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DOLOMITE FOR DETERMINING ATMOSPHERE CONTROL IN THERMAL ANALYSIS*

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ABSTRACT

A generally applicable test using dolomite to detect effects of atmosphere self-generation and to determine atmosphere control in thermal analysis is demonstrated. Either differential thermal analysis (DTA) or thermogravimetry (TG) can be used. In a CO_2 atmosphere dolomite produces two separate thermal decompositions, but in a CO_2-free atmosphere dolomite decomposes in a single reaction. If two peaks or a shoulder appear on the decomposition response in air, effects of self-generated CO_2 are proven. If the reaction in air is not complete by 800°C, self-generated CO_2 around the sample is strongly indicated. The dolomite decomposition at lower temperature in CO_2, essentially independent of CO_2 pressure, can be used to establish a temperature reference point for this atmosphere testing. Thin layers of sample and a gas stream flowing over the sample are shown to be necessary for atmosphere control in thermal analysis.

INTRODUCTION

Chemical equilibrium requires that product gases around a reacting sample influence the progress of its thermal decomposition in thermal analysis[1]. This fact was recognized early in the development of thermal analysis, and specification of the atmosphere over a sample has long been recommended in reporting thermal analysis data. However, obtaining the specified atmosphere is rarely achieved because product gases from the sample create their own atmosphere around the sample. In thermal analysis literature many results given with specified atmospheres conceal the effects of atmosphere self-generation (see refs. 2 and 3, for example). Efficient product gas removal is essential to atmosphere control in thermal analysis, but no generally useful means for detecting or determining such atmosphere effects has been available. How-

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ever, from studies of the thermal behavior of carbonate minerals in Green River Formation oil shale, we found that dolomite ($MgCO_3 \cdot CaCO_3$) can perform this function. This paper describes the use of a National Bureau of Standards dolomite sample to define for most thermal analysis equipment whether product gases can be removed adequately and whether atmosphere control can be achieved.

THERMAL ANALYSIS BACKGROUND

Rowland and Lewis[2] evaluated the influence of a product gas atmosphere on the progress of a gas-producing reaction as follows, using calcite as an example:

> "When calcite is heated in air in the differential thermal apparatus, its dissociation begins to be registered at about 650°C and the reaction progressively becomes more vigorous until a peak is reached at about 925°C. When the reaction starts, the CO_2 content of the air surrounding the $CaCO_3$ is very low but progressively increases as CO_2 is evolved from the sample. If the furnace is filled with CO_2 at approximately one atmosphere pressure, the reaction does not begin until a temperature of 925°C is reached, whereupon it proceeds vigorously until completion.
>
> These phenomena may be interpreted in terms of the basic thermodynamics of the calcium carbonate–calcium oxide–carbon dioxide system. For the reaction:
>
> $$CaCO_3 \rightleftharpoons CaO + CO_2$$
>
> the equilibrium constant may be written as
>
> $$K_P = \frac{P_{CO_2} \times P_{CaO}}{P_{CaCO_3}}$$
>
> Since the partial pressure of the solid phase is constant, this can be written as
>
> $$K_P = P_{CO_2}.$$
>
> The equilibrium constant at a given temperature is determined only by a function of the partial pressure of the carbon dioxide evolved, which will, in turn, depend on the pressure of the CO_2 in the surrounding atmosphere".

They continued by pointing out that $CaCO_3$ begins to dissociate at the temperature where the partial pressure of the CO_2 from calcite first exceeds partial pressure of CO_2 in the surrounding atmosphere.

> ".... at higher temperatures, the system in which all three phases CaO, $CaCO_3$ and CO_2 are present continuously attempts to adjust to equilibrium conditions by releasing more CO_2 and forming more CaO at the expense of $CaCO_3$. As the furnace temperature increases, the partial pressure of CO_2 continues to rise until it approaches atmospheric pressure, which it cannot exceed since the sample is not enclosed. At this point the rate of dissociation becomes a maximum.... A similar explanation applies to the dissociation of all carbonate minerals...."

In this way Rowland and Lewis demonstrated the dependence of carbonate decomposition temperatures on the CO_2 pressure of the atmosphere around the sample. Because the DTA signal and the rate of weight loss in thermal analysis of carbonates depend on CO_2 evolution rates, the CO_2 partial pressure over the sample also effects these measurements. In their paper, titled *Furnace atmosphere control in differential thermal analysis*, Rowland and Lewis[2] published DTA curves for dolomite decomposition in air and in CO_2 (Fig. 1).

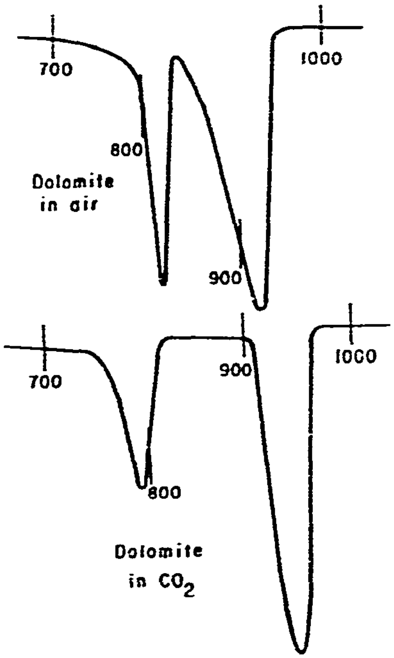

Fig. 1. Dolomite DTA in air and in carbon dioxide (ref. 2).

The change of dolomite's thermal decomposition with CO_2 pressure which we exploit to evaluate atmosphere control was first described by Haul and Heystek[3]. With DTA they studied the thermal decomposition of dolomite under CO_2 pressures down to 1 mm Hg. Figure 2 reproduces their DTA curves obtained at different CO_2 pressures. Because the CO_2 pressure given was also the total pressure in their reaction vessel, they had problems with sample material being expelled from the holder by rapidly evolving CO_2. However, these problems cannot obscure the fact that above 100 mm CO_2 pressure the dolomite decomposition is a two-stage reaction, while below 20 mm CO_2 pressure it is a single reaction.

Haul and Heystek report that in the pressure range where dolomite decomposes in two stages the following reactions occur:

Lower peak: $CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2$

Upper peak: $CaCO_3 \rightarrow CaO + CO_2$

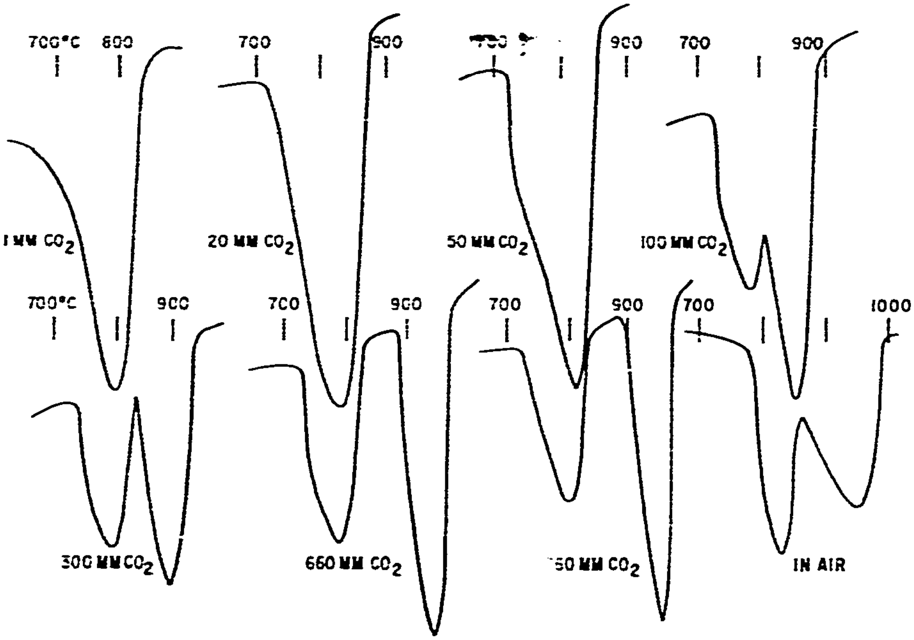

Fig. 2. Dolomite DTA at different CO_2 pressures (ref. 3).

At lower CO_2 pressures they report that decomposition occurs in only one stage, as follows:

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2$$

The curves in Fig. 2 indicate that as CO_2 pressure decreases the temperature of the lower dolomite peak remains fixed while the temperature of the upper peak decreases. Haul and Heystek concluded that the temperature of the lower decomposition is controlled by diffusion processes in the dolomite crystal and is not influenced by CO_2 pressure variations. The decomposition of the remaining $CaCO_3$, however, is subject to the CO_2 pressure effects described by Rowland and Lewis. Consequently in dolomite thermal analysis, the second or $CaCO_3$ peak moves toward and gradually merges with the lower peak as CO_2 pressure decreases. The shoulder on the 50 mm CO_2 curve (Fig. 2) is their last evidence of separate reactions.

Both Haul and Heystek (Fig. 2) and Rowland and Lewis (Fig. 1) published DTA curves for dolomite decomposition in air. Both show two separate DTA peaks, although in normal air the partial pressure of CO_2 is substantially less than 1 mm Hg. Both sets of thermal analysis equipment, designed specifically for atmosphere control, produced self-generated atmospheres of CO_2 around their samples. In each case the CO_2 partial pressure around the sample was significantly higher than that present in air. These two examples illustrate how in thermal analysis literature many results given with specified atmospheres conceal the effects of atmosphere self-generation.

EXPERIMENTAL

Apparatus, sample holders, and run conditions capable of providing sample atmosphere control, together with a commonly used sample holder completely unable to provide atmosphere control, will be described. Thermal analysis results on a standard dolomite sample are presented to illustrate the proposed atmosphere control test. Temperature calibrations of these thermal analysis results are also presented.

Standard sample

The dolomite sample used in these demonstrations was NBS Sample No. 88 obtained from the United States Bureau of Standards*. This specimen has little isomorphous substitution[4], is almost entirely dolomite, is obtained ground and mixed, and needs only gentle drying to be ready for testing. Although any other pure, unsubstituted dolomite can perform adequately as a test specimen, this NBS No. 88 sample is a convenient standard test material.

Equipment

Atmosphere control in thermal analysis is impossible without a flowing gas because product gases must be removed from the sample. The gas stream must sweep over the sample holder efficiently, and the evolving gases must escape from the sample very quickly in order to prevent a local build-up of product gases. The two thermal analysis units used in this demonstration provide the necessary flowing gas atmosphere, and the sample holders developed for each unit permit rapid escape of the product gases.

The first unit, capable of simultaneous DTA, TG, DTG, and EGA, was developed by the U.S. Bureau of Mines for study of oil shale and other solid fuels[5-8]. Because atmosphere control was vital to these studies, the flat pan sample holders illustrated in Fig. 3 were developed. These holders (Pt–3.5% Rh) are 3/4 inch (approximately 19 mm) in diameter and approximately 1 mm deep[8]. They hold 100–400 mg of sample and are suspended from an electrobalance in a gas stream which flows down around the sample holders.

The second thermal analysis unit used to demonstrate atmosphere control is the commercial Mettler thermoanalyzer†, used by one of us (M. M.-V.) for the study of minerals[9]. Description of this apparatus, capable of simultaneous DTA, TG, and DTG, is readily available from commercial literature. The platinum flat pan illustrated in Fig. 4 was prepared for use in the Mettler apparatus during these tests. This pan will hold up to 100 mg of dolomite.

The DTA reference materials were calcined alumina for the Bureau of Mines apparatus and calcined kaolinite for the Mettler apparatus. The heating rate for all

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*Now available as standard number 88a. Fifty-gram specimen with analysis, $36. Order from Office of Standard Reference Materials, Room D314 Chemistry Building, National Bureau of Standards, Washington, D.C. 20234, U. S. A.

†Reference to specific equipment or trade names does not imply endorsement by the Bureau of Mines.

runs reported was 10 °C min^{-1}. Sample weights and gas flow rates are given with the results. To insure absence of CO_2 from air and other gases, these gas streams were passed through a CO_2 absorbent before they were admitted to the thermal analysis units. All runs were made at atmospheric pressure except as noted.

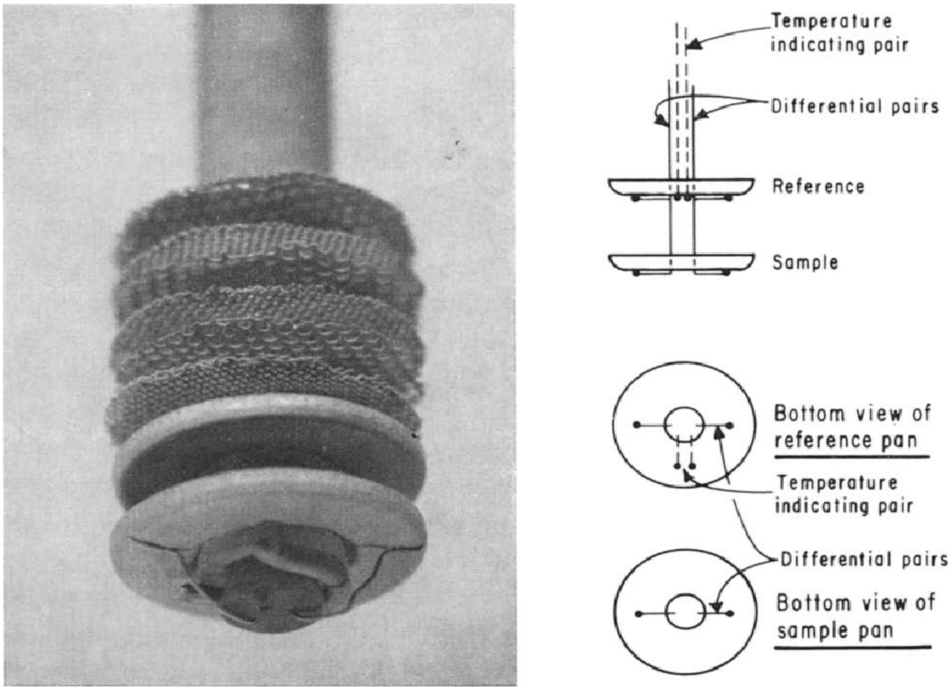

Fig. 3. Bureau of Mines sample holders.

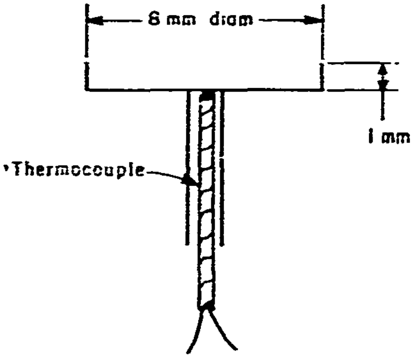

Fig. 4. Mettler flat plan.

RESULTS

Thermal analysis of the standard dolomite in a CO_2 atmosphere using the Bureau of Mines apparatus is presented in Fig. 5. Two separate decompositions are

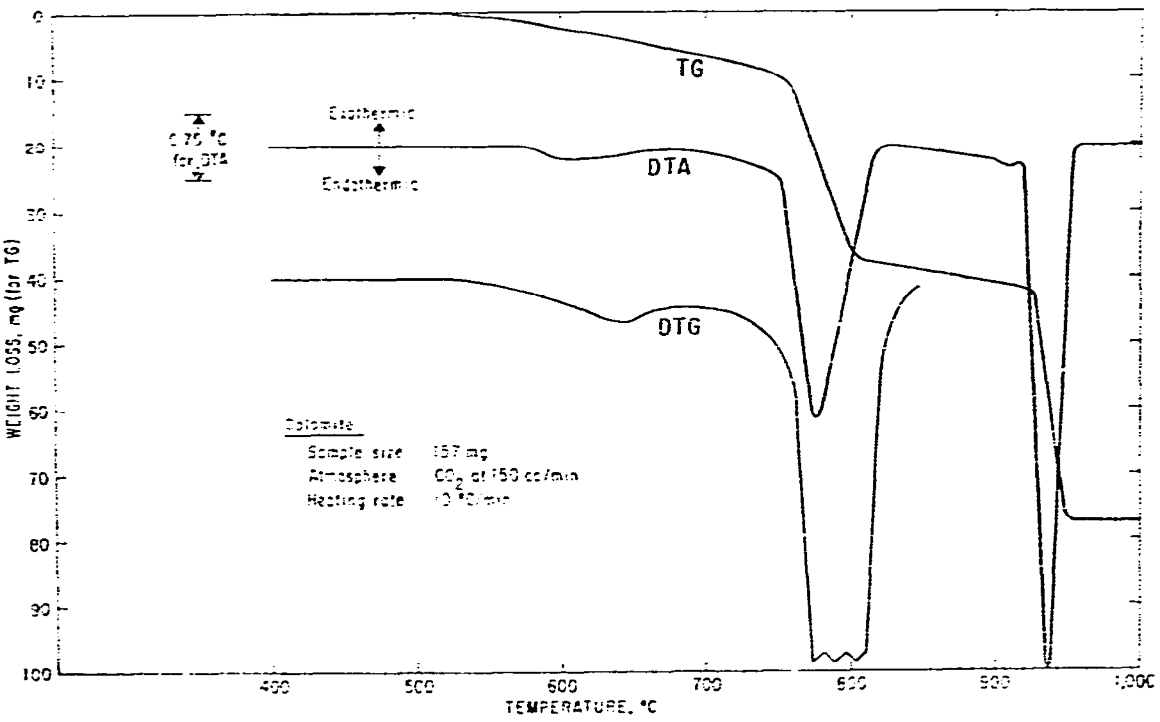

Fig. 5. Thermal analysis of dolomite in CO_2—Bureau of Mines apparatus.

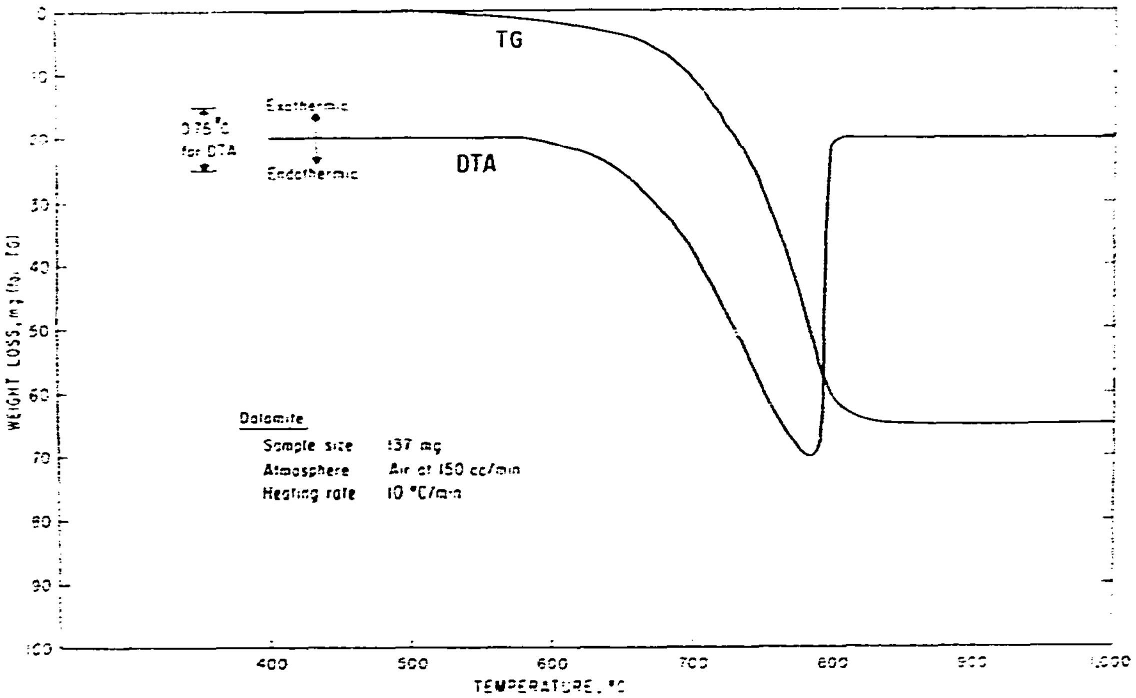

Fig. 6. Thermal analysis of dolomite in air—Bureau of Mines apparatus.

clearly defined by both DTA and TG. The derivative of the TG signal (DTG) is presented for the first decomposition to illustrate comparability of the DTA and TG responses and to emphasize that either DTA or TG can be used in testing atmosphere control.

Figure 6 presents the thermal analysis results on dolomite in air using the Bureau of Mines apparatus. A single and continuous reaction is evident on both DTA and TG results. Both weight losses and both DTA energies from the two reactions in Fig. 5 appear to be included in the single responses in Fig. 6. Similar single reaction results were obtained with other CO_2-free gases, including nitrogen, helium, and argon.

Three DTA curves for dolomite run in Mettler flat pan are given in Fig. 7. The upper curve was run in CO_2, and the lower two were run in air. The DTA response in

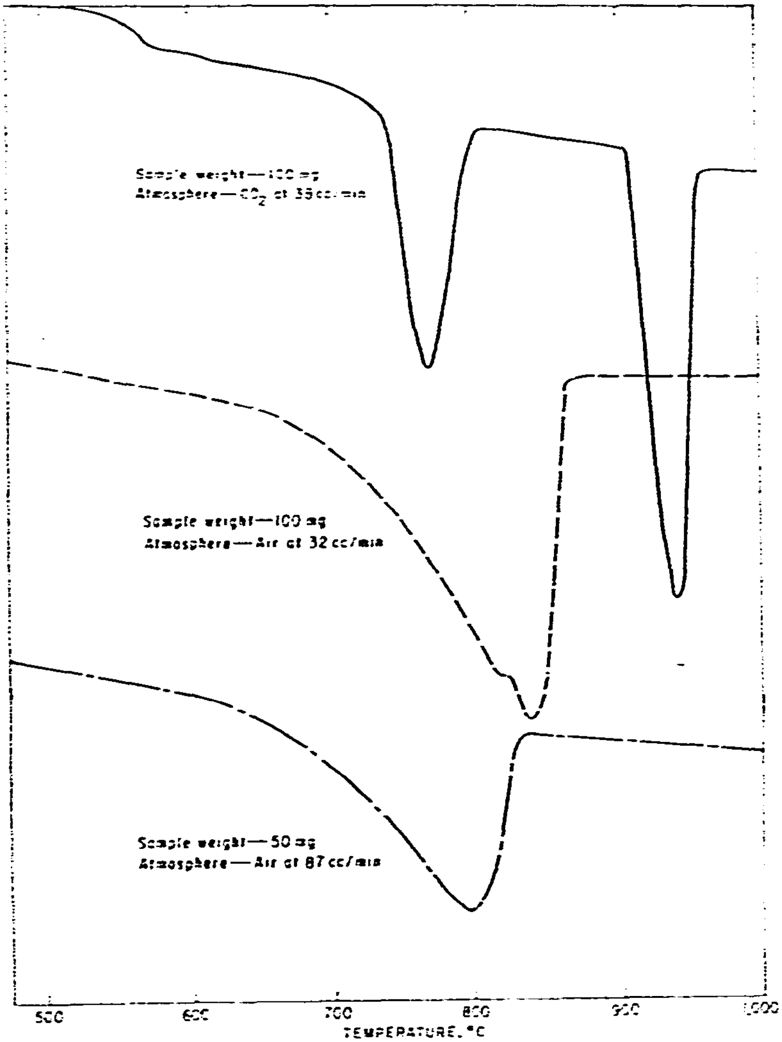

Fig. 7. Dolomite DTA in Mettler flat pan.

CO_2 shows two independent decompositions, and the DTA response with a 50 mg sample in air at a high gas flow rate shows only a single continuous reaction. The middle DTA curve run with 100 mg sample and a slower air flow rate shows a shoulder and an increase in the temperature of the endotherm. Both the DTA shoulder and the temperature increase indicate the presence of a self-generated CO_2 atmosphere around the sample.

To illustrate the effect of sample geometry on atmosphere control, DTA tests were made on dolomite in a commercial vacuum-pressure sample holder. This equipment contains the sample in a cylindrical well 6.35 mm in diameter and 11.2 mm deep. The thermocouple is inserted into the sample from the bottom of the well. The holder system was evacuated, and a pressure below 0.1 mm Hg was maintained over the

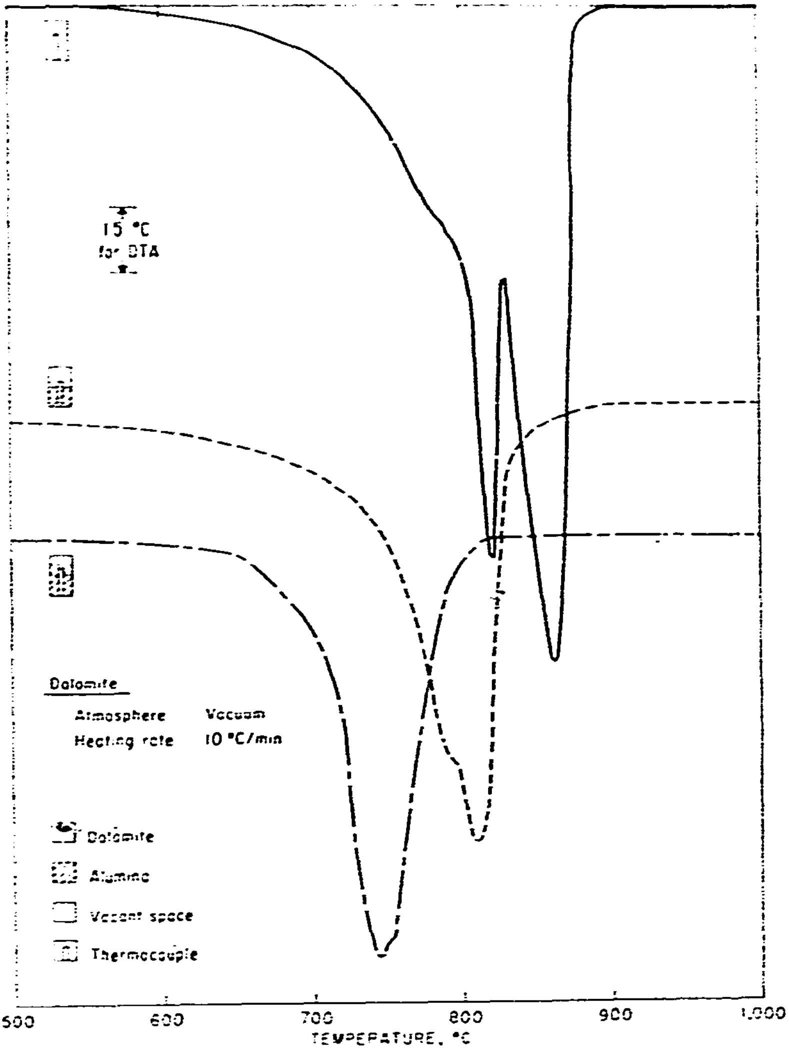

Fig. 8. Dolomite DTA in a cylindrical sample holder.

sample during DTA determinations. This continuous evacuation should produce the best possible conditions for removal of evolving CO_2 without a gas stream.

Results of three DTA runs made with this apparatus are given in Fig. 8. The sample arrangement in the sample well is illustrated at the low-temperature side of each curve. For the top curve the sample well was completely filled with dolomite. In spite of the continuous evacuation, a double DTA response was obtained with both peaks occurring above 800 °C. For the middle curve the bottom half of the sample well was filled with inert alumina with dolomite occupying the rest. A shoulder or break still appears on this DTA curve which also peaks well above 800 °C. For the bottom curve the dolomite thickness was cut to only about $\frac{1}{4}$ of the well depth (<3 mm) with the sample supported around the end of the thermocouple. The DTA curve produced resembles the Haul and Heystek curve for dolomite DTA at 1 mm CO_2 (Fig. 2).

Temperature calibration

Precise temperature measurements are not necessary to determine atmosphere control by thermal analysis of dolomite. We are reluctant to specify temperatures in this test because such temperatures are subject to too many unspecifiable variables. The temperatures indicated in the thermal diagrams are uncorrected machine readouts sufficiently accurate for our purposes. However, peak temperatures measured by the two thermal analysis units on materials from the NBS-ICTA temperature standards 759 and 760 are compared in Table I with the consensus mean peak values. The differences indicated may be used to adjust the temperatures in Figs. 5, 6, and 7.

TABLE I

TEMPERATURE CALIBRATION WITH NBS-ICTA STANDARDS

Standard material	*NBS-ICTA peak temp. (°C)*	*USBM*		*Mettler*	
		Peak temp. (°C)	*Deviation*[a]	*Peak temp. (°C)*	*Deviation*[a]
$KClO_4$	309	315	+6	313	+4
Ag_2SO_4	433	435	+2	439	+6
SiO_2	574	578	+4	575	+1
K_2CrO_4	673	679	+6	674	+1
$BaCO_3$	819	825	+6	821	+2
$SrCO_3$	938	946	+8	946	+8

[a] Deviation from NBS-ICTA peak temperature.

DISCUSSION

The marked difference between the DTA or the TG measurements in air and in CO_2 furnishes a positive test for atmosphere control in thermal analysis. If the single continuous decomposition can be obtained in air or other CO_2-free gas, the produced gases are being removed rapidly enough to prevent self-generation effects. Even small

CO_2 partial pressures introduce the discontinuity into the thermal analysis traces (see Figs. 2, 7, and 8). The disappearance of the two peaks in Fig. 8 and the decrease in reaction temperature with the decrease in sample thickness demonstrates the importance of a thin layer of sample to atmosphere control. Dilution of the dolomite sample with inert materials is not recommended because such dilution increases the length of the CO_2 escape path. The first expression of self-generated CO_2 is elevation of the reaction temperature. This may be used to detect small self-generation effects. For example, in air the single reaction for the Bureau of Mines run (Fig. 6) is complete 30 degrees before that for the 50-mg Mettler run (Fig. 7, bottom curve), indicating that some CO_2 pressure was still affecting the determination in the Mettler pan.

In their recent study on kinetics of the thermal decomposition of $CaCO_3$, Gallagher and Johnson[10] discuss CO_2 partial pressure as a possible reason for their observed dependence of Arrhenius kinetic parameters on sample weight. After assuming that diffusion of gaseous products from their sample is faster than diffusion of heat into the sample, they conclude that self-generated CO_2 pressure is a minor kinetic factor. Our results indicate that it may not be minor. The significance of self-generated CO_2 to kinetic factors can be checked with dolomite.

The Haul and Heystek[3] proposal for direct and complete decomposition of dolomite at low CO_2 pressures according to the equation given earlier appears correct. X-ray diffraction of a dolomite sample heated to 770 °C in N_2, then quickly cooled, showed only dolomite and the daughter products CaO and MgO. No intermediate calcite was detected.

The fine grinding (<200 mesh) that NBS dolomite sample No. 88 was subjected to before it was mixed and packaged by the National Bureau of Standards probably explains the small thermal reaction which appears near 600 °C in CO_2. This event was observed in curves from both the Bureau of Mines apparatus (Fig. 5) and the Mettler equipment (Fig. 7). In a dolomite grinding experiment, Bradley and others[11] observed that as dolomite is ground a new DTA peak begins to appear near the magnesite ($MgCO_3$) decomposition temperature. With continued grinding this peak increased in size at the expense of the normal lower dolomite peak. Apparently this process had begun in NBS No. 88. This does not interfere with the use of the major reactions of this standard dolomite to test for atmosphere effects. However, it does prevent use of departure points or intersection points as criteria. On TG the standard dolomite also has a slightly larger weight loss than theoretically available from pure dolomite, but this has no effect on its use for atmosphere control testing.

The temperature range of the first dolomite decomposition in CO_2 is virtually duplicated in the DTA responses included in this paper (Figs. 1, 2, 5, and 7). Stability of this response has been noted frequently in thermal analysis literature (see ref. 11, for example). Consequently, the lower peak obtained from dolomite decomposition in CO_2 may furnish a temperature reference point for any equipment being tested for atmosphere control.

CONCLUSIONS

Dolomite can be used to define atmosphere control and to determine if self-generated atmospheres are influencing thermal analysis results. Use of a National Bureau of Standards dolomite specimen is recommended. Thermal analysis of dolomite should be run in CO_2 and in CO_2-free gas such as air with the gas flowing over the sample. Either differential thermal analysis or thermogravimetry can be used. In CO_2 the dolomite produces two sharp and distinct decompositions, but in air only a single continuous decomposition appears. The reaction at lower temperature in CO_2 is useful for establishing a reference point unaffected by sample atmosphere. If the DTA or TG curve in air shows any shoulder or break in the single response, effects of self-generated CO_2 are proven. If these curves show that the reaction is not complete by 800°C (Fig. 6), self-generated CO_2 around the sample is strongly indicated. Atmosphere control can be improved by decreasing the sample thickness or by increasing the flow of sweep gas over the sample holder.

REFERENCES

1 S. Glasstone, *Textbook of Physical Chemistry*, 2nd ed., Van Nostrand, New York, 1946, p. 845.
2 R. A. Rowland and D. R. Lewis, *Amer. Mineral.*, 36 (1951) 80.
3 R. A. W. Haul and H. Heystek, *Amer. Mineral.*, 37 (1952) 166.
4 J. R. Goldsmith and D. L. Graf, *Amer. Mineral.*, 43 (1958) 84.
5 J. W. Smith and D. R. Johnson, in H. G. McAdie (Ed.), *Proc. 2nd Toronto Symposium on Thermal Analysis*, 1968, p. 95.
6 J. W. Smith and D. R. Johnson, in R. F. Schwenker and P. D. Garn (Eds.), *Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 1251.
7 J. W. Smith and D. R. Johnson, *Amer. Lab.*, January 1971, p. 8.
8 D. R. Johnson and J. W. Smith, *U.S. Bur. Mines Rept. Invest.*, 7429 (1970) 17.
9 M. Müller-Vonmoos and R. Bach, in R. F. Schwenker and P. D. Garn (Eds.), *Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 1229.
10 P. K. Gallagher and D. W. Johnson, Jr., *Thermochim. Acta*, 6 (1973) 67.
11 W. F. Bradley, J. F. Burst and D. L. Graf, *Amer. Mineral.*, 38 (1953) 207.