

## CLAY-CARBONATE-SOLUBLE SALT INTERACTION DURING DIFFERENTIAL THERMAL ANALYSIS

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### ABSTRACT

In the majority of fine grained soils the qualitative and even quantitative determination of carbonate minerals, calcite and dolomite, by DTA, is a relatively simple matter. However, in some soils it has been found that as much as 40 per cent carbonate may completely escape detection by DTA. Thermograms are presented to show that this anomalous behavior arises from a combination of factors. The data reveal that in the most severe cases soluble salts react with some of the more active silicate from the clay; then the product of this reaction reacts with the carbonate mineral to produce the observed anomalous thermal effects. The thermograms indicate that the anomalous behavior is as pronounced for calcite as for dolomite. Even in the absence of soluble salts, some hydrous micas seriously distort the characteristic calcite thermogram.

### INTRODUCTION

Differential thermal analysis (DTA) is a very common method of determining the kind and amount of carbonate minerals present in fine grained soils. The most common carbonate minerals, calcite and dolomite, have thermal reactions at somewhat higher temperatures than the most important clay reactions. Because of the large amount of heat adsorbed in the carbonate thermal reaction, detection of a few per cent carbonate mineral is expected by differential thermal analysis. In the majority of soils, clay and carbonate thermal reactions occur independently; therefore, detection of a few per cent of carbonate by DTA is realized. Unfortunately, DTA records only the net heat effect which may result in seriously distorted thermograms when several reactions proceed simultaneously. In fact, as much as 40 per cent calcite and/or dolomite may go undetected by DTA because of the complex reactions occurring between clay, soluble salts and the carbonates.

Berg (1943) and Graf (1952) observed that readily soluble salts have a pronounced influence upon the first endotherm of dolomite. Berg (1943) remarked that the salt had no effect upon the dissociation of calcite; therefore, the effects reported here are different from any previously reported anomalies because the soluble salt appears to have a strong influence upon the calcite decomposition.

### NATURAL SOILS

The types of anomalous differential thermal behavior encountered in natural soils are shown by illustrative examples in Fig. 1. Other perti-

ment data for these soils are given in Table 1. Prior to DTA<sup>1</sup> the samples were treated as follows:

- a. Natural soil—the minus 74 micron fraction, air dried and crushed.
- b. Water washed—a 10 gram subsample from “a,” extracted five times with 200 ml. portions of water, air dried and crushed.
- c. Water washed plus NaCl—NaCl added to a suspension of a subsample from “b” to bring the conductivity of the suspension to that of the natural soil, air dried and crushed.
- d. Minus carbonates—natural soil digested with 2N acetic acid to completely destroy all carbonate minerals, washed free of salts, air dried and crushed.

TABLE 1. SALT CONTENT, CARBONATE MINERAL, AND PHYLLOSILICATE CLAY FOR TYPICAL SOILS WITH ANOMALOUS THERMOGRAMS

Soil Number	Soluble Salts (g. NaCl/100 g. Soil)*	Carbonate Mineral		Phyllosilicate† Clay
		Species	g./100 g. Soil	
633	1.16	Dolomite	25	K, I, M
366	0.48	Calcite	40	I, M

\* Computed from conductivity of a 2:1 water clay suspension assuming all soluble salts are NaCl.

† K = kaolinite, I = illite, M = montmorillonoid.

From the thermograms on the natural soils Curves A and E, Fig. 1, the presence of carbonate minerals to the extent of 25 to 40 per cent would hardly be anticipated. Thermograms obtained after the samples were water washed, treatment *b*, clearly show carbonate mineral thermal reactions, Curves C and G, Fig. 1. Treatment *c*, where NaCl was added to the soil that had been washed free of salt, restored the thermogram to nearly that of the natural soil, Curves B and F, Fig. 1.

<sup>1</sup> DTA Experimental Conditions:

Heating rate: 12.5° C./min with maximum variation of less than 1° C./min.  
 Thermocouples: Pt-Pt (10% Rh)  
 Temperature Couple: In Ni steel block, peak temperature uncorrected  
 Sample Pre-treatments: As indicated; no relative humidity control so the thermogram below 400° C. is not reproduced in the figure. Approximately 1 gram samples.  
 Calibration: 50% quartz and 50% BaCO<sub>3</sub>  
 Quartz  $\alpha \rightleftharpoons \beta$  at 573 ± 3° C.  
 BaCO<sub>3</sub> to  $\alpha$  at 819 ± 3° C.  
 BaCO<sub>3</sub> to  $\beta$  at 988 ± 3° C.

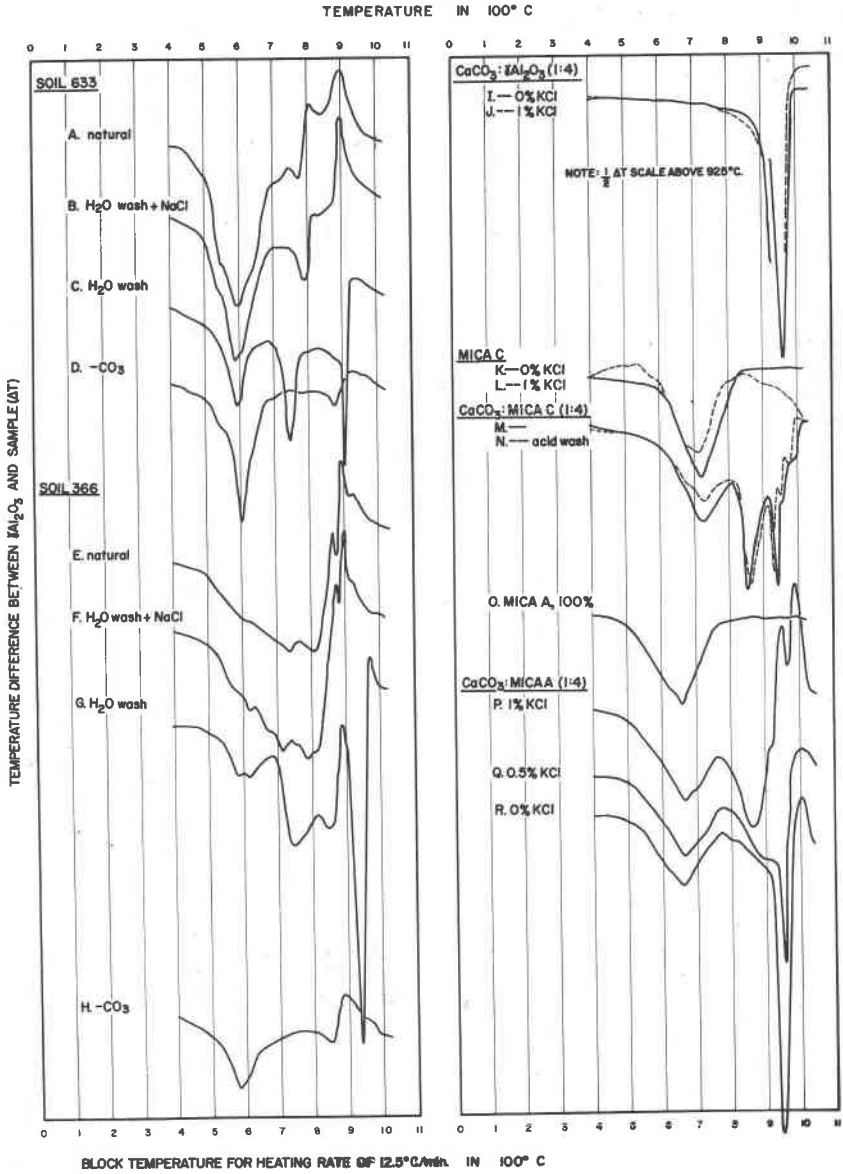


FIG. 1. Thermograms on natural soils and prepared mixtures showing anomalous carbonate peaks.

These results demonstrate that even a trace amount of NaCl (<1 per cent) may be sufficient to mask completely normal carbonate mineral thermal reactions even when the carbonate mineral is calcite. Graf (1952)

found that chloride salts of the alkali and alkaline earth elements were about equally effective in changing the low temperature endotherm of dolomite. That the same group of salts are responsible for the thermal effects observed here is indicated by the fact that LiCl, which has a much lower melting point than NaCl, produced the same thermal effect as NaCl.

The shape of the anomalous thermogram bears no relation to the kind of carbonate mineral nor to the particle size of the carbonate so long as the particles are less than 74 microns. Where the natural soil displays an anomalous thermal reaction, the removal of soluble salt yields a repressed thermal peak for both calcite and dolomite.

The dolomite thermal peaks for soil No. 633 (Curve C, Fig. 1) are both about 1/3 as large as they should be for the 25 per cent dolomite present in this soil. The thermogram for soil No. 366 (Curve G, Fig. 1) after removal of soluble salt shows a typical calcite reaction of approximately 1/2 the amplitude expected from the calcite percentage present. There is, in addition to the calcite peak, an anomalous endothermic reaction between 700 and 900° C. The endotherm between 700 and 900° C. is truly anomalous because careful *x*-ray examination of the sample showed clay minerals and calcite as the only components that could contribute to the thermal curve. Further, after complete removal of carbonates from soil No. 366, the addition of 40 per cent c.p. CaCO<sub>3</sub> gave a thermogram very similar in both shape and size to that obtained for the natural soil washed free of soluble salts.

Additional evidence as to the influence of soluble salt on the carbonate mineral decomposition was obtained from samples heated in the differential thermal analyzer to various temperatures, air quenched, and the products examined by *x*-ray diffraction. The soil used, No. 634, gave an anomalous thermogram similar to soil No. 633; however, the *x*-ray patterns showed that the soil No. 634 contained calcite and dolomite. Nevertheless, the changes in the *x*-ray patterns enumerated in Table 2 verify, qualitatively, that soluble salts lower the carbonate decomposition temperature.

#### ARTIFICIAL MIXTURES

In an attempt to evaluate the effect of soluble salt and clay on the decomposition of carbonate minerals, a few exploratory DTA investigations have been made: (a) calcite plus soluble salt, (b) mica plus soluble salt, (c) mica plus calcite, and (d) mica plus calcite plus soluble salt. Ground mica was chosen as the clay because by varying the method of preparation, differences in availability of the various clay constituents should be obtained. Total potash content of mica prepared by different methods is given in Table 3.

TABLE 2. EFFECT OF A SOLUBLE SALT ON THE DECOMPOSITION TEMPERATURE OF CARBONATE MINERAL IN A NATURAL SOIL

		Relative Intensity of X-ray Reflections after Heating to Temperature Indicated					
		Soil No. 634—Natural			Soil No. 634—Water Washed		
d value	Temperature °C	25	700	800	700	800	900
	3.03 Å (Calcite Reflection)		10	10	—	10	10
2.88 Å (Dolomite Reflection)		10	—	—	10	—	—

During DTA the alkali metal ions of hydrous micas may be released. If the clay structure permits rapid release of alkali ions, these ions may interact with the carbonate minerals in a manner similar to alkali ions obtained from soluble salt. Generally, this release of alkali ions is inadequate to affect the carbonate thermal reactions. Graf (1953) found no effect on the thermograms of dolomite from the addition of illite.

As evidenced by the similarity of Curves I, and J, Fig. 1, addition of 1 per cent KCl to a mixture of 25 per cent  $\text{CaCO}_3$  and 75 per cent  $\gamma\text{-Al}_2\text{O}_3$  had no significant effect upon the calcite decomposition, confirming

TABLE 3. PREPARATION METHOD AND TOTAL POTASH CONTENT FOR MICA\*

Sample	Preparation	Total Potash Content (%)
A	Mica batch No. 1 ground wet in a muller grinder. Sieved wet to minus 74 microns	7.8
B	Mica batch No. 2 prepared same as Sample A. Fine size fraction.	8.15
C	Mica batch No. 2; prepared same as Sample A; intermediate size fraction	8.75
D	Sample C(5g) extracted 6 times with 200 ml portions of 6N HCl; washed free of chlorides	8.70
E	Mica batch No. 2; ground dry in mechanical mortar and pestle; sieved wet to minus 74 microns	6.40

\* Muscovite mica, batch No. 1 and No. 2 gave identical x-ray diffraction patterns.

Berg's observation that soluble salts have no direct effect upon the calcite decomposition. Therefore, soluble salts must act through the clay to produce the observed anomalous calcite thermogram. Evidence that soluble salt acts first on the clay is shown by the effect of 1 per cent KCl on ground mica, compare Curves K and L, Fig. 1.

In the absence of soluble salt, clay-carbonate interactions may be quite marked as indicated by natural soils, Curves C and G, Fig. 1, and representative thermograms for mica mixed with 25 per cent  $\text{CaCO}_3$ , Curves M, N, and R, Fig. 1. Although all of the thermograms for ground mica and  $\text{CaCO}_3$  are not shown, in every instance there was a reaction between the mica and calcite. When mica rather than alundum was used to dilute the calcite, the carbonate reaction was either greatly reduced or occurred as a double endothermic peak. Since mica Sample C showed the greatest interaction between mica and calcite, a subsample of mica C was extracted with strong acid (Sample D), in the hope that all readily extractable potassium ions would be removed and thereby alter the thermal effects. The acid extraction changed neither the thermal effects, compare Curves M and N, Fig. 1, nor the potash content. Mica Sample E which gave an endothermic reaction  $130^\circ\text{C}$ . lower than did mica C and which had 24 per cent less  $\text{K}_2\text{O}$  than did mica C, showed anomalous calcite decomposition identical to that revealed by mica C plus calcite. Acid extraction of mica E, as with mica C, changed neither the thermal effects nor the total potash content.

From these few experiments it would appear that some component other than alkali ions is a major cause for the anomalous thermal behavior of calcite mixed with mica clay. The  $850^\circ\text{C}$ . endothermic peak on Curves M and N in Fig. 1 must arise from interaction between mica and calcite since this peak is not present in the thermogram for either component. A possible reaction could be silicate from the mica and Ca ions from the calcite combining to form a calcium silicate. To check this hypothesis, a thermogram was obtained on a mixture containing 25 per cent Na silicate, 25 per cent  $\text{CaCO}_3$  and 50 per cent  $\text{Al}_2\text{O}_3$ . The resultant thermogram gave endothermic peaks at  $840$  and  $960^\circ\text{C}$ . that were just slightly larger than the  $860$  and  $930^\circ\text{C}$ . peaks on Curve M in Fig. 1. A thermogram on Na silicate diluted with  $\text{Al}_2\text{O}_3$  gave no thermal reaction above  $400^\circ\text{C}$ . Therefore, anomalous thermal behavior of calcite and clay mica has been traced to a reaction between the silicate and calcium. The reason that many soils containing calcite reveal no anomalous thermal behavior is probably due to differences in the reactivity of the silicate in the temperature range  $800$  to  $950^\circ\text{C}$ .

The addition of KCl to a mica-carbonate mixture produces thermal effects similar to those observed for natural soils containing carbonates and

soluble salts (see Curves P, Q, and R, Fig. 1) and these thermal effects are much more pronounced than those observed for mica-carbonate mixtures in the absence of KCl. These data confirm the hypothesis that the soluble salts act on the clay and then some product of this first reaction produces the anomalous carbonate decomposition.

#### CONCLUSIONS

It is concluded from this investigation that as much as 40 per cent carbonate mineral may escape detection by DTA. The cause of this anomalous thermal behavior is demonstrated to result from the interaction of hydrous mica clay and soluble salts with the carbonate minerals. Hydrous mica clay has a direct influence on the calcite decomposition because hydrous mica can distort the calcite thermal reaction. Soluble salts have an indirect influence on the carbonate decomposition because while trace quantities of soluble salt in addition to certain hydrous micas completely obscure the calcite decomposition, soluble salts have no effect on the calcite thermal peak in the absence of the hydrous mica.

#### REFERENCES

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