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LIMESTONE INVESTIGATIONS

DIFFERENTIAL THERMAL ANALYSIS OF NATURAL LIMESTONES AND MIXTURES OF LIMESTONE WITH VARIOUS MATERIALS

by

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ABSTRACT

The method of differential thermal analysis was used to examine various naturally occurring limestones, mixtures of limestone with various minerals and clays, chemically precipitated mixtures of calcium carbonate and hydrated silica, and calcium oxide-quartz and calcium oxide-clay mixtures.

Inspection of differential traces and measurement of the endothermic peak due to the reaction $CaCO_3 \rightleftharpoons CaO + CO_2$ led to the conclusion that no exothermic reactions of any significance occurred between calcium oxide and the various other materials present as impurities.

1. INTRODUCTION

Following a visit to Australia in 1958 by Victor J. Azbe of the Azbe Corporation, St Louis, U.S.A., his recommendations for investigation of limestone deposits were submitted by Hydrated Lime Limited. Item 3, which was headed "Exothermic Reaction of Limestone under Heat Treatment", was considered the only one suitable for investigation in the Chemistry Section.

No record is available of the results of work done by Azbe for Hydrated Lime Ltd, hence it is extremely difficult to know the exact nature of his experimental procedure and results. However, it appears that he used blocks of several naturally occurring limestones hollowed into the centre to accomodate a thermocouple. The sample was heated in a furnace, and the temperatures of the block and the furnace atmosphere were recorded at selected time intervals. It was stated that after calcination was complete i.e. after the removal of all the carbon dioxide, the temperature inside the block was higher than that of the furnace atmosphere. Azbe concluded that an exothermic reaction occurred after calcination was complete and suggested that silica, argillaceous matter, or some other impurity reacted exothermically with the calcination product.

The object of the investigation described in this report, was to examine various natural limestones in an attempt to reproduce this effect and to examine mixtures of limestone with various minerals and clays.

The investigation concerned heat of reaction of limestone at various temperatures. A differential thermal study using the equipment and technique described in another report by the author, (O'Connor, 1960) was therefore undertaken.

The differential trace for a limestone normally shows one large endothermic peak due to the loss of carbon dioxide at approximately 900°C. Any appreciable exothermic reaction occurring after this calcination is complete should be evident as a peak on the differential trace. It also appeared possible, but unlikely, that the postulated exothermic reaction could occur simultaneously with the loss of carbon dioxide. This would cause a reduction in the size of the endothermic peak which could be distinguished by measurement of the peak area.

Some natural limestones contain impurities which were co-precipitated with the limestone during deposition. Attempts were made to simulate such conditions by chemically precipitating calcium carbonate and silica mixtures and examining them by differential thermal analysis.

2. SUMMARY

Standardization of the differential thermal analysis equipment in this laboratory showed that the area of the endothermic peak for the raction $CaCO_3 \rightleftharpoons CaO + CO_2$ at approximately 900°C., could be measured and reproduced with an error of four per cent. Samples containing more than 60 per cent $CaCO_3$ could be analysed with this accuracy.

When a sample of high-grade limestone (containing 99.6 per cent $CaCO_3$) was employed as a standard, the purity of various limestones calculated from the endothermic peak areas, was almost identical with results obtained by chemical analysis. This behaviour indicated that no exothermic reaction occurred simultaneously with the endothermic reaction. In no instance was a separate exothermic reaction detected.

Examination of mixtures of free lime with quartz or clay gave no evidence of an exothermic reaction below 1100°C. Although thermodynamic calculation showed that the reaction between calcium oxide and silica is exothermic and may proceed at 900°C, the formation of compounds is slow until approximately 1200°C.

Chemically co-precipitated mixtures of calcium carbonate and silica were examined but again no exothermic reaction was identified below 1100°C. Mixtures of a high grade limestone and minerals often found associated with limestone deposits were examined by differential thermal methods. Measurement of peak areas and examination of differential traces showed no evidence of exothermic reaction between the limestone and impurities. In several cases e.g. when pyrite was added, an exothermic reaction was detected but this was due to the added mineral itself.

3. MATERIALS EXAMINED

3.1 Limestone Samples

Five samples of naturally occurring limestones were investigated:-

L1 - Marble from Angaston, South Australia.
W1 - Limestone from Warooka, South Australia.
K2 & K3 -- Travertine limestones from Yorke Peninsula, South Australia.
S1 - Marble from Stockwell, South Australia.

Each sample was crushed to pass a 150 mesh Tyler screen. Analysis of the samples is shown in Table 1

TABLE 1. ANALYSIS OF LIMESTONE SAMPLES

Sample No.	Acid insol %	SiO_2 %	Acid sol Gp III Oxides %	CaO %	MgO %	CO_2 %	Total H_2O %
L1	0.4	0.3	0.6	55.8	0.1	43.1	0.6
W1	1.6	1.2	0.9	53.3	0.1	42.0	2.0
K2	8.4	6.6	3.6	46.7	0.7	37.5	2.7
K3	7.4	5.4	2.0	44.5	1.5	37.3	2.9
S1	0.4	0.98	0.50	54.1	0.8	43.41	0.16

3.2 Clay Samples

Samples of clay from Blanche Point (A) and Hackham (B), South Australia, were crushed to pass a 150 mesh Tyler screen. The results of chemical analysis are shown in Table 2.

TABLE 2. ANALYSIS OF CLAYS

	Blanche Point (A) %	Hackham (B) %
SiO_2	55.1	58.9
Al_2O_3	18.08	10.81
Fe_2O_3	6.46	9.09
FeO	0.11	Nil
MgO	1.9	2.84
CaO	0.54	1.24
Na_2O	1.06	0.82
K_2O	2.44	1.20
TiO_2	1.10	0.78
SO_3	0.02	0.07
Cl	0.10	0.04
H_2O at 100°C.	7.51	8.38
H_2O above 100°C	5.64	5.66

3.3 Mineral Samples

Samples of Nairne pyrite, quartz, cassiterite, serpentine and rutile supplied by the Mineralogy and Petrology section, were crushed to pass a 150 mesh Tyler screen and used in experiments.

4. ANCILLARY MATERIALS

Calcium carbonate of analytical reagent grade and granular calcium chloride (B.D.H.) were used.

An aqueous solution of sodium silicate containing 60 per cent SiO_2 was also used.

5. EQUIPMENT

5.1 Differential Thermal Analysis Equipment

The equipment described in another report (O'Connor, 1960) was used for differential thermal analysis investigations.

The sample and inert material (calcined alumina) were placed in the two compartment steatite cell, which was contained in a stainless steel block with a tight fitting lid. The thermocouples were platinum-platinum + 10 per cent rhodium and the temperature measuring couple was always placed in the sample.

A heating-rate of 400°C. per hour was maintained from room temperature to 1100°C.

The differential recorder was operated at a sensitivity of 0.3 millivolts corresponding to a full-scale deflection on the differential trace of approximately 30°C. Chart speed for the proportional and differential recorders was 16 centimetres per hour.

5.2 Peak-area Measurement

Peak areas were measured with an "OTT" compensating polar planimeter accurate to ± 0.02 square inches.

6. EXPERIMENTAL PROCEDURE AND RESULTS

Techniques used for all differential thermal analysis examinations are described fully elsewhere (O'Connor, 1960).

6.1 Standardization of Differential Thermal Analysis Equipment

The instrument was standardized for both temperature and peak area measurement.

6.1.1 Temperature

The $\alpha \rightleftharpoons \beta$ transition of quartz at 573°C. was adopted for temperature standardization.

Pure quartz, crushed to pass a 150 mesh Tyler screen was packed into the steatite cell.

An endothermic peak occurred on the differential trace at 574°C. and hence it was considered that temperatures measured were accurate and needed no correction.

6.1.2 Peak Area

Since peak areas were to be measured quantitatively to determine relative heats of reaction, it was necessary to standardize the equipment, and sample L1 was chosen for this purpose because of its high purity (99.6 per cent $CaCO_3$).

Preliminary experiments showed that when various wights of L1 were subjected to differential thermal analysis, measurement of the area of the endothermic peak due to the loss of carbon dioxide at approximately 900°C. could be reproduced with an error of 4 per cent. The following example illustrates this.

(1) 0.40g of L1 gave a peak area of 5.10 square inches.

(2) 0.33g of L1 gave a peak area of 4.05 square inches.

The second sample should give an area of $\frac{5.10 \times 0.33}{0.40}$

or 4.2 square inches. Hence the error involved is:-

$$\frac{0.15}{4.05} \times 100 \text{ or } 4 \text{ per cent}$$

Mixtures containing various proportions of sample L1 and calcined alumina were mixed thoroughly by grinding in a mortar. Weighed samples were subjected to differential thermal analysis and the endothermic peak was measured. Table 3 shows the results of this investigation, and the error involved in the method.

TABLE 3: AREAS OF ENDOTHERMIC PEAKS OF MIXTURES OF L1 AND CALCINED ALUMINA

Composition of mixture (L1 %)	Sample Wt g	Area of endothermic peak (sq in)	Error %
100	0.33	4.05	4
80	0.30	3.15	4
60	0.29	2.0	5
40	0.25	1.02	18

6.2 Examination of Limestone Samples

Samples L1, W1, K2, K3 and S1 were examined by differential thermal analysis. The samples were weighed by the difference method and packed firmly into the cell by means of a glass plunger.

The area of the endothermic peak at approximately 900°C. was measured and results are shown in Table 4. This table also shows the calculated percentage purity of each limestone compared with sample L1 which is considered as pure $CaCO_3$.

TABLE 4: AREA OF ENDOTHERMIC PEAK AND PERCENTAGE PURITY OF LIMESTONES

Sample	Sample Wt g	Area of endothermic peak (sq ins.)	Calculated purity. ($CaCO_3$%)	Chemical analysis ($CaCO_3$%)
L1	0.33	4.05	100	100
W1	0.26	2.95	92	95
K2	0.30	3.00	80	83
K3	0.32	3.00	77	79
S1	0.32	3.98	97	98

The percentage purity was calculated as follows:-
0.33 g L1 (100% $CaCO_3$) gave an area of 4.05 square inches thus 0.26 g of sample W1 if 100 % $CaCO_3$ should give an area of $\frac{4.05}{0.33}$ x 0.26 or 3.20 square inches. However, the measured area is 2.95 square inches and hence percentage purity of W1 is $\frac{2.95}{3.2}$ x 100 or 92 per cent.

Differential traces showing peaks and temperatures are shown in Figure 1.

6.3 Lime-quartz and Lime-clay Mixtures

Free lime was prepared by heating sample L1 at 950°C. for four hours. The product on cooling was mixed immediately with quartz to give a mixture containing ten per cent quartz by weight. This mixture was ground for ten minutes in a mechanically operated agate mortar to ensure intimate mixing.

A similar procedure was used to prepare a mixture of lime and Hackham clay (B).

A mixture containing alumina and ten per cent by weight Hackham clay was also prepared.

Weighed samples were examined by differential thermal analysis and the differential traces are shown in Figure 2.

6.4 $CaCO_3$-SiO_2 Mixtures

Mixtures of calcium carbonate and hydrated silica were prepared by precipitation from calcium silicate with carbon dioxide.

Sodium silicate solution (containing approximately 60 per cent SiO_2) was treated with granular calcium chloride dissolved in distilled water. The gelatinous product was stirred vigorously with a mechanically operated glass stirrer and carbon dioxide was bubbled continuously into the suspended product for five hours. Calcium oxide, prepared by heating calcium carbonate for three hours at 1000°C., was added during one of the experiments.

The products were filtered on a Buchner funnel, washed thoroughly with distilled water to remove water soluble impurities, and then dried at 60°C. for 24 hours. Analysis of products is shown in Table 5.

TABLE 5: ANALYSIS OF $CaCO_3$-SiO_2 MIXTURES

Sample No.	CaO %	SiO_2 %	CO_2 %	Gp III Oxides %	Total H_2O %
1	15.2	64.4	11.8	1.1	7.5
2	41.7	18.1	32.2	0.5	7.5

Weighed samples were subjected to differential thermal analysis and the differential traces obtained are shown in Figure 3.

6.5 Limestone-mineral mixtures

Mixtures of Angaston marble (L1) and various minerals often found associated with limestone deposits were prepared as in 6.3. Each mixture contained 10 per cent by weight of the added mineral. These mixtures, containing quartz, pyrite, serpentine, rutile and cassiterite were examined by differential thermal analysis.

Results in Table 6 show sample weight, and the measured area of the endothermic peak due to the loss of carbon dioxide from the limestone.

TABLE 6: ENDOTHERMIC PEAK AREA: L1 MINERAL MIXTURES

Added Mineral 10% w/w	Sample Weight %	Area of Peak sq. in.
Quartz	0.32	3.65
Pyrite	0.31	3.70
Serpentine	0.33	3.95
Rutile	0.34	4.10
Cassiterite	0.36	4.00

Differential traces of these mixtures are shown in Figure 4.

6.6 Limestone-clay Mixtures

Weighed samples of clays (A) and (B) were mixed thoroughly with sample L1, the mixtures containing 10 per cent of the clay by weight.

Differential thermal analyses were carried out using weighed samples and the traces obtained are shown in Figure 5.

Sample weights and the measured area of the endothermic peak near 900°C. are shown in Table 7.

TABLE 7: ENDOTHERMIC PEAK AREAS: L1 – CLAY MIXTURES

Sample	Sample Weight g	Area of Endothermic Peak Sq. in.
10% A	0.32	3.70
10% B	0.32	3.65

7. DISCUSSION

7.1 Lime-quartz and Lime-clay Mixtures

Differential thermal analysis traces obtained for mixtures containing lime with 10 per cent quartz and clay show no evidence of an exothermic reaction at temperatures below 1100°C., since the traces are straight lines with little deviation from the baseline.

Thermodynamic calculations using values from Kubaschewski and Evans (1955), for the reactions $CaO+SiO_2 \rightarrow CaSiO_3$

and $2CaO+SiO_2 \rightarrow Ca_2SiO_4$ gave the following information:-

(1) for the reaction $CaO+SiO_2 \rightarrow CaSiO_3$-

$\Delta H_T = -22,750 + 0.37T + 0.29 \times 10^{-3}T^2 + 4.86 \times 10^5T^{-1}$ cals/mole and $\Delta G_T = -21,300 + 0.12T$

ΔH = heat of formation

ΔG = free energy

(2) for the reaction $2CaO + SiO_2 \rightarrow Ca_2SiO_4$-

$\Delta H_T = -30,420 - 1.88T + 2.37 \times 10^{-3}T^2 + 3.92 \times 10^5T^{-1}$ cals/mole and $\Delta G_T = -30,200 -1.2T$

Thus the heat of reaction in both cases at temperatures between 900 and 1000°C. is highly exothermic and the free-energy equations show that the reactions may proceed in this temperature range.

However, the calculations do not indicate probable rates of reaction; it was found in fact that calcium oxide and silica do not combine to form appreciable amounts of such compounds until approximately 1200°C. (Remy 1956). This is illustrated in the trace for the calcium oxide-silica mixture, since no peaks are evident below 1100°C.

There was insufficient information available to enable evaluation of the thermodynamic relationships in the calcium oxide-clay reaction. The absence of any indication of an exothermic peak below 1100°C. on the differential trace for this reaction, shows that the clay did not react exothermically with the lime. A small endothermic reaction at 980°C. is evident for both the lime-Hackham clay and calcined alumina-Hackham clay mixture and is characteristic of the clay itself.

7.2 $CaCO_3$-SiO_2 Mixtures

These mixtures were prepared in an attempt to co-precipitate finely divided calcium carbonate and hydrated silica, since finely divided solids often react at temperatures below those expected, (Cohn, 1948).

Examination of the differential traces shows no evidence of exothermic reation in either case at temperatures below 1050°C.

It is apparent, however from Figure 3 that the decomposition of the calcium carbonate was complete at a lower temperature for sample 1. This is due to the high proportion of impurity in relation to the amount of calcium carbonate present.

7.3 Limestone Samples

The decomposition of limestone is accompanied by a large endothermic heat reaction.

Calculation of the thermodynamics for the reaction $CaCO_3 \rightleftharpoons CaO+CO_2$ shows that the heat of reaction at a temperature T°K is :-

$\Delta H_T = 44,600 - 2.57T - 1.0 \times 10^{-3}T^2 - 2.5 \times 10^5T^{-1}$ cals./mole.

Differential thermal analysis is particularly suited for the study of reactions where the amount of heat involved is of this order since readily measurable peaks may be obtained on the differential trace.

It was found by measurement of peak areas representing the decomposition of limestone, that results could be reproduced with an error of approximately four per cent. Other experiments described in Section 6.1.2 showed that samples containing greater than 60 per cent $CaCO_3$ could be expected to give results with approximately this reproducibility.

The samples of limestone which were examined, contained various amounts of impurities such as silica, and chemical analysis showed them to contain different amounts of calcium carbonate. Thus, the size of the endothermic peaks at approximately 900°C., should be correspondingly smaller than the peak obtained when sample L1, which contains 99.6 per cent $CaCO_3$ was used.

Table 4 shows that, compared with results of chemical analysis, the measured area corresponds closely to the expected value. There is thus no indication of an exothermic reation occurring simultaneously with the limestone decomposition since this would result in a decrease in the size of the peak on the differential trace.

The differential traces show no evidence of exothermic reactions at temperatures up to 1050°C.

7.4 Limestone-mineral and Limestone-clay Mixtures

Minerals which are often associated with limestone deposits were mixed with the reference sample of limestone since it was thought possible that they might react exothermically with lime near the calcination temperature of the limestone.

However, the measured areas of the peaks at approximately 900°C. were extremely close to the expected values and it was concluded that in no instance did a simultaneous exothermic reaction occur.

The serpentine-limestone mixture showed an exothermic peak at 805°C. on the differential trace, but examination of the mineral alone showed that this peak was characteristic of the serpentine itself and was not due to any reaction with the limestone. In no other instance was there evidence of an exothermic reaction near the calcination temperature of the limestone.

The differential trace for the pyrite-limestone mixture shows an exothermic reaction at 500°C. but this is due to oxidation of the pyrite, and not to reaction with limestone.

Mixtures of two clays with limestone showed no exothermic reaction at temperatures below 1100°C. and it was considered unnecessary to investigate the effect of other clays.

8. CONCLUSIONS

Measured areas of the endothermic peaks due to decomposition of impure limestone were as expected, when the sample of Angaston marble was used as a standard. This behaviour indicated that simultaneous exothermic reactions did not occur and no separate exothermic reactions were identified. No evidence was obtained during investigations in this laboratory of the exothermic reaction referred to by Azbe.

Mixtures of limestone with various minerals and clays when analysed by the differential thermal method also failed to show any evidence of exothermic reaction between the limestone and the mineral or clay.

No evidence of chemical reaction was obtained when mixtures of lime with quartz or clay were examined.

Chemically precipitated calcium carbonate-silica mixtures also showed no evidence of exothermic reaction.

While thermodynamic calculations favour the exothermic reaction of lime with silica at temperatures between 900°C. and 1000°C., the rate of reaction is very slow and hence no appreciable reaction occurs until the temperature reaches 1200°C.

It would be impractical to heat limestones to this temperature since the lime obtained would be "dead burned" and worthless for slaking purposes.

The investigations have not indicated in any instance the occurrence of exothermic reactions either in naturally occurring limestones or in artificially prepared mixtures of high grade limestone with various minerals and clays as impurities.

9. REFERENCES

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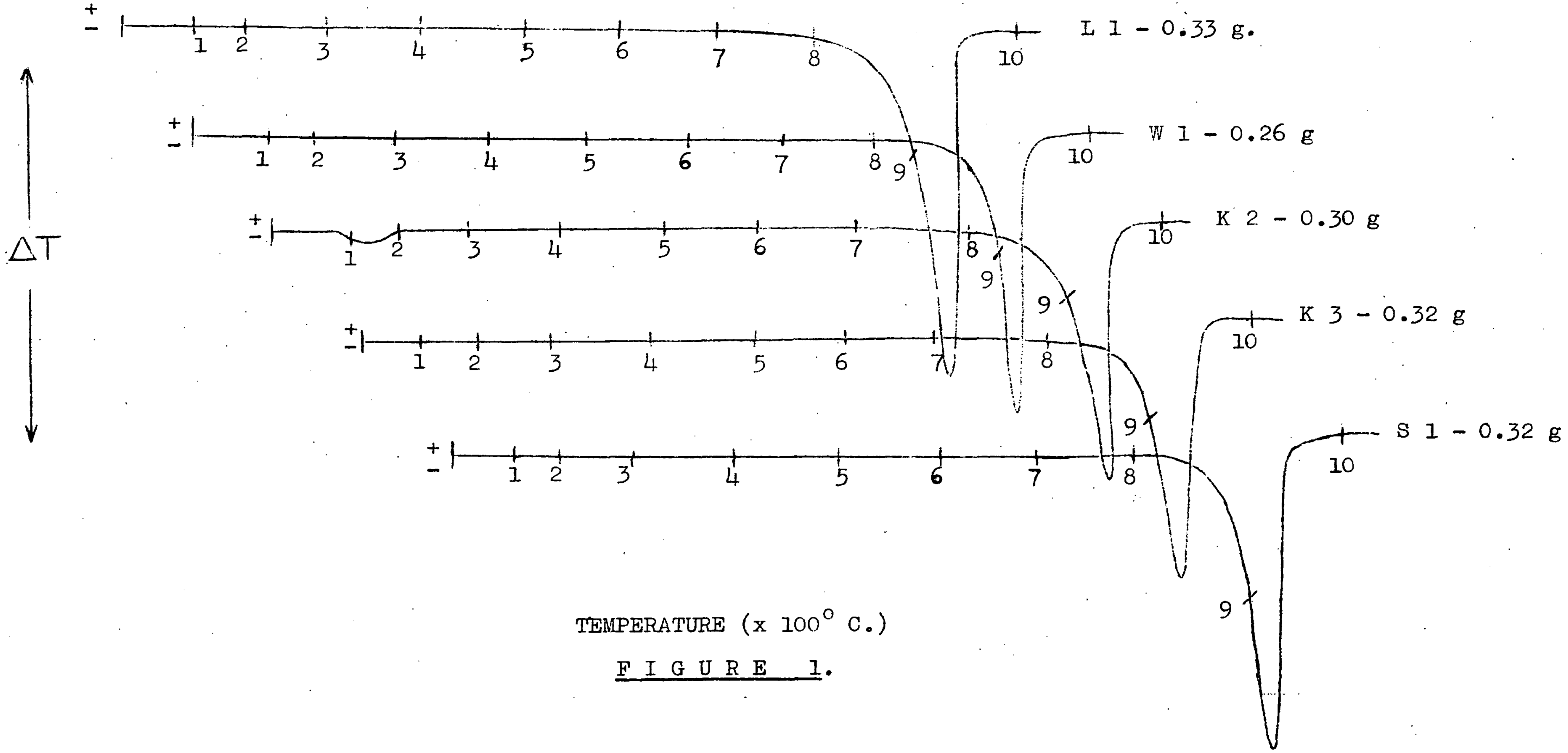
Kubaschewski & Evans, 1955.	Metallurgical Thermochemistry. Pergamon Press Ltd.
O'Connor, M.J., 1960.	Australian Mineral Development Laboratories. Report No. 59
Remy, H., 1956.	Treatise on Inorganic Chemistry. Elsevier Publishing Co. New York. p744

DIFFERENTIAL TRACES - Limestone Samples.

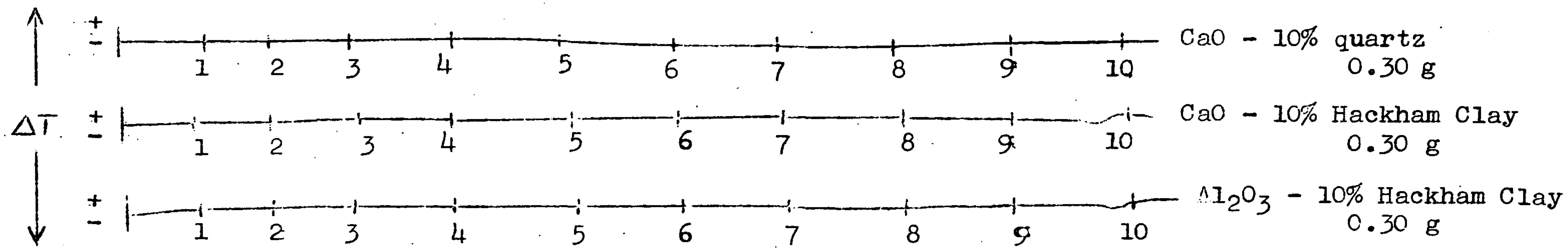


TEMPERATURE (x 100° C.)

FIGURE 1.

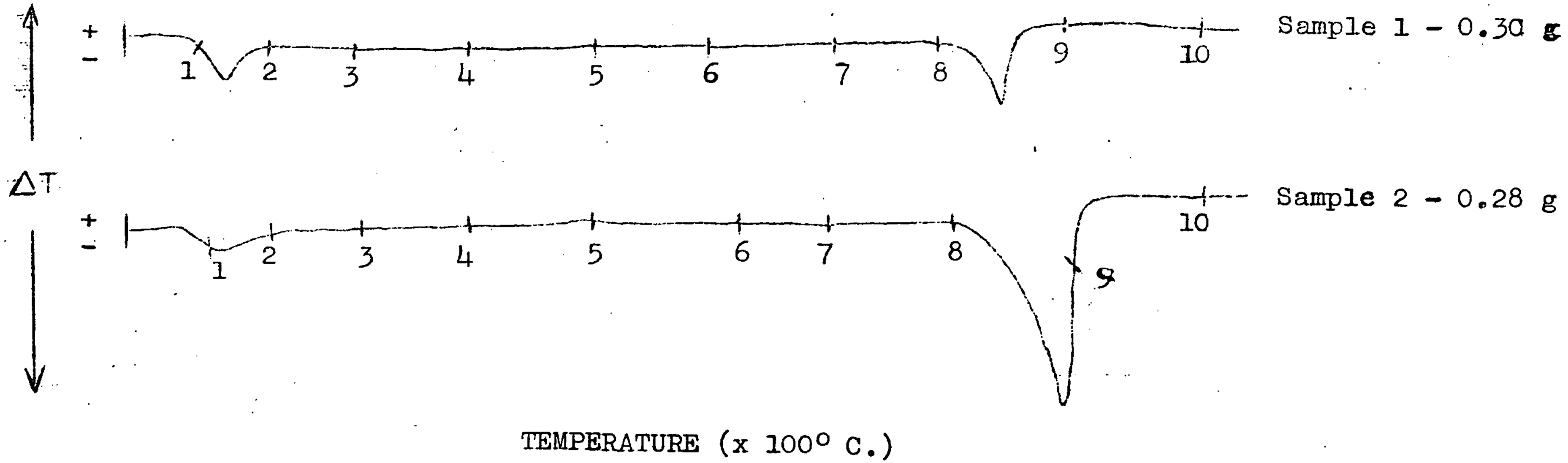
DIFFERENTIAL TRACES: Lime-Quartz and Lime-Clay Mixtures.

FIGURE 2.

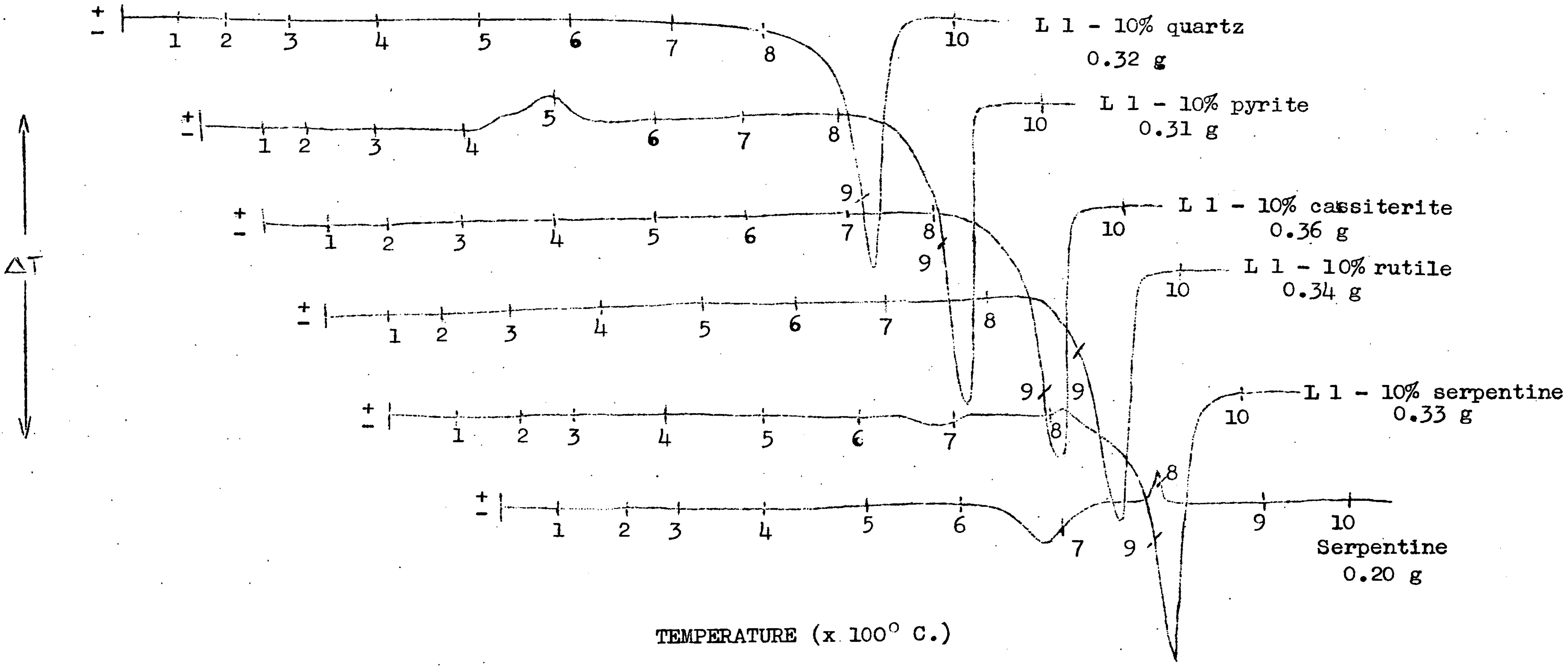


DIFFERENTIAL TRACES: $CaCO_3$-SiO_2 Mixtures.

FIGURE 3.



DIFFERENTIAL TRACES: Limestone-Mineral Mixtures.



TEMPERATURE (x 100° C.)

FIGURE 4.

DIFFERENTIAL TRACES: Limestone-Clay Mixtures.

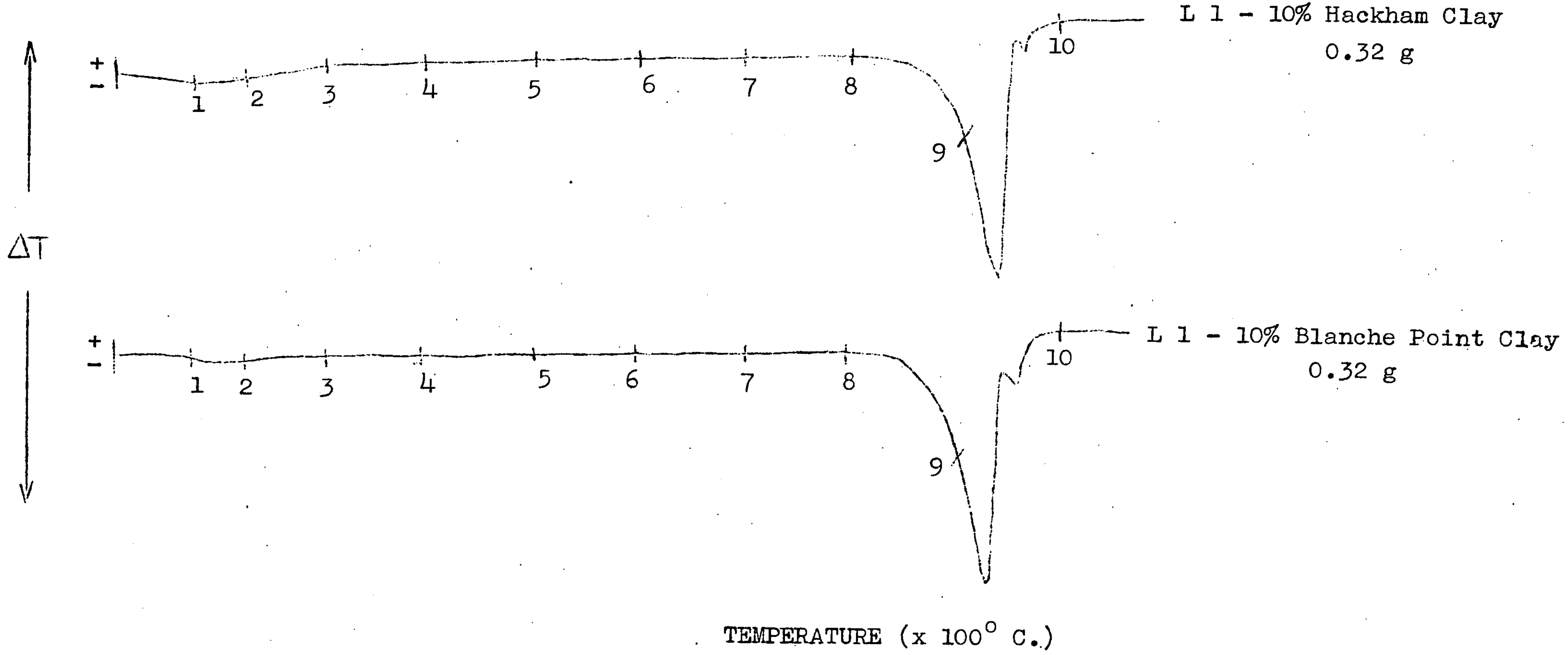


FIGURE 5.