

DIFFERENTIAL THERMAL ANALYSIS OF PYRITE AND MARCASITE

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ABSTRACT

Pyrite and marcasite were investigated by differential thermal analysis using a modification of a technique described by Kopp and Kerr (1957). Distinctive curves were obtained for both species. The initial oxidation peak of pyrite occurs at about 538° C. for a 50 mg. sample (125-149 micron fraction). Under the same conditions the initial oxidation peak of marcasite is noted at about 460° C. The writers believe that the lower peak temperature reflects the relative instability of marcasite in contrast to pyrite.

The thermal reaction products at 1000° C. are hematite and sulfur dioxide for both pyrite and marcasite. During the analysis pyrrhotite and other iron oxides may form as intermediate products. These may include maghemite and magnetite. At the completion of the oxidation reactions an endothermic reaction marks the Curie point.

Peak temperatures of both pyrite and marcasite are lowered by a decrease in grain size. The initial oxidation peak of marcasite merges with an adjacent higher peak for samples consisting of grains finer than 74 microns and only an inflection in the curve is noted.

Peak areas increase with increase in sample weight in a relatively uniform manner and greater detail is obtained for samples weighing more than 30 milligrams. Minor reactions which occur with increasing sample weight may result from oxygen depletion of the sample atmosphere. The heat evolved from the same weight of several pyrite and marcasite samples is found to be essentially the same.

INTRODUCTION

The differential thermal behavior of pyrite was briefly investigated during a preliminary study using a new apparatus designed for the analysis of minerals containing corrosive elements such as sulfur and arsenic (Kopp and Kerr, 1957). Subsequent work on sphalerite (Kopp and Kerr, 1958) has emphasized the importance of controlled conditions. A similar detailed study of pyrite and marcasite was undertaken in an attempt to enlarge fundamental data through use of the differential thermal method.

The chemical relationship of pyrite and marcasite has long been a subject of interest. Buerger (1934) states that, "The control of the precipitation of pyrite and marcasite by chemical environment suggests that these two minerals are not a dimorphous pair in the usual sense of the term, but rather that they are chemically distinct compounds. A critical study of all available analyses indicates that pyrite corresponds very closely to ideal FeS₂, but marcasite is definitely sulfur-low."

Hiller and Probsthain (1956), in their DTA investigations of the sulfides in an inert atmosphere, studied a group of Cu-Fe-S minerals including pyrite and marcasite. They note a small exothermic reaction for marcasite at about 520° C. Debye-Scherrer powder diagrams of material heated to about 500° C. produced only marcasite lines, but at 630° C.

the material yielded a true pyrite pattern. The authors conclude that under the conditions of differential thermal analysis a monotropic inversion from marcasite to pyrite occurs, and the Buerger equation may hold only for the formal character of pyrite and marcasite.

ACKNOWLEDGMENTS

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PROCEDURE

The method used is a modification of the technique previously described (Kopp and Kerr, 1957). Heating rate, grain size and sample weight were controlled within critical limits. The effect upon the peak parameters of sphalerite by changes in these factors has been noted (Kopp and Kerr, 1958). It was considered desirable in this study to determine whether heating rate, grain size and sample weight would influence the DTA curves of pyrite and marcasite in a similar way. Here peak temperatures appear to decrease with grain size as noted for sphalerite. However, sphalerite produced only one peak which increased in intensity with sample weight, but pyrite and marcasite exhibit additional peaks with increasing weight.

Samples were screened and those portions in the size range 125–149 microns were selected for analysis. Grain size ranges from >297 to <44 microns were also tested to ascertain the effect of size upon peak parameters. Sample weights of 50 ± 1 and 10 ± 1 mg. were used for analysis. Samples were mixed with alumina powder (250 microns) in glass vials and transferred directly to the sample well. The heating rate was kept at 12° to 13° C. per minute. No correction appeared necessary since all peaks were formed with this heating rate. All analyses were made at an amplification of $20\times$.

DIFFERENTIAL THERMAL BEHAVIOR OF PYRITE

Pyrite from Bingham, Utah (sample K-1) was crushed, sieved and the resulting grain size distributions subjected to differential thermal analysis. The effect of grain size was studied by testing various size fractions using the same sample weight (50 ± 1 mg.). The effect of sample weight was observed for 5 to 50 mg. samples of the 125–149 micron fraction.

The Effect of Grain Size

Several grain size fractions between 149–297 microns and <44 microns were analyzed under standard conditions. The results (Table 1 and Fig.

1) indicate a general decrease in temperature with grain size for the several oxidation peaks.

In general a decrease in peak temperature corresponds to a decrease in grain size, especially below 44 microns. With finer sizes certain peaks are not distinct, and only an inflection in the curve is observed. The final endothermic reaction at about 670° C. is small and may escape detection. This peak appears as two endothermic peaks for material finer than 44 microns. The first is almost negligible compared to the larger peak at 673° C.

TABLE 1. EFFECT OF GRAIN SIZE ON PEAK TEMPERATURE,
PYRITE, BINGHAM, UTAH (SAMPLE K-1)

Sieve No. Range	Diameter Range (Microns)	Peak Temperatures (° C. ± 5° C.)					
50-100	149-297	(555 ↑)	595 ↓	602 ↑	—	—	—
100-120	125-149	(537 ↑)	578 ↓	600 ↑	—	—	—
120-200	74-125	540 ↑	582 ↓	600 ↑	—	—	—
200-325	44- 74	(530 ↑)	580 ↓	605 ↑	—	—	668 ↓
>325	<44	(512 ↑)	554 ↓	-574 ↑	605 ↓	628 ↑	673 ↓

540 ↑ Exothermic; 582 ↓ Endothermic; 554 ↓ -574 ↑ Inflection; (555 ↑) Estimated temperature for peak off record.

Discussion

The effect of grain size upon the shift in peak temperature is of interest. The temperature of the first exothermic peak decreases with grain size (see Table 1 and Fig. 1). This is because of the increased surface area available for oxidation as the grain size decreases. The intensity of the second exothermic peak ranges, and for material finer than 44 microns only an inflection between 553°-574° C. is observed. The intensity of the second peak indicates the amount of pyrite or other unoxidized material which remains after the initial supply of oxygen is depleted.

The 44-74 micron fraction yields a small endothermic peak at about 668° C. The thermal curve for the fraction finer than 44 microns shows an endothermic peak at about 673° C. several times as intense as that for the 44-74 micron fraction. Also, it is preceded by a minor endothermic peak. The cause of this peak at about 670° C. was investigated. It should be noted that before the reaction, at about 600° C., the material is magnetic, although outwardly appearing to be hematite. According to Mason (1943):

“Confusion is especially marked with respect to the magnetic properties of α -Fe₂O₃. It has mostly been described as paramagnetic, the ferromagnetism reported by some workers

being put down to the presence of intermixed magnetite or other ferrites. However, other investigators have positively stated that α - Fe_2O_3 even when quite free from Fe_3O_4 is ferromagnetic; thus Chaudron and Forestier even determined the Curie point of α - Fe_2O_3 and found that it was at 675° , considerably higher than that of magnetite (590°). This might be considered to settle the question, were it not for the recent experiments by Michel on γ - Fe_2O_3 stabilized by the addition of small amounts of sodium ferrite. He found that the

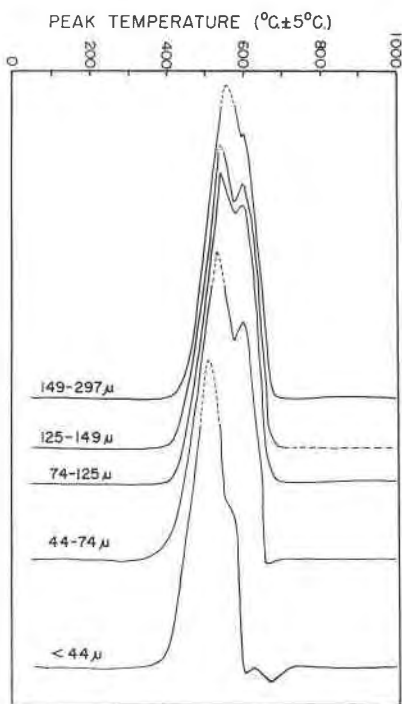


FIG. 1. The effect of grain size on peak temperature. Pyrite (sample K-1), 50 milligram samples.

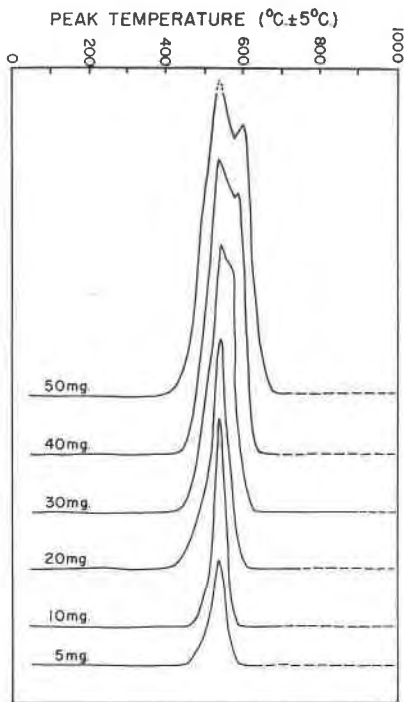


FIG. 2. The effect of sample weight on the peak parameters. Pyrite (sample K-1) 125-149 microns.

(extrapolated) Curie point for γ - Fe_2O_3 was exactly at 675° . The supposed ferromagnetic character of α - Fe_2O_3 is thus very doubtful, since a small amount of γ - Fe_2O_3 in the material investigated by Chaudron and Forestier would suffice to explain their results very well without the necessity of ascribing ferromagnetic properties to α - Fe_2O_3 ."

Schmidt and Vermaas (1955) investigating the differential thermal properties of magnetite report, "The temperature of 580° C. where the second reaction begins, remains absolutely constant for all samples examined and is preceded by a very small endothermic peak, the intensity of which is depressed by the second exothermic reaction. It is interesting

to note that the so-called Curie point, where the ferromagnetism of magnetite changes to paramagnetism occurs at 590° C.”

It appears then that the Curie point may be recognized by differential thermal analysis. The endothermic peak determined for pyrite at about 670° C. appears to be somewhat high compared to the Curie point of magnetite at 590° C. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is also ferromagnetic, and as pointed out by Mason (1943), the extrapolated Curie point of $\gamma\text{-Fe}_2\text{O}_3$ is about 675° C.

Pyrite (sample K-1; less than 44 microns, 50 milligrams) was heated in air to 610° C. at which time the furnace was removed and the material allowed to cool in air. The resulting material was ferromagnetic. An x-ray powder diagram of this material contained lines which do not belong to hematite. At least one of these lines at 2.87 Å may result from either magnetite or maghemite. This spacing is slightly low compared to the 2.97 Å line of magnetite or the 2.95 Å line of maghemite. However, a similar pattern of marcasite at 620° C. has a less intense line at about 2.99 Å. The spacing and intensity of this line may vary during the oxidation process. A weak line at about 2.04 Å corresponds closely with the strongest line of $\alpha\text{-Fe}$ (Swanson, *et al.*, 1955).

The interplanar spacings and their intensities for pyrite heated to 610° C. are listed in Table 2.

The intensity of the endothermic reaction appears to increase with decreasing grain size. It is also apparent (Figs. 1 and 3) that the intensity of the corresponding peak for marcasite is much greater than that of pyrite, and this endothermic reaction is observed for all the grain size ranges of marcasite tested, whereas it is only observed for fractions finer than 74 microns for pyrite. The peak temperature of the endothermic peak appears to increase with decreasing grain size for both pyrite and marcasite.

The following interpretation for the thermal reactions of pyrite varying with grain size is based upon the differential thermal curves and x-ray study of the material. The peak temperature of the first oxidation reaction decreases with grain size as a result of the increased surface area available for oxidation. The second oxidation peak varies somewhat in intensity and reflects the amount of unoxidized material still present after the first peak. The second peak is inhibited until sufficient oxygen becomes available for oxidation to proceed. The endothermic reaction at about 670° C. represents the Curie point of the ferromagnetic material formed during the oxidation reaction. This is only apparent for the finer grain sizes. Since the finer grain sizes oxidize more rapidly and produce sulfur dioxide more rapidly, there is a greater possibility that incomplete

TABLE 2. REACTION PRODUCTS OF PYRITE (SAMPLE K-1)
HEATED IN AIR TO 610° C.

Pyrite (K-1) ¹ At 610° C.		Hematite ²		Magnetite ³		Maghemite ⁴	
<i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I
—	—	—	—	—	—	5.90	2
—	—	—	—	4.86	30	4.82	5
—	—	—	—	—	—	4.18	1
3.66	20	3.68	70	—	—	3.73	5
—	—	—	—	—	—	3.41	2
2.87	30	—	—	2.97	60	2.95	34
—	—	—	—	—	—	2.78	19
2.68	100	2.69	100	—	—	—	—
2.51	80	2.51	80	2.530	100	2.52	100
—	—	—	—	2.425	10	2.41	1
—	—	—	—	—	—	2.32	6
2.20	30	2.20	70	—	—	—	—
2.07	5	2.07	10	2.097	50	2.08	24
2.04	10	—	—	—	—	—	—
1.834	40	1.837	70	—	—	1.87	0.5
1.691	60	1.691	80	1.714	40	1.70	12
—	—	1.634	10	—	—	—	—
1.597	30	1.596	40	1.615	60	1.61	33
—	—	—	—	—	—	1.55	0.5
—	—	—	—	—	—	1.53	1
1.483	40	1.484	70	1.484	70	1.48	53

¹ Copper radiation, Debye-Scherrer camera, 11.46 cm. diameter.

² Rooksby, H. P., (1951), X-ray Identification and Crystal Structure of Clay Minerals, G. W. Brindley, ed., Mineralogical Society, London, p. 264.

³ *Ibid.*, p. 264.

⁴ A.S.T.M. X-ray Powder Data File, Card No. 4-0755 (original reference unobtainable).

oxidation will occur. For material finer than 44 microns the larger peak is preceded by a smaller endothermic reaction. The peak at 670° C. may represent the Curie point of the maghemite present while the preceding peak that of magnetite or other partially oxidized iron present.

The Effect of Sample Weight

Samples of pyrite from Bingham, Utah (sample K-1) were analyzed to determine the effect of weight on the peak parameters (temperature and area). Since composite peaks result for samples weighing more than 30 milligrams, peak heights and widths were not measured. However, the

peak areas were measured with a polar planimeter to the nearest 0.1 inch. Peak temperatures and areas for pyrite weighing from 5 to 50 milligrams were determined. These data are presented in Table 3 and illustrated in Fig. 2. For samples weighing less than 30 milligrams, only one peak (at about 540° C) appears in the thermal record. At about 30 milligrams an inflection in the curve is first noted, and for samples weighing 40 milligrams or more a second exothermic peak appears.

TABLE 3. THE EFFECT OF SAMPLE WEIGHT ON THE PEAK PARAMETERS, PYRITE, BINGHAM, UTAH (SAMPLE K-1)

Sample Weight (±1 mg.)	Peak Temperatures (° C. ±5° C.)			Total Area Under Peaks (In. ² , Planimetric)
5	544 ↑	—	—	0.5
10	538 ↑	—	—	1.2
20	541 ↑	—	—	2.3
30	541 ↑	563 ↓	- 573 ↑	3.7
40	538 ↑	580 ↓	588 ↑	4.7
50	(537 ↑)	578 ↓	600 ↑	5.9 est.

544 ↑ Exothermic; 580 ↓ Endothermic; 563 ↓ -573 ↑ Inflection; (537 ↑) Estimated temperature for peak off record.

Discussion

Earlier curves for the same material (Kopp and Kerr, 1957) also show two exothermic peaks for the oxidation reaction for a sample to inert filler ratio of about 1:15. At this time it was stated that the two peaks might result from two exothermic reactions, or that they might result from the effect of the reaction products which "will alter the reaction rate and peak temperatures, and may even introduce secondary reactions by surrounding the material with an atmosphere other than air."

Hiller and Probsthain (1956) working in an atmosphere of nitrogen, determined that under these conditions of differential thermal analysis, pyrite did not dissociate into FeS, but rather to pyrrhotite (Fe₇S₈). To determine the nature of the second peak pyrite (sample K-1; 44-74 microns, 50 mg.) was heated in air to 580° C. and then cooled rapidly in carbon dioxide. The resulting material was analyzed by x-ray powder photography with the Debye-Scherrer camera. The results (Table 4) indicate that the major reaction product is hematite.

The strongest line of pyrite at 1.6332 Å appears to be absent, indicating that almost all of the pyrite has been oxidized. A small amount, sufficient

TABLE 4. REACTION PRODUCTS OF PYRITE (SAMPLE K-1)
HEATED TO 580° C.

Pyrite at 580° C. Sample K-1 ¹		Hematite ²		Pyrite ³	
<i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I
3.70	40	3.68	70	—	—
—	—	—	—	3.128	36
2.70	100	2.69	100	2.709	84
2.52	80	2.51	80	—	—
—	—	—	—	2.423	66
2.20	30	2.20	70	2.2118	52
—	—	2.07	10	—	—
—	—	—	—	1.9155	40
1.839	50	1.837	70	—	—
1.693	50	1.691	80	—	—
—	—	1.634	10	1.6332	100
1.598	20	1.596	40	—	—
—	—	—	—	1.5640	14
—	—	—	—	1.5025	20
1.483	40	1.484	70	1.4479	24

¹ Copper radiation, Debye-Scherrer camera, 11.46 cm. diameter.

² Rooksby, H. P., (1951), *X-ray Identification and Crystal Structure of Clay Minerals*, G. W. Brindley, ed., Mineralogical Society, London, p. 264.

³ Swanson, H. E., Gilfrich, N. T. and Ugrinic, G. M. (1955), *Standard X-ray Diffraction Powder Patterns: NBS Circ. 539*, v. V, p. 30.

to produce the second exothermic peak might not be observed by the *x*-ray powder method. The strong pattern of hematite may mask the presence of other iron compounds. For example, the two strongest lines of maghemite (γ -Fe₂O₃) occur at 2.52 Å and 1.48 Å (A.S.T.M. Card No. 4-0755). Magnetite's strong lines are 2.530 Å and 1.484 Å (Rooksby, 1951). Pyrrhotite has its most intense line at 2.06 Å (Harcourt, 1942). Minor amounts of any of these compounds might escape detection. Also, since several reactions may be taking place during the oxidation, some of the products may not attain sufficient size to reflect the *x*-ray beam.

Based on the thermal pattern observed and *x*-ray study of the material obtained before the reaction has gone to completion, the following interpretation is given for the reaction: small amounts of pyrite when subjected to differential thermal analysis in air are oxidized essentially to hematite (this material is magnetic until heated to about 700° C.). Small amounts of pyrite may remain, and the presence of other iron compounds may be masked by the large amount of hematite formed. Although Hiller

and Probsthain (1956) noted that pyrite was converted to pyrrhotite when heated in nitrogen, pyrrhotite was not detected in the x-ray study of the material heated in air. Apparently, the relatively large amount of sulfur dioxide formed by a sample of pyrite weighing more than 30 mg., impedes the reaction until sufficient oxygen becomes available for the reaction to continue. With the supply of additional oxygen the small amount of remaining pyrite (or possibly the small amount of pyrrhotite formed under non-oxidizing conditions) then oxidizes causing the second exothermic peak. This peak increases in intensity and peak temperature as the amount of sample increases.

DIFFERENTIAL THERMAL BEHAVIOR OF MARCASITE

Marcasite from Ottawa County, Oklahoma (sample K-11) was crushed and sieved. The resulting grain size distributions were analyzed to determine the effect of grain size and sample weight under standard conditions.

The Effect of Grain Size

Several grain size fractions from >297 microns to <44 microns were tested using a sample weight of 50 ± 1 mg. The results (Table 5 and Fig. 3) indicate a general decrease in temperature with grain size for the several oxidation peaks.

A general decrease in peak temperature for the oxidation reactions is noted with decreasing grain size, especially below 44 microns. The first exothermic peak gradually coalesces with the second exothermic peak as the grain size decreases. The peak temperature of the final endothermic peak appears to increase with decreasing grain size. Also, this peak appears to subdivide into a few smaller peaks besides the major peak as the grain size decreases. The intensity of the final endothermic peak from about 645° – 692° C. appears to increase with decreasing grain size.

Discussion

The effect of grain size for 50 ± 1 mg. samples of marcasite was determined. The peak temperatures of the exothermic peaks decrease with grain size (see Table 5 and Fig. 3). The initial peak temperature decreases from about 462° C. for material larger than 297 microns to an inflection between 410 – 422° C. for material finer than 44 microns. The second exothermic peak decreases from about 562° C. for material larger than 297 to about 475° C. for material finer than 44 microns. The major endothermic reaction increases in peak temperature from about 645° C. for material larger than 297 microns to 692° C. for material finer than 44 microns. There is also a marked increase in intensity for this endothermic

TABLE 5. EFFECT OF GRAIN SIZE ON PEAK TEMPERATURE, MARCASITE, OTTAWA COUNTY, OKLAHOMA (SAMPLE K-11)

Sieve No. Range	Diameter Range (Microns)	Peak Temperatures ($^{\circ}\text{C} \pm 5^{\circ}\text{C}$)									
<50	>297*	462 \uparrow	492 \downarrow	(562 \uparrow)	—	—	—	—	—	—	645 \downarrow
50-100	149-297	456 \uparrow	482 \downarrow	(550 \uparrow)	—	—	—	—	—	—	652 \downarrow
100-120	125-149	440 \uparrow	482 \downarrow	530 \uparrow	564 \downarrow	575 \uparrow	—	—	—	—	655 \downarrow
120-200	74-125	445 \uparrow	472 \downarrow	525 \uparrow	556 \downarrow	-565 \uparrow	—	—	—	—	662 \downarrow
200-325	44-74	422 \uparrow	-437 \downarrow	(495 \uparrow)	—	—	—	585 \downarrow	626 \uparrow	—	673 \downarrow
>325	<44	410 \uparrow	-422 \downarrow	(475 \uparrow)	548 \downarrow	565 \uparrow	597 \downarrow	628 \uparrow	692 \downarrow	—	—

* 38 ± 1 mg. sample.

462 \uparrow Exothermic; 492 \downarrow Endothermic; 555 \downarrow -565 \uparrow Inflection; (562 \uparrow) Estimated temperature for peak off record.

peak as the grain size decreases. One or two additional minor endothermic peaks are observed for material finer than 125 microns. X-ray powder photographs of marcasite (sample K-11; 44-74 microns, 50 mg.) heated in

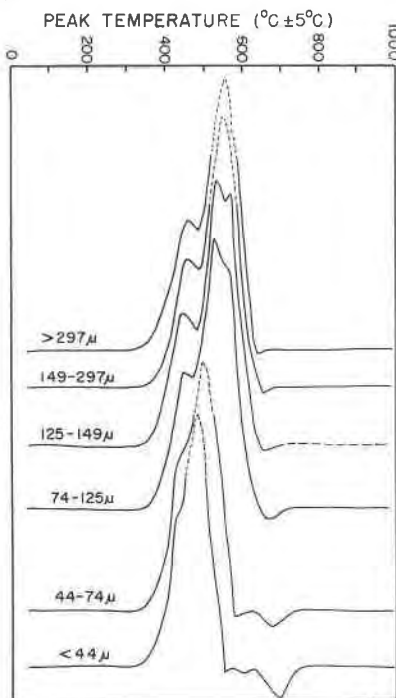


FIG. 3. The effect of grain size on peak temperature. Marcasite (sample K-11), 50 milligram samples.

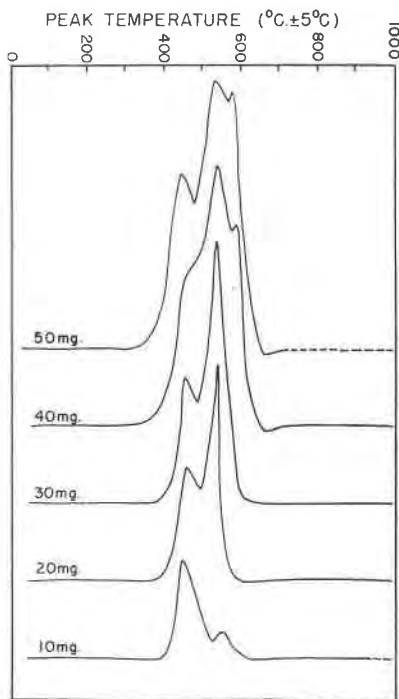


FIG. 4. The effect of sample weight on the peak parameters. Marcasite (sample K-11), 125-149 microns.

TABLE 6. REACTION PRODUCTS OF MARCASITE (SAMPLE K-11)
HEATED TO 620° C.

Marcasite at 620° C. ¹		Hematite ²		Maghemite ³		Magnetite ⁴	
<i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I
—	—	—	—	5.90	2	—	—
—	—	—	—	4.82	5	4.86	30
—	—	—	—	4.18	1	—	—
3.65	30	3.68	70	3.73	5	—	—
—	—	—	—	3.41	2	—	—
2.99	10	—	—	2.95	34	2.97	60
—	—	—	—	2.78	19	—	—
2.70	100	2.69	100	—	—	—	—
2.52	80	2.51	80	2.52	100	2.530	100
—	—	—	—	2.41	1	2.425	10
—	—	—	—	2.32	6	—	—
2.20	20	2.20	70	2.23	0.5	—	—
—	—	2.07	10	2.08	24	2.097	50
1.836	30	1.837	70	1.87	0.5	—	—

¹ Copper radiation, Debye-Scherrer camera, 11.46 cm. diameter.

² Rooksby, H. P. (1951), *X-ray Identification and Crystal Structure of Clay Minerals*, G. W. Brindley, ed. Mineralogical Society, London, p. 264.

³ A.S.T.M. *X-ray Powder Data File*, Card No. 4-0755 (original reference unobtainable).

⁴ Rooksby, *op. cit.*, p. 264.

air to 630° C. indicate that maghemite and magnetite may be present. These data are listed in Table 6.

The interpretation for the variation in thermal reactions of marcasite with grain size is based upon the differential thermal curves and *x*-ray study of the material. The peak temperatures of the oxidation reactions decrease with grain size as a result of the increased surface area available for oxidation. The initial peak occurs at a lower temperature than for pyrite under the same test conditions (see Tables 1 and 5, and Figs. 1 and 3). This is thought to reflect the relative instability of marcasite compared with pyrite. The second exothermic reaction occurs at about the same temperature as the initial pyrite reaction, and may indicate that a transformation to pyrite occurs at the surfaces of the unoxidized marcasite. This pyrite would be oxidized rapidly to hematite and the magnetic iron oxides. The endothermic reaction (Curie point) which occurs at about 650–690° C. increases in peak temperature with decreasing grain size. As the grain size decreases, oxidation will proceed more rapidly. This in turn produces sulfur dioxide more rapidly, allowing the reaction to proceed in a reducing—rather than an oxidizing—environment. Under

these conditions, maghemite or the partially oxidized iron compounds may form.

Effect of Sample Weight

The peak parameters for marcasite (sample K-11) were determined for samples weighing 10 to 50 mg. These data are presented in Table 7 and illustrated in Fig. 4. An initial exothermic peak at about 450° C. is observed for all samples. A second exothermic peak at about 535° C. also occurs, and for samples weighing more than 30 mg. two peaks are noted in a manner similar to pyrite. A final minor peak (endothermic) occurs at about 655° C. for samples weighing more than 30 mgs.

TABLE 7. THE EFFECT OF SAMPLE WEIGHT ON THE PEAK PARAMETERS, MARCASITE, OTTAWA COUNTY, OKLAHOMA (SAMPLE K-11)

Sample Weight (±1 mg.)	Peak Temperatures (° C. ± 5° C.)						Total Area Under Peaks (In. ² , Planimetric)
10	445 ↑	520 ↓	540 ↑	—	—	—	1.1
20	455 ↑	492 ↓	535 ↑	—	—	—	2.5
30	449 ↑	484 ↓	535 ↑	—	—	—	3.5
40	452 ↑	482 ↓	534 ↑	573 ↓	582 ↑	655 ↓	5.0
50	440 ↑	482 ↓	530 ↑	564 ↓	575 ↑	655 ↓	5.9

445 ↑ Exothermic; 520 ↓ Endothermic; 452 ↑-482 ↓ Inflection.

Discussion

The initial exothermic reaction of marcasite (125-149 microns) heated in air occurs at about 450° C. or about 90° C. below the corresponding initial exothermic reaction of pyrite. The intensity of this first peak increases slightly with increased sample weight, but not proportionally. The second exothermic peak occurs at about 535° C. and increases rapidly in intensity. For samples weighing more than 30 milligrams this peak becomes two peaks as was observed for pyrite. The close correspondence of the second exothermic peak of marcasite at 535° C. with the first exothermic peak of pyrite at about 540° C. suggests that a transformation from marcasite to pyrite may have occurred. However, x-ray powder photographs of marcasite (sample K-11; 125-149 microns, 50 mg.) heated to 480° C. and cooled rapidly in carbon dioxide indicate that hematite is the major reaction product. Some marcasite remains, and the presence of pyrite at this stage is doubtful since the strongest line of pyrite at 1.6332 Å is not present. The results are presented in Table 8.

Hiller and Probsthain (1956) working in an inert atmosphere noted a

small flat exothermic peak for marcasite at a temperature of about 520° C. Above this temperature the thermal curve corresponds to that of pyrite. (They also state that the same inversion point has been found by ordinary thermal analysis to be 520–535° C.) X-ray photographs of material heated to 500° C. produced only marcasite lines, while a test of material heated to 630° C. yielded a true pyrite pattern.

TABLE 8. REACTION PRODUCTS OF MARCASITE (SAMPLE K-11)
HEATED TO 480° C.

Marcasite at 480° C. ¹		Hematite ²		Marcasite ³		Pyrite ⁴	
Sample K-11 <i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I
3.67	10	3.68	70	—	—	—	—
3.43	5	—	—	3.44	60	—	—
—	—	—	—	—	—	3.1280	36
2.96	5	—	—	2.96	40	—	—
2.70	100	2.69	100	2.70	100	2.7088	84
2.52	60	2.51	80	2.55	20	—	—
2.41	10	—	—	2.41	70	2.4281	66
2.30	10	—	—	2.31	70	—	—
2.20	10	2.20	70	—	—	2.2118	52
—	—	2.07	10	2.10	20	—	—
—	—	—	—	2.05	20	—	—
—	—	—	—	1.94	40	—	—
1.908	10	—	—	1.91	60	1.9155	40
1.834	20	1.837	70	1.87	10	—	—
1.755	20	—	—	1.76	90	—	—
—	—	—	—	1.72	30	—	—
1.691	20	1.691	80	1.69	50	—	—
—	—	—	—	1.67	40	—	—
—	—	1.634	10	—	—	1.6332	100

¹ Copper radiation, Debye-Scherrer camera, 11.46 cm. diameter.

² Rooksby, H. P. (1951), *X-ray Identification and Crystal Structures of Clay Minerals*, G. W. Brindley, ed., Mineralogical Society, London, p. 264.

³ A.S.T.M. X-ray Powder Data File, Card No. 2-0908 (original references unobtainable).

⁴ Swanson, H. E., Gilfrich, N. T. and Ugrinic, G. M. (1955), *Standard X-ray Diffraction Powder Patterns*: NBS Circ. 539, v. V, p. 30.

A small endothermic reaction at about 655° C. occurs for samples weighing more than 30 mg. (125–149 microns). As in the case of pyrite this endothermic reaction is believed to represent the Curie point of the ferromagnetic material formed during the oxidation.

Based on the thermal records produced and x-ray study of the material

obtained before the reaction has gone to completion, the following interpretation is given for the reactions: marcasite, when heated in air starts to oxidize at a lower temperature than pyrite. At the completion of this first peak, hematite and marcasite appear to be the major components. Pyrite is not detected. The reaction may produce this initial peak either as a result of the early depletion of oxygen, or the initial peak may represent the surficial oxidation of marcasite to hematite. As the temperature is raised the transformation of marcasite to pyrite may take place at the surfaces of the remaining marcasite, and this "nascent" pyrite is oxidized rapidly producing the second exothermic reaction. As the sample weight is increased a small endothermic peak is observed at about 655° C. which represents the Curie point of the ferromagnetic material formed during the oxidation.

A COMPARISON OF SEVERAL PYRITES AND MARCASITES

Four additional samples of pyrite and three of marcasite were analyzed to determine the variations in peak parameters for different samples. Samples weighing 10 and 50 mg. were analyzed. The grain size used was 125–149 microns. The sample localities are listed in Table 9.

TABLE 9. SAMPLE LOCALITIES

Sample Number	Locality
Pyrite	
K-1	Bingham, Utah
K-2	Yak Mine, Leadville, Colorado
K-3	Isle of Elba
K-4	Brazil
K-10	Saratoga Mine, Central City, Colorado
Marcasite	
K-11	Ottawa County, Oklahoma
K-12	Joplin, Missouri
K-13	Brux, Bohemia
K-14	Pitcher, Oklahoma

Thermal curves for these samples are illustrated in Fig. 5 and 6. The peak parameters are listed in Tables 10 and 11.

Under equivalent conditions (sample weight, heating rate and grain size) several samples of pyrite appear to agree closely in the general appearance of thermal curves and peak parameters. In general for a 10 mg. sample only one exothermic peak is observed at 543° C. \pm 5° C. For a 50 mg. sample, two exothermic peaks are observed, the first at 538° C.

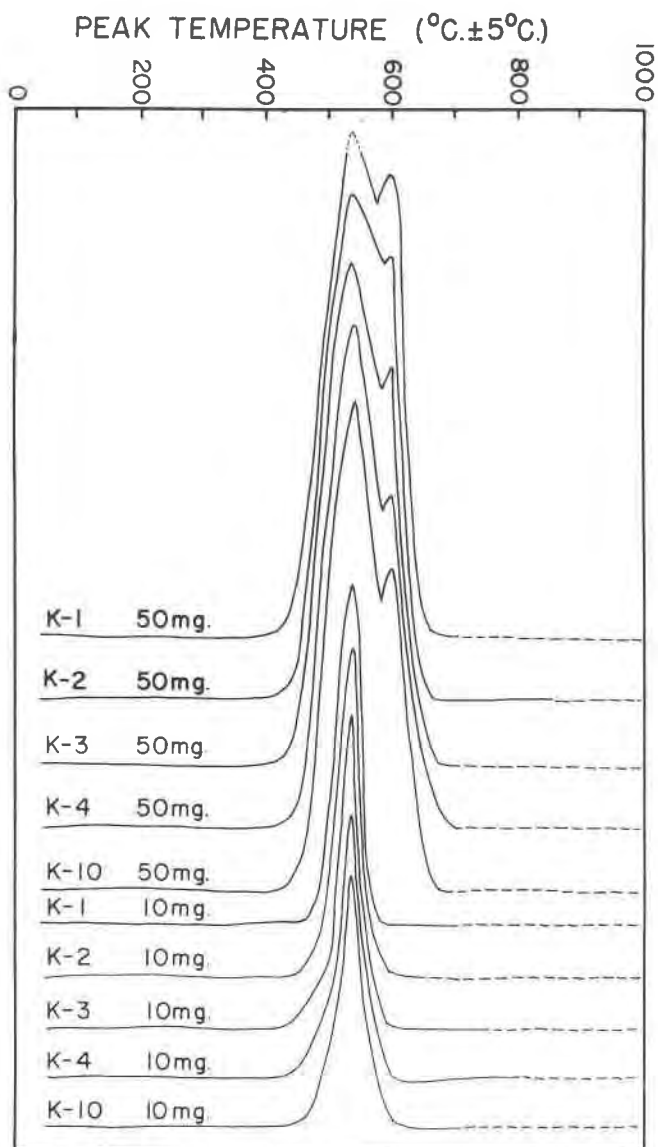


FIG. 5. Selected pyrite DTA curves. 125–149 micron fraction, 10 and 50 milligram samples.

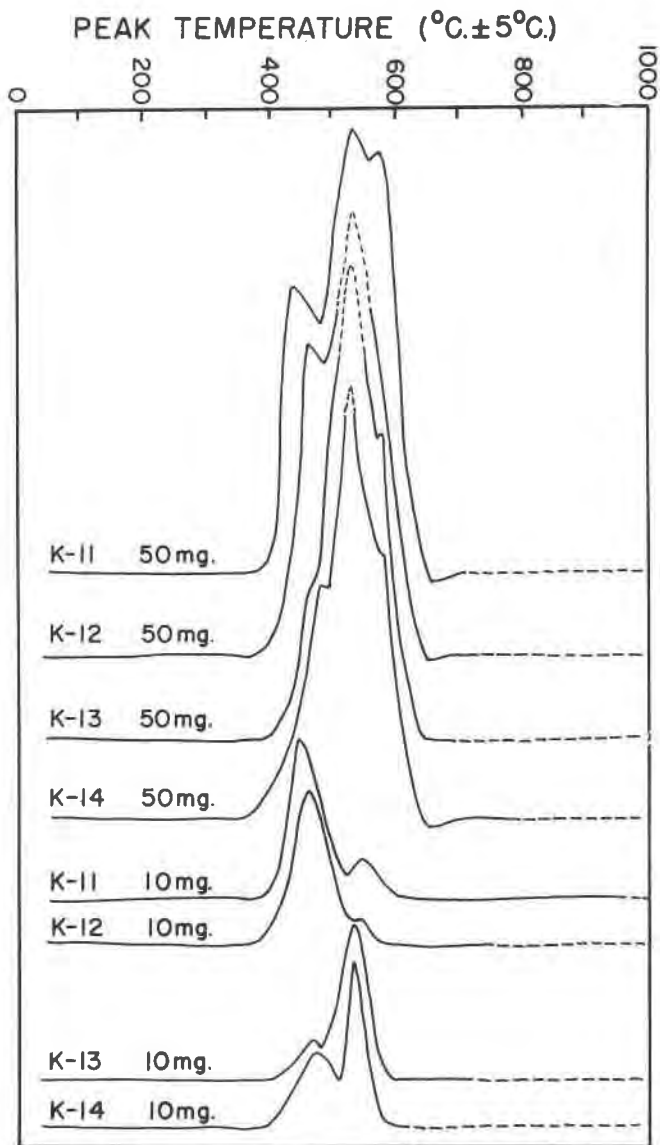


FIG. 6. Selected marcasite DTA curves. 125-149 micron fraction, 10 and 50 milligram samples.

TABLE 10. PEAK PARAMETERS FOR SEVERAL PYRITES (125-149 MICRONS)
(10 ± MILLIGRAM SAMPLES)

Sample Number	Peak Temperatures (° C. ± 5° C.)			Peak Areas (In. ² , Planimetric)
K-1	538 ↑			1.2
K-2	544 ↑			1.2
K-3	545 ↑			1.4
K-4	548 ↑			1.1
K-10	542 ↑			1.0
(50 ± 1 Milligram Samples)				
K-1	(537 ↑)	578 ↓	600 ↑	5.9 est.
K-2	(538 ↑)	590 ↓	598 ↑	6.2 est.
K-3	535 ↑	585 ↓	608 ↑	5.9
K-4	540 ↑	585 ↓	600 ↑	6.0
K-10	(541 ↑)	581 ↓	600 ↑	6.2 est.

535 ↑ Exothermic; 578 ↓ Endothermic; (537 ↑) Estimated peak temperature for peak off record.

TABLE 11. PEAK PARAMETERS FOR SEVERAL MARCASITES (125-149 MICRONS)
(10 ± 1 MILLIGRAM SAMPLES)

Sample Number	Peak Temperatures (° C. ± 5° C.)				Peak Areas (In. ² , Planimetric)			
K-11	445 ↑	520 ↓	540 ↑		1.1			
K-12	462 ↑	528 ↓	538 ↑		1.1			
K-13	465 ↑	475 ↓	528 ↑		1.3			
K-14	470 ↑	504 ↓	529 ↑		1.0			
(50 ± 1 Milligram Samples)								
K-11	440 ↑	482 ↓	530 ↑	564 ↓	575 ↑	655 ↓	5.9	
K-12	465 ↑	488 ↓	(532 ↑)	—	—	655 ↓	6.4 est.	
K-13	455 ↑	—	480 ↓	(530 ↑)	580 ↓	583 ↑	—	6.2 est.
K-14	480 ↑	490 ↓	(535 ↑)	585 ↓	595 ↑	658 ↓	6.2 est.	

440 ↑ Exothermic; 482 ↓ Endothermic; 455 ↑-480 ↓ Inflection; (532 ↑) Estimated temperature for peak off record.

± 5° C. and the second at 603° C. ± 5° C. The peak areas agree closely, the area for a 50 mg. sample being approximately 6.1 in.² and the area for a 10 mg. sample about 1.2 in.²

Several samples of marcasite under the same test conditions also have the same general thermal curves and peak parameters. However, the

agreement is not as close as for pyrite. This may be attributed to the relative instability of marcasite compared with pyrite. For a 10 mg. sample two exothermic peaks are observed. The first occurs at $458^{\circ}\text{C.} \pm 13^{\circ}\text{C.}$ and the second at $534^{\circ}\text{C.} \pm 6^{\circ}\text{C.}$ For a 50 mg. sample two exothermic reactions are also observed for all samples, the first at $460^{\circ}\text{C.} \pm 20^{\circ}\text{C.}$ and the second at $532^{\circ}\text{C.} \pm 3^{\circ}\text{C.}$ A third exothermic peak may be observed at $585^{\circ}\text{C.} \pm 10^{\circ}\text{C.}$, and an endothermic reaction may be observed at about 655°C. It is of interest to note that the peak showing the widest variation in peak temperature is the initial oxidation peak of marcasite which is believed to represent the instability of marcasite compared with pyrite. The peak areas agree closely with each other and also with the peak areas of pyrite. The measured peak areas for 50 mg. samples average about 6.2 in.² and for 10 mg. samples approximately 1.1 in.².

CONCLUSIONS

Pyrite and marcasite analyzed under standard conditions of heating rate, grain size and sample weight yield distinctive differential thermal curves. The initial oxidation peak of marcasite occurs at about 460°C. for a 50 mg. sample (125–149 micron fraction) while under the same conditions the initial oxidation peak of pyrite does not occur until about 538°C. Marcasite appears to oxidize at a lower temperature because of its relative instability compared with pyrite.

The inversion of marcasite to pyrite was not observed for samples heated in air. Upon completion of the initial oxidation reaction, X-ray powder patterns indicate the presence of a mixture of hematite and marcasite.

Oxidation peak temperatures decrease with grain size for both species. The peak temperature of the Curie point (endothermic) which is observed for pyrite finer than 74 microns and for the entire size range of marcasite tested (>297 to <44 microns; 50 ± 1 mg. samples) appears to increase with decreasing grain size. Peak areas for both pyrite and marcasite increase in an essentially linear manner with sample weight and under standard conditions of grain size and sample weight do not differ significantly.

The final reaction products for both pyrite and marcasite are hematite and sulfur dioxide. When the sulfur dioxide produced during the oxidation depletes the sample atmosphere of oxygen, pyrrhotite and other iron oxides including magnetite and maghemite may form as intermediate products.

REFERENCES

- American Society for Testing Materials X-ray Powder Data File, Card No. 2-0908.
- American Society for Testing Materials X-ray Powder Data File, Card No. 4-0755.

- BUERGER, M. J. (1934), The pyrite-marcasite relation: *Am. Mineral.*, **19**, 37-61.
- HARCOURT, G. A. (1942), Tables for the identification of ore minerals by x-ray powder patterns: *Am. Mineral.*, **27**, 63-113.
- HILLER, J. E. AND PROBSTHAIN, K. (1956), Differentialthermoanalyse von Sulfidmineralen: *Geologie (Berlin)*, **5**, 607-616.
- KOPP, O. C. AND KERR, P. F. (1957), Differential thermal analysis of sulfides and arsenides: *Am. Mineral.*, **42**, 445-454.
- KOPP, O. C. AND KERR, P. F. (1958), Differential thermal analysis of sphalerite: *Am. Mineral.*, **43**, 732-748.
- MASON, B. (1943), Mineralogical aspects of the system $\text{FeO-Fe}_2\text{O}_3\text{-MnO-Mn}_2\text{O}_3$: *Geol. För. Förh. Stockholm*, **65**, 97-180.
- ROOKSBY, H. P. (1951), X-ray Identification and Crystal Structure of Clay Minerals, G. W. Brindley, ed., Mineralogical Society, London, 345 p.
- SCHMIDT, E. R. AND VERMAAS, F. H. S. (1955), Differential thermal analysis and cell dimensions of some natural magnetites: *Am. Mineral.*, **40**, 422-431.
- SWANSON, H. E., FUYAT, R. K. AND UGRINIC, G. M. (1955), Standard X-ray diffraction powder patterns: *NBS Cir.* **539, IV**.
- SWANSON, H. E., GILFRICH, N. T. AND UGRINIC, G. M. (1955), Standard X-ray diffraction powder patterns: *NBS Cir.* **539, V**.

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