DIFFERENTIAL THERMAL ANALYSIS OF SOME CARBONATE MINERALS†

F. L. CUTHBERT* AND R. A. ROWLAND**

ABSTRACT

Differential thermal analysis curves are presented for ten of the more common carbonate minerals of known purity. The characteristic curves given should aid in detecting the presence of these minerals when they occur in clays or soils being analyzed by this method. The use of differential thermal analysis is suggested for industries utilizing carbonate minerals or their by-products.

INTRODUCTION

Differential thermal analysis, as applied to soils and clays has become increasingly popular within the last few years, and its value for determining the composition of these materials has been proven (1, 2). Consequently, many research and control laboratories have built apparatus designed to yield differential thermal curves. While most of these vary slightly in operation and design they give similar results, and the thermal curves from different laboratories can thus be compared.

In the course of studying and analyzing many clays in the laboratories of the Illinois State Geological Survey it was noticed that frequently samples contained a carbonate mineral which produced a distinct and characteristic thermal reaction (3, 4). The following work was undertaken to characterize the thermal reactions of several of the common carbonate minerals by means of the type of differential thermal apparatus now popular. All of the work was carried out in the laboratories of the Illinois State Geological Survey.

The carbonate minerals analyzed by the differential thermal method and their source are listed in Table 1.

PROCEDURE

The particular differential thermal apparatus used has been described in detail in another paper and is very similar to those in use in other laboratories (3). A heating rate of about 10° C. per minute was used. The carbonate minerals selected for analysis were specimens chosen for their purity. They were prepared for analysis by grinding in a porcelain mortar to minus 60 mesh and carefully picking out impurities under a microscope. Chemical analyses for each of the purified minerals are given in Table 1.

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† This work was undertaken while the authors were members of the staff of the Illinois State Geological Survey.

* Research and Development, Baroid Sales Division, National Lead Company, Los Angeles, California.

** Exploration and Production Research, Shell Oil Company, Houston, Texas.

Because of the fact that the thermal reactions of many of the carbonate minerals are quite vigorous, thermally inert Al_2O_3 was used as a diluent in the proportion of 25% mineral and 75% Al_2O_3, the two materials being carefully mixed. This allowed all of the minerals to be analyzed without reducing the sensitivity of the differential thermocouple circuit and eliminated the danger of losing a part of the sample because of a vigorous reaction. All of the samples were dried at 90° C. before thermal analysis.

RESULTS

The thermal curves which were obtained using the above procedure are shown in Figs. 1 and 2. All temperatures are noted in degrees centigrade.

Calcite: The differential thermal curve of calcite shows a rather intense broad endothermic reaction starting at about 625° and ending about 890° with a peak at 840°.

Aragonite: This curve also shows a broad endothermic reaction. However, the reaction starts at about 600°, ends at 920° and has its peak at 860°.

Magnesite: The thermal curve for magnesite shows a broad, vigorous endothermic reaction which starts about 400°, ends at 690° and has a peak at 650°. There is also a much smaller endothermic reaction of a much different character immediately following the first.

Dolomite: Two endothermic reactions are shown in the dolomite curve, both of which are sharper than either calcite or magnesite. The first starts about 600° and has a peak at 780° and the second has a peak at 830° and ends about 900°.

Witherite: The thermal curve for witherite shows two small, sharp endothermic reactions; one about 810°, and another about 980°.

Cerussite: Three rather small endothermic reactions are shown in the thermal curve for cerussite. The first starts about 250° and has a peak at 338°, the second immediately follows the first with a peak at 400°, and the third reaction is small and sharp at 855°.

Siderite: Siderite shows a single exothermic reaction starting at about 450° and ending about 625°, reaching a maximum at 560°.

Smithsonite: A single small broad endothermic reaction starting about 300° and ending about 510°, with its peak at 455° is shown in this curve.

Strontianite: A series of relatively small endothermic reactions starting about 800° and continuing past 1000° are shown.

Rhodochrosite: The thermal curve for rhodochrosite shows an endothermic reaction between 500° and 685° with a peak at 625°, and a second rather broad endothermic reaction from 800° to 1000°.

TABLE 1*

Mineral	Source	% Cation	% CO_2
Calcite	Cleavage frag.	CaO— 55.62	44.11
Aragonite	Patterson Pass, Calif.	CaO— 56.21	43.38
Magnesite	Stevens Co., Wash.	MgO—45.98	50.54
Dolomite	Cleavage frag.	CaO— 31.25 MgO—20.13	46.92
Witherite	Northumberland, Eng.	BaO— 74.98	22.40
Cerussite	Embreeville, Tenn.	PbO— 83.33	16.41
Siderite	Roxbury, Conn.	FeO— 53.80	38.21
Smithsonite	Grant Co., N. Mex.	ZnO— 50.74	30.99
Strontianite	Westphalia, Ger.	SrO— 67.80	30.89
Rhodochrosite	Butte, Mont.	MnO—57.20	38.46

* Analyses by L. D. McVicker, Illinois State Geological Survey.

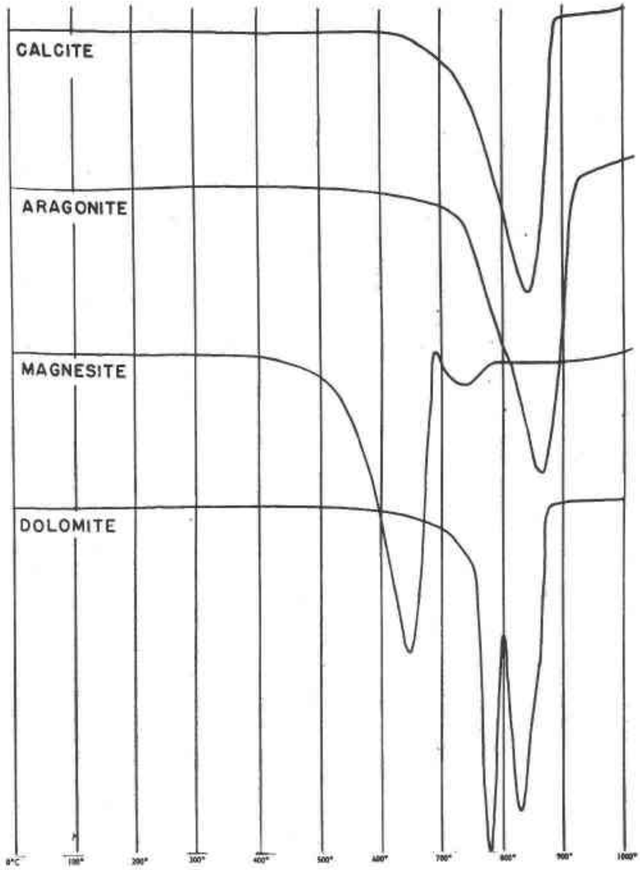

FIG. 1. Differential Thermal Curves.

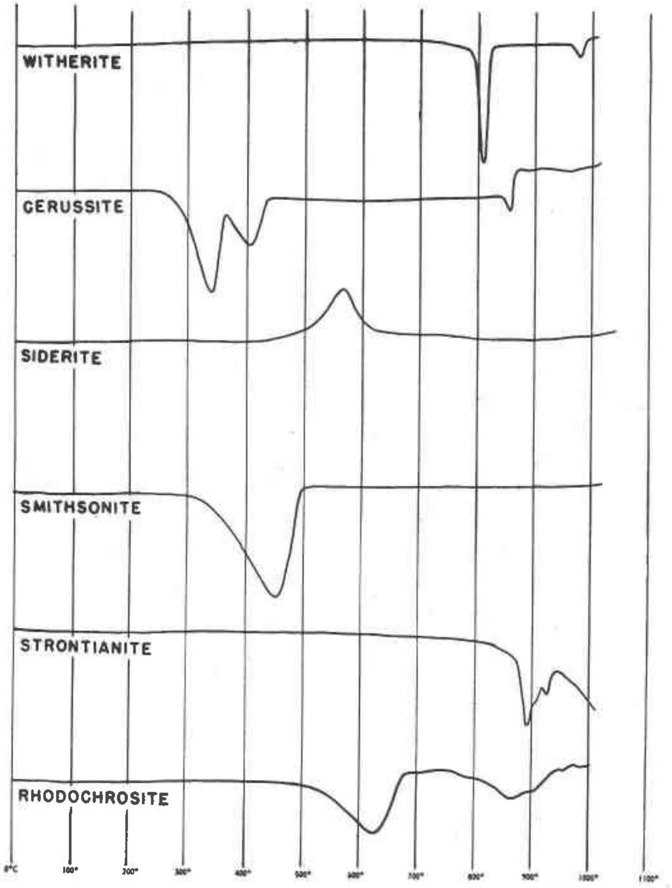

FIG. 2. Differential Thermal Curves.

DISCUSSION

The influence of particle size and heating rate on the decomposition temperatures of carbonates has been recognized for some time (5). Both a decrease in particle size and an increase in the rate of heating, will result in an increase of the rate of decomposition. Also, an increase in the heating rate will cause an increase in the temperature at which the reaction is completed. In view of this, slight differences in the heating rate and particle size of the mineral may cause slight changes in both the slope of the curve, which is characteristic of the rate of decomposition, and the temperature at which the reaction is completed. Consequently some variation may be expected between results obtained in different laboratories.

The differential thermal curves of calcite, aragonite, magnesite, and dolomite can be considered best as a group. Dissociation temperatures for calcite have been recorded in the literature as occurring from about 825° C. to as high as 915°, largely dependent upon the rate of heating (5). Aragonite, when heated above 450° changes more or less spontaneously into calcite and the thermal curves, as obtained, show no significant difference. The dissociation of magnesite occurs at a lower temperature than that of calcite as shown in Figure 1. Wells believes 545° is about right (6). The second endothermic reaction shown in the magnesite curve is probably due to the presence of a small amount of calcite. When double magnesium and calcium carbonates are present, as in dolomite, the thermal curve resulting is not exactly what would be expected by merely combining the curves for magnesite and calcite. A higher temperature is necessary in order to start the decomposition than is required for magnesite and the decomposition proceeds until practically no magnesium carbonate exists before any CaO is formed. This fact is used commercially to separate MgO and CaO.

The thermal curve of witherite shows no dissociation reaction since it does not start to dissociate until about 1100° is reached. However, the two endothermic reactions that do show, serve as an excellent means of identification. They are the transition points to the alpha and beta forms of the mineral occurring at 811° and 982° respectively. Transition points characteristically result in a sharp reaction in contrast to the broad decomposition reactions.

Siderite was the only mineral tested in this series which gave an exothermic reaction. The exothermic reaction is a result of the heat balance between the decomposition of the $FeCO_3$ and the immediate oxidation of the resulting FeO to Fe_2O_3 (7).

Cerussite showed three distinct endothermic reactions which are believed to be an indication of three steps during the dissociation of $PbCO_3$. Tzentnershver reports evidence for the existence of three stages; $3\,PbO\cdot 5PbCO_3$, $2PbO\cdot PbCO_3$, and $PbO\cdot PbCO_3$ (8).

The thermal curve of smithsonite, which shows a peak at 455° is in good agreement with that noted for its dissociation in other work (9).

The dissociation temperature of strontianite is reported to be 1340° (10). However, Dutoit reports a dissociation pressure of 20 mm. at 952°, of 298 mm. at 1175° (11). In view of this, the series of reactions shown in the strontianite curve are believed to represent the beginning of dissociation. It is also possible that the small amount of impurity present as shown in the chemical analysis may account for part of these reactions.

Krustinsons reports the dissociation of manganese spar as beginning at 407.5° and ending about 700° (12). This may be considered in good agreement with that obtained in this work for rhodochrosite, in which the reaction started about 500° and was completed about 684°, reaching a maximum at 625°. The second endothermic reaction shown in the rhodochrosite curve may be due to the small amount of impurity present.

SUMMARY

The type of differential thermal analysis apparatus used for studies of clays and soils produces excellent results when applied to the carbonate minerals. Ten of the more common carbonates are analyzed and characteristic curves are given which should aid in identification of the minerals when they occur in clays and soils.

The decomposition temperatures of the carbonates and the inversion temperatures of witherite shown in this study agree very well with those obtained using other methods.

The possibility of using the method for research and control of plant products in various industries is suggested. Industries that produce and utilize limestones and dolomites for example, might well find the method applicable for control, particularly inasmuch as the analysis, as performed in this manner, requires only about two hours for completion, and is capable of detecting small amounts of carbonates which would be easily overlooked otherwise. Another advantage of the method is the relatively small amount of material which is needed for analysis, about 0.3 to 0.5 of a gram.

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