

APPLICATIONS OF THERMAL ANALYSIS TO CARBONATE MINERALOGY

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ABSTRACT

Thermal analysis (TA) methods have proved to be particularly applicable to the detection, identification and evaluation of the content, composition and decomposition reactions of carbonates in general and the anhydrous species in particular. The use of variable atmosphere TA conditions for the elucidation of such carbonates, singly or in mixtures, has further improved identification and detection limits. It also provides valuable models for the wider applications of these techniques, in relation to carbonate isomorphous substitution series, carbonate-containing deposits, mixtures, economic accumulations and to other mineral groups.

INTRODUCTION

The use of the technique of “variable atmosphere” thermal analysis (TA) and in particular its application to differential thermal analysis (DTA) and to a lesser extent to thermogravimetry (TG), evolved gas analysis (EGA) and thermomagnetometry (TM) has proved to be of very considerable basic and applied value, e.g. refs. 1, 2 and 3, respectively.

This variable atmosphere aspect has been strongly developed and widely applied by Warne whose published results are best summarised in ref. 4 and to whom Earnest [5] has attributed the introduction of the term “Variable Atmosphere Differential Thermal Analysis”.

The techniques have wide applications, to the detection, identification, content appraisal, composition and decomposition reactions of carbonate minerals and carbonate bearing deposits. Applications may be to carbonates singly [1], in mixtures [4], to isomorphous substitution series [6], while under conditions of flowing CO₂ DTA is capable of detecting contents down to ~ 0.25% [4].

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VARIABLE ATMOSPHERE EFFECTS—OVERVIEW

With this variable atmosphere technique, the furnace atmosphere gas surrounding the sample under test may be selected as to type or mixture (i.e. $N_2:O_2$ ratio) and whether or not it has been made to replace the original furnace air in a static way. Alternatively, it may be self-generated, or constantly made to flow over, or through, the sample under test, where the terms flowing or dynamic are used respectively. Additional modes are at ambient, increased pressure or the converse, under variable degrees of vacuum.

Thus, by the use of different furnace gas atmospheres (e.g. N_2 , O_2 or CO_2) individual DTA peaks may be suppressed, enhanced, attenuated and preferentially moved up or down the temperature scale (the last being produced by increasing or decreasing the partial pressure of CO_2 from flowing to vacuum conditions, respectively). The exception is crystallographic inversion/reversion reactions which are unaffected by gas conditions [4,7]. In this way specific types of reaction may be identified and peak superpositions preferentially resolved [8].

DTA CURVE CONFIGURATIONS AND DETECTION LIMITS IN AIR AND NITROGEN

It has been established from sequences of artificial mixtures of specific anhydrous carbonate minerals, diluted with progressive proportions of inert calcined alumina (Al_2O_3), that the detection limits in static air atmospheres are of the order of 1–1.5% by weight [8] with the exception of siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$), which behave similarly and in the following manner.

Siderite breaks down endothermally, releasing CO_2 to form FeO , which *immediately* oxidises exothermally in the presence of O_2 to form Fe_2O_3 . Thus the resultant endothermic and exothermic peaks are usually partially superimposed, which results in both being recorded with reduced peak size (Fig. 1, curves 1–4). Of these, the exothermic reaction is somewhat greater [9]. Thus under conditions of low siderite contents, where the CO_2 release is too small to decrease the O_2 availability, or when O_2 is readily available under conditions of flowing O_2 , only a relatively small resultant exothermic peak is recorded [10] (Fig. 1 curves 1 and 5). Resultant siderite DTA curve configurations are therefore strongly variable and may be surprisingly small in air/ O_2 and its detection limit poor. Thus for accurate diagnostic purposes and content evaluations, determinations must be made under flowing inert atmosphere conditions, e.g. O_2 free N_2 [4,10] (Fig. 1, curve 6).

In addition, the presence of siderite in the original sample containing no other *oxidisable residues* after DTA in an inert gas may be confirmed by

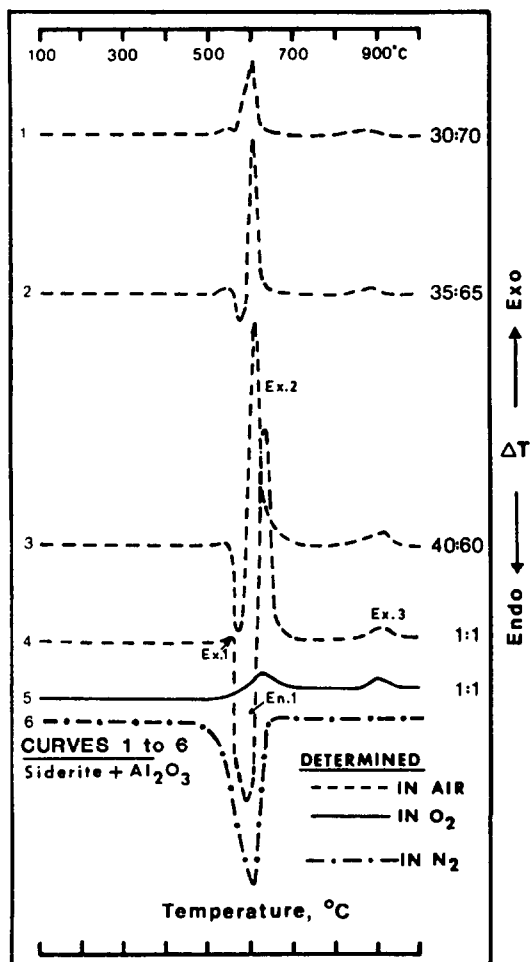


Fig. 1. DTA curves 1–6 are from siderite diluted with 70, 65, 60, 50, 50 and 50 wt% of Al₂O₃, respectively, determined in the gases indicated. Note the progressive superposition of the exothermic peak with dilution until it shows as a small resultant at ~30% in air or at ~50% in flowing O₂, and the removal of exothermic effects in N₂.

allowing the access of O₂ at the high-temperature end of the DTA heating or cooling curve. Under these conditions an immediate exothermic reaction peak will be produced by the oxidation of the FeO, decomposition product of siderite, to Fe₂O₃.

Rhodochrosite, MnCO₃, behaves similarly, decomposing endothermally to MnO, which rapidly oxides exothermally to Mn₂O₃ if O₂ is available.

A further complexity with the use of DTA curves, determined in air or N₂ for carbonate mineral identifications, concerns those with multi-peaked endothermic decomposition curves, e.g. dolomite CaMg(CO₃)₂ and ankerite, Ca(Mg,Fe)(CO₃)₂. As the content of these minerals in samples decreases,

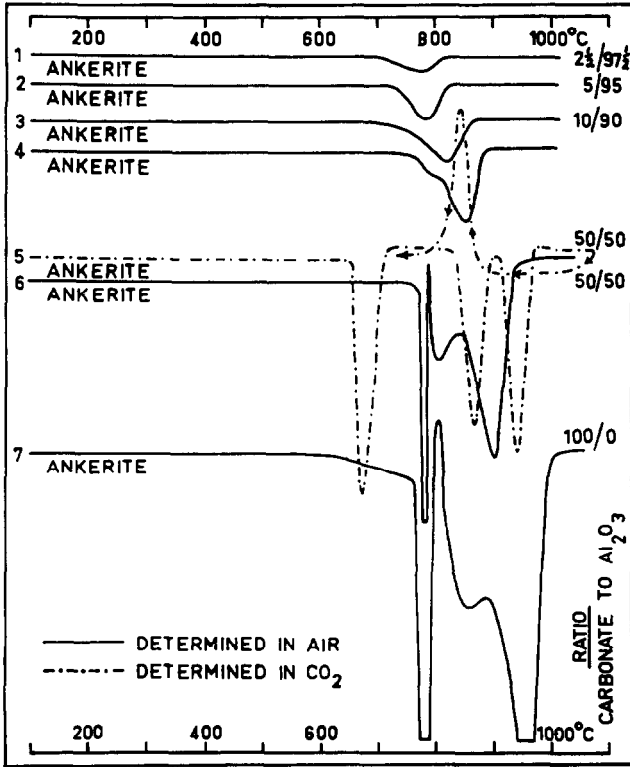


Fig. 2. DTA curves of ankerite diluted with Al_2O_3 as indicated. Curves 1, 2, 3, 4, 6 and 7, determined in air, show progressive peak coalescence as ankerite content falls. Curve 5 shows effects of determination in flowing CO_2 and the exothermic CaCO_3 re-carbonation cooling curve peak. (After Wolf et al., [11].)

their multip peaked DTA curve configurations progressively fuse into a single composite peak (Fig. 2, cf. curves 1–7, excluding 5). Thus small contents (< 20%) are represented by a much less diagnostic, broader endothermic feature [8,11].

This trend is even more pronounced in vacuum, which negates the effects of increased partial pressures, as even self-generated CO_2 gas cannot build up and the decomposition temperatures and peaks fall. As a result, even at high contents of these multi-peaked minerals, little or no peak separation takes place [15,31] and a major identification characteristic is lost.

It is relevant that the peak temperature and separation/fusion movements are so responsive to gas (CO_2) partial pressure changes that the DTA of dolomite has been suggested as a method of evaluating atmosphere control [15]. With this in mind, two standard reference dolomites of established composition are available for purchase, i.e. British Chemical Standard 368 and U.S. National Bureau of Standards, Standard Dolomite 88a.

It is noteworthy that if inert gases other than N_2 are used, the resultant

DTA peak areas from duplicate samples will differ predictably, i.e. those determined under He and Ar compared to N₂ are much smaller and somewhat larger, respectively, due to the thermal conductivities of He and Ar being ~ 6 times and $\frac{2}{3}$ that of N₂ [12].

A further example is that the oxidation (burning) reaction of coal (and oil shale) may be prohibited or enhanced in flowing oxygen-free nitrogen or air conditions, respectively. Within the temperature range of this large exothermic feature lie the very much smaller peaks of the minerals found in coal which are thus negated and fail to be recorded [14]. However, in inert atmosphere conditions the DTA of coal (or oil shale) can be reduced to a relatively featureless curve on which endothermic mineral-caused modifications, particularly carbonates, may be clearly identified [4,8,13]. Conversely, determinations under flowing air conditions enhance the *exothermic* burning effects of carbonaceous materials to the extent that even small amounts of organic material (down to ~ 0.25%) * may be detected in materials of wide diversity [14] and even in carbonate rocks where the endothermic peak of calcite (CaCO₃) occurs at a considerably higher temperature.

DTA CURVE CONFIGURATIONS AND DETECTION LIMITS IN CARBON DIOXIDE

From artificially prepared dilution sequences of individual anhydrous carbonate minerals (with Al₂O₃) it has been established that DTA determinations in flowing CO₂ furnace atmosphere conditions have several important effects compared to comparable determinations in N₂ or air. These differ depending on whether the carbonates decompose with single or multiple endothermic, CO₂-liberating decomposition reactions.

The group with one decomposition peak contains, in order of increasing peak temperature, the minerals smithsonite ZnCO₃, siderite FeCO₃, magnesite MgCO₃ and calcite CaCO₃, while the multi-peaked curves are produced, for example, by dolomite CaMg(CO₃)₂, ferroan dolomite-ankerite Ca(Mg,Fe)(CO₃)₂ and cerussite PbCO₃.

In CO₂ the single endothermic peak of minerals in the first group occurs with the same area, but is narrower and has a much greater peak height. Also, this whole peak, characterised by its initial, peak and final temperatures, moves up scale to occur at considerably higher temperatures [16]. Furthermore, with diminishing carbonate mineral content (dilution) the single peak maintains its temperature position (peak temperature) [17]. This is in contrast to the decreasing content-related progressive falls in peak temperature, in air, which form the basis of the valuable "Proben-Abhan-

* Such effects are further enhanced by determinations in flowing oxygen.

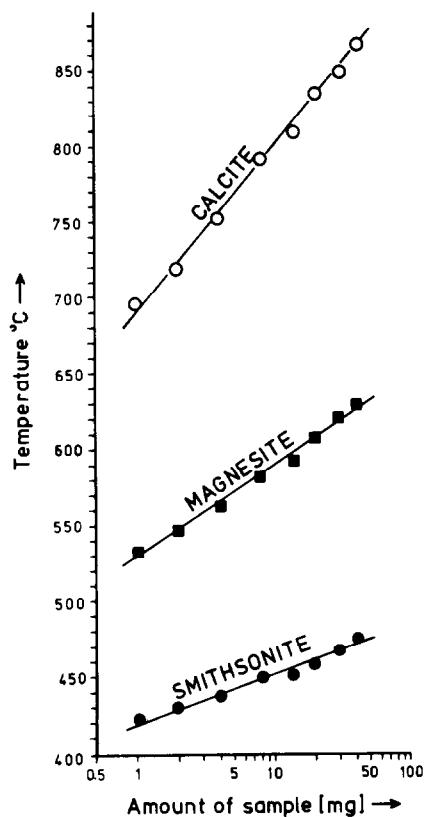


Fig. 3. Examples of PA curves of calcite, magnesite and smithsonite to illustrate diagnostic differences between minerals: (a) different sets of peak temperatures (position of PA curves); and (b) contrasting rates of peak temperature falls (slope of PA curves). (Original curves determined in air with a Du Pont 900 DTA Unit.)

gigkeit" (PA) curves method established in detail by Smykatz-Kloss [18]. Such (PA) curves represent the plot of change in peak temperature (t) on a normal scale (ordinate) against the known sample content (in mg) of each mineral present, on a logarithmic scale (abscissa) (Fig. 3). From such curves obtained from samples of identical mass, individual mineral contents may be determined, but not for carbonates if determined in flowing CO_2 conditions due to their stable peak temperature as described above [19].

Under the same CO_2 purging conditions, the multiple endothermic peaks of the second group behave differently. The initial peak appears displaced somewhat down scale, while the higher temperature peak (dolomite) or peaks (ankerite) move considerably up scale and show increased attenuation [20] (Fig. 2, cf. curves 5 and 6). Thus markedly improved peak definition and separation takes place. Furthermore, this much increased peak separation, as shown by their peak temperatures, remains essentially constant

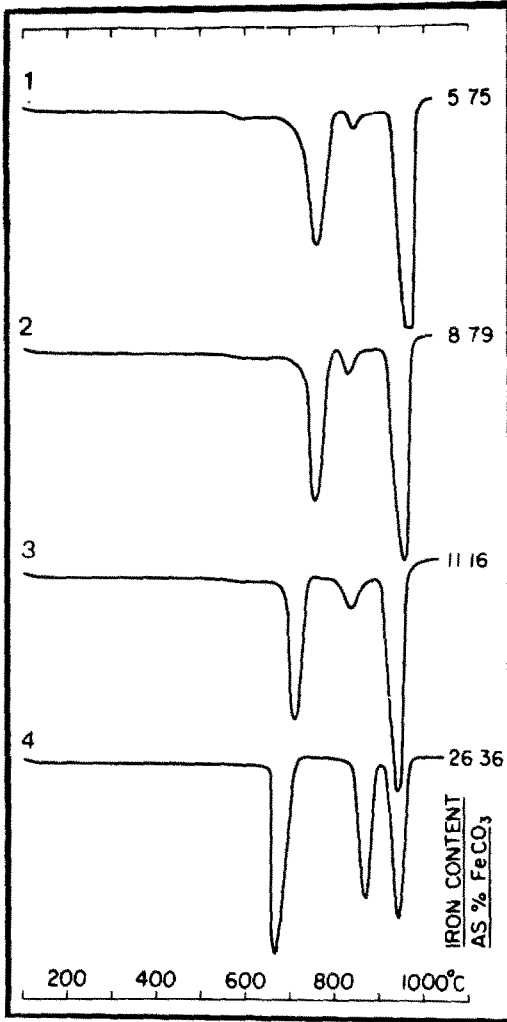


Fig. 4. DTA curves of members of the ferroan dolomite-ankerite series determined in flowing CO_2 showing increased middle peak size and falling first peak temperature with increasing Fe content. (After Warne et al. [6].)

with decreasing content (progressive dilution with Al_2O_3) [17]. Thus these diagnostic peaks (e.g. dolomite and ankerite) remain individually recognisable right down to their limits of detection [17] *. They therefore do not coalesce into the single, broad endothermic features of poor diagnostic value which typically result from medium to low content determinations in air, N_2 or vacuum [8,11,15,31].

* First peak characteristics of dolomite in CO_2 have been related to chemical composition, structural deviation and grain size [32] and are also affected by salts [27], while determinations at above ambient CO_2 pressures cause further increased peak separation [33].

The isomorphous substitution series, dolomite-ferroan dolomite-ankerite, results from the progressive substitution of Fe for Mg in the dolomite lattice. Of the three endothermic peaks clearly resolved in flowing CO₂ (when Fe is present), the middle one represents the Fe content [21]. Later, detailed research on this series [6] established that increasing Fe contents are directly relatable to progressive enlargement of the second peak and first peak temperature falls (Fig. 4). The accuracy of this method for identifying members of this series is considered better than obtainable with X-ray diffraction. In addition, Fe substituted in the dolomite structure may be distinguished from that of siderite, even when both minerals are present together [6].

In CO₂, the peak attenuation, up scale movement of single peaks, together with enlarged (and preserved) peak separation on DTA curves of carbonates, increases their limits of detection (down to ~ 0.25%) and identification [16]. Such peak movements are not only of diagnostic value, as non-carbonate decomposition peaks [8] and crystallographic inversions [7] are not affected, but also aid in the resolution of superimposed peaks if caused by carbonate and non-carbonate mineral decompositions [8,22].

Cooling curves in CO₂ are also of value, as CaO alone of the decomposition products of carbonate minerals will recarbonate to form CaCO₃, producing a clear *exothermic* peak (Fig. 2, curve 5). In this way the CaO content, whether from calcite, dolomite or ankerite, may be monitored free from interference of other peaks on the heating curve. Pertinent to this aspect is that strontianite SrCO₃ and witherite BaCO₃ show one (~ 875°C) and two (~ 750 and 970°C) crystallographic reversion peaks, respectively, on their DTA cooling curves, irrespective of furnace atmosphere conditions. However, their presence on cooling curves produced under flowing N₂ distinguishes them from the CaO re-carbonation peak which will be absent.

CURVE CONFIGURATIONS (TG) IN CARBON DIOXIDE

For the same reasons that the increased partial pressure of CO₂ causes greater DTA peak, attenuation, separation and up scale movement, so also do the weight losses associated with these reactions behave in a similar way. Milodowski and Morgan [2] have shown how the three individual decomposition weight loss reactions of ankerite are virtually completely separated and therefore quantifiable when determined in flowing CO₂, also for dolomite [4]. Such quantifiable weight losses have been related to the complex decomposition mechanism of ankerites [2].

A further advance has been made using simultaneous TG/DTA equipment in relation to the quantification (by weight-related loss) of individual diagnostic DTA peaks obtained from natural materials containing carbonates. Good examples in relation to carbonates in oil shale have been described [23].

EVOLVED GAS ANALYSIS

Morgan and his co-workers have developed the application of simultaneous evolved gas analysis (EGA) and DTA by passing the gaseous product from TA directly into non-dispersive infrared detectors for the continuous measurement of CO_2 and CO contents. The equipment used [24] and the CO_2 and CO gas evolution profiles of ankerite have been described [2], while CO_2 evolution profiles of the major anhydrous carbonates have been shown not only to be diagnostically different but to be detectable down to the 100 ppm level [25]. A further example, extending EGA, involving the application of simultaneous DTA, TG and MS (mass spectroscopy) to the complex carbonate caledonite $\text{Pb}_5\text{Cu}_2(\text{CO}_3)(\text{SO}_4)_3(\text{OH})_6$, has been described using a Stanton-Redcroft prototype unit [26].

THERMOMAGNETOMETRY

The technique and applications of thermomagnetometry (TM) have been reviewed in the present volume [28], and it is potentially applicable to materials which show ferromagnetic properties due to their contents of Fe, Co and Ni (together with a number of rare-earth elements at low temperatures [29]). However, it has only been applied, to date, to the Fe-bearing carbonates siderite and ankerite, i.e. to study their decomposition (Fig. 5), indicate the presence of the major impurities Mg and Mn, to relate the increasing impurity of resultant spinels to progressive falls in Curie points (T_c) [2,3] and for the determination of the Fe contents of coal [30].

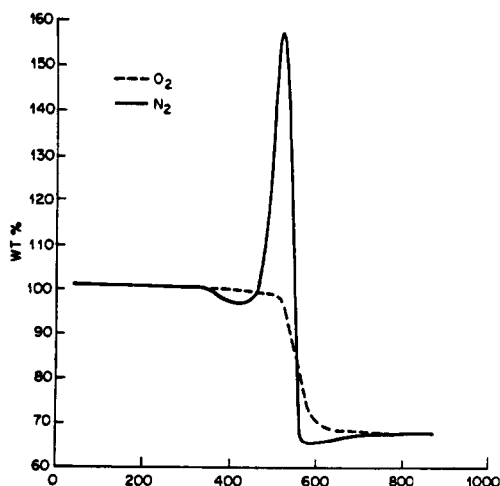


Fig. 5. Comparison of TG and TM curves of siderite with magnet above the sample (for TM) to illustrate the detection of a transient magnetic phase during the decomposition of siderite. (After Gallagher and Warne [3].)

CONCLUSIONS

Comprehensive coverages by DTA curve configurations, determined in air, have been published by Webb and Krüger [27] and Smykatz-Kloss [18]. These compilations form the basis upon which carbonate mineral identification and evaluation, using TA methods, is based. Thus they not only indicate the type and temperature of the reactions involved, on heating, but provide vital comparative and diagnostic data. With this information available, other methods, i.e. variable atmosphere TA, DTA, TG, EGA and TM, may be applied under known preset conditions to measure additional related TA properties (as described above). These in turn aid in the detection, identification and evaluation of content, composition and decomposition reactions of carbonate minerals singly, in mixtures, as isomorphous substitution series and as components of deposits of economic value.

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