VARIATIONS IN DIFFERENTIAL THERMAL ANALYSIS CURVES OF SIDERITE*

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ABSTRACT

The several reported variations in DTA curves of siderite are reproduced from samples of the same siderite by varying the particle size, dilution, and tightness of packing. The relationship between these variables and the suppression of the endothermic loop associated with the loss of CO_2 is shown by a set of curves. By controlling the ambient furnace atmosphere, with a cover over the sample or with an inert gas, the exothermic loops accompanying the oxidation of the iron oxide resulting from decomposition of the $FeCO_3$ can be delayed or completely suppressed. The results of x-ray diffraction studies of samples heated to several different temperatures are used in interpreting the DTA curves.

The method of differential thermal analyses is based on the simultaneous heating in a furnace of two substances, one, the material to be analyzed, the other, an inert substance which is known to undergo no phase changes nor chemical reactions in the temperature range to be studied. As the temperature of the furnace is raised at a regular rate, the difference in temperature between the two substances is measured and recorded. By convention, exothermic deflections, when the sample temperature is greater than the temperature of the inert material, are oriented upwards, and endothermic deflections are oriented downward.

With the recent improvement of DTA techniques and their application to the study of fine-grained sediments, there has developed the problem of detecting and identifying non-argillaceous minerals that may be present in sediments. Differential thermal analysis curves for various clays are reasonably well defined, and the relatively pure minerals can usually be recognized. However, while the presence of some accessory minerals has but little effect on the characteristic clay curve, others, even in small quantity, interfere with the diagnostic portion of the curve. One such mineral, which is frequently associated with petroleum-bearing sediments, is siderite, and with it perhaps the entire iron-manganese carbonate series.

The differential thermal analysis of siderite has been the subject of considerable comment since the publication by Cuthbert and Rowland (*Am. Mineral.*, 1947, p. 114) of a siderite curve with a single exothermic peak at about 560° C. They attributed this peak to "the heat balance between the decomposition of $FeCO_3$ and the immediate oxidation of the resulting FeO to Fe_2O_3." This curve was part of a preliminary study of some carbonate minerals, each of which was diluted 1:3 with γ-Al_2O_3.

The experimental work was completed in 1941 but delayed in publication by the authors' preoccupation with National Defense. That other workers were obtaining siderite curves consisting of an endothermic peak followed by an exothermic peak was recognized by the authors in a letter to the editor (*Am. Mineral.*, 1947, p. 591). Shortly thereafter Kerr and Kulp (*Am. Mineral.*, 1947, p. 679) published curves of siderite from a dozen different localities. Each of these curves had an endothermic peak between 520° and 650° C. followed after an interval by a variety of exothermic peaks. They raised the question as to how immediate is the oxidation of FeO to Fe_2O_3 after the loss of CO_2. Frederickson (*Am. Mineral.*, 1948, p. 373) confirmed the immediate oxidation of the FeO after the loss of CO_2 but was unable to duplicate the curve of Cuthbert and Rowland.

The effect of heating on siderite involves conditions not generally encountered in the thermal analysis of most minerals. When decomposition takes place and CO_2 is liberated from the $FeCO_3$, the remaining FeO is very susceptible to oxidation. Whether the oxidation occurs simultaneously with, immediately after, or somewhat later than the loss of CO_2 may be dependent on the rate at which the CO_2 can escape and allow air to enter.

Assuming that the reactions are:

$$FeCO_3 \rightarrow FeO + CO_2$$
$$4FeO + O_2 \rightarrow Fe_2O_3,$$
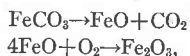
the volume of oxygen gas required to complete the oxidation stage is about one fourth of the volume of CO_2 given off in the decomposition stage. In terms of air volume required to supply the necessary oxygen, for ideal gas behavior, this amounts to approximately 325 cc. of air at 500° C. for 0.5 gram sample. If the final product is $FeO \cdot Fe_2O_3$, then approximately 235 cc. of air at 500° C. would be required. The effect of varying the tightness of packing, particle size, and dilution on the diffusion of these gases through the sample, as reflected in the character of the differential thermal analysis curve, has been partially investigated here.

The differential thermal analysis apparatus with which this study was made is similar to that described by Grim and Rowland (*Am. Cer. Soc.*, 1944, p. 65) except that the furnace temperature is measured by a recording potentiometer, and the deflections of the temperature-difference galvanometers are visibly recorded by Beckman Photopen Recorders. The sample well holds approximately 0.5 gram, and is 0.25 inch in diameter and 0.375 inch deep. The heating program for each sample was 10° C. per minute from room temperature upward. A specimen of Roxbury,

Connecticut, siderite, supplied by Ward's Natural Science Establishment, was ground to pass the 60-mesh screen and used as the supply from which each of the samples used in the following experiments was taken. Each of the curves considered was duplicated several times and the following figures represent more than 100 differential thermal analyses.
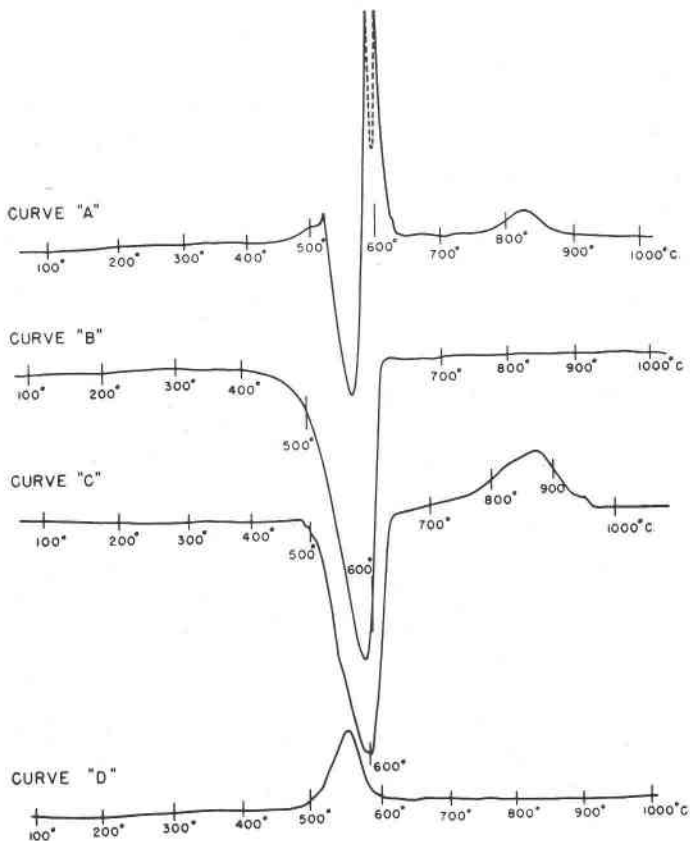

FIG. 1

Figure 1 shows the curves obtained when samples of this siderite were heated under different conditions. Curve "A" was obtained by firmly packing the ground siderite into the sample well and omitting the cover on the sample holder so that the top of the specimen was exposed to the furnace atmosphere. The endothermic peak accompanying the loss of CO_2 is interrupted by an exothermic peak presumably arising from the oxidation of FeO. Curve "B" was produced when a similarly packed

sample was heated in a furnace atmosphere of nitrogen; here the exothermic peaks are suppressed. A similar curve is obtained in a CO_2 atmosphere. Curve "C" was obtained with a cover over the top of a sample otherwise prepared and heated as in curve "A." The broad exothermic peak, which occurs after the endothermic peak associated with the loss of CO_2 is completed, varies in shape and temperature of occurrence even when representing the same sample. The curve is similar to those published by Kerr and Kulp. Curve "D" was obtained when very finely ground siderite was loosely packed in an uncovered sample well. The curve, with its single exothermic peak, is like the curve published by Cuthbert and Rowland, and is also similar to the curve "H" in Fig. 2, obtained by diluting siderite with alundum.

An x-ray diffraction study was made of the products obtained when the heating was stopped at 700° C. At 700° C. each sample contains hematite and a spinel, the diffraction pattern of which resembles magnetite. Samples heated and cooled to room temperature in an atmosphere of nitrogen (curve "B") have only spinel lines and the $d = 4.27$ Å line of magnetite is strong. Samples heated with a cover, curve "C," contain more than 90 per cent of this spinel. Samples heated without a cover, curve "A," contain about 60 per cent spinel and 40 per cent hematite. The product obtained from loosely packing fine-grained siderite, curve "D," contains about 30 per cent spinel and 70 per cent hematite. Chemical analysis of a sample heated without a cover, curve "A," shows less than 0.4 per cent ferrous iron; x-ray diffraction studies of the products at 1000° C. show essentially the same constituents but an increased amount of hematite. In each case, the material is magnetic.

In order to learn whether the exothermic dome between 750° C. and 850° C., curve "A," is associated with an oxidation, a sample was heated in a nitrogen atmosphere, like curve "B," to 1000° C. and cooled in the same atmosphere to 300° C. When the nitrogen was replaced with air an exothermic deflection commenced immediately. When this exothermic deflection was complete the sample was again heated to 1000° C. in an atmosphere of nitrogen. The curve obtained had an exothermic dome between 750° and 850° C. The absence of this dome in a nitrogen atmosphere after the loss of CO_2, and its presence even when material which has been exposed to the air is heated through this range in an atmosphere of nitrogen, suggests that the dome is not associated with an oxidation but probably indicates a change in one of the products of the previous oxidation. The nature of this change is unknown but it may be that the material at 700° C. contains an appreciable amount of γ-Fe_2O_3 which is not readily identifiable when mixed with magnetite, and which may change over to hematite between 750° and 850° C. This

may also account for the increase in hematite observed between 700° and 1000° C.

The corresponding dome on curve "C" is very much larger and is located on a gently sloping exothermic deflection. The absence of a sharp exothermic peak following the endothermic peak is due to a cover over the sample. This cover prevents the rapid escape of CO_2 and does not allow air to enter readily. Of six curves prepared in the same fashion, not one duplicated the shape or position of the exothermic dome. Apparently it is impossible to adjust the cover so that its effect on the passage of gas is reproducible. Furthermore, the endothermic peak is not fully representative of the heat absorbed by the loss of CO_2 because the air trapped in the sample is enough to oxidize some of the FeO. The oxidation seems to take place just after the decomposition of $FeCO_3$ begins and is thought to account for the difference between curves "B" and "C" between 400° C. and 500° C. Curve "B" undergoes no oxidation in this range while curve "C" represents the net heat effect resulting from the loss of CO_2 and the immediate oxidation of the resulting FeO. Curve "A" represents a sample having free access to the air at the outset; consequently, this net effect is more pronounced. Curve "D" not only had free access to the air but also an adjusted rate of evolution of CO_2 and demand for air. Consequently as each grain of siderite decomposes, the CO_2 can escape and the FeO can be oxidized. The curve then represents a heat balance between the decomposition of $FeCO_3$ and the immediate oxidation of the resulting FeO. The curves obtained in passing from a curve like "A" to one like "D" are illustrated in Fig. 2.

The curves in Fig. 2 were produced from sized siderite at several different dilutions with sized alundum. The siderite was ground to pass the 240-mesh screen and to remain on the 270. The alundum passed the 80-mesh screen and remained on the 100. Each sample was packed into the sample holder so that the effect of packing would be as nearly identical as possible. It can be seen that as the amount of siderite decreased, the endothermic peak associated with the loss of CO_2 decreased more rapidly than did the following exothermic peak until in curve "H" the endothermic peak is suppressed. It is thought that this progressive suppression of the endothermic effect is due to the increased ease with which the CO_2 can escape and allow the FeO to come into contact with the air. Some of the factors which may control this are: the permeability of the packed sample, dependent on both the tightness of packing and the sorting of grain size; and the amount of CO_2 evolved at a given point, dependent on the dilution of the siderite, its grain size and its distribution over the surface of the diluent. A tight packing or an unassorted distribution of siderite makes passage of gas more difficult. A diluted sam-

ple reduces the quantity of CO_2 and leaves a proportionate larger amount of air in contact with the grains. Increased surface area permits decomposition and unhindered loss of CO_2 as soon as each grain reaches the proper temperature and thereby allows the reaction to become complete as soon as possible. No steady stream of CO_2 then prevents the access of air to the FeO.

CURVE "E"
40% SIDERITE
60% AL_2O_3

CURVE "F"
35% SIDERITE
65% AL_2O_3

CURVE "G"
33% SIDERITE
67% AL_2O_3

CURVE "H"
30% SIDERITE
70% AL_2O_3
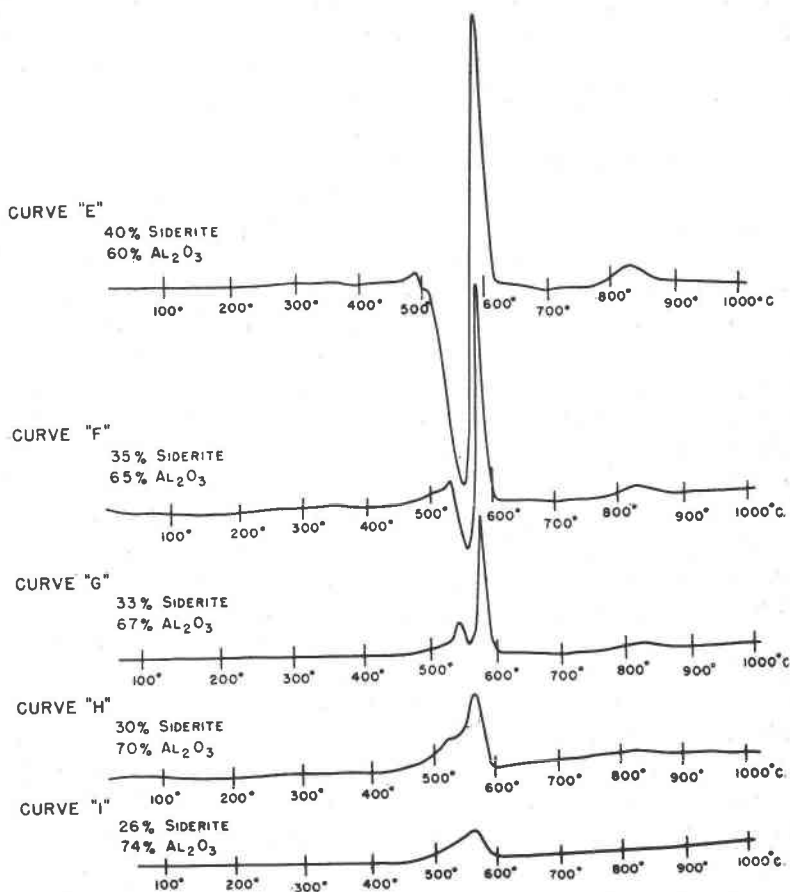
CURVE "I"
26% SIDERITE
74% AL_2O_3

FIG. 2

Higher permeability and easier access for incoming air exists between the wall of the sample well in almost any granular packing. Therefore, it is to be expected that some of the FeO will be oxidized immediately after the loss of CO_2. Furthermore, some air is trapped in the sample even when a cover is used. The exothermic deflection near 500° C. on

curve "C," by contrast with curve "B," is thought to result from this effect.

Several sets of differential thermal curves, similar to those presented in Fig. 2, were obtained for mixtures of different sizes of siderite and alundum. In each set of differential thermal curves for a given siderite-alundum size ratio when the siderite content was reduced to a certain percentage, the endothermic loop between 500° C. and 600° C. did not go below the zero line (like curve "G"). Figure 3 presents a summary of
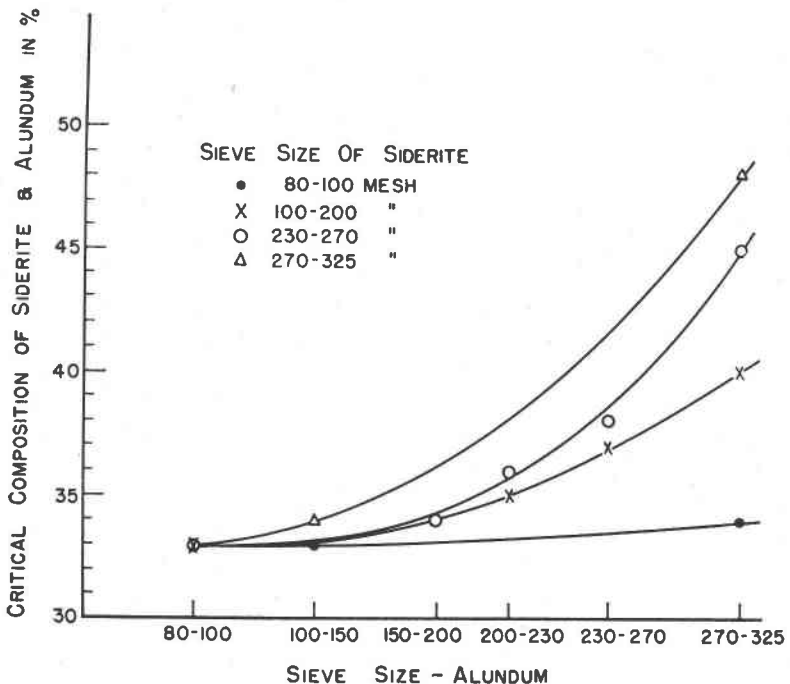

FIG. 3

these differential thermal curves. It should be emphasized that the numerical values associated with these curves are a characteristic of the apparatus employed. Similar curves, with perhaps different numerical values, should be obtainable with any apparatus not employing a cover over the specimen-well. In Fig. 3 the percentage of siderite is plotted as the ordinate, the sieve size of the alundum as the abscissa, while the points on each curve indicate the sieve size of the siderite. These curves present the effect of two conditions of heterogeneous packing with low porosity and permeability and two conditions of open packing of nearly

equidimensional grains. When the grain size of either constituent is large with respect to the other, the percentage of siderite at which the endo-thermic loop is suppressed is about the same (33 per cent). In the open packing when the grains of both siderite and alundum are small, the suppression begins at a higher percentage of siderite. When both siderite and alundum are coarse the suppression is obtained only when the sider-ite is reduced to a percentage about that of the heterogeneous mixture. Even with an open packing, larger grains of siderite increase the total time during which the evolution of CO_2 occurs, and this apparently slows up the entry of air enough to prevent the immediate oxidation of the FeO. Since three of the four conditions give similar results perhaps greater reproducibility can be obtained from artificial mixtures so pre-pared. When siderite is found disseminated through a sediment, a hetero-geneous distribution is most likely. If the siderite constitutes less than 25 per cent of the sediment, the differential thermal analysis curve prob-ably will be a single exothermic loop.

From this study of siderite one aspect of the method of differential thermal analysis has been partially clarified. The variety of thermal analysis curves which are obtained for siderite under various controlled conditions such as: with the top of the specimen well open to the air, covered, and in an inert gas, clearly indicates the effect of the ambient furnace atmosphere. Its accessibility to the sample is varied by control-ling the grain size, dilution, and tightness of packing of the sample.

Thermal analysis curves for minerals which decompose rapidly are not reproducible when made with the sample-well covered because the pressure and rate of diffusion are not controlled. When the evolved gas is allowed to escape freely, this complication is eliminated. If the product remaining after the gas is evolved is susceptible to oxidation, air either must be excluded completely by an inert furnace atmosphere, or allowed to enter freely. When the product is allowed to oxidize, the resulting temperature-difference curve represents the net effect of the heat balance between decomposition and oxidation if the two reactions take place in the same temperature range.

A furnace atmosphere of inert gas suppresses the oxidation reaction. The resulting curve indicates the temperature at which the decomposi-tion begins and represents only the heat involved in the decomposition. The oxidation reaction can be accelerated to such an extent by using finer grain size, by diluting the sample with inert solids, or by packing the sample more loosely, that the decomposition is entirely masked by the oxidation reaction and a curve with only an exothermic deflection re-sults. Because siderite disseminated in petroleum-bearing sediments is both fine-grained and dilute, the exothermic deflection by itself is the

most frequently encountered indication of the presence of siderite in such sediments.

Certain other minerals such as rhodochrosite, cerussite, and some of the basic carbonates, whose thermal decomposition is followed by an oxidation, would be expected to give similarly variable thermal analysis curves.

REFERENCES

CUTHBERT, F. L., AND ROWLAND, R. A. (1947), *Am. Mineral.*, **32,** 111–116.
FREDERICKSON, A. F. (1948), *Am. Mineral.*, **33,** 372–374.
GRIM, R. E., AND ROWLAND, R. A. (1944), *J. Am. Cer. Soc.*, **27,** 65–76.
KERR, PAUL F., AND KULP, J. L. (1947), *Am. Mineral.*, **32,** 678–681.