DIFFERENTIAL THERMAL ANALYSIS OF THE DOLOMITE DECOMPOSITION*

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ABSTRACT

Samples of dolomite, calcite, and magnesite have been submitted to differential thermal analysis under various carbon dioxide pressures and the results obtained are discussed in relation to the reaction mechanism of the thermal decomposition of dolomite. Differential thermal peak temperatures are also compared with equilibrium dissociation temperatures of calcite and magnesite.

INTRODUCTION

In earlier communications in this series, the thermal decomposition of dolomite has been investigated by *x*-ray diffraction (Haul and Wilsdorf, 1951), and by studies of the exchange of carbon-13-dioxide between dolomite and gaseous carbon dioxide at elevated temperatures (Haul, Stein and Louw, 1951). As a further aid to the elucidation of the mechanism of this reaction, the technique of differential thermal analysis (*DTA*) has now been applied.

Differential thermal curves for dolomite have been described by various authors (Table 1) although merely as a means for its identification in minerals. Schwob (1947, 1950), however, concluded from the peaks observed at about 800° C. and 930° C. that the reaction takes place in two distinct stages; the first corresponding to the formation of magnesium oxide and calcite, and the second to the dissociation of calcite. In the presence of small amounts of sodium carbonate, the first peak was shifted to lower temperatures, approximating to the peak temperature observed for pure magnesite (700° C.). Schwob, therefore, suggested that the first phase of the decomposition of dolomite consists of a primary dissociation into magnesium and calcium carbonates. The magnesium carbonate formed in this way is unstable at that temperature and decomposes immediately, followed by the decomposition of the calcium carbonate at a higher temperature. The addition of alkali carbonate merely catalyses the separation of the constituent carbonates.

So far *DTA* work has been done by heating of samples only in air. It was felt, however, that further information on the decomposition of dolomite could be obtained only by investigating the samples under a range of constant carbon dioxide pressures. Investigations along these lines were already completed when Rowland and Lewis (1951) em-

* Communication No. 3 on the thermal decomposition of dolomite.

phasized the importance of controlling the atmosphere in *DTA* work. Among various minerals investigated the above authors also compared mineral carbonates when decomposed in air and in an atmosphere of CO_2. The peaks obtained appeared to be more distinct in CO_2, and the peak temperatures were different. These results were in line with experience in this laboratory and the present paper records an extension of the work in which the effect of various carbon dioxide pressures on the decomposition of dolomite, calcite and magnesite, is illustrated in detail.

Apparatus and Experimental Technique

(*A*) *DTA apparatus*

The automatic *DTA* apparatus used in this laboratory has been described by Theron (1951) and consisted of:

(i) a horizontal kanthal A-wound Alundum tube furnace.
(ii) a differential thermocouple as well as a thermocouple controlling and measuring the furnace temperature, both made out of 0.5 mm. dia. Platinum-Platinum (13%) Rhodium wire.
(iii) a sample holder of two platinum micro crucibles (2 cm.^{3}) suspended in the reaction vessel by means of a chrome-nickel plate as illustrated in Fig. 1.
(iv) an automatic temperature controlling system which utilizes a motor driven variac operated by a proportioning electronic temperature controller.
(v) an automatic recording of the amplified differential voltage and the furnace temperature by a six point recording millivoltmeter.

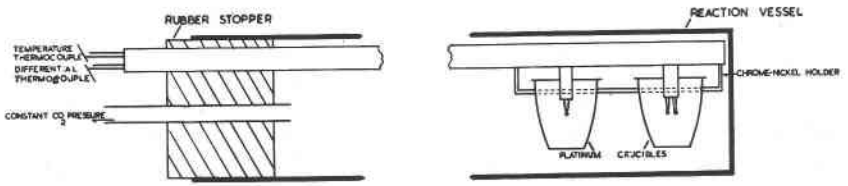

FIG. 1. Reaction vessel with *DTA* sample holder.

(*B*) *Apparatus for controlling the CO_2 pressure*

The platinum crucibles with sample and inert material (calcined Al_2O_3), together with the thermocouples, were placed in a reaction vessel of vitreous silica, 40 cm. long and 4 cm. inner dia. open at one end. This was closed by means of a rubber stopper through which were introduced an alundum tube carrying the thermocouple wires and a glass tube connected with the pressure controlling system. The thermocouple wires were sealed in at the outside end of the alundum tube with picein

wax. This method, though simple, was quite satisfactory, as no leaks occurred during the experiments.

Any desired pressure up to 760 mm. (about 100 mm. above local atmospheric pressure) could be maintained constant by means of the apparatus illustrated in Fig. 2. A capillary tube (1.5 mm. inner dia.) connected with the reaction vessel was suspended inside a glass tube 1 m. long filled with mercury to the desired height and evacuated throughout the duration of an experiment. As soon as the pressure increased inside

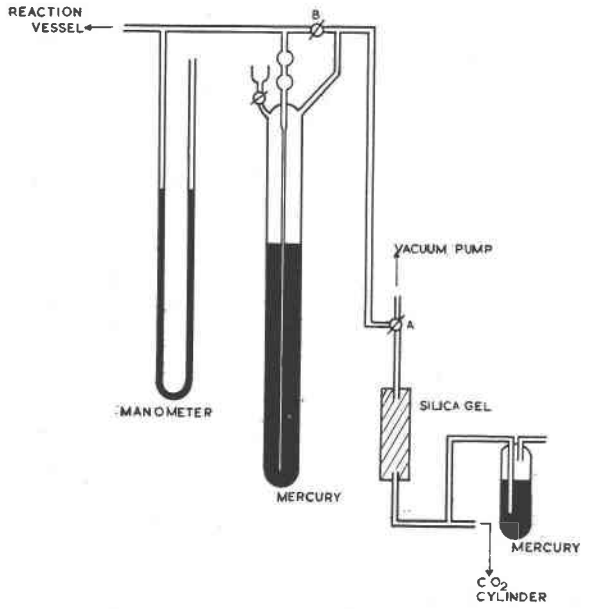

FIG. 2. Apparatus for maintaining constant CO_2 pressures.

the reaction vessel due to heating or evolution of gas by decomposition of a carbonate, the gas escaped through the capillary until the original pressure determined by the mercury height was again obtained. Before starting an experiment, the reaction vessel was repeatedly evacuated and then filled with carbon dioxide dried over silica gel using the three-way stopcock *A*. During this manipulation stopcock *B* was kept open and was closed only after the last filling of the reaction vessel with carbon dioxide.

(*C*) *Experimental technique*

Due to the vigorous gas evolution occurring when carbonates, especially magnesite, decompose at low pressures, some material was lost out

of the crucible. It was, therefore, found expedient to use material of 40 to 60 mesh in preference to finely ground samples and to fasten down the crucible lid in experiments at pressures lower than 100 mm. For the same reason, in some runs magnesite was diluted using a mixture of 10% magnesite and 90% of the same magnesite previously ignited to 1000° C. In all experiments 1.5 g. of sample were used.

Normally, a *DTA* heating rate of 15° C./min. is used in this laboratory. The additional temperature lag caused by the insertion of the silica reaction vessel into the *DTA* furnace, however, made satisfactory control of the furnace temperature difficult. At a heating rate of 7° C./min. good control could be maintained and this rate was used throughout these experiments.

The inversion temperature of α, β quartz (575° C.) was used for temperature calibration. In an initial run in an air atmosphere, a peak temperature of 570° C. was obtained with a standardized thermocouple. If, however, the inversion temperature was measured under carbon dioxide pressures of 40 and 760 mm. respectively, the peak occurred at 550° C. It is thought that this discrepancy may be due to the difference in heat conductivities of air and carbon dioxide. All temperatures given in this paper were corrected accordingly.

The origins and chemical analyses of the samples used are listed in Tables 1 and 2.

Results and Discussion

(1) *Comparison of differential thermal peak temperatures of various dolomites*

In Table 1 peak temperatures of dolomites recently reported in differential thermal investigations on carbonates are listed together with results obtained in the present work.

When comparing these results, and excluding runs with impure and diluted samples, it is found that the first peak maximum occurs at 810 ± 15° C., and the second peak maximum at 940 ± 25° C. Considering that the *DTA* apparatus used by the various authors differed to some extent, e.g. sample holder, differential thermocouple, rate of heating, and that dolomites of various purity, particle and crystal size were investigated, this agreement is surprisingly good. The somewhat bigger variation in the temperature of the second peak maximum may be explained by the dependence of this peak on the carbon dioxide pressure, as will be shown later.

In the present experiments four different dolomites were also run at a constant carbon dioxide pressure of 660 mm. The peak temperatures on comparison are close together, though the first peak of the rather impure

TABLE 1. COMPARISON OF *DTA* PEAK TEMPERATURES OF VARIOUS DOLOMITES

Samples		*DTA* technique	Atm.	First Peak temp. °C.			Second Peak temp. °C.			Remarks	Author
Source	Analysis			Beginning	Maximum	End	Beginning	Maximum	End		
Cleavage frag.	CaO :31.25% MgO:20.13% CO_2 :46.92%	Nickel block sample holder, Pt. Pt. 10% Rhod. Thermocouple 10° C./min. 60 mesh. Mixtures 75% dolom. +25% Al_2O_3	Air	600	780	(800)	(800)	830	880	peaks not completely separated	Cuthbert & Rowland (1947)
West Roxbury, Vt., U.S.A.	ω=1.684 ϵ=1.502	Nickel block sample holder, Chromel P. Alumel Thermocouple 12° C./min. 100/200 mesh	Air	750	815	845	855	965	985	peaks separated	Beck (1950)
Lee, Mass., U.S.A.	—	Platinum crucible, Chromel P.		760	800	830	830	950	970		
Rochester, N.Y., U.S.A.	with calcite	Alumel Thermocouple 6.7° C.	Air	800	810	840	840	965	1000	peaks separated	Gruver (1950)
Pearl Spar, Joplin, Mo., U.S.A.	with magnesite	/min. 80 mesh		650	760	830	830	940	970		
Milville, West Va., U.S.A.	not stated	not stated	Air	—	792	—	—	926	—	peaks separated	Faust (1949)
Quillan, France	CaO :32.7% MgO:20.8% CO_2 :46.2%			780	825	(880)	(880)	940	1020		
Baudean, France	CaO :32.0% MgO:20.0% CO_2 :46.7%	Porcelain crucible divided by nickel wall	Air	780	800	(860)	(860)	920	1000	not completely separated	Schwob (1950)
Bédarieux, France, dolomite spar	CaO :30.4% MgO:21.6% CO_2 :47.8%			710	800	(860)	(860)	930	1000		

Samples		*DTA* technique	Atm.	First Peak temp. °C.			Second Peak temp. °C.			Remarks	Author
Source	Analysis			Beginning	Maximum	End	Beginning	Maximum	End		
Not stated	Not stated	Nickel block sample holder, Pt. Pt. 10% Rhod. Thermocouple 10° C./min.	Air	(750)	810	840	840	920	940	peaks nearly separated	Rowland & Lewis (1951)
			CO_2	760	790	810	910	940	960	peaks separated	
Thornwood, N.Y., U.S.A.	CaO :30.8% MgO:21.8% CO_2 :46.1%	Platinum crucible Pt. Pt. 13% Rhodium Thermocouple 7° C. /min.	Air (660 mm.)	775	825	(870)	(870)	945	995	peaks not completely separated	
			CO_2 (760 mm.)	735	795	855	890	965	990	peaks separated	
			(660 mm.)	730	790	835	885	950	975	peaks separated	
Lee, Mass., U.S.A.	CaO :30.7% MgO:21.8% CO_2 :45.8%	Platinum crucible Pt. Pt. 13% Rhodium Thermocouple 7° C. /min.	(660 mm.)	730	800	855	885	955	990	peaks separated	Haul and Heystek (1951)
Cape, South Africa	CaO :29.9% MgO:20.6% CO_2 :45.0%	Platinum crucible Pt. Pt. 13% Rhodium Thermocouple 7° C. /min.	(660 mm.)	710	770	810	890	960	995	peaks separated	
Krugersdorp, Transvaal, South Africa	CaO :28.7% MgO:19.8% CO_2 :46.0%	Platinum crucible Pt. Pt. 13% Rhodium Thermocouple 7° C. /min.	(660 mm.)	720	790	820	880	955	985	peaks separated	

TABLE 2. *DTA* PEAK TEMPERATURES OF DOLOMITE, MAGNESITE, AND CALCITE OBTAINED AT VARIOUS CO_2 PRESSURES

CO_2 pressure mm.	Dolomite, Thornwood, CaO:30.8%; MgO:21.8%; CO_2:46.1% peak temperatures °C.			Magnesite, S. Rhodesia, Big Dyke MgO:46.7%; CaO:0.7%; loss ign. 51.4% peak temperatures °C.			Calcite, clear cleavage frag. Cherokee County, Kansas, peak temperatures °C.		
	beginning	maximum	end	beginning	maximum	end	beginning	maximum	end
1	645	795	855	595	705	775	645	(820)	890
20	700	825	885	585	685	750	690	(860)	925
50	715	825	875	600	695	775	725	865	925
100	1. 735	790	(815)	575	725	800	755	895	940
	2. (815)	860	910						
300	1. 735	795	(835)	600	740	815	815	955	1025
	2. (835)	895	935						
660	1. 730	790	835	600	745	815	870	995	
	2. 885	950	975						
760	1. 755	810	950	595	765	825	895	1015	1055
	2. 900	975	1000						
Air	1. 775	825	(870)	(545)	765	(835)	(725)	985	1045
	2. (870)	945	995						

South African Cape dolomite is somewhat lower. The same specimens were also investigated by determining the loss of weight when heated at 100 mm. CO_2 for 150 minutes at various temperatures in the range of 550° to 850° C. The pure Thornwood, New York, and Lee, Massachusetts, dolomites gave duplicate curves, while the curves of the Cape and especially the Krugersdorp, Transvaal, dolomites differed considerably in that a gradual decomposition starting at lower temperatures was indicated. In this respect, the thermo-gravimetric method provides more information than the *DTA* method.

(2) *Influence of carbon dioxide pressure on differential thermal curves of dolomite.*

When dolomite is decomposed in air, the two peaks appearing in the *DT* curves are well separated in some experiments, while in others the second peak starts before the first is completed, as already mentioned by Rowland and Lewis (1951). These variations are due to the fact that the partial pressure of carbon dioxide increases within the sample holder

when CO_2 is released during decomposition. When the above mentioned authors, in their experiments, used an atmosphere of CO_2, they found that the peaks were then well separated.

In the present investigations various, but constant, carbon dioxide pressures were maintained during decomposition, as already described. The *DT* curves obtained are reproduced in Fig. 3. The peaks, which were clearly separated at 760 mm. CO_2 pressure, gradually approach one another and finally merge as the pressure is decreased below about 100

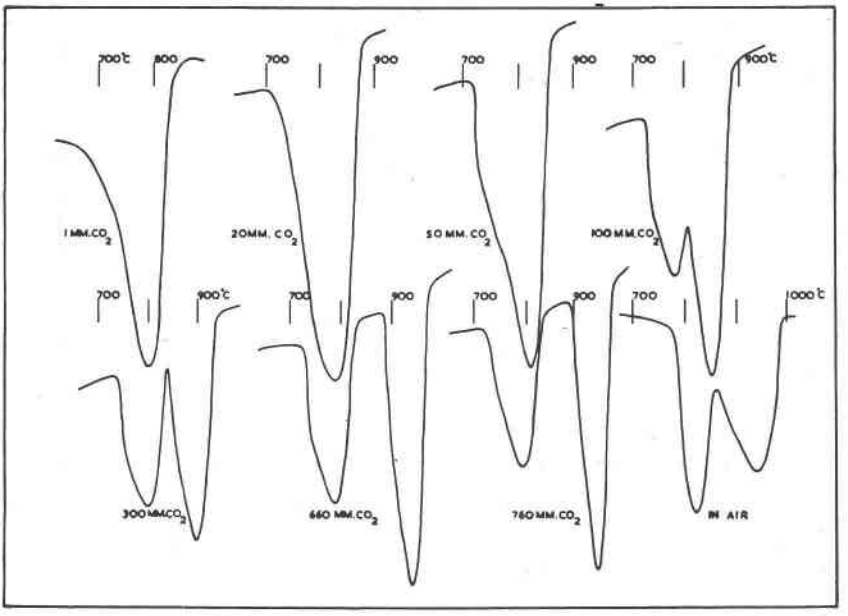

FIG. 3. Differential thermal curves of dolomite at different CO_2 pressures.

mm. The peak temperatures are listed in Table 2, and the maximum peak temperatures are plotted in Fig. 4. From this it can be seen that the first peak due to formation of MgO and $CaCO_3$ is not at all affected by the CO_2 pressure; the peak maximum remains at about 795° C. However, the second peak maximum corresponding to the decomposition of the primarily formed calcite is shifted to higher temperatures with increasing pressure, from about 800° C. to 970° C. The curve (Fig. 4) is very similar to that obtained with pure calcite, but shows that the second peak maximum of dolomite occurs about 50° lower than the peak of mineral calcite at different CO_2 pressures. This is obviously due to smaller crystal size as well as to lattice distortion present to an appreciable degree in calcite formed from dolomite, as was found by *x*-ray study. (Haul and Wilsdorf, *loc. cit.*)

Unfortunately, with the method used, it was difficult to investigate the decomposition of dolomite at CO_2 pressures lower than about 40 mm., as some substance was always lost out of the crucible. Thus the peak temperatures at pressures in this low range may be somewhat in error. They clearly correspond, however, to the calcite decomposition.

Although it was found that the first dolomite peak is not affected by

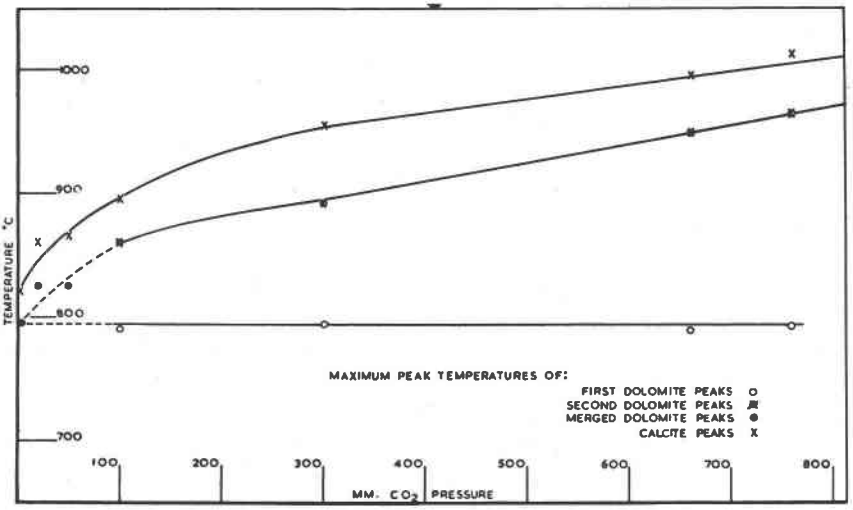

FIG. 4. Maximum differential thermal peak temperatures of dolomite and calcite at various CO_2 pressures.

varying the CO_2 pressure, this fact is only applicable in the pressure range where dolomite is decomposed in two stages according to:

$$\text{first peak:} \quad CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \tag{1a}$$

$$\text{second peak:} \quad CaCO_3 \rightleftarrows CaO + CO_2. \tag{1b}$$

The reaction mechanism is different when the maintained CO_2 pressure is decreased sufficiently below the dissociation pressure of calcite. This is evident from a kinetic investigation of the decomposition of dolomite by Bischoff (1950), as well as from thermo-gravimetric experiments carried out by Noll (1951) and in this laboratory.* Under these conditions, the decomposition occurs instantaneously in one stage.

$$MgCa(CO_3)_2 \rightarrow CaO + MgO + 2CO_2. \tag{2}$$

For this reason the *DTA* results are of significance only in connection with the reaction mechanism involved in the partial decomposition to MgO and $CaCO_3$. Haul and Wilsdorf (1951) have discussed various mechanisms suggested for this decomposition in the light of their *x*-ray

* To be published elsewhere.

study of thermally decomposed single crystals of dolomite and have shown that the following mechanisms do not apply:

(i) Formation of solid solutions of carbonates or oxides during decomposition (Baikov 1913; Mitchell 1923; Gel'd and Esin 1949.)
(ii) Primary dissociation into separate carbonates followed by their independent decomposition (Potapenko 1932; Conley 1939; Fagueret 1940; Schwob 1947, 1950.)
(iii) Primary dissociation into oxides and recombination of CaO with CO_2 from the gas phase to calcite (discussed by Flood 1950).

An interpretation of the first differential thermal peak as due to the "decomposition of the $MgCO_3$ part of the dolomite structure" (Beck 1950) is irrelevant. In the crystal structure of dolomite it is implicit that it must be treated as a definite compound when considering the thermal decomposition.

From the x-ray results, it was concluded that calcite is directly formed from the original dolomite lattice. This was indicated by the fact that calcite was present as crystallites oriented in exactly the same way as the original dolomite, thus resulting in an x-ray diagram equivalent to that of a calcite single crystal. The transition of dolomite into the isotype calcite lattice can easily occur, as only interchange of magnesium and calcium ions and expansion of the lattice to less than 4% are necessary. Due to the difference in crystal structure and lack of suitable corresponding atomic arrangements, the magnesium oxide crystals are not oriented to the original dolomite crystal, but grow from nuclei formed at random when a sufficient excess of magnesium ions has accumulated.

While the dependence of the second peak on the CO_2 pressure can easily be understood from basic thermodynamics, the fact that the first peak is not affected requires some explanation. As the change in free energy of the formation of dolomite from magnesite and calcite is rather small (1.6 kcal. Roth, 1936) the dissociation pressure thermo-dynamically calculated for a reaction according to equation (1*a*) will be slightly less than that for magnesite. This pressure at e.g. 800° C. is 7500 atm. Therefore in the temperature range of the first dolomite peak, the theoretical dissociation pressure exceeds the carbon-dioxide pressure maintained in the experiments by far. Consequently, the first stage of dolomite decomposition should occur at considerably lower temperatures than experimentally observed. However, the rate of this solid state reaction is determined by diffusion of the components within the lattice. It is well known that the rate of these activated processes is exponentially dependent on the temperature, i.e.

$$D = D_0 C^{-\lambda/RT}$$

where D is the average diffusion coefficient; D_0 a constant and λ the activation energy. Therefore, the lattice constituents can be expected to reach sufficient mobility for the reaction (1*a*) to proceed in a rather narrow temperature range.

These considerations explain the experimental finding that the first stage of the dolomite decomposition is independent of the CO_2 pressure and always occurs within the same narrow temperature range.

(3) *Comparison between differential thermal peak temperatures and equilibrium dissociation temperatures of calcite and magnesite.*

The equilibrium constant of the thermal decomposition of carbonates

$$MeCO_3 \rightleftarrows MeO + CO_2$$

as is well known, may be written

$$K_p = \frac{p_{CO_2} \times p_{MeO}}{p_{MeCO_3}} \equiv p_{CO_2}$$

and furthermore the relation between partial pressure of carbon dioxide and dissociation temperature is given by

$$\log p_{CO_2} = -\frac{H_T}{4.57 \cdot T} + \frac{S_T}{4.57}$$

where H_T and S_T represent the differences in heat content and entropy for the initial and final products at the temperature T for 1 Mol. By means of this equation, the thermodynamic equilibrium pressures can be calculated for various temperatures and these values are plotted in Fig. 5. While for calcite there is quite good agreement between the experimental determined (Johnston, 1910) and calculated values (Margulesco, 1946), for magnesite most investigators have recorded pressures far less than those corresponding to equilibrium. Only recently has Cremer (1949) succeeded, by the use of special experimental conditions, in getting data near the thermodynamically calculated values.

When comparing the differential thermal peak maximum temperatures for calcite with the equilibrium values (Fig. 5.) at different CO_2 pressures, the former temperatures are about 120° higher. However, if the temperatures at which the peaks start are compared, a fairly good agreement is obtained, though the measurement of this point on the DT curve is sometimes difficult. Therefore, the temperatures of the beginning of the peaks are more significant as far as the equilibrium temperature is concerned. The peak maximum temperatures are more affected by the conditions of heat conductivity, particle size, etc. For mineralogical analysis, of course, the commonly used peak maximum is sufficient and also more convenient to measure.

When considering magnesite (Fig. 5), it is found that the peak maximum temperatures exceed the corresponding equilibrium temperatures by about 400° C. Even when magnesite is diluted with magnesium oxide (1:9) the peak maximum is still about 300° C. too high. This discrepancy is due to the fact that the rate of diffusion processes within the solids determines the temperature range where the reaction occurs, as already discussed in connection with the mechanism of the first stage of dolomite decomposition. According to this, there should also be no dependence of

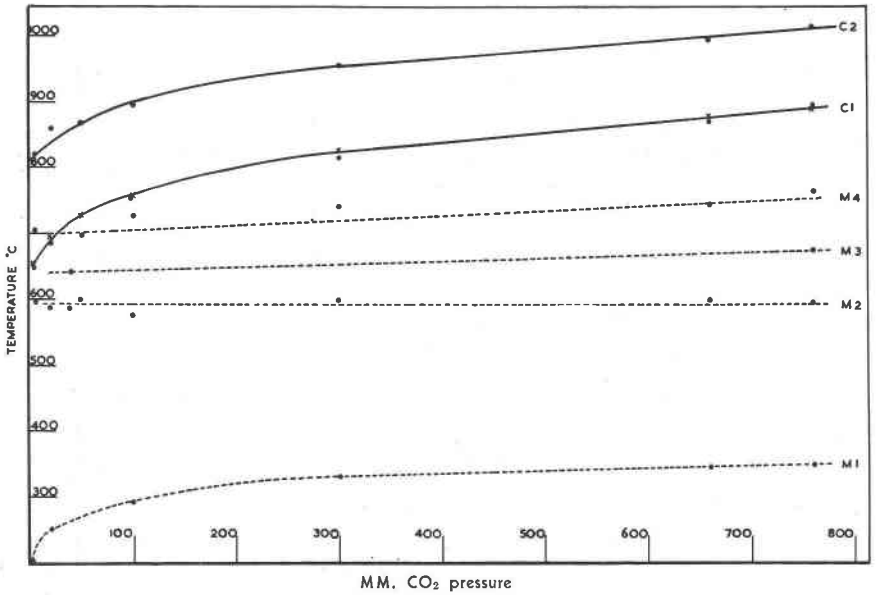

FIG. 5. Comparison of *DT* peak temperatures of calcite and magnesite with equilibrium dissociation temperatures:

C_1—equilibrium dissociation temperatures for calcite,
·—temperatures of the beginning of calcite peaks,
C_2—maximum temperatures of calcite peaks,
M_1—equilibrium dissociation temperatures for magnesite,
M_2—temperatures of the beginning of magnesite peaks,
M_3—maximum peak temperatures for magnesite diluted with magnesium oxide (1:9),
M_4—maximum peak temperatures for magnesite.

the peak temperature on the CO_2 pressure. The experimental values, however, indicated a small difference (35 degrees) between the maximum differential thermal peak temperatures at 40 and 760 mm. CO_2 respectively. When the temperatures of the beginning of the peaks are considered, no dependence on CO_2 pressure is observed (Fig. 5). The slight influence of different CO_2 pressures on the maximum temperature of the

differential thermal peaks may be due to variations in heat conductivity and diffusion of carbon dioxide through the sample.

Conclusions

(1) Comparison of various dolomites has shown that although different apparatus and techniques have been used by different authors, the *DTA* peak temperatures obtained are in reasonable agreement. The first peak occurs at $810 \pm 15°$ C. and the second at $940 \pm 25°$ C.

(2) A variation in carbon dioxide pressure in the range 760 to 0.5 mm. Hg resulted in a lowering of the second peak temperature of the dolomite decomposition with decreasing pressure while the first peak was not influenced. Below about 100 mm. CO_2 the two peaks merged.

(3) These results are in agreement with a reaction mechanism of the thermal decomposition of dolomite derived from a previous *x*-ray study. As far as decomposition in two stages is concerned, the calcite in the first stage is directly formed from the isotype dolomite structure by the diffusion of its constituents within the lattice. The rate of these activated diffusion processes and not the thermodynamic given dissociation pressure determine the temperature range when the first stage of the decomposition occurs. Therefore, the first differential thermal peak is not influenced by a variation of the carbon dioxide pressure.

(4) While the maximum peak temperatures of calcite are about 120° C. higher than the equilibrium dissociation temperatures in the above pressure range, the temperatures of the beginnings of the peaks are in fair agreement with the equilibrium temperatures. The peak temperatures of calcite decomposition increase with an increase of CO_2 pressure, as can be expected thermodynamically.

(5) The differential thermal peak temperatures of magnesite are much higher than the calculated dissociation temperatures and the beginnings of the peaks show no dependence on the CO_2 pressure. This is due to the fact that the rate of decomposition is determined by diffusion processes within the solid state.

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