QUANTITATIVE DIFFERENTIAL THERMAL ANALYSES OF CLAY AND OTHER MINERALS

H. W. van der Marel,
*Agricultural Experiment Station and Institute for
Soil Research, T.N.O., Groningen, Netherlands.*

Abstract

The shape and the intensity of the thermal curve of minerals, when analyzed by the *d.t.a.* method, are strongly influenced by amorphous coatings and disordered structures on the surface of the particles (Beilby layer), and furthermore by differences in particle and/or crystallite size, the degree of crystallinity of the crystallites and ion substitutions in the crystal structure. Examples are given.

Especially in the group of natural clay minerals, variations in these phenomena are numerous. Consequently an accurate quantitative determination of the amount of a clay mineral in a sample by means of the *d.t.a.* method, is impossible. Thus it was found that even kaolinite from pure well known deposits has a heat of transformation which varies from 100 to 176 and from 23 to 43 cal./g. for its endothermal (ca 600° C.) and exothermal reaction (ca 980° C.) respectively.

For other minerals reliable results can be obtained only if the conditions under which the specimens are formed in nature are practically always the same and the minerals are moreover of pure chemical composition, i.e., circumstances, which are mostly seldom found. These conclusions are based on experiments where errors due to the differential thermal analysis *d.t.a.* apparatus are eliminated by calibration of the instrument with a standard chemical, use of the same sample holder and thermocouple, dilution of the mineral with the inert reference material and packing the mixtures always in the same way in the sample holder.

Introduction

Quantitative *d.t.a.* has been applied by several authors as a rapid, inexpensive and accurate method for the determination of the amount of a mineral—see e.g. Norton (1940) for kaolinite, hydrargillite and diaspore in bauxites from Dutch Guiana, Kiyoura and Sata (1950), and Murray et al. (1951) for calcite in limestones. This method of analysis was also used by Vold (1949) to determine the amount of stearic or benzoic acid in a sample from its heat of fusion. The result should be accurate to within a few per cents according to the authors. Grimshaw and Roberts (1953) suggest that the accuracy of the *d.t.a.* method can be increased by diluting the samples 1:3 with inert (calcined) alumina before the test. For in this case the conductivity of the samples investigated should be nearer to that of the inert α-Al_2O_3 reference material which is used in a *d.t.a.*

However, Speil et al. (1945) found for undiluted samples of kaolinite from various origins, deviations of about 30% in their heats of transformation. De Bruijn and Van der Marel (1954) who investigated aside from kaolinite also other minerals from various localities, arrived at

deviations of 100 to 200%. These large deviations cannot be ascribed merely to the heat of conductivity being unequal for all the samples investigated. According to the authors, they should be caused by differences in particle size, degree of crystallinity of the crystallites and substitutions in the crystal structure of the samples investigated. Another factor is that loss of heat flowing away from the samples through the various thermocouples cause deviations of ca 30% according to De Josselin de Jong (1955).

It is the purpose of this article to obtain data about the variation in thermal effects of minerals from various origins, and also about the most important factors by which heat of transformation of a certain mineral is affected. All the *d.t.a.* tests described in the experimental part of this article have been performed with the apparatus constructed and described by De Bruijn (1954) and which has been in operation in the Laboratory of Soil Mechanics at Delft (Netherlands) since 1952.[1]

The nickel-block oven contains 6 holes in which 5 samples can be analyzed simultaneously, the remaining hole being reserved for the inert reference material, usually α-Al_2O_3 previously heated for several hours at ca. 1300° C. It is provided with Pt/Pt, Rh thermocouples, a Boersma amplifier and a Brown recorder.

EXPERIMENTS

Factors by which the thermal transformations of a mineral are affected when it is heated and the effect registered by the *d.t.a.* method, are:

(1) *Particle size of the mineral investigated*

Many authors have found that the finer the particle size of the sample, the lower is the actual temperature at its transformation and the smaller is the peak area—see Van Nieuwenberg (1929), Speil et al. (1945), Laws and Page (1946), Lippman (1952), Martin and Russell (1952) and Robertson et al. (1954) for kaolinite, Caillère and Hénin (1947) for antigorite, Kerr and Kulp (1948) for dickite, Van Schuylenborgh and Arens (1950) and Kulp and Trites (1951) for goethite, Perkins (1950) and Martin and Russell (1952) for montmorillonite, Sabatier (1950) for chlorite, Barshad (1950) for paragonite, Barshad (1950), Mackenzie and Milne (1953), De Bruijn and Van der Marel (1954) for muscovite. De Bruijn and Van der Marel (1954) for pyrophyllite, Faust (1949), Graf

---

[1] The author is indebted to Prof. Ir. E. C. W. A. Geuze, Director of the Laboratory for Soil Mechanics, Delft, for use of this apparatus and to H. Labrie for assistence in the analyses.

(1952), Bradley et al. (1953) for dolomite, Kulp et al. (1951) for calcite. Also quartz when occurring in nature as small crystallites (chalcedony), which after x-ray analysis shows a perfect structure, only demonstrates a small negligible α/β d.t.a. effect—see Berkelhamer (1944) and Fieldes (1952).

Apparently, the smaller the particle or the crystallite size, the smaller are the forces needed for the transformations inside the crystals. Even a qualitative identification of many minerals may be impossible because by differences in particle size the peak temperature may be shifted about 200° C. to lower temperatures and the intensity of the endothermal effect may be largely decreased—see the examples in Speil et al. (1945) for kaolinite, Caillère and Hénin (1947) for antigorite and De Bruijn and Van der Marel (1954) for muscovite and pyrophyllite. Figure 1 shows examples demonstrating the large effect of particle size on the thermal reactions of quartz, chalcedony, muscovite, biotite, pyrophyllite and calcite.

Another difficulty is that when particle size decreases there is an increased influence of the amorphous or vitreous—so called Beilby (1921) —layer on the thermal effects. This layer has chemical-physical properties quite different from those of the original crystalline material. Thus Laws and Page (1946), Perkins (1950), Parkert et al. (1950), Dragsdorf et al. (1951) found that by grinding kaolinite in a ball mill, the original 600° C. endothermal reaction was almost completely lost and a severe fogging appeared on the x-ray photo. Moreover, the cation exchange capacity of the material has largely increased. After treatment with 0.1 n HCl the residue gave sharp diffraction patterns identical with those of the unground sample. Their conclusion was that by grinding, amorphous permutite-like substances or amphoteric $Al(OH)_3$ and H_4SiO_4 groups are formed, coating the particles with a thin layer and having a quite different physical-chemical behaviour as compared with the original mineral.

Fieldes (1952), using the silt fraction of a New Zealand soil, which after x-ray diffraction contained 50% of α-quartz, found only 5% of it by a d.t.a., the mineral having its usual 573° C. inversion peak. Quantitative analysis of quartz by means of x-ray and differential thermal analysis and the occurrence of an amorphous layer on the surface of fine quartz particles has been extensively studied, because fine dust in the air of mining districts may contain quartz which causes a lung disease (silicosis) when inhalated continuously.

It was found that the Beilby layer could be removed by treating the sample with a borate buffer—see Clelland et al. (1952)—or by etching with HF—see Clelland and Ritchie (1952), Nagelschmidt et al. (1952).
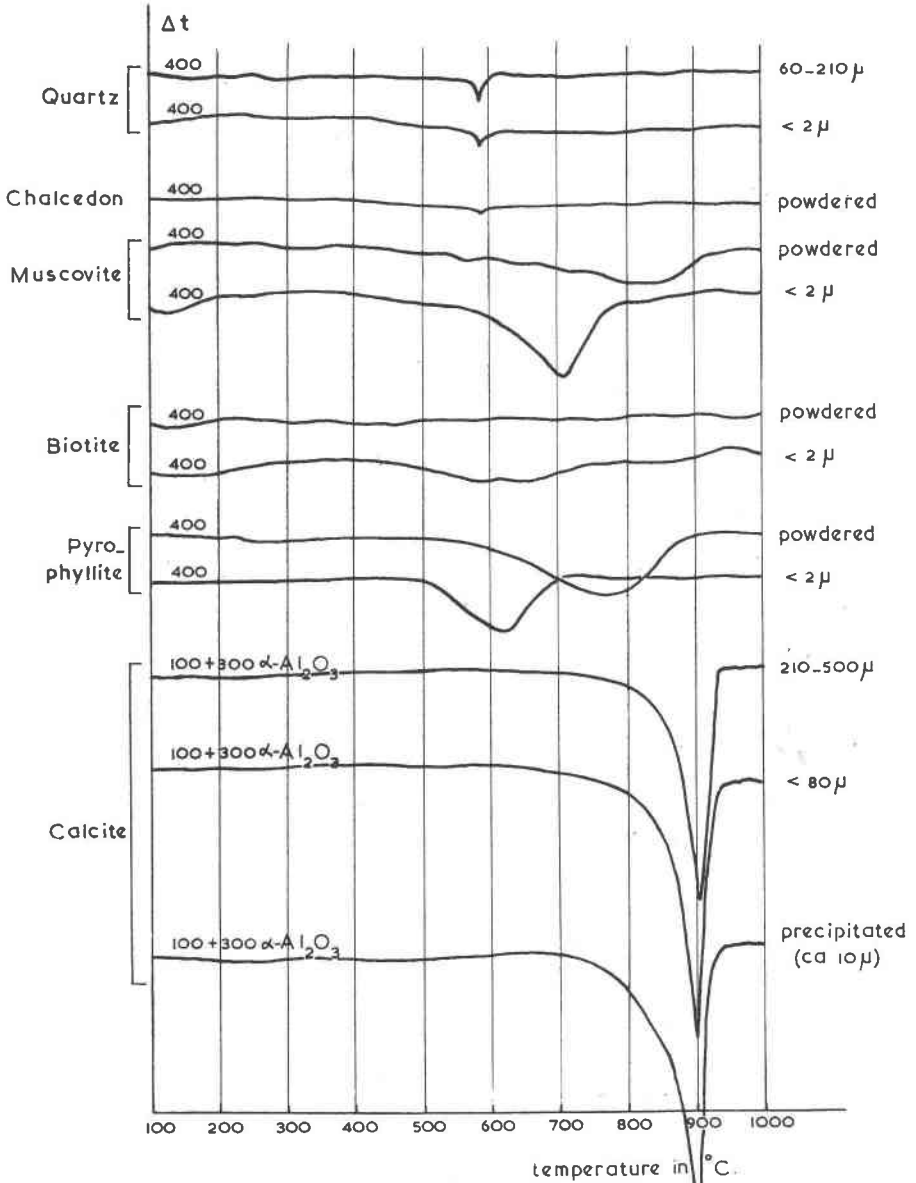
FIG. 1. *D.t.a.* of various minerals in different grades of fineness.
Weight of samples analyzed in mg.

Grimshaw and Roberts (1953)—and that the intensity of the original
α/β transformation could be restored.[2]

(2) *Degree of crystallinity of the mineral investigated*

According to Grimshaw et al. (1945), Grim (1947) and Murray (1954)
the endo- and exothermal reaction of the poorly crystallized kaolinites
(fire clay, ball clay) are broader, of less intensity and they begin at a
lower decomposition temperature than the corresponding reactions of
the better crystallized ones. The first is caused by loss of OH from the
crystal structure and the latter by the formation of γ Al_2O_3.

Caillère and Hénin (1948*b*) ascribe the difference in peak temperature
of the endothermal reaction of dickite, kaolinite and metahalloysite,[3] be-
ing ca. 580° C., 550° C. and 525° C., respectively, to differences in the de-
gree of crystallinity. The first is the best crystallized and the last the
poorest. Apparently a mineral with a high degree of crystallinity needs
more energy for its transformation to a new structure than a mineral of
poor crystallinity. According to Speil et al. (1945), Kerr and Kulp (1948),
Bramao et al. (1950, 1952) and Glass (1954), metahalloysite (and hal-
loysite) may also be distinguished from kaolinite by the shape of the en-
dothermal reaction, *i.e.* the peak for metahalloysite (halloysite) returns
to the base line at a faster rate than it departs, whereas well crystallized
kaolinites show about equal rates. The shape ratio of the thermogram,
i.e. tan α/tan β, in which α = the angle between the perpendicular to
the peak and the descending side and β = the corresponding angle on the
ascending side, has been proposed by Bramao et al. (1952) as a conven-
ient means to distinguish kaolinite from metahalloysite (halloysite). The
reason of this different behaviour of the above minerals is, according to
Kerr and Kulp (1948), that the sheets in the metahalloysite (halloysite)
structure are superimposed in a less orderly manner than in kaolinite.
The occurrence of halloysite (metahalloysite) in nature as small lath-
shaped and not as plate-like particles such as kaolinite, is also supposed

---

[2] The thickness of the Beilby layer on quartz particles was computed by Clelland (1951),
Dempster (1951), Clelland et al. (1952), Clelland and Ritchie (1952) and Dempster and
Ritchie (1952, 1953) from the decrease in density, the decrease in *d.t.a.* effect and the in-
crease in SiO_2 dissolved by the borate buffer between the original and the ground kaolinite
sample. They found 0.03–0.05 μ, 0.11–0.15 μ and 0.02–0.03 μ respectively. Nagelschmidt
et al. (1952), Gibb et al. (1953) found from x-ray and electron diffraction analyses 0.03 μ
and 0.03–0.06 μ, respectively. Meldau and Robertson (1952) arrived at 0.03 to 0.20 μ
for augite, hornblende, fluorite and aragonite by electron diffraction analysis.

[3] In this paper the terms halloysite and metahalloysite, the latter resulting from the
former by heating at ca. 45° C., have been used to designate the phases $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$
and $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, respectively, also called endellite and halloysite, respectively by
other investigators.

to be caused by stresses in the crystal resulting from this particular structure.

By x-ray analysis the poorer degree of crystallinity of halloysite and metahalloysite as compared with kaolinite can easily be observed on the photo—see e.g. van der Marel (1950). Therefore, due to a lack of perfection of the individual crystallites, rather than to their smaller size, the *d.t.a.* curve of halloysite (metahalloysite) is not symmetrical as in kaolinite, but asymmetrical. However, de Bruijn and van der Marel (1954) and Robertson et al. (1954) observed many well crystallized kaolinites, verified by x-ray analysis, to have an asymmetric endothermal reaction. In Plate I are some examples. Thus the size of the crystallites and amorphous coatings—see under (1)—on the particles have also affected the shape and the intensity of the endothermal effect of kaolinite.

(3) *Ion substitutions in the crystal structure of the mineral investigated*

According to Orcel (1935) and afterwards Kelley and Page (1943), Caillère and Hénin (1947, 1948*a,b*, 1949), Kulp et al. (1951), Graf (1952) the introduction of iron into the structure of a mineral, substituting aluminum, magnesium or silicon, shifts the endothermal peak temperature to lower grades and changes its intensity. According to Caillère and Hénin (1947, 1948*a,b*, 1949) the kind of binding of OH in the crystal structure of a mineral is related to its decomposition temperature. In this way OH of talc, antigorite and brucite is bound with decreasing strength in the same order as here mentioned as they have endothermal effects at 950° C., 650° C. and 400° C., respectively.

Page (1943) and Kelley and Page (1943) found that when Al is the predominant constituent of the octahedral sheet of the 2:1 minerals, the water is given off at a lower temperature than when Mg is the predominant constituent. Grim and Rowland (1942) found that iron-free Texas montmorillonite does not show its exothermal peak (caused by the formation of a spinel) until at ca. 1050° C. As a contrast magnesium-rich Otay montmorillonite does not show a distinct exothermal reaction because enstatite is formed at ca. 950° C. instead of spinel—see Earley et al. (1953). In Fig. 2 is demonstrated the evident effect of ion substitutions on the shape and the intensity of the *d.t.a.* curve for some montmorillonites, kaolinites and carbonates—see also the examples given by other investigators.

(4) *Different exchangeable cations in the mineral investigated*

Hendricks et al. (1940), Caillère and Hénin (1944), Barshad (1948, 1950) and Arens (1951) found that the kind of exchangeable cation affects the shape and the intensity of the low temperature endothermal
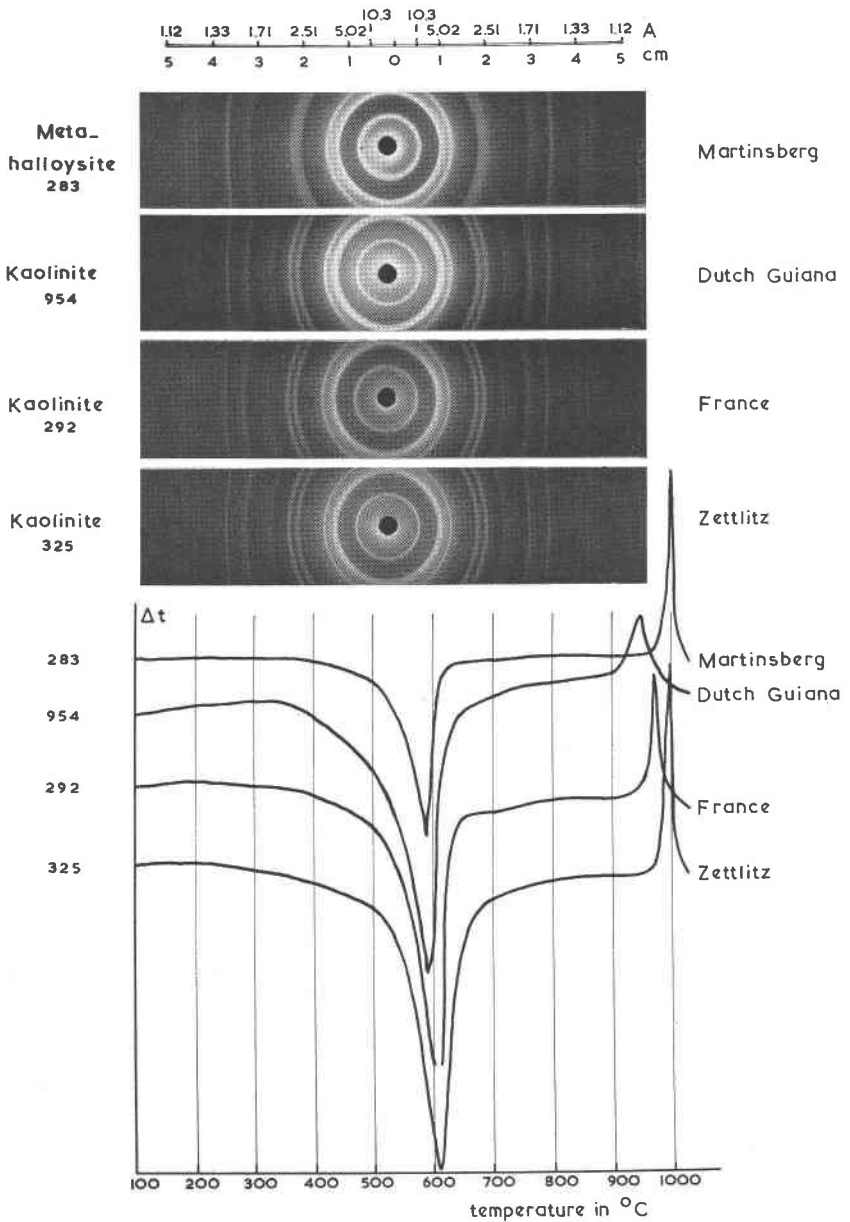
Note: all the samples were dried 1 hour at 105° C. before the *d.t.a.*

PLATE I. X-ray and *d.t.a.* analyses of metahalloysite and kaolinite <2μ with an asymmetric shape of their endothermal reaction at 600° C. Furthermore of kaolinite <2μ from Zettlitz (Czechoslov.) with a symmetric shape as usual.
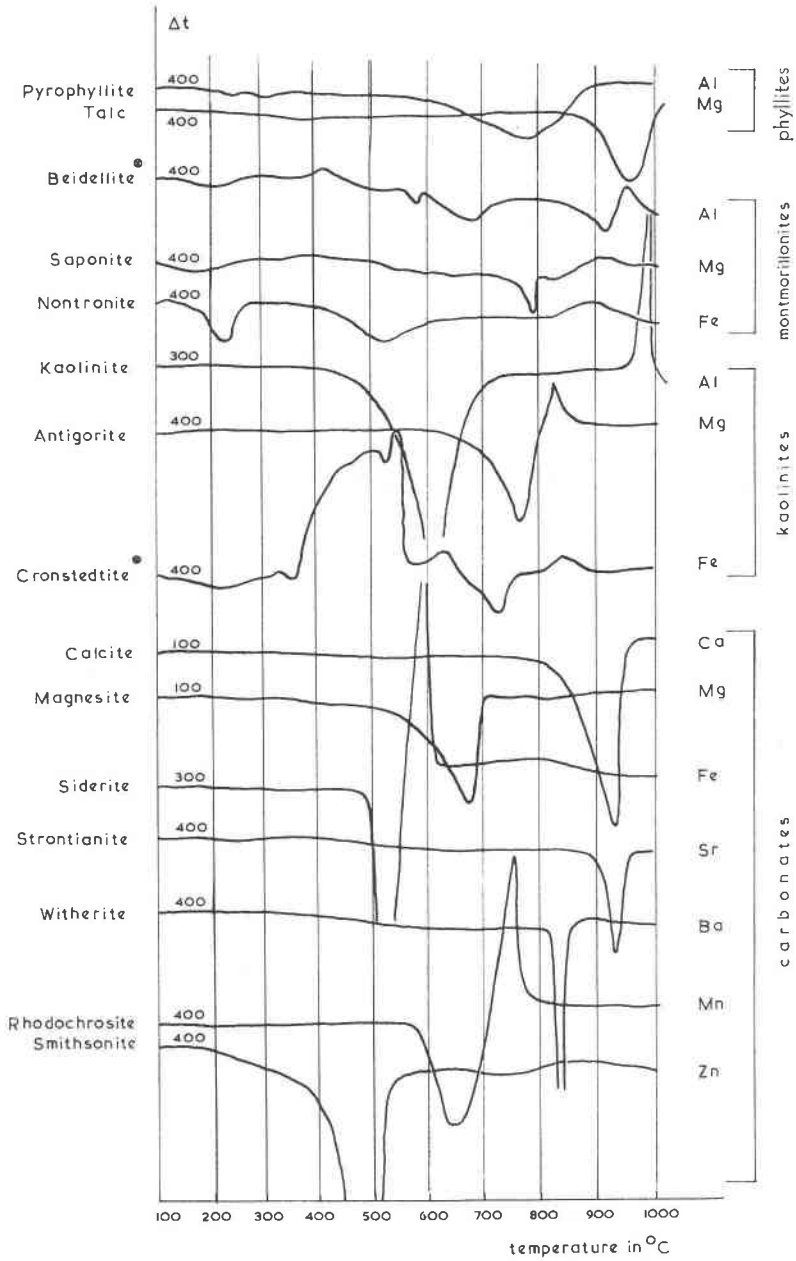
⊗ The author is indebted for these valuable samples to Dr. S. B. Hendricks, U. S. Department of Agriculture, Beltsville, Maryland, (U.S.A.).

FIG. 2. *D.t.a.* of pyrophyllite and talc and some montmorillonites, kaolinites and carbonates. Weight of samples analyzed in mg.

reaction of montmorillonite. Faust (1951) arrived at the same result for sauconite, *e.g.* a mineral representing the Zn-end member of the montmorillonite series.[4] The low endothermal reaction of montmorillonite is caused by loss of planar water, broken bound water and water bound to adsorbed cations. The latter is the most firmly held and thus has an endothermal reaction at higher temperature than the foregoing.

A very large effect on the *d.t.a.* diagram of saturating a mineral with different cations, has been observed for vermiculite by Barshad (1948), Walker and Milne (1950) and Arens (1951). This mineral contracts its plates when saturated with K^+, NH_4^+, Rb^+ and Cs^+ ions thereby expelling the water molecules between the layers, when saturated with Ca^{++}, Mg^{++}, or Sr^{++} ions—see Gruner (1939), Barshad (1948, 1950), Walker (1950). Mackenzie (1950) has attempted to correlate the peak temperatures as found by Hendricks et al. (1940) for montmorillonite saturated with various cations, with the hydration energies of these ions according to Bernal and Fowler (1933). A correlation was found, except for lithium. However Greene-Kelley (1953) pointed out that the activation energy detected by the *d.t.a.* method is not directly related to the hydration energy of the cation concerned. It will also depend on the charge density between the layers. In this way cations which give double peaks for vermiculite, may give single peaks for montmorillonite. Of course minerals with a small cation exchange capacity such as kaolinite—see Arens (1951)—will not manifest significantly the phenomenon of its *d.t.a.* curve being influenced by the kind of adsorbed cation. In Fig. 3 are some examples demonstrating the effect of the kind of adsorbed cations on the low temperature thermal reaction of vermiculite and open illite (ammersooite). The latter mineral also contracts its plates when treated with K^+, NH_4^+, Rb^+ and Cs^+ ions thereby expelling its cation bound H_2O molecules from between the layers—see Van der Marel (1954). In order to eliminate the disturbing effect of the weaker bound H_2O molecules, the samples were dried (in this case 1 hour at 105° C.) before they were analyzed by the *d.t.a.* method. Moreover the samples were analyzed under conditions where errors due to the apparatus could not disturb the results. As pointed out by De Josselin de Jong (1956) these errors are: dilution of the sample with the inert reference material (α-Al_2O_3), packing the samples always in the same way in the sample holder, covering the thermocouples with sufficient material so that the heat flow in the neighbourhood of the thermocouples always follows the same geometrical (cylindrical) pattern. Finally the sample holder+its

[4] By montmorillonite is meant here, as in common usage, the high aluminum member of the montmorillonite series with some slight replacement of Al^{3+} by Mg^{2+} and no replacement of Si^{4+} by Al^{3+}.

thermocouple was calibrated with a standard chemical (in this case $CuSO_4 \cdot 5H_2O$) before and after each mineral/α-Al_2O_3 mixture was analyzed.

As may be observed from the results, the effect of the kind of exchangeable cation is smaller for the open illite as for vermiculite. However, the total cation exchange capacity of the open illite is only ca. 65 m.e./100
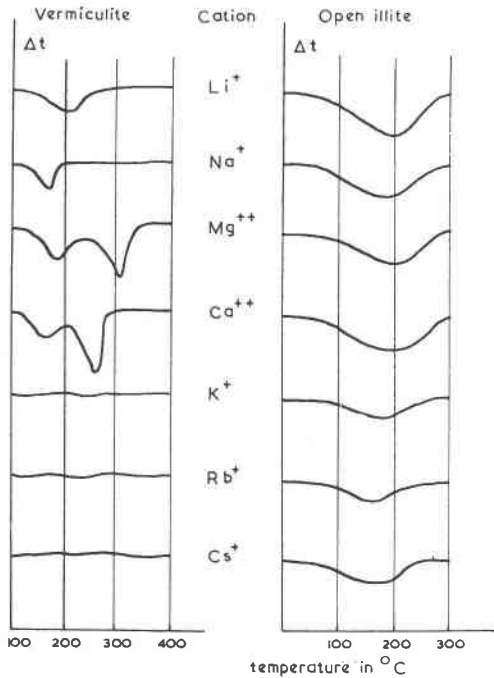
Note: All samples dried 1 hour before the *d.t.a.* and diluted 3:1 with α-Al_2O_3.

FIG. 3. *D.t.a.* of vermiculite and open illite (ammersooite) saturated with different cations.

g. as against ca. 120 m.e./100 g. for vermiculite. Therefore, also the total amount of H_2O molecules which influence the thermal effect of open illite is smaller than that of vermiculite.

(5) *Chemical reactions between minerals in the sample investigated*

Decomposition of pure dolomite, $CaMg(CO_3)_2$ takes place in two steps. First the magnesite component loses its CO_2 at ca. 800° C. and thereafter the calcite component loses its CO_2 at ca. 900° C.—see Flood (1950). However, Stutterheim et al. (1951), Heady (1952) and Webb

(1953) found that in an intimate mixture of dolomite and $Ca(OH)_2$, the normal large endothermal reaction due to the decomposition of $MgCO_3$ in the dolomite, was hardly noticeable. This effect was caused by the instantaneous, exothermal reaction between the CO_2 evolved from the $MgCO_3$ fraction of the dolomite with the CaO resulting from the prior decomposition of the $Ca(OH)_2$. In consequence the first endothermal effect of dolomite was almost completely cancelled, but the second endothermal effect of dolomite was enlarged as its effect was increased by the endothermal reaction of the formed $CaCO_3$ having the same peak temperature as the $CaCO_3$ component of dolomite. On the other hand Webb (1953) found for molar mixtures of $MgCO_3$ and CaO or $Ca(OH)_2$, that a $MgCO_3$ peak was obtained which was followed by only a small $CaCO_3$ peak. Thus the same reaction took place as in the foregoing example but only less readily. In mixtures of quartz and calcite, the endothermal reaction of calcite is hindered by an exothermal reaction of calcium silicate, following immediately upon the former—see Lippmann (1952).

(6) *Other disturbing components in the sample investigated*

According to Grimshaw et al. (1945), Heady (1952) and De Bruijn and Van der Marel (1954) exothermal effects caused by small amounts of organic matter (humus) are often so pronounced as to reduce, or even to eliminate any endothermal effect which may take place simultaneously. By treating the sample before the *d.t.a.* with H_2O_2, slightly decomposable organic material may be oxidized. Many soils and shales, however, contain organic matter which cannot be destroyed with H_2O_2, e.g. cellulose, lignin and elemental carbon. According to Mackenzie and Lakin (1953) graphitic (crystallized) carbon is less easily oxidized in air than amorphous carbon and thus shows an oxidation peak at a much higher temperature.

It should be mentioned here that Allaway (1949) could magnify the endothermal effect of montmorillonite, beidellite and nontronite by investigating samples saturated with piperidine. The latter is first reduced to carbon and then yields hydrogen with the water vapour escaping from the crystal at its decomposition temperature and which has a great heat of combustion when reacting with the oxygen of the air. However, for kaolinite having only a small base exchange capacity, or for samples mixed with finely divided carbon, this method has proved to be valueless. Evidently, a mechanical mixture of inert clay with piperidine or carbon burns in a way much different from a clay which contains adsorbed piperidine cations.

If organic matter is present, the only way to avoid errors is to analyze the sample in vacuum or argon atmosphere—see Rowland and Lewis

(1951). A number of workers—see Budnikov and Bobrovink (1938), Berg (1943, 1945), Schwob (1950) and Graf (1952)—have described the evident, decreasing effect of only small amounts of soluble alkali and alkaline earth chlorides and carbonates, upon the thermal decomposition of dolomite. Caillère and Hénin (1948*b*) observed for mixtures of NaCl
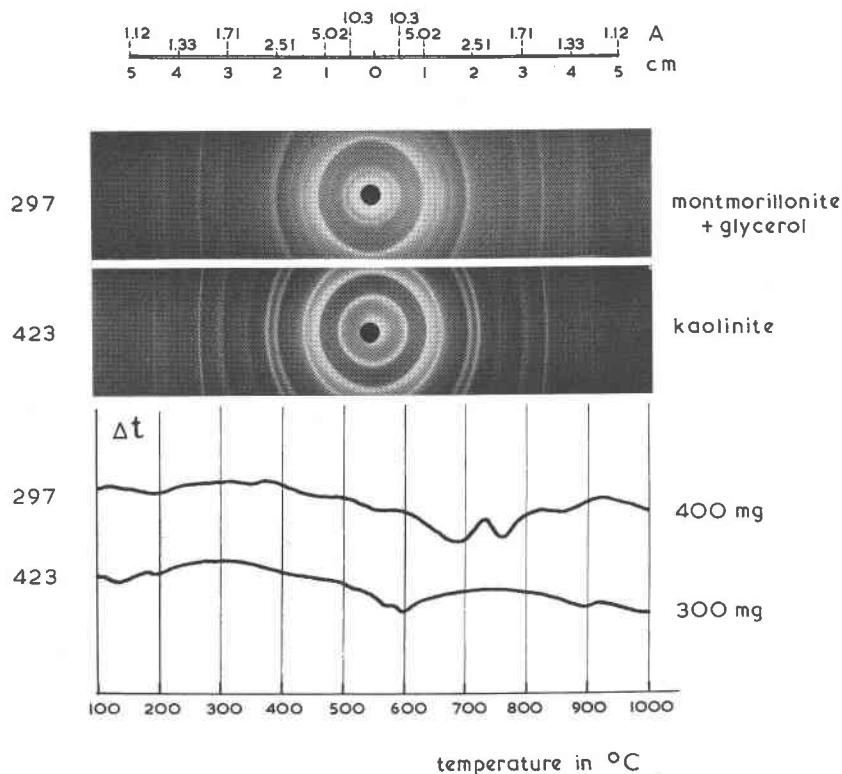
Note: the samples were dried 1 hour at 105° C. before the *d.t.a.*

PLATE II. *X*-ray and *d.t.a.* analysis of montmorillonite $<2\mu$ and kaolinite $<2\mu$ which contain Na_2CO_3.

and KCl that the endothermal peak temperature—being for each component in its pure state ca. 800° C.—is even shifted to 660° C. in the 50% mixture. Moreover, they found for NaCl, KCl, $CaCO_3$, $CaSO_4$ mixtures that the endothermal reaction of calcite at 900° C. may disappear completely and that new ones are produced. This is due to various reactions occurring during the heating of the sample. Gruver et al. (1949) found a strong suppression of the thermal reactions of kaolinite when 5% NaCl

or 5% Na_2CO_3 was added to the sample and that the suppression of the exothermal reaction was decreased more than that of the endothermal reaction.

Plate II shows the results of x-ray and d.t.a. analyses of kaolinite and montmorillonite which have been purified by sedimentation in Atterberg cylinders, 0.01 N NaOH being used as peptisator. As with these fine clays the NaOH could not be washed off entirely, the dried samples which were analyzed, still contained (ca 4%) Na_2CO_3 (through absorption of CO_2 from the air). It may be concluded that the thermal curves of these samples, which by x-ray analysis are pure well crystallized kaolinite and montmorillonite, have evidently been changed by the impurity.

(7) *Volume changes in the sample investigated*

Shrinking, sintering or melting of the sample during heating, affect its thermal properties and therefore also the shape and the intensity of the d.t.a. curve—see Norton (1939), Berg (1945) and De Josselin de Jong (1956). In Fig. 4 are some striking examples—see also the examples given by other investigators. Thus magnesite, calcite, brucite, hydrargillite lose ca. 52%, 44%, 30% and 30% respectively of their weight at the decomposition temperature. As a result of the decreased conductivity, after the decomposition of these minerals, the base line comes at a higher level than before. This effect may be decreased by mixing the samples with α-Al_2O_3. Zinnwaldite and lepidolite melt at their decomposition temperature = ca. 900° C. Thereby the thermocouple is covered with a tight glassy substance and the contact between the sample and the sample holder is disturbed. As a result of the decreased conductivity of the sample, the d.t.a. curve moves downwards, thus making any quantitative analysis impossible. Another inconvenience is that after the test the thermocouple has become useless for further analysis. Incomplete oxidation of carbo lignin during heating caused by lack of sufficient oxygen, is manifested by a gradually downward movement of the d.t.a. curve. In this case only reliable results for the heat of combustion of this organic—see Fig. 4—can be obtained if the sample is diluted 1:29 with α-Al_2O_3.

From the above it may be concluded that with a d.t.a. great differences may be expected in the intensity, the area and the shape of the thermal peaks of minerals from different origins. This holds especially for clay minerals where variations in particle size of the crystallites and chemical composition (ion substitutions) in the tetrahedral and octahedral layers, may be numerous in nature—see f.e. the analyses of Ross and Hendricks (1954) and Early et al. (1953)—and the minerals being moreover, mostly coated with various kinds of amorphous substances which also influence the thermal reactions.

Figure 5 shows the *d.t.a.* results of $<2\mu$ samples of montmorillonite[5] from various, pure deposits. They were obtained by sedimentation of the original samples in Atterberg cylinders with 0.05 N NH$_4$OH as peptisa-
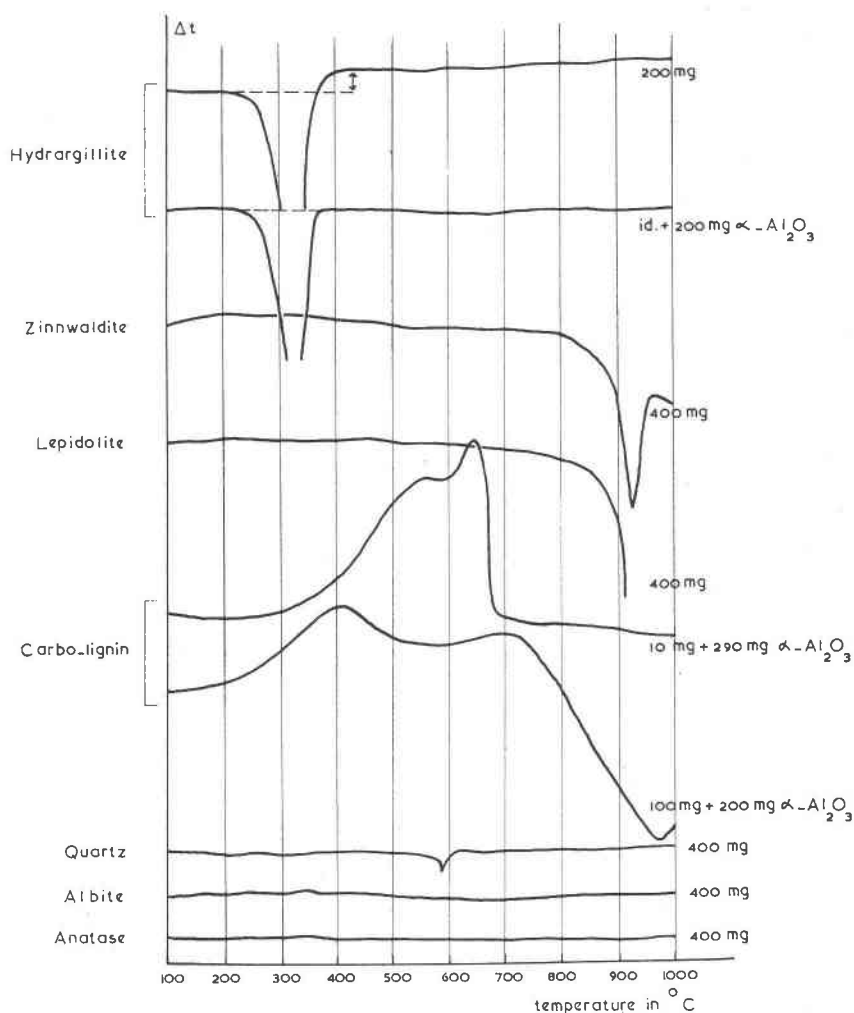

FIG. 4. *D.t.a.* of minerals which lose large amounts of water (hydrargillite), which melt (zinnwaldite, lepidolite) or which burn off (carbo-lignin) when heated. Furthermore of quartz and of some inert minerals (albite, anatase).

tor. The excess of electrolytes was washed out by filtration and the purity of the dried samples was checked by *x*-ray diffraction after the glycerol method of MacEwan (1946). The curves show evidently that the peak

[5] See for this qualification note 4.

temperature, the intensity and even the relative intensities between the high temperature endothermal and exothermal reaction of this clay mineral vary considerably when it is registered by the *d.t.a.* method.

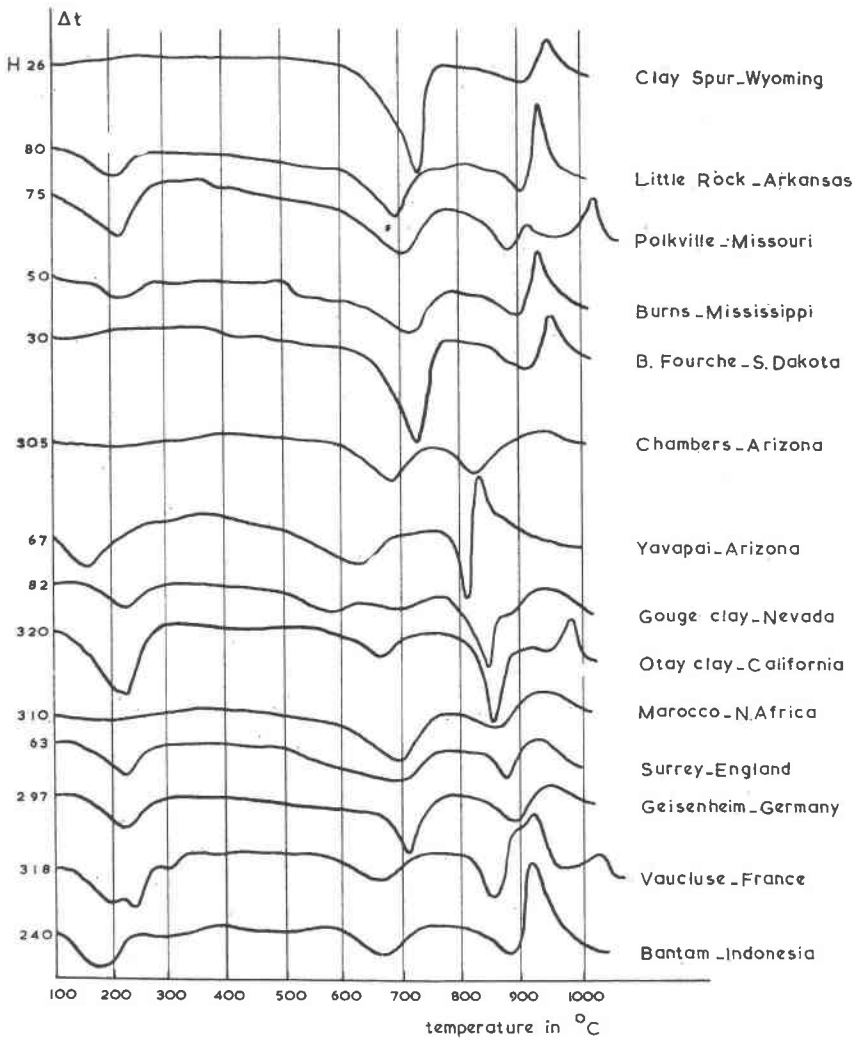Figure 6 shows the *d.t.a.* results of the $<2\mu$ separate of soils of various

FIG. 5. *D.t.a.* of dried (1 hour at 105° C.) samples <2 μ, each 400 mg. of pure (verified by *x*-ray analysis) montmorillonite from different localities.
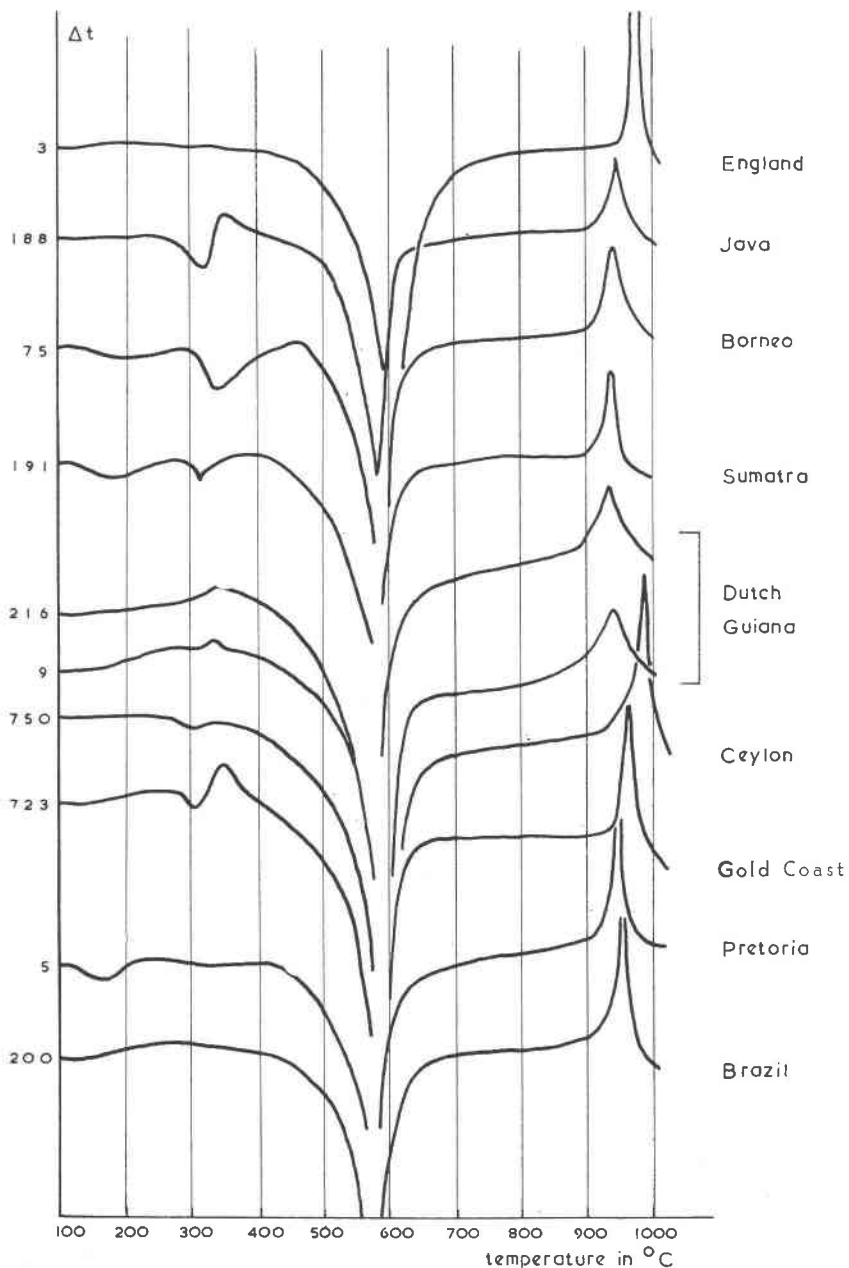
Note: Endothermal effect at ca 325° C. and exothermal effect at ca 350° C. of some samples caused by small amounts of hydrargillite and iron oxides respectively.

FIG. 6. *D.t.a.* of dried (1 hour at 105° C.) samples $<2\mu$, each 300 mg. of pure white kaolinite from Cornwall (England). Furthermore of high graded kaolinites $<2\mu$ from soils from different localities.

origin which after x-ray analysis contain practically only kaolinite. The separate was obtained by first treating the original samples with H_2O_2 (to destroy easily decomposable organic matter). They were afterwards treated in the same way in Atterberg cylinders, etc., as is described for montmorillonite. The d.t.a. curves show that also in this case, the peak temperature, the intensity and the relative peak areas of the endothermal

TABLE 1. PEAK AREA OF PURE, WHITE, WELL CRYSTALLIZED (VERIFIED BY x-RAY ANALYSIS) DRIED (1 HOUR AT 105° C.) KAOLINITE $<2\mu$ AND OF DRIED (1 HOUR AT 105° C.) POWDERED $CuSO_4 \cdot 5H_2O$ (STANDARD) DILUTED WITH α-Al_2O_3 1.50:2.50 EQUALLY PACKED IN THE SAMPLE HOLDER AND ANALYZED WITH THE SAME THERMOCOUPLE. D.t.a. OF KAO-LINITES ALTERNATING WITH THOSE OF STANDARD $CuSO_4 \cdot 5H_2O$ SAMPLES

No.	Origin	KAOLINITE			STANDARD
		Endothermal (ca 600° C.) in cm.²	Exothermal ca(950° C.) in cm.²	Endothermal / Exothermal	Endothermal (ca 150° C.) in cm.²
					31.8
39	Dutch Guiana	19.8	4.6	4.30	33.3
954		14.6	3.4	4.29	32.8
1220	Gabon, Congo	22.0	4.8	4.58	32.2
163	Cornwall, England	26.6	5.6	4.75	32.6
325	Zettlitz, Tsechoslov	19.5	4.7	4.15	32.0
40	Provence France	22.2	4.8	4.62	31.2
292	Reims	17.2	4.0	4.30	32.6
460	Java	18.8	4.4	4.27	33.4
14	Bangka	22.3	5.3	4.21	31.8
653	Pem. Siantar Sumatra	21.8	4.4	4.95	32.6
128	Tandj. Balei	20.9	3.9	5.13	31.5
202	Dhong Thuan, Thailand	17.2	3.5	4.91	33.2
326	Murfreesboro, Ark.	24.7	6.0	4.12	31.7
327	Bath, Carol.	26.5	6.3	4.21	30.3
329	Macon, Georgia U.S.A.	22.1	6.0	3.68	30.7
330	Dry Branch, Georgia	24.0	5.5	4.36	33.5
115	New Jersey	22.7	4.7	4.83	31.1
328	Mesa Alta, Nw. Mexico	25.7	5.5	4.67	30.5
					32.3
	Arithmetical mean (x)				32.06

Note: By calculation was found for the $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2O$ transformation at ca 150° C.:
Standard error of the mean $(s_{\bar{x}})$ $=0.22$ cm.²$=0.69\%$.
Standard error of the single determination $(s) =0.97$ cm.²$=3.02\%$.

and the exothermal reaction vary considerably.

To determine the magnitude of the variations in the heat of transformation of kaolinite, being the least variable clay mineral, d.t.a. were performed on the $<2\mu$ separates of pure, white, well crystallized (verified by x-ray analysis) kaolinite and under conditions where errors due the d.t.a. method are eliminated.

The results are summarized in Table 1. It may be concluded that under these optimum conditions, the measured heat of transformation of the

standard chemical used, is practically constant. It has a standard deviation of the single determination (s) of only 3.02% for its first ($CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2O$) endothermal effect (peak temperature = ca. 150° C.). However, the endothermal and the exothermal reaction of kaolinites from different origin has a peak area which varies from 14.6 cm.^{2} to 25.7 cm.^{2} and from 3.4 cm.^{2} to 6.3 cm.^{2} respectively.[6] The relative intensities of the two thermal reactions varies from 3.7 to 5.1. Another difficulty is that many minerals have reactions which overlap each other for a large part e.g. kaolinite and quartz, kaolinite and illite, glauconite and illite— see for further samples also Table 1 of De Bruijn and Van der Marel (1954), Part II, page 412. Only exceptionally the overlapping can be eliminated by use of a slow-heating rate, or by heating the sample in vacuum-, in nitrogen- or in carbon dioxide atmosphere—see for the latter Rowland and Lewis (1951) and Rowland and Beck (1952) in case of dolomite.

Then there is still the difficulty that varieties of a mineral may occur in nature, which are of the same structure and composition, but differing largely in their thermal effect—see for α quartz McDowall and Dunn (1947), McDowall and Vose (1947, 1952), Fieldes (1952), Keith and Tuttle (1952) and Lewcook and Wylde (1953).

DISCUSSION

Particle size, degree of crystallinity of the crystallites, kind and amount of ion substitutions and amorphous coatings (Beilby layer) may vary considerably for a certain mineral of different origin. As they greatly influence the heat of transformation of a mineral as registered by a *d.t.a.* the application of this method for quantitative purposes will therefore be very restricted. This conclusion holds especially for the group of clay minerals. The same factors have so far resisted also a quantitative determination of this group of minerals by the *x*-ray method.

The quantitative *d.t.a.* method can only be applied to well crystallized minerals of well defined chemical composition if they give sharp diagrams of great intensity and if they are formed in nature under practically the same conditions. However, attention should also be paid in this case to the sample investigated, as very fine crystallites and small amounts of chlo-

---

[6] For the decomposition of 150 mg. $CuSO_4 \cdot 5H_2O$ to $CuSO_4 \cdot H_2O$ at ca 150° C. 33 calories are needed (see tables of constants). This thermal effect is registered by the *d.t.a.* apparatus here used as a peak area of 32.06 cm.^{2} (standard deviation of the mean = 0.22 cm.^{2}). Thus the variation in the thermal transformations of pure kaolinite when heated in a *d.t.a.* oven, is as follows:

endothermal reaction 100 to 176 cal. per gram
exothermal reaction 23 to 43 cal. per gram

rides or carbonates of alkali and alkaline earths may largely disturb the thermal effects. However, there lies an open and at present only accidentally explored field for the *d.t.a.* method in the study of the heat of transformation of H_2O and other polar molecules bound to rest valences at the surface of minerals, or to the exchangeable cations of these minerals. Another possibility for the *d.t.a.* method is the study of ion substitutions in a certain mineral and their place in the crystal structure in combination with chemical and x-ray analysis. In these cases small differences in the physical behaviour of the H_2O molecules (e.g. when stirred to an ice-like state) or in the strength by which OH ions are bound in a crystal, may cause large differences in the peak area or the peak temperature of a *d.t.a.* Their registration can be made more accurate and therefore the application of the *d.t.a.* technique as a very sensitive calorimetric method for quantitative purposes enlarged, (1) by carrying out the analyses at a high heating rate in vacuum-, argon- or carbon dioxide atmosphere; (2) by use of the more sensitive Au, Pd/Pt, Rh (Pallaplat) thermocouple which is also resistant to oxidation at the higher oven temperatures;[7] (3) by placing the thermocouple not inside the sample holder as usual, but as recently suggested by Boersma (1955), outside it. In that case the peak area is no more dependent on the heat conductivity, the heat capacity or volume changes of the mineral investigated, but merely on the produced reaction heat of the mineral sample and a certain calibration constant of the apparatus.[8]

ACKNOWLEDGMENT

REFERENCES

ALLAWAY, W. H. (1949), Differential thermal analysis of clays treated with organic cations as an aid in the study of soil colloids: *Soil Sci. Soc. Amer. Proc.*, **13,** 183–188 (1948).

ARENS, P. L. (1951), A study on the differential thermal analysis of clays and clay minerals: Thesis Agricult. Univ. of Wageningen (Netherlands) 131 pp.

BARSHAD, I. (1948), Vermiculite and its relation to biotite as revealed by base exchange reactions, x-ray analysis, differential thermal curves and water content: *Am. Mineral.*, **33,** 655–678.

[7] Manufactured by W. C. Heraeus, G.M.B.H., Hanau (Germany). It has a E.M.F. at 100° C., 300° C., 600° C. and 900° C. of 2.86, 10.60, 24.72 and 40.35 mV, respectively. The corresponding thermal effects of a Pt/Pt, Rh thermocouple are 0.64, 2.31, 5.23 and 8.45, respectively.

[8] See for details on the factors affecting the application of quantitative mineral analysis with the commonly used *d.t.a.* equipments and the construction and the perspectives of the Boersma sample holder, the articles by De Josselin de Jong (1956) and Boermsa (1955).

BARDSHAD, I. (1950), The effect of the interlayer cations on the expansion of the mica type of crystal lattice: *Am. Mineral.*, **35**, 225–238.

BEILBY, G. (1921), Aggregation and flow of solids: Macmillan, London.

BERG, L. G. (1943), Influence of salt admixtures upon dissociation of dolomite: *Compt. Rend. (Doklady) de l'Acad. d. Sci. de l'U.R.S.S.*, **38**, 24–27.

BERG, L. G. (1945), On area measurements in thermograms for quantitative estimations and the determination of heats of reaction: *Compt. Rend. (Doklady) de l'Acad. d. Sci. U.R.S.S.*, **49**, 648–651.

BERKELHAMER, L. H. (1944), Differential thermal analysis of quartz: *U. S. Bur. Mines, Rept.* **3763**.

BERNAL, J. D., AND FOWLER, R. H. (1933), A theory of water and ionic solution with particular reference to hydrogen and hydroxyl ions: *J. Chem. Phys.*, **1**, 515–548.

BOERSMA, S. L. (1955), Theory of differential thermal analysis and new methods of measuring and interpretation: *J. Am. Ceram. Soc.*, **38**, 281–284.

BRADLEY, W. T., BURST, J. F., AND GRAF, D. L. (1953), Crystal chemistry and differential thermal effects of dolomite: *Am. Mineral.*, **38**, 207–217.

BRAMAO, L., CADY, J. G., AND HENDRICKS, S. B. (1950), The determination of halloysite and its use in the study of red soils: *4th Internatl. Cong. Soil Sci., Part.* **I**, pp. 313

BRAMAO, L., CADY, J. G., HENDRICKS, J. B., AND SWERDLOW, M. (1952), Criteria for the characterization of kaolinite, halloysite and a related mineral in clays and soils: *Soil Sci.*, **73**, 273–287.

BRUIJN, C. M. A. DE, AND MAREL, H. W. VAN DER, (1954), Mineralogical analysis of soil clays. Part I: Introduction and differential thermal analysis; Part II: Examples of mineral analysis by x-ray diffraction and differential thermal analysis: *Geologie en Mijnbouw*, **16** (nw. ser.), 69–83, and 407–428, respectively.

BUDNIKOV, P. P., AND BOBROVINK, D. P. (1938), The influence of admixtures on the decarbonation of dolomite: *J. Appl. Chem. (U.S.S.R.)*, **11**, 1151–1154.

CAILLÈRE, S., AND HÉNIN, S. (1944), Sur l'Origine de quelques anomalies, présentées par les courbes thermiques de certains montmorillonites: *C. R. Acad. Sci.*, **219**, 685–686.

CAILLÈRE, S., AND HÉNIN, S. (1947) Application de l'analyse thermique differentielle à l'étude des argiles des sols: *Ann. Agron.*, **17**, 23–72.

CAILLÈRE, S., AND HÉNIN, S. (1948*a*), Essais de synthèse des mineraux argileux: *Verre et Silic. Ind.*, **13**, 63–64.

CAILLÈRE, S., AND HÉNIN, S. (1947) Sur une synthése de l'antigorite à basse température: *C. R. de l'Acad. et Sci.*, **224**, 1439–1440.

CAILLÈRE, S., AND HÉNIN, S. (1948*b*), l'Analyse thermique et son interpretation: *Actes Congr. Internatl. Céram. Hollande, Scheveningen*, 137–151.

CAILLÈRE, S., and HÉNIN, S. (1949), Sur la signification des resultats de l'analyse thermique differentielle: *Verre et Sil. Ind.*, **13**, 114–118.

CLELLAND, D. W. (1951), Thesis University of Glasgow, England.

CLELLAND, D. W., CUNNING, W. M., AND RITCHIE, P. D. (1952), Physico-chemical studies on dusts: I A high-solubility layer on silicious dusts surfaces: *J. Appl. Chem.*, **2**, 31–41.

CLELLAND, D. W., AND RITCHIE, P. D. (1952), Physico-chemical studies on dusts: II Nature and regeneration of the high-solubility layer on silicious dusts: *J. Appl. Chem.* **2**, 42–48.

DEMPSTER. P. B. (1951), Thesis University of Glasgow, England.

DEMPSTER, P. B., AND RITCHIE, P. D. (1952), Surface of finely ground silica: *Nature*, **169**, 538.

DEMPSTER, P. B., AND RITCHIE, P. D. (1953), Examination of finely ground quartz by differential thermal analysis and other physical methods: *J. Appl. Chem.*, **3**, 182–192.

DRAGSDORF, R. D., KISSINGER, H. E., AND PERKINS, A. T. (1951), X-ray study of the decomposition of kaolinite: *Soil Sci.*, **71**, 439–448.

EARLY, J. W., MILNE, J. H., AND MC. VEAGH, W. J. (1953), Thermal dehydration and x-ray studies on montmorillonite: *Am. Mineral.*, **38**, 770–783.

EARLY, J. W., OSTHAUS, B. B., AND MILNE, J. H. (1953), Purification and properties of montmorillonite: *Am. Mineral.*, **38**, 707–724.

FAUST, G. T. (1949), Dedolomitization and its relation to a possible derivation of a magnesium-rich hydrothermal solution: *Am. Mineral.*, **34**, 789–823.

FAUST, G. T. (1951), Thermal analysis and x-ray studies of sauconite and some zinc minerals of the same paragenetic association: *Am. Mineral.*, **36**, 795–822.

FIELDES, M. (1952), Abnormal thermal behaviour of α-quartz from some New Zealand soils: *Nature*, **170**, 366–367.

FLOOD, H. (1950), Note on the thermal decomposition of dolomite: *Det. Kongelige Norske Videnskabers Selskab Fordhandlinger*, **22**, 188–192.

GIBB, J. G., RITCHIE, P. D., AND SHARPE, J. W. (1953), Electron optical examination of finely ground silica: *J. Appl. Chem.*, **3**, 213–218.

GLASS, A. D. (1954), High temperature phases from kaolinite and halloysite: *Am. Mineral.*, **39**, 193–207.

GRAF, D. L. (1952), Preliminary report on the variations in the differential thermal curves of iron-low dolomites: *Am. Mineral.*, **37**, 1–27.

GREENE-KELLEY, R. (1953), Interpretation of *d.t.a.* diagrams; the low temperature endothermic peak: *Clay Min. Bull.*, **2**, 79–83.

GRIM, R. E., AND ROWLAND, R. A. (1942), Differential thermal analysis of minerals and other hydrous materials: *Am. Mineral.*, **27**, 746–761, and 801–818.

GRIM, R. E. (1947), Differential thermal curves of prepared mixtures of clay minerals: *Am. Mineral.*, **32**, 493–501.

GRIMSHAW, R. W., HEATON, E., AND ROBERTS, A. L. (1945), II Thermal analysis methods: *Trans. Brit. Ceram. Soc.*, **44**, 76–92.

GRIMSHAW, R. W., AND ROBERTS, A. L. (1953), The quantitative determination of some minerals in ceramic materials by thermal means: *Trans. Brit. Ceram. Soc.*, **52**, 50–61.

GRUNER, J. W. (1939), Ammonium mica synthesized from vermiculite: *Am. Mineral.*, **19**, 557–575.

GRUVER, R. M., HENRY, E. C., AND HEYSTEK, J. (1949), Suppression of thermal reactions in kaolinite: *Am. Mineral.*, **34**, 869–873.

HEADY, H. H. (1952), Differential thermal study of Colorado oil shale: *Am. Mineral.*, **37**, 804–811.

HENDRICKS, S. B., NELSON, R. A., AND ALEXANDER, L. T. (1940), Hydration mechanism of the clay mineral montmorillonite saturated with various cations: *J. Amer. Chem. Soc.*, **62**, 1457–1464.

JOSSELIN DE JONG, G. DE, (1956), Calibration of the differential thermal analysis apparatus for quantitative purposes: To appear in *J. Am. Ceram. Soc.*

KELLEY, W. P., AND PAGE, J. B. (1943), Criteria for the identification of the constituents of soil colloids: *Soil Sci. Soc. Amer. Proc.*, **7**, 175–181 (1942).

KEITH, M. L., AND TUTTLE, O. F. (1952), Significance in variation in the high-low inversion of quartz: *Am. J. Sci.*, **1**, 203.

KERR, R. F., AND KULP, J. L. (1948), Multiple differential thermal analysis: *Am. Mineral.*, **33**, 387–419.

KIYOURA, R., AND SATA, T. (1950), The quantitative analysis of the $CaCO_3$-$Ca(OH)_2$-$Mg(OH)_2$ system by differential thermal analysis: *J. Ceram. Assoc. Japan*, **58**, 3–6.

KULP, J. L., AND TRITES, A. (1951), Differential thermal analysis of natural hydrous ferric oxides: *Am. Mineral.*, **36**, 23–44.

KULP, J. L., KENT, P., AND KERR, P. F. (1951), Thermal study of the Ca-Mg-Fe carbonate minerals: *Am. Mineral.*, **36**, 643–670.

LAWS, W. D., AND PAGE, J. B. (1946), Changes produced in kaolinite by dry grinding: *Soil Sci.*, **62**, 319–336.

LEWCOOK, W., AND WYLDE, J. H. (1953), The behaviour of silica bricks on reheating: *Transact. Brit. Ceram. Soc.*, **52**, 225–258.

LIPPMANN, F. (1952),—see Dreiziger Jahrestagung der Deutschen Mineralogischen Gesellschaft von 1. bis 10. September 1952 in Regensburg referred to in *Tonind. Ztg.*, **76**, 315.

MACEWAN, D. M. C. (1946), The identification and estimation of the montmorillonite group of minerals, with special reference to soil clays: *Soc. Chem. Ind.*, **65**, 298–307.

MACKENZIE, R. C. (1950), Some notes on the hydration of montmorillonite: *Clay. Min. Bull.*, **1**, 115–119.

MACKENZIE, R. C., AND MILNE, A. A. (1953), The effect of grinding of micas: I Muscovite: *Mineral. Mag.*, **30**, 178–185.

MACKENZIE, J., AND LAKIN, J. R. (1953),—see the Discussion at the end of the article of Grimshaw, R. W., and Roberts, A. L. (1953) in *Trans. Brit. Ceram. Soc.*, **52**, 50–61.

MAREL, H. W. VAN DER (1950), Identification of minerals in soil clay by x-ray diffraction patterns: *Soil Sci.*, **70**, 109–136.

MAREL, H. W. VAN DER (1954), Potassium fixation in Dutch soils: *Mineralogical analysis: Soil Sci.*, **78**, 163–179.

MARTIN, R. T., AND RUSSELL, M, B. (1952), Clay minerals of four Southern New York Soils: *Soil Sci.*, **74**, 267–279.

MCDOWALL, I., AND DUNN, L. R. L. (1947), New Zeal. *Pottery and Ceram. Res. Assoc. Techn. Pap. no.* **1**.

MCDOWALL, I., AND VOSE, W. (1947), New Zeal. *Pottery and Ceram. Res. Assoc. Techn. Pap. no.* **1**.

MCDOWALL, I., AND VOSE, W. (1952), Anomalous properties in quartz: *Nature*, **170**, 366.

MELDAU, R., AND ROBERTSON, H. S. (1952), Die Bruchflächen feingemahlener Mineralpulver: *Tonind. Ztg.*, **76**, 365–368.

MURRAY, J. A., FISCHER, H. C., AND SHADE, R. W. (1951), Thermal analysis of limestones: *Proc. 49th Annual. Conv. Natl. Lime Assoc., Washington.*

MURRAY, H. H. (1954), Structural variations of some kaolinites in relation to dehydrated halloysite: *Am. Mineral.*, **39**, 97–108.

NAGELSCHMIDT, G., GORDON, R. L., AND GRIFFIN, O. G. (1952), Surface of finely ground silica: *Nature*, **169**, 538.

NIEUWENBERG, C. J. VAN, AND PIETERS, H. A. J. (1929), The dehydration vapour pressure of kaolin: *Rec. Trav. Chim. Pays Bas.*, **48**, 406–416.

NORTON, F. H. (1939), Critical study of the differential thermal method for the identification of the clay minerals: *J. Amer. Ceram. Soc.*, **22**, 54–63.

NORTON, F. H. (1940), Analysis of high alumina clays by the thermal method: *J. Amer. Ceram. Soc.*, **23**, 281–282.

ORCEL, J. (1935), l'Emploi de l'analyse thermique differentielle dans la determination des constituents des argiles des laterites et des bauxites: *7th Congr. Internatl. Mines. Met. Geol. Appl. Paris, Section Geol. appl.*, **1**, 359–373.

PAGE, J. B. (1943), Differential thermal analysis of montmorillonite: *Soil Sci.*, **56**, 273–283.

PARKERT, C. W., PERKINS, A. T., AND DRAGSDORF, R. D. (1950), Decomposition of minerals by grinding: *Kans. Acad. Sci. Trans.*, **53**, 386–397.

PERKINS, A. T. (1950), Reactions of bentonite as influenced by adsorbed cations and grinding: *Soil Sci. Soc. Amer. Proc.*, **14**, 93–96 (1949).

ROBERTSON, R. H. S., BRINDLEY, G. W., AND MACKENZIE, R. C. (1954), Mineralogy of kaolin clays from Pugu Tanganyika: *Am. Mineral.*, **39**, 118–138.

ROSS, CLARENCE, S., AND HENDRICKS, S. B. (1945), Minerals of the montmorillonite group: *U. S. Depart. Int. Profess. Pap.* **205-B**, 23–79.

ROWLAND, R. A., AND LEWIS, D. R. (1951), Furnace atmosphere control in differential thermal analysis: *Am. Miner.*, **36**, 80–91.

ROWLAND, R. A., AND BECK, C. W. (1952), Determination of small quantities of dolomite by differential thermal analysis: *Am. Mineral.*, **37**, 76–82.

SABATIER, G. (1950), Sur l'influence de la dimension des cristaux de chlorites sur leurs courbes d'analyse thermique differentielle: *Bull. Soc. Franc. Mineral.*, **73**, 43–48.

SCHUYLENBORGH, J. VAN, AND ARENS, P. L. (1950), The electrokinetic behaviour of freshly prepared α and γ FeOOH: *Rec.d. Trav. Chim. Pays Bas*, **69**, 1559–1565.

SCHWOB, Y. (1950), Les carbonates rhomboédriques simples et complexes de calcium, magnésium et fer: *Publication technique no. 22, Centre d'Études et de Recherches de l'-Industrie des Liants Hydrauliques*, Paris, 105 pp.

SPEIL, S., BERKELHAMER, L. H., PASK, J. A., AND DAVIES, B. (1945), Differential thermal analysis, its application to clays and other aluminous materials: *U. S. Bur. of Mines, Techn. Paper no.* **664**.

STUTTERHEIM, N., WEBB, T. L., AND URANOVSKY, B. (1951), Developments in research on the burning and hydration of lime and on its use in building: *Proc. Brit. Bldg. Res. Congr. Part.* **2**, 120–126.

VOLD, MARJORIE, J. (1949), Differential thermal analysis: *Anal. Chem.*, **21**, 683–688.

WEBB, T. L. (1953), Some applications of differential thermal analysis and findings using this technique: *S. African Ind. Chem.*, **7**, 224–232.

WALKER, G. F. (1950), Trioctahedral minerals in the soil clays of northeast Scotland: *Mineral. Mag.*, **29**, 72–84.

WALKER, G. F., AND MILNE, A. (1950), Hydration of vermiculites saturated with various cations: *Trans. 4th Internatl. Congr. Soil Sci. Amsterdam*, **2** 62–67.

Manuscript received April 22, 1955.