Differential Thermal Analysis of Selected Borate Minerals

GEOLOGICAL SURVEY BULLETIN 1036-K

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By ROBERT D. ALLEN

A CONTRIBUTION TO GEOCHEMISTRY

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By ROBERT D. ALLEN

ABSTRACT

Differential thermal analysis curves of bakerite, borax, colemanite, ginorite, howlite, kernite, meyerhofferite, priceite, probertite, sassolite, searlesite, tincalconite, and ulexite were prepared with a portable differential thermal analysis apparatus. These minerals yield distinctive endothermic curves between 50° C and 650° C. Thermal curves of synthetic mixtures of colemanite and ulexite demonstrate the practicality of semiquantitative analysis of borate mineral mixtures with the portable apparatus.

INTRODUCTION

In 1953 the writer began a differential thermal analysis study of selected borate minerals. The possibility of using differential thermal analysis methods on borates was discussed with George T. Faust of the Geological Survey who pointed out that the low fusion temperatures of the borate minerals and their well known glass-forming tendencies would set an upper temperature limit to the practical range of investigations. Preliminary investigations confirmed these views and showed the inadvisability of heating borate minerals to temperatures approaching 1000° C. The resulting fusion product may bind the thermocouple and crucible with such tenacity that the two can be separated only by breaking the thermocouple. Furthermore, the fused borate is removed from the crucible only with great difficulty.

Three modifications in the usual differential thermal analysis procedure obviate the difficulty pointed out above: (1) the run is discontinued at a temperature of 650° C or less; (2) several of these minerals are mixed with equal weights of aluminum oxide to lessen the adhesive effect; (3) the crucible is removed from its pedestal immediately after completing a run.

Differential thermal analysis used in conjunction with microscopic examination is found to be a satisfactory method for the identification of the 13 borate minerals investigated. Although these minerals can usually be identified with the petrographic microscope, positive identification is not always possible, especially for fine-crystalline varieties. The following minerals and pairs of minerals are occasionally troublesome: bakerite, borax, colemanite-howlite, ginorite, howlite-priceite, meyerhofferite, probertite, sassolite, searlesite, tincalconite, and ulexite.

A portable differential thermal analysis unit such as the one used in this investigation can be operated after a few hours of practice; such a unit is relatively inexpensive, costing about $500 at current market prices.

ACKNOWLEDGMENTS

Acknowledgments are due the following colleagues in the Geological Survey: The study was suggested by Ward C. Smith. The first experimental work was done with the assistance of Paul D. Blackmon. The methods of differential thermal analysis and the application to the borate minerals were discussed with George T. Faust. Their application to semiquantitative analysis of borate mineral mixtures was suggested by Earl Ingerson.

APPARATUS AND EQUIPMENT

Hendricks, Goldich, and Nelson (1946) described a portable differential thermal analysis unit which they used in the study of bauxitic clays. An improved model of this apparatus has been in use on various problems in the past eight years. Parker, Hathaway, and Blackmon (1956) have prepared a set of reference curves, chiefly clays, with the modified Eberbach unit. This apparatus has been found very well adapted to the differential thermal analysis study of borates.

A variable transformer calibrated to read voltage drop was used in place of the variable resistance supplied with the above unit.

EXPERIMENTAL PROCEDURE

Starting with a cold furnace, a heating rate of 30° C per minute was found to give greater amplitude and more measured area under the curve than the more conventional slower heating rates of 10° C or 15° C per minute. The relation between heating rate and measured area under the curve has been described by Wittels (1951). The heating rate of 30° C per minute was obtained with the following voltage drop settings on the transformer:

Degrees centigrade	*Voltage drop*
0–200	82
200–300	85
300–400	90
400–500	100

Between 500° C and 650° C, a temperature range utilized in the examination of bakerite and howlite, the 100-volt setting gave a heating rate of 25° C per minute. The endothermic troughs for these two minerals would probably occur at slightly higher temperatures if the 30° C per minute heating rate were used in the 500° C to 650° C range. Temperature readings were made at 10° C intervals, the smallest interval on the thermometric scale of this unit. Galvanometer deflections were read to the nearest quarter-of-a-scale division.

Crucibles no. 1, 2, and 3 were used interchangeably without calibration of their respective thermocouples; errors introduced by this procedure are below the resolution range of the instrument. Samples were sieved to $-50+200$ mesh, a size range that is satisfactory for this work, and tamped lightly into the crucibles. Faust (1950, p. 215)

has pointed out that very fine sizes tend to broaden the base of an endothermic trough. Extremely tight packing was avoided because the amplitude and inflection temperatures for a given trough appeared to increase and because tightly packed samples were often difficult to remove after the runs were completed.

The following minerals were considered:

Bakerite	$Ca_5B_{10}Si_6O_{35}\cdot 6H_2O$
Borax	$Na_2B_4O_7\cdot 10H_2O$
Colemanite	$Ca_2B_6O_{11}\cdot 5H_2O$
Ginorite	$Ca_2B_{14}O_{23}\cdot 8H_2O$
Howlite	$Ca_2SiB_5O_9(OH)_5$
Kernite	$Na_2B_4O_7\cdot 4H_2O$
Meyerhofferite	$Ca_2B_6O_{11}\cdot 7H_2O$
Priceite	$Ca_4B_{10}O_{19}\cdot 7H_2O$
Probertite	$NaCaB_5O_9\cdot 5H_2O$
Sassolite	$B_2O_3\cdot 3H_2O$
Searlesite	$NaB(SiO_3)_2\cdot H_2O$
Tincalconite	$Na_2B_4O_7\cdot 5H_2O$
Ulexite	$NaCaB_5O_9\cdot 8H_2O$

The minerals, many of which are from type localities (indicated adjacent to the differential thermal analysis curves), were examined microscopically to ascertain identity and purity. Specimens of bakerite, ginorite, and priceite were also analyzed chemically and identified by X-ray examination (Kramer and Allen, 1956; Allen and Kramer, 1957).

Colemanite, howlite, priceite, probertite, and searlesite were mixed with equal weights of reagent-grade aluminum oxide because preliminary runs had indicated that these minerals are difficult to remove from the crucibles after heating to the requisite temperatures; it was necessary to mix sassolite with Al_2O_3 in the ratio of 1:3. Even with this precaution it is advisable to remove a crucible from its pedestal immediately after finishing a run. This should be done for all borates.

Experimental evidence indicates that reaction between aluminum oxide and these borates is negligible or absent up to the requisite temperature for each mineral. Unheated and heated mixtures of aluminum oxide with colemanite, howlite, priceite, probertite, sassolite, searlesite, and ulexite (the reason for inclusion of ulexite is given below) were X-rayed on a diffractometer. In every mixture the intensities of the respective aluminum oxide peaks were substantially the same in unheated and in heated materials. In contrast, the peaks of the borate minerals were absent in the X-ray patterns of the heated samples. Microscopic examination of the heated samples disclosed (1) aluminum oxide and vitrified borate were present in approximately equal amounts in each, and (2) no evidence of reaction between aluminum oxide and borate minerals was seen.

Priceite and searlesite were run at high sensitivity, whereas all other minerals were run at medium sensitivity.

RESULTS

Differential thermal analysis curves for the 13 borates are arranged alphabetically in figures 19–25. Each mineral was analyzed three or more times. Variations of the results were within the limits of the sensitivity of the apparatus. The three reruns were made to avoid including any gross error in the data.

In all the curves the vertical scale is the same—1 inch equals 10 galvanometer divisions. For purposes of comparison, a curve prepared from barium chloride dihydrate, a common reference material which illustrates stepwise dehydration, is shown in figure 25. This compound was selected because it shows large endothermic troughs in about the same temperature range as that in which most of the borate minerals show their reactions, that is, between 100° C and 500° C; furthermore, the $BaCl_2.2H_2O$ curve was prepared at medium sensitivity with a heating rate of 30° C per minute—the same experimental conditions used for most of the borate curves. (The trough produced by the quartz α–β inversion would be barely visible at this medium sensitivity setting.)

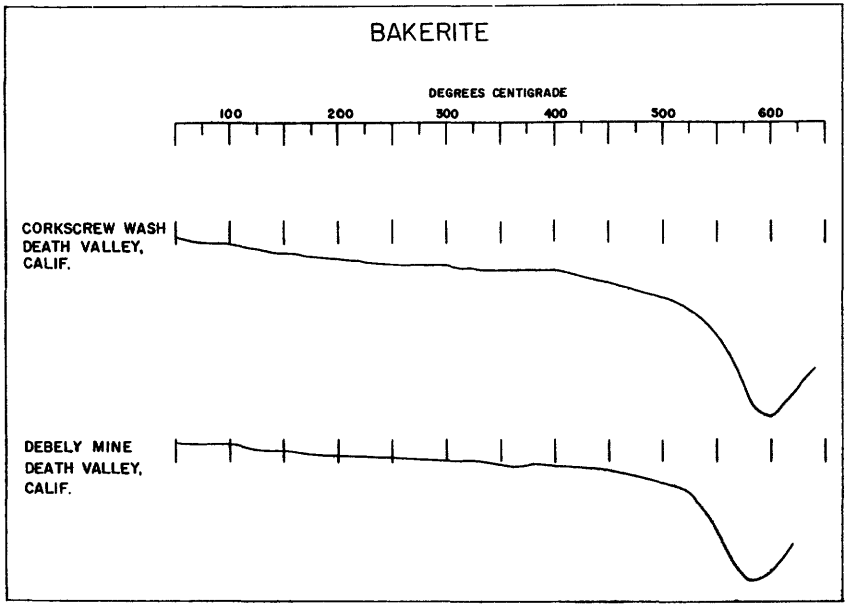
Five curves obtained from probertite from the Lower Biddy McCarthy mine, Death Valley, are presented in figure 23. The initial temperatures of endothermic reaction [1] vary between 80° C and 90° C. The two trough temperatures are essentially the same in all five curves; the trough of lesser amplitude was recorded at 140° C, the trough of greater amplitude at 260° C. Thus, the precision errors in determination of initial temperature and trough temperature for this one sample of probertite are considerably less than ±10° C. Temperature readings were made at 10° C intervals, the smallest readable interval on the thermometer of the portable apparatus.

The initial and trough temperatures (or temperature ranges) for the thirteen minerals studied are tabulated below. Data for colemanite are taken from figure 27 ("ulexite 100 percent") as well as from figure 21.

	Initial temperature (° C)	*Endothermic trough temperature(s) (° C)*
Bakerite	400–450	580–600.
Borax [1]	50	60, 105–110, 160–170.
Colemanite	270–300	370–375.
Ginorite	70–80	100, 150, 310, 360, 470.
Howlite	450–460	525–540.
Kernite	100	185.
Meyerhofferite	160	265.
Priceite	220–270	295 [2], 365–385, 430–435.
Probertite	80–90	140, 260.
Sassolite	120 (?)	160.
Searlesite	350	430.
Tincalconite	60–70	160.
Ulexite	70–90	190–200.

[1] Exothermic peak at 75° C.
[2] In one sample.

[1] Initial temperature of endothermic reaction is hereafter called initial temperature.



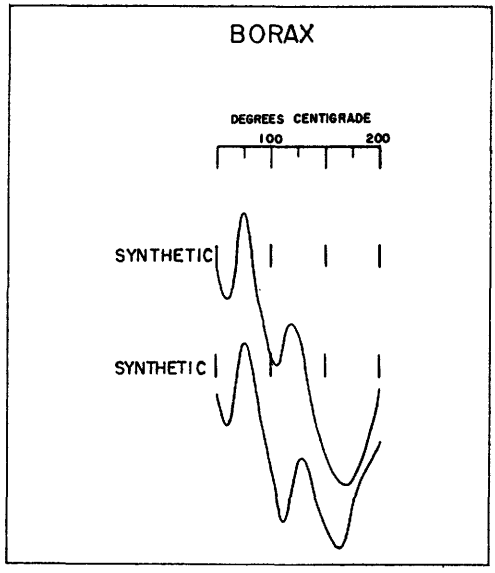


FIGURE 19. Differential thermal analysis curves of bakerite and of synthetic borax.

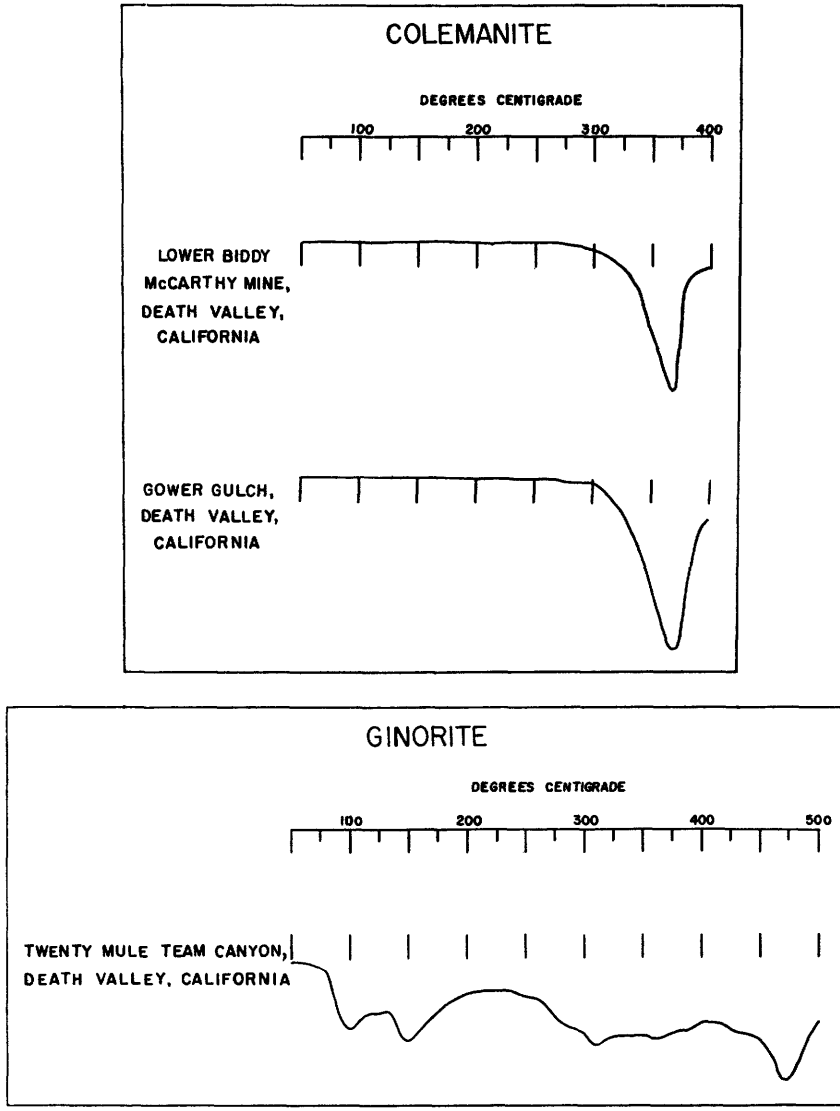
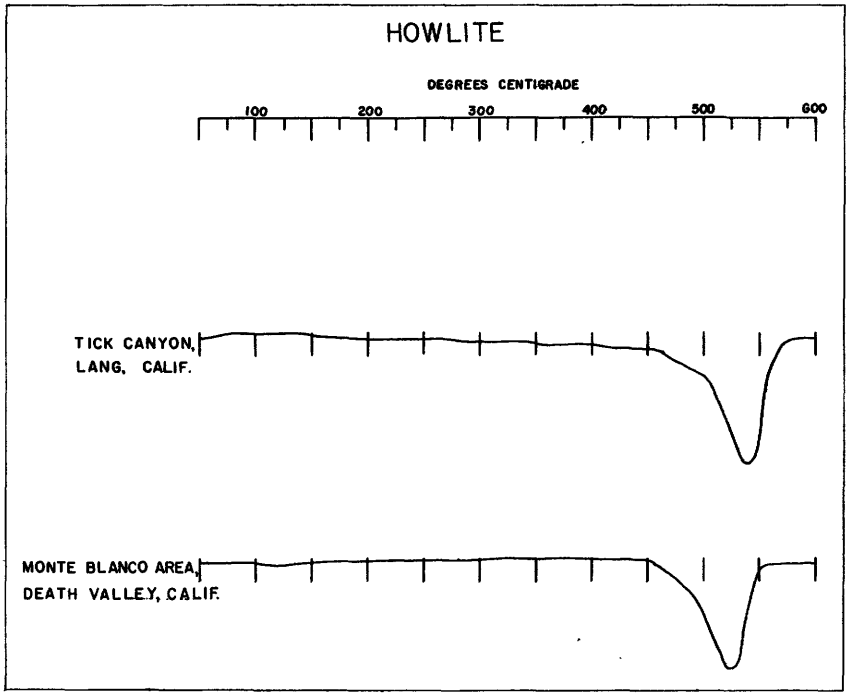


FIGURE 20. Differential thermal analysis curves of colemanite and of ginorite.



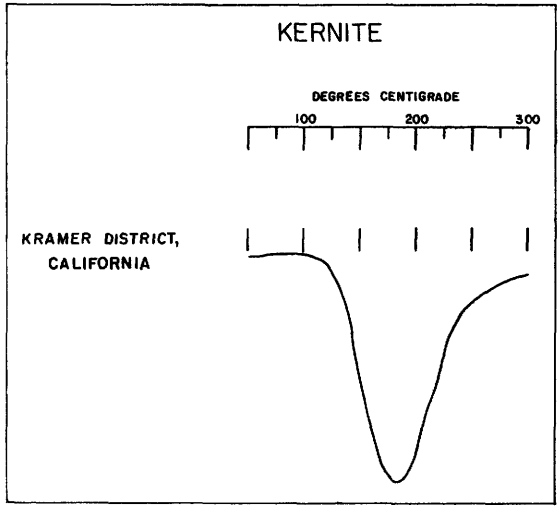
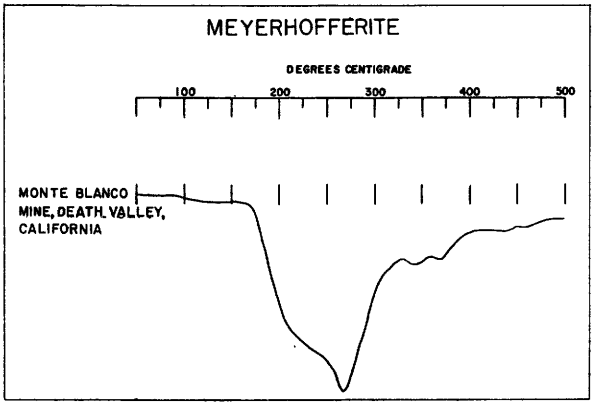


FIGURE 21. Differential thermal analysis curves of howlite and of kernite.



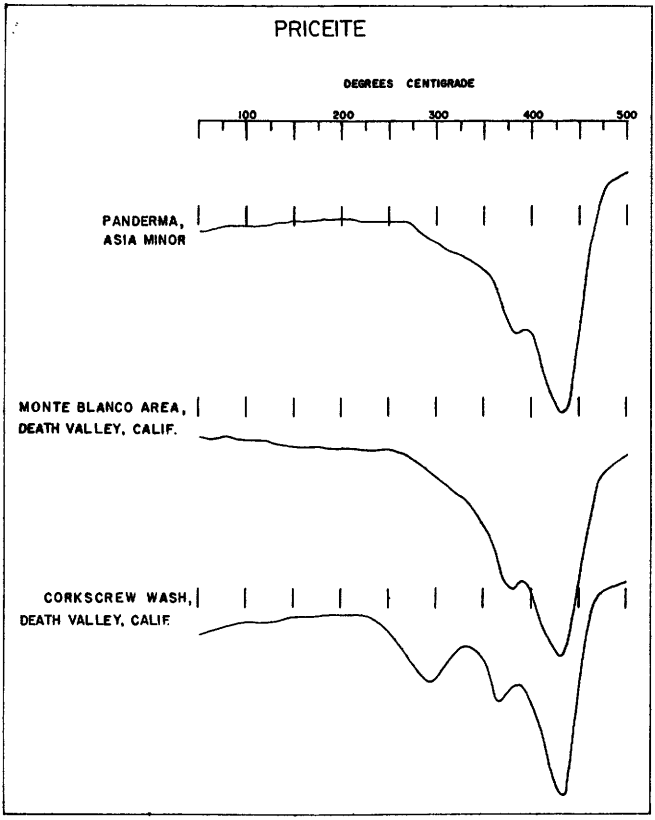
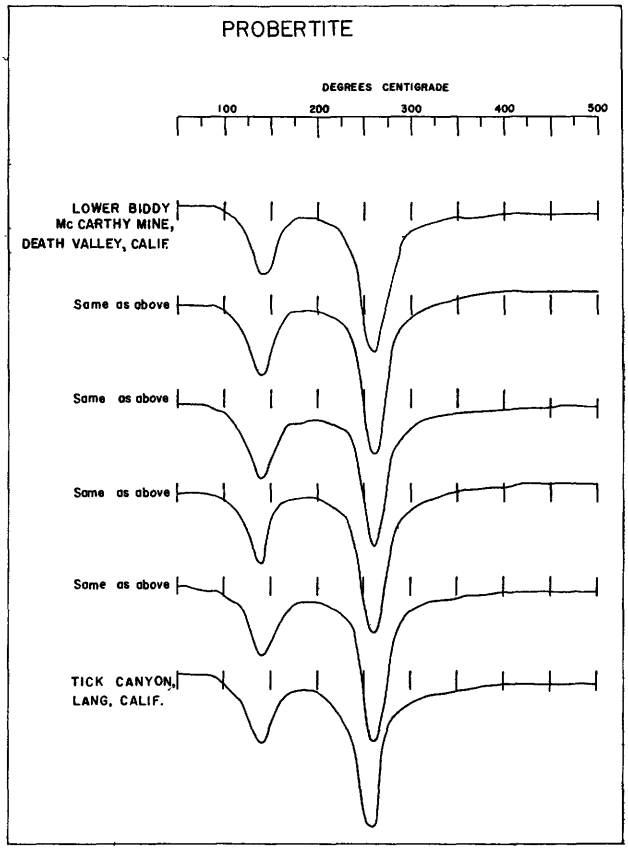


FIGURE 22. Differential thermal analysis curves of meyerhofferite and of priceite.



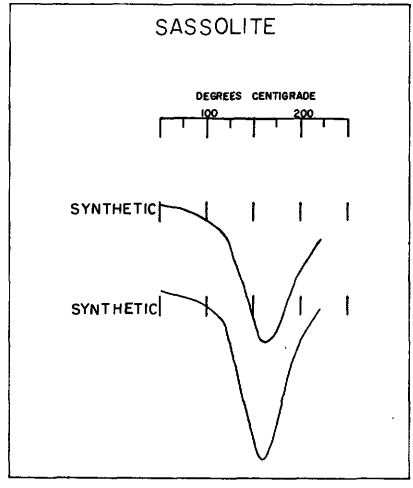


FIGURE 23. Differential thermal analysis curves of probertite and of synthetic sassolite.

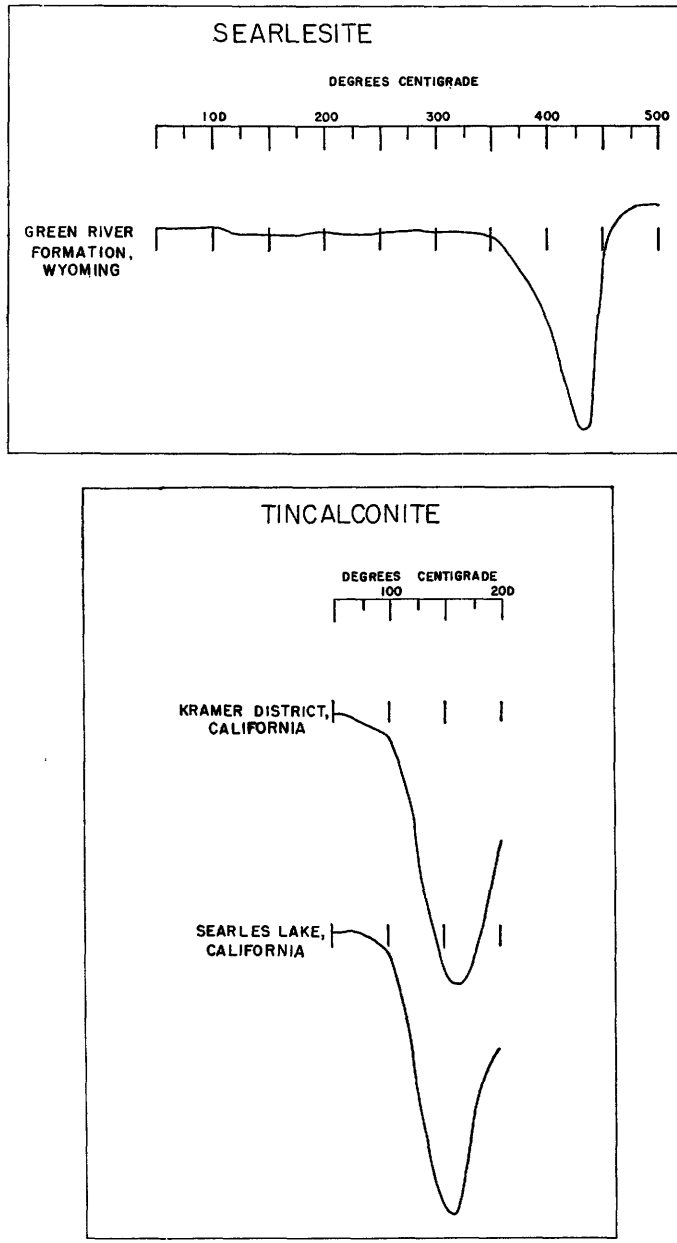
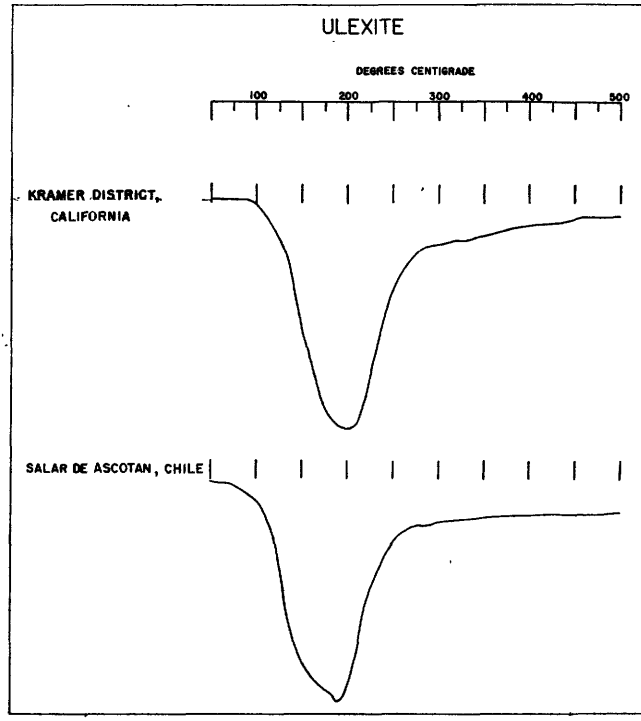


FIGURE 24. Differential thermal analysis curves of searlesite and of tincalconite.



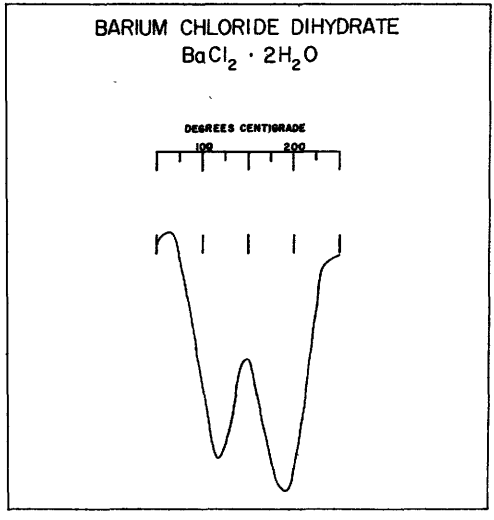


FIGURE 25 Differential thermal analysis curves of ulexite and of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$).

In figure 28 curves of the 13 minerals are presented in order of increasing trough temperatures. Similarities between curves would make identification inconclusive for the following mineral pairs: (1) kernite-ulexite; (2) priceite-searlesite; (3) sassolite-tincalconite.

Borax, whose principal endothermic reaction begins at 120° C, decrepitates and expands at about 200° C. Colemanite, whose endothermic reaction begins at 270° C, decrepitates violently between 350° C and 400° C. Moderately coarse crystalline tincalconite from Searles Lake whose endothermic reaction begins at 80° C, decrepitates and expands between 130° C and 200° C. Borax, colemanite, and tincalconite runs, therefore, were discontinued at 200° C, 400° C, and 200° C, respectively.

The meyerhofferite curve shows a minor peak at 370° C that is probably accounted for by the presence of a minor amount of colemanite (microscopically estimated at 5 percent).

DISCUSSION

In some specimens of the same mineral species variations in the temperatures at which endothermic reactions commence and culminate are traceable to differences in crystal size. Thus, white powdery ulexite from Salar de Ascotan, Chile, shows an endothermic reaction which commences and culminates at temperatures significantly lower than those for colorless compact ulexite from the Kramer district. Microscopic examination of these specimens of ulexite discloses a marked difference in crystal size: Ulexite from Kramer is characterized by much larger crystals than ulexite from Salar de Ascotan. The crystal size effect is even more pronounced in the curves obtained from priceite. Priceite specimens from Panderma, Asia Minor, and Monte Blanco area, Death Valley, yielded nearly identical curves; and both these priceite specimens are characterized by an average crystal diameter of 20 to 25 microns. In contrast, priceite from Corkscrew Wash, Death Valley, yields an endothermic trough at 295° C which is not obtained from the other priceite specimens. The priceite from Corkscrew Wash is characterized by an average crystal diameter of less than 5 microns which probably explains this anomaly. Chemical analyses, X-ray diffraction patterns, and optical examinations had established the fact that the Monte Blanco and Corkscrew Wash specimens are of high purity (Kramer and Allen, 1956).

APPLICATION TO SEMIQUANTITATIVE ANALYSIS OF COLEMANITE-ULEXITE MIXTURES

Synthetic mixtures of colemanite from the Upper Biddy McCarthy mine, Death Valley, and ulexite from the dump at the Eagle Borax Works, Death Valley, were prepared in 10 percent increments to test the method as a tool for semiquantitative mineral analysis. Every

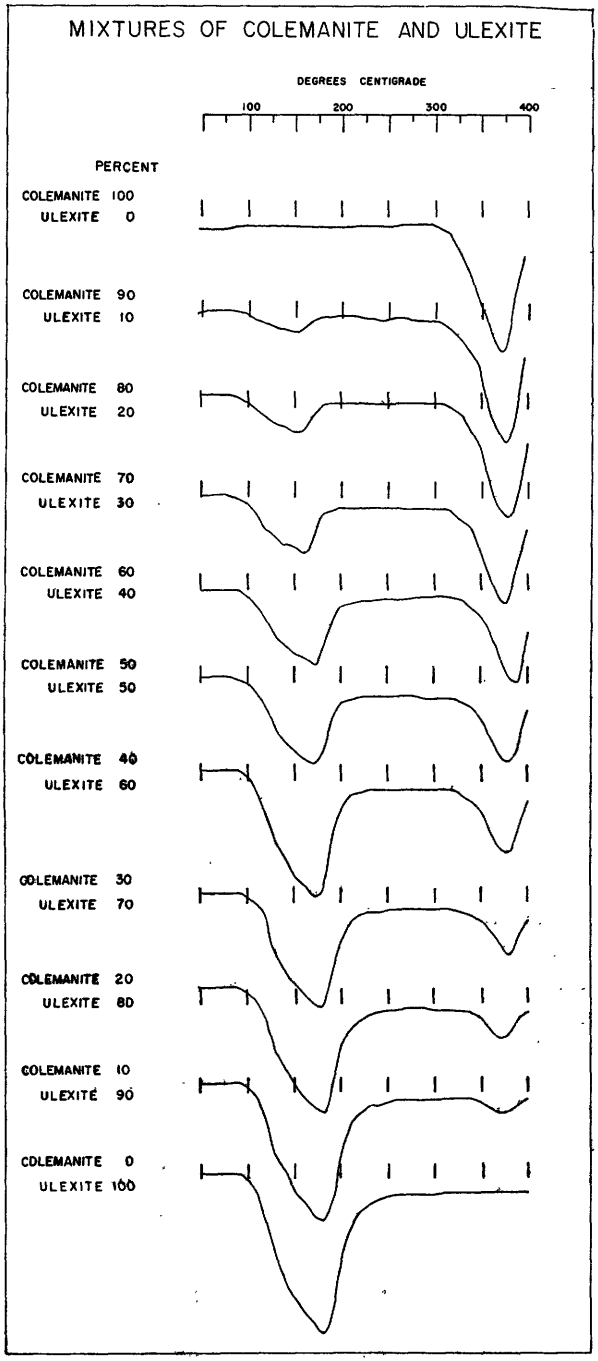


FIGURE 26. Differential thermal analysis curves of mixtures of colemanite and ulexite.

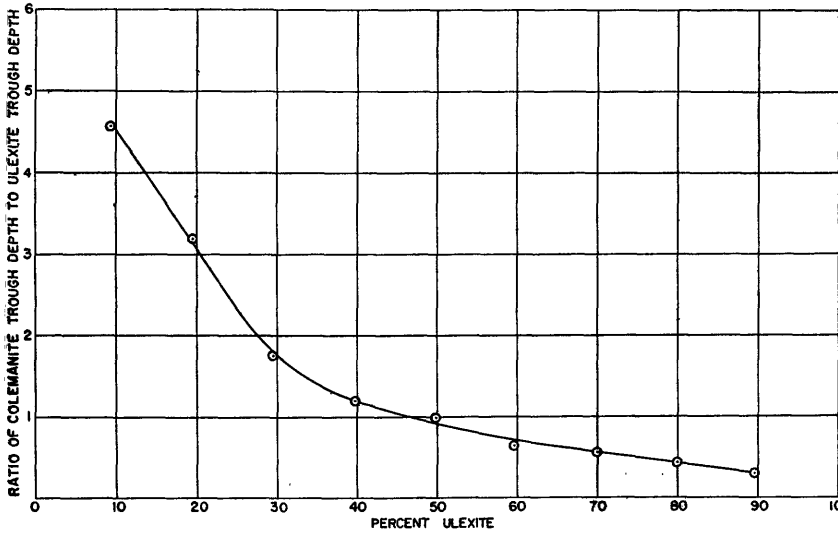


FIGURE 27. Working curve for the semiquantitative determination of colemanite and ulexite.

sample was mixed with an equal weight of aluminum oxide; 350 mg of sample was used for each run. All samples were run at medium sensitivity. Inspection of the curves in figure 26 reveals the proportional relationship between trough depth and concentration for each mineral. A working curve for the semiquantitative determination of ulexite (and colemanite by difference) is depicted in figure 27. This curve was obtained by plotting the ratio of colemanite trough depth (in units of galvanometer deflection) to ulexite trough depth against percent ulexite. This method of analysis is recommended because the trough depth ratio is considered to be more reliable than a single trough depth. In a sense, each mineral acts as an internal standard for the other. The ratio should not be seriously affected by an error in weighing of samples.

Four synthetic mixtures of colemanite and ulexite whose proportions were unknown to the analyst were determined by the procedure used to obtain the curves in figure 26. The colemanite percentages obtained from the working curve in figure 27 are compared with the actual colemanite percentages in the columns below.

Colemanite added (percent)	*Colemanite recovered (percent)*
50	52
80	84
10	10
30	37

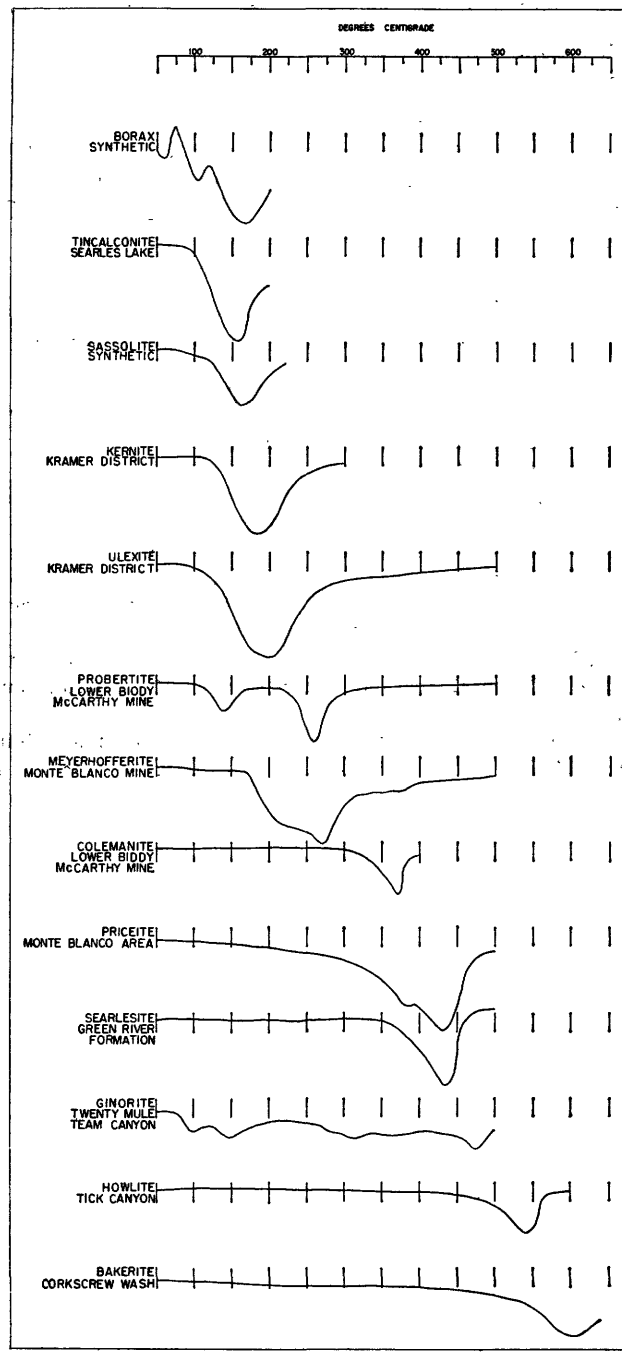


FIGURE 28. Differential thermal analysis curves of 13 borates.

These results give some indication of expectable precision in this analytical method.

It is noteworthy that the trough temperature for ulexite from Eagle Borax Works ranges from 155° C for the sample containing 10 percent ulexite (with respect to colemanite) to 180° C for the sample containing 100 percent ulexite. These trough temperatures are not directly comparable with those reported for ulexite from Kramer or Salar de Ascotan because the latter were not mixed with Al_2O_3. The trough temperatures for colemanite from Upper Biddy McCarthy mine vary between 370° C and 385° C; no proportional relationship between percent colemanite and trough temperature was noted.

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