THERMAL ANALYSIS STUDIES ON CARBONATES
I. ARAGONITE AND CALCITE[1]

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ABSTRACT

Differential thermal analysis studies were made on eight different samples of aragonite, seven of calcite, and one natural mixture of aragonite and calcite. The transformation of aragonite to calcite gave a thermal effect that was easily observed with the continuous-photographic-recording type of differential thermal analysis apparatus. This transformation serves to identify aragonite. The aragonite-calcite transformation and the formation of unstable polymorphs of $CaCO_3$ are discussed.

INTRODUCTION

The writer started his studies on the thermal analysis of carbonate minerals at the U. S. Department of Agriculture in 1942. These data formed the basis of a method for differentiating magnesite and dolomite which was later developed at the U. S. Geological Survey (Faust, 1944). A comprehensive study by thermal analysis of the carbonates and of the hydrous magnesium silicates which was begun in 1944 is now well under way; this paper is the first of a series to be published on studies on carbonate minerals.

A preliminary note regarding the use of the differential thermal analysis method for differentiating between aragonite and calcite was recently published (Faust, 1949).

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DESCRIPTION AND CHEMICAL COMPOSITION OF THE MINERALS

Some of the specimens used in this study were obtained from the U. S. National Museum through the cooperation of Dr. W. F. Foshag and E. P. Henderson, and some were supplied by Drs. C. S. Ross and W. T. Schaller of the U. S. Geological Survey. Some of the specimens were collected by the writer.

The samples used in this study were all carefully selected by hand picking under the binocular microscope. This selected material was then crushed to pass a 58-mesh cloth sieve and re-examined for impurities. The samples were then examined in immersion liquids under the petrographic microscope. Spectrographic analysis of the material and *x*-ray diffraction studies served to verify the purity and the identitity of the minerals.

(*a*) *Aragonite*

ARAGONITE #9. Locality: Chile, South America. (U.S.N.M.—R2554) Labelled cupriferous aragonite. Very pale greenish-blue aggregates. Spectrographic analysis shows 0.01 per cent CuO, 0.12 per cent ZnO, and 0.09 per cent SrO.

ARAGONITE #3 (Zeyringite). Locality: Zeyring, Flatschach, Styria, Austria. (U.S.N.M. #R2548) Green to white masses. This mineral was supposedly nickel-bearing, but spectrographic analysis fails to show nickel as a constituent. The color is probably due to the copper. The chief impurity is strontium, 0.18 per cent SrO corresponding to 0.26 per cent $SrCO_3$. Strunz (1941) states that zeyringite is partly saddle-shaped calcite and partly the variegated variety of aragonite, flos ferri.

ARAGONITE #5. Locality: Enos-Lindsey Cove, Batesville district, Arkansas. White to colorless radiating needles. This is a strontian-barian aragonite containing 0.86 per cent SrO and 0.56 per cent BaO, corresponding to 1.23 per cent $SrCO_3$ and 0.72 per cent $BaCO_3$.

ARAGONITE #6 (Nicholsonite). Locality: Robert Emmett mine, Leadville, Colorado (U.S.N.M. #R2550). White radiating blades arranged in asteriated forms. This variety of aragonite was never fully described. Butler (1913) reports up to 12 per cent zinc. Spectrographic analysis shows the chief impurity of the specimen studied in this investigation to be 0.19 per cent SrO, and no zinc was found.

ARAGONITE #15 (PLUMBOAN). Locality: Mine la Motte, 5–6 miles northwest of Fredericks-town, Madison County, Missouri. Colorless to white radiating needles. Spectrographic analysis shows 1.8 per cent PbO (equivalent to 2.15 per cent $PbCO_3$) and 0.04 per cent SrO.

ARAGONITE #12. Locality: Fifty miles southeast of Roswell and 17 miles east of Lake Arthur New Mexico. Pseudohexagonal cyclic twins. Some of the crystals have a surficial coating of iron oxides. Only the clear cores were used in this study and the success of the separation of the coated grains from the core is attested to by the spectrographic analysis, Table 1, which shows only 0.005 per cent FeO. This aragonite is a strontian aragonite containing 0.73 per cent SrO, equivalent to 1.04 per cent $SrCO_3$.

ARAGONITE #4 (PLUMBOAN) (Tarnowitzite). Locality: Friedrich mine near Tarnowitz, Silesia. (U.S.N.M. #C-2101). Greenish, needlelike crystals of the so-called "grüner stengeliger" variety. Spectrographic analysis shows 3.5 per cent PbO, equivalent to 4.19 per cent $PbCO_3$, and 0.09 per cent SrO. A wide variation in composition for this mineral from the

Friedrich mine is reported in the literature. Doelter (1912) lists an analysis by Traube of the grüner stengeliger variety which shows 4.26 per cent PbO (5.09 per cent $PbCO_3$) and 0.25 per cent SrO.

ARAGONITE #10 (Mossottite). (U.S.N.M. #R2547). Locality: Lias of Gerfalco in Tuscany, Italy. Pale greenish-blue radiating masses. Spectrographic analysis shows 0.18 per cent SrO, 0.10 per cent PbO, and 0.13 per cent ZnO. Doelter (1912) lists an analysis by Lucca of material from this same locality which contains 6.68 per cent $SrCO_3$, 1.21 per cent $CuCO_3$, 0.82 per cent Fe_2O_3.

(b) *Calcite*

CALCITE #2. Locality: Ala-Mar deposit, Currant Creek, Nye County, Nevada. White fine-grained masses containing about 10 per cent of admixed dolomite.

CALCITE #13. Locality: Joplin district, Missouri. Colorless cleavage fragments. This calcite was analyzed by Dr. R. C. Wells (1915) and found to contain SiO_2, 0.09 per cent; MnO, 0.05 per cent; FeO, 0.19 per cent; CaO, 55.80 per cent; MgO, 0.00; CO_2 (calc'd.), 43.99 per cent; total 100.12 per cent. A comparison with the spectrographic analysis by Murata shows Wells' FeO to be too high and his MgO figure to be in error.

CALCITE #F1102. Locality: Franklin Furnace, New Jersey. Orange cleavage masses exhibiting coarse polysynthetic twinning lamellae.

CALCITE #11. Locality: Soda Dam Springs, two miles north of Jemez Hot Springs, Sandoval County, New Mexico. White, radiating columns, paramorphous after aragonite.

CALCITE #7, (Schaumkalk). Locality: Myokenzan, Harima, Japan. (U.S.N.M. #61, 492). Snow-white scaly masses, paramorphous after aragonite. Spectrographic analysis shows 1.2 per cent MnO.

CALCITE #A-3. Locality: Highway cut, one-half mile northeast of Myersville, Maryland. White cleavage masses, showing polysynthetic twinning. See figure I-c in Faust (1944).

CALCITE #18. Locality: Champion Mica mine, Amelia County, Virginia. Vug filling.

(c) *Aragonite-calcite mixture*

ARAGONITE-CALCITE #8. Locality: Monte Neva (formerly Melvin) Hot Springs SW$\frac{1}{4}$SW$\frac{1}{4}$ sec. 24, T.21N. R.63E., 18 miles north of McGill, White Pine County, Nevada. A natural mixture. Spectrographic analysis shows MgO to be the chief impurity.

Complete spectrographic analyses for the minor elements present were kindly made by K. J. Murata of the U. S. Geological Survey and are given in Table 1. It is noteworthy that strontium was noted in all the specimens and barium in most of them.

THERMAL ANALYSIS

(a) *Static method*

The static method of thermal analysis was developed many years ago by mineralogical chemists for the analysis of hydrated minerals. The earliest method of study, and one still used today, consists of heating the sample at a given temperature, cooling in a desiccator, weighing, and then repeating the heating at this temperature until the sample attains constancy in weight. The process is then repeated at other temperatures. The results are commonly plotted as loss in weight of sample

TABLE 1. SPECTROGRAPHIC ANALYSIS OF SOME ARAGONITE AND CALCITE SPECIMENS

K. J. Murata, analyst

Description	Number	MgO	MnO	FeO	SrO	BaO	PbO	ZnO	CuO	NiO	Y_2O_3	V_2O_5	Ag
Aragonite. Chile, South America	9	X	X	0.002	0.09	0.001	0.007	0.12	0.01	X	X	X	X
Aragonite. Styria, Austria	3	0.02	X	0.004	0.18	0.005	X	X	0.04	X	X	X	X
Aragonite. Batesville district, Arkansas	5	0.004	0.002	0.02	0.86	0.56	X	X	X	X	0.006	X	X
Aragonite. Leadville, Colorado	6	0.05	0.001	0.003	0.19	0.02	0.004	X	X	X	X	X	X
Aragonite. Mine La Motte, Missouri	15	0.004	X	0.002	0.04	0.001	1.8	X	X	X	X	X	X
Aragonite. Near Roswell, New Mexico	12	0.01	X	0.005	0.73	X	X	X	X	X	X	X	X
Aragonite. Tarnowitz, Silesia	4	0.009	X	0.003	0.09	0.008	3.5	X	X	X	X	X	X
Aragonite. Tuscany, Italy	10	X	X	X	0.18	0.005	0.10	0.13	0.01	X	X	X	X
Calcite. Currant Creek, Nye County, Nevada	2	2.2	0.04	0.13	0.01	0.003	X	X	X	0.002	X	0.01	X
Calcite. Joplin, Missouri,	13	0.12	0.07	0.10	0.01	X	X	X	X	X	0.005	X	0.0005
Calcite. Jemez Hot Springs, New Mexico	11	0.29	0.15	0.03	0.03	0.004	X	X	X	X	X	X	X
Calcite. Myokenzan, Harima, Japan	7	0.001	1.2	0.08	0.06	X	X	X	X	X	0.008	X	X
Aragonite-calcite mixture. Monte Neva, Hot Springs, Nevada	8	1.5	0.005	0.03	0.02	0.05	X	X	X	X	X	X	X

X, element looked for but not found.
Other elements not found: Sn As Sb Bi Mo W Tl Ge In Co Cd La Cb Ti Zr.

versus temperature. Various improvements in this technique were added from time to time and the apparatus designed and used by Dr. P. G. Nutting (1943), of the U. S. Geological Survey is typical. In this apparatus, the crucible is suspended in the furnace from the balance, which permits the sample to be weighed while in the furnace and eliminates errors introduced by removing the crucible from the furnace.

The static method involves only the determination of the weight of the sample and the measurement of the temperature. It can, therefore, reveal only phenomena associated with a loss or gain in weight. Changes in weight are involved in such reactions as the loss of water or carbon dioxide, and in the oxidation of iron or manganese. The static method cannot detect inversions, for such phenomena are not accompanied by changes in weight.

Dr. Nutting (1948) very kindly examined for the writer by this method two specimens—a calcite from Joplin, Missouri (#13) and aragonite from Enos-Lindsey Cove, Batesville district, Arkansas. The results are given in Fig. 1; they are essentially identical. The temperature of decomposition for both is 615° C.

In the static method of thermal analysis as described here, the process of dissociation is not reversible because carbon dioxide is lost to the atmosphere. The reaction is written:

$$[\mathrm{CaCO_3} + \Delta \rightarrow \mathrm{CaO} + \mathrm{CO_2}\uparrow]$$

the single horizontal arrow implying thermodynamic irreversibility. The

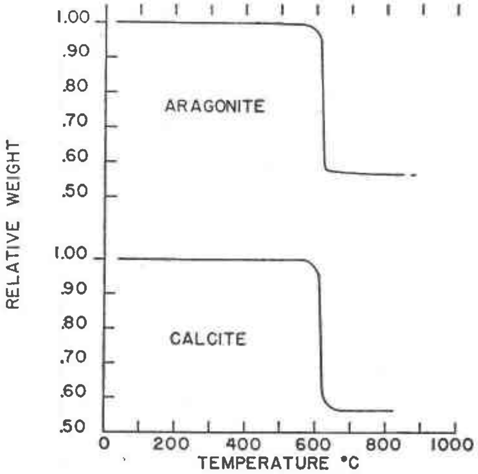

FIG. 1. Thermal analysis curves of aragonite and calcite obtained by the static method. The ordinate is the weight of the sample at each temperature divided by the original weight taken.

temperature of dissociation is, therefore, not an equilibrium value and may vary, depending on such factors as grain size, intergranular texture, presence of impurities, etc.

The data in Fig. 1 are based on relative weight and show a constancy in weight at 0.56. Pure calcite and aragonite contain 56.08 per cent CaO, 43.92 per cent CO_2. The data in Fig. 1 are in accord with this theoretical value and hence the samples were completely dissociated.

The static method is unable to differentiate between calcite and aragonite as it does not reveal the thermal effect that accompanies the transition.

(*b*) *Dynamic method—differential thermal analysis*

(1) General statement

A brief description of the technique employed in this laboratory in making differential thermal analyses and references to the original literature on the apparatus and method are given in a previous paper (Faust, 1948). The curves are produced by the reflection of a light beam from the galvanometer mirrors upon sensitive photographic paper and represent continuous, unhampered recording. The rate of heating for the samples was approximately 12° C. per minute; a complete run required about 80 minutes.

(2) Aragonite curves

The thermal analysis curves for aragonite are given in Fig. 2 and the data are summarized in Table 2. The first four curves C-486, C-484, C-471, C-131 show clear-cut relationships free from complications. In each sample the transition from aragonite to calcite, when it starts, takes place promptly, and the curves show well-defined breaks. In the sample of aragonite from Arkansas (curve C-131) the break is flattened, and this arises from the slightly larger spread in the temperature range over which the transition takes place. The slight hump before the transition break, which appears in this and other records here included, is the result of an accidental instrumental effect and has nothing to do with the aragonite. The straight portions of the curve before and after transition are not noticeably offset, indicating that in this temperature range these two polymorphic forms of $CaCO_3$ have nearly identical specific heats. In the curves showing the inversion of quartz from the low to the high form, the offset in the height of the curves is easily observed (Faust, 1948).

The subsequent dissociation of the calcite paramorphous after aragonite is accompanied by a very large thermal effect. As mentioned previously, the loss of carbon dioxide is approximately 44 per cent of the sample weight. The next six curves, although they show normal relationships

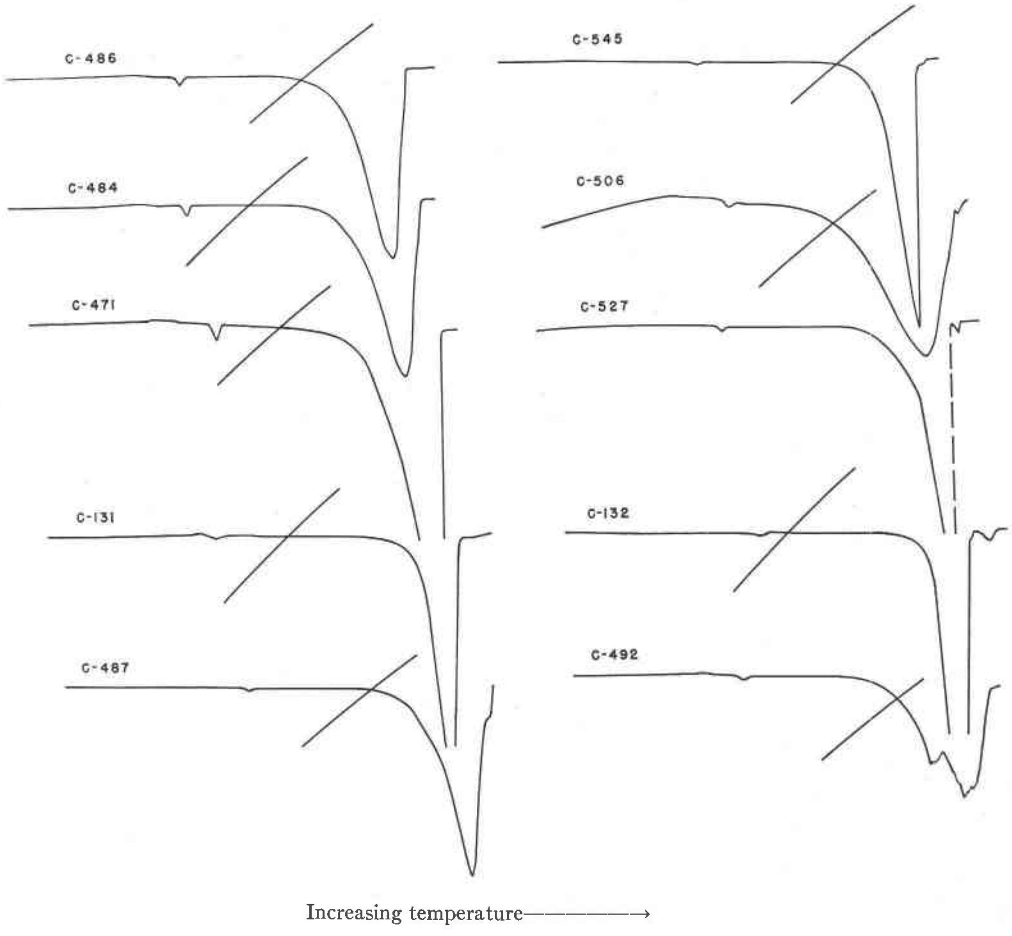

FIG. 2. Differential thermal analysis curves for aragonite. C-486 = aragonite #9, C-484 = aragonite #3, C-471 = aragonite #3, C-131 = aragonite #5, C-487 = aragonite #6, C-545 = aragonite #15, C-506 = aragonite #12, C-527 = aragonite #4, C-132 = aragonite #15, C-492 = aragonite #10. The diagonal line intersecting the curves is a portion of the curve registering the temperature.

TABLE 2. OBSERVATIONS ON THE THERMAL CURVES OF ARAGONITE

Record No.	Sample	Temperature of transition—T_1	Character of break	Temperature of dissociation—T_2	Character of break	Temperature of subsidiary break—T_3	T_2–T_1	T_3–T_2	Locality	Resistance in the galvanometer circuit
C-486	9	447° C.	Sharp	897° C.	Sharp		450° C.		Chile, S.A.	999.9 ohms.
C-484	3	458	Sharp	914	Sharp		456		Flatschach, Styria, Austria,	999.9
C-471	3	462	Sharp	929	Sharp		467		Flatschach, Styria, Austria,	600
C-131	5	400	Rounded	955	Very sharp		555		Batesville district, Arkansas	999.9
C-487	6	461	Rounded	918	Sharp	956 °C.	457	38° C.	Leadville, Colorado	999.9
C-545	15	477	Rounded	943	Very sharp	1156	466	213	Mine La Motte, Missouri	999.9
C-506	12	488	Rounded	890	Rounded	961	402	71	Near Roswell, New Mexico	600
C-527	4	387	Rounded	891	Sharp		504		Tarnowitz, Silesia	600
C-132	15	484	Rounded	959	Very sharp	1019	475	60	Mine La Motte, Missouri	999.9
C-492	10	447	Rounded	870 927 950					Tuscany, Italy	600

at the transition, are complicated at the close of the dissociation of the paramorphic calcite by additional breaks in the curve. These breaks in the curve range from the inflexional change in C-487 and C-545 to the formation of subsequent independent breaks which, for some samples, become more widely separated from the main break, as is shown in records C-506, C-527 and C-132. The sample of aragonite (curve C-492) represents an extreme in that it shows both inflexional alterations of the curve and many subsidiary breaks. The probable origin of these subsidiary breaks will be considered with the discussion of the aragonite-calcite mixtures.

A summary of the observations on these curves is given in Table 2. The temperature of the transition from aragonite to calcite is variable and no relation between this temperature and the content of substituents such as Sr and Pb could be established. The variability of the transition temperature, T_1, and the dissociation temperature, T_2, for duplicate runs is shown clearly in curves C-484 and C-471 obtained with aragonite from Styria, Austria, and C-545 and C-132, aragonite from Mine La Motte, Missouri. These reactions are not reversible and many factors contribute to departures from definite agreement between duplicate runs.

(3) Calcite curves

Thermal analysis curves for calcite are given in Fig. 3, and the data obtained from the curves are summarized in Table 3. All the curves are similar. They all exhibit sharp thermal dissociation breaks. The size of the particles affects the temperature at which dissociation begins, for finer sizes tend to broaden the base of the break.

Theoretically we would expect that the finer particles would cause a spreading of the curve through the onset of dissociation at a lower temperature. Small particles have a much greater surface area than large particles and hence a proportionately greater number of broken bonds. Broken bonds reduce the thermal stability of solids in the boundary layer. As the particles become finer and finer, the importance of the boundary layer increases. Smaller particles also have a greater vapor pressure than larger particles. None of the samples discussed here contained a significant proportion of exceedingly fine particles. It is likely that such fine particles would spread the base of the curve more than was observed.

Twinning of calcite apparently has little if any effect on the character of the thermal analysis curve.

(4) Aragonite with calcite curves

A natural mixture of calcite and aragonite was fortunately available

TABLE 3. OBSERVATIONS ON THE THERMAL CURVES OF CALCITE

Record No.	Sample No.	Temperature of dissociation	Character of the break	Comments	Locality	Resistance in the galvanometer circuit
C-148	2	939° C.	Sharp	Contains some dolomite. (Magnesium is not in the calcite)	Ala-Mar magnesite deposit, Sec. 34 T.12N. R.59E. Nye County Nevada.	600 ohms.
C-89	13	972	Sharp	Analyzed sample of R. C. Wells	Joplin, Missouri	999.9
C-558	F-1102	967	Sharp	Coarsely twinned	Franklin Furnace, New Jersey	999.9
C-552	13	956	Sharp	Analyzed sample of R. C. Wells (−48+65 mesh) = 34% (−200 mesh) = 66%	Joplin, Missouri	600
C-521	13	954	Sharp	Analyzed sample of R. C. Wells (−20+48 mesh) = 24% (−66 mesh) = 76%	Joplin, Missouri	600
C-533	11	937	Sharp	Paramorph after aragonite	Soda Dam Hot Spring deposit, Jemez Springs, New Mexico.	999.9
C-485	7	939	Sharp	Paramorph after aragonite (Scales)	Var. Schaumkalk. Myokenzan Harima, Japan	999.9
F-1*	A-3	952	Sharp	Coarsely twinned.	Highway cut, one-half mile N.E. of Myersville, Maryland.	900
C-307*	18	914	Sharp	Contains pyrite and sericite. Vug filling.	Champion mica mine, Amelia County Virginia. Record by W. Griffitts.	600

* These curves are not given in Fig. 3. The curve for F-1 is given in Faust (1944) on p. 144.

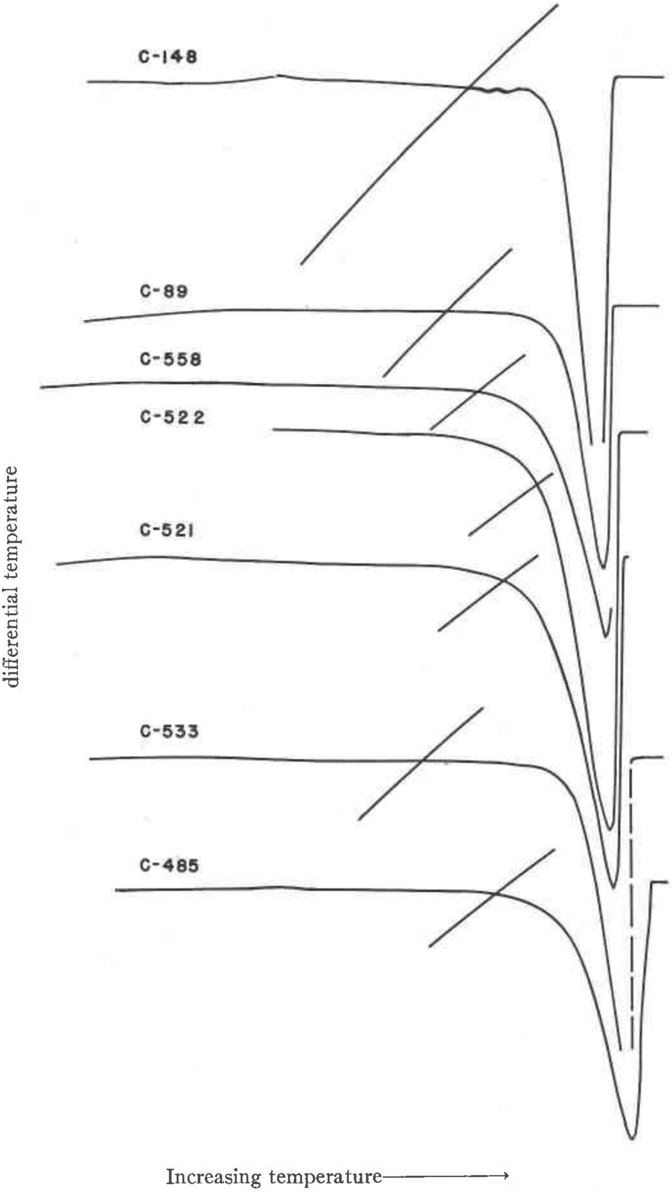

FIG. 3. Thermal analysis curves for calcite. C-148 = calcite #2, C-89 = calcite #13, C-558 = calcite #F-1102, C-522 = calcite #13, C-521 = calcite #13, C-533 = calcite #11, C-485 = calcite #7. The diagonal line intersecting the curves is a portion of the curve registering the temperature.

for study. This material, a spring-water deposit from Monte Neva Hot Springs, Nevada (sample #8), consists of prismatic crystals of aragonite and equant rhombs of calcite. The temperature of the springs that deposited these minerals ranges from 173° F. (78.3° C.) to 193° F. (89.4° C). The thermal curve, C-504, (Fig. 4), shows a small but well-formed peak that corresponds to the transition of aragonite to calcite. The dissociation curve of the calcite is sharp.

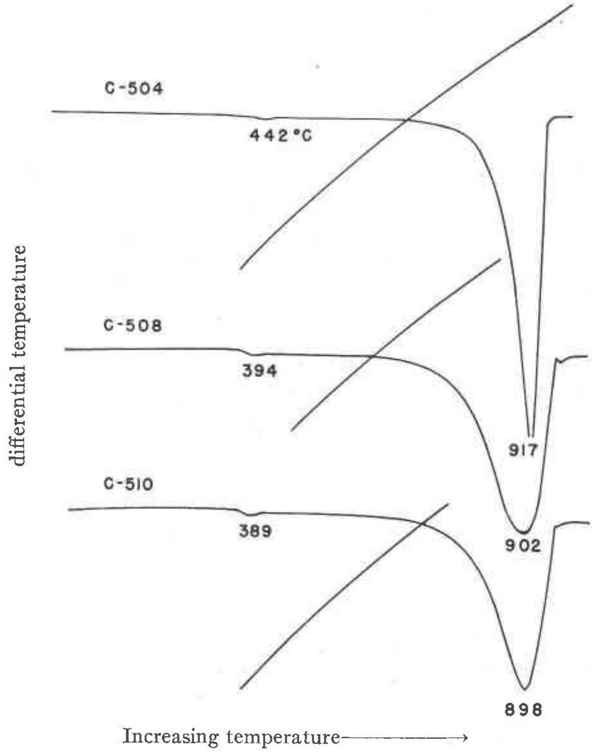

FIG. 4. Differential thermal analysis curves for natural and artificial mixtures of aragonite and calcite. C-504 = natural aragonite-calcite mixture #8, C-508 = mixture of 50% aragonite #5 and 50% calcite #13, C-510 = 90% aragonite #5 and 10% calcite #13. The diagonal line intersecting the curves is a portion of the curve registering the temperature.

In addition to this natural mixture, two artificial mixtures were prepared. The sample used to obtain curve C-508 was made up of 50 per cent of aragonite #5 and 50 per cent of calcite #13, whereas that for curve C-510 was made up of the same minerals in the proportions of 90 per cent aragonite to 10 per cent calcite. Both of the minerals used in the mixtures give normal uncomplicated patterns. The curves, C-508 and C-510, both show the transition of aragonite to calcite as was anticipated. The break showing the dissociation of calcite is markedly different from that of either of the pure minerals used. This break in the curve is a compound break and arises from the presence of two types of calcite, that which results from the transition of aragonite to calcite and that used in the mixture. Each of these types of calcite dissociates at slightly different temperatures, hence the reactions overlap. The break in curve C-508 due to the dissociation of calcite has a very wide base and a rounded top. The temperature of this break is 902° C., much lower than the mean values of the pure minerals used, namely 963° C. The shifting of the temperature of the break in thermal analysis studies on mixtures has been pointed out by many workers. The temperature of this break for the mixture of 90 per cent aragonite and 10 per cent calcite is even lower than that mentioned previously (898° C.) for curve C-510. A curious subsidiary break, of very small size, occurs in curves for mixtures after the curve for the principal dissociation of calcite. This break does not appear in either of the pure mineral curves and is believed to arise through the delayed dissociation of some of the larger grains of calcite. Measurements and observations on these curves are given in Table 4.

The appearance of the subsidiary breaks on the aragonite curves, mentioned earlier, may arise in part as a consequence of difference in size of the particles. It may also be due to intra-particle texture or to the presence of substances in solid solution not uniformly distributed through the fragments, as in zoned crystals. The presence of small amounts of calcite, not produced by the present rapid inversion of aragonite to calcite in the sample, and hence lacking in the strain induced by paramorphism, could also give rise to subsidiary breaks. It should be noted (Fig. 4) that the curve for 50 per cent aragonite and 50 per cent calcite almost was resolved into two breaks (curve C-508).

(5) Measurements of areas under the thermal curves

Areal measurements were made, using a polar planimeter and checking with a simple grid, on five records, all with 999.9 ohms resistance in the galvanometer circuit. These measurements were repeated at least five times for each curve; the agreement between successive measurements on the same curve was satisfactory. From the data for each curve, the area corresponding to the transformation of 1 gram of aragonite to calcite was calculated. The complete lack of agreement among the calculated results was disappointing. The average area arising through the transformation of 1 gram of aragonite to calcite was found to be 30 square millimeters, the maximum being 43.8 square millimeters and the minimum 17.5 square millimeters.

TABLE 4. OBSERVATIONS ON THE THERMAL CURVES OF MIXTURES OF ARAGONITE AND CALCITE

Record number and description	Sample No.	Temperature of transition–T_1	Character of break	Temperature of dissociation–T_2	Character of break	Temperature of subsidiary break–T_3	T_2–T_1	T_3–T_2	Resistance in the galvanometer circuit
C-504. Aragonite and calcite Monte Neva (formerly Melvin) Hot Springs. SW ¼ Sec. 24, T.21.N. R.63E, White Pine County, Nevada.	8	442° C.	Rounded	917° C.	Sharp		475° C.		999.9 ohms
C-508. Aragonite, Batesville District, Arkansas, 50%; Calcite, Joplin District, Missouri, 50%.	5 and 13	394	Rounded	902	Rounded	964° C.	508	62° C.	999.9
C-510. Aragonite, Batesville District Arkansas 90%; Calcite, Joplin District, Missouri 10%.	5 and 13	389	Rounded	898	Sharp	948	509	50	999.9

The heat of transformation of aragonite to calcite is given by Goranson (1942) as $\Delta H = +21$ joules per gram. The positive sign indicates that the reaction is endothermic. The area under the curve, given above, is produced by heat effects of this order of magnitude.

The heat of transformation is given off in the rearrangement of the atoms and groups of atoms in the crystal structure of aragonite as they shift to their new positions in the calcite structure. This rearrangement has been studied by Kôzu and Kani (1934) and the reader is referred to their paper for the details.

The area under the curve for the dissociation of calcite paramorphous after aragonite was also measured for the same series of curves mentioned above. It was found that the dissociation of 1 gram of calcite produces an average area of 5,646 square millimeters, with a maximum of 6,836 square millimeters and a minimum of 4,743 square millimeters. These results apply to curves obtained with 999.9 ohms in the galvanometer circuit. The value of the heat of the reaction, ΔH, for the dissociation of calcite is given by Smyth and Adams (1923) as follows: 9,680 joules at 800° C.; 8,132 joules at 1,000° C.; and 8,654 joules at 1,200° C. The value of ΔH at 898.6° C., the temperature at which $p = 760$ mm. is 9,426 joules. These values of ΔH cover the range of temperatures of 800°–1,200° C. and are computed from data for the system at equilibrium. They indicate the order of magnitude of the heat effect which produces the curves.

The chief difficulty in accurate areal measurement is connected with construction of the straight line used to close the base of the curve. This is further complicated by the steepness of the curve at the onset of transformation. The observations on the measurements of the area under the curve suggest that the use of a simple grid for measurement of the area is entirely adequate.

The variation in the area associated with the transformation of aragonite to calcite imposes a limitation upon quantitative estimates of mixtures of aragonite and calcite. If such estimates are made, it will be necessary to first determine the area under the curve associated with the transformation for the particular aragonite being studied.

THE ARAGONITE→CALCITE TRANSFORMATION

The aragonite→calcite transformation is monotropic in character. It is therefore irreversible and does not take place at a constant temperature.

It has long been well established that merely heating aragonite in air to about 450° C. is sufficient to convert it to calcite. Johnston, Merwin, and Williamson (1916) found that this transformation could be brought about in a few days at temperatures as low as 100° C. by heating in the presence of water. They found that pure dry aragonite was changed to calcite in a few minutes when heated at 470° C., in 90 minutes at 425° C., and in 3 hours at 400° C. Kôzu and Kani (1934) in their studies on the thermal expansion of aragonite crystals observed that the transformation took place, in air, in the range of 450–490° C. More recently, Zimens (1937) using the Hahn radioactive-emanation technique, showed that the transformation of aragonite to calcite begins at about 450° C. These observers all agree on the irreversibility of the aragonite-calcite transformation. The present study shows that at a heating rate of 12° C. per minute, the transformation takes place between 387° and 488° C.

THE FORMATION OF UNSTABLE POLYMORPHS

Credner (1870) made a very thorough study of the synthesis of calcite and aragonite. He found that calcite is precipitated from pure solutions of "doppelt kohlensaurem Kalkes," whereas both calcite and aragonite are precipitated from solutions of calcium bicarbonate that contain limited amounts of lead carbonate, calcium sulfate, or strontium carbonate. He also observed that temperature of precipitation and strength of the solution were not "unique" factors in the cause of the dimorphism of calcium carbonate. This study of Credner is noteworthy, considering the early date of the research. He supported his chemical studies by microscopic examination of the phases and reproduced drawings of the crystals. in his paper. He further tested his conclusion that strontium entered into the aragonite crystals by using a spectroscope to determine its presence. The standard French reference books on mineral synthesis paid no attention to his work and it was soon forgotten. Johnston, Merwin, and Williamson (1916) also observed the formation of aragonite from solutions to which Pb, or sulfate was added.

Bloom and Buerger (1937) have discussed the genesis of polymorphous forms, including the aragonite-calcite relations, and conclude:

> Certain types of impurities present in solution during precipitation of a solid phase often effect the generation of an unstable polymorphous modification. The modification thus generated often contains this impurity, sometimes held so tenaciously as to defy usual chemical treatment for its removal. Under these conditions, the structure containing this impurity shows a remarkable resistance to transformation to the stable structure of the pure substance. The complete removal of the impurity is apparently necessary for the realization of the transformation.

Spectrographic examination showed the presence of barium, strontium, or lead in all of the aragonites used in this study. The total amounts of the oxides of these metals are 0.1 per cent or more. The two specimens of calcite paramorphous after aragonite contain a total of 0.03–0.06 per cent of these oxides. Calcite from Joplin, Missouri, has only 0.01 per cent of these oxides. These results suggest the desirability of further spectrographic studies on these minerals.

TABLE 5. IONIC RADII (IN ANGSTROM UNITS) OF THE CATIONS OF THE CALCITE AND ARAGONITE GROUPS (AFTER BRAGG, 1937)

	Mg	Fe	Zn	Mn	Cd	Ca	Sr	Pb	Ba
Calcite type	0.78	0.83	0.83	0.91	1.03	1.06	—	—	—
Aragonite type	—	—	—	—	—	1.06	1.27	1.32	1.43

The presence of barium, strontium, and lead in solid solution in aragonite is well known. However, zinc does not form an orthorhombic carbonate, and one would anticipate, from consideration of the atomic radii listed in Table 5, that substitution of Ca by Zn would tend to favor the formation of a rhombohedral carbonate. It was of interest, therefore, to re-examine nicholsonite, the reputed zincian aragonite, which Butler claimed (1913), contains as much as 12 per cent zinc. The specimen used in this study was from the Canfield collection of the U. S. National Museum and consists of white radiating blades arranged in asteriated form. Spectrographic analysis failed to reveal determinable quantities of zinc in this sample. The *d* spacings of the powder photograph agree with those of aragonite. Zinc was, however, found in two of the aragonite specimens, which contained 0.12 and 0.13 per cent ZnO. Both of these samples are fine-grained, and neither *x*-ray study nor microscopical observations can unequivocally rule out the possibility of the presence of some minor amount of a zinc mineral. The presence of zinc in solid solution in aragonite thus needs further study.

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