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PRELIMINARY REPORT ON THE VARIATIONS IN DIFFERENTIAL
THERMAL CURVES OF LOW-IRON DOLOMITES

BY
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PRELIMINARY REPORT ON THE VARIATIONS IN
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OF LOW-IRON DOLOMITES*

DONALD L. GRAF

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ABSTRACT

Soluble salts, present to the extent of as much as 0.3 weight per cent, principally potassium, sodium, calcium, and magnesium chlorides, are found to be a major cause of the variations in position and shape of the lower-temperature endothermic deflection in differential thermal analysis curves of a number of low-iron sedimentary dolomites. Finely ground dolomites from which soluble salts have been leached give DTA curves like those of salt-free specimens. Conversely, the curves of essentially salt-free specimens to which dilute salt solution has been added duplicate those of naturally occurring salt-rich dolomites.

The particle size to which specimens are ground before differential thermal analysis becomes increasingly important in more coarsely crystalline rocks and results in the shifting of deflection temperatures without marked change in the shape of the deflections. Dilution of samples with noncarbonate material lowers the deflection temperatures because of reduced CO₂ partial pressure in the furnace atmosphere.

The Na₂O and K₂O present in accessory-mineral illite and feldspar are not released from the lattices of these minerals at the temperatures of the lower dolomite endotherm.

Understanding of the significance of salt-dolomite interaction, and of area measurements under dolomite DTA curves, is believed to be contingent upon a more detailed knowledge of the mechanism of dolomite thermal decomposition.

The kind and amount of soluble salts in dolomites may be characteristic of different

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environments of deposition, but it does not appear to be possible to secure reliable salinity estimates from the extent of distortion of DTA curves of dolomite.

INTRODUCTION

Variations in differential thermal analysis curves of dolomite have been attributed by Faust (1949) largely to grain size and rate of heating. Sprague (1949) was unable to find evidence of cation disorder in a number of specimens, and suggested that a domain structure, destroyed by grinding during preparation of powder x -ray samples, might be responsible for the unusually large separation of the two endothermic deflections for "Ohio dolomite." According to this hypothesis, the grinding of DTA samples, to a coarser size than x -ray samples, would presumably not affect the domains. Murray (1950) noted that the curve for "Ohio dolomite" could be duplicated by soaking "non-Ohio dolomite" in a one-percent solution of sodium chloride overnight, but his DTA curves have not yet been published. A number of workers (Budnikov and Bobrovnik, 1938; Berg, 1943; Schwob, 1950) have described the effect of small amounts of alkali- and alkaline-earth salts upon thermal decomposition of dolomite. The principal findings of Berg's paper are substantiated by the present study.

The present investigation has centered around DTA curves, but the report includes some related stratigraphic and chemical information. Table 1 lists the specimens examined, all of which are low in ferrous iron, as may be seen from Table 2. It was felt that ferrodolomites and ankerites, whose high ferrous iron content is known to modify the curve strongly, would introduce an undesired additional variable into a preliminary study. The Fe^{++} values in Table 2 represent the maximum possible Fe^{++} in these dolomites, for some of the ferrous iron will be shown later in the paper to be present in illite, and furthermore the determination of Fe^{++} by permanganate reduction gives high values if S^- , organic material, or any other reducing substance is present. There is no evidence that significant amounts of Fe^{++} are oxidized to Fe^{+++} during the determination (McVicker, 1951).

The R-series of Illinois sedimentary dolomites are Chicago-area Silurian types from the suite assembled by Willman (1943) for his study of high-purity dolomites of Illinois. The K-series specimens are part of a group of dolomites having different colors, textures, and fossil types, collected from the reef-core and near-reef-flank beds exposed in a quarry north of Kankakee, Illinois.

The writer wishes to express his appreciation to his Illinois Geological Survey colleagues, J. E. Lamar, W. F. Bradley, J. S. Machin, H. B. Willman, W. A. White, and E. C. Jonas, for stimulating discussion and

TABLE 1. SPECIMEN LOCATIONS AND DESCRIPTION

Specimen	Series	Formation	Member	Relation to reefs	Lithology
R-1926	Niagaran	Joliet	Markgraf	Non-reef	Dense, fine-grained, slightly argillaceous, slightly silty, no visible porosity (common type)
R-1927	Niagaran	Joliet	Markgraf	Non-reef	Like R-1926 but more nearly pure, slightly coarser grained, more porous (common type)
R-1928	Niagaran	Joliet	Romeo	Non-reef	Very fine-grained, widespread unit
R-1929	Alexandrian	Kankakee	—	Non-reef	Well-bedded, some greenish shale partings (not in this sample)
R-1930	Niagaran	Brandon Bridge	—	Non-reef	Contains reddish shale partings, reddish crinoid stems
R-1931	Niagaran	Chicago	—	Reef flank beds	Highly porous unit, Thornton reef
R-1932	Niagaran	Chicago	—	Reef flank beds	Less porous than R-1931; Thornton reef
R-1933	Niagaran	Chicago	—	Non-reef (?) but (?) near reef	Rather pure, gray organic (?) banding
R-1934	Niagaran	Chicago	—	Flat non-reef beds just outside dipping reef flank beds	Rather pure, probably made up of reef detritus
R-1935	Niagaran	Elwood	—	Inter-reef	Intermixed silty dolomite and thin greenish clay laminae
K-1	Niagaran	Chicago	—	Fossil and texture varieties from loose blocks; reef core or reef flank near the core.	Very fine-grained, light yellow around vugs and darker elsewhere
K-2	Niagaran	Chicago	—		Fine-grained, porous, crumbling yellow rock
K-3	Niagaran	Chicago	—		Medium-grained porous red unit
K-5	Niagaran	Chicago	—		Mottled, dense medium gray and medium-grained light brown
K-6	Niagaran	Chicago	—		Light yellow replacement and filling of Favosites
K-7	Niagaran	Chicago	—		Coarsely crystalline, non-porous, light brown
K-9	Niagaran	Chicago	—		Porous fine-grained gray rock, rock, light brown zones
Manteno, Illinois Carey, Ohio	Niagaran	Chicago	—	Near-reef-flank beds	Fine-grained non-porous brown rock Fine-grained vuggy cream-colored dolomite
Anna, Illinois	Niagaran	Chicago	—	—	Light pink crystalline aggregates filling cavities in Ste. Genevieve limestone
Lee, Mass.	Niagaran	Chicago	—	—	Fine-grained white dolomite marble (Wards)
Sierra das Eguas, Brazil New York	Niagaran	Chicago	—	—	Large colorless, transparent cleavage fragment (Wards) Cavity lining of 1/8" white crystals in dense black limestone (Wards)

TABLE 2. CHEMICAL ANALYSES OF ILLINOIS DOLOMITES

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Speci- men	CaO	MgO	FeO	CO ₂	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	H ₂ O	100 Total	Maximum possible weight % illite	Maximum possible K ₂ O in illite	Maximum possible Na ₂ O in illite
R-1926	27.72	18.76	0.36	42.45	8.54	0.16	1.50	0.16	0.12	0.73	0.10	100.60	5.85	.38	.02
R-1927	30.09	20.29	0.38	45.60	2.60	0.15	0.35	0.09	0.11	0.20	0.11	100.03	1.36	.09	—
R-1928	30.72	20.92	0.32	46.72	0.98	0.10	0.00	0.06	0.12	0.06	0.11	100.11	—	—	—
R-1929	29.57	20.16	0.29	44.89	3.71	0.11	0.69	0.17	0.10	0.34	0.09	100.12	2.69	.18	.01
R-1930	28.76	19.26	0.40	43.38	6.19	0.13	1.17	0.22	0.13	0.69	0.08	100.41	4.56	.30	.01
R-1931	30.57	21.54	0.07	47.12	0.06	0.00	0.25	0.02	0.11	0.01	0.19	99.94	0.98	.06	—
R-1932	30.91	21.60	0.08	47.38	0.12	0.03	0.19	0.01	0.20	0.03	0.23	100.78	0.74	.05	—
R-1933	30.80	21.56	0.13	46.96	0.36	0.03	0.26	0.12	0.09	0.05	0.08	100.44	1.02	.07	—
R-1934	30.76	21.32	0.18	47.03	0.68	0.02	0.25	0.09	0.15	0.07	0.10	100.65	0.98	.06	—
R-1935	25.86	17.89	0.25	39.16	13.58	0.13	1.85	0.17	0.10	0.95	0.08	100.02	7.21	.47	.02
K-1	30.53	21.60		46.81								(98.94)			
K-2	30.62	21.92		47.33								(99.87)			
K-3	30.63	21.60		47.11								(99.34)			
K-5	30.70	21.29		46.70								(98.69)			
K-6	30.60	21.50		46.82								(98.92)			
K-7	30.91	21.50		47.04								(99.45)			
K-9	30.65	21.26		46.50								(98.41)			
Pink	32.23	20.20		47.14								(99.57)			

Cupric nitrate staining tests (Rodgers, 1940; Hugi, 1945) reveal calcite intergrown with the Anna dolomite, as suggested by its MgO/CaO molar ratio of 0.870. Calcite was also found in small amount in several R- and K-series specimens examined, usually as a vug lining presumed to be secondary, but rarely intergrown with the dolomite as isolated grains that may be remnants of original CaCO₃ before dolomitization.

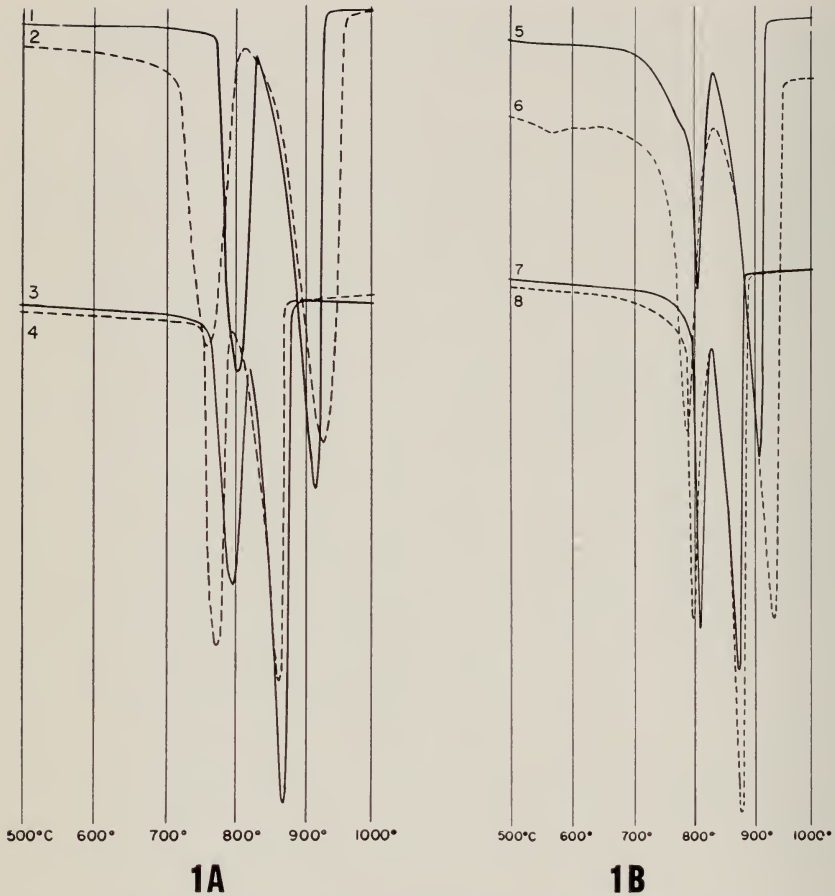
helpful criticism, and for reading part or all of the final manuscript. J. E. Melvin, State Geologist of Ohio, kindly furnished the specimen of Ohio glass-grade dolomite.

DIFFERENTIAL THERMAL ANALYSES PROCEDURE

The equipment used for differential thermal analyses has been described (Grim and Rowland, 1942). The procedure for preparing samples used in the present study involves grinding the entire sample to minus 325-mesh in a mullite mortar, to minimize as much as possible the effect upon the curves of grain-size in coarsely crystalline rocks. In this way, too, the final portion of the sample used in the analysis is representative of the original rock, which might not be true of a specific size fraction. The dolomite powder is next mixed with an equal weight of α - Al_2O_3 , prepared from $\text{Al}(\text{OH})_3$ held at 1380°C . for 7 hours which dilutes the sample enough so that none of it is expelled from the sample block by rapid evolution of CO_2 . Because of the dilution and the consequent lower partial pressure of CO_2 in the furnace atmosphere, temperatures at which the endothermic deflections occur are somewhat lower than those customarily reported for undiluted specimens. The details of the complex lower-temperature deflection are better resolved because of the dilution, and the higher-temperature deflection is unusually sharp because of the increased amplification used for diluted-sample curves.

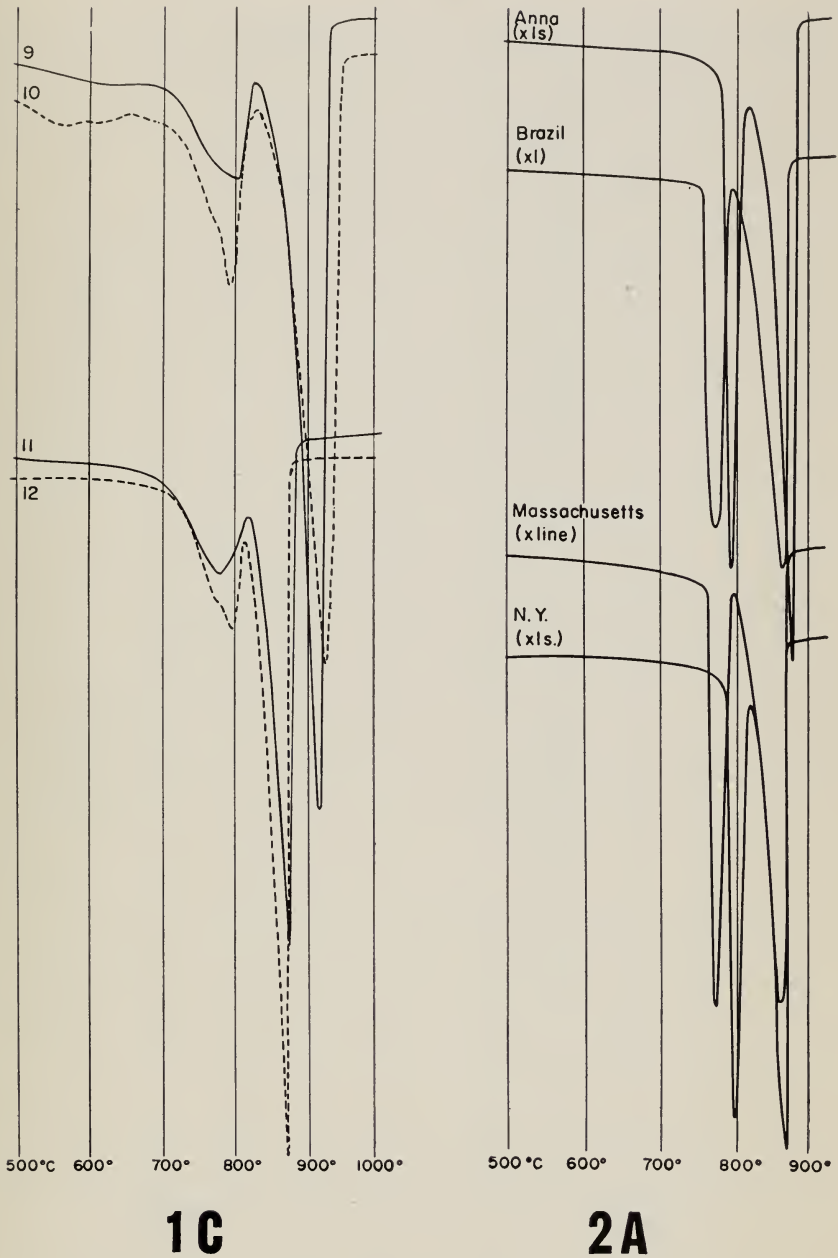
The effect upon the DTA curves of particle-size obtained by grinding, and of dilution, is shown in Fig. 1 for a dolomite marble, a dense sedimentary dolomite (K-7), and a sedimentary dolomite (K-2) which readily breaks into a coarse sand. It is sufficient at this point to note from Fig. 1 that any dolomite DTA curve must be regarded as valid in detail only for a set of experimental conditions which have been arbitrarily selected; these curves are discussed at greater length below. The curves shown in figures 2, 3, 4, and 6 were run under conditions identical with those for curve 4 in Fig. 1.

Throughout the paper, DTA curves of salt-containing dolomites, diluted with α - Al_2O_3 , are discussed, and the question of DTA deflection from reaction between the alkali- and alkaline-earth salts and the α - Al_2O_3 arises. DTA curves of mixtures of several of the pure salts and α - Al_2O_3 show no deflection below the melting points of the salts. Therefore there is apparently no solid-state reaction between salts and alumina which has a sufficiently rapid heat effect to be detected. The melting points of the chlorides and sulfates of K, Na, Mg, and Ca are at or above the temperature of maximum deviation from baseline of the sensitive lower-temperature dolomite deflection for diluted samples. Thus it

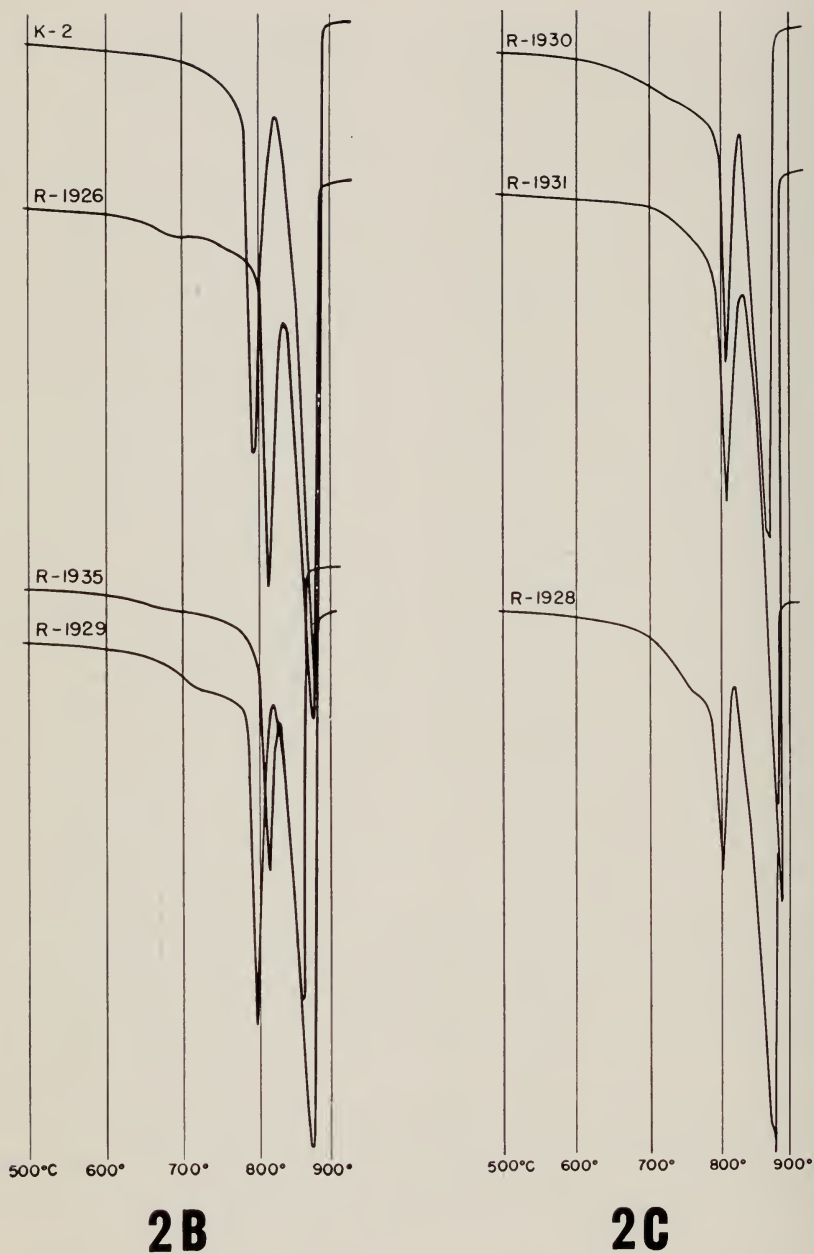


FIGS. 1A, 1B, and 1C. DTA curves of dolomite samples of varying particle size and dilution. Curve 1 Brazilian dolomite—65 mesh, 0.345 gram, 300 ohms resistance in series. Curve 2. Brazilian dolomite—325 mesh, 0.345 gram, 300 ohms. . . . Curve 3. Brazilian dolomite—65 mesh, 0.14 gram+0.14 gram α - Al_2O_3 , 200 ohms. . . . Curve 4. Brazilian dolomite—325 mesh, 0.14 gram+0.14 gram α - Al_2O_3 , 200 ohms. . . . Curves 5-8. Specimen K-2. Curves 9-12. Specimen K-7.

seems unlikely that a chloride or sulfate melt has an opportunity to attack the α - Al_2O_3 before completion of the deflection, although the possibility of local melting of salt mixtures should be considered further. The validity of the diluted-sample curves is further indicated by the fact that the order of undiluted-sample curves arranged in a progression toward increasing "abnormality," a term that will be defined below, duplicates that of the diluted samples, even though the general shape of the lower-temperature endothermic deflection in the undiluted-sample curves is somewhat different.



Little importance has been attached to actual lengths of deflections, especially the sharp ones, because several different furnaces and thermocouple wire assemblies, yielding somewhat different sensitivities for the



FIGS. 2A, 2B, 2C, and 2D. DTA curves of dolomite samples, diluted with 50 wt. percent α - Al_2O_3 .

same resistance in series, had to be used. The curves in Fig. 1, which should be directly comparable, are an exception. The shapes of deflections, ratios of deflection lengths within the same curve, and ratios of areas under the two deflections of a single curve are considered to be meaningful; limitations on their quantitative accuracy will be discussed.

DIFFERENTIAL THERMAL ANALYSES CURVES

Typical curves for pure, low-iron dolomite are given by the specimens from Brazil, Massachusetts, New York, and Anna, Illinois, at the top of Fig. 2. The sharp break from the gently sloping low-temperature portion of the curve into the lower-temperature endothermic deflection is characteristic. Even among these specimens, however, there is a difference of 30° C. in the temperature of that deflection maximum, and some variation in the sharpness of both deflections.

The curves of a few sedimentary dolomites, such as K-2, are similar to those of the highly crystalline specimens, but for the most part the sedimentary dolomite curves have a smaller ratio of [lower-temperature deflection height]/[higher-temperature deflection height], a more gradual beginning of the lower-temperature deflection, and a lower-temperature deflection complicated by a shoulder (R-1928), a vague preliminary deflection (R-1929), or an actual separate deflection (R-1934). The curves are arranged approximately in order of increasing abnormality, using the criteria just enumerated.

All the curves from R-1927 to K-10 have higher-temperature endothermic deflections very similar in shape and length to that shown for R-1933, and the others have been omitted to save space.

The effect of soluble salts on DTA curves

In order to determine the composition and approximate amount of soluble salts in the specimens studied, two-hundred gram portions of Massachusetts dolomite, Ohio dolomite, a composite of the K-series Kankakee specimens, and Manteno dolomite were ground in a mullite mortar to a fine powder, placed in 400 ml. of distilled water, stirred intermittently for 8 hours, and filtered through Whatman #42 filter paper.

The leachate analyses are given in Table 3, both in weight per cent and in milliequivalents per 200 gram sample. The Massachusetts dolomite contains a much smaller amount of soluble salts than the sedimentary dolomites. The chloride content is from 6 to 30 times that of sulfate; inasmuch as DTA curves of dolomites artificially enriched with several per cent of various sulfates are not distorted, the sulfate content of the leachate analyses is not regarded as significant to the present discussion.

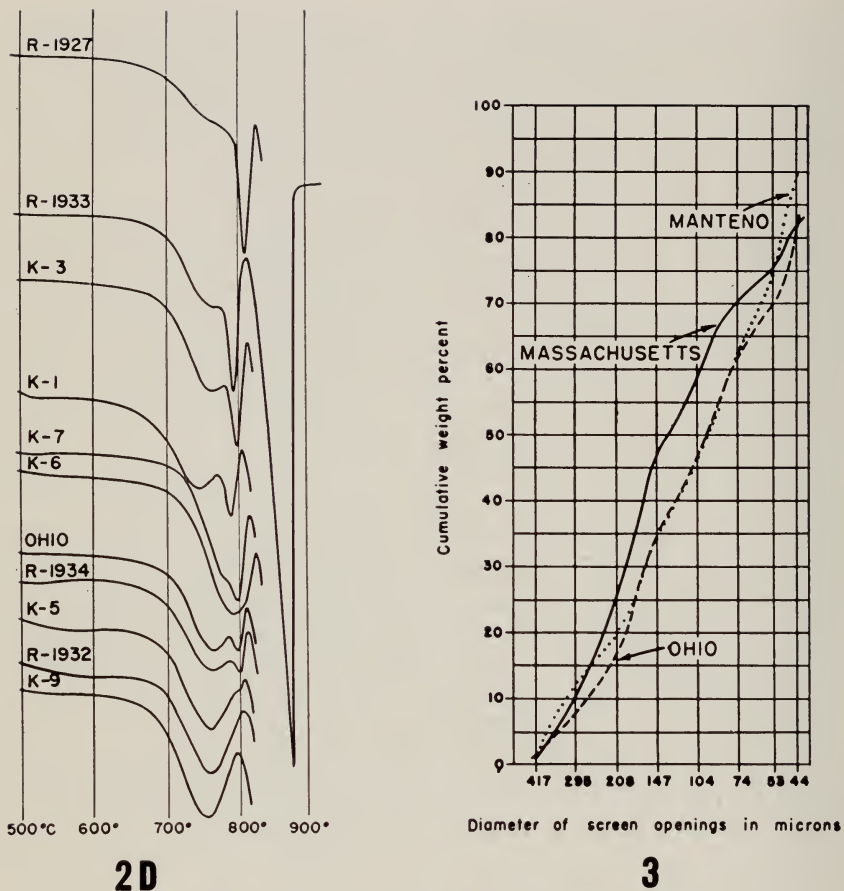


FIG. 3. The particle size distribution of several dolomite powders used in leachate experiments.

The amount of Na_2O is from 2 to 9 times that of K_2O , the reverse of the ratio in the total analyses given in Table 2.

As the soda and potash in the leachates satisfy a little less than one-third of the chloride and sulfate, alkaline-earth chlorides must be present in the specimens. At least part of the MgO and CaO left (column 5 of Table 3) after these calculations results from the solution of dolomite, but no attempt has been made to give the contribution from this source, both because of uncertainty in published values of dolomite solubility and because the dolomite in these experiments was almost certainly not in the water long enough to give an equilibrium solubility. Iron chloride, which might result from the oxidation of small amounts of pyrite, was

TABLE 3. LEACHATE ANALYSES

Specimen	Weight % of original rock						Milliequivalents/original 200 gm. sample						Meq. (CaO + MgO) remaining after satisfying SO ₄ ²⁻ and Cl ⁻	
	CaO			Total			CaO			Total				
	MgO	K ₂ O	Na ₂ O	SO ₄ ²⁻	Cl ⁻	Total	MgO	K ₂ O	Na ₂ O	SO ₄ ²⁻	Cl ⁻	Total		
Massachusetts ¹	.003	.013	0.0005	.0007	.000	0.0182	0.11	1.30	0.02	0.05	0.04	1.52	-0.03	1.41
Ohio ²	.006	.010	.002	.011	.001	0.060	0.43	1.00	0.08	0.71	0.04	1.67	0.92	0.20
Kankakee ³	.011	.019	.004	.009	.0025	0.1005	0.79	1.90	0.17	0.58	0.10	3.14	2.49	0.59
Manteno ⁴	.007	.013	.002	.009	.0025	0.0645	0.50	1.30	0.08	0.85	0.10	1.77	1.21	0.51

Analyst: L. D. McVicker.

¹ Crystalline dolomite, Lee, Massachusetts.

² High-purity dolomite, Carey, Ohio.

³ Composite of Kankakee, Illinois, quarry specimens (K-series specimens in table 1).

⁴ Niagaran dolomite, Manteno, Illinois.

not determined and could account for some of the variation in column 5 of Table 3. It is unlikely that any dolomite particles passed through the filter paper.

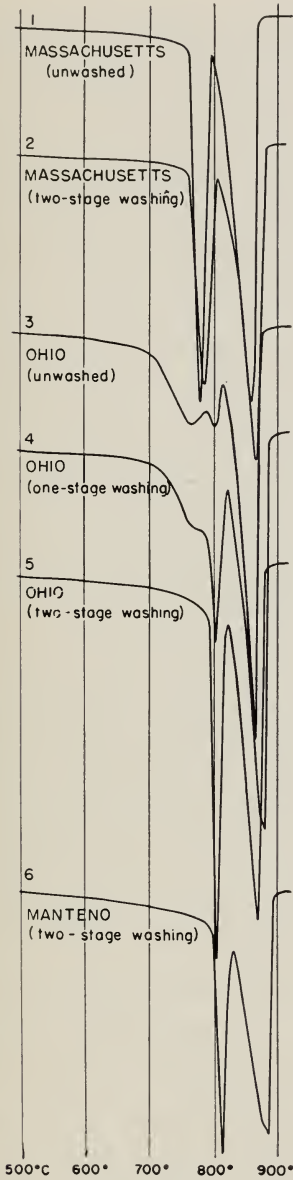
Not all the salts were leached from the dolomites, but a considerable fraction, believed to be representative, was recovered. The particle-size distribution of the fine powders used in the initial leachate experiments is given in Fig. 3. The differences among the three samples reflect variations in the ease with which the dolomites pulverized. The difference in particle-size distribution for the several powders presumably affected the quantity recovered.

The DTA curve of the unleached Ohio dolomite with the particle-size distribution of Fig. 3 is number 3 in Fig. 4. The next curve, which represents this material after it was leached, dried, and reground to pass 325 mesh (44 microns), is definitely more "normal" according to the criteria previously discussed. A 5-gram portion of the leached Ohio dolomite, reground to minus 325 mesh and then continuously agitated in 200 ml. of distilled water by means of a motor-driven stirrer for 8 hours, gave curve 5, which is typically "normal."

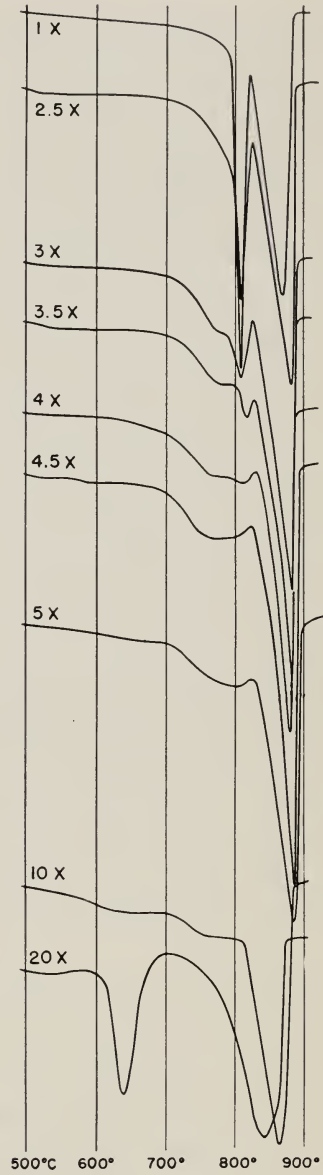
The Manteno dolomite, whose original DTA curve was very similar to that of the Ohio material, gave curve 6 after the two-stage washing described above. However, the Massachusetts dolomite, which as a "normal" curve, retained about the same ratio of deflection lengths after washing, although the deflections are somewhat less sharp.

The foregoing suggests that soluble salts are responsible for the DTA anomalies and that it should be possible to produce these anomalies in the curve of the Massachusetts dolomite by adding salts to it. Therefore a moderately concentrated distilled-water solution was prepared with HCl, H₂SO₄, MgO, CaO, KOH, and NaOH, in which the ratio Cl⁻:SO₄⁼:Na⁺:K⁺:Mg⁺⁺:Ca⁺⁺ in milliequivalents was 2.16:0.08:0.53:0.11:1.10:0.50, a close approximation to the average of the leachate analyses for the three sedimentary dolomites of Table 3. By diluting portions of this solution to different volumes, it was possible to add 0.3 ml. of solution to 0.14 gm. dolomite in each case and yet to use different salt concentrations. The ground dolomite samples were placed in the centers of watch glasses, and the solution added from a graduated pipette. After drying, the dolomite was briefly reground and the standard 0.14 gm. of α -Al₂O₃ diluent added.

DTA curves of the salt-treated samples, arranged according to the multiple of the original leachate concentration added, are given in Fig. 5, and closely duplicate the curves of the untreated dolomites. The temperature of the lower-temperature endothermic deflection in these artificial mixtures is somewhat higher than in most of the comparable natural curves for sedimentary dolomites, and the sharpness of that



4



5

FIG. 4. The effect of distilled water leaching upon the DTA curves of dolomite.

FIG. 5. DTA curves of Massachusetts dolomite with added salts. The figures given are multiples of the average of salt content in leachates of three sedimentary dolomites (Table 3).

deflection in the "4.5X" and "5X" curves of Fig. 5 is not comparable, for example, with its equivalent in the K-9 and K-5 curves of Fig. 2. The curves of numerous other artificial mixtures investigated indicate clearly that small variations in the particle size of the added salts and in the ratios of the several ions of which they are composed would be enough to alter the shape of the lower-temperature deflection. The position of the deflection varies with particle size; thus the difference in position noted here may be due to the finer grain size of the sedimentary dolomites, compared to the Massachusetts dolomite marble.

It appears from a comparison of the "1X" curve of Fig. 5 with that of the original Massachusetts dolomite in Fig. 2 that the addition of a very small amount of the salts actually sharpens the lower-temperature deflection. Conversely, the Massachusetts dolomite curve in Fig. 4, after washing, has a more blunted lower-temperature deflection than before. It does not necessarily follow from the sharpness of the lower-temperature deflections in the curves of the Ohio and Manteno dolomites after two-stage washing (Fig. 4) that these specimens still contain a small amount of salts; although this is probably true. The difference in grain size between these specimens and the Massachusetts dolomite is an additional variable.

The leachate analysis figures, which are much too low, give 0.060, 0.101, and 0.064 wt. per cent total soluble salts for the three sedimentary dolomites. The curves of artificial salt-dolomite mixtures indicate that concentrations ranging from 2 to 5 times that of the average leachate duplicate the range of curves for the natural salt-containing dolomites. These figures are slightly high because of a small amount of salt film which clings to the watch glass after preparation of the salt-dolomite mixtures and cannot be removed. Accordingly, the maximum amount of soluble salts present in the specimens examined is estimated to be 0.3 wt. per cent.

Detailed discussion of possible mechanisms of salt-dolomite interaction is not included in this preliminary report. It seems desirable, however, to mention the necessity of giving serious consideration to solid-state reaction for which conditions are ideal because: (1) at the temperature of the lower-temperature decomposition, the alkali salts are beginning to show measurable vapor pressures, indicating strong thermal agitation of their component ions, and (2) the magnesium carbonate in dolomite is unstable above about 600°, if appropriate bonds in the dolomite lattice can be weakened enough to permit its segregation.

The effect of particle size

With information regarding the role of soluble salts in dolomite thermal decomposition in mind, the effect of the particle size of the samples

may be better understood. Its effect is to shift the position of the deflection with only a moderate change in deflection shape. This is shown by curves 1-4 of Fig. 1, for an essentially salt-free Brazilian dolomite which is a single crystal, at least in the macroscopic sense. In contrast, the effect of water-soluble salts in increasing amounts is to distort the lower-temperature deflection severely before there is any change in temperature. Curves 9-12, for a salt-rich Kankakee dolomite whose average grain size is only slightly greater than the minus 4-micron particle-size obtained by grinding, illustrate this phenomenon. The amount of salts needed to shift the temperature of the deflection noticeably, as determined from synthetic mixtures ("20X" curve, Fig. 5), has not been encountered in the natural specimens examined, but obviously exists in dolomites from evaporite sequences, for example.

The increase in separation of the two dolomite endothermic deflections when particle size is decreased (Curves 1 and 2, 3 and 4, of Fig. 1) is the result of a lowered temperature for the first deflection. The lowering is generally attributed to the fact that there is a smaller temperature differential between the surface and the center for smaller particles than for large ones, and consequently a lower furnace temperature is needed to raise the center of the particle to a temperature at which dissociation of the center area will take place. A contributing factor is the thickness of the layer of already dissociated material through which the CO_2 has to pass. Smyth and Adams (1923) noted an initial dissociation for calcite, followed by a decrease in heat absorption, after which dissociation increased rapidly. They believed that CO_2 pressure within the crystals had to build up sufficiently to break through the initially formed CaO coating before dissociation could continue. Zawadski and Bretsznajder (1938) note that in the thermal decomposition of coarsely powdered calcite the velocity of the reaction falls almost to zero "at a certain distance from equilibrium."

The sharpness of the lower-temperature deflection is affected by the rapidity with which CO_2 can escape from the sample well, and in turn from the furnace, as well as from within the particle. This is equivalent, of course, to saying that the partial pressure of CO_2 in the atmosphere between the particles is critical in determining how rapidly the dissociation will be completed. Thus, the 0.345 gram sample of minus-325 mesh material used for curve 2 of Fig. 1 had to be packed much more tightly to fit into the sample well than the same weight of minus-65 mesh material for curve 1, and the lower-temperature deflection is accordingly sharper in curve 1 than in curve 2. When the samples are diluted with $\alpha\text{-Al}_2\text{O}_3$ (curves 3 and 4), the quantity of CO_2 which must escape from the sample well is decreased enough so that the partial pressure of CO_2 in the atmosphere around the sample does not approach the

magnitude of that within the particles. Consequently, particle size becomes the critical factor in determining deflection sharpness, and the minus-325 mesh material of curve 4 gives the sharper low-temperature deflection.

The next logical step in this line of investigation is experimentation with gas atmospheres directed through the sample, either to sweep CO_2 away as fast as it is formed, or to maintain the sample in an atmosphere of constant partial CO_2 pressure. Stone (1951) has carried out a similar series of experiments for kaolin, in which the partial pressure of water vapor was controlled.

Differences in the rate of particle-size growth of MgO undoubtedly have some effect upon the slope of the right side of the lower-temperature deflection, but this phenomenon can hardly be independent of the rate at which CO_2 escapes. No simple relation is evident in Fig. 1 between slope of the deflection and either particle size or the temperature of the deflection.

There is some variation in the closeness with which the curve approaches the baseline between the two deflections. The most striking difference can be seen by comparing curves 3 and 4 of Fig. 1. The coarse particle size of the curve 3 sample has brought the lower-temperature deflection to about the upper limit of the range in which it occurs in air at one atmosphere pressure. The higher-temperature deflection is at about the lower limit of the observed range for CaCO_3 decomposition because: (1) the CaCO_3 resulting from the dolomite lattice breakdown is extremely fine grained, and (2) dilution of the sample with Al_2O_3 makes it easy for CO_2 to escape from the sample well. Consequently the lower-temperature deflection partially overlaps the upper one in curve 3.

In this connection it is of interest to note that the doubling of the tip of the high-temperature deflection, as in the curve for specimen R-1929 (Fig. 1), and the shoulder at a similar position in the curve for R-1928 (Fig. 1), can very likely be attributed to a small amount of calcite which occurs in some of the dolomites (see Table 2). This calcite is more coarsely crystalline than that resulting from dolomite dissociation, and consequently should dissociate at a slightly higher temperature.

It is not clear from these curves to what extent finer grinding of the salt-containing dolomites alters the area in contact between salt and dolomite and thus affects the intensity of the salt-dolomite interaction. The gentle endothermic deflections at about 600°C . in curves 6 and 10, not present in curve 4, Fig. 1, may represent accelerated low-temperature decomposition at local points of high salt concentration, or decomposition of a fine fraction created by grinding.

The importance of lattice domains of the order of 0.1 to 0.01 micron diameter as the controlling factor in the rate of diffusion of CO_2 from

the lattice has been suggested for magnesite (Kahler, 1947; Cremer, 1949). Determination of the variation, from one dolomite sample to another, in the size and regularity of these units would be desirable, for these domains are not of constant size and disorientation for a given mineral species and are not necessarily related to the macroscopic particle size and orientation in the rock (see, for example, Ewald and Renninger, 1934). It is also known that grinding of ideal crystals or non-ideally imperfect crystals produces or increases domain structure in a surface layer so that the manner in which these dolomite samples have been prepared for thermal analysis may be important in determining the initial rates of nucleation of MgO and diffusion of CO₂.

Areas under curves

Berg (1943) states that the ratio of areas under the lower- and higher-temperature deflections changes from about 1.65 to about 1.25 if NaCl is added to depress the temperature of the lower-temperature deflection. It is not clear how much NaCl was added and how much the temperature was lowered. In accordance with his view that there is a preliminary dissociation of dolomite into CaCO₃ and MgCO₃, Berg cites the change of heat of dissociation of MgCO₃ with temperature to explain the differences in ratios.

The amount of soluble salts present in the Niagaran specimens is sufficient only to blunt the lower-temperature deflection, not to lower its temperature appreciably. The principal practical use of the area ratios—to determine the relative amounts of calcite and dolomite in dolomitic limestone—would thus not be affected by changes of carbonate heat of dissociation for specimens of this type. Likewise, the fact that soluble salts modify the shape of the lower-temperature deflection should not affect the heat of dissociation, for these salts are present in such small amounts that their action must be viewed as a catalytic or surface-active one rather than a true chemical reaction. To the extent that deflections become broader and shallower, errors in drawing the baseline have a greater percentage effect on the accuracy of area measurement. Beyond a certain point the sensitivity of the equipment to gentle prolonged heat drops off. There is probably some error because of differences in recrystallization. Experience thus far suggests that the combined effect of these errors is not great enough to mar the usefulness of area ratios as a routine semi-quantitative procedure. Berg (1945) obtained calcite and dolomite percentages from area measurements which agreed within two per cent with those from chemical analyses, even though the baseline for his area measurements is not completely defensible on theoretical grounds.

The accuracy of measurement and thoroughness of interpretation re-

quired for meaningful comparisons of area ratios for various pure dolomites and slightly salty dolomites is believed to be considerably greater than for estimating calcite/dolomite ratios. Measurement of areas for the curves in this paper has accordingly been deferred until a better understanding of certain fundamentals has been obtained:

(1) The precise mechanism of dolomite thermal decomposition has not been determined satisfactorily. Berg's concept of preliminary dissociation into CaCO_3 and MgCO_3 must compete with the idea of high-temperature carbonate solid solutions, and that of a preliminary dissociation into oxides followed by a recombination, $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$, as well as more specific hypotheses of ion migration and oxide nucleus formation within the disintegrating dolomite lattice (Hall, Stein, and Louw, 1951; Wilsdorf and Hall, 1951). Until this mechanism is understood in detail, the effect of specific cations and anions upon it, and perhaps indirectly upon the areas under curves, can hardly be appreciated.

(2) There seems at present to be no means of estimating from DTA curves the exothermic effect resulting from particle-size growth of newly formed MgO and CaO which is superimposed, respectively, upon the latter portions of the lower- and upper-temperature endothermic deflections. Bradley and Grim (1951) have recently discussed this problem of how energy changes resulting from the gradual formation of new phases are recorded in DTA curves. The recrystallization of CaO has been shown by Noda (1939, 1940) to be accelerated by the presence of salts like those found in sedimentary dolomites. The area ratio may thus be affected by the presence of these salts if MgO recrystallization is affected more than that of CaO , or vice versa, or if the supply of salts has been partly volatilized before the CaCO_3 dissociates.

(3) There is some uncertainty as to what areas under the curve should be measured, and what they mean. The curve for many specimens does not return to baseline between the two deflections, indicating that the two reactions overlap. The question may be raised whether a perpendicular from this point to the baseline, for example, gives two meaningful areas for measurement. A long sliver of area at lower temperatures results, at least in large part, from gradual CO_2 loss, because the partial pressure of CO_2 in the dolomite is greater than that in the atmosphere, at these temperatures. The sliver should, therefore, be measured, even though slight differences in the position of a baseline projected from below 400°C . unfortunately result in very considerable differences in the sliver area.

(4) There are questions of the behavior of equipment, and its effect upon some of the details of the DTA curves, which this paper does not

attempt to answer. The response of a moving-coil, ribbon-suspension type of galvanometer like that used in this study is not perfectly linear for the outer portions of the long endothermic dolomite deflections and in the setup used this instrument is not in a perfect critically damped condition when the various resistances are put in series with it, even though another resistance used in parallel minimizes deviation from critical damping. Likewise, the use of a nickel block of high heat capacity makes it necessary to be very careful in positioning all thermocouples exactly at the centers of the alumina-filled wells, if the baseline in the lower portion of the curves is to be straight enough for projection. It is generally believed that these instrumental errors can be avoided by experienced workers, but only detailed testing of individual setups will prove the point.

A further evaluation of instrumental performance is relevant to an explanation of the variation in baseline position of dolomitic DTA curves after complete dissociation (Fig. 6). Differences in heat of solution of MgO samples formed by calcining MgCO_3 were related to the particle size and lattice perfection of the oxide by Kahler (1947) and Treffner (1950). By analogy, it is possible that the variation in baseline position of the dolomite curves results from differences in heat diffusivity and specific heat related to the size and perfection of the CaO and MgO lattice blocks present.

SUGGESTED PROCEDURES FOR DOLOMITE

The specific procedure followed in making DTA curves of dolomite can be varied in accordance with the main objective of the study. As the design of the equipment currently in use in most laboratories is still being perfected, it is well to realize that the outlook presented here may soon require amplification and revision.

Measurement of areas under curves, in order to estimate calcite/dolomite ratios, requires a straight baseline and sharply-defined deflections as large in area as possible. The use of a rather large resistance in series to minimize baseline variation, plus undiluted samples to give larger areas under the curves, plus a CO_2 atmosphere (Rowland and Lewis, 1951) to sharpen the beginning of the lower-temperature deflection, plus a capping layer of $\alpha\text{-Al}_2\text{O}_3$ to prevent ejection of part of the sample from the well by rapid CO_2 evolution, would seem to be called for.

On the other hand, it has been shown that dilution of the sample is useful in resolving details of the lower-temperature deflection in samples containing soluble salts, because of the decreased partial pressure of CO_2 . Studies of the relation between deflection shapes, areas under deflections, temperature of CO_2 evolution, and amount of specific salts added

could probably be carried out best on curves of diluted samples.

Berg (1943) noted that there were still differences in dolomite DTA curves after soluble salts had been leached out, and tentatively attributed them to water-insoluble salts that affected the dolomite dissociation, or to "admixture of calcite and magnesite in solid solution."

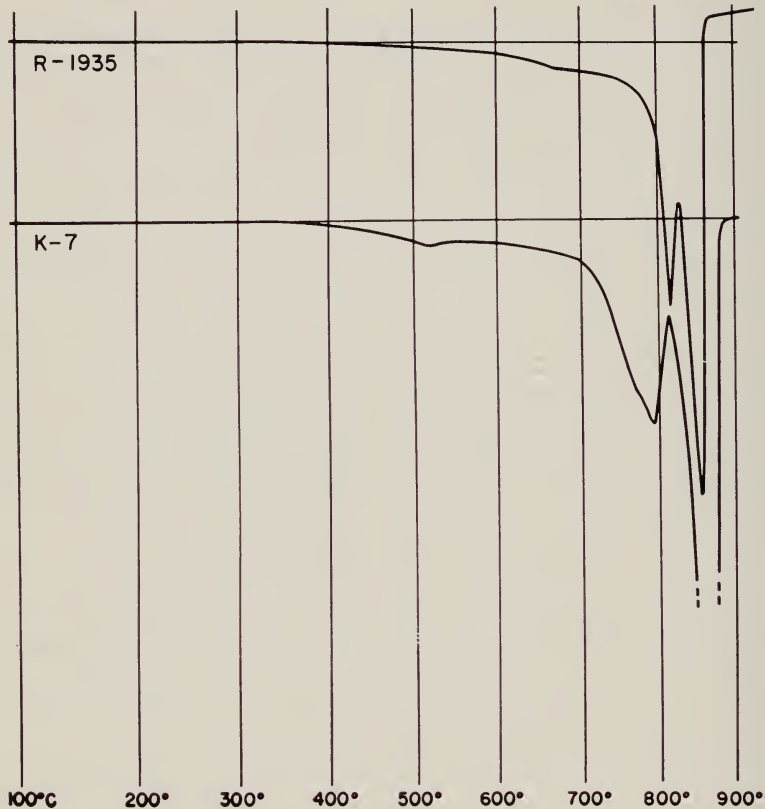


FIG. 6. Variation in baseline position after dolomite decomposition.

If further studies are to be undertaken of the effect of particle size, isomorphous substitution as in ferrodolomites and ankerites, and possible lattice disorder, the soluble salts present should first be removed as completely as possible, as Berg suggested, because their effect upon the curves is comparable to that of any of the other factors.

MINERALOGICAL DISTRIBUTION OF CATIONS IN THE SEDIMENTARY DOLOMITES

It is desirable to know accurately the mineralogical distribution in the sedimentary dolomites of K, Na, Mg, and Ca which are not present

as soluble salts, to be certain that there are no difficultly soluble accessory minerals which affect the dolomite deflections. The compilation of analyses of carbonates by Ford (1917), even though not accompanied by *x*-ray data, indicates that departures from a 1:1 molar Mg:Ca ratio occur in some iron-free single crystals of dolomite. It is impossible to determine the actual Mg/Ca ratio in the Illinois sedimentary dolomite minerals accurately enough to allot, for example, a small amount of excess Ca to clay minerals, feldspars, and anhydrite or gypsum. A number of comments can be made, however, about the distribution of K and Na.

A comparison of the R-series curves in Fig. 2 with the analyses of Table 2 shows that there is no correlation between increasing abnormality of the curves and total percentage of K_2O , Na_2O , or (K_2O+Na_2O) . Much of the alkali may be presumed to be combined in insoluble accessory minerals, from which it is not released at temperatures up to that of the lower-temperature dolomite endotherm.

Muscovite, illite, and the feldspars are possible sources of alkalis. No muscovite could be found in an immersion study of the coarser fraction of the HCl-insoluble residue of a composite of the K-series specimens, but potash feldspar and Na-rich plagioclase together made up perhaps 15 or 20 per cent of the coarser residue. It was not possible to secure accurate determinations of the alkali content of these small amounts of feldspar, for the individual K-series specimens were too small to permit chemical analyses of the low percentages of insoluble residue in each of them.

The less-than-1 micron fraction of the insoluble material from a 200-gram composite of the K-series specimens was obtained, using 1 N acetic acid, and Na polyphosphate as a deflocculating agent. The *x*-ray powder diffraction pattern of this material gives a basal spacing of 10.0 Å, which does not expand on treatment with glycol. The presence of an illite-group clay mineral is thus confirmed, according to the agreement reached at the International Soils Science Congress, Amsterdam, 1950, that illite should be used as a general, nonspecific term for both heptaphyllite and octaphyllite mica-clay minerals which show no significant swelling characteristics and which give a first order basal reflection of about 10 Å which is unaffected by mild chemical or thermal treatments. This determination is in agreement with the finding of Grim, Lamar, and Bradley (1937) that illite is abundant in Niagaran limestones from Illinois, some of which contain considerable kaolinite as well.

It is possible to estimate the maximum amount of alkalis which could be contained in the accessory mineral illite of these dolomites. The average of a number of illite analyses assembled by Grim and Bradley (1949) gives 6.5 wt. per cent K_2O , 0.3 Na_2O , and 25.6 Al_2O_3 for a "typical" illite from well-indurated sedimentary beds. These figures are not fun-

damentally different from the average of the percentages given for illite with associated chlorite, or for illite with some mixed layers of montmorillonite. This average illite composition, obtained chiefly from analyses of illites from shales, probably applies as well to illites from dolomites, for laboratory experiments indicate (White, 1951) that K is able to remain in only 3 to 5 per cent of the exchange positions in the presence of a considerable excess of Ca, a situation which obtains in most natural environments. In an extreme situation such as a bed containing alkali halide brine, of course, the amount of alkali ions in base-exchange position could increase sharply and the average figures cited would not be valid. Degraded illites (Grim, Dietz, and Bradley, 1949) low in alkali are formed during weathering, but regain most or all of the alkali loss when carried into a marine environment; therefore the illites in the Niagaran samples should not be degraded.

Column 15 of Table 2 indicates the amount of illite, expressed as weight per cent of the dolomite rock, that would exist if all the alumina in the analysis were converted to a "typical" illite containing 25.6 weight per cent alumina. Column 16 gives the maximum amount of K_2O , expressed as weight per cent of the dolomite rock, which could be tied up in the illite. For specimens high in K_2O , only about half can be accounted for in this manner. Figs. 7 and 8, based upon the chemical analyses of Table 2, indicate that the alkali/alumina ratios for the dolomite specimens lie between that for illite and that for orthoclase.

The predominance of Na over K in the soluble salts is suggested by comparison of Fig. 8, in which the band of $(Na_2O + K_2O)/Al_2O_3$ plots intersects the positive side of the horizontal axis, indicating that some alkali oxide is not combined with Al_2O_3 , with Fig. 7, in which the band of K_2O/Al_2O_3 plots goes through the origin.

Dolomite-illite interaction

In order to determine whether any of the alkalis in base exchange position in illite are released to affect the lower-temperature dolomite deflection, a mixture of 85 wt. per cent Massachusetts dolomite marble and 15 wt. per cent $<2\mu$ Fithian illite was thoroughly ground together in a mullite mortar and mixed with an equal weight of $\alpha-Al_2O_3$ diluent in accordance with the usual procedure. The Massachusetts rock is very low in alkalis (Table 2) and has a sharp lower-temperature deflection. The quantity of illite added is greater than that which could possibly be present in any of the dolomites examined. In the DTA curves of this mixture, the lower-temperature deflection is completely undistorted, and characteristic illite deflections are not developed at the instrumental sensitivity and dilution used. Nor did any recognizable illite deflections occur in the DTA curves of the natural specimens.

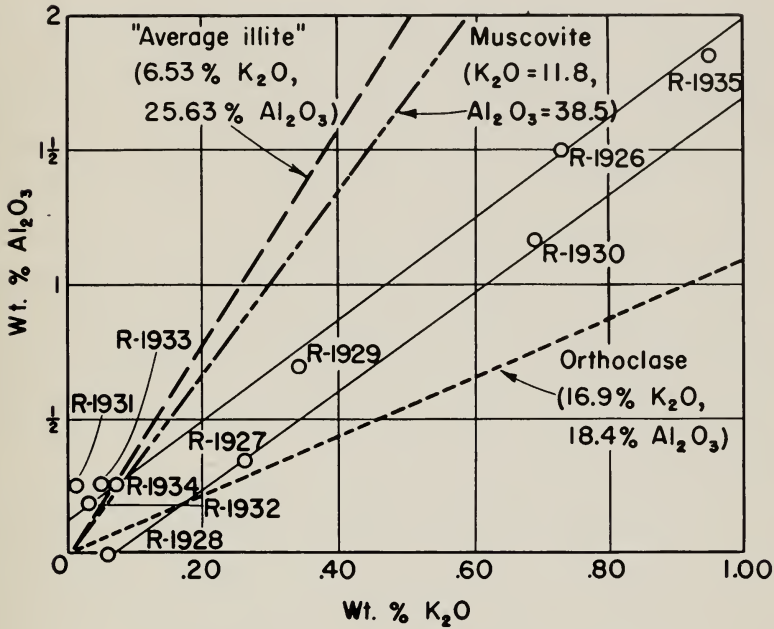


Fig. 7. K₂O-Al₂O₃ relations for R-series specimens

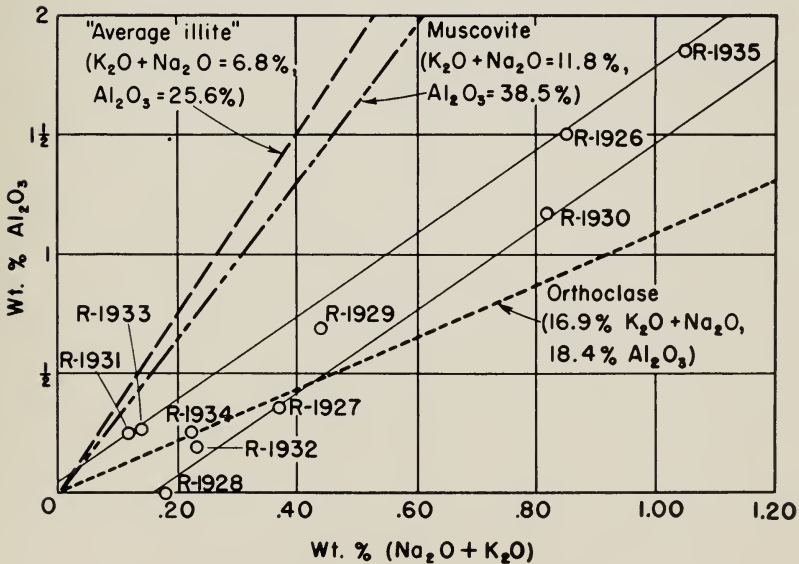


Fig. 8. (K₂O+Na₂O)-Al₂O₃ relations for R-series specimens

Grim (1942) found that the degree of intimacy of mixing of layer lattice minerals, particularly certain poorly crystallized varieties, had a significant effect upon the DTA curves, and accordingly allowed mixtures to settle from a water suspension. Interaction between alkalis in illite, and in dolomite, whether expressed in terms of mobilities of ions at elevated temperatures or very low vapor pressures, should be related to the area in contact between the two compounds per unit weight. Although no structural relationship comparable to the interlayered clay minerals has ever been suggested for illite and dolomite, a certain doubt as to the validity of artificial dolomite-illite mixtures should remain until more is known of the physical relationship of these two minerals in natural dolomites. In the present case, this doubt is largely dispelled by the fact that illite-containing dolomites give undistorted curves after washing (Fig. 4), a procedure which is quite inadequate for the removal of base-exchange cations from the illite.

Another method of evaluating possible dolomite-illite interaction involves consideration of the detailed thermal behavior of illite. Grim and Bradley (1940) state that destruction of the "anhydrous modification" of illite is completed around 800 or 850° C., at which temperature spinel begins to form from the middle sheet of the illite lattice, while the alkalis and the silica from the outer sheets go to amorphous glass. An indication of the effect of temperature on the equilibrium existing between cations in base-exchange positions and those in fixed positions, below 850° C., is given by Hofmann's studies (Hofmann and Endell, 1939; Hofmann and Klemen, 1950) of the decrease in base-exchange capacity of montmorillonite on heating. The loss of 80 per cent of exchange capacity by Li-saturated montmorillonite after heating to 200° C. over a protracted period is attributed to the migration of Li ions from the surfaces to the interiors of the silicate sheets. Higher temperatures are required, in the order Li^+ , H^+ , Ca^{++} , Na^+ to achieve comparable effects for these larger ions, whose movement into the lattice is believed to be more difficult. K^+ , of course, is even larger, but is not discussed by Hofmann. Wear and White (1951) found that illite, heated to 105° C. for 12 hours after its base-exchange positions had been saturated with K^+ , fixed the least K^+ , 2.4 milliequivalents, of the several clay minerals so treated. They attribute this to the fact that the large amount of K^+ already present in the lattice almost balances the negative charge existing in the tetrahedral layers.

The differential thermal analysis of dolomite-illite mixtures in the present study does not correspond precisely to any of the experimental situations described in the preceding paragraph, for the base-exchange positions of the illite are assumed to be largely filled by Ca^{++} and Mg^{++} , and the times used are less and the temperatures greater than in the

other experiments. Nevertheless, the evidence seems to indicate that the base-exchange cations are held more and more tightly, whatever their final position in the lattice, with rising temperature and progressive dehydration, and that by the time the illite lattice breaks down to release these cations into a liquid alkali silicate phase, the sensitive lower-temperature dolomite reaction has already occurred.

SOLUBLE-SALT CONTENT AS AN ENVIRONMENTAL INDICATOR

The sensitivity of the lower-temperature deflection to tiny amounts of salts suggests, on first thought, that examination of routine DTA analyses might furnish information about the salinity of the environments of deposition of carbonate rocks. Thus, the variability of DTA curves for the Niagaran specimens contrasts with the virtual identity of a series of slightly abnormal curves for specimens from a section through the Prosser member of the Ordovician Galena formation near Galena Junction, Ill. More of the Niagaran specimens from reef-core and near-reef-flank beds have highly abnormal curves than those from inter-reef and non-reef areas.

On further consideration, however, it becomes clear that there are several inherent limitations in the use of DTA analyses of dolomite in estimating salinity of depositional environments. These limitations, which are in addition to the usual difficulty involved in selecting a sampling method that integrates local variation, are: (1) Alkali- and alkaline-earth chlorides and alkali carbonates distort the curves, but sulfates do not, so that specimens having a high sulfate content will give misleading curves. Likewise, it is unlikely that the cations in a salt mixture will have a simple additive effect upon decomposition, regardless of whether they act as a melt or by solid-state reaction. (2) It seems likely that in many cases a portion of the soluble salt cations in the sea water trapped in carbonate sediment would be used in forming authigenic feldspar and illite, changing the relative proportions of the cations remaining in solution. (3) Because groundwater movement after lithification may redistribute soluble salts present as intergranular films, determinations of salt content of liquid inclusions within grains, where they exist, would be highly desirable. A crushing and leaching procedure which will preferentially remove intergranular salt films, so that only the liquid inclusion material remains to affect the DTA curves, is not apparent from this study, for it cannot be assumed that compact dolomites will break apart into their component grains before breaking across these grains.

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