THE AMERICAN MINERALOGIST, VOL. 43, JULY–AUGUST, 1958

DIFFERENTIAL THERMAL ANALYSIS OF SPHALERITE

OTTO C. KOPP AND PAUL F. KERR, *Columbia University, New York, N. Y.*

ABSTRACT

A relationship between iron content and differential thermal reaction temperature is shown to exist for sphalerite. Samples were heated in air using a modification of a recently developed technique described by Kopp and Kerr (1957). The thermal reaction products consist essentially of sulfur dioxide and zincite, but zinc ferrite or magnetite also appear as the iron content increases.

Several sphalerite samples covering a considerable range in iron content were subjected to differential thermal analysis under controlled conditions using quartz as an internal standard. Peak temperatures decreased from 821° C. for low iron sphalerite ($<0.1\%$ Fe) to 767° C. for sphalerite with 13% Fe. Plots of data shown indicate a relationship between D.T.A. peak temperature, iron content and the lattice constant.

Heating rate, grain size and sample weight require close control in determining peak temperature. Peak temperatures are found to decrease at about 3° C. for each ° C. per minute the heating rate is lowered. In the range between 7° C. and 12° C. per minute this correction may apply. Peak temperatures also decrease with a diminution in grain size, especially below 44 microns. The grain size found most suitable for analysis lies in the range 125–149 microns. Peak temperature shows a variation of less than $\pm 3°$ C. for a sample weight between 40 and 60 milligrams. Samples weighing less than 40 milligrams show a decrease in peak temperature.

INTRODUCTION

Recent studies by Hiller and Probsthain (1955) and Kopp and Kerr (1957) have made possible the application of differential thermal analysis to sulfide and arsenide minerals. Sphalerite has been selected for investigation as a part of a series of studies directed toward enlarged application of the D.T.A. method. The wide range in the iron content and common occurrence of sphalerite make it an interesting subject for study.

Kullerud (1953) has offered the significant suggestion that the iron content of sphalerite crystallized in an iron saturated environment is indicative of the temperature of formation. Differential thermal analysis is suggested as a possible supplement to chemical analysis or lattice constant determination in investigating the temperature range of sphalerite.

PROCEDURE

The method of differential thermal analysis used is a slight modification of the technique described by Kopp and Kerr (1957). The heating rate, grain size and sample weight were controlled within essential limits. Since differences of a few degrees are significant, quartz was used as an internal standard to establish a reference peak for temperature control.

The differential thermal peak temperature for quartz with the equipment used was found to be 580±2° C.*

Samples used to obtain a curve showing the relation between iron content and peak temperature were screened.† Only that portion lying in the range 125–149 microns was used. Sample weight was standardized at 50±1 milligrams. Only those thermal curves in which the heating rate showed an average of 11° C. to 12° C. per minute during the oxidation reaction were used, although several tests indicated that it may be sufficiently accurate to apply a correction factor to heating rates as low as 7° C. per minute. All analyses were made at the 200 scale reading on the recorder which corresponds to an amplification of 20× (Kulp and Kerr, 1949).

The samples were mixed with quartz (149–297 microns) in small glass vials and transferred directly to the sample well. The relatively large grains of quartz pack in a uniform manner as they are poured into the sample well. There was no apparent change in packing when the surface of the sample was tamped with a tool fashioned from copper tubing.

As far as possible specimens consisting of single crystals were selected for analysis, but this is difficult for black sphalerite with a high iron content. Megascopic pyrite, pyrrhotite, galena, chalcopyrite and other impurities were removed prior to grinding and the sieved samples were examined with the binocular microscope at 45× magnification. Minor amounts of impurities were removed by hand picking. In general the sphalerite specimens varied in color, except for the high iron sphalerites which were black. Since the peak temperature obtained is thought to reflect the iron present in the sphalerite lattice, the presence of exsolved pyrrhotite will affect the resultant curve. The chemical determination of iron does not in itself distinguish between iron present in sphalerite as FeS from that present as (Zn,Fe)S.

---

* Keith and Tuttle (1952) determined the inversion temperature for a number of quartz specimens and state that, "Approximately 70 per cent of all natural quartz specimens studied show an inversion break within the range 572.5°–573.5° C." The differential thermal peak temperature for quartz determined without the use of known standards is ordinarily about 7° C. high because it is determined under nonequilibrium conditions.

† For the convenience of the reader standard sieve sizes considered in these experiments are listed as follows:

Sieve No.	*Opening in Microns*
50	297
100	149
120	125
200	74
325	44

SPECTROCHEMICAL DETERMINATION OF IRON CONTENT

The authors are indebted to Mr. Arnold Silverman of Columbia University for suggesting the following method of analysis for iron in the sphalerite samples, and providing a standardized curve from which the per cent of iron could be read directly. The method involves dissolving a fixed weight of sample in nitric acid and converting the oxidized material to ferric chloride. The resulting solution is examined by means of the Cary Spectrophotometer. The procedure is as follows:

1. Weigh 0.250 gram of sample.
2. Slowly add 15 milliliters of concentrated nitric acid and after the reaction has subsided, 3 milliliters of 30% hydrogen peroxide.
3. Evaporate to dryness at constant heat.
4. Add 10 milliliters of concentrated hydrochloric acid and boil until all the residue is dissolved.
5. Allow to return to room temperature and bring volume back to 10 milliliters with constant boiling (760 mm. pressure) hydrochloric acid.
6. Decant the solution for an absorption curve on Cary Spectrophotometer.
7. Run the curve in the visible spectrum using slow chart speed; read wavelength in angstroms at optical density 0.5 as pen returns to the base line.

In most cases there was only enough sample for a single iron determination, but the analyses are considered to be accurate to within ±5% of the determined values.

CONTROL OF TECHNIQUE

The range in effects due to heating rate, grain size and sample weight indicates that unless these factors are adequately controlled, peak changes result which exceed the effect of iron content in decreasing the peak temperature of sphalerite. The importance of controlled conditions may be illustrated by noting that the observed temperature range for sphalerite from less than 0.1% to 13% Fe is approximately 54° C., while variations in grain size alone may produce a change in excess of 100° C. Thus prior to any discussion of the range in peak temperature with iron content it becomes necessary to consider the effects of heating rate, grain size, sample weight and proper control.

The Effect of Heating Rate

Ordinarily in D.T.A. determinations, other factors remaining the same, a heating rate between 10° C. and 15° C. per minute yields useful curves. In the current study, however, heating rate variations of as little as 1° C. per minute were observed to cause perceptible changes in peak temperature.

If grain size, sample weight, and heating rate are kept constant, peak temperatures for the same sample analyzed several times agree within

±3° C. However, due to the absence of tight seals in the apparatus, drafts may cause a considerable lowering of the heating rate. In general the heating rate was at least 10° C. per minute, but in a few cases it fell below (as low as 6° C. per minute in one instance). Analyses which showed critical lowering of heating rates were repeated. A group of corresponding peak temperatures obtained for identical samples with different heating rates is shown in Fig. 1. Dashed lines connect points which indicate peak temperatures for the same sample at different heating rates. The lines correspond in slope.

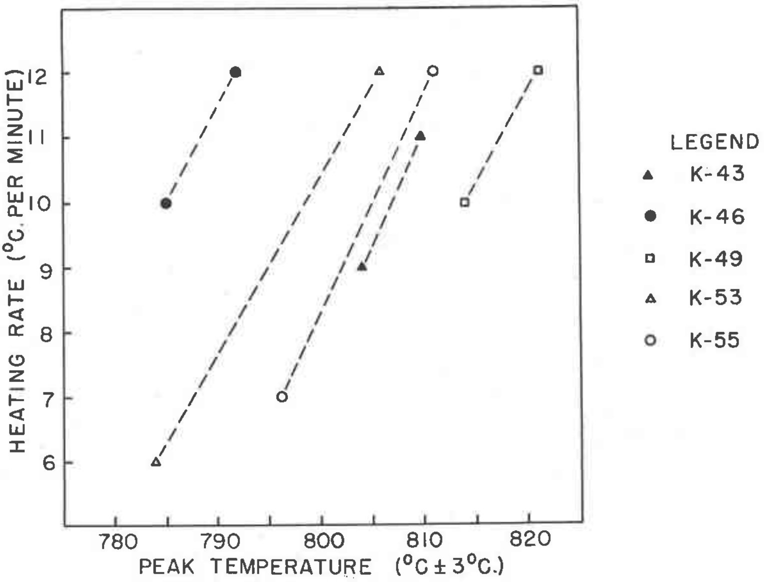

FIG. 1. Heating rate vs. peak temperature. Corresponding slopes of dashed lines connecting data for identical samples at different heating rates indicate an essentially linear relationship between peak temperature and heating rate.

The correction found applicable to low heating rates is illustrated in Fig. 2. The difference in peak temperature noted for the same sample at two different heating rates is plotted against the difference in heating rate for the two runs. A heating rate of 12° C. per minute is considered most satisfactory and serves as a datum for all corrections. Peak temperatures appear to decrease at the rate of about 3° C. for each degree per minute lowering of the heating rate. The slope of the curve appears to change at heating rates below 7° C. per minute.

It appears possible to correct curves in which the heating rate varies between 7° C. per minute and 12° C. per minute. However, in the curve relating sphalerite peak temperature to Fe content only those differential thermal curves which have a heating rate between 11° C. and 12° C. per minute over the range of the peak were used. A correction of +3° C. was added to peak temperatures obtained at 11° C. per minute and +1° C. to those obtained at 11.5° C. per minute.

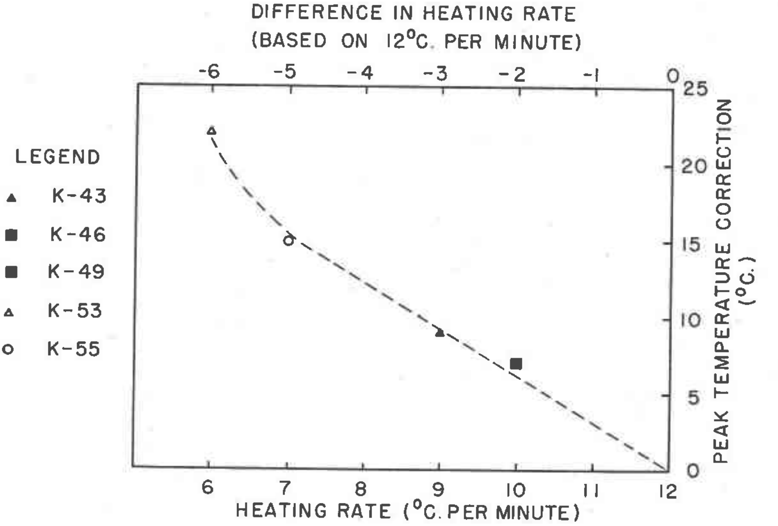

FIG. 2. Peak temperature correction. A correction of about 3° C. for each ° C. the heating rate is lowered appears applicable to heating rates below 12° C. per minute.

Effect of Grain Size

An attempt was made to evaluate the effect of grain size upon the differential thermal peak temperature. Sphalerite from Santander, Spain (Sample No. K-49) was crushed and sieved. The resulting grain size distributions were subjected to differential thermal analysis using a sample weight of 50±1 milligrams (except where noted). The results discussed below indicate that the most suitable grain size for analysis lies in the range 125–149 microns.

The peak temperatures obtained for several size distributions were plotted against the average grain size in microns. The average grain sizes for those samples less than 44 microns and larger than 297 microns are uncertain. The data are listed in Table 1. In order to establish the correct peak temperatures for the various grain sizes, the correction (3° C. per ° C. per minute) was applied.

Figure 3 illustrates a progressive decrease in peak temperature with

TABLE 1. THE EFFECT OF GRAIN SIZE UPON PEAK TEMPERATURE

Sieve No. Range	Diameter Range (Microns)	Peak Temperature (° C.±3° C.)	Heating Rate (° C. per Min.)	Correction (° C.)	Corrected Peak Temperature (° C.±3° C.)
< 50	>297	856	7	+15	871
< 50*	>297	851	8	±12	863
50–100	149–297	835	9	+ 9	844
50–100	149–297	833	9	+ 9	842
100–120	125–149	812	9	+ 9	821
100–120	125–149	816	10	+ 6	822
120–200	74–125	802	10	+ 6	808
200–325	44– 74	796	11	+ 3	799
>325	< 44	752	11	+ 3	755

* Sample Weight: 38±1 Milligrams.

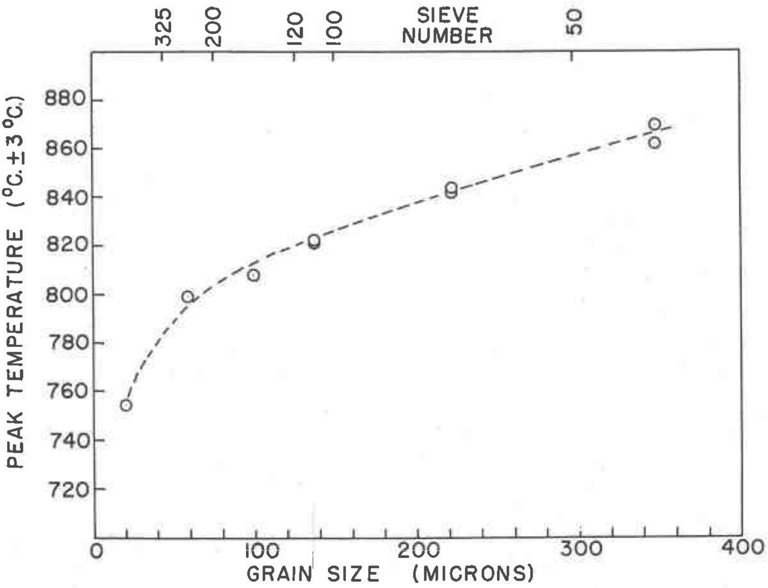

FIG. 3. Grain size vs. peak temperature. Peak temperature decreases with grain size, especially for particles finer than No. 325 sieve.

grain size. This reflects an increase in surface area for the same sample weight as the grain size decreases. Since the reaction is one of oxidation, it is assumed to proceed more rapidly when a greater surface area is available.

The diameter range from 125–149 microns was selected as most suitable for the following reasons:

1. Samples falling within this size range have the smallest possible variation in grain size, i.e. 24 microns, for the sieves available. The next smallest size range lies between 44–74 microns.
2. Samples within this size range lie on a relatively flat portion of the curve. If it were possible to prepare samples consisting essentially of the limiting grain sizes (125 microns and 149 microns) these peak temperatures would not appear to vary by more than ±3° C. from the temperature obtained from the average sample. On the other hand, between 44 and 74 microns the curve is relatively steep and the variation in peak temperatures of the end members might exceed 20° C. Below 44 microns the curve appears to be quite steep. Since the lower size limit cannot be controlled, variations in the average grain size will result in a wide peak temperature range.
3. Samples within this size range are relatively large and inspection under the binocular microscope is not too tedious.
4. During preparation of the specimens for differential thermal analysis, when the grains are mixed in a glass vial with quartz (or alumina) the particles do not adhere to the walls of the vial. This may occur with the finer particles, especially below 44 microns.

Effect of Sample Weight

Samples of sphalerite from Santander, Spain (Sample No. K-49) ranging in weight from 10 milligrams to 60 milligrams (in increments of 10 milligrams) were run to determine the effect of sample weight on peak position and shape.

The peak temperatures, peak heights, peak widths (at one-half the peak height) and estimated peak areas (obtained by multiplying the peak height by the peak width at one-half the peak height) are listed in Table 2. An evaluation of data appears in Fig. 4. Peak temperatures are corrected for heating rate variations.

TABLE 2. EFFECT OF SAMPLE WEIGHT ON PEAK TEMPERATURE (125–149 MICRONS)

Weight (Mg.)	Peak Temp. (° C. ±3° C.)	Heating Rate (° C. per min.)	Correction (° C.)	Corrected Peak Temp.	Height (Mm.)	Width (Mm.)	Area (Mm.^{2})
10	809	12	—	809	22	22	484
20	810	11	+3	812	39	23	897
30	809	10	+6	815	59	24	1316
40	820	11	+3	823	71	24	1704
50	819	12	—	819	94	25	2350
60	820	11	+3	823	103	26	2678

A sample weight of 50 milligrams was found most suitable for comparison. This weight lies on the flat portion of the temperature curve. The variation in peak temperature between 40 and 60 milligrams is within ±3° C. The total error in the sample weight analyzed, including possible weighing errors and losses during mixing and transfer of material to the sample well is thought to be within ±5% and in most cases within ±2% of the sample weight.

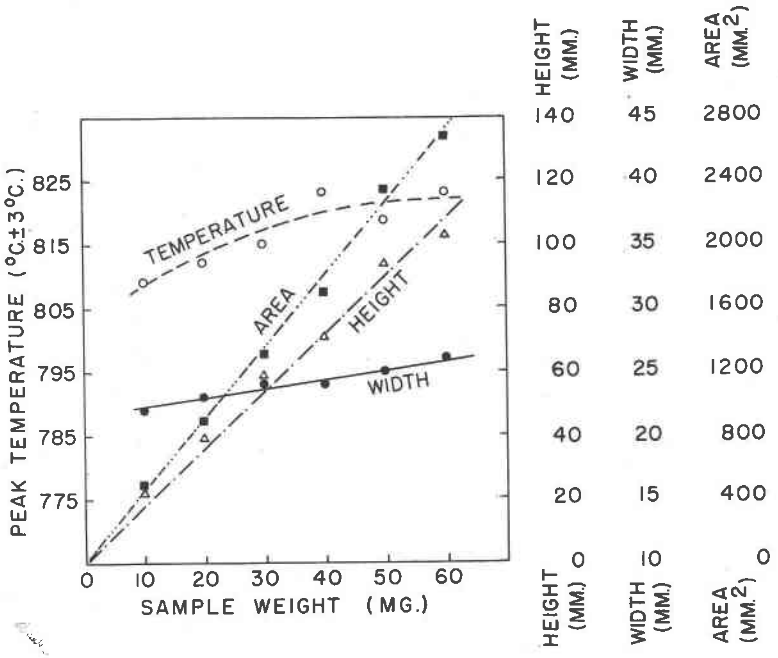

FIG. 4. Sample weight vs. peak dimensions. Peak height, width and area appear to be related linearly to the sample weight. Peak temperature decreases slightly below 40 mg.

A decrease in peak temperature occurs for samples weighing less than 40 milligrams, although the total decrease is only on the order of 10–15° C. The determination of peak temperature for samples weighing less than 40 milligrams becomes increasingly more difficult because the peaks spread and become broader as the sample weight decreases. Peak width decreases slowly compared with peak height. This results in a broader peak for a small sample weight.

The decrease in peak temperature for samples weighing less than 40 milligrams may be of interest. During the oxidation of the sphalerite, sulfur dioxide is produced. This gas must escape from the sample well before oxidation can proceed. The escape of sulfur dioxide and supply of additional oxygen appear to occur simultaneously. As the amount of sample decreases, the volume of sulfur dioxide produced also decreases. Proportionately more oxygen becomes available and causes more rapid oxidation. Thus, with more rapid oxidation a slightly lower peak temperature may be observed.

Possible application in the determination of the relative constituents of a mineral mixture is suggested by the decreasing size of peaks with respect to height, width and area. For a single specimen, peak height, width and area decrease in a substantially uniform manner. Quantitative determinations may be best related to peak area since peak height and width may vary for the same weight of sample for different specimens.

THE NATURE OF THE REACTION

Sphalerite and other zinc sulfide polymorphs are converted to zinc oxide when heated in air. Prewitt-Hopkins and Frondel (1950) state, "Crystals or small cleavage pieces of the five known polymorphs of zinc sulfide when heated in air for 16 hours at 800° C. were found by *x*-ray study to be converted in every instance to the ordinary form of zinc oxide (zincite)."

X-ray examination of sphalerite from Santander, Spain (Sample K-49) indicates that oxidation occurs during the differential thermal analysis of the sample. During the course of the exothermic reaction, the sulfur is oxidized to sulfur dioxide and the zinc to zinc oxide (zincite). The differential thermal curve appears to indicate that the reactions occur simultaneously. The final product is found by *x*-ray study to be zincite (Table 3).

TABLE 3. REACTION PRODUCT OF SPHALERITE (SAMPLE K-49)

Sample K-49 Residue*		Zincite†	
d(Å)	I	*d*(Å)	I
2.819	70	2.816	71
2.615	40	2.602	56
2.484	100	2.476	100
1.912	20	1.911	29
1.625	30	1.626	40
1.477	30	1.477	35
—	—	1.407	6
1.379	20	1.379	28
1.360	10	1.359	14

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

† Swanson, H. E. and Fuyat, R. K., 1953, Standard *X*-ray Diffraction Powder Patterns, N.B.S. Circ. 539, v. II, p. 26.

Copper radiation, high angle diffractometer.

The nature of the reaction for sphalerite containing iron is of interest. Sphalerite from Troy, Montana (Sample K-52) which contains 6.9% Fe was examined by means of *x*-ray diffraction after oxidation had been accomplished during differential thermal analysis. Zincite still appears to be the major component, but some additional lines are observed. The spacings of these lines is such that the material formed could be either zinc ferrite or magnetite (Table 4).

Table 4. Reaction Products of High Iron Sphalerite (Sample K-52)

Sample K-52 Residue*		Zincite†		Zinc Ferrite‡		Magnetite§	
d(Å)	I	*d*(Å)	I	*d*(Å)	I	*d*(Å)	I
—	—	—	—	4.84	20	4.86	30
2.97	5	—	—	2.98	50	2.97	60
2.816	70	2.816	71	—	—	—	—
2.601	40	2.602	56	—	—	—	—
2.547	10	—	—	2.53	100	2.53	100
2.473	100	2.476	100	—	—	—	—
—	—	—	—	2.43	10	2.425	10
—	—	—	—	2.10	40	2.097	50
1.912	30	1.911	29	—	—	—	—
—	—	—	—	1.72	40	1.714	40
1.622	50	1.626	40	1.62	70	1.615	60
1.487	5	—	—	1.49	80	1.484	70
1.474	30	1.477	35	—	—	—	—
1.377	20	1.379	28	—	—	—	—
1.357	10	1.359	14	—	—	—	—

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

† Swanson, H. E. and Fuyat, R. K., 1953, Standard *X*-ray Diffraction Powder Patterns, N.B.S. Circ. 539, **II**, 26.

‡ Posnjak, E., 1930, The crystal structures of magnesium, zinc and cadmium ferrites, *Am. Jour. Sci.*, 19, 67.

§ Rooksby, H. P., 1951, Oxides and hydroxides of aluminum and iron; *X*-ray Identification and Structures of Clay Minerals, G. W. Brindley, ed., Mineralogical Society, London, 345 pp.

The differential thermal curves for high iron sphalerites indicate that the oxidation reactions occur simultaneously. Sulfur is oxidized to sulfur dioxide, zinc goes to zinc oxide (zincite) and the iron present yields either zinc ferrite, magnetite or both. The pattern obtained is too weak to discern many of the zinc ferrite or magnetite lines. They are closely related in structure and spacings (Table 4), and would be difficult to distinguish even if complete patterns were available. Particles of the

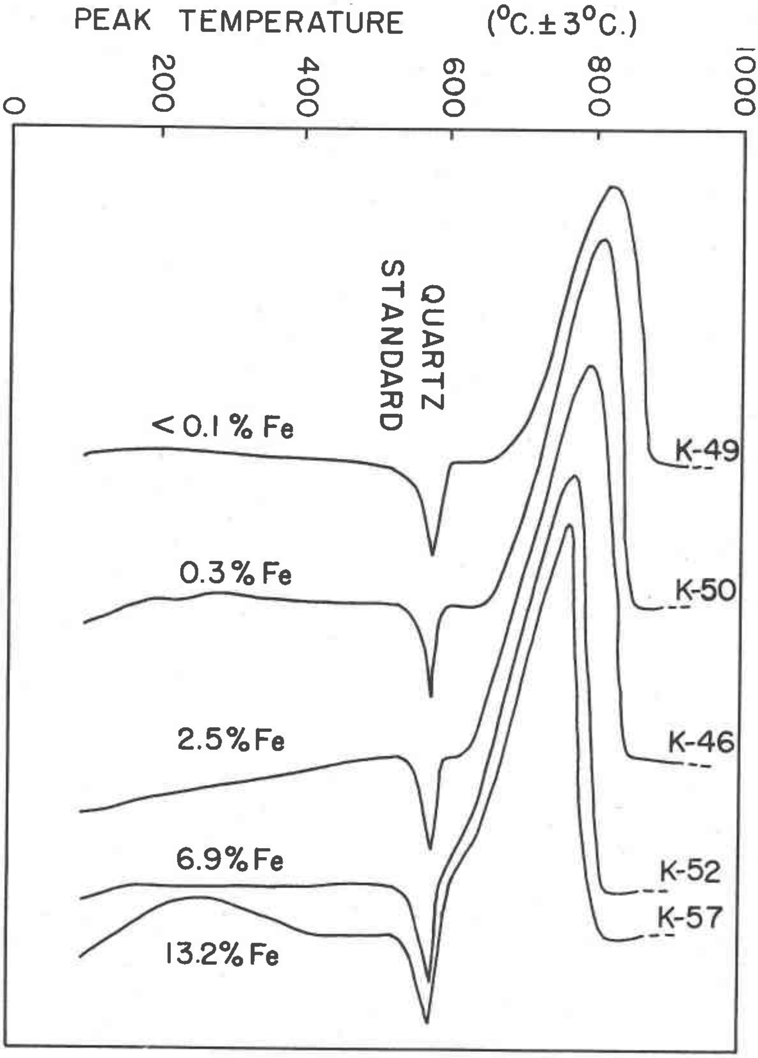

FIG. 5. Selected differential thermal curves of sphalerite. The peak temperature of sphalerite decreases with increasing iron content.

oxidized material tested with an Alnico magnet exhibit no magnetic properties.

IRON CONTENT AND PEAK TEMPERATURE

The peak temperature of sphalerite was observed to decrease with increasing iron content as illustrated in Figs. 5 and 6. Twenty-four samples were selected for analysis as outlined in the section on procedures. Of these samples twelve were rejected for one or more of the following reasons:

1. Presence of lead, copper or cadmium as indicated by the *x*-ray spectrograph. (Some manganese was present in the high iron samples.)
2. Presence of exsolved pyrrhotite or other impurities in the 125–149 micron fraction visible under 45× magnification.
3. Presence of additional peaks in the thermal record (other than quartz).
4. Peak area of differential thermal curve less than 2000 mm.^{2} for a 50 mg. sample.

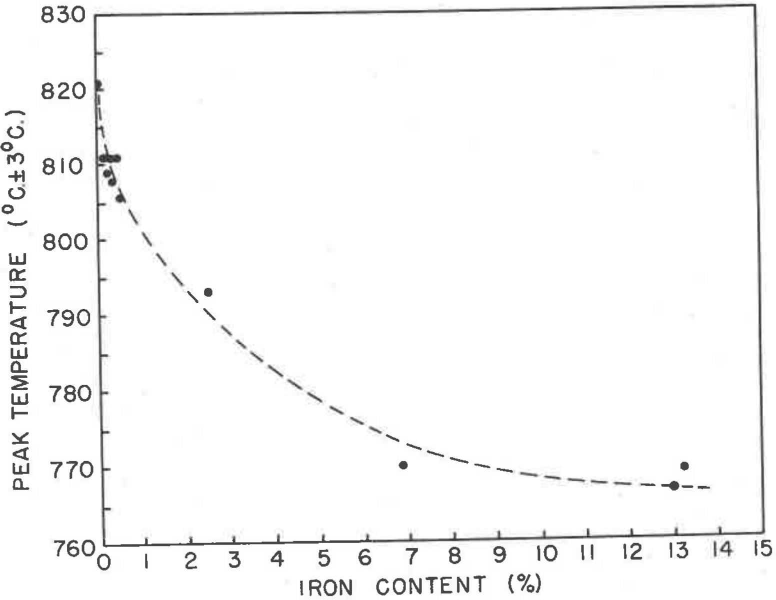

Fig. 6. Iron content vs. peak temperature. The presence of iron in the sphalerite lattice causes a decrease in the peak temperature. Iron contents greater than 7 per cent do not appear to materially affect the peak temperature.

Data for the twelve remaining samples are listed in Table 6 and illustrated in Figs. 5 and 6. Corrected peak temperatures were determined by adding to the observed peak temperatures the correction based on the heating rate and also a correction based on the peak temperature of the quartz standard. This accounts for a temperature difference of ±2° C., corresponding to the peak temperature range of 580±2° C. (Table 5).

Thermal records in which the quartz peak did not fall within these limits were rejected. The variation of the quartz peak temperature is apparently due to minor shifts of the thermal head in the furnace.

TABLE 5. QUARTZ PEAK CORRECTION

Quartz Peak (° C.)	Correction (° C.)
578	+2
579	+1
580	0
581	−1
582	−2

TABLE 6. DATA FOR SPHALERITE VS. IRON CONTENT CURVE

Sample Number	Location	Color of Grains	Iron Content (%) (±5% of Value)	Peak Temperature (° C. ±2° C.)	Quartz Peak (° C. ±2° C.)	Heating Rate (° C. (° C. per Min.)	Correction (° C.)*	Peak Temperature Corrected (±3° C.)
K-49	Santander, Spain	Colorless—Yellow	less than 0.1	819	578	12	+2	821
K-30	Friedensville, Pennsylvania	Colorless—Yellow	0.1	808	580	11	+3	811
K-44	Cananea, Mexico	Colorless—Orange	0.2	810	580	11.5	+1	811
K-50	Oklahoma	Yellow—Orange	0.3	810	579	12	+1	811
K-43	Minaret, Germany	Yellow—Orange	0.5	810	580	11.5	+1	811
K-33	Kiffin, Ohio	Colorless—Orange	0.2	809	580	12	—	809
K-59	Jasper Co., Missouri	Colorless—Orange	0.3	808	580	12	—	808
K-53	Barren Grounds, N.W. Territory	Colorless—Black	0.5	808	582	12	−2	806
K-46	Cumberland, England	Colorless—Orange	2.5	792	580	11.5	+1	793
K-52	Troy, Montana	Black	6.9	768	579	11.5	+2	770
K-57	Rodna, Transylvania	Black	13.2	771	582	12	−2	769
K-58	Kokomo, Colo.	Black	13.0	768	581	12	−1	767

* The correction applied includes both heating rate changes and also the variation in the peak temperature of quartz.

Figure 6 illustrates the decrease in peak temperature for sphalerite with increasing iron content. The slope of the curve is quite steep at first, but it gradually decreases. Peak temperatures do not decrease appreciably for iron contents greater than 7%, but the validity of the curve in this region is uncertain. Most sphalerite containing iron in excess of 6% is black and it is difficult to determine whether all the iron is present in the sphalerite lattice, or if part of the iron has exsolved as pyrrhotite. In the event that exsolution has occurred, the curve will be displaced, since only that iron which is in the lattice is believed to affect the peak temperature.

Peak Temperatures and Lattice Constants

Kullerud (1953) has shown that the lattice constant of sphalerite increases with replacement of Zn by Fe, Mn and Cd. Replacement by iron causes the lattice constant to increase from 5.3985±0.0001 Å for synthetic sphalerite containing 0% Fe to 5.4134±0.0002 Å for sphalerite containing 36.5% Fe. The rate of increase in lattice constant when Mn substitutes for Zn is greater than for Fe, and the rate of increase when Cd substitutes for Zn is even greater. Kullerud states, "Thus the increase obtained when 1.0 mol. % CdS is dissolved in the ZnS lattice is equal to that caused by 3.6 mol. % MnS or to 11.5 mol. % FeS."

The relationship between the differential thermal peak temperature and the lattice constant appears to be of interest. It was hoped that some correlation could be made between Kullerud's lattice constant determinations based on iron content and the differential thermal peak temperature based on iron content. However, several problems exist. The lattice constant for a synthetic sphalerite (Swanson and Fuyat, 1953) containing 0.01 to 0.1% Cu, 0.001 to 0.01% B, Fe, Mg and Si, and less than 0.001% of Al and Ca was determined to be 5.4060 Å. If this value is placed in Kullerud's curve relating lattice constant with Fe content, the specimen would yield an anomalous 19% Fe. Also, Smith (1955) determined the lattice constants of forty natural specimens of sphalerite. The lattice value ranged from 5.4073 to 5.4246 Å (one specimen from Bolivia had a lattice constant of 5.4806, but this specimen proved to be hexagonal rather than isometric). The relationship of lattice constant to specimen color appears to be rather vague although color is thought to be a good indicator of replacement by foreign ions. Smith also showed that varying amounts of hexagonal packing are to be found in isometric sphalerites.

The lattice constants of seven sphalerite specimens were determined using the Debye-Scherrer method. Iron radiation was used, the period of exposure being from 32 to 48 hours. Films were corrected for shrinkage by the Straumanis technique. All measurements were made on a device capable of readings to 0.05 mm. The lattice constants were determined from the (511) reflections (Table 7).

Table 7. Lattice Constants of Selected Sphalerite Specimens*

Specimen Number	Lattice Constant†	Per Cent Fe	Peak Temperature (±3° C.)
K-49	5.4082	less than 0.1	821
K-50	5.4087	0.3	811
K-46	5.4103	2.5	793
K-52	5.4160	6.9	770
K-57	5.4196	13.2	769

* Lattice constants for samples K-30 and K-53 are omitted from Table 7 and Figures 7 and 8. Sample K-30 appears to contain a relatively large amount of hexagonal packing which may affect the lattice constant determination. Sample K-53 exhibits a color range from colorless to black which is the widest color range of any of the specimens considered in the entire problem. The lattice constant determined for this specimen is probably questionable, and therefore was not used.

† Fourth place uncertain.

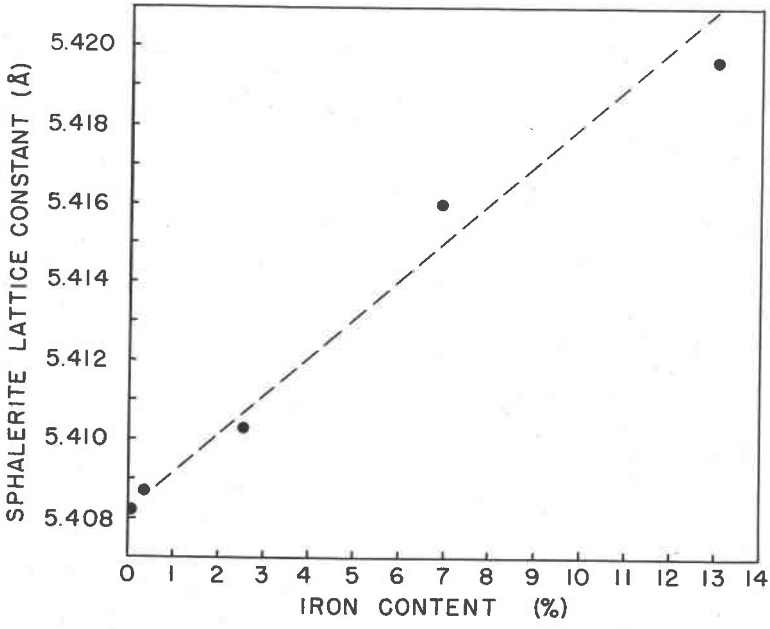

Fig. 7. Iron content vs. lattice constant. The lattice constant appears to increase linearly with increased iron content.

The lattice constant appears to increase with increasing iron content. The relationship of lattice constant to iron content is illustrated in Fig. 7, and that of lattice constant to differential thermal peak temperature is shown in Fig. 8.

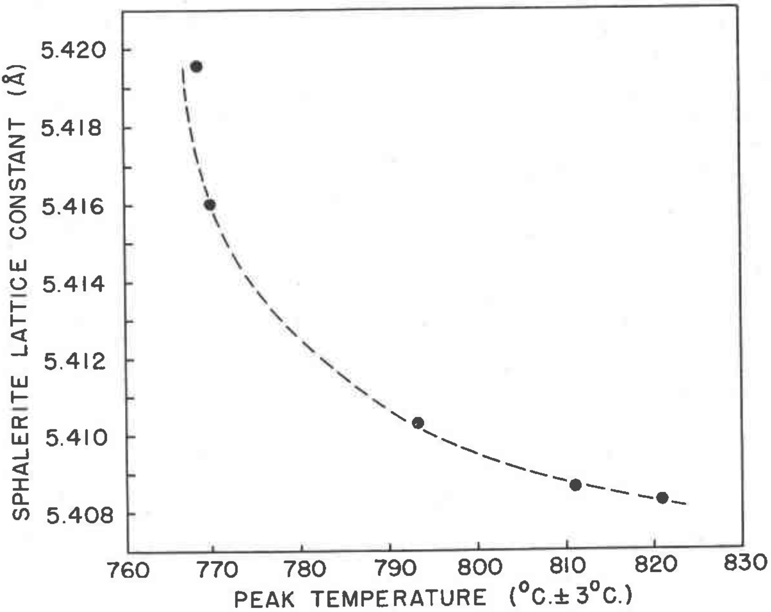

FIG. 8. Peak temperature vs. lattice constant. The peak temperature of sphalerite appears to decrease with increasing lattice constant as a result of increasing iron content.

CONCLUSIONS

Differential thermal analysis has been applied to sphalerite showing a relatively wide range in iron content. The observed progressive change in peak temperature with composition is of interest in investigating composition changes in relation to other factors such as lattice constants and temperatures of formation. Similar studies with other sulfides and arsenides may be possible. Quantitative as well as qualitative mineralogical determinations may be realized if the relation of the peak area to the amount of sample is consistent both in ore mixtures and in purified samples.

REFERENCES CITED

HILLER, J. E. AND PROBSTHAIN, K. (1955), Eine apparatus für die differentialthermoanalyse von sulfiden: Erzmetall, **VIII,** 257–267.

KEITH, M. L. AND TUTTLE, O. F. (1952), Significance of variation in high-low inversion of quartz: *Am. Journ. Sci.,* **Bowen Vol.,** 203–280.

KOPP, O. C. AND KERR, P. F. (1957), Differential thermal analysis of sulfides and arsenides: *Am. Mineral.*, **42,** 445–454.

KULLERUD, G. (1953), The FeS-ZnS system, a geological thermometer: *Norsk Geol. Tidssk.*, **32,** 61–147.

KULP, J. L. AND KERR, P. F. (1949), Improved differential thermal analysis: *Am. Mineral.*, **34,** 839–844.

POSNJAK, E. (1930), The crystal structures of magnesium, zinc and cadmium ferrites: *Am. Jour. Sci.*, **19,** 67–70.

PREWITT-HOPKINS, J. AND FRONDEL, C. (1950), Thermal decomposition of zinc sulfide polymorphs: *Am. Mineral.*, **35,** 116.

ROOKSBY, H. P. (1951), Oxides and hydroxides of aluminum and iron: *X*-ray Identification and Structures of Clay Minerals, G. W. Brindley ed., Mineralogical Soc., London, 345 pp.

SMITH, F. G. (1955), Structure of zinc sulphide minerals: *Am. Mineral.*, **40,** 658–675.

SWANSON, H. E. AND FUYAT, R. K. (1953), Standard *X*-ray Diffraction Powder Patterns: *U. S. Bur. Stands. Circ.* **539.**

Manuscript received November 14, 1957