Thermochimica Acta, 109 (1986) 243–252
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

APPLICATIONS OF VARIABLE ATMOSPHERE DTA (IN CO_2) TO IMPROVED DETECTION AND CONTENT EVALUATION OF ANHYDROUS CARBONATES IN MIXTURES *

S.St.J. WARNE

Department of Geology, The University of Newcastle, Shortland, N.S.W. 2308 (Australia)

(Received 7 July 1986)

ABSTRACT

The identification, content evaluation and detection limits of anhydrous carbonate minerals are greatly improved by the technique of variable atmosphere DTA. In particular, determinations under reproducible conditions of flowing CO_2 produce marked and predictable DTA curve modifications. These, due to resultant peak height increase, attenuation, separation, up and down scale (temperature) movements, have improved greatly their recognition and detection limits when present singly or in mixtures and have considerable application to problems of carbonate mineral identification due to peak superposition and unsatisfactory definition.

INTRODUCTION

The identification and content evaluation of the common anhydrous carbonate minerals individually, as mixtures together, or as components in other deposits are constantly under investigation: e.g. the identification of dolomite ($CaMg(CO_3)_2$) from ankerite ($Ca(Mg, Fe)(CO_3)_2$) [1]; the differentiation of mixtures of magnesite ($MgCO_3$) and calcite ($CaCO_3$) from dolomite ($CaMg(CO_3)_2$) [2]: and the determination of the carbonate mineral contents of coal and oil shales [3,4].

This forms an important aspect of the appraisal of mineralogical deposits and materials, e.g. in relation to their use in the ceramic, refractory, coal fuel, smelting, glass, cement, plaster, building stone, roadstone, agricultural, insulation, glaze, polishing powder and chemical industries. The degree and process of dolomitisation are important in petroleum geology, as are carbonate compositional variations in relation to ore bodies, environments of deposition and, for SO_2, complexing and recovery from flue gases in relation to acid-rain mitigation.

---

* Dedicated to Professor Syûzô Seki in honour of his contribution to Calorimetry and Thermal Analysis.

Pertinent aspects of the DTA curves of simple anhydrous carbonates have been documented in general [2] in relation to: solid hydrocarbon fuels [3,4], determinations in steam [5,6], in vacuum [7], above ambient gas pressures [8]; siderite ($FeCO_3$) for a range of gases and thermomagnetometry [9,10]; and dolomite [11]. The dolomite group has been reviewed [12], the rare member kutnahorite ($CaMn(CO_3)_2$) detailed [13], and the curve modifications with progressive Fe substitution in the dolomite-ferroan dolomite-ankerite series established [14].

Although the overall applications of thermal analysis to carbonate mineralogy have just been reviewed by Warne [15], no detailed study has been made of mixtures of carbonate minerals under the optimum peak resolution conditions of flowing CO_2 gas at ambient pressure.

EXPERIMENTAL

The identity and relative purity of the carbonate minerals used has been confirmed by X-ray diffraction.

Details of the DTA unit used have been published previously [1]. Determinations were made with alundum sample holders on samples ground to −150# (BS sieve) in flowing CO_2 (2 l min^{-1}) with a heating rate of 15°C min^{-1}, using Cr/Al thermocouples.

RESULTS AND DISCUSSION

Curve modifications produced in flowing CO_2

The decomposition of carbonates is an equilibrium reaction controlled by the pressure (or partial pressure under atmospheric pressure conditions) at the reaction interface [16]. Thus, with increasing partial pressure conditions of flowing CO_2 (compared to air), the following takes place.

For the single-endothermic-peaked carbonates, such as smithsonite ($ZnCO_3$), siderite, magnesite and calcite:

(a) the individual single peaks become narrower and more sharply defined;
(b) peak heights increase considerably;
(c) the complete peaks move up scale to occur at higher temperatures.

In addition, for the multi-peaked curves of the dolomite/ankerite series:

(a) the initial, lowest temperature endothermic peak moves down scale to occur at a lower temperature;
(b) the higher temperature endothermic peak (dolomite) or peaks (ankerite) move up scale to occur at higher temperatures (the four peaks of Mg kutnahorite behave similarly [13]);
(c) these peak movements are markedly spread over a greater temperature range and result in the complete separation and resolution of all peaks;

(d) in particular the middle and smallest endothermic peak is completely separated from the others and can therefore be clearly recognised and evaluated (important because its size is relatable to the Fe content substituted for Mg in the dolomite lattice [14]).

Effects of progressive reduction in carbonate contents—dilution

For single-endothermic-peaked carbonates, earlier work has shown that in air or N_2 [3,17], the peak temperature falls on progressive dilution with inert Al_2O_3, while for the multi-peaked carbonates, the peaks progressively coalesce into a simple endothermic feature whose peak temperatures also fall with decreasing contents [3].

By contrast, in flowing CO_2 all peak temperatures are maintained, despite progressive dilution, right down to the limits of detection [18].

APPLICATIONS

In the present study bi-mineral mixtures of anhydrous carbonate minerals have been studied by DTA under conditions of flowing CO_2 to temperatures of 1000°C. Resultant DTA curves obtained from artificially prepared mixtures containing each pair of minerals in the ratios of 5 : 95, 50 : 50 and 95 : 5 (by weight) are featured in Figs. 1–7 to illustrate peak resolution and detection limits.

Siderite with dolomite

The DTA curves of mixtures of siderite with dolomite (Fig. 1) show that in all proportions the characteristic endothermic peaks, one for siderite (S) and two for dolomite (D), are completely separated, with the curve returning to the baseline between each. The detection limit indicated is ~ 1%.

Magnesite with dolomite

For mixtures of magnesite with dolomite (Fig. 2) the single peak of magnesite (M) is not always separated from the lower temperature peak of the two diagnostic of dolomite (D). This peak superposition, due to the higher peak temperature characteristic of magnesite compared to siderite, occurs for mixtures with high magnesite and low dolomite contents (cf. curves 3 and 2, Fig. 2). However, the presence of dolomite, even with high amounts of magnesite, is indicated by the presence of the small, but clearly delineated, higher temperature peak of dolomite (Fig. 2, curve 3). Again detection limits of ~ 1% are indicated.

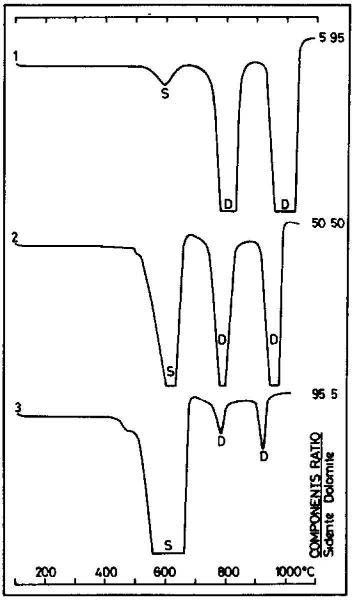

Fig. 1. DTA curves of artificial mixtures of siderite with dolomite, to illustrate the identification and detection limits of these two carbonate minerals when present together. Determined in flowing CO_2. Peaks for siderite and dolomite are marked S and D, respectively.

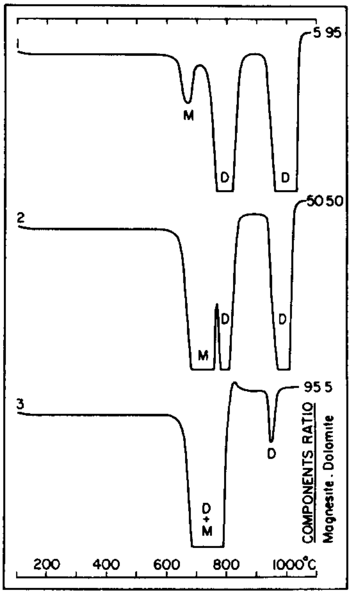

Fig. 2. DTA curves of artificial mixtures of magnesite with dolomite, to illustrate the identification and detection limits of these two carbonate minerals when present together. Determined in flowing CO_2. Peaks for magnesite and dolomite are marked M and D, respectively.

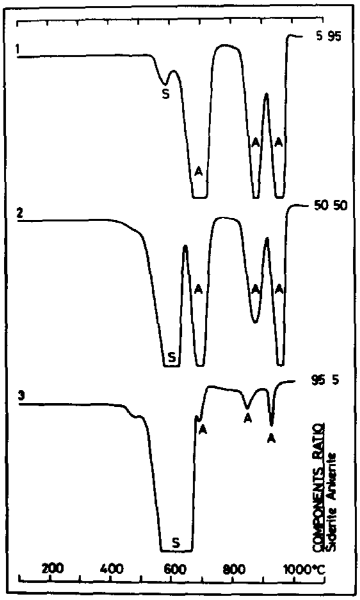

Fig. 3. DTA curves of artificial mixtures of siderite with ankerite to illustrate the identification and detection limits of these two carbonate minerals when present together. Determined in flowing CO_2. Peaks for siderite and ankerite are marked S and A, respectively.

Siderite with ankerite

In all mixtures of siderite with ankerite (Fig. 3) the single peak of siderite (S) and the three peaks of ankerite (A) are resolved and clearly identifiable. Even for high siderite–low ankerite mixtures the first or lowest temperature peak of ankerite is either resolved (Fig. 3, curve 3) or close to the limits of detection, and shows as an inflection on the otherwise straight return limb of the siderite peak. Furthermore, the presence of ankerite is confirmed by the clearly defined presence of its other two higher temperature peaks (Fig. 3, curve 3).

Magnesite with ankerite

In the case of mixtures of magnesite with ankerite (Fig. 4) it is only for relatively low contents of magnesite that its single peak (M) is clearly separated from the three diagnostic peaks of ankerite (A). With contents of 50% or more of magnesite, its single peak and the lowest temperature peak of ankerite are completely superimposed to form a single composite peak (Fig. 4, curves 2 and 3). However, the presence of the two perfectly resolved, higher temperature peaks of ankerite clearly indicates the presence of small amounts of ankerite with large amounts of magnesite.

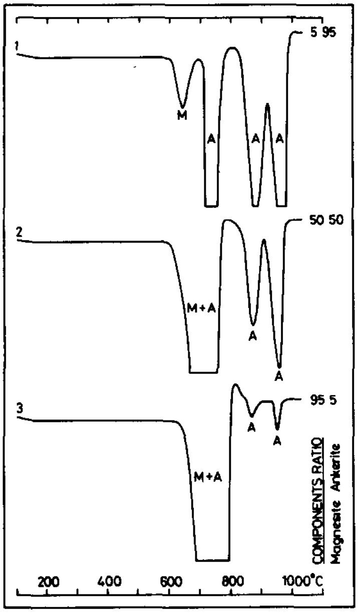

Fig. 4. DTA curves of artificial mixtures of magnesite with ankerite to illustrate the identification and detection limits of these two carbonate minerals when present together. Determined in flowing CO_2. Peaks for magnesite and ankerite are marked M and A, respectively.

Dolomite with ankerite

Figure 5 shows the DTA curves of mixtures of dolomite with ankerite, and includes also the two- and three-peaked curves obtained from 100% samples of dolomite (D) and ankerite (A) (cf. curves 1 and 5, Fig. 5). From these it can be seen that, except for the superposition of the highest temperature peak of both dolomite and ankerite, all the other three peaks of these two minerals are clearly resolved and therefore indicate the presence of these two minerals in all proportions down to the detection limits.

Calcite with dolomite or ankerite

The behaviour of mixtures of calcite with dolomite or ankerite is somewhat different. The single peak of calcite (C) which occurs at ~ 1000 °C for all contents, appears completely superimposed on the highest temperature peaks of both dolomite (D) and ankerite (A) (Figs. 6 and 7).

The presence of calcite in high contents with low amounts of dolomite (Fig. 6) can be seen by comparing the fully recorded double-peaked portion of the curve containing 5% dolomite (Fig. 1, curve 3) with the curve of the same amount of dolomite with calcite (Fig. 6, curve 1). For the latter, the

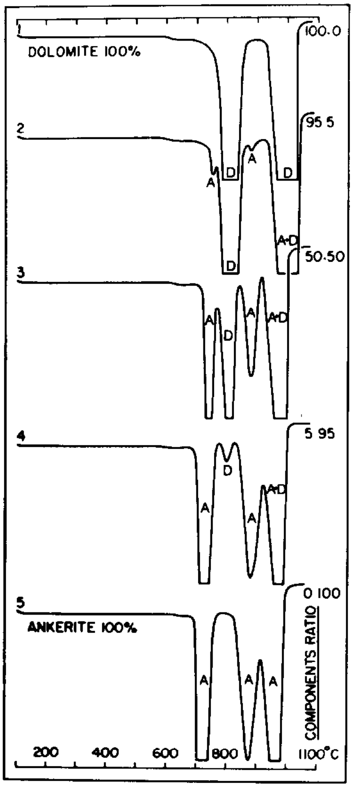

Fig. 5. DTA curves of artificial mixtures of dolomite with ankerite to illustrate the identification and detection limits of these two carbonate minerals when present together. Determined in flowing CO_2. Peaks for dolomite and ankerite are marked D and A, respectively.

first (low temperature) peak of dolomite (D) may be clearly seen, whilst the second (higher temperature peak) of dolomite shows as a slight inflection on the low-temperature limb of the large, superimposed single peak of calcite. Further confirmation of this modest inflection feature may be obtained by differential thermogravimetry (DTG) runs of duplicate samples.

Except for mixtures of high dolomite and low calcite contents (Fig. 6, curve 3) the presence of calcite is indicated by the unexpectedly large ~ 1000°C peak of dolomite due to the additional superposition of the calcite peak (cf. Fig. 1, curve 2 for the two dolomite peaks with Fig. 6, curve 2 for dolomite plus calcite).

The same applies to mixtures of calcite with ankerite. Here the highest temperature peak of ankerite (see Fig. 4, curve 3), shows again only as an inflection on the low-temperature limb of calcite (for high calcite contents, e.g. Fig. 7, curve 1). Also, the large, highest temperature peak of ankerite is disproportionately enlarged due to its superposition by the peak of calcite, thus indicating the presence of calcite (see Fig. 7, curves 1 and 2). However,

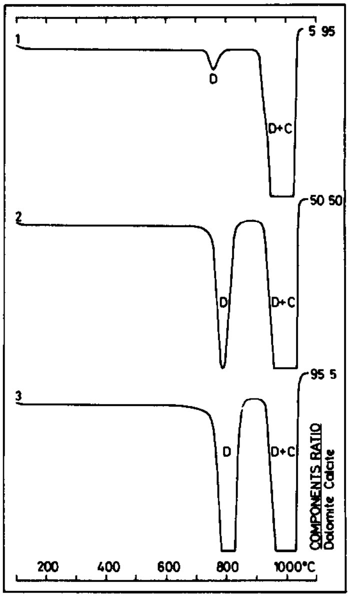

Fig. 6. DTA curves of artificial mixtures of dolomite with calcite to illustrate the identification and detection limits of these two carbonate minerals when present together. Determined in flowing CO_2. Peaks for dolomite and calcite are marked D and C, respectively.

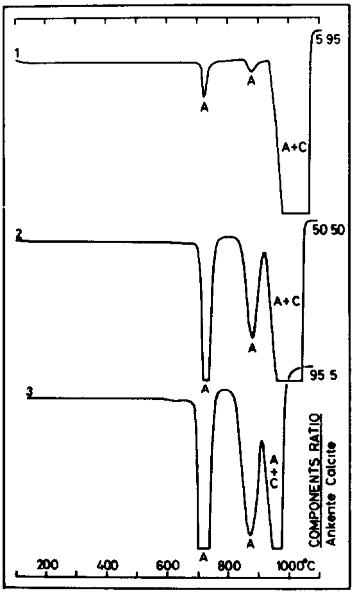

Fig. 7. DTA curves of artificial mixtures of ankerite with calcite to illustrate the identification and detection limits of these two carbonate minerals when present together. Determined in flowing CO_2. Peaks for ankerite and calcite are marked A and C, respectively.

small amounts of calcite, when present with large contents of ankerite, are not detectable (Fig. 7, curve 3), see Fig. 5, curve 5 for comparison.

Furthermore, dolomite ($CaMg(CO_3)_2$) may be distinguished from a 50 : 50 mixture of calcite ($CaCO_3$) and magnesite ($MgCO_3$) of the same chemical composition [2]. This can be seen by comparison of Fig. 1, curve 1 which shows a 95% curve of dolomite with peak temperatures at ~ 800 and 1000°C, and Fig. 2, curve 3 together with Fig. 7, curve 1 which show curves from 95% magnesite and calcite which, respectively, occur with peak temperatures of ~ 725 and 1025°C. Thus the much closer position of the two peaks of dolomite distinguishes this mineral from a mixture of magnesite and dolomite.

Associated detailed research, in flowing CO_2, on the dolomite-ferroan dolomite-ankerite series has already been published [14]. This established that three endothermic peaks were present for all members containing Fe, that with increasing Fe content the second peak size progressively increased and the first peak temperature decreased. The limit of detection of Fe (expressed as $FeCO_3$) appears to be ~ 1% by weight.

CONCLUSIONS

Differential thermal analysis determinations of anhydrous carbonate minerals under furnace atmosphere conditions of flowing CO_2 greatly improve peak height, attenuation and separation. As a result, the identification, content evaluation and detection limits are much improved when present singly or in mixtures, and the application of DTA to elucidate carbonate-bearing materials is enhanced.

REFERENCES

1 S.St.J. Warne, J. Inst. Fuel, 48, (1975) 142.
2 K.H. Wolf, A.J. Easton and S.St.J. Warne, in G.V. Chilinger, H.J. Bissell and R.W. Fairbridge (Eds.), Carbonate Rocks, Pt.B. (Physical and Chemical Aspects), Elsevier, New York, 1967, pp. 253–341.
3 S.St.J. Warne, in C. Karr, Jr (Ed.), Analytical Methods for Coal and Coal Products, Vol. III, Academic Press, London, 1979, pp. 447–477.
4 S.St.J. Warne, Thermochim. Acta, 76 (1984) 179.
5 D.A. Young, Decomposition of Solids, Pergamon Press, London, 1966.
6 F.Z. Bischoff, Anorg. Chem., 262 (1950) 288.
7 R.A. Haul and H. Heystek, Am. Mineral., 37 (1952) 166.
8 H. Henmi, T. Hirayama, N. Mizutani and M. Kato, Thermochim. Acta, 96 (1985) 145.
9 S.St.J. Warne, Chem. Erde, 35 (1976) 251.
10 P.K. Gallagher and S.St.J. Warne, Thermochim. Acta, 43 (1981) 253.

11 S.W. Smith, D.R. Johnson and M. Müller-Vonmoos, Thermochim. Acta, 8 (1974) 45.
12 R. Otsuka, Thermochim. Acta, 100 (1986) 69.
13 K. Iwafuchi, C. Watanabe and R. Otsuka, Thermochim. Acta, 60 (1983) 361.
14 S.St.J. Warne, D.J. Morgan and A.E. Milodowski, Thermochim. Acta, 51 (1981) 105.
15 S.St.J. Warne, Thermochimica. Acta, 110 (1987) in press.
16 K.H. Stern and E.L. Weise, High Temperature Properties and Decomposition of Inorganic Salts, Part 2, Carbonates, Natl. Bur. Stand., Washington, D.C., National Standard Reference Data Series, 1969.
17 S.St.J. Warne and R.C. Mackenzie, J. Therm. Anal., 3 (1979) 49.
18 S.St.J. Warne and B.D. Mitchell, J. Soil. Sci., 30 (1979) 111.