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Analysis of the Oxidation of Chalcopyrite, Chalcocite, Galena, Pyrrhotite, Marcasite, and Arsenopyrite

By G. W. Reimers and K. E. Hjelmstad

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**UNITED STATES DEPARTMENT OF THE INTERIOR
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	kcal/mol	kilocalorie per mol
cm ³	cubic centimeter	μm	micrometer
cm ³ /min	cubic centimeter per minute	mg	milligram
°C	degree Celsius	min	minute
°C/min	degree Celsius per minute	mm	millimeter
g	gram	pct	percent
h	hour	wt pct	weight percent

ANALYSIS OF THE OXIDATION OF CHALCOPYRITE, CHALCOCITE, GALENA, PYRRHOTITE, MARCASITE, AND ARSENOPYRITE

By G. W. Reimers¹ and K. E. Hjelmstad²

ABSTRACT

Conditions in the underground mine environment can cause self-heating of sulfide ores as a result of exothermic oxidation reactions, which may result in mine fires. This Bureau of Mines report describes thermal analyses of finely ground chalcopyrite, chalcocite, galena, pyrrhotite, marcasite, and arsenopyrite, to characterize their responses under oxidizing conditions. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were used, in the temperature range 100° to 500° C.

Chalcopyrite showed an initial weight gain, due to formation of sulfates, a weight loss, caused by ignition of iron sulfide to iron oxide, and a final weight gain, indicating the conversion of copper sulfide to sulfate. Chalcocite did not ignite in the temperature range studied but exhibited a rapid weight gain, because of the rapid conversion of copper sulfide to sulfate. Likewise, galena failed to ignite but underwent a steady weight gain when oxidized in a moist atmosphere, showing conversion of lead sulfide to sulfate below the ignition point. Marcasite underwent a rapid weight loss, indicating ignition, at 200° C. Moisture in the oxidizing atmosphere lowered the ignition point of marcasite and arsenopyrite but not that of pyrrhotite. All the sulfides exhibited exothermic behavior at temperatures below the ignition point.

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INTRODUCTION

This report describes the results of laboratory thermal analysis experiments conducted to follow the oxidation of chalcopyrite, chalcocite, galena, pyrrhotite, marcasite, and arsenopyrite. These tests are part of a broader Bureau of Mines research program to develop methods of controlling the oxidation of sulfide ores in underground mines, thus preventing spontaneous combustion mine fires.

Previously, Ninteman (1)³ completed an extensive literature review of the nature and problems associated with the oxidation and combustion of sulfide minerals in underground metal mines. Sulfide oxidation is an exothermic process that produces heat, which, if not dissipated, causes a temperature rise within the mineral mass. If the temperature begins to rise, a thermal runaway situation may develop that will cause the sulfide and other combustibles to burn.

Reactions similar to those that cause spontaneous combustion in underground mines can also be responsible for the self-heating of sulfides during shipment. Kirshenbaum (2) described many such incidents, involving both rail and ship carriers of sulfide concentrates. His review provided details of the conditions that led to the oxidation and self-heating of sulfide cargoes and, ultimately, to combustion. Mention was also made of the high levels of toxic SO₂ generated during such events, which impeded fire control efforts.

The spontaneity and prolonged incipient stage (weeks or months) of these fires make their occurrence difficult to predict and to detect. Furthermore, these fires often start in abandoned, backfilled, and/or caved areas where abundant fuel is present but where access for fire fighting is difficult or in some cases impossible. Since detection and suppression are so difficult, a high priority is placed on fire prevention. However, the chemical reactions giving rise to

spontaneous combustion in sulfide deposits are not well understood. Thus, current efforts by mine personnel to control spontaneous combustion problems, regardless of how well intended, are not always based on sound engineering and technical principles. The intent of this research is to delineate the thermal behavior of sulfide minerals exposed to oxidizing conditions, thereby providing a background of data that will enable mine personnel to undertake fire prevention efforts with maximum effectiveness.

In his monograph on chalcopyrite, Habashi (3) refers to work by Tafel and Greulich, who followed the oxidation of powdered chalcocite in air. They found that both cupric sulfate and ferrous sulfate were formed slowly at about 350° C. Ferrous sulfate reached its maximum formation at 400° C; at 500° C, its rate of formation equaled its rate of decomposition. Cupric sulfate reached its maximum formation at 550° C. Above 550° C, it gradually decomposed to copper oxysulfate. Habashi also cited the work of Meunier and Vanderpoorten in studying the oxidation of chalcopyrite cubes (2 to 3 cm³) in the temperature range of 300° to 900° C. At 330° C, they noted oxidation on the surface of the cube. At 500° C, the surface film was thick enough that when the cube was sectioned the red outer layer could be identified as ferric oxide. Work by Razouk and others to study the oxidation of chalcopyrite by TGA was also reviewed (3). Razouk proposed a mechanism for the temperature range of 350° to 400° C, suggesting that chalcopyrite oxidized to form ferric sulfate and cuprous sulfide. Between 450° and 600° C, the cupric oxide and ferric sulfate reacted to form cupric sulfate and ferric oxide. This interpretation seems to contradict that of other researchers, but it does propose the formation of sulfates during oxidation.

Larger scale Bureau research experiments in progress on the low-temperature (90° to 200° C) oxidation of pyrite have shown that ferrous sulfate was formed on the surface of pyrite in the presence of moist air. In these same tests, the

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

temperature of the pyrite increased substantially during oxidation. However, in similar tests conducted in the absence of water vapor, only a slight temperature rise was noted and the presence of sulfate on the pyrite surface was not detected by X-ray diffraction (XRD) analysis. The role that moisture has in promoting the oxidation of pyrite to sulfate is not completely understood. However, the water vapor may assist the oxygen in permeating the sulfate layer formed on the pyrite surface. Simpson and Herbert (4), among others, have also suggested that the formation of sulfates contributes to the self-heating of sulfides.

Table 1 lists the molar heats of reaction of a number of common sulfides to form oxides and sulfates (5). Only the anhydrous forms of the sulfates are reported, as the degree of hydration would be influenced by the humidity level and the temperature at which the sulfates were formed. It should be noted that the reactions responsible for forming the sulfates produce more energy (heat) than do the reactions that precede ignition and form oxides. However, assuming that sulfide self-heating is only caused through the formation of sulfates is probably oversimplifying a complex process. Previous research indicates that a number of other factors and reactions, such as the presence of free sulfur, can contribute to sulfide self-heating (6-7).

In this investigation, the weight changes occurring during oxidation of chalcopyrite, chalcocite, galena,

TABLE 1. - Standard heats of reaction (ΔH_{298}°)

Mineral	Oxidation product	ΔH_{298}° kcal/mol
Chalcocite.....	CuO,CuSO ₄	-202.1
	Cu ₂ ,SO ₄	-160.2
Chalcopyrite....	FeSO ₄ ,CuSO ₄	-361.6
Galena.....	PbSO ₄	-197.0
Marcasite.....	Fe ₂ O ₃ ,SO ₂	-200.4
	FeSO ₄ ,SO ₂	-253.7
Pyrrhotite.....	Fe ₂ O ₃ ,SO ₂	-132.1
	FeSO ₄ ,SO ₂	-178.9
Pyrite.....	Fe ₂ O ₃ ,SO ₂	-199.4
	FeSO ₄ ,SO ₂	-252.7

pyrrhotite, marcasite, and arsenopyrite were measured in the temperature range 100° to 500° C. This weight change information, the XRD analysis of the oxidized products, and the results obtained from DTA were used to characterize the oxidation of the subject sulfide minerals. These data, together with previously published data on the oxidation of pyrite (8), will be used to develop models that describe the kinetics and mechanisms of sulfide oxidation reactions. A detailed understanding of these reaction kinetics and mechanisms is expected to lead to optimized strategies for preventing spontaneous combustion fires.

EQUIPMENT AND TEST PROCEDURE

The thermal analysis equipment used in this study consisted of the following Perkin Elmer⁴ components: a TGS-2 thermogravimetric analyzer and a DTA 1700 differential thermal analyzer, in conjunction with a system 7/4 thermal analysis controller. Data from the analyzers were continuously fed to a thermal analysis data station (TADS), and the test results were displayed on paper by a TADS-1

plotter. Modifications to the TGS-2 analyzer included the installation of a heating tape around the glass tube shell that surrounds the furnace assembly, in order to reduce moisture condensation on the balance hangdown wire assembly. The balance was also continually purged with a few cubic centimeters per minute of helium to prevent corrosion from moisture and SO₂.

Compressed gas cylinders were used to supply the nitrogen, air, and oxygen used in the tests. In the TGA tests, a flow rate of 500 cm³/min was used for purging

⁴Reference to specific products does not imply endorsement by the Bureau of Mines.

the system with nitrogen and for supplying air or oxygen during the oxidation tests. To add moisture to the system, the oxidizing gas (air or oxygen) was bubbled into water contained in a heated flask and routed to the TGA furnace through an insulated tube to prevent condensation. The water content of moist gas streams was verified over measured time intervals by weighing the water collected in drying tubes filled with a drying agent. When moisture was added to the gas stream, the flow rate of the oxidizing gas was reduced to compensate for the volume of the added water vapor, keeping the total flow rate of 500 cm³/min. A flow rate of 40 cm³/min was used in tests with the DTA equipment.

For the TGA tests, approximately 40 mg of sulfide was used. The sample was loaded into the balance pan, and the system was closed by raising the furnace assembly into position. The system was then purged with nitrogen while the sample was heated to 100° C. At this point,

the nitrogen was replaced with the oxidizing gas, and the sample was heated at 25° C/min. A starting temperature of 100° C was used to prevent condensation of moisture on the sample when water vapor was added to the oxidizing-gas stream. Selected sulfide samples were also tested isothermally under oxidizing atmospheres at fixed furnace temperatures, using the TGA system. These tests were run at temperatures near the ignition point or near the point where rapid weight change occurred. The same system loading procedure was used, and the sulfides were heated in nitrogen until the desired test temperature was reached.

DTA tests used a sample weighing about 30 mg. After the sample pan was filled, the furnace assembly was locked into position, and the assembly was purged with nitrogen while the sample was heated to 100° C. At 100° C, the oxidizing gas was allowed to flow into the assembly, and the thermal behavior of the sample was monitored at a heating rate of 25° C/min.

SAMPLE PREPARATION

The sulfide minerals used in this investigation were specimens purchased from a commercial supplier. The primary crushing of the minerals involved breaking with a sledge hammer, followed by roll-crushing in several stages, along with sorting to remove visible gangue. After being crushed to minus 6 mm, the sulfides were split into 20-g lots for

further size reduction in a Bleuler-brand mill. Table 2 lists the partial chemical analysis of the various samples. XRD analysis was used to confirm their compositions. Pyrite was present as a minor constituent in the samples designated "chalcopyrite A" and "pyrrhotite A" and in the marcasite and arsenopyrite.

TABLE 2. - Partial chemical analysis of sulfide samples, weight percent

Element	Chalcopyrite			Chalcocite		Galena	Pyrrhotite		Marcasite	Arsenopyrite
	A	B	C	A	B		A	B		
Fe.....	37.4	33.3	30.8	5.3	5.6	0.26	45.6	44.0	45.6	28.5
Cu.....	21.2	30.7	33.3	71.4	68.0	.24	.10	.14	ND	ND
Pb.....	ND	ND	ND	ND	ND	82.2	ND	ND	ND	ND
S.....	31.8	33.0	31.6	20.7	19.0	12.1	30.2	24.2	50.7	13.4
Al.....	.68	<.20	<.20	.31	.37	<.20	<.20	2.4	ND	.31
As.....	ND	ND	ND	ND	ND	ND	ND	ND	ND	27.6
Ca.....	<.50	<.50	<.50	<.50	<.50	<.50	1.8	1.9	ND	<.30
Mg.....	.42	<.01	<.1	<.1	<.1	<.1	.16	2.0	ND	<.10
Ni.....	ND	ND	ND	ND	ND	ND	.08	3.8	ND	ND
Si.....	1.7	.48	1.1	.34	2.2	<.10	.77	8.5	ND	9.7
Zn.....	ND	ND	ND	ND	ND	<.01	ND	ND	ND	ND

ND Not determined.

In previous tests, it was found that the reactivity of sulfides increased as the particle size decreased; therefore, the samples in this study were ground in the Bleuler mill to fine sizes, to reduce the time required to conduct the experiments. This was achieved by milling 20-g batches for either 15, 30, 60, or 120 min. To decrease the possibility of oxidation during this final size-reduction step, the samples were milled and stored in heptane. Just prior to thermal analysis, a portion of the sample slurry was withdrawn from the storage bottle, dried in air at room temperature, and then loaded into the analysis units.

Table 3 illustrates the size distribution of chalcopyrite, chalcocite, and

galena samples that were ground for 15 and 120 min. The mean and median particle sizes for the various samples are indicated in the table footnotes. A Leeds and Northrup Microtrac particle size monitor was used to collect the size information on the ground sulfides. Heptane was evaporated from the samples before they were added to the water carrier used with the monitor. The average particle size of these sulfides was in the range of 5.8 to 8.7 μm and 3.4 to 4.8 μm for the 15- and 120-min grinding times, respectively. Under the assumption that grinding would produce similar sizes in all samples, the remaining milled samples were not measured.

RESULTS AND DISCUSSION

ORE-TYPE SULFIDES

Several sulfides that are commonly mined for their metal content were examined first: two copper sulfides, chalcopyrite and chalcocite, and the lead sulfide galena.

Thermal Gravimetric Analyses

Chalcopyrite

Chalcopyrite was the first ore-type mineral selected for examination in the series. It is a sulfide of copper and iron and has a typical formula of CuFeS_2 and a tetragonal crystal structure (9). Figure 1 shows the results of TGA tests conducted on chalcopyrite sample A, milled for 15, 30, 60, and 120 min, in the temperature range of 100° to 400° C in dry air. In these tests, the ignition temperature, shown as the point where a rapid weight loss occurred due to the oxidation of iron sulfide to the oxide, decreased with increasing milling time (decreasing particle size). Replacing air with oxygen had little effect on the ignition point. This indicates that the oxygen content of the air atmosphere was not limiting the results illustrated in figure 1. The addition of moisture to the oxidizing atmosphere was found to

increase the sample weight gain prior to ignition.

Figures 2A and 2B illustrate the test results of oxidizing the chalcopyrite A sample with the finest particles at 290° C. An increase in weight was observed when water vapor was added to either air or oxygen. Figure 2A also illustrates that an increased rate of weight gain can be initiated when moisture is added to the atmosphere even after exposing the sample to dry air for 60 min. When this test was repeated at 300° C, the sample immediately ignited when exposed to the moist-air oxidizing atmosphere. Ignition was verified by the rapid weight loss and the glow observed through the glass wall of the furnace. After cooling, the sample was noted to have the red color characteristic of hematite. XRD analysis of the sample after oxidation confirmed that ferric oxide (hematite) had been formed.

The TGA results for chalcopyrite B (15- and 120-min grinds) oxidized in oxygen containing 40 pct water vapor are shown in figure 3A. This figure illustrates that over the temperature range of 100° to 400° C the finer material ignited at a lower temperature. Similar effects were noted when these samples were oxidized in air and in air containing moisture. The TGA data also indicate a weight gain in

TABLE 3. - Particle size analyses of chalcopyrite A, chalcocite A, and galena

Particle size fraction, μm				Sample cumulative volume, pct undersize		Sample volume, pct	
				15-min grind	120-min grind	15-min grind	120-min grind
CHALCOPYRITE A ¹							
Minus 42.21 plus 29.85.....				100.0	100.0	4.2	0.0
Minus 29.85 plus 21.10.....				95.8	100.0	7.1	.0
Minus 21.10 plus 14.92.....				88.7	100.0	5.3	.0
Minus 14.92 plus 10.55.....				83.3	100.0	7.5	.0
Minus 10.55 plus 7.46.....				75.7	100.0	4.8	.0
Minus 7.46 plus 5.27.....				70.9	100.0	20.6	15.1
Minus 5.27 plus 3.73.....				50.2	84.8	25.0	30.2
Minus 3.73 plus 2.63.....				25.2	54.6	7.9	18.9
Minus 2.63 plus 1.69.....				17.2	35.6	9.0	11.3
Minus 1.69 plus 1.01.....				8.2	24.2	6.1	13.8
Minus 1.01 plus 0.66.....				2.1	10.4	1.5	7.4
Minus 0.66 plus 0.43.....				.5	3.0	.5	2.2
Minus 0.43 plus 0.34.....				.0	.8	.0	.8
Minus 0.34 plus 0.24.....				.0	.0	.0	.0
CHALCOCITE A ²							
Minus 42.21 plus 29.85.....				100.0	100.0	0.0	0.0
Minus 29.85 plus 21.10.....				100.0	100.0	.0	.0
Minus 21.10 plus 14.92.....				100.0	100.0	.0	.0
Minus 14.92 plus 10.55.....				100.0	100.0	7.8	.0
Minus 10.55 plus 7.46.....				92.1	100.0	13.5	3.4
Minus 7.46 plus 5.27.....				78.6	96.5	30.8	31.3
Minus 5.27 plus 3.73.....				47.8	65.2	31.9	39.2
Minus 3.73 plus 2.63.....				15.8	26.0	11.6	16.7
Minus 2.63 plus 1.69.....				4.2	9.2	1.9	5.4
Minus 1.69 plus 1.01.....				2.2	3.8	1.6	2.3
Minus 1.01 plus 0.66.....				.5	1.4	.5	1.4
Minus 0.66 plus 0.43.....				.0	.0	.0	.0
GALENA ³							
Minus 42.21 plus 29.85.....				100.0	100.0	0.0	0.0
Minus 29.85 plus 21.10.....				100.0	100.0	5.5	.0
Minus 21.10 plus 14.92.....				94.5	100.0	6.9	1.8
Minus 14.92 plus 10.55.....				87.6	98.2	10.5	1.9
Minus 10.55 plus 7.46.....				77.1	96.3	14.5	5.3
Minus 7.46 plus 5.27.....				62.6	91.0	27.8	28.3
Minus 5.27 plus 3.73.....				34.9	62.7	24.3	32.4
Minus 3.73 plus 2.63.....				10.5	30.2	5.3	14.2
Minus 2.63 plus 1.69.....				5.2	16.0	2.9	9.9
Minus 1.69 plus 1.01.....				2.3	6.0	2.3	3.7
Minus 1.01 plus 0.66.....				.0	2.3	.0	1.2
Minus 0.66 plus 0.43.....				.0	1.1	.0	1.1
Minus 0.43 plus 0.34.....				.0	.0	.0	.1

¹Mean and median particle sizes: for the 15-min grind, 8.68 and 5.31 μm , respectively; for the 120-min grind, 3.40 and 3.42 μm , respectively.

²Mean and median particle sizes: for the 15-min grind, 5.78 and 5.55 μm , respectively; for the 120-min grind, 4.72 and 4.68 μm , respectively.

³Mean and median particle sizes: for the 15-min grind, 8.44 and 6.27 μm , respectively; for the 120-min grind, 4.83 and 4.43 μm , respectively.

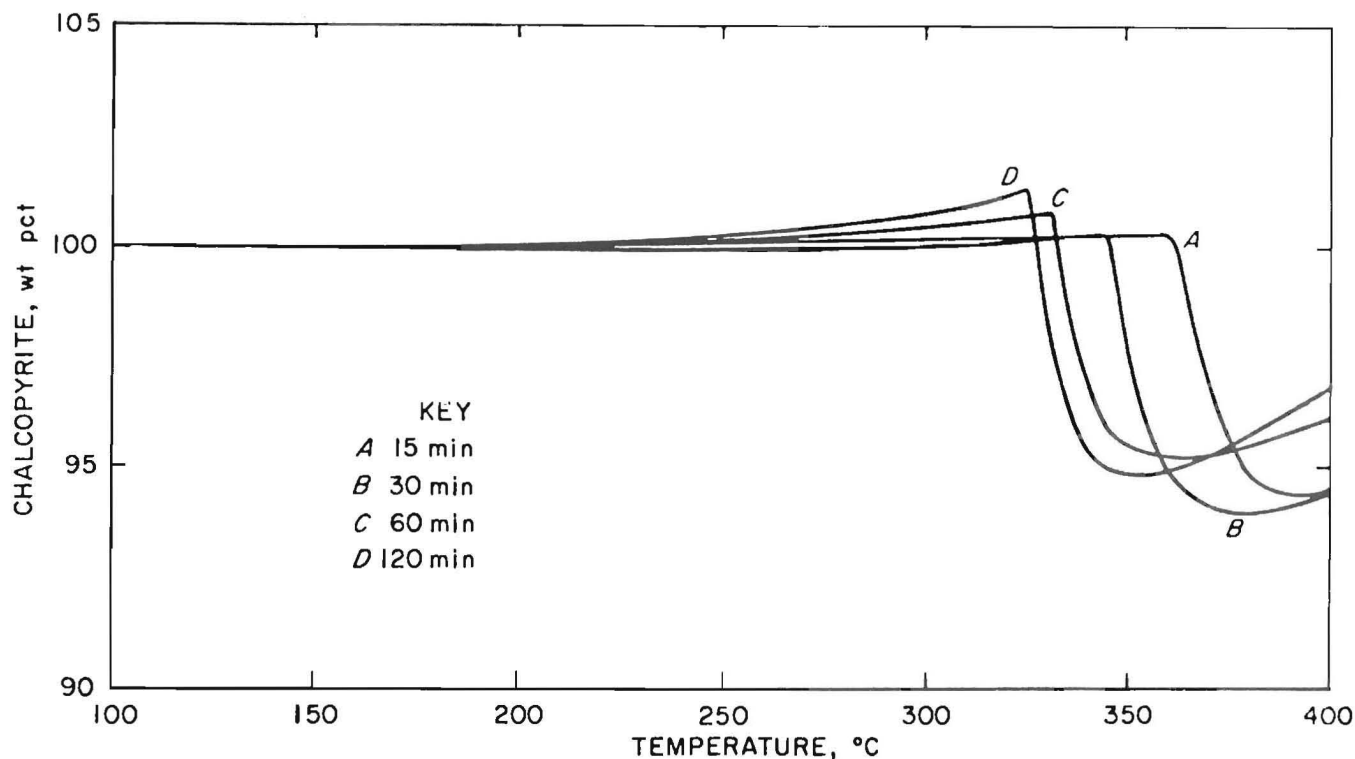


FIGURE 1.—Thermal gravimetric analysis illustrating effect of milling time on oxidation of chalcopyrite A in air.

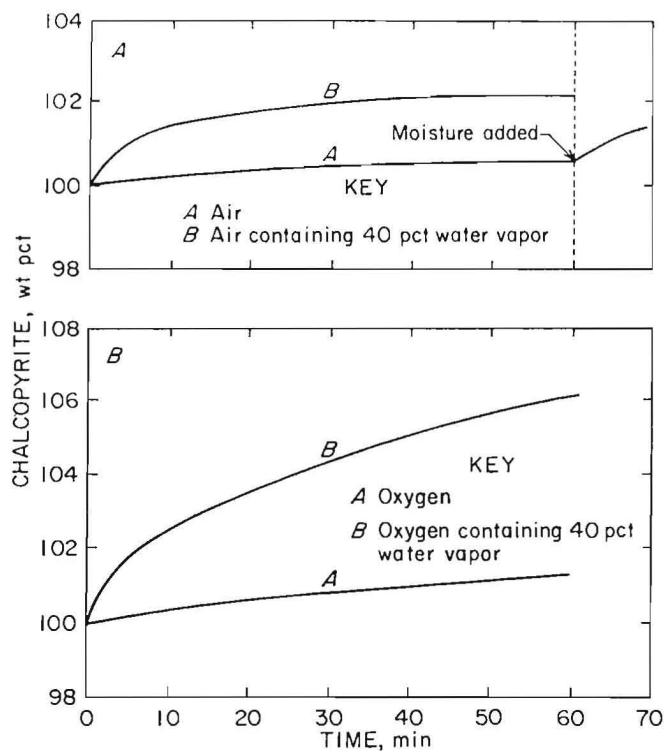


FIGURE 2.—Isothermal oxidation of chalcopyrite A at 290° C, (A) with air and air containing 40 pct water vapor and (B) with oxygen and oxygen containing 40 pct water vapor.

the sample prior to the rapid weight loss associated with ignition of the sulfide.

From these curves, the occurrence of several reactions can be postulated. The first reaction, as evidenced by the slight gain in sample weight prior to the rapid weight loss, was probably the partial oxidation of the iron sulfide fraction of the chalcopyrite sample to the sulfate. Although iron sulfate was not detected by XRD analysis of the partially oxidized samples, its presence was confirmed by dissolving the soluble sulfate from partially oxidized samples and then analyzing the leach solution by chemical methods. The rapid weight loss indicates a second reaction, the burning of iron sulfide to the oxide, which in turn provided additional heat to accelerate the subsequent rapid weight gain associated with a third reaction, the formation of copper sulfate. XRD analysis confirmed the presence of iron oxide in a sample of chalcopyrite B whose oxidation during TGA was interrupted when the sample reached its maximum weight loss. Analysis of a sample that was oxidized to a final temperature of 450° C indicated the presence

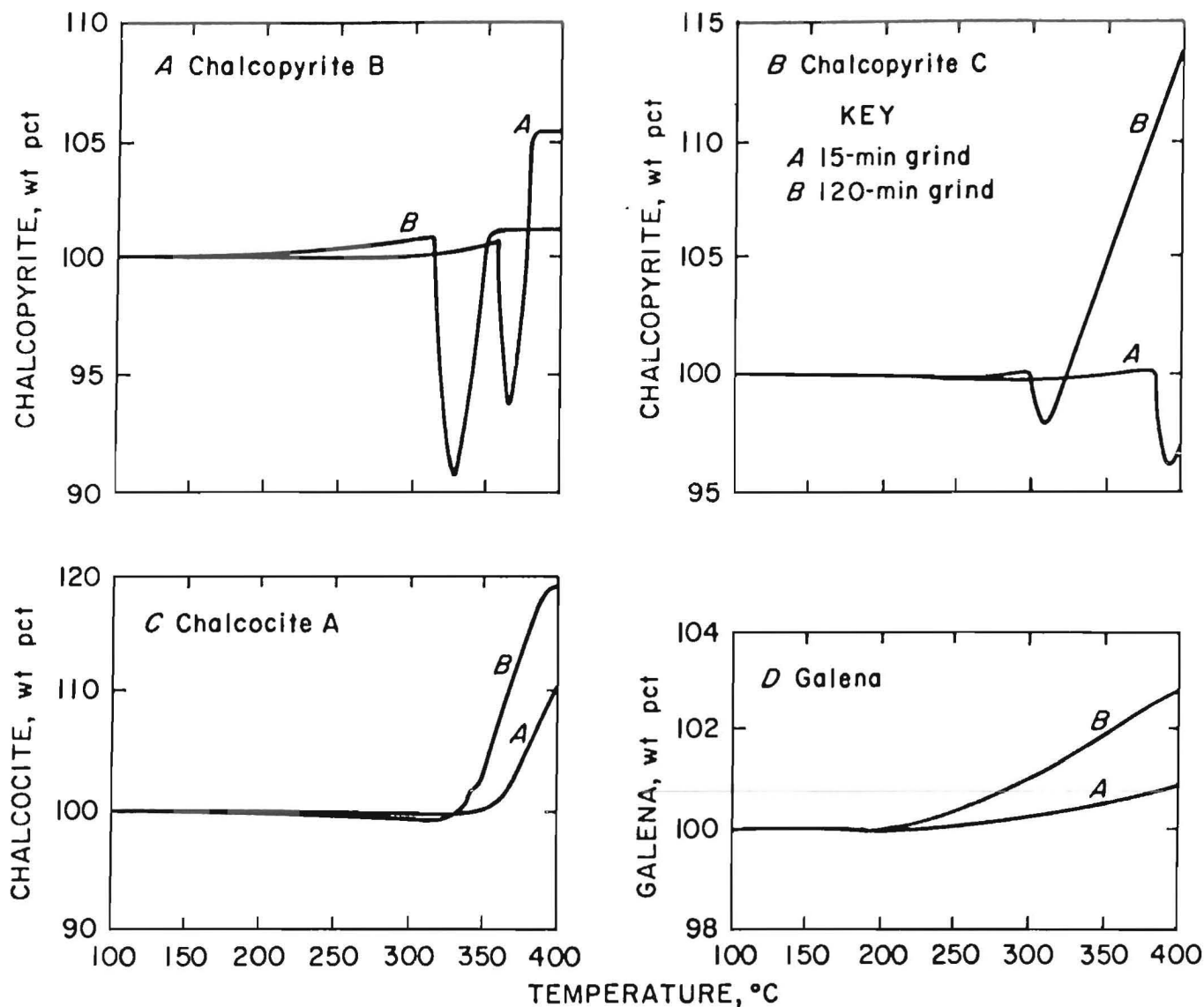


FIGURE 3.—Thermal gravimetric analyses of (A) chalcopyrite B oxidized with oxygen containing 40 pct water vapor, (B) chalcopyrite C oxidized with air, (C) chalcocite A oxidized with air, and (D) galena oxidized with oxygen containing 40 pct water vapor.

of iron oxide, copper sulfate, and cupric oxide.

Samples of chalcopyrite B that were ground to the finest particle size and then oxidized in air for 60 min at constant furnace temperatures of 280°, 310°, and 320° C are shown in figure 4A. The rate of sample weight gain increased as the test temperature increased. At 320° C, the sulfide was found to ignite, as indicated by the rapid initial weight loss. Following the weight loss, the chalcopyrite gained weight, indicating the conversion of copper sulfide to copper sulfate. In similar tests where

moisture was added to the oxidizing atmosphere, an increase in the rate of weight gain was noted at temperatures below the ignition point.

TGA results for sample chalcopyrite C, ground for 15 and 120 min and oxidized in dry air, are shown in figure 3B. The finest fraction of chalcopyrite C ignited at a lower temperature than was noted for samples A and B. It also underwent a smaller weight loss at ignition, which was probably a result of its lower iron content. Sample C also exhibited a tendency to gain weight prior to the rapid weight loss that occurred at ignition.

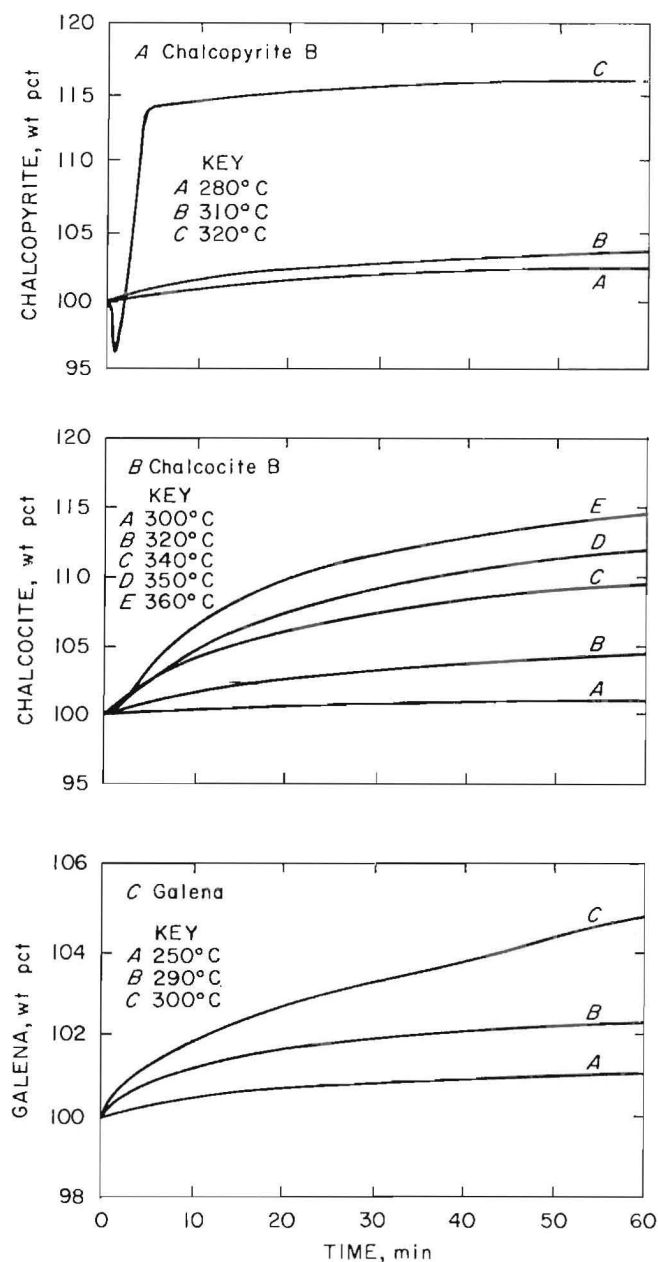


FIGURE 4.—Isothermal oxidation of (A) chalcopyrite B with air, (B) chalcocite B with air, and (C) galena with oxygen containing 40 pct water vapor.

Chalcocite

Chalcocite is copper sulfide having an orthorhombic crystal structure and the formula Cu_2S (9). TGA results for chalcocite A ground for 15 and 120 min are shown in figure 3C. In this test, the sulfide was oxidized in dry air, and the results indicate that in the range of 340° to 380° C the sample underwent a rapid weight gain, consistent with the

weight gain associated with copper sulfate formation. XRD analysis of the chalcocite after oxidation confirmed the presence of copper sulfate. The addition of moisture to the oxidizing gases had only a small effect on the behavior of the samples during TGA. The effect of moisture in the oxidizing atmosphere was also studied at a constant furnace temperature of 300° C. When the chalcocite ground to the smallest particle size was oxidized for 60 min in air containing 40 pct water vapor, it gained about 4 wt pct. This compares with a gain of 2 wt pct for samples oxidized in dry air.

TGA tests were also conducted on a second sample of chalcocite (sample B). The results of the analysis were very similar to those obtained for sample A. At test temperatures ranging from 300° to 360° C, weight gains were noted. Results of oxidizing sample B, ground to the smallest particle size, in dry air at fixed furnace temperatures ranging from 300° to 360° C, are shown in figure 4B. This figure illustrates the weight gain due to the formation of copper sulfate as a function of temperature. It also indicates that if chalcocite underwent slow heating in an oxidizing atmosphere, the sulfide would tend to be converted to the sulfate rather than igniting to form an oxide.

Galena

Galena (PbS), a lead sulfide, is the most common ore of lead and occurs as cubic crystals (9). TGA results for the galena sample oxidized in oxygen containing 40 pct water vapor are shown in figure 3D. This figure illustrates the higher reactivity of the finer samples. As the galena was heated to 400° C, a gradual gain in weight was seen. The abrupt weight change common to the copper sulfide samples was absent. Substituting air for oxygen had no measurable effect on the weight change results; however, the presence of moisture promoted the weight gain. Results of tests conducted on the finer sample of galena at constant furnace temperatures of 250°, 290°, and 300° C, with oxygen containing 40 pct moisture, are shown in figure 4C. XRD

analysis of the sample oxidized isothermally at 300° C confirmed that lead sulfate was formed.

Differential Thermal Analyses

DTA was also conducted on the various types of ore sulfides. These tests were conducted in an atmosphere of dry air and spanned a temperature range from 100° to 500° C. All of the sulfides were ground for 120 min prior to testing.

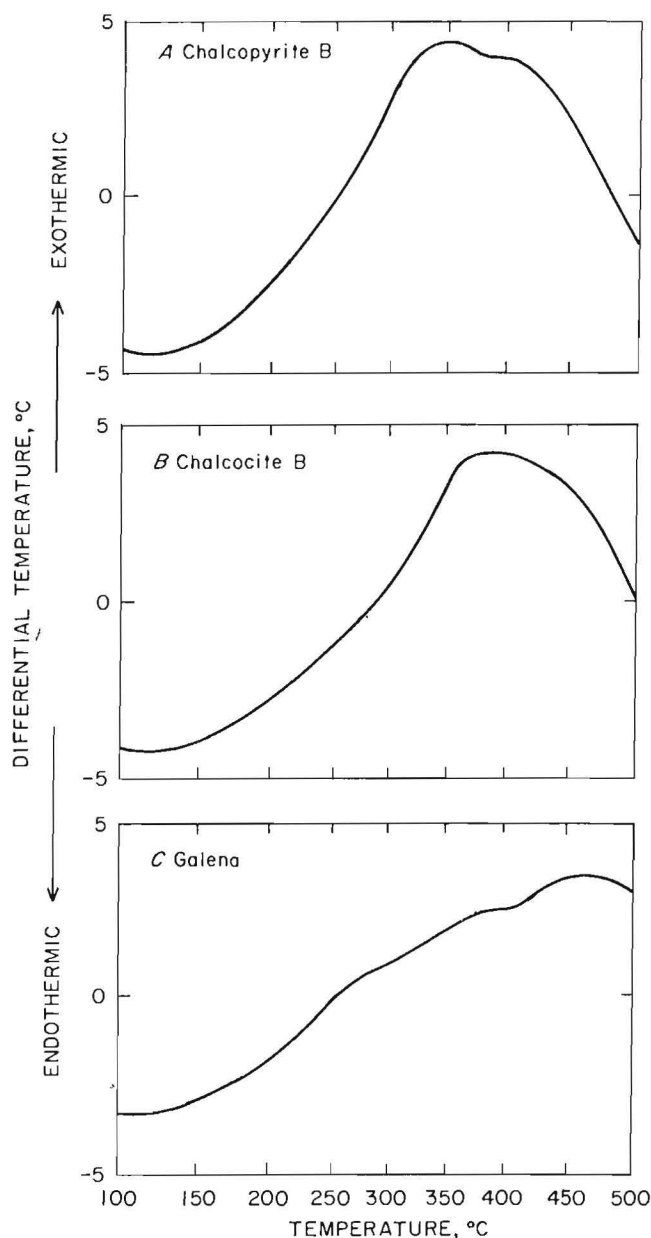


FIGURE 5.—Differential thermal analyses of (A) chalcopyrite B, (B) chalcocite B, and (C) galena milled for 120 min and oxidized with air.

Examination of the DTA results (fig. 5) indicates that exothermic behavior for both of the copper sulfides was initiated at about 150° C. The exothermic peak for the chalcopyrite is at about 310° C; the exothermic peak for the chalcocite is at about 370° C. These values are fairly close to the temperatures at which rapid weight change was first noted during TGA. The behavior of galena indicated a steady increase in exothermic behavior until the peak occurred at about 440° C. This is consistent with the steady gain in weight measured by TGA.

Discussion

The results of the thermal analysis experiments conducted on chalcopyrite, chalcocite, and galena samples show that increasing the grinding time, which should be synonymous with generating finer particles, increased the reactivity of the sulfides and caused them to ignite or undergo weight change at lower temperatures. Because the chalcopyrite samples contained about 50 pct iron sulfide, the evidence of ignition was based on the rapid weight loss during TGA and the red color of the sample after oxidation. In addition, the presence of ferric oxide in the oxidized samples was verified by XRD analysis. In the case of the chalcocite and galena, there was little color change following oxidation. However, in tests in which the chalcocite underwent rapid weight gain, it became sintered, indicating that the sample attained a temperature higher than the furnace temperature.

The thermal analysis data also revealed that oxygen did not strongly affect the ignition point, compared with the results obtained in an air atmosphere. However, the presence of moisture in the oxidizing atmosphere, whether air or oxygen, had the strongest promoting effect on increasing the weight gain of the chalcopyrite and galena samples. This was verified in tests where the sample was scanned over the temperature range of the experiment and in isothermal tests. This weight gain of the chalcopyrite sample prior to ignition was assumed to be due to the formation of sulfates. However, as the weight gain was small, the

presence of sulfates was not detected by XRD analysis. Further verification of sulfate formation by other methods and the role water vapor has on promoting its formation are areas for further research.

NON-ORE-TYPE SULFIDES

Sulfides that are considered gangue or byproducts were examined next: pyrrhotite, marcasite, and arsenopyrite.

Thermal Gravimetric Analyses

Pyrrhotite

Pyrrhotite was the first non-ore-type mineral examined in this test series. Pyrrhotite is expressed as $\text{Fe}_{n-1}\text{S}_n$, with n ranging from about 5 to 16. This iron sulfide mineral crystallizes in the hexagonal system (9). Results of tests conducted on pyrrhotite A, milled for 15 min, in the temperature range of 100° to 450° C, are shown in figure 6A. The sample weight change was monitored in nitrogen, air, and air containing 40 pct water vapor. For this pyrrhotite sample, the presence of water vapor failed to have an effect on the ignition point of the sample or the sample weight change at temperatures below 300° C. The sample weight loss while heating in nitrogen was likely due to the volatilization of sulfur. (The information on the sample weight change in a nitrogen atmosphere was included, because this group of minerals tended to exhibit a more pronounced weight loss during heating than was observed for the copper and lead sulfides. A similar observation at higher temperatures was reported by Chaubal and Sohn (10).)

Figure 6B illustrates the results of TGA on pyrrhotite A ground to a finer particle size by increasing the milling time to 120 min. Decreasing the sulfide particle size lowered the ignition point by about 50° C. Water vapor had little effect on the ignition point, and no effect was observed on oxidation in the lower temperature regions. At the completion of the oxidation tests, the samples were red, and XRD analysis confirmed the conversion of the sulfide to ferric

oxide. This sulfide was also tested isothermally at 330° C, and XRD analysis of the sample after oxidation for 2 h indicated that partial conversion to ferrous sulfate had occurred.

Results of TGA of pyrrhotite B milled for 120 min are shown in figure 6C. As observed for the previous pyrrhotite sample, the presence of water vapor had little effect on the ignition point of this sample. Water vapor did, however, promote the weight gain of this sample at lower temperatures. Ferrous sulfate was also detected in this sample after isothermal oxidation in air containing water vapor.

Marcasite

TGA conducted on the marcasite sample indicated that this was the most reactive sulfide tested to date. Marcasite is often called white iron pyrite and has the same chemical formula, FeS_2 , as pyrite. It is the orthorhombic dimorph of pyrite and is considered less stable (9). Figure 6D illustrates the TGA results for a sample ground for 120 min. It shows the weight changes during oxidation of the sulfide in air and in air containing 40 pct water vapor, as well as under inert conditions. The presence of water vapor in the oxidizing atmosphere had a strong influence on the ignition point of this sulfide. It was found to lower the ignition point to 257° C, which was 65° C below the value obtained in dry air. XRD analysis of the samples at the completion of testing indicated that the sulfide had been converted to ferric oxide.

The results of isothermal tests conducted on marcasite milled to the finest particle size and oxidized with air containing 40 pct water vapor are shown in figure 7. This figure illustrates the curves that were obtained for tests run at 190° and 200° C. At 190° C, the sample was found to slowly gain weight, and XRD analysis of the sample after oxidation for several hours indicated that the formation of ferrous sulfate had occurred. At 200° C, the sample immediately ignited. During thermal analysis of various sulfides, it has been observed, in the isothermal test, that the temperature

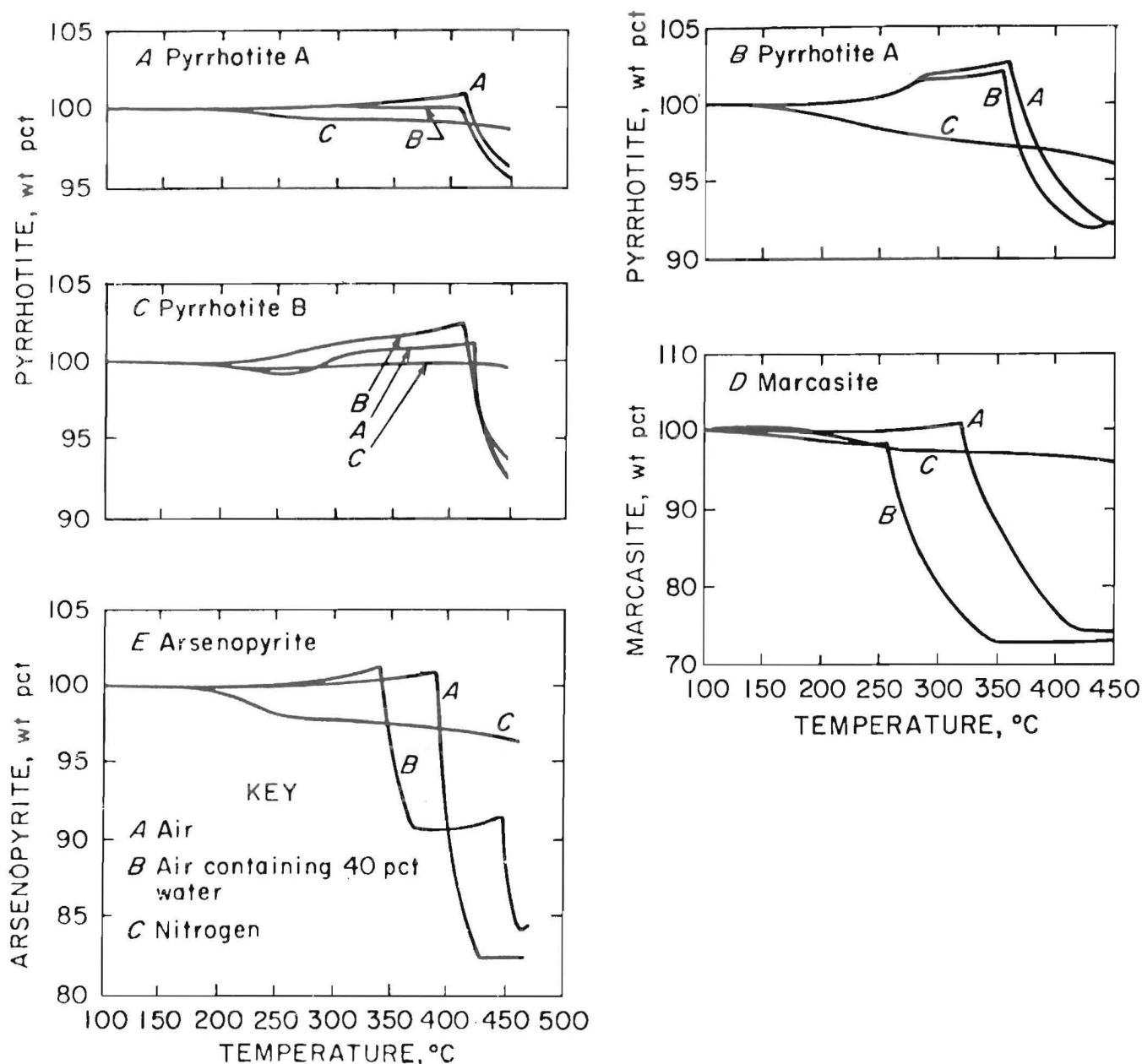


FIGURE 6.—Thermal gravimetric analyses of (A) pyrrhotite A milled for 15 min, (B) pyrrhotite A milled for 120 min, (C) pyrrhotite B milled for 120 min, (D) marcasite milled for 120 min, and (E) arsenopyrite milled for 120 min.

rise produced when oxygen reacts with the fresh sulfide surface induces ignition at lower temperatures than are obtained when the sulfide is being oxidized as it is heated during the TGA run.

Arsenopyrite

The final sulfide tested in this series was a sample of arsenopyrite. In this mineral, arsenic replaces a sulfur in

pyrite, making it a sulfarsenide of iron, FeAsS . This mineral crystallizes in the monoclinic system, with the crystals having a pseudo-orthorhombic symmetry because of twinning (9). Figure 6E illustrates the TGA results for a sample milled for 120 min. This figure shows that water vapor had the effect of lowering the ignition point of the sulfide and causing the sample to gain weight more rapidly at lower temperatures. For this

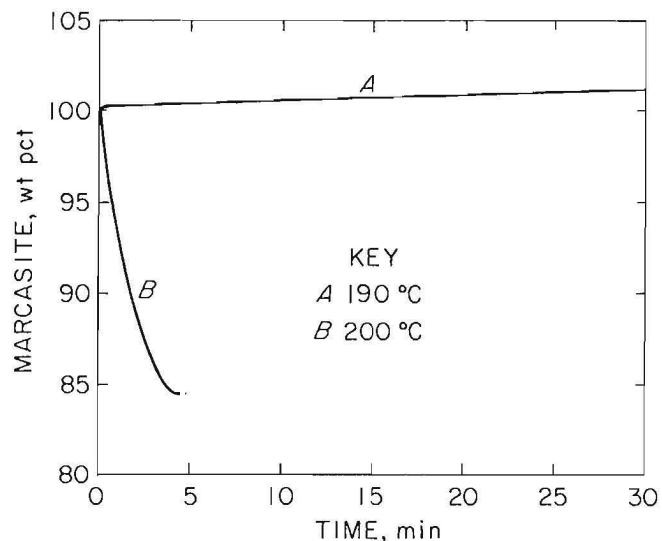


FIGURE 7.—Isothermal testing of marcasite milled for 120 min and oxidized with air containing 40 pct water vapor.

sample, water vapor lowered the initial ignition point from 372° to 337° C. The final temperature in these TGA tests was raised to slightly above 450° C to better illustrate the unusual double weight loss that occurred when the arsenopyrite was oxidized to the end of the first step, which was about a 10-pct sample weight loss. XRD analysis indicated the presence of hematite, but it failed to indicate if the iron sulfide or iron arsenide component of the mineral had oxidized.

Differential Thermal Analyses

The results of DTA on pyrrhotite A milled for 120 min are shown in figure 8A. This sample was oxidized in air containing 4.5 pct water vapor, and the DTA trace shows two prominent peaks in proximity to the areas of most rapid weight gain and weight loss shown in figure 6B. Based on the TGA results and XRD analysis, the exothermic peaks shown in figure 8A correspond to the formation of iron sulfate and then iron oxide. The DTA trace of pyrrhotite B was similar to that for sample A and included two exothermic peaks at 305° and 400° C. The DTA analysis of marcasite oxidized in an atmosphere of air containing 4.5 pct water vapor is shown in figure 8B. The single

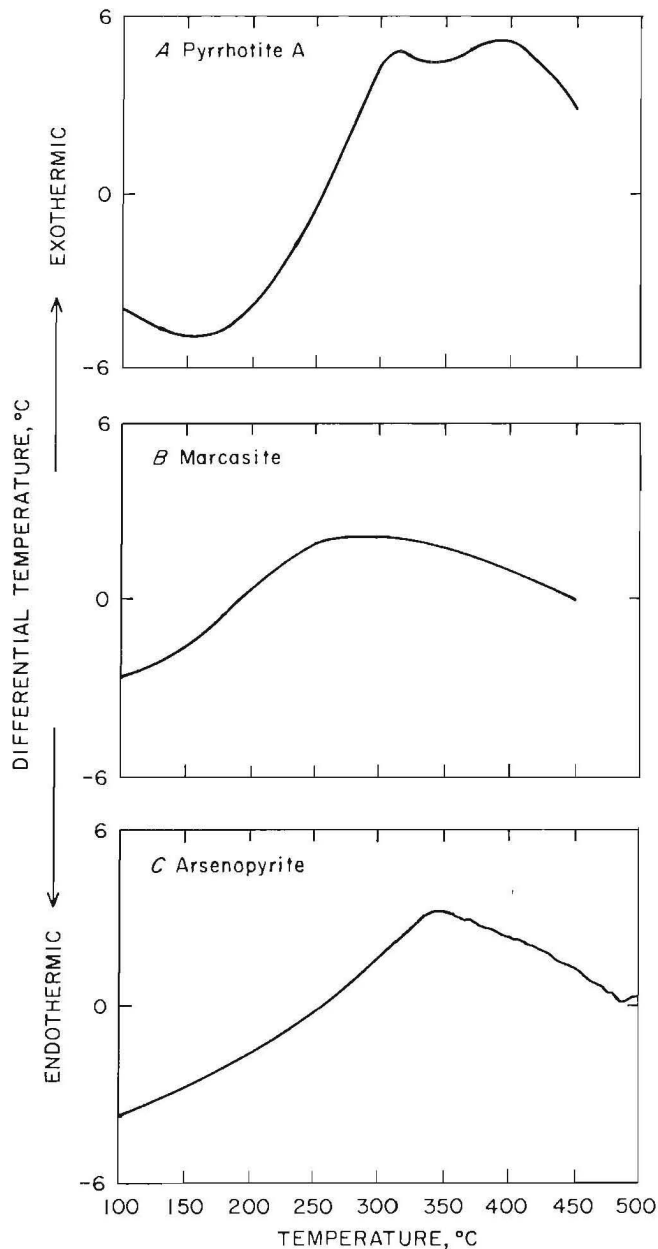


FIGURE 8.—Differential thermal analyses of (A) pyrrhotite A, (B) marcasite, and (C) arsenopyrite milled for 120 min and oxidized with air containing 4.5 pct water vapor.

broad peak reaches its maximum value at about 300° C. A shift of this peak to the left would be expected if additional water vapor could be added to the furnace assembly. Figure 8C is the DTA plot of arsenopyrite during oxidation in air containing 4.5 pct water vapor. A large peak was found at about 340° C, along with a minor peak that initiated at 480° C.

Discussion

The results of thermal analysis conducted on fine pyrrhotite, marcasite, and arsenopyrite showed that decreasing the particle size of the sulfide lowered the ignition point. Decreasing the particle size also increased the volatility of the sulfur, shown as sample weight loss during heating in nitrogen. Adding water vapor to the oxidizing atmosphere had little effect on the ignition point of the pyrrhotites tested in this investigation. The presence of water vapor did not enhance the weight gain or sulfate formation for pyrrhotite sample A, but it accelerated the weight gain prior to ignition for sample B. Ferrous sulfate was found in pyrrhotite samples following oxidation for several hours at temperatures below the sulfide ignition point.

The ignition point of marcasite was significantly lowered when water vapor was present during oxidation. Partial conversion of the sulfide to the sulfate below 200° C was verified.

Arsenopyrite was found to undergo an unusual double-step weight loss during oxidation in the presence of water vapor. XRD analysis was used to compare the oxidation products following the first weight loss and the second weight loss; however, the analysis failed to indicate

if the iron sulfide or iron arsenide component of the mineral underwent a single weight loss on ignition.

DTA indicated that marcasite and arsenopyrite reacted in an exothermic manner after oxidation was initiated at 100° C. However, pyrrhotite required heating to 140° to 150° C before exothermic behavior was initiated. This result suggests that the self-heating of pyrrhotite in a mine may be initiated by a mechanism other than sulfate formation from oxidation by air.

In this investigation, the sulfides were milled to very fine particle size to increase their reactivity. This enhanced the degree of weight change and allowed the completion of isothermal testing in a reasonable time span. From the thermodynamic data listed in table 1, it is apparent that the reactions that form sulfate could be a possible source of heat generation in a sulfide mine. The thermal analysis tests were conducted with equipment that has a high thermal loss, but future experiments are planned that will use larger samples in tests that will retain the heat from exothermic reactions. These tests are expected to verify if the sulfates formed by air oxidation in a warm, moist mine environment are part of the mechanism that leads to spontaneous combustion.

SUMMARY AND CONCLUSIONS

Common sulfide minerals, including chalcopyrite, chalcocite, galena, pyrrhotite, marcasite, and arsenopyrite, were subjected to thermal analysis using TGA and DTA methods. One condition of the thermal analyses required grinding of the sulfides to very fine sizes to promote their reactivity. This allowed the thermal analysis to be conducted at relatively low temperatures, and in experiments with fairly short timeframes. Samples were tested in atmospheres of nitrogen,

air, or oxygen with or without the addition of water vapor. Using the weight change of the samples under the various test conditions and the XRD analysis of the oxidized samples, reactions were proposed that could promote the heating of sulfides and eventually lead to a mine fire.

As expected, the sulfide samples that had the finest particle size were the most reactive. This increased reactivity provided test results indicating that

chalcopyrite, a common copper ore, underwent a weight gain prior to ignition. Evidence was found that this weight gain is related to the formation of ferrous sulfate, which is similar to the reactions that precede the ignition of pyrite. Upon ignition, or weight loss, of the chalcopyrite, some of the iron present in the sulfide is oxidized to ferric oxide. Following the weight loss, the chalcopyrite rapidly gained weight during the formation of copper sulfate. Chalcocite and galena did not exhibit the weight loss indicative of oxide formation in tests conducted below 450° C. However, chalcocite exhibited a rapid weight gain at a temperature just slightly above the ignition point of chalcopyrite. This weight gain was due to the formation of copper sulfate, and if an initial source of heat were present, the chalcocite could display a strong exothermic response. Galena underwent a steady weight gain as determined by the TGA method, and no rapid gain in weight was observed during the conversion of lead sulfide to lead sulfate. Based on the thermal analysis results, it appears that neither chalcocite nor galena would tend to ignite during the long periods of time that are usually associated with self-heating of sulfides in the mine environment. However, because both chalcocite and galena appear to form sulfates, they could contribute to the problem of self-heating.

For all three of the non-ore-type minerals, an exothermic weight gain was observed prior to the ignition point, caused by the formation of iron sulfate. The TGA results show that the ignition point of both marcasite and arsenopyrite was decreased when water vapor was included in the oxidizing atmosphere. Water vapor appeared to have little effect on the ignition point of pyrrhotite, and it had a mixed effect on promoting the formation of iron sulfate at temperatures below the ignition point of the sulfide. This suggests that water vapor has a lesser role in the exothermic behavior of this mineral. The self-heating of pyrrhotite is often suggested as the principal cause of spontaneous combustion fires in sulfide ore mines. However, of the minerals examined in this report, marcasite was found to be the most reactive in that it exhibited a self-heating tendency at the lowest temperature. As marcasite may be associated with pyrrhotite, but in much smaller quantities, its role in the spontaneous heating event may incorrectly be attributed to the pyrrhotite. The apparent higher reactivity of the marcasite could also be a result of specific parameters employed in the test program that differ from in-mine conditions. Further study is thus indicated to define the mechanism responsible for these self-heating tendencies.

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