THERMAL STUDY OF RHODOCHROSITE

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Contents

Abstract

Representative specimens of rhodochrosite from many localities have been examined by the method of differential thermal analysis in order to establish the form and variations of the thermal curve of the mineral, and to study the effect of cation substitution on its thermal behavior. The optimum conditions of sample and apparatus providing reproducible thermal curves for this mineral group are discussed.

The endothermic peak was found to reproduce more consistently than the exothermic, varying from 609° C. to 724° C. but only one specimen gave an endothermic peak higher than 667° C. The majority range from 609° C. to 635° C. The temperature at which the endothermic peak occurs is raised by the presence of Ca and Mg and is lowered if iron substitutes for manganese in the lattice.

The materials used in the thermal work were checked by means of powder *x*-ray patterns and semi-quantitative tests for the cations in question.

Several specimens of manganocalcite varying widely in manganese content indicate that the substitution of Mn for Ca in the series calcite-rhodochrosite is probably continuous and unlimited.

I. INTRODUCTION

The members of many mineral groups may be distinguished by the method of differential thermal analysis since the temperatures at which reactions involving appreciable energy changes take place differ for the several members of the group. The relations between crystal structure and the stability of minerals with increasing temperature have been recognized by structural chemists and mineralogists for over 60 years but it is only within the last decade that these have been utilized as a practical aid in the identification and study of minerals.

The most extensive applications of differential thermal analysis have been in the field of clay mineralogy (Grim and Rowland, 1942), (Speil, Berkelhamer, Pask, and Davies, 1945), (Kerr and Kulp, 1947, 1948). Reconnaissance studies indicate the usefulness of the technique in the investigation of such mineral groups as the hydrous oxides, sulfates, phosphates, zeolites, and carbonates.

Little is known concerning the thermal behavior of the minerals of the carbonate group and even less about the influence on the thermal curves of ionic substitution among the cations of this group. The present investigation attempts to define the type thermal curve of rhodochrosite and its variations in order to study the extent of cation substitution in rhodochrosite as indicated by correlated thermal, *x*-ray and chemical data.

The authors are especially indebted to Prof. Paul F. Kerr, at whose suggestion the problem was undertaken. His helpful advice and critical reading of the manuscript are greatly appreciated. They also wish to thank Professor Charles H. Behre, Jr., with whom certain aspects of the paper were discussed. Dr. Frederick H. Pough, Curator of Mineralogy, American Museum of Natural History, made available several specimens of manganocalcite which added much to the study.

II. EXPERIMENTAL EQUIPMENT AND PROCEDURE

A. General Method. Many minerals when heated at a constant rate to about 1000° C. undergo thermal reactions (gain or loss of heat) due to (1) loss of either absorbed or lattice (OH) water, (2) chemical combination, (3) decomposition, or (4) changes in crystal structure. The reactions usually are characteristic of a given mineral, and thus may be used for identification. Further, since the intensity of reaction is roughly proportional to concentration, a quantitative estimate of the proportions of the component minerals in mechanical mixtures can be obtained.

In practice the thermal properties of a mineral are detected by comparing its temperature with that of an inert material as both are heated at the same constant rate. One terminal of a two-headed thermocouple is placed in the mineral, the other in the inert material (alundum). Voltage across the terminals of the pair is detected only when there is a difference in temperature between them. If the temperature differential is plotted against the temperature of the inert material, thermal reactions of the mineral appear as exothermic or endothermic peaks on an otherwise straight line curve. The shape and temperature position of these peaks usually are characteristic of a particular mineral, and can be readily measured and studied. (For details of method see Speil et al., 1945 and Kerr and Kulp, 1948.)

B. Apparatus. The apparatus used was the multiple thermal analysis unit in the Mineralogical Laboratory of the Department of Geology, Columbia University. Both apparatus and technique are fully described elsewhere (Kerr and Kulp, 1948). *X*-ray diffraction equipment using iron radiation was employed in obtaining Debye powder patterns.

C. Procedure. The specimens studied were obtained from the Mineralogical collection of Columbia University, except for certain manganocalcites obtained from the American Museum of Natural History. Specimens from the following localities were made use of:

Locality	No. of specimens sampled
Lake County, Colorado	3
Saguache County, Colorado	1
Park County, Colorado	1
Austin, Nevada	1
Branchville, Connecticut	1
Cummington, Massachusetts	1
Butte, Montana (various mines)	3
Whitehall, Montana	1
Stassfurt, Germany	1
Staffel, Bavaria	1
Oberneisen, Nassau	1
Lahnstein, Prussia	1
Franklin, New Jersey	6

A preliminary study of the influence of fragment size on the thermal curve was made by separating fractions of four different size ranges and testing them simultaneously in the thermal apparatus. The fragment sizes used were: (1) 50–80 mesh; (2) 80–120 mesh; (3) 120–200 mesh; and (4) minus 200 mesh. No appreciable change was observed in the shape of the thermal curves, but the endothermic peak temperature varied slightly with fragment size. The differences in peak temperatures given by (80–120) and (120–200) mesh fragments were negligible. The endothermic peak temperatures of the (50–80) mesh fraction was about 5° C. above the average for the (80–200) mesh range, and fragments which passed 200 mesh had an endothermic peak about 5° C. below. Therefore preparation procedure was standardized so that only (80–200) mesh fragments were used for the thermal analysis work. The samples were heated to 1000° C. at a near-constant rate of 12° C. per minute.

Qualitative and semi-quantitative chemical tests for Ca, Mg, Mn and Fe, and *x*-ray powder patterns (Debye) were obtained for all samples and each sample was examined with the aid of a petrographic microscope for impurities.

Shifts in the endothermic peak temperatures were correlated with corresponding shifts in the high angle lines of the *x*-ray powder patterns, and with the evidence of substitution of Ca^{++}, $Mg,^{++}$ and Fe^{++} for Mn^{++} in the crystal lattice indicated by the results of the chemical analyses.

A quantitative study of the effects of impurities on the thermal curve of rhodochrosite was made using artificially prepared mixtures of rhodochrosite with calcite, dolomite, siderite and chemically pure $CaCO_3$ powder. The shift in endothermic peak temperature, and the relation between area under the curve and percentage of a given constituent were investigated.

D. Exothermic Peak Reproducibility. Experimental work indicated that the exothermic (oxidation) peak which follows the large endothermic decomposition reaction varies considerably in shape and peak temperature, while the endothermic peak remains reasonably constant. (The endothermic and exothermic reactions will be discussed more fully later.) In most cases the exothermic peak appears as a long, low arch rather than a sharp, pointed peak, like that produced by the endothermic reaction. This exothermic reaction is believed to be a result of air oxidation of the lower valence manganese oxide produced in the decomposition of rhodochrosite, and in the furnace it was evident that something inhibited the immediate oxidation of the decomposition product, manganous oxide. An attempt was made to obtain a reproducible exothermic peak by varying (1) the fragment size and (2) the position of the cover disc. A rhodochrosite specimen* from the Anaconda Mine, Butte, Montana, was selected for the exothermic peak study. Experiments were made under the following conditions:

(1) Minus 80 mesh fragments; cover on.
(2) Same.
(3) Minus 50 plus 120 mesh fragments; cover off.
(4) Minus 50 plus 120 mesh fragments; cover on.
(5) Minus 80 plus 200 mesh fragments; cover off.

These experiments demonstrate that particle size is not a critical factor in obtaining reproducible exothermic peaks. It is clear, however, that the cover disc had restricted the free access of oxygen to the rhodochrosite decomposition product. When the cover was removed the curves showed sharp exothermic peaks which are largely reproducible from one experiment to the next. The remaining differences in exothermic peak shape are to be attributed to the thermocouple position and the nature of the weld. The curves in Figs. 1 and 2 illustrate the results obtained in the five experiments listed above. Those of Fig. 1 were obtained with the cover on. The peak due to the oxidation reaction is not appreciably developed and

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* The double endothermic peak indicates an intergrowth of two rhodochrosites which differ in the foreign cations substituted for Mn in the lattice. This specimen is discussed in detail later.

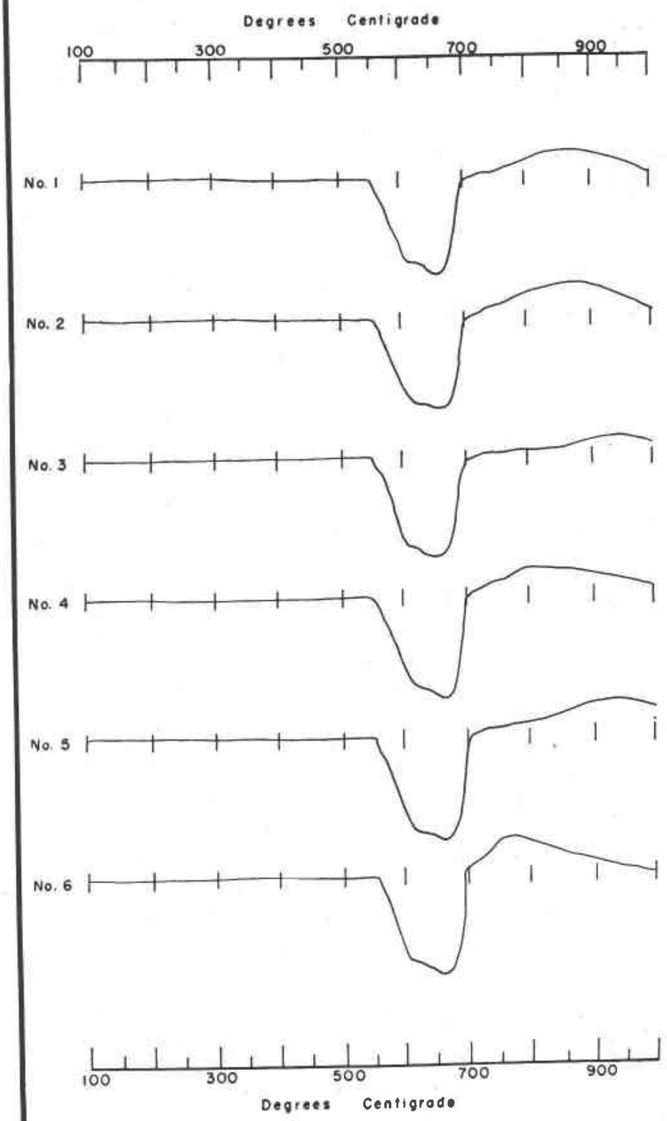

FIG. 1. Exothermic Peak Study. Cover on, restricting free access of air to sample. (50–120 mesh fragments.)

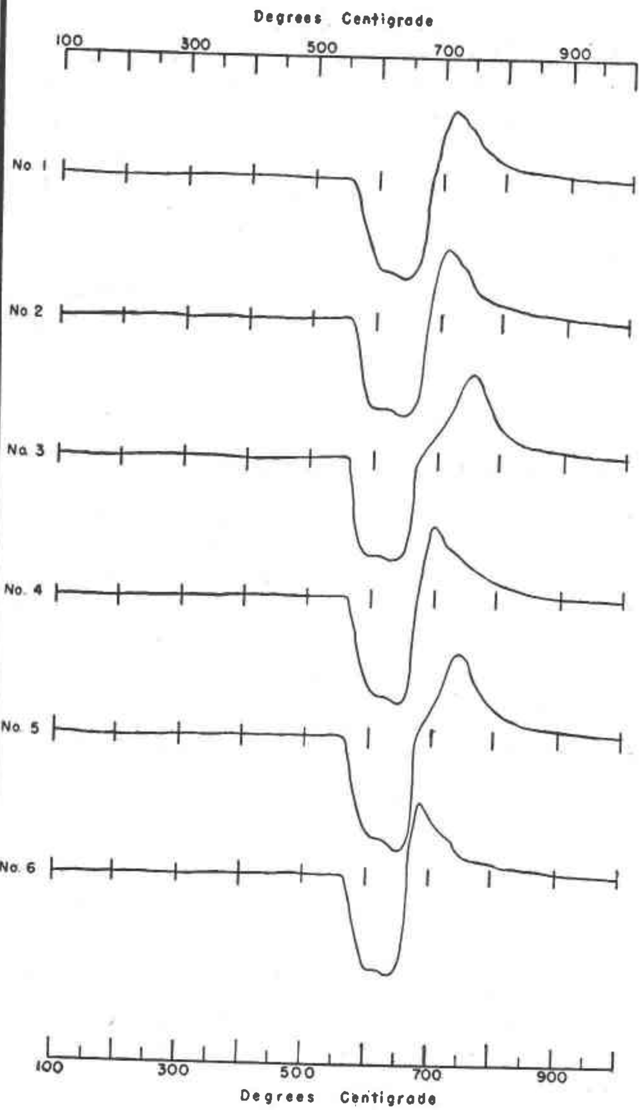

FIG. 2. Exothermic Peak Study. Cover off, permitting free access of air to sample for oxidation. (50–120 mesh fragments.)

there is little relation among the individual curves. These were not reproducible from one experiment to the next. The curves in Fig. 2, on the other hand, show the sharp exothermic peak produced by removing the cover. Under these conditions the peaks are reproducible for a particular thermocouple in successive experiments, but the curves obtained for different thermocouples during the same experiment differ somewhat due to differences in position of the thermocouple head. Curves Nos. 3 and 5 exhibit a delayed peak because the thermocouple head was considerably below the center of the sample.

From this study it is evident that reproducible thermal curves of rhodochrosite or other minerals that undergo air oxidation could not be obtained with the sample holder cover in place. Accordingly, a special cover was made with small supports, which leaves about $\frac{1}{8}''$ space between cover and sample holder. This permits free access of oxygen to the samples but shields them from direct furnace radiation. This innovation was used for all of the subsequent thermal curves discussed in this paper.

III. SUBSTITUTION IN RHODOCHROSITE

The mutual substitution of the common divalent metallic ions in the carbonate minerals is tacitly assumed in most mineralogical texts. An examination of the ionic radii of Ca^{++}, Mg^{++}, Fe^{++} and Mn^{++} in relation to the crystal structure of the carbonates indicates that such substitution seems possible. The clearest demonstration of this phenomenon was provided by the work of Krieger (1930), who showed that in manganoan calcite Mn^{++} can substitute for Ca^{++} to at least 40%. He demonstrated that this substitution may be correlated with a linear shift in the indices of refraction, specific gravities and the position of the lines in the *x*-ray diffraction patterns.

The present investigation provides further evidence of this phenomenon in the case of the substitution of Ca^{++}, Mg^{++}, and Fe^{++} for Mn^{++} in rhodochrosite. This is particularly interesting since the temperature of decomposition is necessarily related directly to the bonding energies in the lattice. Since the shift in peak temperature on a thermal curve is more pronounced than the corresponding shift in the high angle lines of the *x*-ray pattern, differential thermal analysis is an expeditious technique for detecting this phenomenon. This is particularly true of carbonates that contain more than 60% "impurity."

If a single carbonate ion surrounded by its nearest neighbor cations is considered, it is evident that the temperature of decomposition will be directly dependent upon the strength of the cation-carbonate bond. Decomposition will occur at the temperature at which the internal energy of the carbonate ion just exceeds the bonding energy, thus freeing the CO_2

molecule. Further, the cation-carbonate bonds progress in strength from siderite through rhodochrosite and magnesite to calcite, since each succeeding mineral has a higher decomposition temperature.

This is illustrated by comparing the thermal behavior of magnesite and dolomite (Faust, 1944). Magnesite decomposes with a single exothermic peak into periclase (MgO). The temperature of the lower endothermic peak of dolomite is about a hundred degrees above that of magnesite and is due to the decomposition of dolomite into periclase and fine calcite. The carbonate ion most closely associated with the magnesium ion in the dolomite lattice, therefore, due to the calcium-carbonate bonds, has additional stability over the carbonate ion in magnesite.

From this it follows that the random substitution of calcium or magnesium ions for manganese ions in the rhodochrosite lattice will strengthen the cation-carbonate bond and thereby increase the decomposition temperature. Furthermore, since the lattice is sufficiently open to allow substitution of calcium for manganese ions without introducing appreciable strain, a continuous shift of decomposition temperature from pure rhodochrosite to pure calcite is to be expected. In the present study, endothermic peak shifts indicate substitution of calcium for manganese ions to the extent of approximately 40%. Further, a specimen of manganocalcite from Franklin, New Jersey, which probably contains about 10% Mn^{++} in Ca^{++} positions (estimate based on shift in x-ray diffraction lines compared with patterns obtained by Krieger on analyzed material) showed a shift of about 30° downward in the endothermic peak temperature. By analogy, specimens in which iron has substituted for manganese will show lowered endothermic peak temperatures, and magnesium for manganese substitution likewise will result in raised peak temperatures. Such substitution in the natural rhodochrosite specimens has been observed by means of shifts both in x-ray diffraction lines and peaks in thermal curves.

A tabulation of data on a selected group of rhodochrosite-manganocalcite specimens illustrating this substitution phenomena is given in Table 1. The shift in x-ray diffraction lines is consistent with the chemical and thermal data. With increasing Ca^{++} substitution, the thermal curve peaks are shifted upward in temperature and the x-ray lines move from the rhodochrosite to the calcite positions.

IV. Thermal Curves of Rhodochrosite-Carbonate Mixtures

Artificially prepared mixtures of rhodochrosite with other carbonates were tested thermally in order to study the extent to which the percentage composition of naturally occurring intergrowths of rhodochrosite with other carbonates could be determined by means of differential

TABLE 1

Specimen	Approximate cation composition*				Endothermic peak temperature	"d" outermost strong α_1 line
	Ca^{++}	Mg^{++}	Fe^{++}	Mn^{++}		
(Ideal rhodochrosite)	—	—	—	(100%)	(615° C.)	—
Oberneisen, Nassau	—	Trace	—	100%	615° C.	1.001
Butte, Mont. #2	5–10%	—	10%	80%	640° C.	1.000
Butte, Mont. #1 (2nd peak)	10–15%	—	5%	75%	660° C.	1.001
Whitehall, Mont.	15–20%	—	5%	75%	670° C.	1.003
Cummington, Mass.	30%	—	—	70%	730° C.	1.017
Franklin, N. J. (manganocalcite #5)	90%	—	—	5–10%	935° C.	1.024
(Iceland spar)	100%	—	—	—	990° C.	1.045

* Determined by semi-quantitative semi-micro methods using known mixtures as standards. The error is estimated to be ±5% below 30% and ±10% above 70%.

thermal analysis. The resulting thermal curves are reproduced in Figs. 3, 4, and 5.

Figure 3 shows the curves obtained from mixtures of Lake County, Colorado, rhodochrosite (80–200) mesh with chemically pure calcium carbonate powder.

#1 90% $MnCO_3$–10% $CaCO_3$
#2 75% $MnCO_3$–25% $CaCO_3$
#3 60% $MnCO_3$–40% $CaCO_3$
#4 40% $MnCO_3$–60% $CaCO_3$
#5 25% $MnCO_3$–75% $CaCO_3$
#6 10% $MnCO_3$–90% $CaCO_3$

The endothermic peak temperature lowered progressively from 592° C. with 90% $MnCO_3$ to 550° C. with 25% $MnCO_3$. The peak temperature decreased more rapidly in the low $MnCO_3$ range than in the high. The lowering effect of impurity on the endothermic peak temperature may be seen equally well in the case of the $CaCO_3$ peak.

No rhodochrosite peak was obtained for the 10% $MnCO_3$–90% $CaCO_3$ mixture, yet an appreciable $CaCO_3$ peak occurred for the mixture with 10% $CaCO_3$. (See curve #6.) The explanation of this appears to be quite simple. Similar phenomena have been observed with siderite ground to the same fragment size (80–200 mesh). When the rhodochrosite is diluted to the point where the oxygen in the air spaces immediately surrounding a rhodochrosite fragment is sufficient to oxidize completely the

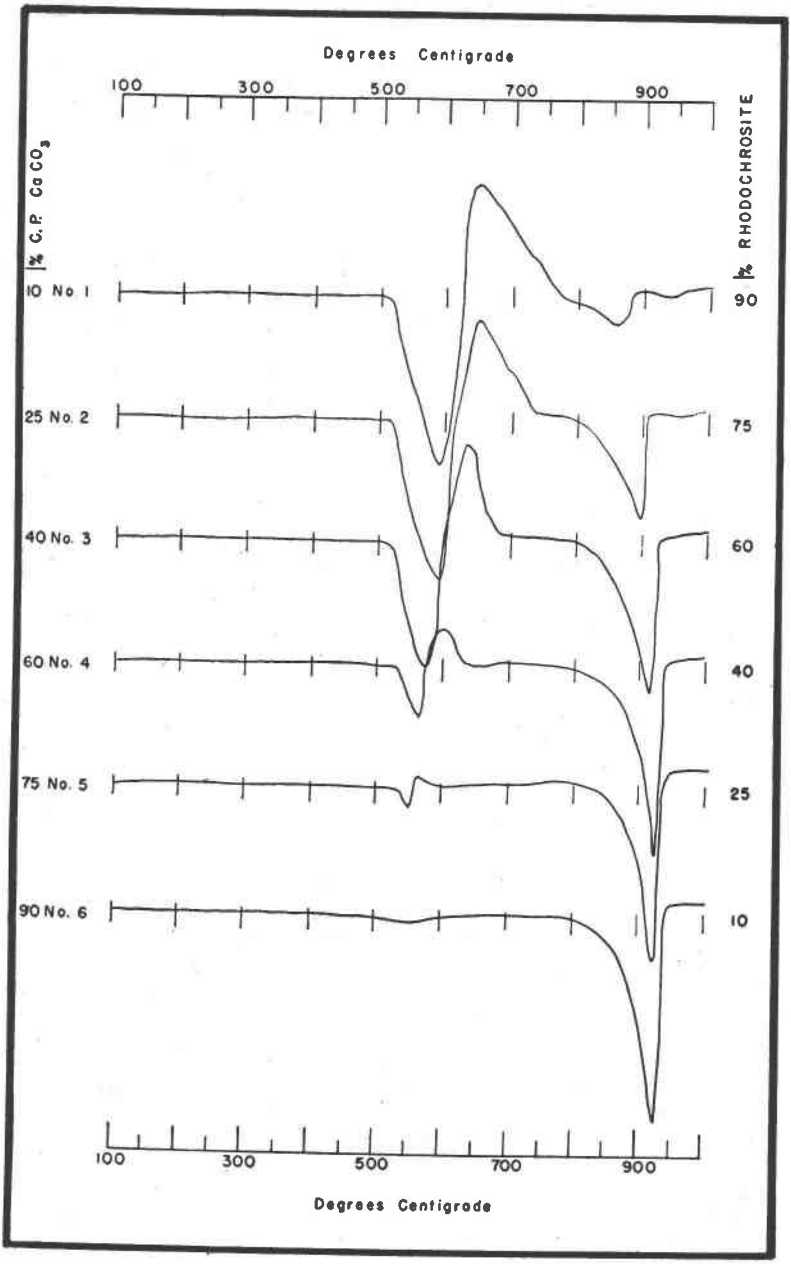

FIG. 3. Differential Thermal Curves of Mixtures of Rhodochrosite with C.P. Calcium Carbonate.

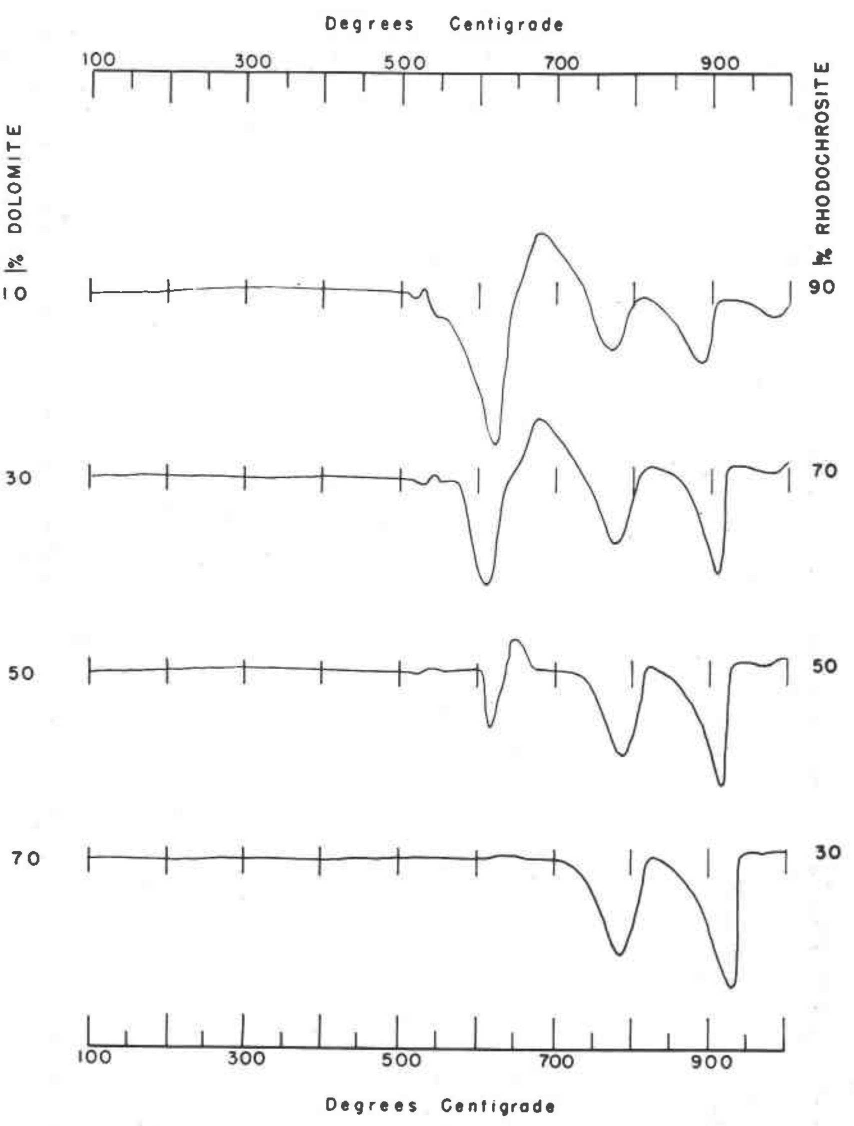

FIG. 4. Differential Thermal Curves of Mixtures of Rhodochrosite with Dolomite.

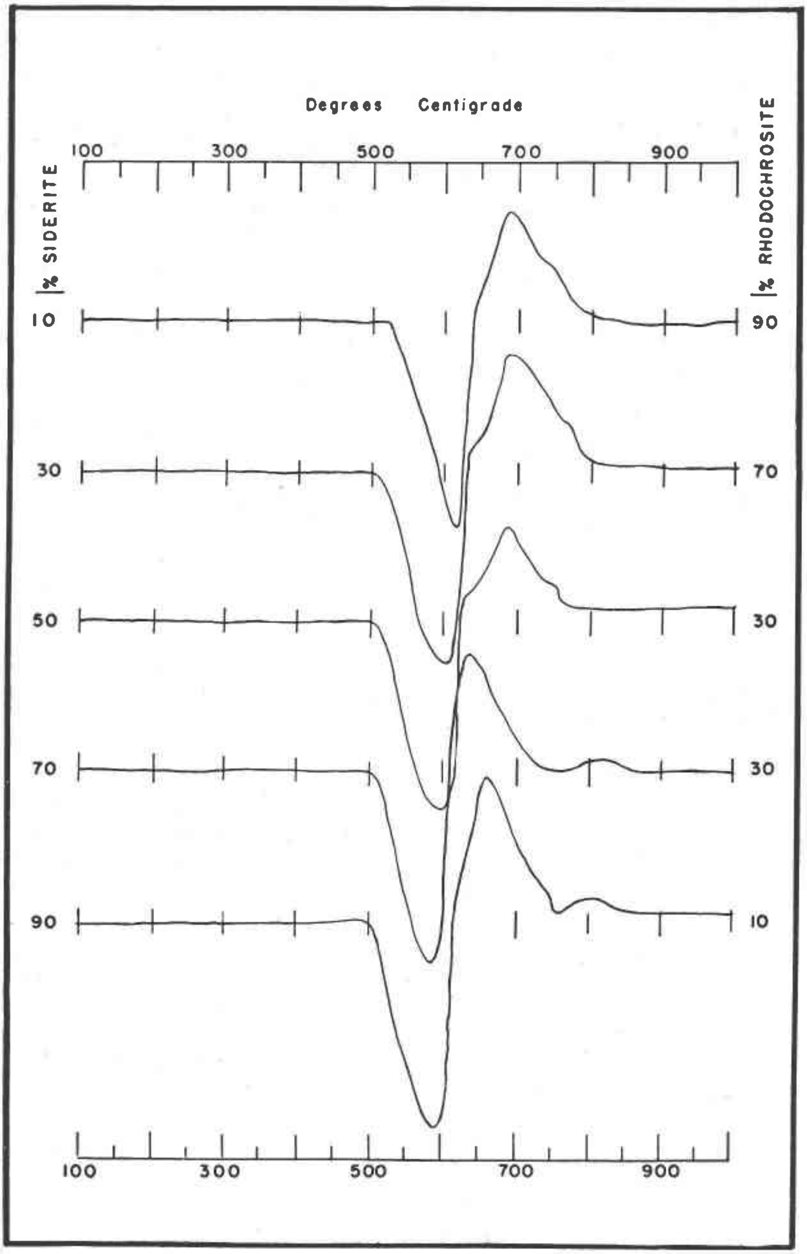

FIG. 5. Differential Thermal Curves of Mixtures of Rhodochrosite with Siderite.

MnO formed from its decomposition, the oxidation reaction immediately follows the decomposition. Since the energy changes involved in both processes are about equal but in opposite directions, the effects cancel out and the thermal curve shows no peaks. Presumably, if the thermal analysis of a 10% rhodochrosite sample were run in an atmosphere of CO_2, an endothermic peak with the appropriate amplitude would be observed. This effect should vary with the nature of the foreign constituent and the particle size.

The slight endothermic peak at 940°–950° C. in curves #1 and #2 is the same as that appearing in the Lake County #1 curve, Fig. 6.

A similar series of mixtures with Iceland spar ground to 200 mesh gave analogous results. The most striking difference is the fact that the extremely fine $CaCO_3$ powder (chemical precipitate) gives an endothermic peak at 938° C. as compared to 950° C. for Iceland spar ground to 200 mesh in 90% calcite mixture.

The curves obtained from the mixture of Lake County rhodochrosite with Oberdorf, Styria, dolomite are grouped in Fig. 4.

#1 90% $MnCO_3$ – 10% Ca,Mg(CO_3)
#2 70% $MnCO_3$ – 30% Ca,Mg(CO_3)
#3 50% $MnCO_3$ – 50% Ca,Mg(CO_3)
#4 30% $MnCO_3$ – 70% Ca,Mg(CO_3)

The rhodochrosite endothermic peak shifts from 620° C. for 90% $MnCO_3$ to 613° C. for 50% $MnCO_3$. In the 30% rhodochrosite mixture no appreciable rhodochrosite peak appeared for reasons given above. The upper dolomite peak shifts from 885° C. for the 10% dolomite mixture to 930° C. for 70% dolomite, whereas the lower dolomite peak temperature increases only about 20° C. with increasing concentration in the same range. The small endothermic and exothermic dips occurring at 500°–550° C. in the first three curves are due to an impurity in the rhodochrosite used. The specimen was from Lake County, Colorado, as was that used for the $CaCO_3$ mixtures, but probably contained more $FeCO_3$. The small endothermic dip occurring at 980° C. is probably the same as that found in the $MnCO_3$-$CaCO_3$ mixture runs, and is believed due to an unidentified impurity in the rhodochrosite.

$MnCO_3$-$FeCO_3$ Mixtures. The curves for mixtures of Lake County rhodochrosite with Roxbury, Connecticut, siderite are reproduced in Fig. 5.

#1 90% $MnCO_3$ – 10% $FeCO_3$
#2 70% $MnCO_3$ – 30% $FeCO_3$
#3 50% $MnCO_3$ – 50% $FeCO_3$
#4 30% $MnCO_3$ – 70% $FeCO_3$
#5 10% $MnCO_3$ – 90% $FeCO_3$

The thermal curve of siderite is the most similar to that of rhodochrosite of all the carbonate curves. (This is to be expected from the close similarity in ionic radii and lattice constants.) The endothermic peak of the siderite curve occurs about 50° C. lower than that of rhodochrosite.

Because the shapes of the curves and the peak temperatures are so closely similar for the two components, the result is a blending of the two with only a suggestion of two peaks where the percentages of the two components are approximately equal. Curves #2, #3, and #4, Fig. 5, show considerable broadening near the peak. A progressive lowering of peak temperature from 615° C. with 90% rhodochrosite to 591° C. with 90% siderite is seen. The exothermic bulge at about 810° C. in #4 and #5 is due to an unidentified impurity in the siderite. The exothermic peak follows the downward trend with the endothermic peak.

In summary, mixtures of rhodochrosite with other carbonates produce thermal curves which show the following general characteristics:

(1) "Mixture" curves are a combination of the curves typical of each component.
(2) The greater the amount of impurity present, the lower the temperature at which the endothermic (and generally the exothermic) peak occurs (Kerr and Kulp, 1947).
(3) The lowering of the endothermic peak temperature is not a linear function of the amount of impurity present, but is greater for a given change in amount of impurity where the amount of impurity is large, than for the same change where the amount of impurity is small.
(4) The area under the endothermic or exothermic peak is roughly proportional to the amount of the constituent producing this peak (Kerr and Kulp, 1947).

V. THERMAL CURVES OF RHODOCHROSITE

A. General. For the rhodochrosite specimens tested, a range in endothermic peak temperature of 609° C. to 724° C. was found, but only one specimen showed a peak temperature higher than 667° C. Considerable variation in exothermic peak temperature was observed, which was not surprising in view of the variability of conditions affecting the exothermic reaction, discussed previously.

Variations in the endothermic peak temperature are traceable to two major factors: (1) replacement of Mn^{++} by other cations such as Fe^{++}, Ca^{++} and Mg^{++} in the crystal lattice, and (2) the presence of thermally active or inactive impurities.* As pointed out earlier, substitution may elevate the endothermic peak temperature, as in the case of the Mg^{++} and Ca^{++} ions, or lower the peak temperature, as with the Fe^{++} ion. It has been shown by other workers (Kerr and Kulp, 1947), (Speil, Berkel-

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* Throughout this discussion the term "impurities" will refer to mechanically admixed foreign constituents in the rhodochrosite specimens, not to cations substituting in the rhodochrosite lattice.

hamer, Pask and Davies, 1945), (Cuthbert and Rowland, 1947) that the presence of impurities invariably results in a lowering of endothermic peak temperatures. The difficulties in duplicating conditions of packing and maintaining thermocouple head sensitivity and geometry, impose a limit of error which probably does not exceed ±5° C. in peak temperature.

B. Discussion of Individual Curves. Figures 6 and 7 show the thermal curves for the most interesting and typical rhodochrosites. They will be discussed successively in the following section.

Lake County, Colorado.

The three specimens tested yielded endothermic peaks of similar shape and amplitude, with the peak temperatures spread over a relatively small range, 8° C. Fe^{++} was found in appreciable quantity (estimated 10–30% of cations) by qualitative chemical analysis. The double exothermic peak of #3 cannot be satisfactorily explained at present. It may be due to the formation and decomposition of an Fe-Mn oxide complex. The endothermic dip at about 850° C. in samples #2 and #3 is probably due to a small percentage of included calcite.

Saguache County, Colorado

This sample showed a double endothermic peak, with the lower peak at 652° C., the upper at 698° C. Even the lower of the twin peaks is at a temperature considerably higher (25° C. to 30° C.) than the peak temperatures of the Lake County samples, and the upper peak is well out of the general range found to be characteristic for rhodochrosite. Qualitative chemical analysis indicated the presence of Ca^{++}, Mg^{++} and Fe^{++} ions in appreciable quantities. It is estimated that Ca^{++} is the principal substitution ion in the Mn^{++} positions in the lattice, possibly to the extent of 25%. The double peak indicates an intergrowth of two rhodochrosites of different compositions. Ca^{++} and Mg^{++} substitutions are possible in both constituents, but Fe^{++} is probably prominent in the lower member. It is suggested that the lower member is at least a tricomponent rhodochrosite (Ca, Fe, Mn) while the higher member is at least a di-component (Ca, Mn) rhodochrosite. An intergrowth of two closely similar substituted rhodochrosites is also indicated by the abnormal line broadening apparent in the high angle lines of the *x*-ray patterns. The exothermic peak does not occur until the second rhodochrosite is decomposed due to the fact that the decompositions overlap and oxygen cannot readily get to the sample until the evolution of CO_2 has ceased.

Park County, Colorado

The curve is regular and indicates no appreciable impurity. The endothermic peak temperature of 664° C. is high for rhodochrosite. Qualitative chemical analysis showed, besides Fe, an appreciable amount of the

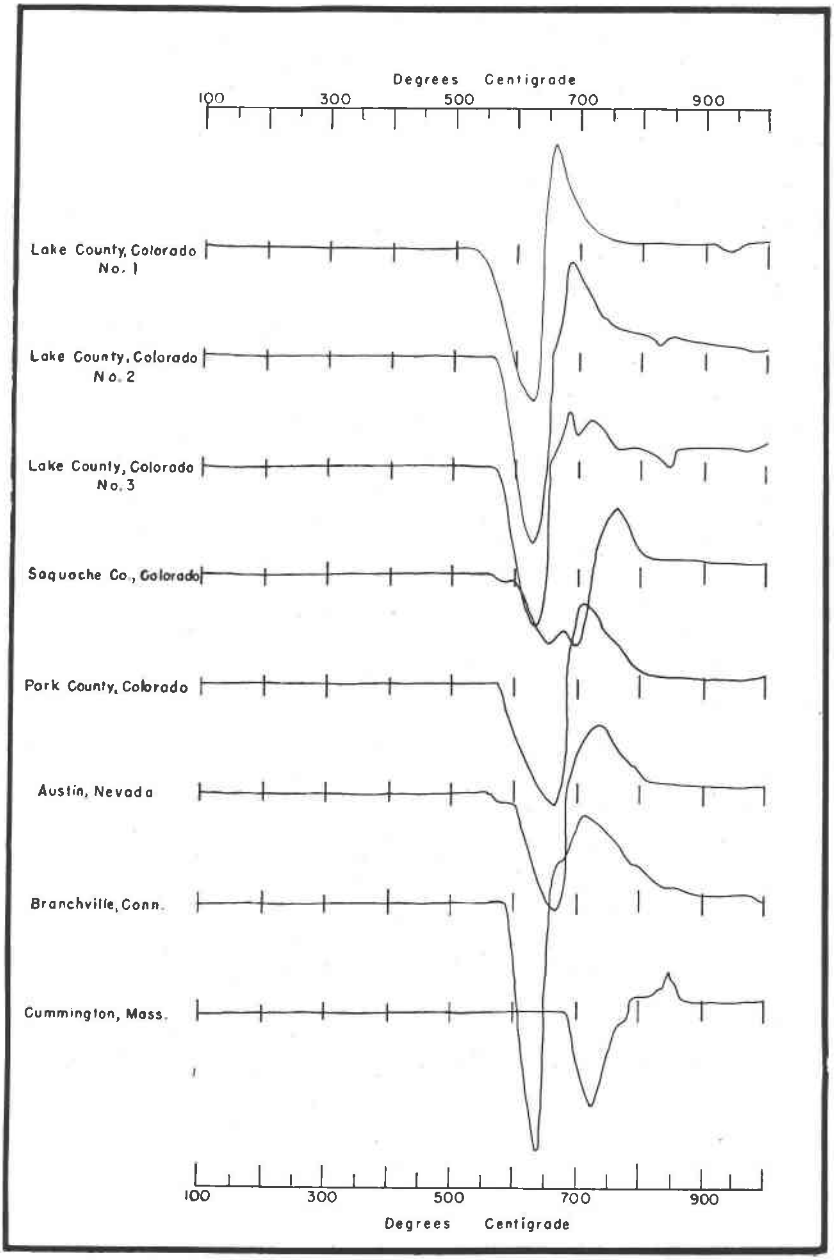

FIG. 6. Differential Thermal Curves of Rhodochrosite. Specimens from various localities.

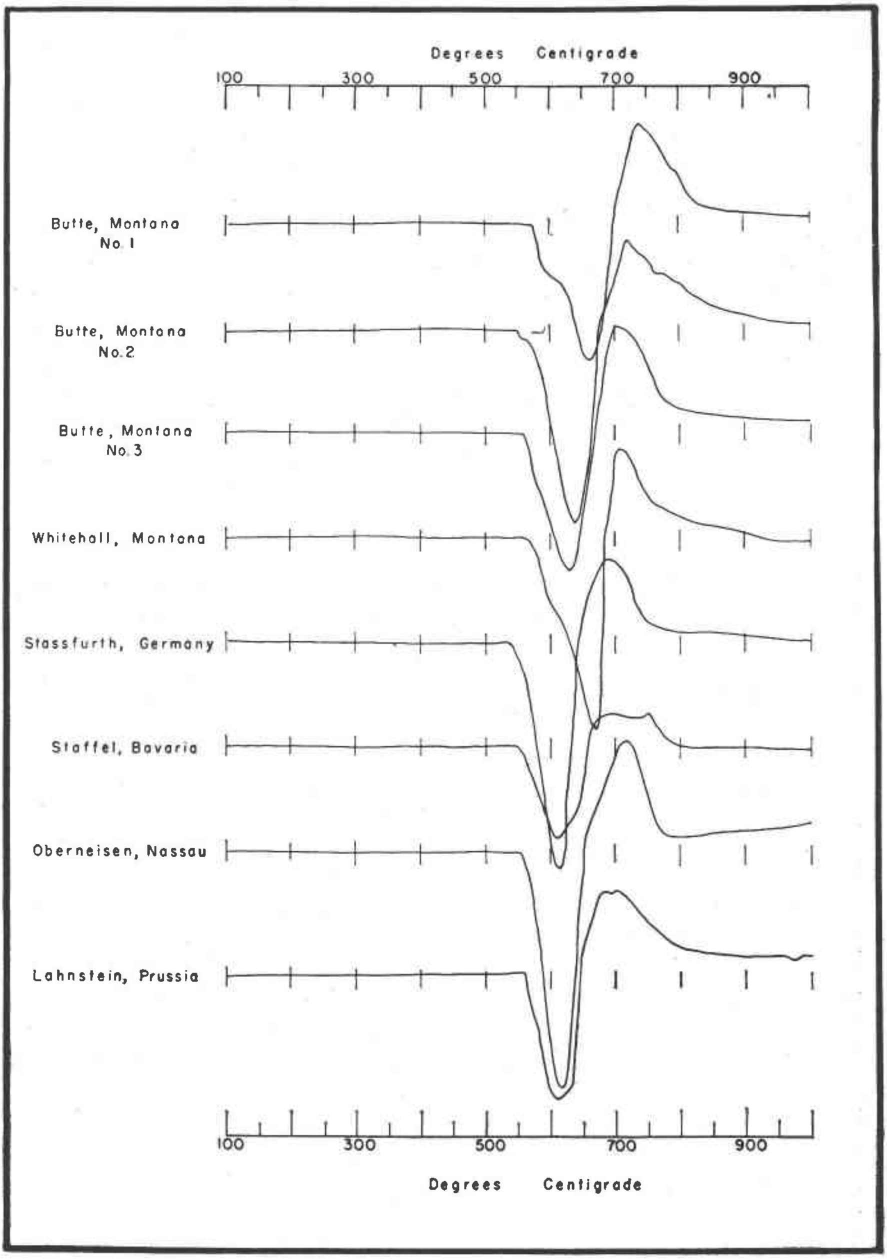

FIG. 7. Differential Thermal Curves of Rhodochrosite. Specimens from various localities.

Mg^{++} ion. Since there is no appreciable irregularity in the shape of the curve, the magnesium probably occupies manganese positions in the lattice, and this would account for the upward shift in endothermic peak tempeature. On the basis of the absence of lines due to magnesite in the *x*-ray patterns it is believed that Mg^{++} substitution in the rhodochrosite lattice is a more probable explanation of the chemical results than an intergrowth of magnesite and rhodochrosite.

Austin, Nevada

This curve is similar to that given by the Lake County sample in general shape and endothermic peak temperature, although the exothermic peak is not as sharp and occurs at a higher temperature. An endothermic dip occurs at approximately 575° C. and is possibly due to siderite impurity. Semi-quantitative analysis indicated the presence of calcium, representing about 10–20% of the cation positions in the lattice. This accounts for the high endothermic peak temperature (666° C.). Lines in the *x*-ray diffraction pattern are shifted toward calcite, but no siderite lines were detected.

Branchville, Connecticut

This material gave an exceedingly narrow, sharp endothermic peak, indicative of uniform grain size. No significant irregularities appear. Qualitative chemical analysis showed the presence of moderate Ca^{++} and Fe^{++}, which probably substitute for manganese in the lattice. The endothermic peak is only slightly increased due to the counterbalancing effect of Fe^{++} and Ca^{++}.

Cummington, Massachusetts

The curve produced by this material is remarkable for the high endothermic peak temperature, 724° C. Qualitative chemical analysis indicates that a large amount of Ca^{++} (estimated 35%) is present; in fact more than in any of the other specimens tested. The high endothermic peak temperature indicates that the Ca^{++} ion probably occupies Mn^{++} lattice positions, representing approximately 35% of the total Mn^{++} lattice positions. The small size of the exothermic peak may be attributed at least in part to Ca^{++} for Mn^{++} substitution, since the calcium oxide remaining after decomposition of calcium carbonate is not oxidized to a higher valence state of the cation as is manganous oxide (MnO). The smaller endothermic area may be attributed in part to the presence of inert impurities, whose presence was indicated by the fine-granular nature and brownish color of the material.

Butte (including Whitehall), Montana

The unusual breadth of the curve across the base line and the changes in slope along the lower temperature side of the endothermic part of the curve possibly reveal another case of two intimately intergrown rhodochrosites in the cases of the Butte #1 and Whitehall specimens. These were shown by qualitative analysis to have a strong Fe^{++} content and moderate Mg^{++}. It is suggested that the low temperature variety is (Fe-Mn) and the high temperature member (Mn-Mg). The presence of Fe^{++} was indicated for Butte #2 and #3. The Fe^{++} and Mg^{++} may be assumed to be present in the lattice rather than in an impurity since the the thermal curve shows no appreciable irregularities.

The specimen used for the exothermic peak studies, Figs. 1 and 2, came from the Anaconda Mine, Butte, Montana. Instead of a single endothermic peak, a doublet is apparent. Since the area under the curve is essentially the same as the single peak rhodochrosites and the qualitative chemical analysis indicates moderate concentration of Fe^{++} and Mg^{++} as foreign cations, it seems probable that this specimen is an intimate intergrowth of Fe-rhodochrosite and Mg-rhodochrosite. This hypothesis is consistent with the mottled appearance of the specimen. The *x*-ray diffraction photograph shows abnormally broad lines, but only rhodochrosite lines. This is not the case in a diffraction pattern of a single rhodochrosite exhibiting substitution in its lattice. Further, a sample of this material was heated to 610° C. and cooled quickly. According to the explanation given above, this should have essentially decomposed the lower temperature Fe-rhodochrosite but left the higher temperature Mg-rhodochrosite. An *x*-ray diffraction pattern of the residue yielded the lines of hausmannite (the normal decomposition product of rhodochrosite) and sharp lines of rhodochrosite shifted slightly toward the low angle range of the film compared to those of Lake County rhodochrosite. The above hypothesis appears to account satisfactorily for this interesting rhodochrosite doublet.

The lower peak may be due to manganoan siderite rather than to ferroan rhodochrosite. However, the *x*-ray diffraction lines more closely approximate rhodochrosite than siderite.

Stassfurt

This curve approaches the ideal for rhodochrosite. The narrow, sharp endothermic peak occurs at 612° C., and is followed by a typical exothermic peak with no irregularities. A trace of Mg^{++} as well as Fe^{++} appeared in the qualitative analysis but no effect can be seen on the thermal curve. This is to be expected for quantities of the substituting ions under 50%. When they occur as admixed impurities, the presence of even 5% is sometimes observable on the thermal curve as shown by the calcite in the Lake County specimen. On the basis of chemical and thermal analysis, this specimen appears to be the purest rhodochrosite studied.

Staffel, Bavaria

The peaks produced by this material are broad and of small amplitude.

The flat-topped exothermic peak is unusual and is believed to be due to the relatively lower position of the thermocouple in the sample holder used. The greater difficulty of penetration by oxygen may account for the broadening and flattening of the exothermic peak. Qualitative analysis indicated an appreciable amount of Fe^{++}.

Oberneisen, Nassau

Like the Stassfurt specimen, this material closely approximates the type curve. The sharp endothermic peak occurs at 616° C. and is followed by a relatively sharp exothermic peak. Qualitative analysis indicates appreciable Fe^{++} content, and a trace of Ca.$^{++}$ The amount of the latter probably is too small to affect the curve.

Lahnstein, Prussia

The curve produced by this specimen shows an endothermic peak at 609° C. followed by an exothermic peak which is typical except for the slight endothermic dip at the peak. Another slight endothermic dip at about 975° C. cannot be accounted for by the qualitative chemical data, which shows only a trace of Ca^{++} but appreciable Fe^{++} content.

C. Type Thermal Curve for Rhodochrosite. The thermal reaction in rhodochrosite which is responsible for the endothermic peak is the breakdown of the crystal structure, which involves the absorption of heat energy. Carbon dioxide is evolved and a low valence manganese oxide is formed. This is subsequently oxidized to a higher valence manganese oxide (hausmannite) and the heat liberated in the process is responsible for the exothermic peak (Beck, 1946). The areas under the peaks are a measure of the energy transformations involved.

The type thermal curve for rhodochrosite may be derived by the analysis of the mineral specimens already discussed. The purity of the specimen tested, as indicated by qualitative chemical analysis, *x*-ray powder patterns and optical study, and the size, shape and temperature of the endothermic and exothermic peaks of the differential thermal curve, are significant in determining the ideal rhodochrosite curve.

No specimen of pure rhodochrosite was sampled. Microscopic examination indicated that most of the specimens contained little impurity aside from other carbonates. All specimens except three showed some iron; in most, it was estimated to make up approximately 5–20% of the cations present. A number of samples showed iron as the only foreign cation. Of these, only two on the basis of the shape of the curve and the optical data appeared to be suitable as standards. Several others, especially Lake County #1 and #2 and Butte #2 showed smooth thermal curves with large amplitudes. These minerals, however, gave evidence of substitution in the lattice as shown by the upward shift of the endothermic peak and the semi-quantitative chemical analysis.

The Stassfurt and Oberneisen specimens, which appear of highest purity and whose thermal curves probably approximate the ideal rhodochrosite curve, are shown in Fig. 7. Qualitative analysis of the material from these localities showed only a trace of iron in the Oberneisen specimen and traces of Fe^{++} and Mg^{++} in the Stassfurt specimen. Both curves are remarkable for smoothness and regularity. Their peaks occur in the lower part of the rhodochrosite range at 612° C. for the Stassfurt specimen, and 616° C. for the Oberneisen specimen. Since Fe^{++} in small but appreciable quantities does not affect the thermal curve peak to any noticeable extent, it may be assumed that these specimens give thermal curves that are close to pure $MnCO_3$.

In summary, it appears that an ideal rhodochrosite thermal curve shows a sharp endothermic peak at about 615° C., followed immediately by a somewhat less sharp exothermic peak in the range of 690° C. to 735° C. and a generally smooth, regular form. The exothermic peak temperature depends largely upon the geometry of the thermocouple. The high temperature side of the endothermic peak is much steeper than the low temperature side, which is characteristic of carbonates in general. In contrast, the low temperature side of the exothermic peak is steeper than the high temperature side. Finally, the temperature at which the curve breaks for the endothermic peak is fairly constant for specimens of high purity and uniform grain size.

D. Manganocalcite. A group of manganocalcite specimens from Franklin, New Jersey, was examined for fluorescence, manganese content, color after heating to 1020° C., and thermal peak temperature. The results, summarized in Table 2, show a continuous downward shift in thermal peak temperature with increasing Mn content as qualitatively determined by controlled borax and soda bead tests and color of the powder after heating. Specimen #5 in the table indicated the highest percentage of Mn^{++}. An *x*-ray diffraction pattern of this specimen showed an appreciable shift of the lines toward rhodochrosite. (See Table 1.)

Conditions were maintained approximately constant in determining the fluorescence intensity, the concentration of Mn^{++} by bead tests and the thermal curves. A quartz-mercury lamp with a filter to eliminate the visible part of the spectrum from the source light was used.

W. L. Brown (1934) studied the fluorescence of manganocalcite as a function of manganese content. He showed that weak fluorescence was observable at 0.1% manganese, the maximum was reached at about 3.5%, was weak again at 10% and absent at 17%. This is consistent with the data in Table 2. An assumption of 10% manganese in specimen #5 on the basis of the shift in the *x*-ray diffraction lines is quite reasonable both in terms of the thermal curve shift, the fluorescence intensity, and the qualitative analysis.

That the fluorescence phenomena should go through a maximum while

TABLE 2. MANGANOCALCITE SPECIMENS, FRANKLIN, N. J.

No.	Description	Fluorescence	Qual. Chem. Analysis Bead Tests	Color after heating to 1020° C.	Thermal peak temperature
Iceland spar	clear transparent	none	no Mn	white	990° C.
#2	with zincite	very weak	no Mn	cream	980° C.
#3	coarsely crystalline with garnet	weak	trace	light brown	970° C.
#1	minor franklinite and willemite	moderate	trace–weak	light brown	975° C.
#6	white without other minerals	moderate	weak	medium brown	975° C.
#4	coarsely crystalline spotted with willemite	strong	moderate	chocolate brown	960° C.
#5*	minor willemite	weak	strong	dark brown	935° C.
rhodochrosite	Lake Co., Colo.	none	—	black	615° C.

* This specimen, American Museum of Natural History No. 10964, is estimated to have 5–10% Mn in cation position.

the thermal peak and *x*-ray line shifts appear to be linear is readily explained by the mechanism of the fluorescence postulated by Brown.

"If only a few atoms of manganese occupy similar positions to the calcium atoms in the crystal structure, their influence would be very small on the crystal as a whole and the atomic spacing would be practically that of pure calcite. This would produce a state of unstable equilibrium in the manganese atom, as it would occupy a larger space than it would require when in equilibrium in its own rhodochrosite structure. . . . As the number of replacing manganese atoms increases, it would be expected that the fluorescent emission would rapidly increase. With a further increase of replacing manganese atoms, however, there is a gradual shrinkage of the crystal structure, allowing the manganese atom less and less freedom for the separation of the electrons."

Finally a condition of stability would be reached in which fluorescence would no longer occur. Experimentally this occurs when roughly 20% of the calcium positions have been taken by manganese atoms.

In the course of this investigation several other "manganocalcites" were run from Franklin, New Jersey, Nordmark, Sweden, and Elbingerode, in the Hartz. These specimens proved to have several components including dolomite or ankerite. Peaks corresponding to manganocalcite with Mn^{++} occupying up to 25% of the cation positions were distinguishable. The manganocalcite peaks had the following values which were qualitatively consistent with the concentration of manganese detected by bead tests: Nordmark 915° C., Franklin 880° C., and Elbingerode (labelled "rhodochrosite") 780° C.

Therefore, it seems that the substitution of Ca^{++} for Mn^{++} is continuous from rhodochrosite to calcite and this substitution results in a continuous shift of the *x*-ray lines and in a single endothermic thermal curve peak. A double endothermic peak clearly indicates the presence of more than one carbonate mineral.

The "*d*" values for some of the strong lines in the *x*-ray diffraction patterns of the samples, selected on the basis of the thermal and chemical data, as representative of various positions in the calcite-rhodochrosite series, have been computed. Although the line positions throughout each pattern exhibit measurable deviations from the positions of corresponding lines in the other patterns of the series these variations become more conspicuous in the outer "high angle" range. In Table 1 the calculated "*d*" values for the outermost strong high angle line in each pattern is given. The figures indicate a correlation of the *x*-ray data with that obtained from the thermal and semi-quantitative chemical studies.

VI. CONCLUSIONS

A study has been made of the differential thermal curves yielded by specimens of rhodochrosite and manganocalcite. Variations in curves have been critically examined in the light of *x*-ray, chemical, and optical data. The effect on the thermal curves of rhodochrosite produced by cation substitution in the crystal lattice has been investigated. The curves obtained from artificially prepared two-component mixtures of rhodochrosite with other carbonates have been analyzed for effects produced on the thermal curve by carbonate impurities.

The following conclusions have been reached on the basis of the above data.

1. In the examination of rhodochrosite by differential thermal analysis optimum results will be obtained if the following precautions are observed:

(1) The fragment size should be restricted (minus 80, plus 200 mesh proved satisfactory) to obtain consistent thermal curves; larger fragments tend to raise the endothermic reaction temperature while smaller fragments tend to lower it appreciably.

(2) In order to obtain reproducible exothermic peaks, the cover on the sample holder should be raised somewhat to allow free circulation of air. Furthermore, the geometry of the thermocouple head must be constant from one run to the next.

2. For the sixteen specimens tested, a range in endothermic peak temperature of 609° C. to 724° C. was found. Only one specimen showed a peak temperature higher than 667° C., and the majority showed endothermic peaks in the lower part of the range (609° C. to 635° C.).

3. The temperature at which the endothermic peak appears depends on the amount of substitution of Ca, Mg, and Fe for Mn in the lattice, and to a smaller extent on the concentration of the mechanically admixed impurities present. Ca and Mg tend to raise the endothermic peak temperature because substitution of Ca or Mg for Mn strengthens the cation-carbonate bond, and consequently a greater amount of energy is required to destroy this bond. For analogous reasons, substitution of Fe for Mn tends to lower the endothermic peak temperature.

4. The thermal curves of the Oberneisen, and Stassfurt specimens most closely approach the theoretical curves for pure rhodochrosite. This theoretical curve has a sharp endothermic peak at about 620° C., followed immediately by a less sharp exothermic peak. The areas under the two peaks are of the same order of magnitude.

5. Two-component mixtures of rhodochrosite prepared in varying proportions with calcite, dolomite and siderite showed:

(1) A combination of the curves typical for each component.
(2) A decrease in endothermic peak temperature with increasing foreign constituent.
(3) A greater decrease in endothermic peak temperature per unit change in percentage composition in the high percentage impurity range than in the low percentage impurity range.
(4) A direct relationship between area under the peak and percentage composition of the constituent responsible for the peak.

Thus a specimen containing intimately intergrown calcite and rhodochrosite can readily be distinguished from a specimen of rhodochrosite which has appreciable calcium substituting for manganese. The former would show two endothermic peaks of decreased amplitude and peak temperature. The latter would show a single peak well above that for pure rhodochrosite.

The thermal results obtained from mixtures of rhodochrosite with other carbonates indicate that it is possible to determine the percentage composition of a mixture within about 10–15% by noting the size of the endothermic and exothermic peaks, and the temperatures at which they occur.

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