

Gaylussite: Thermal Properties by Simultaneous Thermal Analysis

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Abstract

Simultaneous thermal analysis apparatus was used to determine the thermal properties of gaylussite over a temperature range from ambient to 1000°C at 10° per minute in several carefully controlled atmospheres. In a dry atmosphere, dehydration occurs in a single step, while in the presence of water, dehydration occurs in two steps. Dehydration converts gaylussite to the double carbonate, $\text{Na}_2\text{Ca}(\text{CO}_3)_2$, which generates the thermal effects above 250°C. From 250°C to 500°C thermal analysis indicates one major crystal change and two crystal inversions in the double carbonate. Above 500°C the thermal properties of the double carbonate are controlled by the presence or absence of CO_2 in the atmosphere surrounding the sample. In a CO_2 atmosphere $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ first melts, then decomposes to form Na_2CO_3 and CaO . In a CO_2 -free atmosphere the double carbonate decomposes to form Na_2CO_3 and CaO . Melting is again detected by thermal analysis; however, the material that melts is Na_2CO_3 formed from decomposition of the double carbonate.

Introduction

Gaylussite ($\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$) is found in Wyoming in Eocene Green River Formation oil shales (Fahey, 1962). Because minerals contained in oil shale are heated in the retorting process, a knowledge of the thermal properties of these minerals contributes to a basic understanding of oil shale's thermal behavior. Literature on thermal analysis of gaylussite is limited to Beck's (1950) interpretation of his differential thermal analysis curve that shows water loss in two steps. He suggests that the remaining "highly irregular" curve is produced by slow fusing of the mineral. His large exotherm between 500° and 600°C could not be duplicated in this study. Thermal properties of the double carbonate similar to the residue formed after gaylussite loses its water of hydration have also been discussed in the literature—Smith, Johnson, and Robb (1970); Billhardt (1969); Wilburn, Metcalfe, and Warburton (1965); and Niggli (1916). Because little is known about gaylussite, this paper reviews briefly the mineral's history and presents new data on the thermal properties of natural and synthetic gaylussite. The importance of the effect of different atmospheres on the thermal analysis of gaylussite is demonstrated.

History and Literature of Gaylussite

Gaylussite was first found at Lagunilla near the City of Merida, Venezuela, by J. B. Boussingault (1826) who named it after the French chemist, L. J. Gay-Lussac. Occurrences of gaylussite at Searles Lake, San Bernardino County, and Borax and Mono Lakes, Lake County, California (Haines, 1959; Pratt, 1896); Railroad Valley and Soda Lake of Ragtown, Nevada (Free, 1914); Sweetwater County, Wyoming (Fahey, 1962); Dtabusu-nor Lake in Inner Mongolia (Okada, 1937; Niinomy, 1930); and Tchaad Lake in Chad, Africa (Maglione, 1968), have been reported.

A mineral description for gaylussite is given in the standard text, *Dana's System of Mineralogy* by Palache, Berman, and Frondel (1951). X-ray powder patterns and crystal data are given on Card No. 12-255, Card No. 20-1088, and Card No. 21-343 in the JCPDS powder diffraction file. An X-ray powder pattern for a low-temperature form of $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ is given on Card No. 2-970 in the JCPDS file. The X-ray powder patterns for the high-temperature form are given by Billhardt (1969) and by Smith, Johnson, and Robb (1970).

Infrared spectra of gaylussite are reported by Estep, Kovach, Hiser, and Karr (1970), Adler and Kerr (1963), and Huang and Kerr (1960); and

luminescence studies are given in a paper by Parzanov and Sheveleva (1953). Manganese and strontium contents in naturally occurring gaylussite are presented in papers by Vinokurov, Zaripov, and Stepanov (1964) and Asari (1950). Commercial utilization of gaylussite found in Railroad Valley, Nevada, was considered in a paper by Free (1914).

Sources of Gaylussite

Naturally occurring gaylussite for this study was found in oil shale from Diamond Alkali Co., Reid No. 1 Corehole located 150 feet W/E and 1,251 feet N/S, Section 24, Township 16N, Range 109W, Sweetwater County, Wyoming. The gaylussite occurred in two $\frac{1}{8}$ -inch thick bands within a 3-inch band of gray clayey dolomite at a depth of 848.9 feet. The X-ray powder pattern for this sample is given on Card No. 12-255 in the JCPDS powder diffraction file. Because only a small amount of naturally occurring gaylussite was available for this study, synthetic gaylussite was prepared for use in some of the thermal analysis experiments. Methods for preparing synthetic gaylussite were used by Butschli (1907), Sherwood and Newlon (1964), and Brooks, Clark, and Thurston (1950); however, we found the following method to be quicker. An equimolar mixture of sodium carbonate and calcium carbonate was ground for 5 minutes in a mechanical grinder to produce fine particles and close contact necessary for reaction between the carbonates (Smith, Johnson, and Robb; 1970). The carbonate mixture was heated to 550°C under a CO₂ atmosphere for about 12 hours and then cooled and mixed. The heating-cooling-mixing step was repeated four times. After final cooling, a thick slurry was made by adding a small amount of water to the carbonate mixture. The slurry was air dried for several days to produce crystalline gaylussite which was checked for purity by X-ray. Small amounts of CaCO₃ and Ca(OH)₂ were present as contaminants. Except for peaks from CaCO₃ and Ca(OH)₂, the X-ray pattern of the synthetic gaylussite was essentially identical to the pattern for the natural gaylussite on Card No. 12-255 in the JCPDS file.

Experimental Work

Thermal behavior of gaylussite was investigated from ambient to about 1000°C by thermal analysis apparatus developed by the U.S. Bureau of Mines (Johnson and Smith, 1970). This apparatus pro-

vides simultaneous differential thermal analysis (DTA), thermogravimetric analysis (TG), and evolved gas analysis (EGA) on a single sample under controlled conditions (Smith and Johnson, 1967 and 1971). An important feature for providing accurate thermal analysis data is the thin, flat-pan sample and reference holders with differential temperature thermocouples spot welded directly to the bottom of each holder. The flat platinum pan is 0.003 inch thick, 0.75 inch in diameter, 0.05 inch deep, and weighs about 500 mg. The temperature-measuring thermocouple is spot welded to the bottom of the reference pan. DTA and temperature-measuring thermocouples are Platine¹ wire, 0.012 inch in diameter. A sample on the thin flat-pan holder in a layer no thicker than 0.05 inch is not affected by the usual thermal analysis problems of sample packing, gas evolution, expansion, and shrinkage during heating. The thin sample layer provides quick removal of gases evolving from the sample to prevent significant recondensations, interactions, and reevolutions.

An alternate, deep-well sample holder that limits passage of gases from a sample was used for studies in a self-generated atmosphere (Garn and Kessler, 1960). The deep-well sample and reference chambers are $\frac{1}{4}$ inch in diameter by $\frac{7}{8}$ inch deep in an Inconel block. Differential-temperature thermocouple junctions are in the center of the sample and reference chambers. The temperature-measuring thermocouple is in the reference chamber. Temperature-measuring and differential-temperature thermocouple wires are Chromel-Alumel, 0.012 inch in diameter.

A set of four figures are presented in this paper to demonstrate the thermal properties of gaylussite. In addition, the four figures serve to demonstrate the following specific features. Figure 1 presents simultaneous DTA-TG-EGA on naturally occurring gaylussite in a helium atmosphere. Figure 2 demonstrates that the thermal behavior of synthetic gaylussite at temperatures up to 800° is essentially the same as that of naturally occurring gaylussite. Figure 3 shows the thermal behavior of gaylussite in a CO₂ atmosphere. Figure 4 shows the thermal behavior of gaylussite in a deep-well sample holder, where gas evolution from gaylussite partially provides the atmosphere surrounding the sample (self-

¹ Reference to specific brand names is made for identification only and does not imply endorsement by the U.S. Bureau of Mines.

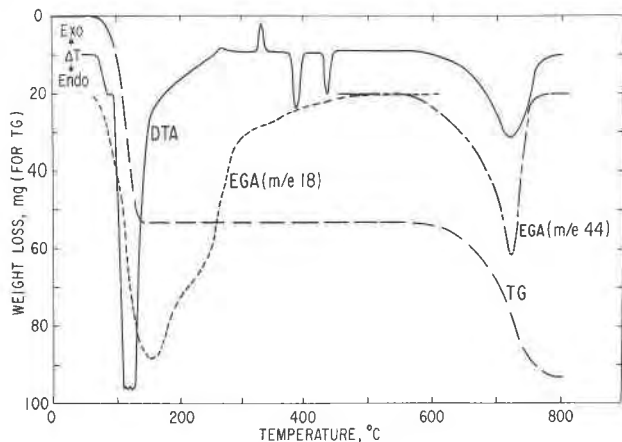


FIG. 1. Simultaneous DTA-TG-EGA on 198 mg sample of Wyoming gaylussite in a helium atmosphere.

generated atmosphere). Many commercial instruments are furnished with this type of holder. Hence the results obtained from these instruments would be expected to be similar to the results shown in Figure 4.

Experimental parameters for thermal analysis for the four figures presented in this paper are listed in Table 1. Gas flow rate around the sample was at a rate of 150 cc/min through a $\frac{1}{8}$ -inch I.D. sample chamber at atmospheric pressure. DTA peak locations on Figures 1 to 3 differ from peak temperatures discussed in the text. For Figures 1 through 3, the recorded temperatures shown on the figures have been corrected for inclusion in the text as recommended by the Committee on Standardization for the International Confederation for Thermal Analysis in a report by McAdie (1969). Corrected temperatures for Figures 1 through 3 are listed in Table 2. Because the authors were primarily interested in the results from the flat-pan sample holder,

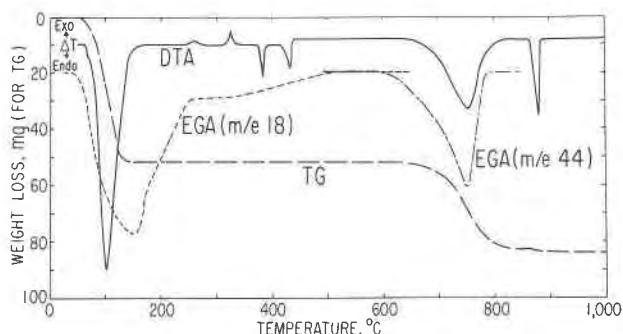


FIG. 2. Simultaneous DTA-TG on 211 mg sample of synthetic gaylussite in a helium atmosphere.

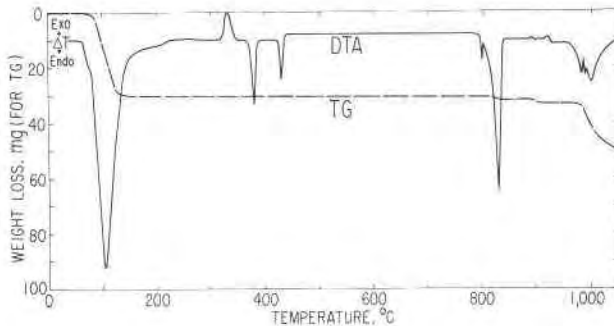


Fig. 3. Simultaneous DTA-TG on 121 mg sample of synthetic gaylussite in a CO_2 atmosphere.

only the flat-pan system was calibrated for temperature measurement. Onset temperatures listed in Table 2 are arbitrarily defined as the first detectable deviations of the DTA curves from the baselines preceding DTA peaks.

Heated samples were cooled to ambient temperature for examination by X-ray diffraction.

Results and Discussion

Gaylussite's thermal behavior consists of three main features: (1) Dehydration up to 250°C; (2) Crystal transformations between 250° and 500°C; and (3) Melting and carbonate decomposition from 500°C to a maximum of 1050°C.

Dehydration

In a water-free atmosphere, dehydration of gaylussite occurs in a single step to produce a single DTA peak, a single EGA water peak, and a single

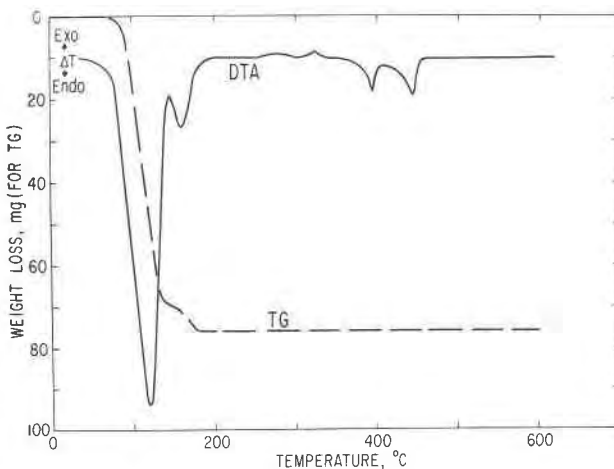


Fig. 4. Simultaneous DTA-TG on 311 mg sample of synthetic gaylussite in a self generated atmosphere.

TG weight loss (Figs. 1 and 2). Natural gaylussite in a dry helium atmosphere (Fig. 1) shows water evolution beginning above 50°C with a DTA peak at 133°C, an EGA peak at 190°C, and a TG weight loss curve with no inflection point, indicating that gaylussite is the only source for water evolution. The DTA and EGA peak temperatures in Figure 1 are different because the EGA peak is primarily a function of the transfer rate of water vapor from the sample to the quadrupole mass spectrometer detector, while the DTA peak is a function of the water evolution rate from the sample. Unfortunately, water does not move as rapidly through the EGA system as CO₂ or most other gases. Total water loss measured from the TG curve in Figure 1 shows less water than pure gaylussite would produce—25.5 percent compared to the theoretical 30.4 percent. Figure 2 shows 25.1 percent water loss from synthetic gaylussite.

Gaylussite dehydration does not result in the formation of the lower hydrate, pirssonite [Na₂Ca(CO₃)₂·2H₂O], as claimed by Fahey (1962). In the deep-well sample holder, gaylussite generates its own water-containing atmosphere. Under these conditions two DTA peaks representing the energy for the loss of water are produced (Fig. 4). If gaylussite loses water to form pirssonite, then the second DTA water loss peak would be from pirssonite. However, the thermogravimetry curve in Figure 4 shows that the weight loss associated with the second peak is equivalent to only 1/3 mole water, rather than to the 2 moles of water associated with pirssonite. X-ray diffraction data on gaylussite samples heated to 100°, 120°, 150°, 180°, and 200°C, then cooled to room temperature, show direct conversion of gaylussite to the low-temperature form of the double carbonate with no intermediate phase containing pirssonite. In addition, X-ray diffraction on gaylussite heated in dry air at 75°C for 96 hours showed poorly crystallized Na₂Ca(CO₃)₂ in its low-temperature form with almost total disappearance of the gaylussite peaks. No pirssonite was detected. Because gaylussite and the double carbonate have no X-ray diffraction peaks where pirssonite shows its largest peak, the presence of even small quantities of pirssonite should be easily detected. The source of energy that produces the second DTA dehydration peak, formed only in a self-generated or water-filled atmosphere, remains unexplained.

The small shoulder on the leading edge of the large DTA peak at 133°C (Figs. 1, 2, and 3) could

TABLE 1. Experimental Parameters for Thermal Analysis for Figures 1, 2, 3, and 4

	Figure 1	Figure 2	Figure 3	Figure 4
Gaylussite source	Natural	Synthetic	Synthetic	Synthetic
Sample weight, mg	198	211	121	311
Heating rate, °C/min	10	10	10	10
Atmosphere	Helium	Helium	CO ₂	Self-generated
Flow rate, cc/min	150	150	150	150
DTA sensitivity, °C/inch				
Ambient to 250°	0.75	1.5	1.5	1.5
250° to max.	0.375	0.75	0.75	0.75
TG sensitivity, mg/inch	10	10	10	10
EGA sensitivity	Arbitrary units	Arbitrary units	-	-

be the loss of a small amount of absorbed water or the loss of water from an impurity such as a hydrate of sodium or calcium carbonate. No change in X-ray powder pattern occurs in gaylussite heated just above the DTA shoulder.

Dehydration converts gaylussite to the low-temperature form of the double carbonate, Na₂Ca(CO₃)₂, which is discussed in the next section.

Crystal Transformation

This section describes the thermal properties of Na₂Ca(CO₃)₂ from 250° to 500°C. All DTA peaks included in this section show neither associated weight loss nor gas evolution. As expected for phase changes, the peak locations are independent of atmosphere surrounding the sample. Minor variations in temperatures for Figures 1, 2, and 3 probably result from differences in the thermal conductivities of the gases and from impurities in the gaylussite samples.

TABLE 2. Corrected Peak Temperatures for Figures 1, 2, 3, and 4

Description of event or reaction	Corrected peak temperature, °C for Figure No.			Corrected onset temperature, °C for Figure No.		
	1	2	3	1	2	3
Dehydration	133	121	131	63	71	79
Transformation, LTF to HTF ¹	328	340	345	308	333	333
α-β inversion	390	395	392	364	384	376
β-γ inversion	435	442	440	423	419	432
Na ₂ Ca(CO ₃) ₂ decomposition, solid ²	723	746	n/a	618	600	n/a
Na ₂ Ca(CO ₃) ₂ melting	n/a ³	n/a	819	n/a	n/a	768
Na ₂ CO ₃ melting	--- ⁴	866	n/a	--- ⁴	843	n/a
Na ₂ Ca(CO ₃) ₂ decomposition, liquid ²	n/a	n/a	982	n/a	n/a	943

¹ LTF to HTF transformation is the conversion of the low-temperature form of Na₂Ca(CO₃)₂ to the high-temperature form.

² Two Na₂Ca(CO₃)₂ decompositions are listed. Listed first is the decomposition of solid Na₂Ca(CO₃)₂ that occurs in a CO₂-free atmosphere; listed second is the decomposition of liquid Na₂Ca(CO₃)₂ that occurs in a CO₂ atmosphere.

³ n/a - Not applicable under specific experimental conditions.

⁴ The dash in the space indicates that thermal analysis was discontinued before reaching the temperature at which the corresponding event would be expected to produce a DTA peak.

A small exothermic peak between 280°C and 305°C occurs in both natural and synthetic gaylussite. The peak is irreversible; that is, it does not occur on the cooling curve. X-ray diffractions on a sample heated to 250°C and then to 310°C show no change in the poorly crystallized, low-temperature form of the double carbonate as indicated by the short, broad X-ray peaks for the low-temperature form of the double carbonate, regardless of its temperature history. The source of the thermal event occurring between 280°C and 305°C could not be identified by X-ray diffraction or thermal analysis.

Between 325° and 350°C another exothermic peak occurs on the DTA curve. This irreversible crystal transformation from the low-temperature form of $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ to the high-temperature form is easily identified by X-ray diffraction. In contrast to those of the low-temperature form, the X-ray peaks of the high-temperature form are narrow and intense, suggesting good crystallinity. This high-temperature form of the double carbonate is the same material that is formed when a mixture of Na_2CO_3 and CaCO_3 is repeatedly heated and cooled (before the addition of water) by the method we described earlier for preparation of synthetic gaylussite. At a heating rate of 10° per minute, the high-temperature form of the double carbonate goes through two crystal inversions to generate two reversible, endothermic peaks: (1) α -to- β crystal inversion between 390° and 400°C and (2) β -to- γ crystal inversion between 435° and 445°C. On the cooling curve the γ -to- β inversion is near 435°C and the β -to- α inversion is near 360°C.

Melting and Carbonate Decomposition

Above 550°C the thermal analysis pattern for gaylussite is dependent on the partial pressure of CO_2 surrounding the sample. In the decomposition of the double carbonate represented by the reaction, $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{CaO} + \text{CO}_2$, removal of the CO_2 encourages decomposition to begin as low as 640°C. The sample, in a flat pan with CO_2 -free carrier-gas flow over it, is essentially in a CO_2 -free atmosphere where the decomposition reaction will begin near 620°C (Figs. 1 and 2). In a CO_2 atmosphere at atmospheric pressure (Fig. 4), decomposition begins as high as 930°C, this approximately 300°C spread in decomposition temperatures being controlled by the partial pressure of CO_2 .

A sharp, melting-point DTA peak is observed regardless of the atmosphere surrounding the sample,

although the material undergoing fusion is different depending on the presence or absence of CO_2 in the atmosphere. When decomposition of the double salt is shifted to a higher temperature by a CO_2 atmosphere as shown in Figure 3, then the double carbonate melts with a DTA peak at 819°C. Its X-ray pattern is still the high-temperature form of the double carbonate. In a CO_2 atmosphere, the double carbonate decomposes with a DTA peak at 982°C. The X-ray pattern following decomposition shows CaO and Na_2CO_3 . If the sample atmosphere is free of CO_2 , then the double carbonate decomposes before its melting temperature (Fig. 2) and X-ray shows no double carbonate—only CaO and Na_2CO_3 . The peak observed after decomposition is actually the fusion peak for Na_2CO_3 at about 866°C (Fig. 3).

Quantitative measurements on CO_2 loss from the CaCO_3 part of natural and synthetic gaylussite are quite different, probably because of contaminants in the samples. Naturally occurring gaylussite showed a weight loss of 20.2 percent for CO_2 , while synthetic gaylussite showed a weight loss of 14.7 percent. The theoretical weight loss, 14.8 percent, is only one-half of the total CO_2 in gaylussite because the Na_2CO_3 part of gaylussite is stable to more than 1000°C. Because the water loss value for naturally occurring gaylussite is lower and the CO_2 loss value is higher than the theoretical values, some of the contaminants are probably carbonates without water such as dolomite, calcite, shortite, northupite, and/or bradleyite. The presence of these and other oil-shale minerals in conjunction with gaylussite in the Green River Formation has been documented by Fahey (1962). Other contaminants probably include illite, quartz, and feldspars in extremely fine particles (Fahey, 1962; Tisot and Murphy, 1960) and in small quantities. In addition, $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ could be present as a product of dehydration of gaylussite. None of the contaminants was detected by X-ray; therefore, probably no individual mineral was present as a major contaminant.

The synthetic gaylussite had enough CaCO_3 and $\text{Ca}(\text{OH})_2$ to be detected by X-ray diffraction. The presence of some $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ probably contributed to the low water loss value for the synthetic material.

Two small DTA peaks at 863°C and 890°C on Figure 3 were not studied because of the severe effects of the melt on the sample support. Probably some dissociation of the double carbonate occurred

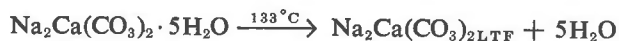
when it melted to provide enough CaCO_3 to produce the DTA peak at 890°C (CaCO_3 would decompose at 890°C in CO_2). The peak at 864°C could be melting of Na_2CO_3 , although the peak occurs at a higher temperature than expected for a small amount of material.

The irregular shape of the endotherm at 982°C in Figure 3 is caused by bubbles of CO_2 escaping from the melted sample. A small narrow peak on the leading edge of the melting endotherm at 785°C is also probably caused by bubbles of CO_2 leaving the melted sample, as evidenced by a small weight loss resulting from decomposition of part of the CaCO_3 in the double carbonate.

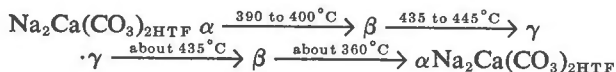
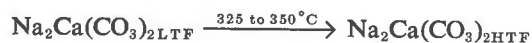
Summary

Thermal behavior of gaylussite from ambient to 1000°C is given in the following set of equations:

(1) Dehydration

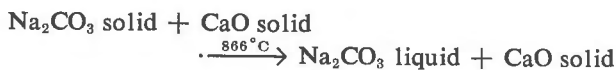
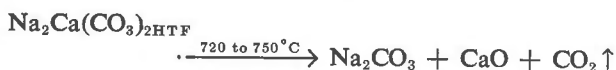


(2) Crystal transformations

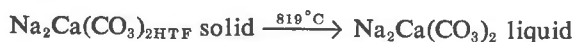


(3) Melting and carbonate decomposition

(a) CO_2 -free atmosphere



(b) CO_2 atmosphere



where LTF = low temperature form and HTF = high temperature form.

The data show that synthetic and natural gaylussite have almost identical thermal decomposition curves. A dehydration doublet DTA peak is produced only in a water-containing atmosphere. Pirssonite is not formed during dehydration of gaylussite in either a water-containing atmosphere or a dry atmosphere. Gaylussite apparently dehydrates directly

to form the low-temperature form of $\text{Na}_2\text{Ca}(\text{CO}_3)_2$. Decomposition temperature of the double carbonate varies by more than 200°C (onset temperatures), depending on the presence or absence of an atmosphere of CO_2 . The double carbonate melts only in a CO_2 atmosphere; otherwise, decomposition occurs and the DTA peak represents the fusion of sodium carbonate. A description of gaylussite's thermal behavior must include a precise description of the atmosphere surrounding the material during analysis for the data to be meaningful.

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