

THE THERMAL DISSOCIATION OF SOME CARBONATE MINERALS

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Detailed differential thermal studies on mixtures of *natural* carbonate minerals have confirmed the peak-temperature shifts recently reported for mixtures of *synthetic* carbonates and have established that such shifts can be attributed entirely to dilution effects. The exception, where magnesite in the presence of siderite maintains its peak position, is due simply to the fact that both minerals give similarly sized peaks at approximately the same temperature.

In a recent paper Gokhale and Rao [1] have reported a general lowering of the temperature of the dissociation peaks on DTA curves for synthetic samples of magnesite, dolomite and calcite when these are in admixture. They have also recorded that the presence of siderite does not affect the peak temperature of magnesite and suggest that these phenomena warrant more intensive study.

In view of the well-established fact that dilution alone reduces the temperatures of DTA peaks due to decomposition reactions [2–5], and consequent on recent studies on carbonates in nitrogen [6] and in air atmospheres [7], it appeared to the authors that the main observations of Gokhale and Rao [1] were consistent with simple dilution effects. The results of a detailed study of mixtures of *natural* carbonate minerals are given below: these agree in general with those for *synthetic* carbonates [1] and confirm the hypothesis that the peak shifts observed can be accounted for by dilution.

Experimental

Materials. Natural samples of magnesite, calcite, dolomite and siderite of a known degree of purity were employed to prepare the mixtures used. Localities of origin and purity as determined by chemical analysis are given in Table 1. Calcined alumina was used as reference material and as diluent (when employed). All materials were crushed (but not ground) to pass a 200-mesh B.S. sieve.

Method. A Du Pont 900 Differential Thermal Analyzer equipped with a 1200° furnace, platinum sample cups and matched platinum/platinum–13% rhodium thermocouples was used. The heating rate was 15°/min and all curves were

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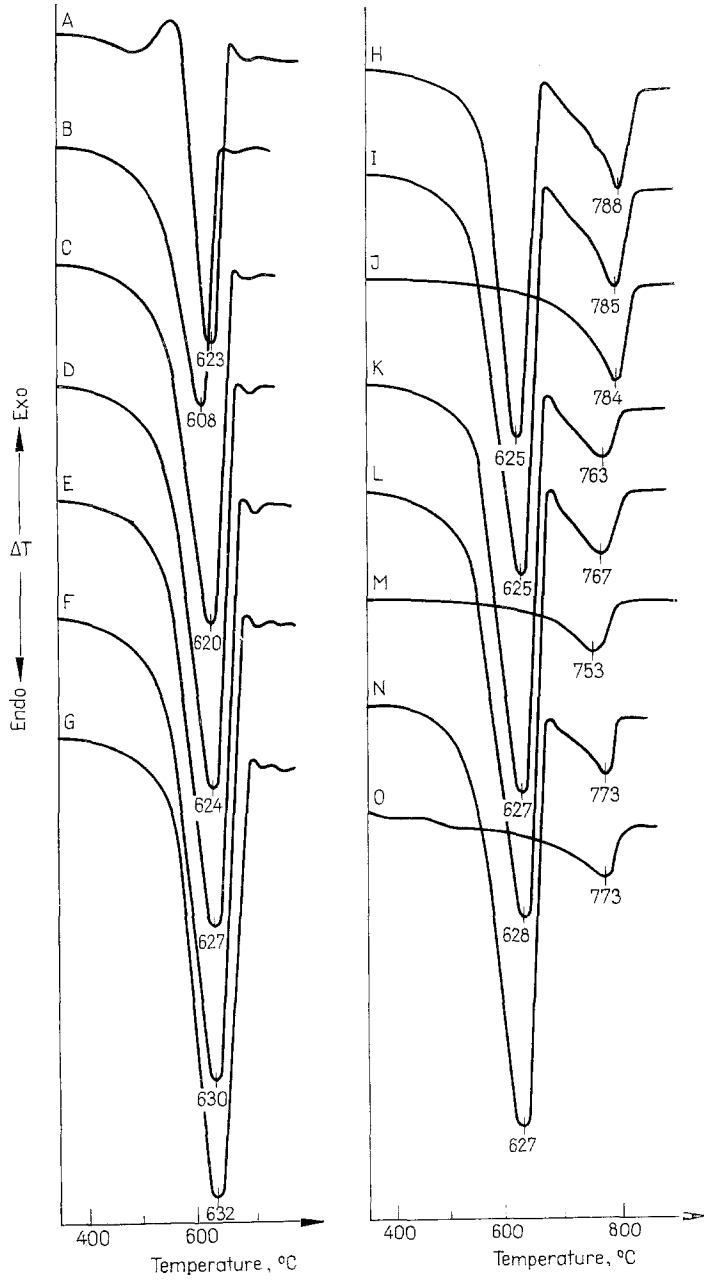


Table 1
Minerals used, locality of origin and purity

Mineral	Locality of origin	CaCO ₃ %	MgCO ₃ %	FeCO ₃ %	MnCO ₃ %
Magnesite	Thuddungra, New South Wales, Australia	—	99.40	0.96	—
Dolomite	Kalgoorlie, Western Australia	51.76	41.41	5.00	0.75
Calcite	Wee Jasper, New South Wales, Australia	98.16	n.d.	n.d.	n.d.
Siderite	Roxbury, U.S.A.	0.86	7.55	85.54	4.07

determined in a static air atmosphere, the ceramic liner tube being left open at the top. Sample and reference material weight was 40 mg and the temperature-measuring thermocouple was located in the sample.

Results and discussion

For easy comparison, the results quoted by Gokhale and Rao [1] are tabulated in Table 2 and those obtained in the present study in Table 3; DTA curves for the various mixtures are reproduced in Fig. 1.

From the phraseology used by Gokhale and Rao [1], it was not immediately obvious whether in stating, e.g., "magnesite with 10% calcite" they had used a mixture of 90% magnesite + 10% calcite* or whether they had added 10% calcite to the same weight of magnesite as used for their "pure magnesite" curve, this increasing sample size. If the latter interpretation were correct then the reduction in peak temperature observed must be real and could not be a dilution effect. This aspect was checked by carrying out experiments with 40 mg mag-

* In the absence of other evidence it was assumed that the percentages quoted in [1] were by weight and were not molar. Percentages and ratios given for the present study are all on a weight basis.

←
Fig. 1. DTA curves for: A — 50% magnesite + 50% siderite; B — 50% magnesite + 50% alumina; C — 70% magnesite + 30% alumina; D — 80% magnesite + 20% alumina; E — 90% magnesite + 10% alumina; F — 100% magnesite; G — 90% magnesite + 10% siderite; H — 70% magnesite + 10% dolomite + 10% calcite + 10% siderite; I — 80% magnesite + 10% dolomite + 10% calcite; J — 10% dolomite + 10% calcite + 80% alumina; K — 80% magnesite + 10% calcite + 10% siderite; L — 90% magnesite + 10% calcite; M — 10% calcite + 90% alumina; N — 90% magnesite + 10% dolomite; O — 10% dolomite + 90% alumina. Note that lettering on curves represents sample indication in Table 2. Each division on the ΔT axis is equivalent to 1° at 700°

Table 2

Peak temperatures quoted in [1] for various mixtures of carbonate minerals

Sample No.	Description	Ratio of components				Peak temperature (s), °C and attribution
		M	D	C	S	
1	Magnesite	100	0	0	0	612 (M)
2	Magnesite with 10% calcite	90	0	10	0	600 (M); 745 (C)
5	Magnesite with 10% dolomite	90	10	0	0	600 (M)
3	Magnesite with 10% siderite	90	0	0	10	612 (M)
—	Calcite	0	0	100	0	798 (C)
4	Dolomite	0	100	0	0	798 (D)
7	Magnesite with 10% dolomite and 10% calcite	80	10	10	0	Not quoted
6	Magnesite with 10% siderite and 10% calcite	80	0	10	10	585 (M)
8	Magnesite with 10% each of siderite, dolomite and calcite	70	10	10	10	590 (M)

Table 3

Peak temperatures for carbonate minerals and their mixtures for constant sample weight of 40 mg

Sample	Ratio of components					Peak temperature (s), °C and attribution
	M	D	C	S	A	
F	100	0	0	0	0	630 (M)
E	90	0	0	0	10	627 (M)
N	90	10	0	0	0	627 (M); 773 (D)
L	90	0	10	0	0	828 (M); 767 (C)
G	90	0	0	10	0	632 (M+S)
D	80	0	0	0	20	624 (M)
I	80	10	10	0	0	625 (M); 785 (D+C)
K	80	0	10	10	0	627 (M+S); 763 (C)
H	70	10	10	10	0	625 (M+S); 788 (D+C)
C	70	0	0	0	30	620 (M)
B	50	0	0	0	50	608 (M)
R	50	25	25	0	0	612 (M)
A	50	0	0	50	0	623 (M+S)
Q	0	100	0	0	0	789 850 (D)
O	0	10	0	0	90	773 (D)
P	0	0	100	0	0	867 (C)
M	0	0	10	0	90	753 (C)
J	0	10	10	0	80	784 (C+D)

Key: M — magnesite; D — dolomite; C — calcite; S — siderite; A — alumina

nesite + 4 mg calcite and 40 mg magnesite + 4 mg calcite + 4 mg dolomite. In neither instance did the peak temperature for magnesite differ from that obtained with 40 mg magnesite alone. Furthermore, for those mixtures listed in Table 3 (samples E, N and L; D and I) with the same weight of magnesite there was no drop in peak temperature on admixture with other carbonate minerals. Indeed, the magnesite peak temperature on a curve for 40 mg of a mixture of 50% magnesite + 25% calcite + 25% dolomite (sample R, Table 3) showed

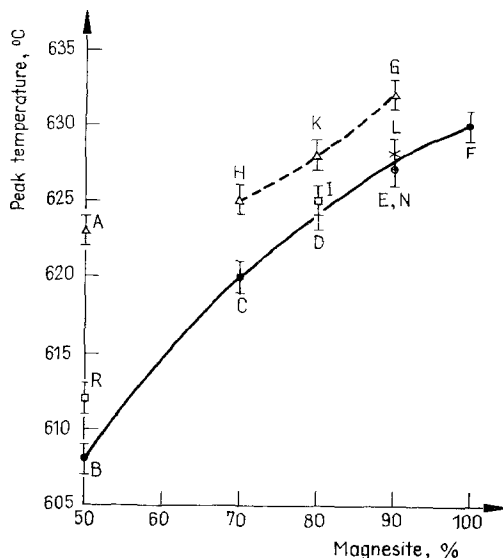


Fig. 2. Relationship between magnesite peak temperature and magnesite content for various mixtures with carbonate minerals and alumina; lettering of points corresponds to sample indications in Table 2 and Fig. 1. ● — Magnesite + alumina; ◐ — magnesite + dolomite; × — magnesite + calcite; □ — magnesite + calcite + dolomite; △ — mixtures containing siderite

a temperature rise when compared with a curve for 40 mg of a mixture of 50% magnesite + 50% alumina (sample B, Table 3). The peak temperature for carbonate dissociation peaks is known to depend markedly on the pressure of carbon dioxide in the sample atmosphere (*cf.* samples L and M, Table 3) and a possible explanation of this effect is that an increased pressure of carbon dioxide is developed in the sample through the simultaneous early decomposition of the other carbonates that are present in high proportion in this mixture. A temperature rise was also observed for samples L and I compared with samples E and D (Table 3), but here the difference is probably within experimental error.

On the other hand, when the peak temperatures for magnesite in 40 mg samples of mixtures of magnesite:dolomite:calcite in the ratios 90:10:0 and 80:10:10 (samples N and I, Table 3) are compared with that for 40 mg magnesite (sample

F, Table 3), drops of 3° and 5° are observed. It would appear, therefore, that these were the conditions of experiment employed by Gokhale and Rao [1] and subsequent studies were carried out on samples of a constant weight of 40 mg with various ratios of carbonates.

The results given in Fig. 1 and Table 3 show that the respective peak temperatures drop continuously as the proportions of magnesite, dolomite or calcite in the mixture decrease; the relationship between magnesite content and peak temperature is clearly expressed in Fig. 2, where vertical lines through the points indicate the possible limits of experimental error. From Fig. 2 it is clear that the lowering of peak temperature on dilution is virtually identical whether the diluent of the magnesite be alumina or other carbonates. The possible reason for the position of point R (and points L and I) in Fig. 2 has already been discussed.

Thus, the reason for the lowering of peak temperatures quoted by Gokhale and Rao [1] is simply the well-known dilution effect [2–5] and no other more complicated mechanism, such as is operative in the lowering of dolomite peak temperatures on admixture with salts [8], need be invoked.

As distinct from additions of calcite and dolomite, addition of siderite to magnesite and mixtures containing magnesite not only counteracts reduction in the temperature of the magnesite peak [1] but, in this study, causes a slight increase (samples A, G, H and K, Table 3 and Fig. 2). Thus, mixtures containing 10% siderite give peak temperatures $3-5^\circ$ above those without siderite (samples G, H and K), while for a mixture with 50% siderite (sample A) the peak temperature increases by 15° . These increases in peak temperature are also accompanied by increases in peak height. From detailed studies on dilution sequences for siderite and magnesite [7] it is clear that the dissociation peaks for the two minerals occur within the same temperature range so that the endothermic peak for siderite is superimposed on and obscured by the endothermic peak for magnesite. The result of this reinforcement is to overcompensate for decrease in magnesite content so that both peak temperature and peak height increase. Since no peak coincidence occurs between siderite and calcite or dolomite this mechanism also explains why the presence of siderite does not affect peak temperature for these minerals [1].

In the DTA apparatus used by Gokhale and Rao [1] and in the present study one other factor can lead to spurious results involving apparent decrease in peak temperature – namely, loss of some of the samples by ejection during heating. This phenomenon has been widely observed with carbonates [8–10] and can be due to decrepitation and/or sudden evolution of gas causing physical removal of material. In the present series of experiments care was taken to ensure that this did not occur.

Conclusions

Decrease in peak temperature for the dissociation peaks of natural samples of magnesite, dolomite and calcite when admixed in decreasing contents of individual carbonates in mixtures of constant weight appears to be due entirely

to the effect of dilution in all mixtures examined. Failure to observe such a decrease in the peak temperature for magnesite when admixed with siderite under comparable conditions is a result of the additive effect of superposition of the peaks for the two minerals.

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RÉSUMÉ — L'étude de mélanges de carbonates *naturels* par les procédés thermiques différentiels a confirmé l'observation faite récemment d'un déplacement de la température au sommet du pic pour des mélanges de carbonates *synthétiques*. On attribue ces déplacements entièrement aux effets de dilution. La magnésite en présence de sidérite constitue une exception. Dans ce cas, la position du pic reste inchangée du fait que ces deux minéraux donnent des phénomènes sensiblement identiques presque à la même température.

ZUSAMMENFASSUNG — Eingehende differentialthermische Untersuchungen von Gemischen natürlicher Karbonatmineralien zeigten ähnliche Spitzentemperaturverlagerungen wie kürzlich bei Gemischen von künstlichen Karbonatgemischen beobachtet wurden. Solche Verlagerungen sind ausschließlich Dilutionserscheinungen zuzuschreiben. Magnesit behielt zwar in Gegenwart von Siderit seine Spitzenpositionen, wofür jedoch der Umstand verantwortlich ist, daß beide Mineralien ähnliche und bei gleichen Temperaturen erscheinende Spitzen besitzen.

Резюме — Детальным исследованием смесей природных карбонатных минералов, проведенным посредством дифференциального термического анализа, подтверждено наличие сдвигов температурных пиков, недавно описанное (1) для смесей синтетических карбонатов, и установлено, что такие сдвиги могут быть всецело приписаны эффектам разбавления. Исключение, представляемое магнетитом, сохраняющим в присутствии сидерита положение своего пика (1), просто обусловлено тем фактом, что оба минерала дают при приблизительно одной и той же температуре пики одинаковых размеров.