

## THE EFFECT OF CO<sub>2</sub> PRESSURE AND ALKALI SALT ON THE MECHANISM OF DECOMPOSITION OF DOLOMITE\*

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### ABSTRACT

A detailed investigation of the mechanism of decomposition of dolomite in a specially designed thermal apparatus has been performed. Results show that much of the published thermal analysis data for dolomite represent decomposition at some unknown but high CO<sub>2</sub> pressure. Detailed results confirm that CO<sub>2</sub> pressure affects both the initial decomposition temperature into MgO and CaCO<sub>3</sub> and the final decomposition temperature of CaCO<sub>3</sub>, but in opposite directions. This demonstrates the existence of different decomposition mechanisms. Alkali salt also affects the decomposition temperature regardless of the gaseous atmosphere, and in some instances may cause decomposition to occur by a completely different mechanism.

### INTRODUCTION

Recently we investigated in detail the effect of atmosphere composition and alkali salt concentration on the decomposition of dolomite. To accomplish this, we used a specially modified differential thermal analysis (DTA) apparatus and experimental procedures. For example, better-than-usual control of the gas atmosphere was achieved by use of a small (2 mg) sample in a small compartment with a dynamic gas flow that rapidly removed decomposition gas from the sample compartment and therefore minimized the effect of the CO<sub>2</sub> evolved on the mechanism and rate of decomposition of dolomite. As a result of this work, we have correlated the changes in mechanism of decomposition of dolomite with differences in published DTA results.

Most studies of dolomite by methods other than DTA show a single decomposition step, whereas the normally published DTA thermograms for dolomite show a two-step decomposition<sup>1-13</sup>. Methods other than DTA show that decomposition occurs at even lower temperatures than shown by DTA methods. Haul and co-

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workers<sup>4,5,14-16</sup> studied the decomposition of dolomite by X-ray, DTA, and carbon isotope methods. They concluded that the decomposition took place in two steps  $[\text{CaMg}(\text{CO}_3)_2 \xrightarrow{780-800^\circ\text{C}} \text{CaCO}_3 + \text{MgO} + \text{CO}_2 \xrightarrow{880-900^\circ\text{C}} \text{MgO} + 2\text{CO}_2 + \text{CaO}]$  at high partial pressures of  $\text{CO}_2$ , but at low partial pressures of  $\text{CO}_2$  the decomposition occurred in one step  $[\text{CaMg}(\text{CO}_3)_2 \xrightarrow{700^\circ\text{C}} \text{CaO} + \text{MgO} + 2\text{CO}_2]$ . Müller-Vonmoos and Bach<sup>17</sup> showed a single DTA decomposition endotherm in both dynamic nitrogen and vacuum, which agrees with data from other methods. Haul and Heystek<sup>4</sup> showed a single decomposition endotherm at low pressure of  $\text{CO}_2$ .

Carbon isotope studies<sup>14</sup> showed that decomposition of dolomite occurs at  $700^\circ\text{C}$ ; calcination studies<sup>18</sup> in air showed complete decomposition between  $650$  and  $700^\circ\text{C}$ ; and evolved gas analysis (EGA) by mass spectrometry showed decomposition below  $700^\circ\text{C}$  in vacuum<sup>17</sup>. Thermogravimetric (TG) methods indicate that the evolution of  $\text{CO}_2$  occurs as a single step between  $640$  and  $720^\circ\text{C}$  in vacuum<sup>17,19</sup>, as a single step in nitrogen<sup>20</sup>, as a single step between  $610$  and  $800^\circ\text{C}$  in air<sup>21</sup>, and as a single step at  $680^\circ\text{C}$  at low  $\text{CO}_2$  pressures<sup>22</sup>.

Haul and Heystek<sup>4</sup> have calculated that dolomite should begin to decompose at the same temperature as magnesite, and further predicted that the temperature at which dolomite begins to decompose is sensitive to the partial pressure of  $\text{CO}_2$ . Hedvall<sup>23</sup> states that dolomite begins to decompose at  $580^\circ\text{C}$  in static air and this corresponds with some values for magnesite decomposition<sup>3,24</sup>, which has been shown to be sensitive to  $\text{CO}_2$  pressure.

A study of the DTA literature shows that the DTA thermograms which are most often published for decomposition of dolomite represent the decomposition at some unknown but high partial pressure of  $\text{CO}_2$ . The partial pressure of  $\text{CO}_2$  is dependent upon the rate of diffusion of  $\text{CO}_2$  from the sample, which is in turn dependent upon sample size, particle size, sample-compartment size, use of sample lids, use of static or dynamic atmosphere, and other factors<sup>25</sup>.

When two endotherms are shown for the decomposition of dolomite, authors agree that the higher endotherm ( $880^\circ\text{C}$ ) represents the decomposition of  $\text{CaCO}_3$ ; the temperature varies directly as the  $\text{CO}_2$  pressure is changed. When concentrations of alkali metal salts, alkaline earth salts, iron carbonate, and other diverse ions are low, most authors agree that the lower temperature endotherm ( $780^\circ\text{C}$ ) results from the decomposition of a portion of the dolomite to  $\text{MgO}$ . However, there is much disagreement on the mechanism of decomposition and whether the lower temperature endotherm is sensitive to  $\text{CO}_2$  pressure<sup>1,4,5,13,18,26</sup>. On the basis of vacuum TG results, Gritton et al.<sup>19</sup> said that the initial reaction was  $\text{CaMg}(\text{CO}_3)_2 \rightarrow \text{MgO} + \text{CaO} + 2\text{CO}_2$  followed by rapid recombination of  $\text{CaO}$  to  $\text{CaCO}_3$  at higher pressures of  $\text{CO}_2$ . However, this conflicts with Haul's X-ray diffraction results<sup>15</sup>, which show that  $\text{CaCO}_3$  is left in the same crystal arrangement as the original dolomite when a large single crystal of dolomite is decomposed.

It has also been shown by X-ray diffraction that the initial decomposition step to  $\text{MgO}$  can be attained at  $600^\circ\text{C}$  if the elapsed time is at least 300 h. Both Haul<sup>5</sup>

and Garn<sup>26</sup> have pointed out that an inverse relationship exists between the low-temperature endotherm and the CO<sub>2</sub> pressure. Garn further suggested that a second mechanism of decomposition involving the exchange of CO<sub>2</sub> is present. Carbon isotope results support the idea of CO<sub>2</sub> exchange. Esin<sup>27</sup> proposed that the initial step in the decomposition is  $\text{CO}_3^{2-} \rightarrow \text{CO}_2 + \text{O}^{2-}$  which is caused by heating. Because of the crystal arrangement and smaller size of the magnesium ion, the initial step is more prevalent around this ion. Because the re-formation of MgCO<sub>3</sub> is not possible<sup>3</sup> and because more exchange reaction would take place at higher concentrations of CO<sub>2</sub>, it appears that the mechanism involving exchange of CO<sub>2</sub> predominates and this is a possible explanation for the inverse temperature relationship of the low-temperature endotherm with CO<sub>2</sub> pressure.

There is a large amount of evidence<sup>7,11,27-30</sup> showing that certain salts affect the low-temperature endotherm when the decomposition of dolomite is occurring in the presence of CO<sub>2</sub>. Esin<sup>27</sup> has proposed that salt catalyzes the first step [ $\text{CO}_3^{2-} \rightarrow \text{CO}_2 + \text{O}^{2-}$ ] of the overall reaction at the magnesium sites, and then further states that the salt catalyzes the rearrangement of Ca<sup>2+</sup>, Mg<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, and O<sup>2-</sup> so as to complete the second step in the reaction (leading to MgO + CO<sub>2</sub> + CaCO<sub>3</sub>). Garn's explanation<sup>26</sup> is that dolomite is unstable below the normal first decomposition endotherm<sup>9</sup>, and the presence of salt distorts the lattice and lowers the activation energy so that the first decomposition step can take place at a lower temperature. The effect of salt not only lowers the temperature of decomposition, but TG<sup>7,18,27</sup> results show that it changes the rate of decomposition. Esin<sup>27</sup> also noted the change of rate being observed by X-ray methods.

An earlier interpretation of the two DTA endotherms for the decomposition of dolomite was based on initial decomposition of dolomite to MgCO<sub>3</sub> and CaCO<sub>3</sub> with subsequent decomposition of the resulting carbonates. Although this has not been proven for relatively pure dolomite, Esin et al.<sup>27</sup> believe that decomposition to individual carbonates is possible with high concentrations of salt in impure dolomites. A survey of abstracts<sup>1,8-10,20,27</sup> of old and recent papers which have presented the possibility of this decomposition to individual carbonates shows that these investigations could be talking about salt-bearing dolomites. Recently Komatsu and Senda<sup>31</sup> published X-ray results showing that in the presence of ferrosilicon and residual reducing material, dolomite decomposed to the individual carbonates. A reinterpretation of some of Graf's<sup>11</sup> results indicates that salt could be catalyzing two different decomposition mechanisms.

Our present systematic study was specially designed to investigate the effect of CO<sub>2</sub> and salt on the decomposition of dolomite. In many instances we have obtained EGA, TG, and X-ray diffraction data to help with the explanation of the DTA observations.

## EXPERIMENTAL WORK\*

Dolomite samples from three different sources and National Bureau of Standards dolomite (Reference Material No. 88) were used in this study (see Table I). All were low in alkali salt concentration except one. Also included in this study were a magnesite sample which is a Research Laboratory petrographic standard, and reagent-grade calcite ( $\text{CaCO}_3$ ). All samples were reduced to  $-100$  mesh, so that little if any effect of particle size would be reflected in the results. A special effort was made to eliminate the effect of other variables, such as iron carbonate, when conducting the experiments.

*DTA experimental procedure*

The basic instrument used in this work was an RL Stone Model 12BC<sub>2</sub>. A sample holder similar to a Stone Model SH-11BR2-INZ with platinel differential thermocouples was used. All gas connections in the DTA instrument were fitted with needle valves capable of controlling the gas flow-rate to less than  $1 \text{ ml min}^{-1}$ . The direction of the gas flow was upward past the sample pan and then out at the periphery of the top of the sample-holder cover. To accomplish this the cover of the sample holder was raised 0.4 mm by use of small platinum blocks. This provided a dynamic gas atmosphere for the sample during the DTA programmed heating.

DTA thermograms were recorded in dynamic atmospheres of  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , Ar, and mixtures of  $\text{CO}_2$  and  $\text{O}_2$  all flowing at  $10 \text{ ml min}^{-1}$ .  $\text{Al}_2\text{O}_3$  was used as an inert reference material. Approximately 1 mg of sample was placed on a round, flat 6-mm-diameter platinum dish. The small sample, dynamic atmosphere, raised lid, and high recording sensitivity ( $0.17^\circ\text{C in.}^{-1}$ ) caused some difficulty in maintaining and reproducing a good baseline, but this was tolerated because of the primary desire to rapidly evolve  $\text{CO}_2$  from the sample area during the DTA determination.

The reference temperature for the change of quartz crystal structure in these experiments was nominally  $590^\circ\text{C}$ , in contrast to  $577^\circ\text{C}$  for the NBS standard, which indicates that the endothermic peaks are about  $15^\circ\text{C}$  high. This agreement was considered satisfactory because the high heating rate, fast dynamic gas flows, and raised sample holder cover would tend to produce small variations in the temperature range over which endotherms are observed. No claims are made for the temperature accuracy of the endotherms, but the difference in temperature of two endotherms being compared is significant and reproducible.

Ultrapure  $\text{O}_2$  and  $\text{N}_2$  and regular-grade  $\text{CO}_2$  and argon were used in these experiments. All samples were purged for 1 h in the sample holder with the atmospheric gas flow-rate at  $40 \text{ ml min}^{-1}$  before the programmed heating at  $10^\circ\text{C min}^{-1}$ . From the volume of the sample holder, the weight of the sample, the rate of decomposi-

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\*It is understood that the material in this paper is intended for general information only and should not be used in relation to any specific application without independent examination and verification of its applicability and suitability by professionally qualified personnel. Those making use thereof or relying thereon assume all risk and liability arising from such use or reliance.

TABLE 1  
COMPOSITION OF DOLOMITE SAMPLES

Sample	Description	X-ray and microscopic data	Composition (%)											
			CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe	Na <sub>2</sub> O	K <sub>2</sub> O	Soluble Na	Soluble K	Soluble Ca	Soluble Mg	Soluble Cl
A	Low salt	Dolomite	NA*	NA	NA	NA	NA	0.01	0.16	0.002	0.011	0.063	0.032	0.046
B	Low salt	Dolomite plus small amount quartz	29.92	21.30	1.65	0.36	0.67	0.01	0.05	0.002	0.004	0.063	0.026	0.007
C	Low salt	Dolomite plus small amount quartz	NA	NA	NA	NA	NA	0.02	0.02	0.003	0.005	0.075	0.042	0.018
D	Salt-bearing	Dolomite	28.96	20.32	0.55	0.15	0.92	0.04	0.05	0.020	0.003	0.11	0.060	0.15
88	National Bureau of Standards	NA	30.49	21.48	0.31	0.07	0.06	0.08	0.03	NA	NA	NA	NA	NA

\* NA = not analyzed.

tion, and the rate of gas flow, it was estimated that the peak  $\text{CO}_2$  pressure in the dynamic  $\text{O}_2$  was 5 to 10 torr.

#### *EGA experimental procedures*

In the Stone apparatus mentioned earlier, the furnace platform, gas-analysis system, gas controls, and sample holder were replaced with equipment built at the Research Laboratory. The sample holder has been described in a previous publication<sup>32</sup>, and was designed to facilitate measurement of the small amounts of gas evolved when milligram quantities of sample are used. A furnace was modified by drilling a 25-mm hole through the top to fit the gas exit train of the sample holder. A dynamic gas flow of  $3 \text{ ml min}^{-1}$  of ultrapure  $\text{O}_2$  was used.

The thermal conductivity of the evolved  $\text{CO}_2$  was monitored by use of a Gow-Mac constant-temperature thermal-conductivity cell and recorder with a sensitivity of  $0.1 \text{ mV in.}^{-1}$ . The response of the thermal-conductivity detector was calculated to be  $23 \mu\text{g}$  of  $\text{CO}_2$  per  $\text{cm}^2$  of peak area when the power supply was set at 16, bridge current at 6 mA, and the gas flow at  $3 \text{ ml min}^{-1}$ .  $\text{CaCO}_3$  was used to calibrate the EGA response. From the observed rate of decomposition, the volume of the sample compartment, a gas flow of  $3 \text{ ml min}^{-1}$ , and the use of a 1-mg sample, it was estimated that the peak partial pressure of  $\text{CO}_2$  was between 50 and 100 torr at the instant of most rapid carbonate decomposition.

As in the DTA determination, the apparatus was purged for 1 h with the atmosphere gas at  $40 \text{ ml min}^{-1}$  before the gas flow was adjusted and the programmed heating at  $10^\circ\text{C min}^{-1}$  was started. EGA temperatures are approximately 70 degrees higher than DTA temperatures because of the time elapsed while the evolved gas travels from the sample compartment to the thermal-conductivity detector. With these experimental conditions, the endotherm for the crystal change of quartz occurs at  $590^\circ\text{C}$  on the DTA scale.

#### *X-ray diffraction studies*

To help in determining the reaction and reaction mechanism, normal and salt-bearing dolomite samples were heated in the same atmospheric gas and at the same heating rate to a temperature just below the temperature at which an endotherm was observed. After reaching the desired temperature, the samples were quickly cooled by turning off the power and removing the furnace or by directing a stream of cold air inside the furnace toward the sample holder. In a similar manner, other samples were heated to a temperature at which the endotherm was recorded, and then the samples were cooled. All samples were then examined by conventional X-ray diffraction methods.

#### *Concentrating salt and removing salt from or adding salt to dolomite*

To better observe the effect of salt on the decomposition of dolomites, 2 g each of a salt-bearing and a low-salt dolomite were stirred in 100 ml of distilled water for 1/2 h. After the coarse particles were allowed to settle for 10 min, the suspended fines

and water were decanted and evaporated to dryness, yielding about 0.1 g of fines in each case. The concentrated salt-bearing sample that initially contained about 0.05% leachable salt now contained about 1% salt by virtue of this concentration step. However, because some of the salt remained on the sides of the evaporating dish and because the salt was present externally on the dolomite rather than being crystallized within the dolomite crystal, it is estimated that the resulting sample was equivalent to a salt-bearing dolomite containing 0.20 to 0.50% NaCl.

To remove salt from the sample, the dolomite was stirred in 100 ml of distilled water for 1/2 h. After the coarse particles were allowed to settle for 10 min, the suspended fines and water were decanted from the coarse particles. The suspension was then filtered to remove the water containing the salt, and the fines were dried for thermal analysis.

Salt was added to normal dolomite samples by stirring 2 g of the dolomite with 100 ml of water containing 1 to 3 mg of NaCl and evaporating this mixture to dryness.

## RESULTS AND DISCUSSION

### *Effect of CO<sub>2</sub> pressure on the mechanism of decomposition*

Curve I of Fig. 1 resembles that most often found in the literature. Endotherm peaks appear at 775 and 870°C. However, this curve represents a special case in which an initial partial pressure of CO<sub>2</sub> of 300 torr or greater exists or is quickly attained, and a partial pressure of 700 torr or more of CO<sub>2</sub> is present by the time calcite is decomposed. Even when air is used, a CO<sub>2</sub> pressure of 300 torr or more is attained with large samples and static atmospheres. In static atmospheres of CO<sub>2</sub>, the decomposition of calcite often occurs at a temperature higher than 870°C, because the pressure of CO<sub>2</sub> exceeds 760 torr and decomposition of calcite is very dependent on the pressure of CO<sub>2</sub>.

A calculation shows that the partial pressure of CO<sub>2</sub> in the sample holder in our apparatus as a result of the decomposition of 1 mg of dolomite is approximately 5 torr. This estimate is based on using a sample holder with a volume of 17.5 ml, using a dynamic gas flow of 10 ml min<sup>-1</sup>, and assuming that the total gas pressure within the sample holder is the same as atmospheric pressure outside the sample holder (730 torr). Therefore, the partial pressure of CO<sub>2</sub> for curve I and subsequent curves in Fig. 1 is essentially the partial pressure of CO<sub>2</sub> in the dynamic gas.

Figure 1 shows that the low-temperature endotherm is indeed sensitive to the partial pressure of CO<sub>2</sub>. This endotherm is present only when dolomite is heated under a CO<sub>2</sub> pressure of at least 200 torr. It is well established that this endotherm is associated with the formation of MgO from partial decomposition of the dolomite. To confirm this, 1 mg of sample was heated to 800°C at 730 torr CO<sub>2</sub> and then quickly cooled; the resultant sample was examined by X-ray diffraction. Patterns for MgO, calcite, and a trace of dolomite were found. It is significant that dolomite was identified, even after heating through the lower temperature endotherm, because

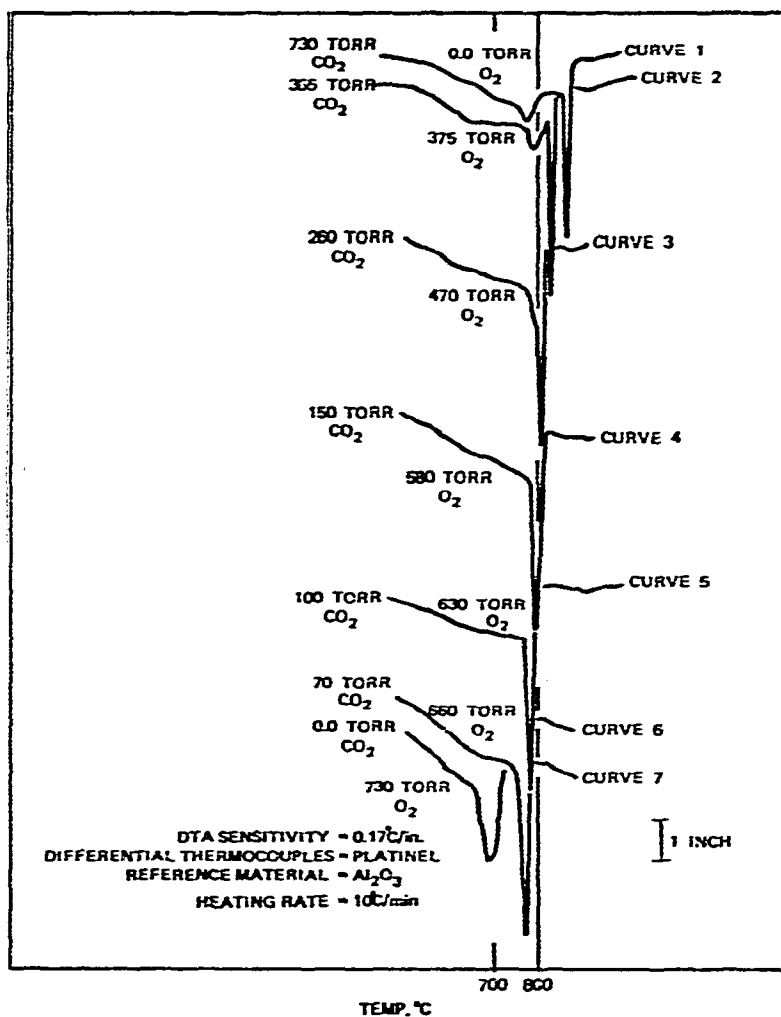


Fig. 1. Effect of partial pressure of CO<sub>2</sub> on decomposition of 1 mg NBS No. 88 standard dolomite.

this tends to confirm that some sort of solid-state rearrangement is the mechanism by which the production of MgO and calcite takes place, rather than decomposition to individual carbonates. Haul and co-workers<sup>4,5,15,16</sup>, in detailed studies with single crystals of dolomite, have stated that the endotherm at 775°C is due to the formation of MgO and also to diffusion in the lattice and direct formation of calcite from dolomite; these results are in agreement with his conclusion.

Esin et al.<sup>27</sup> have proposed that the first step in the lattice rearrangement takes place at the surface of the crystal where carbonate forms CO<sub>2</sub> and oxide ion. When calcite decomposes, as in the case for the high-temperature (870°C) endotherm in curve 1 of Fig. 1, the decomposition temperature is very dependent on CO<sub>2</sub> pressure. Decreasing the CO<sub>2</sub> pressure causes a decrease in decomposition temperature (curve 2 versus curve 1). However, curves 1, 2, and 3 of Fig. 1 show that decreasing the CO<sub>2</sub> pressure has the opposite effect on the low-temperature endotherm (775°C)



which is associated with the decomposition to  $\text{MgO}$  and  $\text{CaCO}_3$ . As the pressure of  $\text{CO}_2$  is decreased, the endotherm occurs at a higher temperature, indicating that the mechanism is complex and not a straightforward decomposition. Garn<sup>26</sup> proposed that at around 700 torr  $\text{CO}_2$  another reaction involving the exchange of  $\text{CO}_2$  between the sample and the atmosphere predominated as the reaction mechanism. (At a lower pressure of  $\text{CO}_2$ , a reaction mechanism similar to that of calcite predominates.)

Studies<sup>13</sup> of  $\text{CO}_2$  have shown that there is such an exchange for both dolomite and calcite<sup>33</sup>. Assuming this reaction path, higher pressures of  $\text{CO}_2$  would bring about decomposition of dolomite to  $\text{MgO}$  and  $\text{CaCO}_3$  at a lower temperature because more exchange takes place. This would be particularly true if recombination of  $\text{MgO}$  was not possible, as shown in Fig. 2. Figure 2 shows that  $\text{CaO}$  can be easily recombined with  $\text{CO}_2$  at temperatures below the decomposition temperature, whereas  $\text{MgO}$  shows very little recombination even when cooled to room temperature in  $\text{CO}_2$  and reheated in  $\text{CO}_2$ .

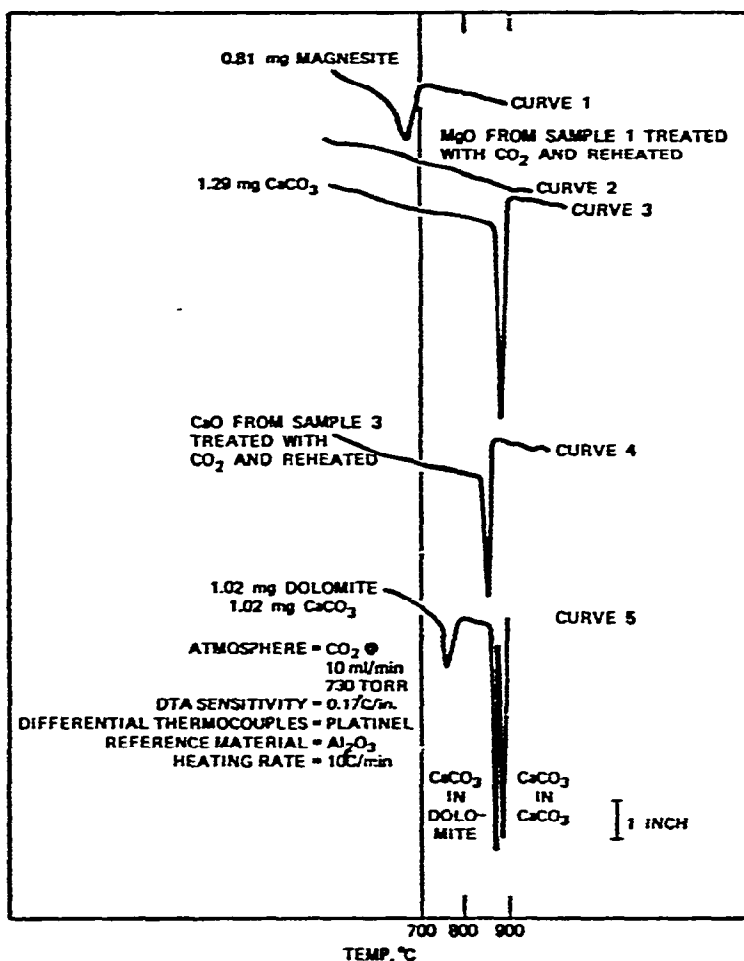


Fig. 2. Comparison of decomposition of recombined  $\text{MgO}$  and  $\text{CaO}$  with decomposition of calcite and magnesite.

If the initial reaction is decomposition of  $\text{CO}_3^{2-}$  to  $\text{CO}_2$  and oxide, then the next step should be the formation of  $\text{MgO}$ . It is generally agreed, from X-ray diffraction data, that there is a solid-state diffusion rearrangement of calcium and magnesium in this step. The calcium can then recombine with  $\text{CO}_2$  unless the partial pressure of  $\text{CO}_2$  is so low that calcite is not stable at the temperature being considered.

Curves 3 and 4 of Fig. 2 also show that when  $\text{CaCO}_3$  is decomposed and then allowed to recombine with  $\text{CO}_2$ , the recombined material decomposes at a lower temperature than the original material. This may be because the recombined material is finer, or has more defect structures, or both. Curve 5 in Fig. 2 shows that the calcite produced in the decomposition of dolomite also decomposes at a lower temperature than pure  $\text{CaCO}_3$ . This may also be caused by the recombining of  $\text{CO}_2$

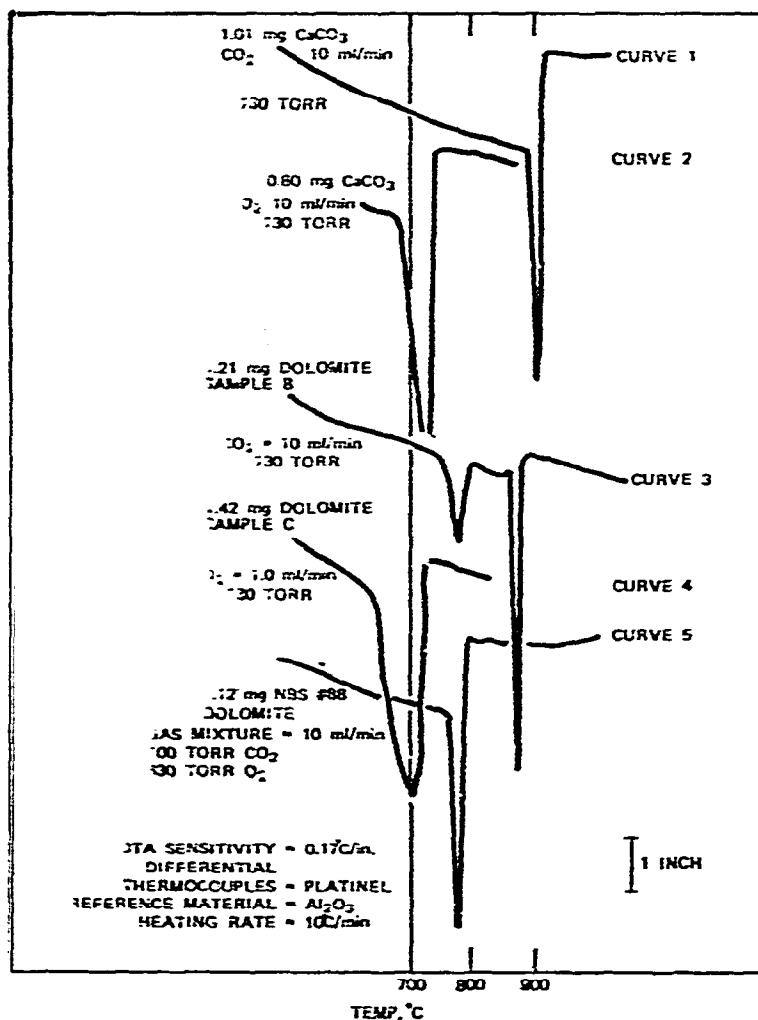


Fig. 3. Comparison of thermograms for decomposition of dolomite and  $\text{CaCO}_3$  and  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{O}_2$ - $\text{CO}_2$ .

and CaO to produce calcite from dolomite, thus producing very fine  $\text{CaCO}_3$  or defect structures.

Curves 4 and 5 of Fig. 1 show that when the partial pressure of  $\text{CO}_2$  is reduced to 150 torr or less, the first and second endotherms merge into one. Curves 2 and 4 in Fig. 3 show that the single endotherm of dolomite very much resembles the single endotherm for calcite at 0 torr  $\text{CO}_2$ . Looking at curves 4 and 5 of Fig. 1, it is impossible to determine whether the initial decomposition takes place at the magnesium bond. If we assume that the initial step involves formation of  $\text{CO}_2$  and oxide ion (and we know that the calcite crystal is not stable at this temperature and pressure of  $\text{CO}_2$ ), then the rate-controlling steps may be a formation of CaO or a simultaneous indiscriminate formation of CaO and MgO rather than preferential formation of MgO. Whatever the mechanism, the results show that the reaction is very fast, and not stepwise.

Curves 4, 5, 6, and 7 in Fig. 1 are in agreement with some TG publications describing dolomite decomposition as a one-step reaction. When the  $\text{CO}_2$  pressure during decomposition of dolomite is decreased to 100 torr or less, there is a change in the reaction rate which is observable in curves 6 and 7 of Fig. 1 as a broadening

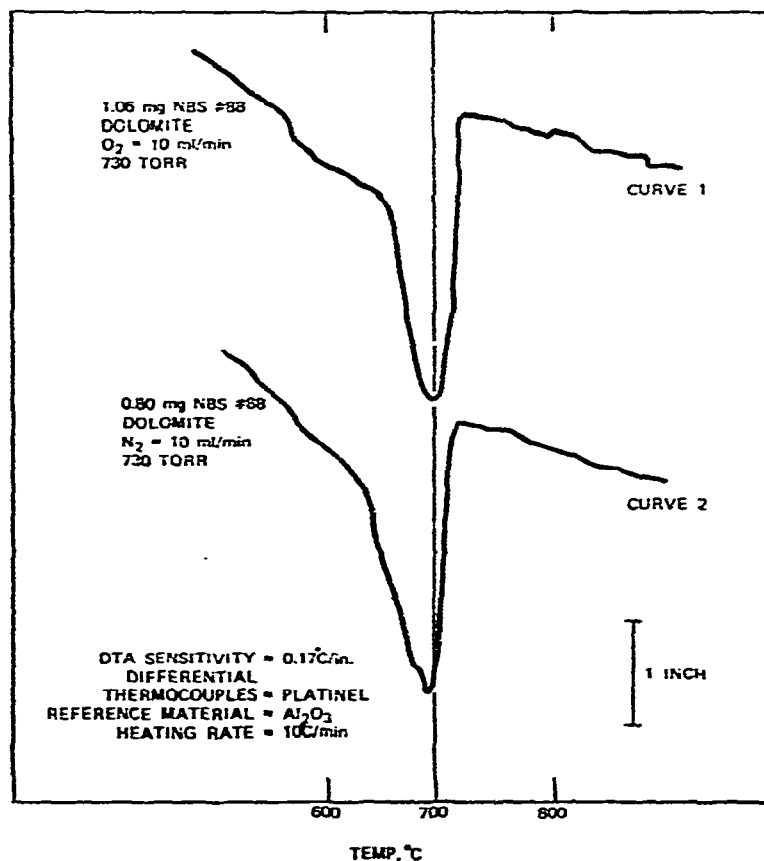


Fig. 4. Decomposition of dolomite in oxygen and nitrogen.

of the decomposition-temperature range. In curve 6, the temperature at which the start of decomposition is detected is 25 degrees lower than in curve 5. Also, the shape of the curve at the temperature at which decomposition commences (750°C) is different in the two curves, indicating that the initial reaction rate has decreased. This may or may not mean that the rate-controlling step in the reaction is once again the formation of MgO, but curve 7 would seem to support this premise.

Curve 7 in Fig. 1 and curves 2 and 4 in Fig. 3 show that the decomposition temperature of dolomite in 10 ml min<sup>-1</sup> oxygen is slightly lower than that for calcite, and the broader temperature range for the decomposition of dolomite indicates a slower rate of decomposition. This appears to indicate that the formation of CaO is no longer a rate-controlling factor. A shoulder was observed in the curves for the decomposition of some dolomites in oxygen, which might indicate preferential decomposition of the magnesium portion of the dolomite. Reducing the heating rate to 2°C min<sup>-1</sup> did not result in the resolution of a separate peak, but did show that dolomite would decompose at a lower temperature (640°C) if enough time elapsed.

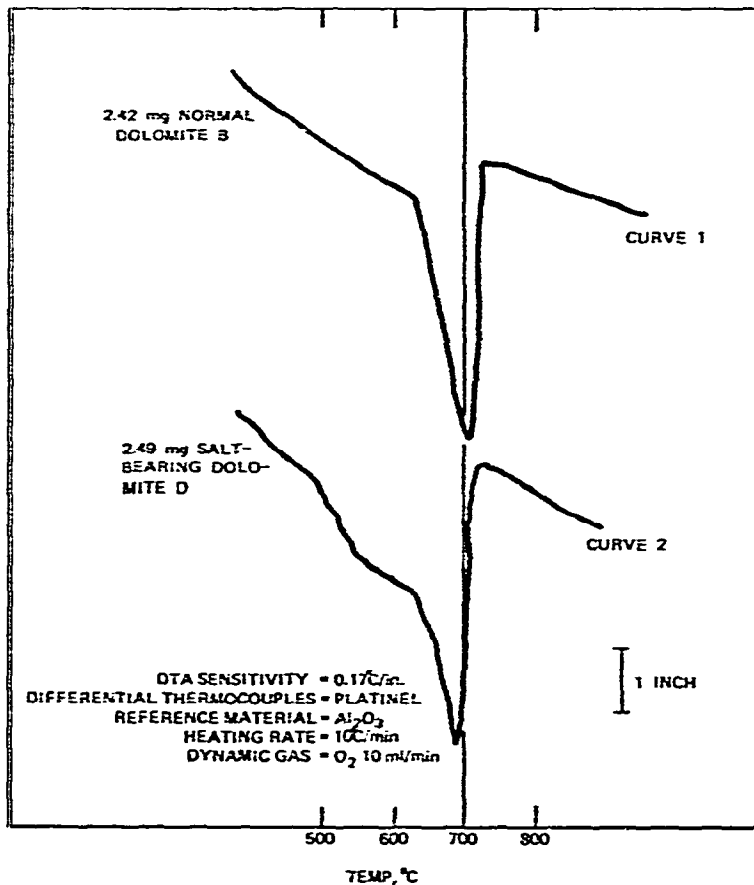


Fig. 5. Thermograms of normal and salt-bearing dolomites.

The results shown in Fig. 1, curve 7, and Fig. 3, curve 4, show that if the partial pressure of  $\text{CO}_2$  is 5 torr or less, then the temperature at which dolomite decomposes in a DTA apparatus is the same as that determined by TG, X-ray, separated isotope, and other methods. This also shows that some of the published DTA data are inaccurate because of inadequate instrumentation and/or faulty experimental procedure. It is particularly important to realize that past decomposition data, stated to have been obtained in static air, really were obtained at some unknown pressure of  $\text{CO}_2$ .

Finally, to check the influence of the oxygen partial pressure, we obtained some differential thermal analysis data in flowing nitrogen and argon. An example is shown in Fig. 4, which compares dolomite decomposition in dynamic oxygen and dynamic nitrogen. This is the largest difference in temperature of the peaks found among the six determinations in argon and nitrogen. The decomposition temperature in nitrogen is between that obtained by Müller-Vonmoos and Bach<sup>16</sup> in vacuum and the value we obtained in oxygen. Müller-Vonmoos and Bach<sup>16</sup> showed that dolomite gave a single decomposition peak at 779°C in nitrogen, which indicates that their use of a 40-mg sample resulted in some partial pressure of  $\text{CO}_2$  in the sample compartment even though they used a nitrogen flow of 33 ml min<sup>-1</sup>.

#### *Effect of alkali chloride on the mechanism of decomposition*

Figure 5 shows the difference in the curves obtained in oxygen for a salt-bearing and a normal dolomite with similar amounts of other impurities. From the water-leachable and total alkali and chloride contents of the sample, the NaCl content of the dolomite sample having the abnormal curve is estimated to be 0.05 to 0.06%. It is certainly less than 0.10%; some  $\text{CaCl}_2$  and  $\text{MgCl}_2$  are also present. Part of the salt content of the dolomite can be leached in water after the sample has been ground to -100 to +200 mesh. Not all the alkali salt can be separated in this manner because some is held within the dolomite crystal.

Figure 6 is the EGA recording of the evolution of  $\text{CO}_2$  from normal and salt-bearing dolomites. This EGA response confirms that the abnormalities in the curve of the salt-bearing dolomite are associated with the evolution of  $\text{CO}_2$  and the decomposition of this material at a temperature lower than normal. The peak endotherm for the decomposition of salt-bearing dolomite also occurs at a lower temperature (Fig. 5) and over a broader temperature range (Figs. 5 and 6) than for normal dolomite. The difference in temperatures of the peaks in Figs. 5 and 6 represents the time necessary for  $\text{CO}_2$  to travel from the sample holder to the EGA detector.

As the concentration of salt is increased, the abnormalities in the curve become more apparent, as shown in curve 2 of Fig. 7. The main endothermic peak is shifted downward to 675°C. According to X-ray diffraction determinations, this represents the decomposition of calcite rather than dolomite, and it therefore means a lowering of the temperature for calcite decomposition by approximately 50 degrees. X-ray results show that some decomposition has occurred at 500°C, and the peak at 550°C represents the formation of MgO and calcite from dolomite.

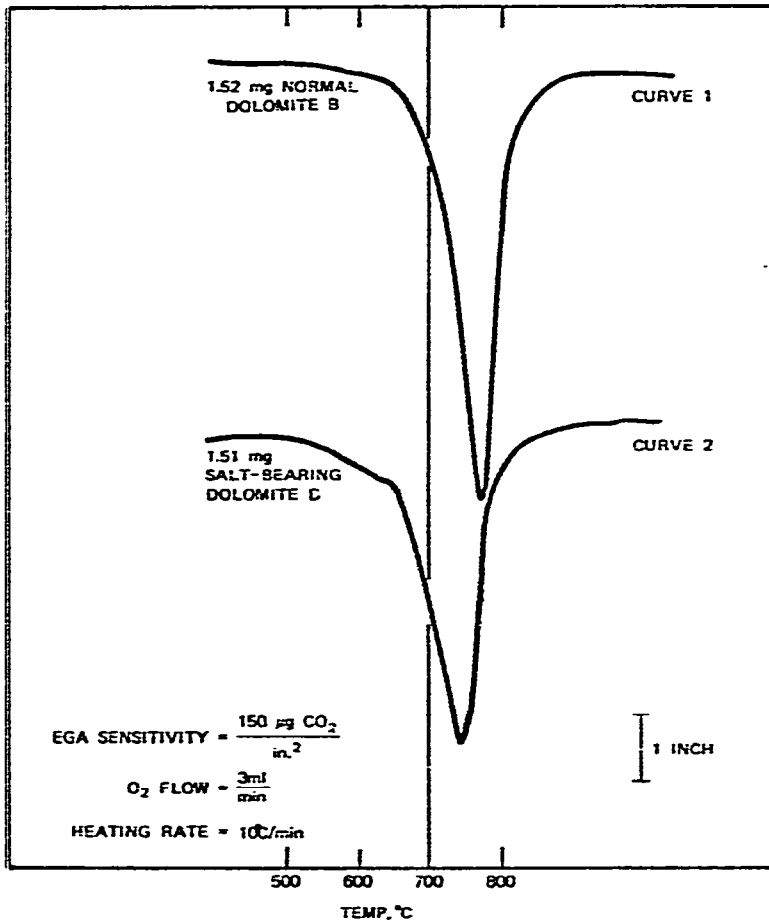


Fig. 6. Comparison of EGA response of normal and salt-bearing dolomites.

The first peak of curve 2 of Fig. 7 occurs at a temperature lower than that for the decomposition of magnesite (curve 5 of Fig. 7). It is known that salt lowers the decomposition temperature of magnesite, and the difference in salt content could account for the difference in temperature between the peaks. Although high concentrations of salt may produce magnesite in a separate step in the decomposition, it seems that rearrangement of the calcium and magnesium ions is more likely when there is only a small amount of salt. More reasons for favoring this explanation will be shown in later curves of salt-bearing dolomites in a CO<sub>2</sub> atmosphere. However, with a salt-bearing dolomite there is preferential formation of MgO when the dolomite is heated in either dynamic oxygen or dynamic CO<sub>2</sub>, and the difference in thermal response of normal and salt-bearing dolomites is due to a shifting of the temperature of formation of MgO. Therefore the presence of salt may be causing the same effect as increasing the CO<sub>2</sub> partial pressure, but to a larger extent.

Curves 3 and 4 of Fig. 7 represent the results obtained after reducing the salt content of a salt-bearing dolomite. Both curves are nearly normal DTA responses

and demonstrate that the abnormal DTA responses result from the effect of salt on the thermal decomposition of dolomite. Curve 3 of Fig. 7 was obtained by leaching a salt-bearing dolomite in water, discarding the leachings, and evaporating to dryness after addition of the leachings from a normal dolomite. Curve 4 of Fig. 7 was obtained after washing the salt-bearing dolomite, discarding the washings, and drying the dolomite.

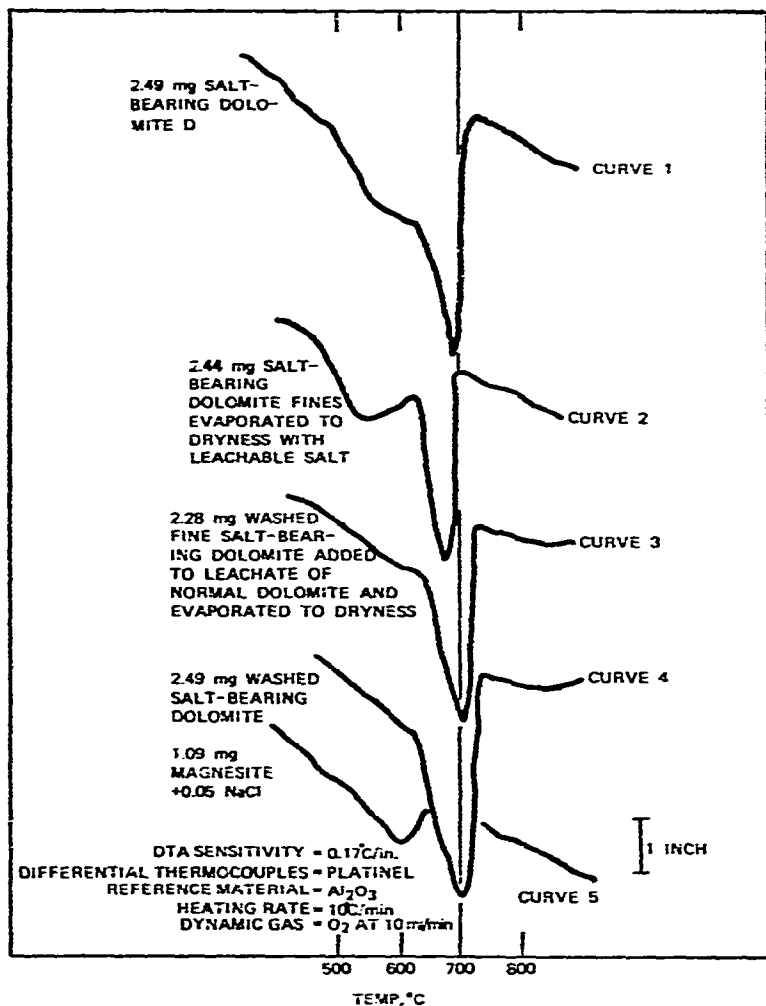


Fig. 7. Effect of enriching and removing salt from a salt-bearing dolomite.

Figure 8 is almost the opposite of Fig. 7 in that salt has been added to a normal dolomite to produce abnormal curves like those obtained for salt-bearing dolomites. Curve 2 of Fig. 8 shows that adding the leachable salt from a normal dolomite to the suspended fines caused only a very slight abnormality. To obtain curve 3, the addition was made by adding leachings from a salt-bearing dolomite and to obtain curve 4 by adding a salt solution. The first endotherm of curve 3 matches that for magnesite

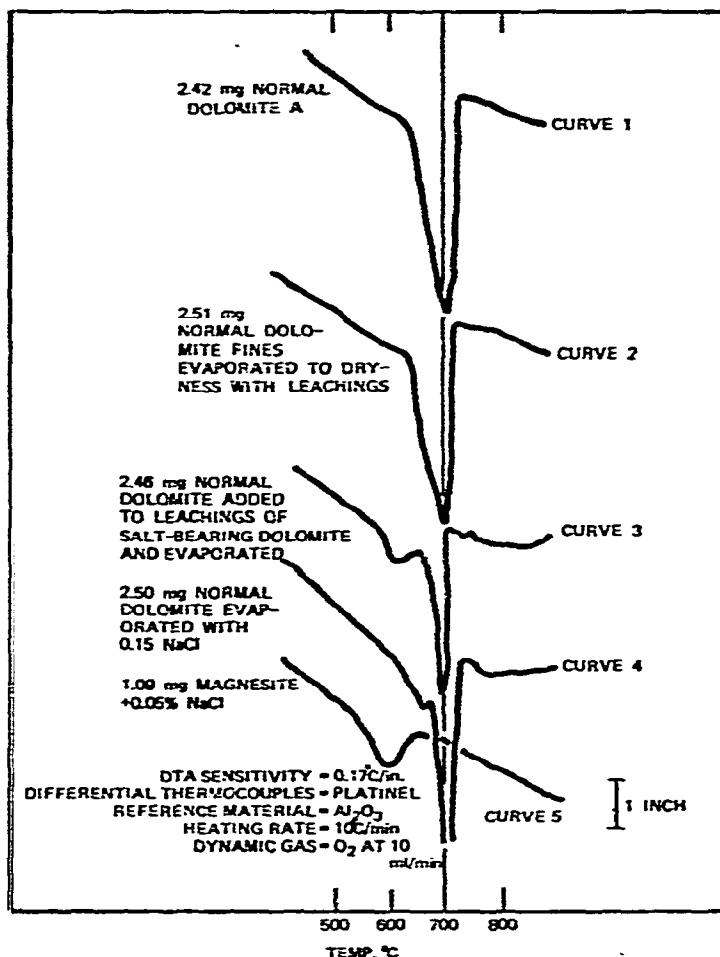


Fig. 8. Effect of adding salt to a normal dolomite.

in curve 5, but the first endotherm in curve 4 does not match this. Similarly, the data obtained on salt-bearing dolomites are difficult to reproduce. EGA results also confirm this observation because they are not reproducible during the first stages of evolution of  $\text{CO}_2$ . As an example, in Fig. 9 several peaks are recorded for the evolution of  $\text{CO}_2$  between 500 and 700°C, which could mean that MgO is formed by more than one reaction mechanism.

The effect of NaCl on the curve obtained in  $\text{CO}_2$  (Figs. 10 and 11) is much more spectacular than the effect on the curve obtained in  $\text{O}_2$  because the temperature of the first endotherm may be lowered 200 degrees or the first endotherm may not appear at all. This endotherm is associated with the formation of MgO and shows that regardless of the atmosphere, the effect of salt is to preferentially form MgO from dolomite at a temperature at which the remaining calcite does not decompose. The disappearance of the peak seems to agree with Garn's theory<sup>26</sup> that the activation



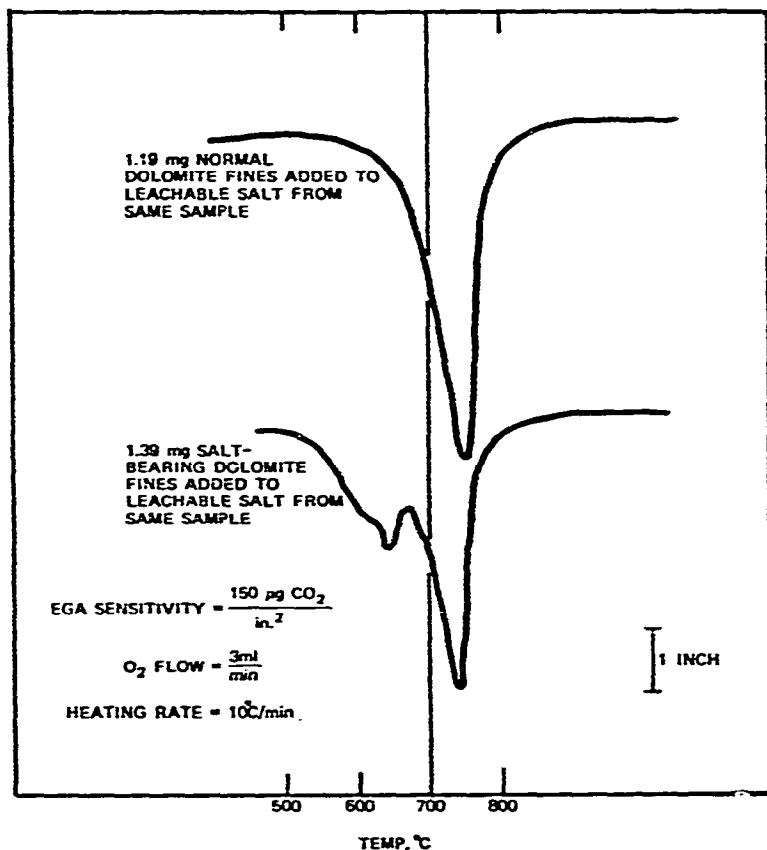


Fig. 9. Comparison of EGA response of salt-concentrated samples of normal and salt-bearing dolomites.

energy for the decomposition is reduced because salt distorts the lattice. The temperatures at which the MgO was formed coincide in some instances for both CO<sub>2</sub> and O<sub>2</sub> atmospheres.

Figure 12, which is a weight-loss curve (TG) for the heating of a salt-bearing dolomite fine plus leachable salt in CO<sub>2</sub>, confirms that decomposition of dolomite occurs as a stepwise process in the presence of salt. The weight loss between 500 and 630°C is exactly what would be expected if all the MgCO<sub>3</sub> in the dolomite were converted to MgO. X-ray diffraction results also confirm that decomposition in either O<sub>2</sub> or CO<sub>2</sub> starts at 500°C, and only calcite and MgO are identified at 650°C in O<sub>2</sub> and at 700°C in CO<sub>2</sub>. The results shown in Fig. 11 also show that NaCl seems to reduce the amount of energy needed to decompose calcite because the 870°C endotherm is smaller. This indicates that salt distorts the calcite lattice and lowers the activation energy needed for decomposition to occur. NaCl does not appear to cause calcite to decompose at a lower temperature in CO<sub>2</sub>, but it does in oxygen.

Figure 13 is made up of three selected curves arranged in increasing concentration of salt (0.02 to 0.25%). These were chosen for several reasons. First, they all

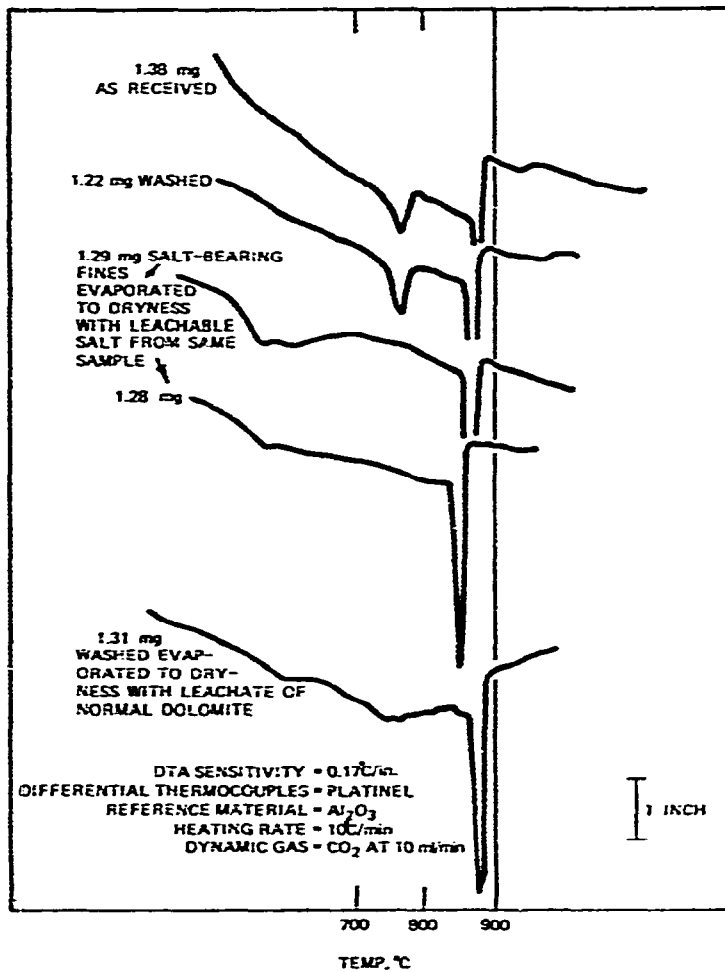


Fig. 10. Effect of increasing and decreasing salt on thermogram of salt-bearing dolomite.

have a small endotherm at 580 or 590°C, which seems to appear on many curves as soon as there is a reduction in the size of the endotherm at 780°C. The endotherm at 580 or 590°C is assumed to be caused by the presence of salt. Second, they also show that as the amount of salt is increased the original 780°C endotherm for the decomposition of dolomite in CO<sub>2</sub> atmosphere occurs at a lower temperature. Third, when the salt concentration is high enough, the original 780°C endotherm is shifted and sometimes coincides with the small endotherm at 580°C. Fourth, the curve for the highest salt content coincides with the data shown in the EGA results in Fig. 9. EGA peaks appear on top of EGA peaks, as is the case with the thermal peaks of the DTA in Fig. 13.

Similar work has been published by Graf<sup>12</sup>, including two endotherms merging into a single response, but no CO<sub>2</sub> pressures, O<sub>2</sub> pressures, or EGA results were correlated with the DTA data. On the basis of these observations, there may be two mechanisms for the decomposition of dolomite in the presence of salt. The known

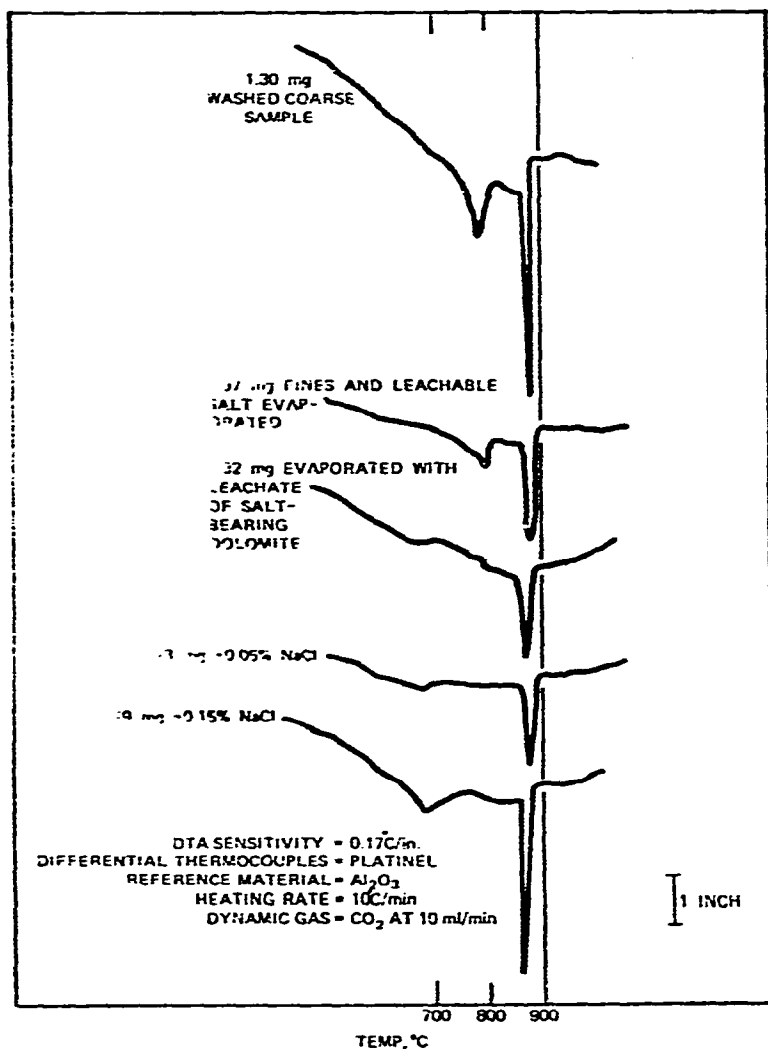


Fig. 11. Effect of increasing salt on thermogram of normal dolomite.

mechanism involves solid-state rearrangement of calcium and magnesium ions to form calcite and MgO. A second mechanism may be the formation of small amounts of magnesite and calcite before formation of MgO, but this has not been detected by X-ray diffraction.

#### CONCLUSION

The decomposition of dolomite has been systematically investigated by using instrumentation and experimental procedures specifically designed to elicit information on the effect of CO<sub>2</sub> pressure and salt concentration. It has been shown that much of the information obtained in the past by thermal analysis has not described

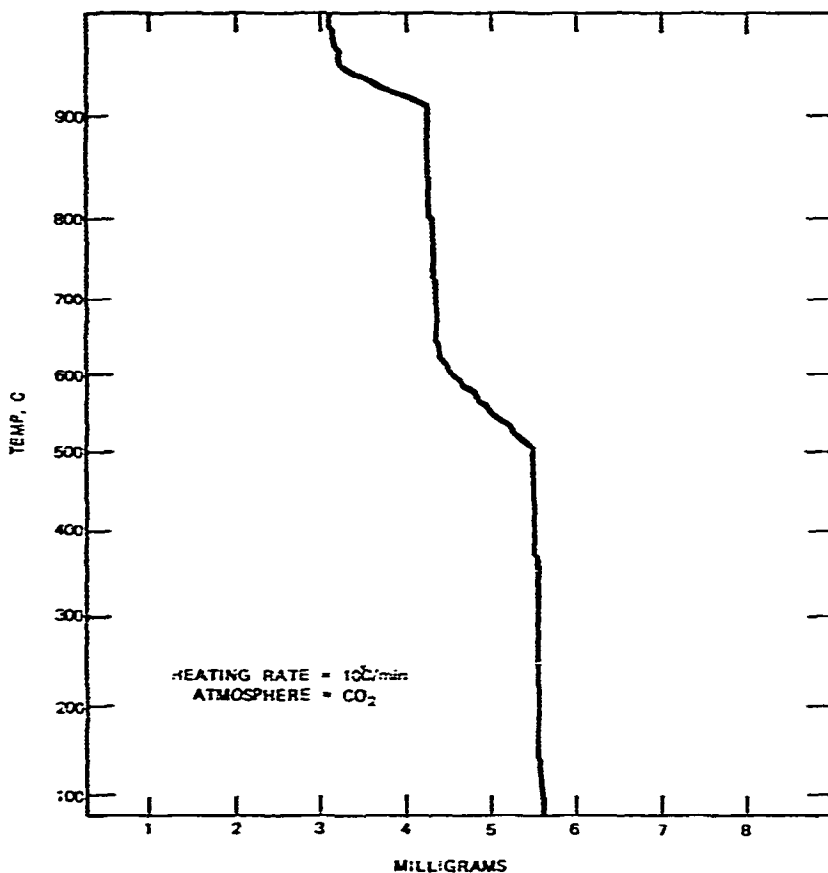


Fig. 12. Decomposition of salt-bearing dolomite evaporated with leachable salt.

the reaction mechanism and reaction rates correctly because of poor instrumental design and failure to consider and control partial pressure of  $\text{CO}_2$  and/or the salt content of the dolomite sample.

This latest work shows that there are several rate-controlling mechanisms or conditions which are independent of the instrument design, and they determine the type of curve which will be observed for dolomite. These are:

1. A two-step decomposition at high  $\text{CO}_2$  pressure in which the first step involves crystalline rearrangement and formation of  $\text{MgO}$  and calcite.

2. A two-step decomposition at high  $\text{CO}_2$  pressure in which the first step involves exchange of  $\text{CO}_2$  between the atmosphere and dolomite and results in the formation of  $\text{MgO}$  and calcite.

3. A rapid one-step decomposition of dolomite to  $\text{CaO}$  and  $\text{MgO}$  at  $\text{CO}_2$  pressures of less than 200 torr.

4. A slow one-step decomposition of dolomite to  $\text{CaO}$  and  $\text{MgO}$  at very low  $\text{CO}_2$  pressures, in which the decomposition of the magnesium carbonate part of the crystal may be the rate-controlling step.

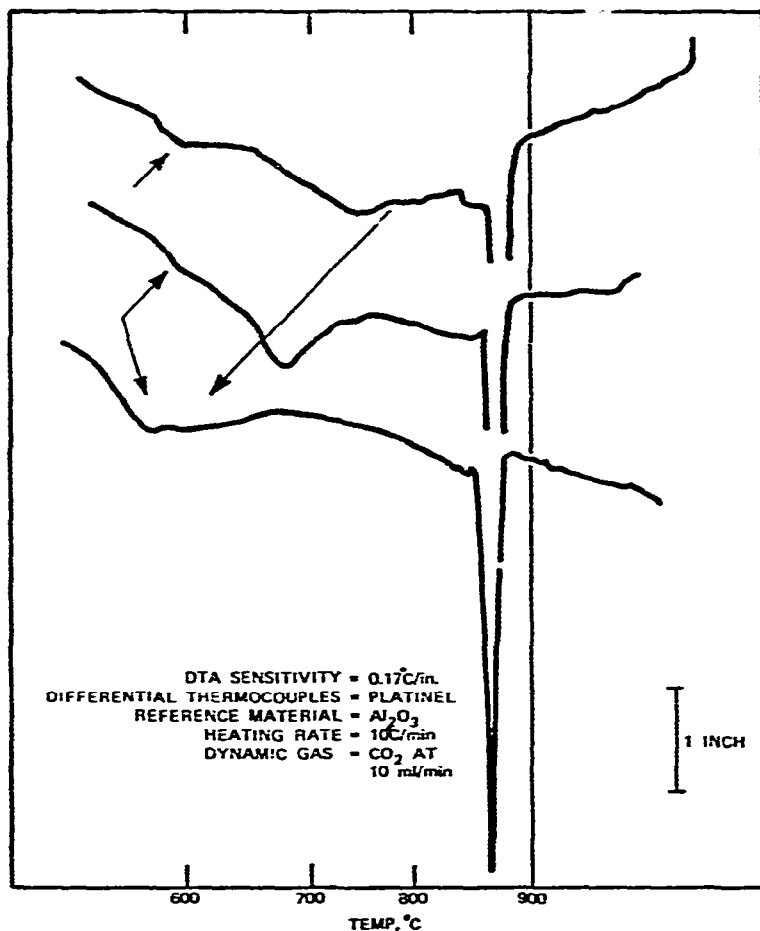


Fig. 13. Effect of increasing salt concentration on formation of MgO from dolomite.

5. A possible decomposition to magnesite and calcite formed by catalytic action of high concentrations of alkali chloride in the dolomite.

In contradiction to most published information, the normal decomposition of a dolomite involves the simultaneous formation of CaO and MgO. No stepwise decomposition is detectable, and the rate-controlling step at some partial pressures of  $CO_2$  may be the decomposition of the  $CaCO_3$  portion of the dolomite crystal rather than formation of MgO as is usually stated.

The commonly published curve showing two endotherms and a stepwise decomposition of dolomite is really a special condition of decomposition in which the partial pressure of  $CO_2$  is greater than 200 torr inside and/or around the dolomite sample. The removal of  $CO_2$ , which is attendant with the solid-state rearrangement of Ca and Mg, occurs with two different mechanisms. The amount of MgO formed by a particular mechanism and the peak temperature of the endotherm are dependent on the  $CO_2$  pressure. Even though most published literature says that the first

endothrm is not sensitive to CO<sub>2</sub> pressure and the second endotherm is, the present experiments prove that both endotherms are sensitive to CO<sub>2</sub> pressure but in opposite ways.

Salt in the dolomite causes early formation of MgO by catalyzing the rearrangement of calcium and magnesium ions regardless of the atmosphere in the sample holder. There is also some evidence that salt catalyzes a second decomposition mechanism involving the intermediate formation of magnesite and calcite, but this has not been proven.

Finally, it was observed that the presence of salt also lowered the decomposition temperature of magnesite and calcite in an oxygen atmosphere.

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