Thermal study of some manganese oxide minerals.

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Introduction.

IN the past decade, differential thermal analysis has developed into a very useful mineralogical technique. The theoretical background for this method has been treated by Speil, Berkelhamer, Pask, and Davies (1945) and has been modified by Kerr and Kulp (1948, 1949). The application of the method to the clay minerals has been carried out with considerable success by a number of workers in Europe and America. In particular, Grim and co-workers (1942, 1947, 1948) have produced a number of significant papers dealing with the thermal analysis of clays. The method has been extended to other mineral groups such as the carbonates (Faust, 1949; Beck, 1946; Kerr and Kulp, 1947; Cuthbert and Rowland, 1947; Kulp, Kent, and Kerr, 1950), phosphates (Manly, 1950), sulphates (Kulp and Adler, 1950), quartz (Faust, 1948), and the hydrous iron oxides (Kulp and Trites, 1950).

Since differential thermal analysis provides both qualitative and quantitative data of the presence of thermally active minerals, it is ideally suited to a study of fine-grained natural aggregates which present a difficult problem to other methods of attack. It appeared that the natural occurrence and importance of the manganese oxide minerals would make a preliminary investigation by thermal analysis desirable. The publication of two papers on the mineralogy of the manganese oxides (Fleischer and Richmond, 1943; and Gruner, 1943) has assisted greatly in understanding the complexities of the group, but no thermal analysis was carried out in these investigations. In this study it has been the objective to define the thermal curves of the simpler manganese minerals and to show how the method may be applied to natural mixtures.

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assisted in taking some of the thermal curves. Dr. H. H. Adler obtained the curve on ramsdellite in the course of another study.

Method.

Under the application of heat substances undergo exothermic and endothermic changes. This application may be carried out dynamically (differential thermal analysis) in which the system is heated at a constant rate. It is called *differential* because the temperature difference between an inert material and the sample is measured as both are being heated at a constant rate.

In order to obtain a satisfactory curve it is necessary to control the rate of heating so that it is uniform and reproducible, to measure the temperature with reasonable precision (2–5° C.), and to record the slight differences in temperature caused by changes in the sample as the temperature is raised. The last is determined by the use of a two-headed thermocouple, one head of which is placed in the sample while the other is placed in an inert material (generally alundum). The connexions are so arranged that the potentials oppose each other. Hence, if there is no reaction in the sample, the potentials balance and there is no net heat flow. Any heat effect in the sample will cause an unbalance and this is picked up on a sensitive recording device. The practical result is a plot which is a straight line when no reaction is taking place, but shows deviations in one direction or the other depending on the nature of the heat effect.

Since it is unlikely that any two minerals have chemical bonds of identical strength, they will decompose, oxidize, or change phase at different temperatures. The temperature at which a peak occurs often indicates which mineral is present. Since many minerals undergo several endothermic or exothermic changes in the temperature range studied, the aggregate peaks at the proper temperatures suffice in many instances to identify the mineral. The relative amplitude and shape of a peak is a function of the type of change, as well as the rate at which it occurs. The amplitude of the peak is related to the concentration of a particular mineral, and hence semi-quantitative estimates are possible by simple inspection. The area under the peak is proportional to the concentration according to the theoretical treatment of the problem.

Since each mineral will ordinarily yield a characteristic set of peaks independent of the foreign constituents, frequently the members of a mixture in a fine-grained aggregate may be defined. Obviously the more complex the mixture and the larger the number of components with

overlapping peaks the more difficult becomes the interpretation. Usually, however, X-ray, petrographic, and thermal data together are adequate to define the major minerals present in a mixture if the group is thermally reactive. In order to obtain quantitative results, it is necessary to prepare comparison curves by diluting pure minerals with some inert materials similar to those in the naturally occurring aggregates. A calibration curve based upon the amplitude of a significant peak is then constructed. The amplitude of the mineral peak in an unknown then yields by comparison the appropriate percentage of the mineral in the unknown. The amplitude is a more convenient measurement than the area under the peak and except for very sharp peaks is reproducible within the limits of experimental error.

Apparatus and procedure.

The apparatus used in this investigation is described by Kerr and Kulp (1948). The most recent modification is shown in fig. 1. It consists of four major components: a vertically mounted, wire-wound electrical resistance furnace; the specimen holder block and necessary attachments; the programme controller for automatically maintaining a constant rate of heating; and a Leeds and Northrup Speedomax electronic recorder with a full scale of 3 millivolts. Recent improvements include changing the recorder from a 6- to a 16-point type, 4 points of which are on absolute temperature while the other 12 are on differential temperature. A direct current electronic pre-amplifier coupled with an automatic synchronized rotary switch makes it possible to obtain sensitivities equal to any galvanometer without the attendant inconvenience and inefficiency of photographic recording.

The mineral specimen is ground to pass 80 mesh and packed into the specimen-holder recess to finger tightness. This procedure permits reproduction of peak amplitudes within the limits of experimental error. Experimentation indicates that processes such as weighing the sample, obtaining a narrow particle-size range, and bringing to constant humidity are unnecessary for most routine work. For special experiments any or all of these factors may require control.

Where quantitative calibration curves are desired, the mixture of the known materials should be prepared to correspond in particle size and intimacy with the natural unknown material. However, in most cases, rough mixture by weight gives the desired result.

All of the amplitudes are strictly comparable since they are corrected to an arbitrary reference curve of standard Georgia kaolinite. The

temperature range used for these studies was 100–1050° C. The heating rate was $12\frac{1}{2}$° per minute and the thermocouples were chromel-alumel.

The samples used were essentially homogeneous. Gangue observable by microscopic observation was rejected. Transparent impurities were identified in so far as possible by study of the powder with a petrographic
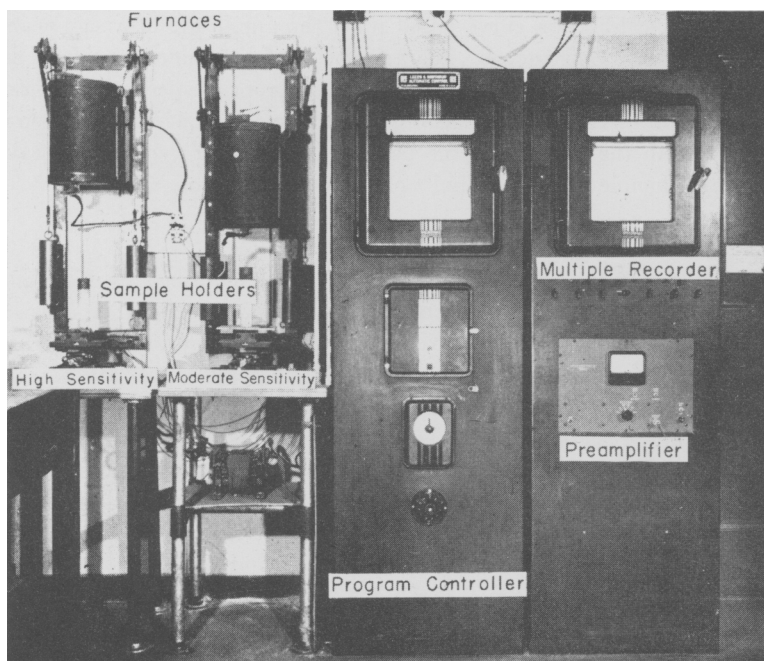

FIG. 1. Differential thermal apparatus at Columbia University.

microscope. Artificial mixtures were prepared from mineral specimens which had been carefully checked for purity by X-ray diffraction, thermal analysis, and petrographic examination.

Debye X-ray powder patterns were obtained on most of the specimens by the use of iron radiation. Patterns of the material heated to temperatures above that of the thermal curve peaks were also obtained so that the resultant phase could be identified.

Typical thermal curves.

Pyrolusite and ramsdellite.—A number of specimens that appear to be high quality pyrolusite were thermally analysed. The results appear

in fig. 2. The typical thermal curve for this mineral shows a major endothermic peak between 670 and 700° C. and a second lesser peak 1000–1010° C. The initial break occurs between 580 and 670° C.

The curve is slightly asymmetrical with a steeper return slope. All of these specimens showed a characteristic pyrolusite X-ray diffraction pattern with no extra lines. A sample (2–9) of the Numadate mine heated to 850° C. gave a distinct pattern similar to bixbyite $(Mn,Fe)_2O_3$.

The data of the heated pyrolusite are given below for the three principal lines and compared with the American Society of Testing Materials Index of X-ray patterns.

	(1)	(2)	(3)
Mn_2O_3	2·68	1·66	1·42
Bixbyite	2·73	1·65	1·41
Pyrolusite heated to 850° C. .	2·69	1·67	1·43

It has been shown that bixbyite has the same crystal structure as Mn_2O_3 (Pauling and Shappell, 1930), hence the product of the 700° C. peak in pyrolusite is due to the endothermic reaction

$$4MnO_2 \rightarrow 2Mn_2O_3 + O_2.$$
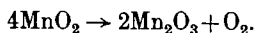
The same specimen heated to 1010° C. gave the pattern of hausmannite. Similar results were obtained with the specimens from Coburg (2–4) and Tenny Cape (2–6).

There are several minor differences in these curves (fig. 2) which are of interest. It is also noteworthy that the water content of these specimens is very low and that most of it is released before 100° C. This is consistent with the coarsely crystalline appearance of these specimens. All specimens except Tabua (2–2) were coarsely fibrous or platy and bright. The Tabua specimen consisted of very uniform fibres with traces of limonitic material. The minor peak at 350° C. is probably due to a few per cent. of goethite. The slight variation in the peak temperatures and amplitude are probably to be attributed to crystallite size. The low temperature (970° C.) of the Mn_2O_3–hausmannite conversion in the Numadate mine (2–9) specimen is not entirely understood.

Fig. 3 shows two curves of pyrolusite. The specimen from France (3–1) contains some inert impurity, probably hausmannite.

The specimen of pure ramsdellite (MnO_2) from the Idorado mine (3–3) is typical. A small amount of capillary water is indicated by the slight endothermic peak at 120° C. The exothermic phase change from ramsdellite to pyrolusite is shown at 500° C. on the differential thermal curve. Subsequent to this reaction the curve is similar to that of pyrolusite as would be expected. Note that in this case as in (2–9) the final
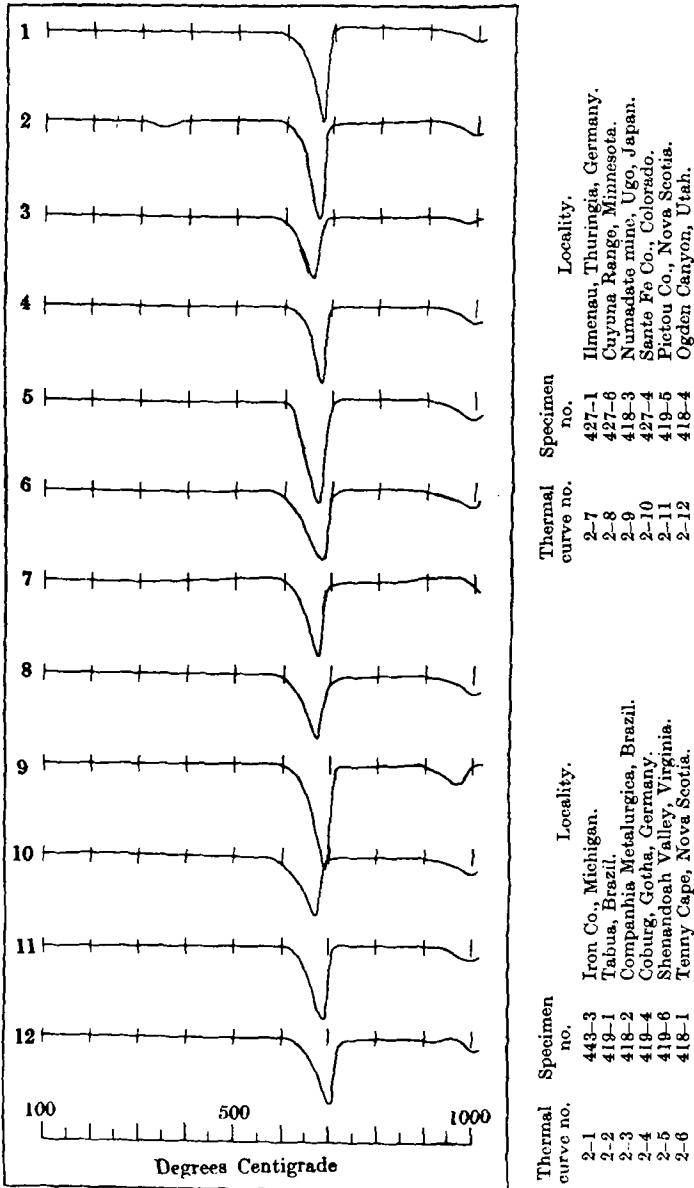
FIG. 2. Thermal curves of representative pyrolusite specimens. All specimens yielded a typical pyrolusite X-ray diffraction pattern without extraneous lines.
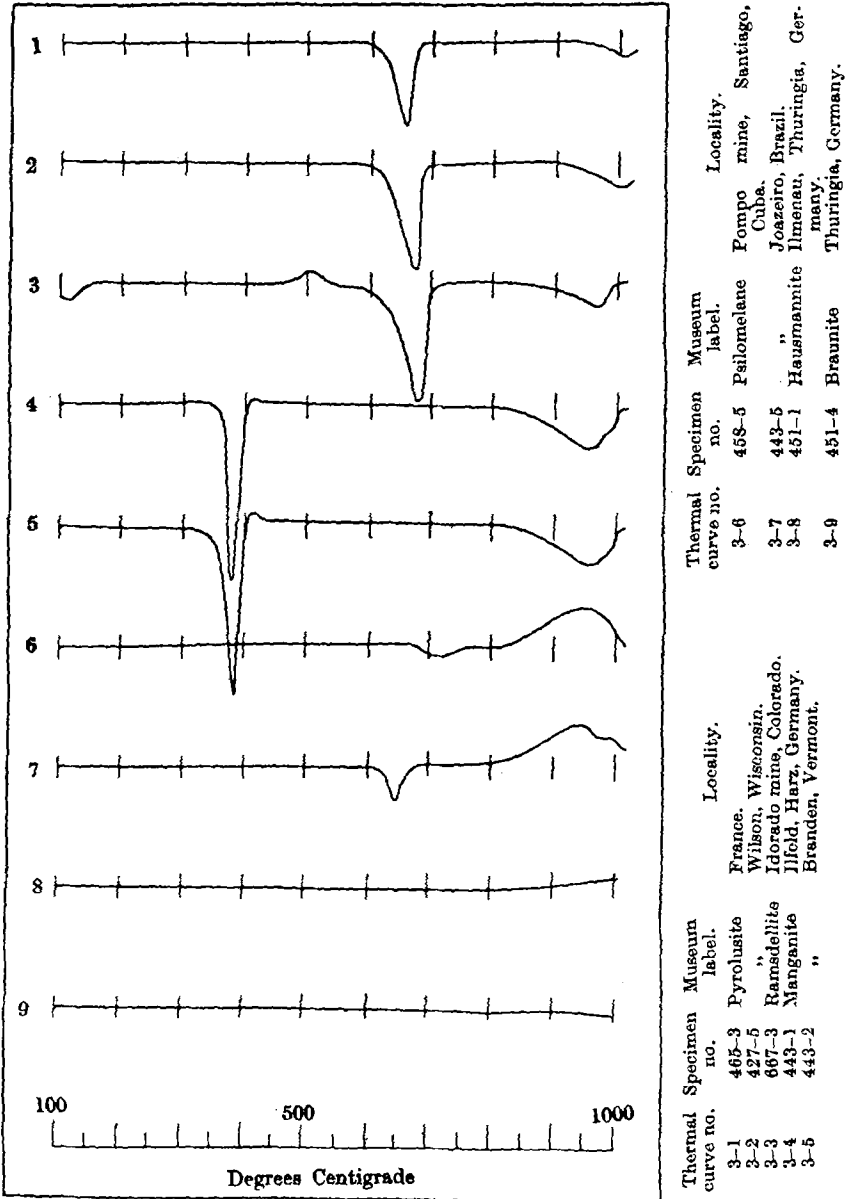
FIG. 3. Thermal curves of various manganese oxides.

endothermic peak temperature is reduced. This is probably to be related to the Mn_2O_3 crystallite size which forms in the pyrolusite decomposition. X-ray diffraction patterns taken at room-temperature (ramsdellite), 200° C. (ramsdellite), 550° C. (pyrolusite), 800° C. (Mn_2O_3), and 1000° C. (hausmannite) are consistent with the above interpretation.

Manganite.—The manganite specimens (3–4 and 3–5) show typical X-ray diffraction patterns with no extra lines. The specimens were shiny black prismatic crystals. The thermal curves show a sharp endothermic peak at 380° C. followed by a broader endothermic peak at 950° C.

The manganite goes over to Mn_2O_3 at 350–400° C. which remains stable until about 800° C. The Mn_2O_3 is less perfectly crystallized from this low temperature of formation (400° C.) as compared to the Mn_2O_3 produced from the pyrolusite decomposition at 700° C. This explains the lower temperature at which the final recrystallization starts. The slight doublet near 980° C. is not clearly understood. An X-ray pattern taken after heating to 900° C. showed only Mn_2O_3 lines, but one taken after heating to 1000° C. showed only hausmannite.

Psilomelane type.—Curves 3–6 and 3–7 of fig. 3 show the thermal curves of two specimens of the psilomelane type. The absence of analytical chemical data made it useless to study the complex members of this group. The broad exothermic reaction from 800 to 1000° C. appears typical of this group. The reaction is probably a recrystallization type of reaction. There appears to be no low-temperature reaction of this mineral. Specimen 3–7 contains about 20 % pyrolusite and gives expected inflections at 650° and 970° C. The presence of pyrolusite in this specimen was confirmed by X-ray diffraction.

Hausmannite and braunite.—One specimen of each of these high-temperature minerals was thermally analysed after X-ray diffraction examination had proved them to be monomineralic. They show no thermal reaction in the temperature range studied. This was confirmed by X-raying the specimen after heating to 1000° C.

Thermal curves of artificial mixtures.

The analysis of the mineral composition of natural aggregates of manganese oxide minerals requires a previous knowledge of the size and shape of characteristic peaks as a function of concentration. To this end a series of artificial mixtures were prepared and thermally analysed. Fig. 4 shows the results for mixtures of pyrolusite, manganite, and quartz. Note the additive effect of the high-temperature endothermic peaks of pyrolusite and manganite. Fig. 5 shows the curves for mixtures of
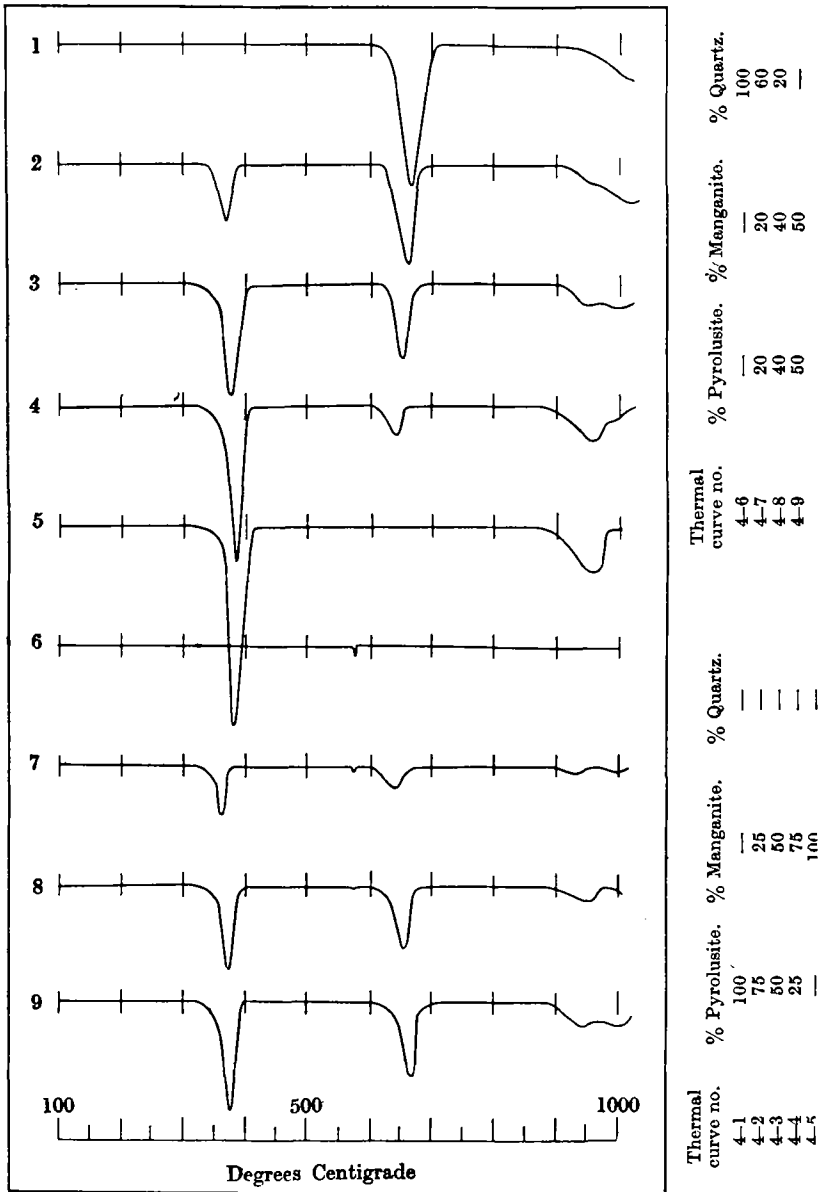
FIG. 4. Thermal analysis of artificial mixtures of pyrolusite, manganite, and quartz.
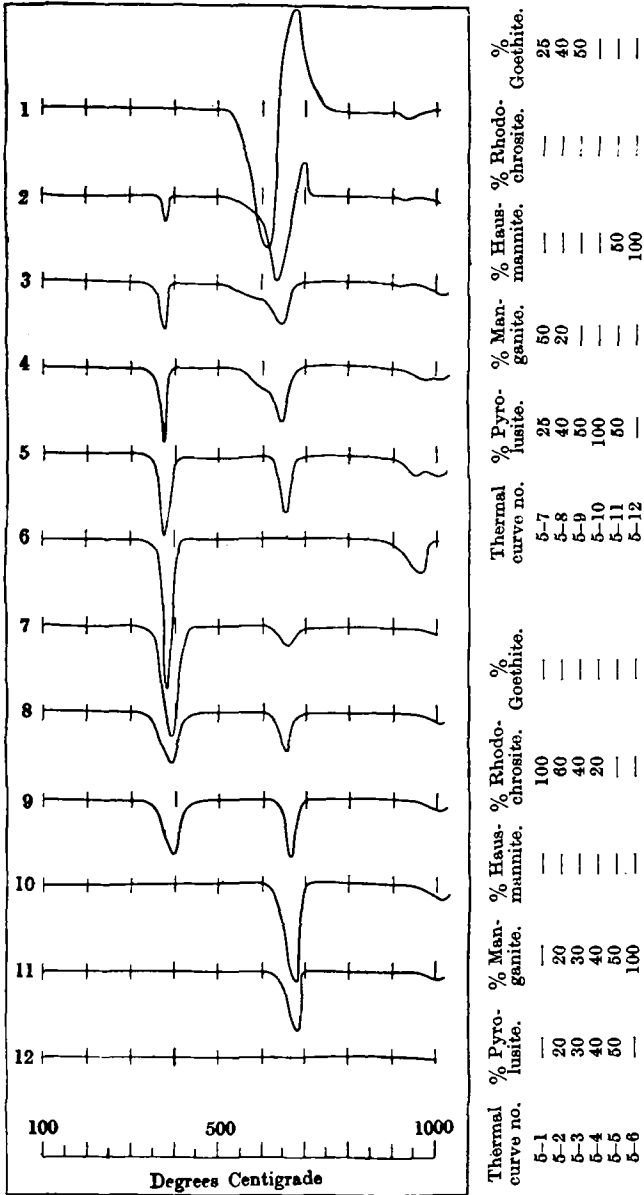
Fig. 5. Thermal analysis of artificial mixtures of pyrolusite, manganite, hausmannite, and rhodochrosite.

pyrolusite, manganite, hausmannite, rhodochrosite, and goethite. Note
the broadening of the manganite peak in the presence of goethite. In
general, the variation of peak amplitude or peak area with concentra-
tion is well established. These curves are used as a basis of estimating
percentages of these minerals in unknown assemblages.

Representative natural aggregates.

Fig. 6 shows the differential thermal curves of fifteen natural man-
ganese oxide aggregates. The names for the specimens as given on the
museum labels are included in the accompanying table. The present
results show that in several cases they had been incorrectly determined.

(6–1) labelled pyrolusite from Thuringia contains 30 % manganite,
25 % pyrolusite, and 10 % (?) psilomelane type mineral in addition to
inert material which includes hausmannite; X-ray diffraction showed
lines of pyrolusite, manganite, and hausmannite. (6–2) contains 40 %
manganite, 10 % dusty pyrolusite, and some hausmannite. (6–3) con-
tains 15 % manganite and goethite (?), and 10 % pyrolusite; X-ray
diffraction showed only hausmannite lines. (6–4) contains 50 % quartz
and 20 % pyrolusite; X-ray diffraction showed only quartz and pyrolu-
site lines. (6–5) shows 80 % pyrolusite with a thermally active but
unidentified material giving a small sharp endothermic peak at 630° C.
(6–6) contains 80–90 % lepidocrocite with possibly 10 % psilomelane
type. (6–7) shows 2–6 % pyrolusite; X-ray pattern showed hausmannite
lines. (6–8) contains 30 % fine pyrolusite; the specimen shows strong
X-ray lines of hausmannite. (6–9) contains 25 % fine pyrolusite as
well as hausmannite. (6–10) shows 20 % fine manganite and goethite (?),
20 % coarse pyrolusite, and 40 % (?) psilomelane type. (6–11) shows
the presence of colloidal water and a small amount of organic matter
which yields the exothermic peak at 210° C. It also contains 10 % coarse
pyrolusite and possibly 10 % psilomelane. (6–12) contains hausmannite
(X-ray) and pyrolusite 15 %. (6–13) is a specimen of high manganite
(80 %) with the presence of some unidentified but thermally active con-
stituent which produces the broad peak at 500–600° C. (6–14) shows the
presence of some organic matter by the exothermic dome at 300–400° C.,
psilomelane type 80 % (?), and fine pyrolusite 10 %. (6–15) shows a
thermal peak of fine calcite and gives an X-ray pattern showing braunite
as the major constituent.

Conclusions.

Representative specimens of the more common manganese oxide
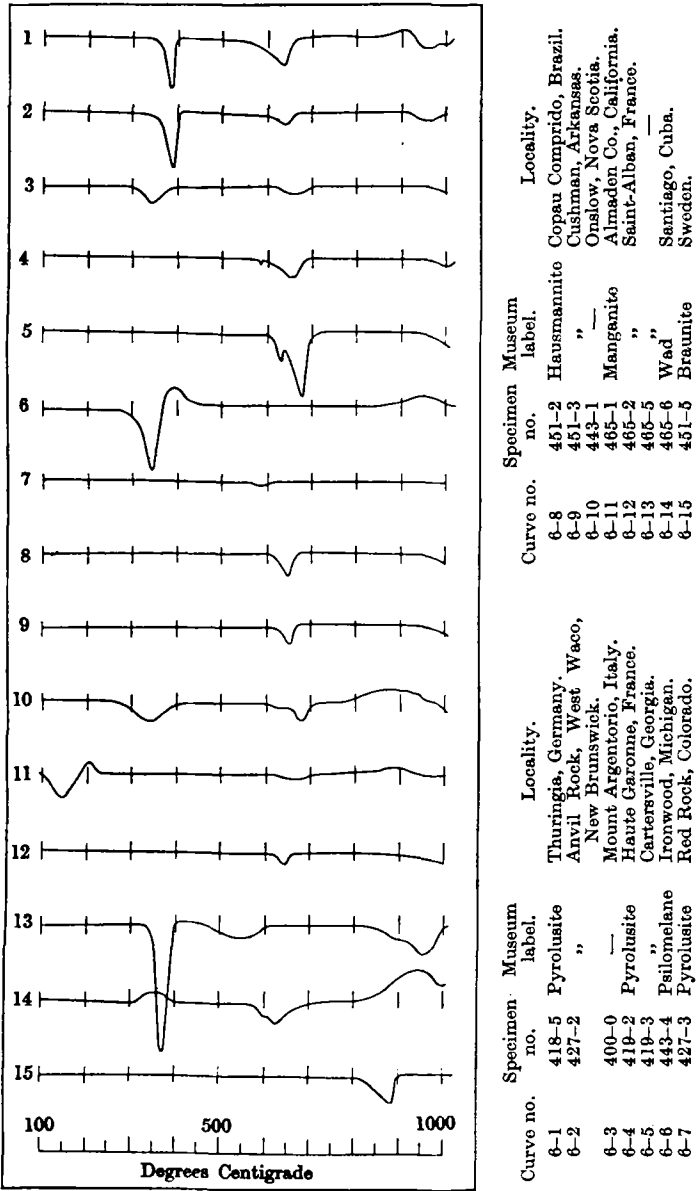minerals have been thermally analysed. Pyrolusite, manganite,

FIG. 6. Thermal curves of natural hydrous manganese oxide aggregates.

ramsdellite, and the psilomelane type minerals give distinctive thermal reactions which may be used in the semi-quantitative analysis of the components of a natural mixture. A group of natural aggregates have been analysed and the concentrations of the various minerals, interpreted in terms of the thermal curves of artificial mixtures. The application of thermal analysis to this group of minerals provides valuable information unavailable by other standard methods of technique.

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