DIFFERENTIAL THERMAL ANALYSIS OF CLAYS AND CARBONATES *

By Richards A. Rowland **

ABSTRACT

Differential thermal analysis (DTA) began soon after the development of the thermocouple. It has progressed through the systematic development of better equipment and the cataloguing of typical DTA curves for a variety of materials until good technique now requires control of the composition and pressure of the furnace atmosphere as well as consideration of the thermodynamics and kinetics of the reactions involved. Although differential thermal analyses have been made for many materials, the major applications have been concerned with clay and carbonate minerals.

In DTA curves for clay minerals the low-temperature endothermic loop associated with the loss of water, and the high-temperature exothermic loop accompanying the formation of new compounds, are changed in shape, temperature, and intensity by the kind of exchange cations. The midtemperature-range endothermic loop has a temperature dependence on the partial pressure of water in the furnace atmosphere.

For the anhydrous normal carbonates the dissociation temperature and its dependence on the partial pressure of CO_2 are in the decreasing order Ca, Mg, Mn, Fe, and Zn. The lower temperature loop of dolomite, the reaction for which must be preceded by an internal rearrangement, is independent of the pressure of CO_2 but may be shifted to a lower temperature by prolonged fine grinding which accomplishes a similar rearrangement.

INTRODUCTION

Differential thermal analysis (DTA), although not a very accurate or definitive method, has found an important place among techniques which allow the characterization of materials. Limited only by the sensitivity of the apparatus, the differential thermal curves record all transformations in which heat is taken up or given off. This includes the dehydration of clays, the decarbonation of carbonates, the reversible change from α- to β-quartz, the burning of materials, and the recombination of elements into more stable forms. When employed alone, the technique can be used to identify a number of reasonably pure compounds and to follow changes in mixtures for control purposes. When used in conjunc- with X-ray diffraction, microscopy, and chemical analysis, otherwise difficult identifications can be made. The technique is not easily standardized, however, and the factors which frequently make it difficult to compare DTA curves prepared in different laboratories are summarized by Ahrens (1950).

The development of differential thermal analysis has progressed through several stages. As early as 1887 le Chatelier described the use of his thermocouple as a difference thermocouple and published DTA curves of kaolinite. From that time until Orcel (1935) began the systematic differential thermal analyses of clays, about twenty miscellaneous DTA papers appeared. Another stage began with the design of good furnaces, sample holders, and photographic recording equipment by Norton (1939) and Hendricks (1939). Refinements of this design by Grim and Rowland (1942) were followed by further developments by Berkelhamer and Spiel (1944). Throughout this period many papers appeared which repeated the thermal curves of the same clay samples and related oxides, and a portable apparatus was developed by Hendricks (1946)[1] for use in studying bauxite deposits in the field. The last development in the basic apparatus was the visual recording of the DTA curves of a number of samples being heated in the same furnace. Simultaneous development of DTA techniques for the elementary study of carbonate minerals took place in the U. S. A., Japan, and the U. S. S. R.

Reconsideration of the thermodynamics of the system gave rise to a very sensitive sample holder (Gruver, 1948) (Kaufman and Dilling, 1950) made of platinum foil. Herold (1948) developed a thin sample holder half platinum and half platinum-10 percent rhodium in which the thermocouple junction, built into the sample holder, was a ring around the middle of the cylindrical sample. Development of static atmosphere control within the furnace was introduced by Saunders and Giedroyc (1950) and Rowland and Lewis (1951). Dynamic atmosphere control within the sample was introduced by Stone (1952)[2] Presently the trend is toward atmosphere control at elevated pressures where DTA reactions begin to approach equilibrium reactions. From the simple approximate measurement of the effective temperature difference obtained by comparing the temperature of the reaction of a sample in its own atmosphere with that of an inert standard, the technique has now progressed to a consideration of the heat exchange under controlled conditions of an inert atmosphere or of a participating gas.

KINDS OF TRANSFORMATIONS

The endothermic and exothermic deflections of a DTA curve record many kinds of changes of state. The only limitation is that $\frac{\partial Ha}{\partial t}$, the rate of change of enthalpy (ΔH), be sufficient for the temperature difference to be registered before dissipation in the system. First-order phase changes, which involve discontinuities in volume, entropy, and the first derivatives of the Gibbs function (ΔF) are represented by two kinds: the reversible allotropic inversion of alpha to beta quartz (Faust 1948) (Grimshaw, et al. 1948) and the irreversible monotropic change of aragonite to calcite (Faust 1950). The change from endellite to halloysite probably is a monotropic phase change. Definite second-order phase changes, in which there is no discontinuous change in volume and entropy while the second derivatives of the Gibbs function change discontinuously, are rather rare. One which is habitually recorded in DTA, employing a nickel block as a sample holder, is the change from ferromagnetic to paramagnetic nickel (Curie point) at 353°C.

Murray and White (1949) have discussed the kinetics of thermal dehydration curves. Most of the chemical reactions recorded by DTA are first-order reactions in which the rate of reaction is directly proportional to the concentration of the reacting substance. The dehydration of clay minerals such as kaolinite and the dissociation of

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[1] This apparatus is available commercially from the Eberbach Corporation, Ann Arbor, Michigan.

[2] Variable pressure DTA apparatus is available from Dr. Robert L. Stone, Austin, Texas.

carbonates are chemical reactions of this type. The very poor curves obtained for muscovite—because the rate of dehydration for the usual heating rates is very slow—also represent a first-order reaction. Second-order reactions in which the rate depends on the concentration of two molecules, and third-order reactions where the concentration of three molecules controls the rate, are not common in the interpretable DTA reactions. Combinations of first- and second-order reactions, and perhaps some third-order reactions, probably take place after the final breakdown of the clay mineral lattice when new high-temperature products are formed.

The kinetics and thermodynamics of the DTA method are actually too complex to permit the application, in any sense other than approximate similarity, of these physical-chemical terms for better-known reactions. This rather incomplete discussion of phase changes and order of chemical reactions is included because it has become increasingly popular to refer to DTA curve deflections as representing a specific kind of chemical reaction or phase change.

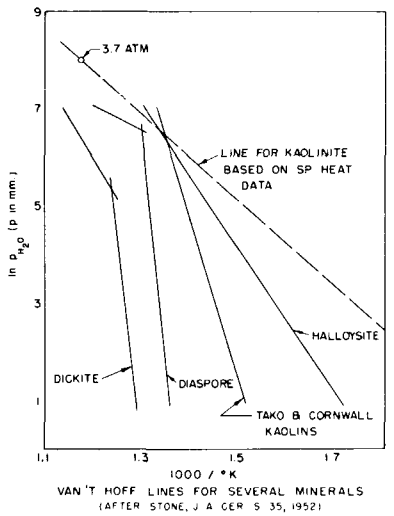

FIGURE 1

THERMAL THEORY

Spiel (1945) and Kerr and Kulp (1948), by opposing the thermal effects—the heat of the thermal reaction and the differential heat flow between the block and the sample—arrived at an expression to show that the area enclosed by the loop and the base line is an approximate measure of the total heat effect and, under certain conditions, is proportional to the amount of thermally active material in the sample. By making a set of calibration curves with prepared mixtures of dolomite and calcite, Rowland and Beck (1952) were able to show that this relationship can be used to determine dolomite in limestone when as little as 0.3 percent is present (fig. 13).

Wittels (1951) varied both the heating rate and the mass of the sample to obtain an expression and calibration so that precise calorimetric measurements can be obtained from DTA curves.

M. Vold (1949) has derived equations for the calculation of heats of transformation from differential heating curves, which are independent of external calibration, by using the rate of restoration of a thermal steady state to

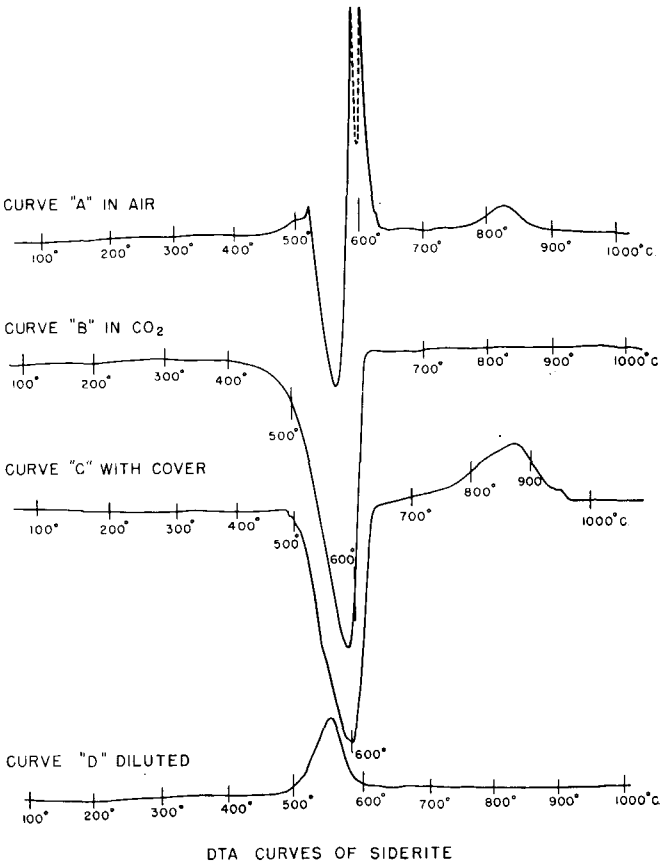

FIGURE 2

establish a relation between the differential temperature and the heat adsorption producing it. Valid results were obtained for such widely differing processes as the melting of stearic acid and the vaporization of water.

A highly significant contribution to the understanding of differential thermal analysis was made by Murray and White (1949). They point out that a Clausius-Clapeyron

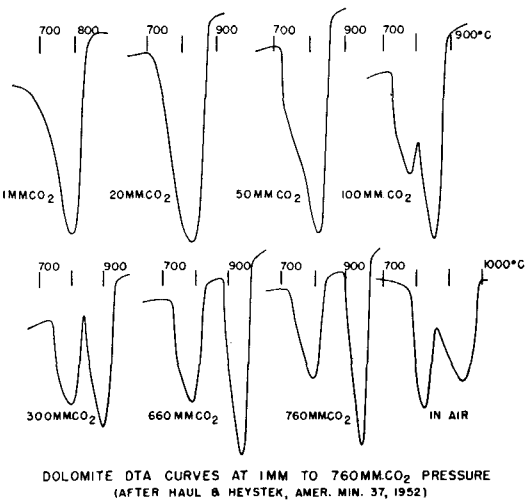

FIGURE 3

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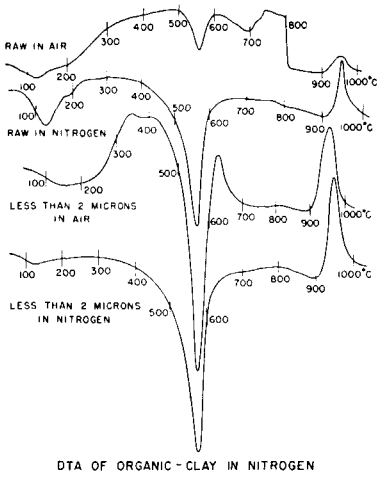


FIGURE 4

type equation can be reduced to a plot of ln p_{H_2O} vs $1/T$ to obtain a straight line of slope—$\Delta H/2R$. By selecting a number of partial pressures of H_2O and observing from the DTA curve the value of t°C. at which the loss of hydroxyl water begins, Stone (1952) assembled data for a van't Hoff line from the slope of which the heat of reaction can be calculated (fig. 1). Comparison of these heats of reaction with values obtained from specific heat data shows that, for minerals of the kaolin group, the temperature at the beginning of the deflection of the DTA curve is considerably higher than equilibrium temperature up to a partial pressure of ln $p = 6.50$ (665 mm). Above ln $p = 6.50$ better agreement is obtained. For calcite, good agreement is obtained at ln $p = 3.8$ (447 mm). Stone concludes from these experiments that at temperatures close to equilibrium in dry air the kaolinite decomposition reaction must be very slow indeed. These experiments show that, even though the clay minerals have very similar structural arrangements, their DTA hydroxyl-loss loops can be shifted selectively by control of the partial pressure of water vapor. Hence, clay mineral DTA curves so obtained should resolve the midrange endothermic loops which interfere when the furnace atmosphere is uncontrolled.

ATMOSPHERE CONTROL

Atmosphere control in differential thermal analysis has taken several different forms. When a sample is heated in air, it builds up its own atmosphere, but not in excess of one atmosphere pressure. A typical example is the dissociation of siderite (Rowland and Jonas 1949) (fig. 2), in which the DTA curve is a compromise between the endothermic effect of CO_2 liberation and the exothermic effect of iron oxidation, until the CO_2 evolution is violent enough to exclude oxygen and the endothermic effect predominates. Oxidation resumes when CO_2 evolution slows down, and the endothermic loop is interrupted by an exothermic loop. A similar effect is shown by the DTA curve when dolomite is heated in air. The curve in air resembles the curve at about 360 mm of CO_2 (Haul 1951) (fig. 3). When a cover is used on the sample holder, the main oxidation loop of siderite is displaced to a higher temperature. Except when the sample well is covered, the pressure of the evolved gas probably never attains one atmosphere pressure and is quickly reduced by diffusion to a much lower concentration. These atmospheric effects are not controlled but are a function of the sample dissociation.

The atmosphere of a furnace may be maintained at about one atmosphere partial pressure by allowing a gas to flow through the furnace (Rowland and Lewis, 1951). This technique is sufficient for many applications where approximately one atmosphere of an inert gas, or a participating gas, is required. A better technique, using a sintered block for a sample holder, has been described by Saunders and Giedroyc (1950). This method insures that the gas surrounds the individual grain of the sample from the beginning of the analysis. Neither of these methods permits control of the partial pressure of the gas, and the composition is maintained only so long as no air is swept in with the gas.

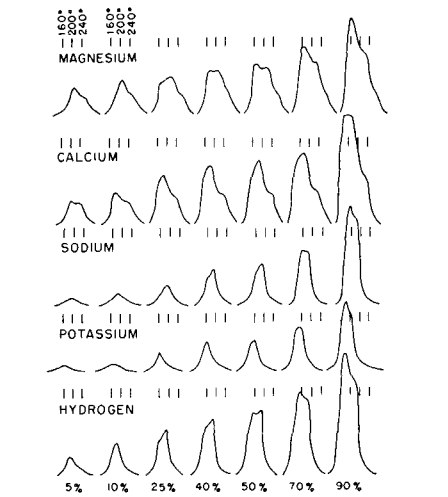
Actual control of the pressure within the furnace has been used as a vacuum technique by Whitehead and Breger (1950). A dynamic system for control of the pressure and composition of the atmosphere surrounding the particles of the sample was described by Stone (1952) who included the sample holder in the gas-handling system. With this arrangement it is possible to maintain a continuous supply of fresh gas moving through the specimen at a predetermined pressure.

Atmosphere control can be used to eliminate unwanted exothermic reactions resulting from the burning of organic matter in clays (fig. 4). DTA curves of some carbonates, particularly calcite and dolomite, are greatly improved by an atmosphere of CO_2. From DTA curves made in a dynamic steam atmosphere van't Hoff lines can be constructed. While van't Hoff lines constructed from DTA curves only approximate equilibrium at elevated pressures, they are a summary of the DTA curves at several pressures and as such may be more characteristic of the material than the original DTA curve.

DTA CURVES OF CLAYS

Aside from a number of papers describing systematic studies of the collections of clays and carbonate minerals to learn what differences could be observed by this technique, there have been a number of studies involving the factors controlling the individual parts of the differential thermal analysis curves. The geometry of a differential thermal curve of a clay is usually made up of three distinct parts. The first is a low-temperature endothermic loop which is registered when atmospheric water departs from the material. A second or midrange endothermic loop accompanies the loss of bound water or the dissociation of hydroxyls from the lattice. The third is a high-temperature combination of loops accompanying the final breakdown of the lattice and the formation of one or more new materials.

Low-temperature Loop. The low-temperature loop, which may cover the interval from 50°C. to about 240°C., is dependent on the kind of clay mineral for its presence; on the type (bivalent-univalent) and amount of exchange cations for its shape; and on the moisture content, or the relative humidity surrounding the clay



DTA CURVES OF MISSISSIPPI MONTMORILLONITE WITH SEVERAL COMMON CATIONS AT DIFFERENT WATER CONTENT (AFTER HENDRICKS, NELSON & ALEXANDER, J.A.C.S. 62, 1940)

FIGURE 5

prior to analysis, for its size. In general, members of the kaolinite group do not show a low-temperature peak. The exception is hydrated halloysite; its peak can be irreversibly destroyed by storage over a period of time in an atmosphere of low relative humidity at room temperature, or by heating to slightly more than 100°C.

The three-layer lattice clay minerals invariably have a low-temperature endothermic loop. Of these, the montmorillonite loops are the largest and most sensitive to moisture content, humidity, and type and amount of exchange cations. Although the illites also exhibit a low-temperature loop, the true micas, such as muscovite and biotite, do not. Chlorite in clay-mineral particle size has a low-temperature endothermic loop, but chlorite from metamorphic rocks does not. The effect of exchange cations on montmorillonites and illites is frequently rather marked. Hendricks (1940) pointed out the effect

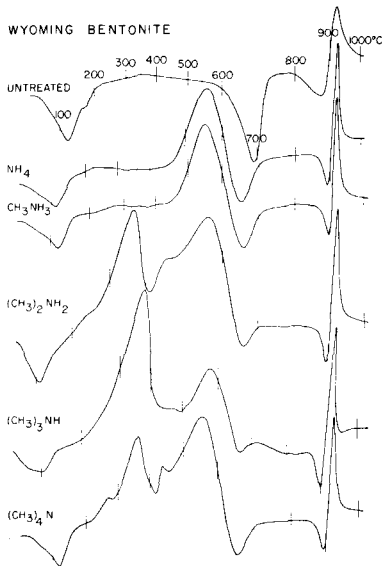
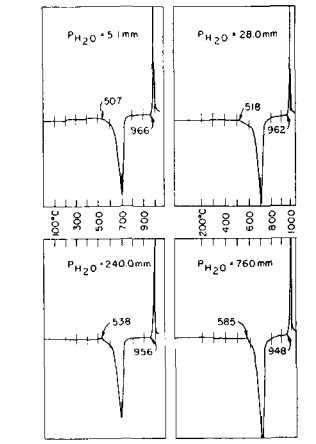


FIGURE 6

of a number of different exchange cations on different bentonites (fig. 5). In general, clays with monovalent cations exhibit one endothermic loop at about 150°C.; most clays with bivalent cations have a second loop or a shoulder on a loop similar to the monovalent loop at a higher temperature (220°C.). Various organic compounds, particularly those which blanket the space between the layers of the lattice, also have their particular effect on the hydration loop, but this is frequently obscured by the immediate volatilization or burning of the organic material.

As yet, no one has succeeded in making use of the area of the low-temperature endothermic loop to determine either the total moisture content or to make a quantitative estimate of the type and amount of exchange cations on the clay.



DTA CURVES OF DICKITE (OURAY, COLORADO) AT DIFFERENT PRESSURES OF WATER VAPOR (AFTER STONE, J. A. CER. S. 35, 1952)

FIGURE 7

High-temperature Loops. At the high-temperature end of the differential thermogram most of the recorded loops are the combined heat effect of several reactions, both endothermic and exothermic in nature. Grim (1948) and Stone (1952) have pointed out that, even in kaolinite, a very small endothermic loop occurs and is interrupted by the large exothermic loop usually associated with the formation of mullite. The high-temperature zone for members of the montmorillonite and illite groups is largely controlled by the chemical composition of the material. This involves the amount and kind of isomorphic substitution within the lattice and the nature of the exchange cations. Most of the three-layer lattice clay minerals undergo an endothermic reaction associated with the final breakdown of the clay mineral lattice (Grim, 1948) and with the loss of a small amount of water which supposedly results from the loss of the last hydroxyls. Different persons have different ideas as to just what happens during this endothermic reaction. McConnell (1950) theorizes that tetrahedral hydroxyls give rise to the small water loss, and occur in groups of four, substituted for silicon in the tetrahedral layer. It is also possible that the hydroxyls are supplied from local substitution of magnesium in the octahedral layer. While there appears to be no reason for one part of the octahedral layer to retain its character at temperatures

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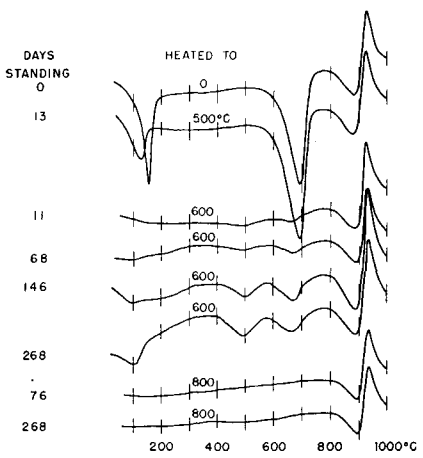
Table 1. Firing products of several clays.

High alumina	900° C.	1000° C.	1100° C.	1200° C.	1300° C.
Kaolinite		mullite (a)		mullite (a) cristobalite (b)	
Endellite		mullite (a)		mullite (a) cristobalite (b)	
Diaspore	α-Al_2O_3 (a)				
Gibbsite	γ-Al_2O_3 (a)	α-Al_2O_3 (a)			
Bauxite (Kaolinite and gibbsite)					
Montmorillonite group					
Beidell, Colo.					mullite cristobalite
Cheto		β-quartz (a) anorthite (?) (c)	β-quartz (a) cristobalite (c) anorthite (?) (c)		cristobalite (a) cordierite (a)
Fairview, Utah				mullite (a) cristobalite (a)	mullite (a)
Harris Co., Tex.		spinel (b) cristobalite (c)	cristobalite (a) spinel (a)	cristobalite (a) spinel mullite (b)	cristobalite (a) mullite (b)
Otay, Calif.		β-quartz (a) enstatite (c)	cristobalite (a) β-quartz (a) enstatite (b)	cristobalite (a) cordierite (a)	cristobalite (c) cordierite (a) periclase (c)
Palmer, Ark.		spinel (a)	spinel (a) quartz (c)	cristobalite (a) spinel (a) mullite (a)	
Pontotoc Co., Miss.		spinel (a) α-quartz (b)	cristobalite (a) spinel (a)		cristobalite (b) cordierite (b)
Sierra de Guadalupe		spinel (a)	cristobalite (a) spinel (a)	cristobalite (a) spinel (a) cordierite (b)	cristobalite (a) cordierite (a)
Tatatila, Vera Cruz		β-quartz (b)			cristobalite (a) mullite (b) cordierite (b)
Upton, Wyo.	spinel (a)	spinel (a) α-quartz (b)	spinel (a) cristobalite (b)		mullite (b)
Wagon Wheel Gap, Colo.	spinel (b)	cristobalite (a) mullite (b) spinel (c)			cristobalite
Woody nontronite					mullite cristobalite spinel

Parenthetic letters signify: (a) important, (b) moderate, and (c) minor. (After Bradley & Grim, 1951.)

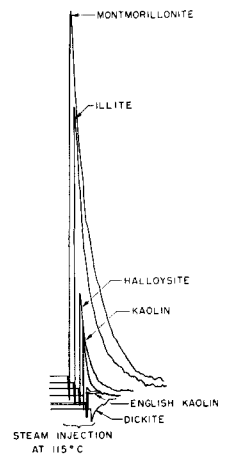
higher than that attained by other parts of the same layer, it is still possible to draw the parallel between the temperature at which gibbsite loses its hydroxyls versus the temperature at which brucite loses its hydroxyls. Other magnesium-bearing minerals, such as talc and chlorite, seem also to lose their hydroxyls at temperatures somewhat higher than encountered in materials consisting primarily of aluminum in the octahedral layer.

Bradley and Grim (1951) have described many of the factors controlling the nature of the immediate high-temperature products (table 1). They point out that the



DTA CURVES OF SODIUM MONTMORILLONITE AFTER HEATING TO INDICATED TEMP. FOR 1 HOUR AND STANDING FOR DIFFERENT PERIODS (AFTER GRIM & BRADLEY, AMER MIN 33, 1948)

FIGURE 8



DTA SHOWING EFFECT OF STEAM INJECTION ON DRIED CLAY MINERALS (AFTER STONE, J. A. CER. S. 35, 1952)

FIGURE 9

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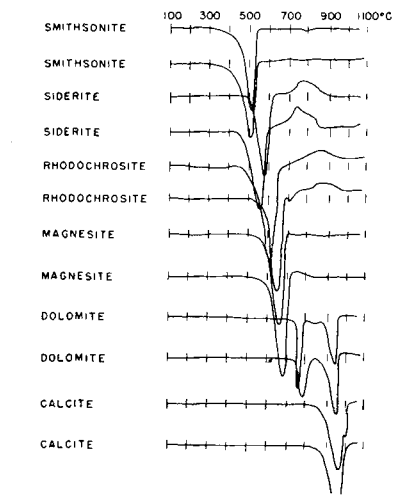
exchange cations can give rise to a variety of spinels and cordierite. When the exchange ion between the layer positions is blanketed with an organic compound so that at elevated temperatures the only exchange cation present is hydrogen, the formation of mullite occurs even with a three-layer lattice clay mineral. In figure 6 the exothermic loop at 930°C. accompanies the formation of a spinel in the untreated sample, mullite and spinel in the NH_4 sample, and mullite in the remaining samples. In some cases where there is a return to the baseline between the endothermic and exothermic reactions and where lithium is present in the clay mineral, the accompanying excess silica appears in the form of beta quartz instead of cristobalite.

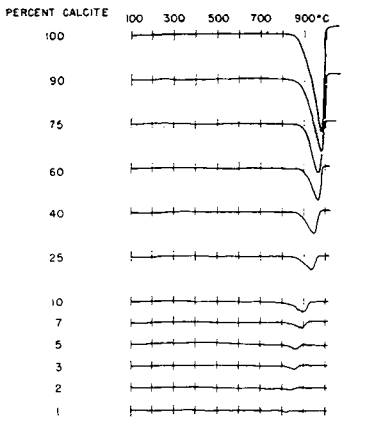
Midrange Loop. The endothermic loop occurring at midtemperature range and associated with the major loss of hydroxyls from the octahedral layer varies considerably from clay to clay. In the kaolinite group this is an intense reaction which probably starts at a much lower temperature but is sufficiently strong to cause deflection at about 450°C. and to peak at about 600°C. Dickite, the most highly organized member of the kaolinite group, has a slightly different differential thermal curve through the range of loss of hydroxyls. The low-temperature side of this loop is quite steep, while the high-temperature side is at a somewhat lesser slope. The result is a loop skewed toward the low-temperature end. The starting and peak temperatures of the midrange loop of both dickite and kaolinite can be shifted by p_{H_2O} of the furnace atmosphere (fig. 7). Wyoming bentonite and other bentonitic materials in which the order of stacking and the organization of the crystals are very good, have a loop beginning at about 575°C. and peaking at about 700°C. When the organization is poor, as is the case with most sediments containing montmorillonite, this loop is approximately 100°C. lower. The loop for nontronite, the iron analog of montmorillonite, also occurs at a somewhat lower temperature.

Members of the illite group lose their hydroxyls over the same approximate range as do some of the less well-



DTA CURVES FOR SOME RHOMBOHEDRAL CARBONATES
(AFTER KERR & KULP, AMER. MIN. 33, 1948)

FIGURE 10



EFFECT OF DILUTION — DTA CURVES OF CALCITE ALUNDUM MIXTURES
(AFTER KULP, KENT, KERR, AMER. MIN. 36, 1951)

FIGURE 11

organized montmorillonites. In sediments which may contain both illite and montmorillonite, it is seldom possible to distinguish between montmorillonite and illite with differential thermal curves. In fact, the shales and clays of the Gulf Coast, at least to the base of the Tertiary, appear to contain both an illite and a very poorly organized montmorillonite which may be in effect a degraded illite in which a large portion of the potassium has been lost.

Previously this loss of hydroxyls was considered to be an irreversible reaction. However, Grim and Bradley (1948) (fig. 8) demonstrated that clays heated to a temperature just below the end of their differential thermogram dehydration loop will reabsorb a considerable amount of moisture as hydroxyls when exposed to an average relative humidity over a period of time. From his experiments using steam atmospheres, Stone suggests (fig. 9) that more rehydration may be obtained at elevated steam pressures.

DIFFERENTIAL THERMAL ANALYSIS OF THE CARBONATE MINERALS

The carbonate minerals are especially amenable to differential thermal analysis. Normal anhydrous carbonates undergo dissociation in an atmosphere of CO_2 at progressively lower temperatures in the order Ca, Mg, Mn, Fe, and Zn (fig. 10). The temperature of the dissociation of calcite is very sensitive to the partial pressure of CO_2. In the absence of CO_2 in the surrounding atmosphere the dissociation starts at about 500°C. When one atmosphere of CO_2 surrounds the sample, the dissociation starts at about 900°C. The other normal carbonates are much less sensitive to change in p_{CO_2}. Rowland and Lewis (1951) have shown that the order of decreasing sensitivity to change in p_{CO_2} is also Ca, Mg, Mn, Fe, and Zn. DTA curves of the anhydrous normal carbonates, with explanations of the reactions represented, have been published by Cuthbert and Rowland (1947), Kerr and Kulp (1948), Gruver (1950), and Beck (1950). In addition to the normal anhydrous carbonates, Beck included DTA curves of samples representative of most of the other carbonate minerals.

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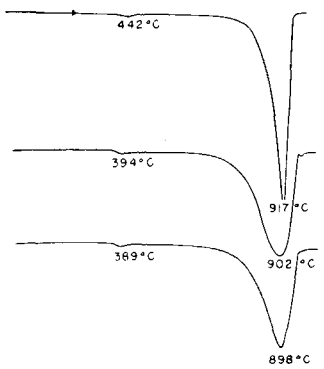


DTA CURVES OF CALCITE ARAGONITE MIXTURES
(AFTER FAUST, AMER. MIN. 35, 1950)

FIGURE 12

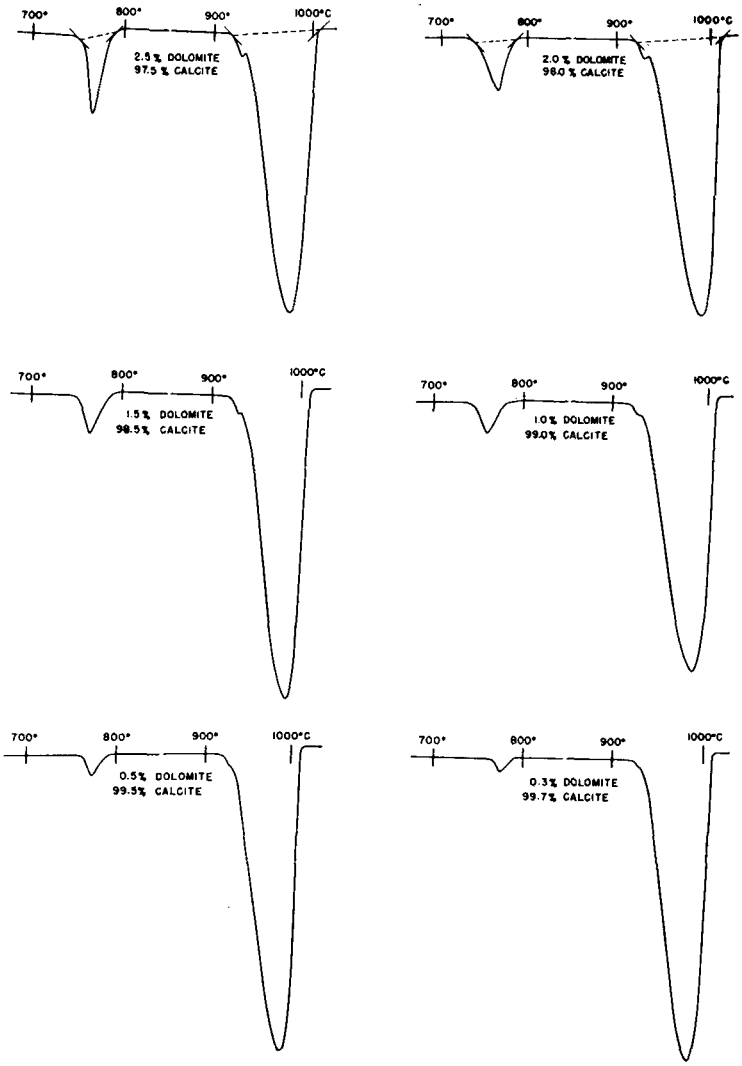
A review of the interpretations of DTA curves indicates the necessity for: (1) determining by other methods, usually X-ray, the nature of the product formed by each reaction; (2) establishing whether each thermal loop represents a single change or is a compromise heat effect resulting from several reactions; (3) investigating the effect of varying the gas pressure within the sample to establish the temperature dependence of the reaction on the gas phase. The data from (3) when plotted as van't Hoff lines almost uniquely describe the thermal characteristics of the materials.

Calcite. The dissociation of calcium carbonate is used in physical chemistry as a classic example of the effect of the partial pressure of a participating gas on heterogeneous equilibria. Perhaps it is for this reason that very little attention has been given to the DTA curves of calcite. Faust (1950) and Kulp, Kent, and Kerr (1951) have shown that the peak temperature and the initial decomposition temperature of pure calcite decrease when the sample is ground to an extremely fine particle size. Kulp et al. (1951) (fig. 11), also show a drop in both temperatures when the sample is highly diluted with alundum. These results were obtained in an ambient furnace atmosphere without control of the CO_2 and are therefore not definitive. Dilution reduces the opportunity for the buildup of a back pressure of CO_2 and consequently lowers the dissociation temperature. This effect is frequently observed in unwashed Ca-clay samples which have been allowed to stand in water open to the atmosphere. The DTA curves exhibit a small endothermic peak at about 750°C., resulting from the calcium carbonate formed from calcium in the solution and CO_2 dissolved from the air.

DTA curves of the aragonite → calcite transformation have been examined by Faust (1950) (fig. 12), who has pointed out that this monotropic transformation does not take place at a constant temperature, and is subject to further variations resulting from the presence of barium, strontium, lead, and perhaps zinc. The transformation temperatures range from 387°C to 488°C at a heating rate of 12°C per minute.

Magnesite. DTA curves of magnesite have been published by Cuthbert and Rowland (1947), Faust (1949), Gruver (1950), Beck (1950), and Kulp, Kent, and Kerr (1951). Pure coarsely crystalline magnesite heated in air yields a simple endothermic peak at 680 to 700°C. The temperature of the peak varies somewhat in the presence of impurities. The magnesite from Stevens County, Washington, shows an exothermic peak at the end of the endothermic peak. Kulp attributes this peak to the presence of small amounts of iron substituted in the lattice. It may also be the heat effect accompanying the organization of magnesium oxide as periclase.

Siderite. Cuthbert and Rowland (1947), Kerr and Kulp (1947), Frederickson (1948), and Rowland and Jonas (1949) have discussed the DTA curve of siderite. Diluted and heated in air, this carbonate yields a small exothermic loop (fig. 2). In an atmosphere of CO_2 the loop is large, endothermic, and at the proper temperature for the Ca, Mg, Fe, Mn, and Zn series. Undiluted and heated in air, the curve first swings in the exothermic direction until enough CO_2 has been liberated to prevent oxidation of the iron. The dissociation of CO_2 is then registered by an endothermic loop which is interrupted by an exothermic loop representing the oxidation of the FeO when the back pressure of CO_2 begins to subside. At a higher temperature the partially oxidized iron is completely oxidized to hematite.



DTA Calibration Curves of Small Percentages of
Bureau of Standards Dolomite and Iceland Spar Calcite

FIGURE 13

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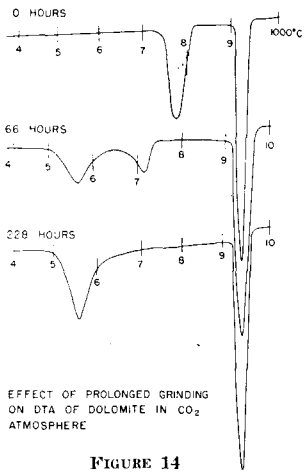

FIGURE 14

Dolomite. Of all of the carbonate minerals of the Ca-Mg-Fe group (Kulp, Kent, and Kerr, 1951) dolomite has received the most attention. Berg (1945) attempted to use the areas under the loops as a quantitative expression of the amount of dolomite in the sample. Rowland and Beck (1952) (fig. 13) succeeded in doing this for samples heated in an atmosphere of CO_2. Haul and Heystek (1952) (fig. 3) have shown that DTA curves for dolomite have only one loop at 1 mm p_{CO2}, two loops, resembling the curve made in air, at 300 mm p_{CO2}, and two distinctly separated loops at one atmosphere of CO_2. This is accomplished entirely by shifting of the second or $CaCO_3$ peak. The apparent immobility of the first peak leads them to suggest that this peak is formed only after a certain amount of diffusion of lattice constituents has taken place. The requirement for this activation energy explains the formation of this peak at a higher temperature than the peak for magnesite dissociation.

Actually, the first dissociation peak of dolomite is not immobile. Bradley, Burst, and Graf (1952) (fig. 14) have shown that during prolonged grinding (250 hours) there first appears another peak about 100°C. lower, which grows in size until the usual first peak is exhausted. At any stage the ratio of the sum of the areas of these two peaks to the area of the calcite is constant. These authors demonstrate by X-ray diffraction studies that, by a process of twin gliding and translation gliding, the Ca and Mg of the dolomite lattice which at first occupied alternate positions around any CO_3 group have now been rearranged so that most of the Mg has magnesium for its nearest neighbors and vice versa. Hence, the temperature delay required to activate these atoms to sufficient mobility so that dissociation can occur is no longer required. The first loop of a dolomite DTA curve is the algebraic sum of the ΔH required to dissociate both $MgCO_3$ and $CaCO_3$ (endothermic), to reform most of the $CaCO_3$ (exothermic), and perhaps to form periclase and some calcium oxide (exothermic).

Dolomite furnishes an excellent example of the effect of small crystallites (not fine grain size) on DTA curves. In figure 13 the endothermic loop beginning at 925°C is preceded by a small shoulder. This shoulder accompanies the dissociation of the extremely fine crystallites of $CaCO_3$ formed from the products of the first loop which dissociate before the more coarse-grained calcite fragments.

Berg (1943) and Graf (1952) have shown that the presence of soluble salts such as encountered in brines will materially affect the shape and size of the first loop of the dolomite curve. In addition, the presence of a sericite-like mica will completely eliminate the second or calcium carbonate peak in a CO_2 atmosphere.

MISCELLANEOUS APPLICATIONS OF DTA

Soaps. Vold and Vold (1941) established that, instead of melting directly from crystal to liquid, sodium salts of long-chain fatty acids pass through a series of forms, each constituting a definite stable phase existing over a definite range of temperature. They calculated heats of transition from the DTA curves of these soaps and have since (Vold, Grandine, and Vold, 1948) delineated the polymorphic transformations of calcium stearate and calcium stearate monohydrate by their technique.

Greases. By the same technique Vold, Hattiangdi, and Vold (1949) have delineated the phase state and thermal transitions of numerous samples of aluminum, barium, calcium, lithium, sodium, and mixed base commercial greases, and of the corresponding oil-free soaps.

CONCLUSION

Differential thermal analysis is well established as a technique for the characterization and control of materials which undergo characteristic changes on heating. It is less well established as a method for investigating the products obtained when such a material is heated, since equilibrium is an inherent impossibility of the method. However, the latter is not an obstacle when thermodynamic considerations control the design of the apparatus and when good recording equipment is employed. With the addition of dynamic atmosphere control much useful information about the products of heating can be assembled in a short time.

Because differential thermal analysis is most useful when the apparatus is designed so that several different techniques can be employed, there should be no standardization of materials, heating rates, etc. Instead, a flexibility should be maintained so that due consideration can be given to the details of the kind of change being analyzed, and these considerations must be presented as a part of the data.

DISCUSSION

J. A. Pask:

In the DTA curves of montmorillonite Rowland mentioned that the exothermic loop at 930°C. is accompanied by the formation of a spinel in the untreated material, mullite and spinel in the NH_4^+-saturated samples, and mullite in the methylamine-saturated samples. Could this be discussed?

R. A. Rowland:

I believe the explanation lies in the nature of the exchangeable cation. When the exchangeable cations are Ca^{++} and Mg^{++}, spinel is formed, but when these are completely absent, as in the case of the methylamine-saturated samples, mullite is formed. The formation of both spinel and mullite in the NH_4^+-saturated sample would indicate that the sample was not completely saturated with NH_4^+; some of the original exchangeable cations must have remained on the clay.

J. A. Pask:

Is the spinel formed by a combination of the exchangeable cation and the aluminum of the lattice?

R. A. Rowland:

This appears to be so from the series of curves which I showed and from other curves run in similar fashion.

G. W. Brindley:

I feel that progress can be made in the use of the various methods of clay identification and estimation by a cooperative effort whereby type mineral specimens would be examined by the various methods by those persons who have had a great deal of experience with a given method.

J. A. Pask:

I think that any one of the methods for clay identification is as good and as useful as any other, provided the operator is thoroughly familiar with the method which he uses.

Isaac Barshad:

Each method yields data which another method does not. That is precisely why the various methods of analysis were developed. Thus, while X-ray analysis is indispensable for crystal structure analysis, DTA is undispensable for recording changes which occur in a mineral during the course of heating. It would be practically impossible to identify and estimate amounts of the various clay minerals in a clay sample derived from a soil unless various methods of analysis are used.

T. F. Bates:

This discussion has further indicated the need for additional fundamental research and for the exchange of clay samples between workers on both sides of the Atlantic.

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