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THE DECOMPOSITION OF ANHYDROUS CARBONATE MINERALS IN COAL AND OIL SHALE ASHES PRODUCED AT TEMPERATURES OF 400 AND 575°C

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ABSTRACT

Several simple anhydrous carbonate minerals found in coal and oil shale decompose at or below 400°C in air. These are siderite, rhodochrosite and magnesite, the decomposition temperatures of which are lowered or raised (compared to air) if determined in atmospheres of flowing N_2 or CO_2, respectively. Decomposition temperatures and rates have been evaluated by thermogravimetry, to constant weight and for isothermal mass change determinations over 40 min at 375, 400, 425 and 575°C. The decomposition data obtained relate directly to the mineralogical composition of coal ash (400°C) and oil shale retorting.

INTRODUCTION

In the excellent paper Mineralogy of Ash of some American Coals: Variations with Temperature and Source, by Mitchell and Gluskoter [1], samples from a wide range of United States coalfields were studied. In these untreated coals and resultant low and high temperature ashes the presence of the anhydrous carbonate minerals, siderite ($FeCO_3$), rhodochrosite ($MnCO_3$), magnesite ($MgCO_3$), witherite ($BaCO_3$), strontianite ($SrCO_3$) and ankerite $Ca(Mg, Fe)(CO_3)_2$ were not detected and therefore not considered.

A number of studies of the mineralogy, chemistry and low/high temperature ashing of coal inorganic constituents undertaken in recent years have been reported [1] and added to [2,3]. From these studies it has been generally concluded [1] that "the minerals found in ash treated at 400°C for 1/2 h are the same as those in low-temperature ash (150–200°C) and, generally, are the original coal minerals". Furthermore, Watt [4], in his review of coal ashing, indicated that most coal minerals are stable up to at least 380°C [1].

In this context three of the above six carbonates (i.e., siderite, rhodochrosite and magnesite) are important because they may be expected to decompose at temperatures in the region of 400°C. Two of them (siderite and ankerite) are listed as common in coals [5], in particular from Australia (siderite) [6,7] and the United Kingdom (ankerite) [4,7,8], respectively.

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In addition, there is the isomorphous series where Fe substitutes for Mg in the dolomite lattice to form the continuous dolomite, ferroan dolomite, ankerite series. Previous work [9,10] has established that as the Fe content of members of this series increases, the decomposition temperature falls.

A wide range of carbonate compositions in this series have been identified from coals and portrayed on triangular diagrams [4]. These are important because of the effects their variable compositions have on ash fusion temperatures [11] and evolved sulphur complexing and retention [12,13]. Additional relationships between ash chemical compositions and fusibility have been reviewed [14].

On the other hand, rhodochrosite, magnesite, strontianite and witherite, although not common in coals [2,15] are included to complete the coverage.

All six of the above minerals, together with calcite and dolomite are known to occur in oil shales [16].

EXPERIMENTAL

Thermogravimetry (TG) and differential thermal analyses (DTA) provide suitable experimental methods for the evaluation of the decomposition

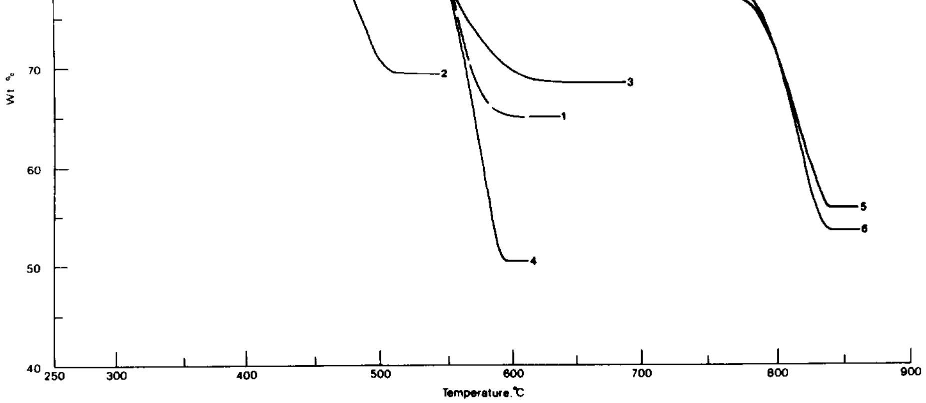

Fig. 1. TG curves of minerals all determined at a heating rate of 5°C min^{-1} in static air. (1 and 2) siderite, (3) rhodochrosite, (4) magnesite, (5) ankerite, and (6) dolomite. Contrasting symbols highlight the marked TG differences shown by siderites 1 and 2. For chemical compositions see Table 1, minerals numbered 1, 2, 6, 9, 10 and 11, respectively.

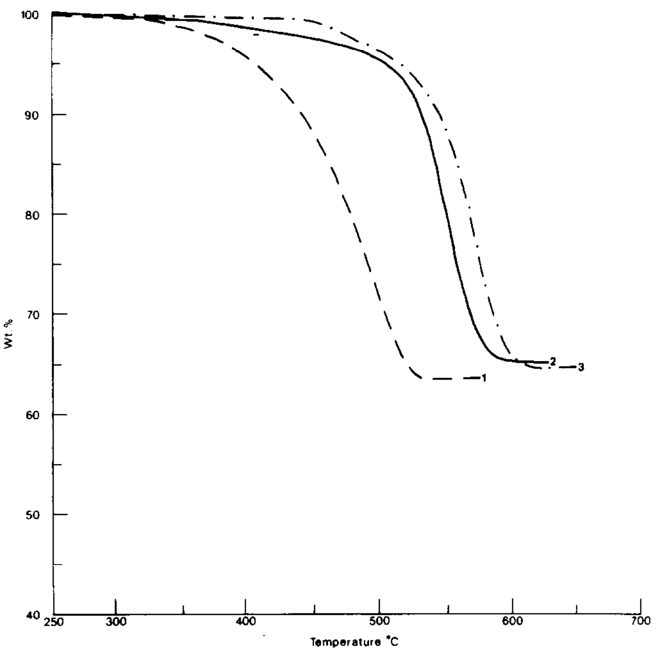

Fig. 2. TG curve of siderite (curve 2 Fig. 1), determined at a heating rate of 5°C min^{-1}, in flowing N_2 (- - - - - -), static air (———) and flowing CO_2 (· — · — ·).

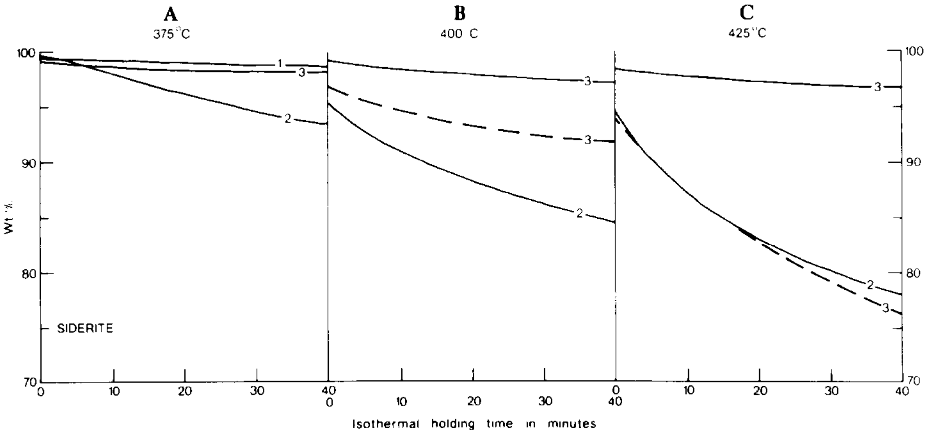

Fig. 3. Isothermal mass change determination curves obtained from natural siderites ($FeCO_3$), at temperatures of 375°C (A), 400°C (B) and 425°C (C) in static air (———) and flowing N_2 (- - - - - -). As siderites 1 and 3 above behaved similarly, curves for sample 1 have been omitted from the 400 and 425°C plots (B and C above). For chemical compositions of siderites used to produce curves 1–3 above, see minerals 1–3 in Table 1, respectively.

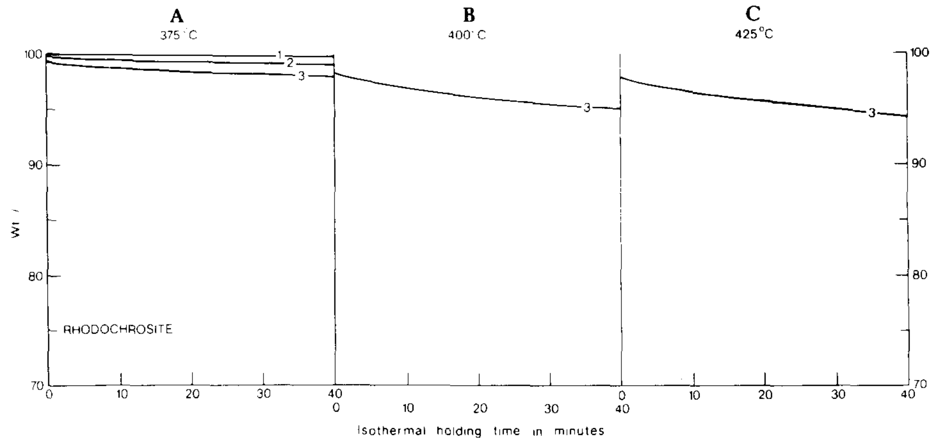

Fig. 4. Isothermal mass change determination curves obtained from natural rhodochrosites ($MnCO_3$), at temperatures of 375°C (A), 400°C (B) and 475°C (C) in static air. For clarity only the most easily decomposed rhodochrosite was determined at 400 and 425°C. For chemical compositions of rhodochrosites used to produce curves 1–3 above, see minerals 4–6 in Table 1, respectively.

behaviour of minerals. In this case TG is preferred as it automatically and continuously records the weight variations of a sample as its temperature is varied at a constant rate (Figs. 1 and 2) or is maintained at a constant (isothermal) temperature (Figs. 3–6).

In this study both these TG methods were used to establish and characterise decompositions which might occur in anhydrous carbonates and particularly those in the region of 400 and 575°C.

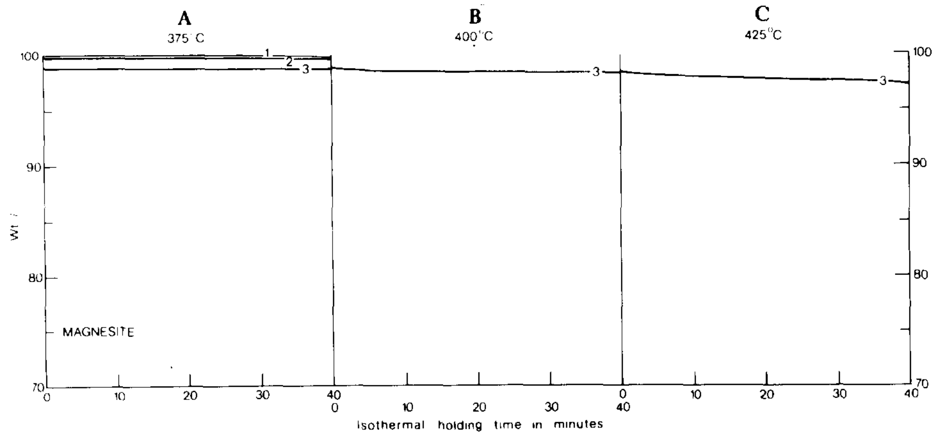

Fig. 5. Isothermal mass change determination curves obtained from natural magnesites ($MgCO_3$) at temperatures of 375°C (A), 400°C (B) and 425°C (C) in static air. For clarity only the most easily decomposed magnesite was determined at 400 and 425°C. For chemical compositions of magnesites used to produce curves marked 1–3 above, see minerals 7–9 in Table 1, respectively.

The identity of the specific minerals investigated was confirmed by the X-ray powder film method and their chemical compositions are listed in Table 1.

The TG runs were determined from 30-mg samples in furnace atmosphere conditions of static air, flowing oxygen-free nitrogen, or flowing high purity carbon dioxide, at ambient pressure, with a constant heating rate of 5°C min^{-1}, using a Stanton Redcroft STA 781 simultaneous TG/DTA unit. Sample holders were of thin-walled platinum crucible type.

The isothermal mass change determinations were made with the same equipment and sample mass.

The first position plotted on the isothermal mass loss curves (Figs. 3–6) represents the weight of each sample when held for zero time at temperatures of 375, 400, 425 and 575°C, respectively.

To reach these zero time points the samples were heated to the required temperatures at a rate of 50°C min^{-1}. The samples were then held at the

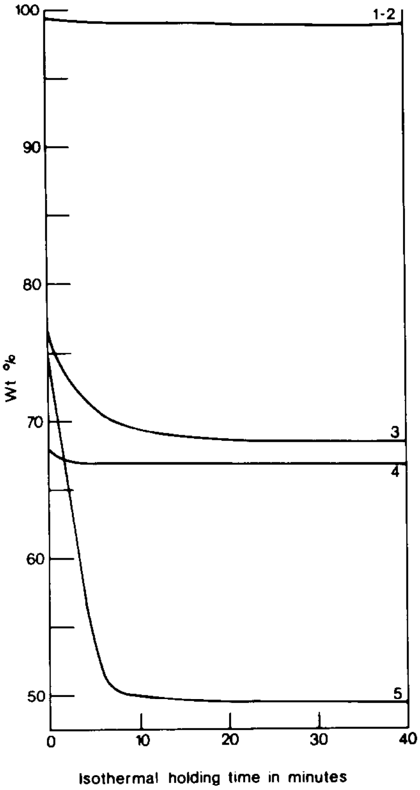

Fig. 6. Isothermal mass change determination curves obtained from natural carbonates at a temperature of 575°C. (1 and 2) dolomite and ankerite, (3) rhodochrosite, (4) siderite, and (5) magnesite. All were determined in static air. Samples took 11 min, at maximum heating rate of 50°C min^{-1}, to reach the 575°C isothermal temperature. For clarity siderite 2 (see Fig. 1) was omitted as complete decomposition occurred before reaching 575°C. It plots as a horizontal line marginally above the constant weight part of curve 3. (The same carbonates as used in Fig. 1.)

TABLE 1

Identity and chemical compositions, expressed as weight percent carbonate components of the eleven natural anhydrous carbonate minerals used for the thermogravimetric investigations

	No.	$CaCO_3$	$MgCO_3$	$FeCO_3$	$MnCO_3$	Fe_2O_3	Insoluble
Siderite	1	0.9	7.6	85.5	4.0	0.1	1.9
Siderite	2	0.4	4.2	95.3			
Siderite	3	0.4	16.4	79.2	1.0	3.0	
Rhodochrosite	4	1.9	6.1	0.9	92.0		
Rhodochrosite	5	5.3	1.4	4.2	88.3	0.6	
Rhodochrosite	6	5.1	4.2	2.3	87.9	—	0.5
Magnesite	7	1.0	93.2	2.1	0.1	0.2	3.3
Magnesite	8	0.9	98.8				0.1
Magnesite	9		98.2				1.6
Ankerite	10	54.5	35.2	11.1			
Dolomite	11	53.7	44.6		0.1	0.3	1.4

preselected temperature and the weight losses measured continuously for 40 min. In each case the loss after 30 min has been clearly indicated.

All samples used were ground to $-150^{\#}$BSS (-75 μm).

RESULTS

Comparison of the detailed thermal analysis data has shown that considerable differences in decompositional characteristics occur between these carbonates.

Furthermore, in order to evaluate the effects of heating minerals isothermally at temperatures in the order of 400°C for 30 min, identical samples have also been heated at ±25°C, i.e., at 375, 400 and 425°C.

Additional isothermal runs at 575°C were made to provide comparative decomposition data relative to oil shale retorting temperatures.

Comparison of carbonate TG curves

In the context of the decomposition of the common carbonate minerals in coal, it has been established by DTA [11,17] that (a) mineral chemical composition, and (b) the composition of the furnace atmosphere, considerably alter the decomposition temperatures and rates.

To place these variations on a comparative basis complete TG curves of the carbonates under discussion were determined (Fig. 1). From this figure it can be seen that under the same experimental conditions, the resultant TG curves show considerable differences.

Thermogravimetric determinations in air

Firstly, based on the increasing temperature at which weight loss/decomposition starts the carbonates fall into the order of siderite followed by rhodochrosite, magnesite, ankerite and dolomite. Strontianite and witherite do not decompose in the temperature range studied, their decomposition peak temperatures being stated as 1200 and 1450°C, respectively [18]. However, it has been demonstrated subsequently that strontianite shows perceptible dissociation under isothermal conditions at temperatures as low as 850°C in air [19].

It is noteworthy that should smithsonite ($ZnCO_3$) be found to occur in coal or oil shale, that its decomposition temperature is significantly below that of siderite [18,20].

Secondly, the amount of weight loss on complete decomposition increases progressively in the order siderite and rhodochrosite (comparable) *, ankerite, dolomite (comparable) and magnesite (Fig. 1).

Thirdly, the decomposition of siderite and rhodochrosite clearly starts below 400°C.

Thermogravimetric determinations in nitrogen and carbon dioxide

It has been established previously that the decomposition temperatures of these carbonate minerals are affected considerably by the composition and properties of the atmosphere surrounding the sample [17,21]. In principle, carbonate decomposition reactions, in order to take place, have to overcome the partial pressure of any CO_2 in the surrounding atmosphere. Thus, as this partial pressure increases from pure N_2 to air to pure CO_2 (at ambient pressure), the decomposition temperatures also rise progressively (Fig. 2).

This factor is considered important because the heating of coal or oil shale samples or charges is unlikely to always be in the equivalent of normal air conditions. Thus, CO_2 content may vary from very low (comparable to N_2 purging) to high for some carbonate rich oil shales (comparable to CO_2 purging).

To illustrate this point, TG curves of a typical siderite were determined in flowing N_2, static air and flowing CO_2 (Fig. 2). The indicated falls and rises in the decomposition onset temperatures compared to air are in the order of 40 and 80°C, respectively. This general pattern persists until decomposition is complete, which occurs at progressively lower temperatures in CO_2, air and N_2, respectively.

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* Smithsonite would be located between rhodochrosite and ankerite and calcite between ankerite and magnesite.

Isothermal mass change determinations

To clarify the mineral decomposition characteristics, i.e., the amount, rate and rate variations, with time, at 400°C (relatable to coal ashing) and 575°C (relatable to oil shale retorting) isothermal mass change determinations on the individual carbonate minerals were made in static air and, where pertinent, also in flowing N_2.

As 400°C appeared to be a marginal temperature, where decomposition has been established, additional runs at ±25°C (i.e., at 375 and 425°C) were made to establish more clearly the potential for decomposition at temperatures close to but significantly above and below 400°C.

Isothermal determinations at 375°C

Isothermal mass change determinations, in static air at 375°C (Figs. 3A, 4A and 5A) show that significant decompositional weight losses have taken place for all the siderites and rhodochrosites, while the samples of magnesite remain unchanged, viz., the weight losses for siderite and rhodochrosite, after 30 min, range from 1.5 to 5.3% and 0.2 to 1.8%, respectively, while the magnesite samples remained essentially unchanged except for a small initial absorbed water loss below 375°C. As the ankerites and dolomites examined herein were stable in the 375–425°C range they were not illustrated. (Calcite is also stable.)

More meaningfully, the weight loss data could be expressed as a percentage of the total weight loss on full decomposition. This would represent the amount of decomposition produced under set conditions. To achieve this, the weight losses figured (Figs. 1–6) would become increased by factors of approximately ×3 for siderite and rhodochrosite and ×2 for magnesite (minerals assumed pure).

The TG curves of siderite exhibit noticeable variation, while those of rhodochrosite do not.

In view of the general lowering of the decomposition temperatures produced in flowing N_2 (Fig. 2), the moderately stable siderite (Fig. 3A, No. 3) and least stable magnesite (Fig. 5A, No. 3) were re-run in flowing N_2 and a small additional weight loss and no weight loss resulted, respectively, compared to duplicate determinations in air.

Isothermal determinations at 400°C

In comparison to those obtained at 375°C the isothermal runs in static air at 400°C (Figs. 3B, 4B and 5B) indicate that after 30 min siderite, rhodochrosite and magnesite exhibit an increased rate and amount of decompositional weight loss. Again ankerite and dolomite show no weight loss.

Due to the variability of the decomposition rate of siderite two curves were featured which represent the range of differences exhibited (Fig. 3B, curves 2 and 3).

The weight losses, after 30 min, are of the order of 2.5–13.7% for siderite, 4.6% for rhodochrosite and 1.0% for magnesite. (Again the amount decomposed may be calculated from these figures.)

The effect of determining the moderately stable siderite (Fig. 3B, No. 3) and the least stable magnesite (Fig. 5B, No. 3) in flowing N_2 produced 5.0 and 0.5% extra weight loss, respectively, after 30 min compared to the determination in air (cf. the two curves marked 3 in Fig. 3B for siderite). Because of curve proximity the curve in N_2 was not included in Fig. 5B.

Ankerite and dolomite (together with calcite) are stable amd show no weight loss.

Isothermal determinations at 425°C

Isothermal runs determined in static air at a temperature increased by a further 25°C (i.e., at 425°C) show further intensification of the decomposition rates and amounts. Ankerite and dolomite (together with calcite) still remain stable.

Weight losses after 30 min are 3.2–20.1% for siderite, 5.0% for rhodochrosite and 2.6% for magnesite (the amount of decomposition may again be calculated).

The effect of determining siderite (No. 3) in flowing N_2 compared to air was very marked after 30 min, i.e., an extra 20% weight loss (cf. the two curves marked 3 in Fig. 3C). For magnesite (No. 3) the extra weight loss in flowing N_2 of only 1.0% was again not clearly plottable in Fig. 4C.

Still ankerite and dolomite (plus calcite) remain stable.

Isothermal determinations at 575°C

In order to provide a comparative set of data obtained at a considerably higher temperature and because of its relevance to oil shale retorting, an additional set of isothermal runs was made in static air at 575°C.

At this temperature, the more unstable minerals suffer rapid decomposition which is complete at 575°C in 0–5.5 min (siderite), 29 min (rhodochrosite) and 10 min (magnesite).

In addition, both ankerite (1.2%) and dolomite (0.6%) show slow decomposition over 30 min. Thus, the production of half calcinated products from members of the dolomite, ferroan dolomite, ankerite series starts at temperatures of approximately 570°C and the high iron content member ankerite starts to decompose at a somewhat lower temperature than the almost iron-free dolomite. (Calcite remains stable.)

The decomposition onset temperatures produced in flowing N_2 compared to air are similar for dolomite, but show significant decreases for ankerite [22]. Similarly, determinations in flowing CO_2 compared to air cause considerable falls in the decomposition onset temperatures of both dolomite and ankerite [17]. Of these the effect on ankerite is considerably greater with temperature falls of up to at least 110°C being recorded [17] as compared to determinations in air.

Finally, the temperature of formation of ashes may be determined by the presence or absence of these minerals. The ash formation temperature range is thus extended significantly below 400°C and more detailed information may be gained for samples heated to temperatures in this region.

CONCLUSIONS

Several simple anhydrous carbonate minerals found in coal and oil shale decompose in air when heated to temperatures in the region of 400°C. Specific isothermal runs at 375, 400, and 425°C indicate that siderite and rhodochrosite start to decompose by 375°C, magnesite by 400°C, while all three minerals undergo considerable decomposition at moderate rates by 425°C.

In this temperature range ankerite and dolomite (plus calcite) are stable and show no weight loss.

The decomposition of siderite and magnesite falls in flowing N_2 and rhodochrosite is assumed to be affected similarly. The application of this technique has produced a measurable decomposition of magnesite at 375°C, whereas it was stable in air.

After heating for 30 min at 575°C, siderite, rhodochrosite and magnesite suffer complete decomposition, while ankerite and dolomite show small weight losses (calcite is still stable).

The rates of decomposition (cf. full TG curves, Fig. 1) in decreasing order of magnitude are magnesite, siderite, rhodochrosite, dolomite and ankerite. Furthermore, the decomposition rate to produce the half calcinated product appears to be faster for dolomite than for ankerite, but starts at a lower temperature for the latter.

The stepwise decomposition profile of dolomite and ankerite, determined in air, results from a number of reactions which take place before full decomposition is achieved [23]. Thus, magnesium oxide (MgO) and dicalcium ferrite ($2\ CaO \cdot Fe_2O_3$; if iron is present in the lattice), result from the early periods of decomposition (half calcination), while the greater part of the CaO remains in the form of $CaCO_3$, until released on decomposition during the last, highest temperature, weight loss period.

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