CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS, OTTAWA

MINES BRANCH

RESEARCH REPORT

R 94

Price 75 cents

THE MINERAL CONSTITUTION OF SOME ORDOVICIAN SHALES OF EASTERN AND SOUTHERN ONTARIO

A. G. SADLER

MINERAL PROCESSING DIVISION

MARCH 1962

Mines Branch Research Report R-94

THE MINERAL CONSTITUTION OF SOME ORDOVICIAN SHALES OF EASTERN AND SOUTHERN ONTARIO

by

A. G. Sadler*

- - -

SYNOPSIS

Ordovician shale specimens from formations belonging to the Richmondian, Maysvillian, Edenian, and Chazyan stages were sampled from several localities in Ontario.

The materials were subjected to various physical and chemical treatments, and examined by DTA, chemical and X-ray diffraction techniques.

The major mineral constituents in the three Queenston shale samples of the Richmondian stage were found to be illite, chlorite, quartz, and calcite. Dolomite was identified as a minor mineral constituent in two of the samples, and X-ray and chemical analyses suggested the presence of minor amounts of a sodium (or sodium-calcium) feldspar. The mineral types present in all three samples were almost identical and the specimens differed only in the relative amounts of each component.

The Dundas and Carlsbad shale samples of the Maysvillian stage had similar mineral constitutions to the Queenston specimens. In addition, small amounts of pyrite and organic matter were identified in the Carlsbad shale. The results and calculations based on chemical tests showed that the samples differed from the Queenston shales in having a higher proportion of ferrous and a lower proportion of ferric ions.

---

* Senior Scientific Officer, Ceramic Section, Mineral Processing Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

The shale from the Billings formation of the Edenian stage resembled the Carlsbad material mineralogically; however, the sample contained more organic matter and pyrite, and calcite was present only as a minor constituent.

The Rockcliffe shale, which belongs to the Chazyan stage, also contained illite, chlorite, quartz, calcite and dolomite. Chemical and X-ray results indicated the presence of appreciable amounts of a potassium feldspar.

Suggestions for future work in this field have been put forward.

• • •

Direction des mines

Rapport de recherches R 94

CONSTITUTION MINÉRALOGIQUE DE CERTAINS SCHISTES ORDOVICIENS DE L'EST ET DU SUD-EST DE L'ONTARIO

par

A.G. Sadler*

RÉSUMÉ

Des échantillons de schistes ordoviciens en provenance de formations qui appartiennent aux étages richmondien, maysvillien, edenien et chazyen ont été prélevés dans plusieurs endroits de l'Ontario.

Les minéraux en question ont été soumis à divers traitements physiques et chimiques et étudiés suivant des procédés de chimie, de radiocristallographie par diffraction et d'analyse thermique différentielle.

Voici les principaux constituants minéraux des trois échantillons de schiste de Queenston (étage richmondien): illite, chlorite, quartz et calcite. Deux des échantillons contiennent également une petite quantité de dolomie, et les analyses tant radiographiques que chimiques indiquent la présence de faibles quantités de feldspath sodique (ou sodique-calcique). Les types minéralogiques présents dans tous les trois échantillons sont presque identiques, les échantillons différant seulement par la proportion relative de chacun des constituants.

Les échantillons de schiste de Dundas et de Carlsbad (étage maysvillien) ont une constitution minéralogique semblable à celle des échantillons de Queenston. Le schiste de Carlsbad renferme aussi de petites quantités de pyrite et de matières organiques. Les résultats et les calculs fondés sur les analyses chimiques démontrent que les échantillons en question diffèrent des schistes de Queenston en ce qu'ils contiennent une proportion plus forte d'ions ferreux et une proportion plus faible d'ions ferriques.

---

*Chargé de recherches principal, Section de la céramique, Division du traitement des minéraux, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

Le schiste de la formation Billings (étage edenien) ressemble à celui de Carlsbad du point de vue minéralogique; toutefois, il contient plus de matières organiques et de pyrite, mais ne contient que peu de calcite.

Le schiste de Rockcliffe (étage chazyen) contient également de l'illite, de la chlorite, du quartz, de la calcite et de la dolomie. Les résultats des analyses chimiques et radiographiques indiquent la présence de quantités assez considérables de feldspath potassique.

L'auteur du présent rapport fait certaines recommandations relativement aux travaux futurs dans ce domaine.

CONTENTS

……

TABLES

TABLES (Continued)

TABLES (Continues)

....

FIGURES

....

INTRODUCTION

In the settled parts of Ontario, there exists a serious shortage of clays and shales suitable for the manufacture of high-quality ceramic ware. There are, however, large deposits of shales that are used for making structural clay products, although in many cases these materials have to be used in conjunction with more plastic surface clays.

The three main sources of raw material used for the production of brick and tile are the shale deposits of the Queenston and Dundas formations and the Quaternary surface clays. The shale formations are of the Palaeozoic era and the Quaternary clays belong to the Cenozoic era.

The positions of the shale deposits of the geological succession are shown in Table 1. Queenston shale, belonging to the Richmondian stage, and Dundas shale, belonging to the Maysvillian stage, are both of the upper Ordovician period of the Palaeozoic era.

TABLE 1

Middle and Upper Ordovician Stratigraphy

Ottawa and Toronto Area (B.A. Liberty *)

Period	Stage	Formations East of the Frontenac Axis (Ottawa Area)	Lithology	Stratigraphy West of the Frontenac Axis (Toronto Area)
Ordovician Upper	Richmondian	Queenston	Red Shale	Queenston
		Russell	Grey shale with heavily interbedded dolomite	Meaford
	Maysvillian	Carlsbad (Lorraine)	Grey shale and sandy, rusty shales with thin dolomitic layers on top	Dundas
	Edenian	Billings	Grey or bluish-grey shale	Blue Mountain
			Brown soft shale Black fissile shale	Gloucester Collingwood
		Eastview	Limestone with a little interbedded shale	Cobourg Sherman Fall Hull Rockland Leray Lowville Pamelia
	Trentonian Blackriveran	Ottawa	Limestone	
Middle	Chazyan	St. Martin Rockcliffe	Impure limestone Olive-green shale with sandstone lenses	

---

* Geologist, Fuels and Stratigraphy Division, Geological Survey of Canada

The shale deposits of the Ordovician period also include the Carlsbad formation of the Maysvillian stage, which has been correlated with the Dundas deposits, the Billings formation of the Edenian stage and the Rockcliffe shale of the Chazyan stage. None of these materials is exploited commercially. The deposits have been described by several authors, notably Wilson (1), for the Ottawa - St. Lawrence Lowland, and Caley (2), for the Toronto-Hamilton area.

Although some of these shales have been used for many years and the stratigraphy of the formations has been studied extensively, very little work has been done on the mineralogy of these deposits.

A raw clay or shale is an agglomeration of different-sized particles of many minerals, a knowledge of the nature and relative amounts of which would be useful in many ways. From a geologist's viewpoint, the information could help to complete his picture of the formation of a deposit. It may aid deduction of the origin of the material, and possibly lead to an understanding of the climatic and geological conditions prevailing at and since the time of deposition. To a ceramist, knowledge of the mineral constitution of a shale could be invaluable in yielding information on what happens during treatment of the material. Present-day ceramic manufacturing techniques call for mass production methods with precise control, and require a complete understanding of all the factors involved. Not the least of these requirements is a knowledge of the raw materials themselves, particularly of the mineral types present and of how their physical state and chemical nature can influence the properties of products during manufacture and in use. A review of the varying effects that can be caused by the same elements in different chemical combinations and physical forms has been given by Searle and Grimshaw (3).

The Queenston formation consists of a uniform reddish-brown shale, massive in appearance but actually very thinly bedded and containing occasional hard layers and greenish-grey bands and patches. According to Caley (2), the narrow greenish bands lie both parallel and at right angles to the bedding planes. The vertical seams appear to lie along small joint fissures, the horizontal ones along what may be zones of greater permeability. The greenish colour was probably caused by the reducing action of percolating waters charged with organic acids in solution. When weathered, the shale breaks down to soft thin laminae which illustrate the actual thin-bedded structure of the deposits. As a consequence of this degradation, many outcrops carry a soft mantle of clay which has originated from the shale by the process of weathering. Deposits of the shale are thick and extensive in southern Ontario, a thickness of over 400 feet being quoted by one authority (4). The formation outcrops as a belt at the base of the Niagara Escarpment from Niagara Falls to Hamilton. From Hamilton it extends north through Halton, Peel, and Dufferin Counties to the Bruce Peninsula. Queenston shale is not known to occur in central Ontario, but it outcrops to the west and north of Russell, Russell County in eastern Ontario.

The Carlsbad and Dundas formations consist predominantly of a greyish-blue, thinly-bedded shale, interspersed with numerous hard sandy layers limited in extent, together with thinner but more continuous limestone layers. The Dundas shale occurs extensively in southern Ontario, where it is locally referred to as Lorraine; it forms the bedrock of a considerable area in York, Peel, and Dufferin Counties. Numerous outcrops occur, particularly in stream banks, but for the most part the deposit is covered by glacial drift. There is no known occurrence of Maysvillian stage shale formations in central Ontario, but the Carlsbad is abundant in Carleton and Russell Counties in eastern Ontario.

The Billings formation consists of a thinly-bedded, black, fissile shale containing bituminous material and pyrite. The shale is found in many places in the eastern part of Ottawa, and the deposit underlies large areas in Cumberland and Gloucester Townships.

In the Ottawa area, the Rockcliffe formation is the earliest deposit of the Ordovician period that contains appreciable quantities of shale. Outcrops occur along the Ottawa River near Ottawa at Green's Creek in Gloucester Township, Carleton County, and at Cumberland in Russell County. The formation consists predominantly of an olive-green shale of a sandy texture, interspersed with occasional bands of sandstone.

METHODS OF INVESTIGATING CLAYS AND SHALES

Numerous methods of investigating the mineral constitution of clays and shales have been established in recent years. The most useful and fundamental of these techniques include chemical analysis, differential thermal analysis (DTA), X-ray analysis, and optical and electron microscopy. In addition, there are many subsidiary methods of investigation applicable to these materials that may serve to confirm the findings of the more fundamental techniques. No one method is capable of establishing with certainty the mineral constituents, and a combination of the different techniques must be utilized.

The complexity of the constitution of a clay or shale, which may often contain certain minerals in the process of chemical degradation or synthesis, makes the evaluation of analytical results extremely difficult. For this reason methods of separating or concentrating the different minerals are essential in order to identify them and establish their nature. In clays and shales the range of particle size is large and variable and, in many cases, certain minerals tend to be present in definite size ranges. Thus, by a means of dispersion, followed by sieving or sedimentation, it is often possible to obtain concentrations of these minerals.

Dispersion

The first essential step is to break the material down to its ultimate particles. This can sometimes be brought about by blunging the raw material in water containing a dispersion agent such as Calgon; for particularly hard shales heat must be applied.

The danger in all dispersion techniques is that the treatment may be so drastic as to remove or change some of the mineral constituents. For instance, blunging with water will remove any soluble salts, and the addition of Calgon may increase the sodium content of a clay by the process of cation exchange.

Sieving

After dispersion the resulting suspension may be passed through a nest of sieves. Many clays contain impurities, such as quartz, ironstone nodules and mica, which have a comparatively large grain size. These minerals predominate in the larger sieve size-fractions, and after thorough washing they may be collected and purified by other methods.

Sedimentation

Following sieving the remaining clay suspension may be separated into further size-fractions if allowed to settle for various lengths of time. The equivalent spherical diameter may be calculated by applying Stokes' Law. The actual sizes of the particles may be determined with an optical or electron microscope.

Centrifuging

For the separation of extremely small particles a centrifuge may be used. In this apparatus the acceleration of the particles can be varied by altering the speed of the centrifuge. The method permits the time for sedimentation of particles of a required size to be greatly shortened.

Although only a rough separation is usually effected by the methods described, the various fractions may be further purified by the application of other techniques such as mechanical separation, heavy-liquid separation, froth flotation, elutriation, and chemical treatment.

In this study seven shale samples were obtained from different localities in Ontario and examined. Details of the specimens are given in Table 2.

TABLE 2

Description of the Shale Samples

Sample No.	Stage	Formation	Locality
1	Richmondian	Queenston	Near Streetsville, Peel County
2	Richmondian	Queenston	Near Ottawa, Russell County
3	Richmondian	Queenston	Nelson Township, Halton County
4	Maysvillian	Dundas	Near Toronto, York County
5	Maysvillian	Carlsbad	Near Ottawa, Carleton County
6	Edenian	Billings	Ottawa, Carleton County
7	Chazyan	Rockcliffe	Rockcliffe, Carleton County

PROCEDURE AND RESULTS

Queenston Shales of the Richmondian Stage

Examination of the Raw Shales

Differential Thermal Analysis

DTA curves of the three raw shales are illustrated in Curves 1, 2, and 3 of Figure 1. They show the following characteristics:

Streetsville Shale (Curve 1, Figure 1)

Endothermic peaks:

120°C - elimination of adsorbed water

590° - loss of structural water from a clay mineral or minerals

645° - further loss of structural water from a clay mineral or minerals

750°to 810° - may be due to loss of CO_2 from magnesium carbonate in the form of dolomite

880° - final decomposition of the dolomite combined with the breakdown of calcite to CaO and CO_2

Exothermic peaks:

350° - small broad peak probably due to the presence of organic material

925° - effect commonly observed at the end of a large calcite peak

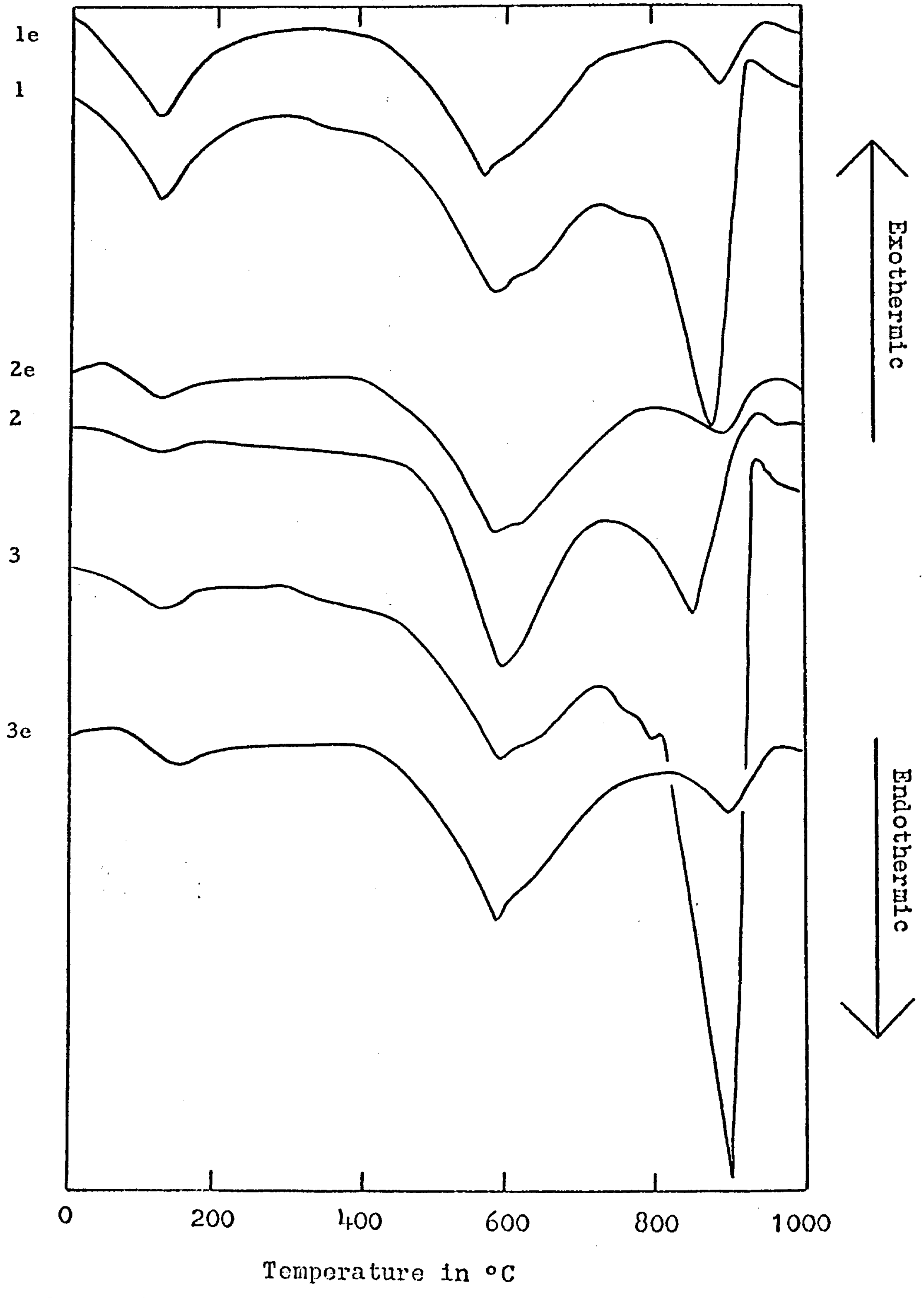

Figure 1. DTA curves of the raw Queenston shales and the dilute hydrochloric acid treated samples.

Ottawa Shale (Curve 2, Figure 1)

Endothermic peaks:

130°C - elimination of adsorbed water

595° - loss of structural water from a clay mineral or minerals

850° - breakdown of calcite to CaO and CO_2

Exothermic peaks:

200° to 400° - uneven baseline probably due to the presence of organic material

950° - effect commonly observed at the end of a large calcite peak

Nelson Shale (Curve 3, Figure 1)

Endothermic peaks:

135° C - elimination of adsorbed water

585° - loss of structural water from a clay mineral

630° - further loss of structural water from a clay mineral

795° - may be due to loss of CO_2 from magnesium carbonate present in the form of dolomite

900° - final decomposition of the dolomite combined with the breakdown of calcite to CaO and CO_2

Exothermic peaks:

210° to 300° - small amount of organic material

925° - effect commonly observed at the end of a large calcite peak

All the DTA curves are similar, although minor differences are evident. The peak temperatures of the major constituents vary because the apparent reaction temperatures depend on the amount of reacting material in the sample. An examination for quartz was carried out on the specimens by obtaining the DTA curve of the calcined (750°C) material and examining the chart for the endothermic alpha to beta quartz reaction at 573° C. All three curves gave evidence of the presence of this mineral.

Examination of the DTA curves indicates that the major constituents of the Queenston shale samples are:

1. A clay mineral which loses structural water at a temperature of approximately 590°C.
2. Calcium carbonate.
3. Quartz.

The DTA curves of the shales from Streetsville and Nelson show endothermic shoulders at about 645° and 630° C respectively, on the main endothermic peaks. The multiple effects were probably caused by the presence of two or more clay mineral types. The curve for the Nelson shale shows a small endothermic peak at 795° C, characteristic of dolomite. The DTA evidence for the presence of this mineral in the Streetsville sample is uncertain, and negative for the Ottawa sample.

Quantitatively, the shales appear to contain similar amounts of a clay mineral or minerals, considerable quartz (more than 15 per cent), and approximately 8, 5, and 20 per cent calcite respectively for the Streetsville, Ottawa, and Nelson samples.

The effect of the large amounts of calcium carbonate in the raw shales obscured other DTA effects at the higher temperatures; therefore samples were treated with dilute hydrochloric acid (1:20) to remove the calcite. The residues were washed and dried, and examined by DTA. The curves are illustrated in Figure 1 (le, 2e, 3e) together with the ones for the corresponding raw shales. The effect of the dilute acid treatment was similar for each shale. A small, sharp, endothermic peak at 575° C has become prominent and indicates a considerable quartz content. The calcite and dolomite peaks have disappeared, revealing a high temperature endothermic clay mineral peak at about 890° C. The form of the curves is now typical of the illite group of clay minerals.

Chemical Analysis

The chemical analyses of the raw shales are shown in Table 3.

Very little information can be obtained from chemical analysis alone. In the case of Queenston shale the relatively large percentages of calcium oxide and carbon dioxide indicate the presence of appreciable quantities of calcite. If all the CO_2 is assumed to be present as calcium carbonate, the weight percentages are 12, 8.4, and 22.2 respectively for the Streetsville, Ottawa, and Nelson samples. However, siderite (iron carbonate) and dolomite (magnesium calcium carbonate) may be present also.

TABLE 3

Chemical Analyses of the Raw Queenston Shales

Constituent	Sample 1 Streetsville	Sample 2 Ottawa	Sample 3 Nelson
SiO_2	56.50 %	56.47%	48.76 %
Al_2O_3	13.81	15.93	14.02
Fe_2O_3	3.62	3.55	3.72
FeO	1.99	2.73	1.42
TiO_2	0.80	0.87	0.58
CaO	6.78	4.80	11.46
MgO	2.75	3.40	2.13
K_2O	3.70	3.80	3.48
Na_2O	0.71	1.00	0.62
CO_2	(5.29)	(3.70)	(9.76)
Moisture	(0.16)	(0.16)	(0.50)
LOI	9.26	7.74	13.30
$H_2O(+110^\circ C)$	(3.81)	(3.88)	(3.04)
Total	99.92	100.29	99.49

The analyses in brackets constitute the LOI

X-Ray Analysis

X- ray diffraction photographs were taken in a 57.54 mm dia. Debye-Scherrer camera, using Co K_{alpha} radiation. The principal diffraction lines and their relative intensities (visual determination) are given in Table 4.

TABLE 4

d-Spacings and Relative Intensities of the Principal X-Ray Diffraction Lines Given by the Raw Queenston Shales

Sample 1 Streetsville		Sample 2 Ottawa		Sample 3 Nelson	
d(A)	Int.	d(A)	Int.	d(A)	Int.
10.1	4	9.9	3	10.0	2
7.1	3	7.1	3	7.1	2
4.97	3	-	-	-	-
4.50	6	4.48	5	4.46	5
4.26	6	4.24	5	4.24	5
-	-	-	-	3.84	2
-	-	3.51	2	-	-
3.35	10	3.35	10	3.33	10
3.20	4	3.18	3	3.18	4
3.03	8	3.02	6	3.02	9
2.57	4	2.57	5	2.56	3
2.28	5	2.28	5	2.28	8
2.13	3	2.14	5	2.12	2
1.82	8	1.82	7	1.81	4
1.54	7	1.54	5	1.54	4
1.38	6	1.38	3	-	-

-

The samples produced similar X-ray patterns and these indicate the presence of clay minerals with basal spacings of about 10A and 7A. Considerable amounts of quartz are present, as shown by the strong lines corresponding to spacings of 4.24A and 3.35A. Calcite is indicated by the characteristic line corresponding to a spacing of 3.024A.

Examination of the Finer Fractions of the Shales

It is an established fact that in clays and shales the clay mineral constituents are concentrated in the finer particle sizes. Therefore, in order to obtain samples containing a greater proportion of clay mineral for further examination, a separation and sedimentation technique was used.

The shales were ground to pass a 10-mesh sieve, then blunged and heated with distilled water for six hours. Each suspension was passed through a 325-mesh screen and allowed to settle in a container for different periods of time. The sediments consisted of fractions of the shale containing particles of less than a certain equivalent spherical diameter. The fractions collected are shown in Table 5.

The equivalent spherical diameter may be calculated by applying Stokes' Law which states:

$$\frac{S}{t} = \frac{2\,gr^2\,(d_1 - d_2)}{9n}$$

where

S = distance of fall in cm

t = time of fall in secs

g = acceleration due to gravity (981 cm/sec^2)

$2r$ = D equivalent spherical diameter (ESD) of the falling particle in cm

n = viscosity of the suspending medium (0.01 poises for water at 20° C)

d_1 = specific gravity of the particles in suspension (clay = 2.5)

d_2 = specific gravity of the suspending medium (water = 1.0)

For a suspension of clay in water the equation may be be simplified to

$$D = 1.84\,(S/t)^{1/2}$$

where D is measured in microns, S in centimetres, and t in hours.

TABLE 5

Size Fractions of the Queenston Shales

Shale Sample			Settling Time (hr)	Height of Suspension (cm)	Equivalent Spherical Diameter (ESD) in microns
Sample 1 Streetsville	Sample 2 Ottawa	Sample 3 Nelson			
1	2	3	-	-	Raw shale
1a	2a	3a	25	16	55
1b	2b	3b	121	16	1.5
1c	2c	3c	Remaining suspension evaporated	-	0.7

Differential Thermal Analysis

The DTA curves of the finer fractions are presented in Figures 2, 3, and 4. They show the following characteristics:

Streetsville Shale (Figure 2)

In the coarse fraction, Curve 1a, the clay mineral peak is smaller and the calcite peak larger than in the raw shale, Curve 1.

Curve 1b shows evidence of an increase in the amount of adsorbed water which is released between 100° and 250° C. The clay mineral occurring between 500° and 600° C has increased in size and the dual nature of the peak is more evident. The small peak at 760° C is characteristic of dolomite, and the large endothermic reaction at 890° C indicates the presence of a considerable amount of calcite.

In Curve 1c the adsorbed water and clay mineral breakdown peaks are even larger. The calcite peak is considerably smaller and now occurs at 780° C. A new endothermic peak is in evidence at 910° C with a small shoulder at 860 °C.

Ottawa Shale (Figure 3)

The Ottawa shale shows effects similar to those of the Streetsville shale. The calcite peak has almost disappeared in Curve 2b, revealing a high-temperature endothermic clay mineral reaction. The large exothermic reaction at 365° C in Curve 2c indicates the presence of a small percentage of organic material or a fine grained mineral such as pyrite or siderite.

Nelson Shale (Figure 4)

The curves are very similar to those obtained from the Streetsville shale samples. However, the calcite peaks are much more prominent.

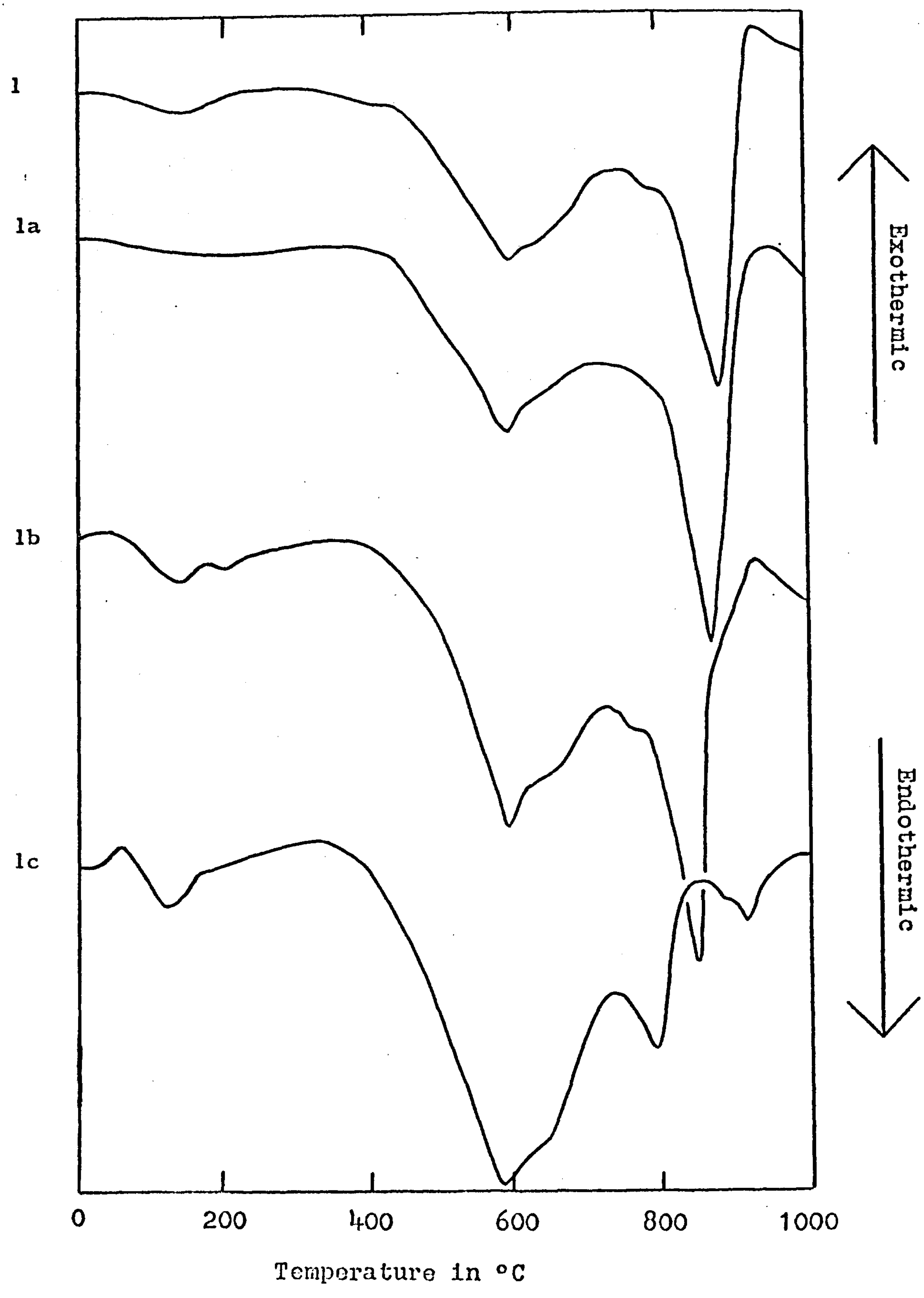

Figure 2. DTA curves of the Streetsville shale fractions.

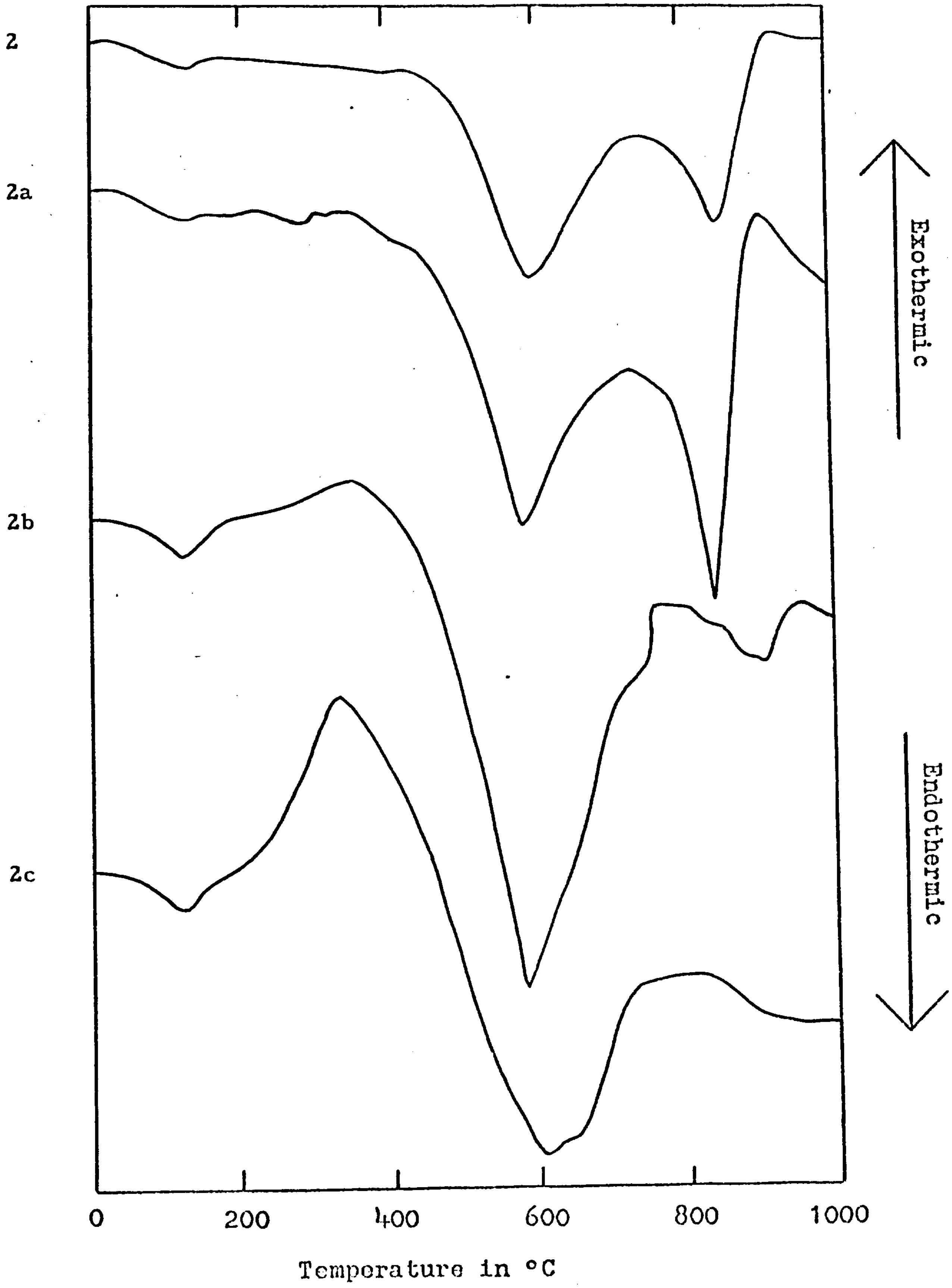

Figure 3. DTA curves of the Ottawa shale fractions.

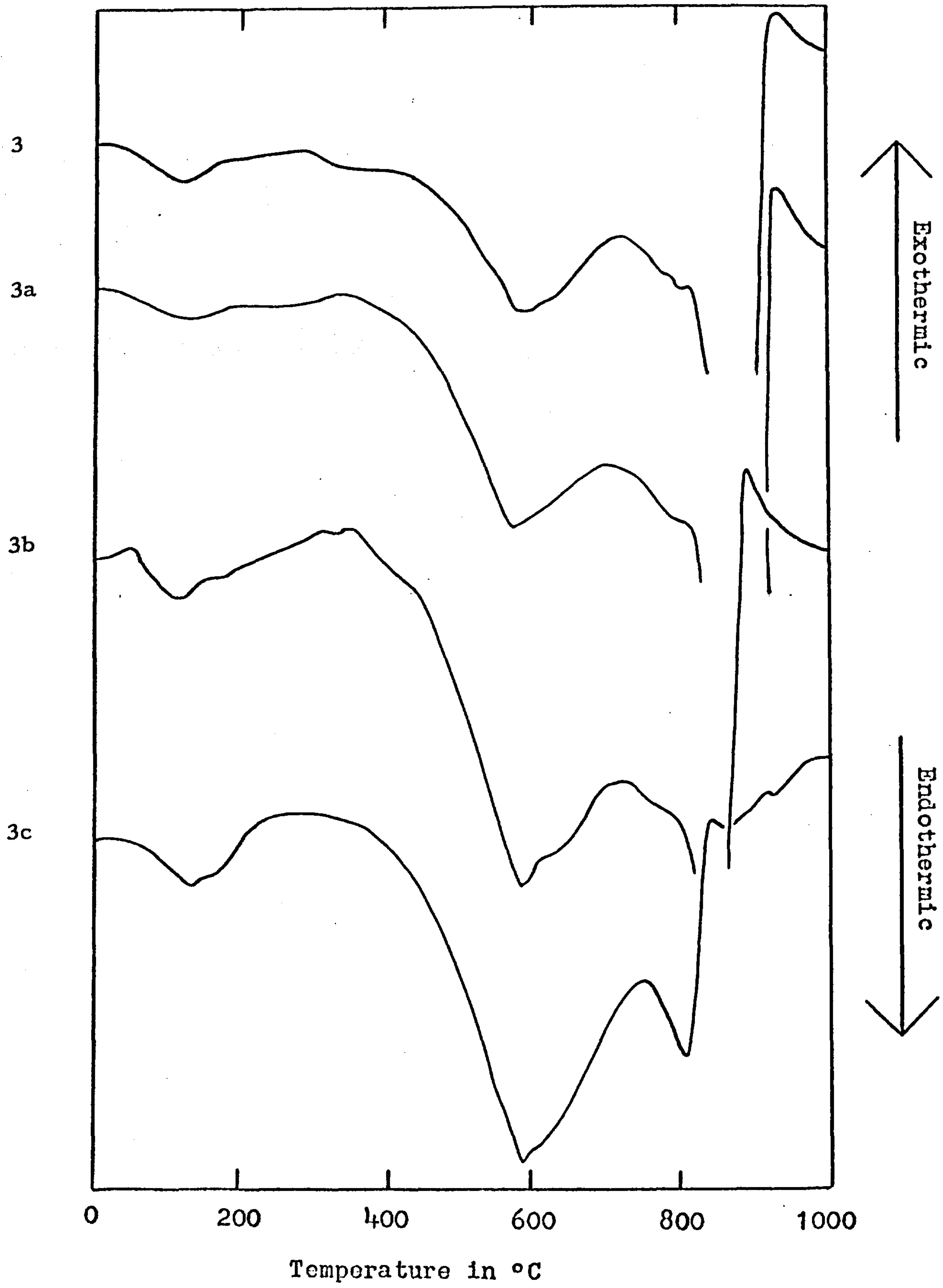

Figure 4. DTA curves of the Nelson shale fractions.

Chemical Analysis

The results of the chemical analysis of the finer fractions are given in Table 6. In all cases, when compared with the undispersed shales, there is a decrease in the relative amounts of SiO_2, CaO, Na_2O and CO_2, and an increase in the percentage weight of all the other constituents. These results are to be expected if the quartz and calcite minerals are concentrated in the coarser fraction of the shales.

The analyses are typical of illite-type clay minerals contaminated with quartz and calcite.

X-Ray Analysis

X-ray diffraction photographs were taken in a 114.83 mm dia. Debye-Scherrer camera, using Co K_{alpha} radiation with an Fe filter. The principal diffraction lines and their relative intensities (visual determination) are listed in Table 7.

By comparing Table 7 with Table 4, it can be seen that a line corresponding to an atomic spacing of 14A has been revealed by the use of the larger diameter camera, and the lines representing 10A and 7A spacings have increased in intensity when compared with the ones for 3.03A, 4.25A and 3.34A (calcite and quartz).

TABLE 6

Chemical Analyses of the Finer Fractions of the Queenston Shales

Constituent	Sample 1c Streetsville	Sample 2b Ottawa	Sample 3c Nelson
SiO_2	52.40%	47.85%	47.52%
Al_2O_3	20.62	23.55	20.60
Fe_2O_3	5.58	6.00	6.00
FeO	2.44	3.22	1.93
TiO_2	0.82	0.78	0.67
CaO	2.92	1.92	5.12
MgO	3.08	3.76	3.31
K_2O	5.27	5.69	5.52
Na_2O	0.36	0.44	0.34
CO_2	(2.04)	(1.76)	(4.46)
Moisture	(0.86)	(0.44)	(0.77)
LOI	6.75	7.20	9.60
$H_2O(+110^\circ C)$	(3.85)	(5.00)	(4.47)
Total	100.24	100.41	100.61

TABLE 7

d-Spacings and Relative Intensities of the Principal X-Ray Diffraction Lines Given by the Fine Fractions of the Queenston Shales

Sample 1c Streetsville		Sample 2b Ottawa		Sample 3c Nelson	
d(A)	Int.	d(A)	Int.	d(A)	Int.
14.2	2	14.2	3	-	-
9.9	3	10.0	5	10.1	-
7.1	3	7.1	4	7.0	2
-	-	5.04	2	-	-
4.49	4	4.50	6	4.50	6
4.26	5	-	-	4.28	4
-	-	4.13	5	-	-
-	-	3.72	4	-	-
-	-	3.53	4	-	-
3.35	10	3.33	10	3.35	10
3.05	5	3.03	4	3.03	8
2.72	3	2.71	4	-	-
2.59	8	2.58	8	2.57	6
2.46	3	-	-	-	-
2.38	3	2.38	3	2.38	3
2.29	4	-	-	2.27	3
2.13	4	-	-	-	-
1.96	3	1.99	3	1.98	2
1.82	4	1.82	3	1.82	3
1.55	4	1.55	4	1.54	3
1.51	4	1.51	5	1.50	3
1.38	3	-	-	-	-

Special Methods of Examination of Raw Shales and Fine Fractions

Crystalline Silica Determination

A chemical method developed by Trostel and Wynne (5) for the determination of crystalline silica was used. The value obtained includes the total free crystalline silica which may be present. The results are given in Table 8.

TABLE 8

Crystalline Silica Determinations, Trostel and Wynne(5)

Shale	Sample	% Crystalline Silica by wt
Streetsville	1	29.20
Streetsville	1c	17.64
Ottawa	2	32.48
Ottawa	2b	9.72
Nelson	3	26.64
Nelson	3c	12.92

Acid Treatment

Although the dilute hydrochloric acid treatment removed the calcite from the shale samples, there was no appreciable attack on the clay minerals themselves. However, it was discovered that the shales were very susceptible to attack by warm, concentrated hydrochloric acid. The red colour of the samples disappeared leaving behind a light grey residue. Chemical tests also revealed the removal of some aluminium, iron, magnesium, and calcium.

The fine-fraction samples 1c, 2b, and 3c, were treated with hot concentrated hydrochloric acid (50%) for 3 hours, and the residues washed and dried.

The DTA curves are illustrated in Figure 5 (1d, 2d, and 3d), superimposed upon the curves of the original fine-fraction materials. In addition to the removal of the carbonate dissociation peaks, there are three major changes:

1. The adsorbed water peak at about 130°C is much larger, and, in Samples 1c and 2b, a second peak at 240° C has appeared.
2. Some material with an endothermic peak temperature at about 590° C has been removed, revealing the multiple nature of the main clay mineral peak.
3. The size of the high temperature endothermic peak at about 900° C has been increased and the reaction seems to have proceeded in a more uniform manner. This is indicated by the absence of the irregularities which are evident in the DTA curves of the untreated fractions.

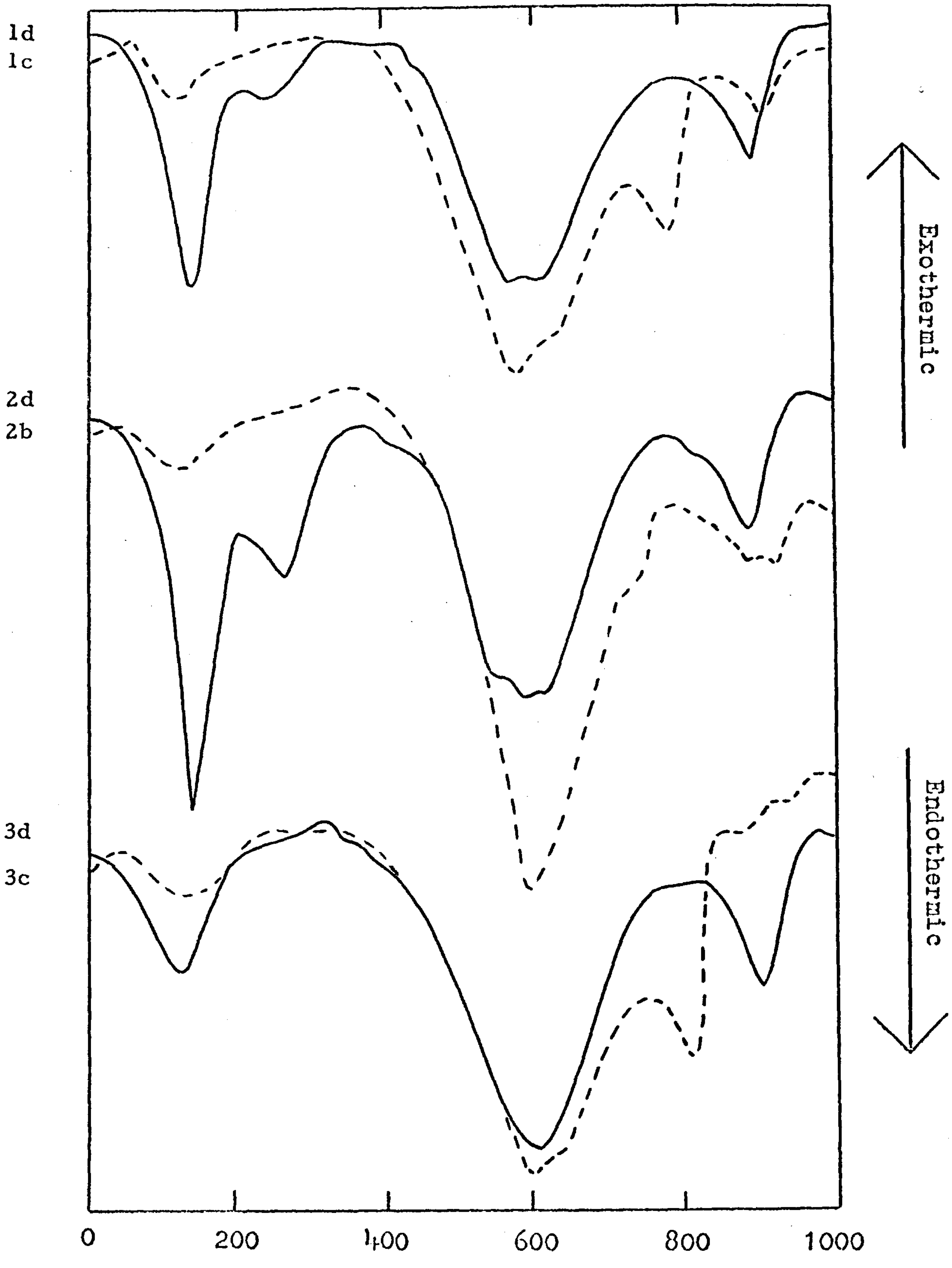

Figure 5. DTA curves of the Queenston shale fine fractions and the concentrated hydrochloric acid treated samples.

X-ray analyses were carried out on the acid-treated samples, using a 114.83 mm dia. Debye-Scherrer camera, Co K_{alpha} radiation and an Fe filter. The results are given in Table 9. The most noticeable effect of acid treatment is that the 14 A line is no longer in evidence and the 7 A line has either disappeared or its relative intensity has been greatly reduced.

Action of Heat

The fine fractions of the Streetsville (1c) and Nelson (3c) shales were heated to various temperatures. The specimens were then examined by means of X-ray diffraction as described above. The results, given in Table 10, indicate that the 7 A line disappears and the 14 A spacing contracts with increasing temperature.

TABLE 9

d-Spacings and Relative Intensities of the Principal X-Ray Diffraction Lines Given by the Fine Fractions of the Queenston Shales After Treatment With Concentrated Hydrochloric Acid

Sample 1c Streetsville		Sample 2b Ottawa		Sample 3c Nelson	
d(A)	Int.	d(A)	Int.	d(A)	Int.
10.1	4	10.1	5	9.9	3
7.1	2	-	-	-	-
4.96	3	5.01	3	4.96	3
4.49	6	4.48	6	4.48	5
4.26	6	4.23	5	4.24	3
-	-	3.72	3	-	-
3.34	10	3.36	10	3.33	10
3.20	3	3.20	2	-	2
-	-	2.70	3	2.67	2
2.57	6	2.57	5	2.57	8
2.45	4	2.47	3	2.45	4
2.38	4	2.38	3	2.38	4
-	-	-	-	2.28	3
2.13	4	2.10	2	-	-
1.98	3	1.98	2	1.98	3
1.81	6	1.82	2	1.81	4
-	-	1.70	2	-	-
1.54	5	1.54	3	1.54	3
1.50	5	1.51	4	1.50	4
1.45	3	-	-	-	-
1.37	5	-	-	-	-

TABLE 10

Effect of Heat Treatment on the d-Spacings and Relative Intensities of the Principal X-Ray Diffraction Lines Given by the Fine Fractions of the Queenston Shales

Shale	300° C		600° C		700° C	
	d(A)	Int.	d(A)	Int.	d(A)	Int.
Streetsville Sample 1c	14.3	3	13.9	3	13.4	3
	10.10	4	10.10	4	10.10	4
	7.40	2	-	-	-	-
	4.99	2	5.04	3	5.17	3
	4.49	7	4.51	7	4.50	8
	4.26	6	4.27	5	4.25	6
	3.35	10	3.35	10	3.34	10
	3.03	7	3.03	5	3.02	4
	2.56	7	2.58	7	2.58	7
	d(A)	Int.	d(A)	Int.	d(A)	Int.
Nelson Sample 3c	15.7	2	13.8	4	13.3	2
	9.90	5	10.1	5	10.2	4
	7.10	2	-	-	-	-
	4.97	2	5.05	3	5.07	3
	4.49	8	4.51	9	4.52	9
	4.24	5	4.26	5	4.27	5
	3.34	10	3.34	10	3.36	10
	3.02	8	3.03	7	3.03	3
	2.56	7	2.58	6	2.58	5

Discussion of the Results for the Queenston Shales

The shapes of the DTA curves of the acid-treated shales (Figure 1) are very similar to those of the illite-type clay minerals, or to mixed-layer minerals with illite as a major constituent.

DTA curves of the finer fractions (Figures 2 to 4) indicate the presence of two or more types of clay minerals. The main endothermic effect (500° to 700° C) appears to be caused by two separate reactions occurring at approximately 590° C and 640° C. The high-temperature endothermic peaks at about 900° C are more irregular than those in the curves of the acid-treated shales. It appears that two reactions take place over the same temperature range, viz., a large endothermic effect and a smaller exothermic one.

A trend can be followed by comparing the curves for the Ottawa shale samples:

Curve 2e, Figure 1, represents the shale treated with dilute acid. The 900° C endothermic peak is large, regular and well defined, indicating a preponderance of the mineral with an illite-type DTA curve.

Curve 2b, Figure 3, represents the fraction where the particles have an ESD of less than 1.5 microns. The high temperature endothermic reaction shows two peaks occurring at 900° C and 920° C. This effect could be explained by hypothesizing that an exothermic reaction is superimposed upon an endothermic one. This explanation is supported by the fact that in Curve 2d, Figure 5, which represents the 2b material treated with concentrated hydrochloric acid, there is a larger, more regular 900° C endothermic peak. The indication is that some mineral has been removed which gave an opposing reaction to the 900° C endothermic peak, viz., an exothermic effect.

In Figure 3, curve 2c, the high temperature endothermic peak has almost disappeared. Therefore, following the trend of the curves (Figure 1, Curve 2c, dilute acid-treated shale; Figure 3, Curve 2b, ESD less than 1.5 microns; Figure 3, Curve 2c, ESD less than 0.7 microns), it appears that the amount of material with an exothermic 900 °C reaction increases with decreasing particle size. This exothermic reaction is in opposition to the endothermic one observed previously and the result is a cancellation of both effects.

Chemical analyses, after allowing for the crystalline silica and carbonate mineral contents, support the evidence that the major clay mineral constituent is illitic in character. Mineral balances are shown in Table 11 and Table 12. The moisture content has been disregarded, the crystalline silica content has been determined by the chemical method of Trostel and Wynne (5), and all the CO_2 has been considered to be present primarily as calcium carbonate. DTA tests indicated the presence of dolomite in the Streetsville and Nelson samples; therefore, any excess CO_2, after computing the calcium carbonate content, has been assigned to the magnesium carbonate part of theoretical dolomite ($MgCO_3.CaCO_3$). The required amount of calcium carbonate has also been assigned to this mineral, and the remainder assumed to be present as calcite. No dolomite could be detected by DTA in the Ottawa shale. However, with the exception of the finest fraction (2c) of this material, no evidence was found for the presence of any other carbonate mineral, therefore the same procedure was followed for this shale as with the Streetsville and Nelson samples. The percentage of crystalline silica, and the calculated amounts of calcite and theoretical dolomite have been subtracted from the corresponding chemical analyses. The remainder has then been recalculated on a 100 per cent basis and the result gives an approximate chemical analysis of the remaining mineral constituents. These calculated analyses are typical of the illite-type clay minerals, the main feature being the large percentage of alkalis. However, there appears to be, at least in the case of the fine fractions of the shales,a deficit of structural water. A typical analysis of illite (6) shows in per cent:

SiO_2, 50.10; Al_2O_3, 25.12; Fe_2O_3, 5.12; FeO, 1.52; CaO, 0.45; MgO 3.93; Na_2O, 0.05; K_2O, 6.93; ignition loss 6.82.

The X-ray results reveal that the clay minerals present have basal spacings of 14 A (chlorite, vermiculite, montmorillonoids), 10 A (mica-type minerals, eg, illite) and 7 A (kaolinite or chlorite type).

Treatment with concentrated hydrochloric acid supports the evidence for the presence of a chlorite-type material. A comparison of Table 7 with Table 9 reveals that the acid treatment removes the minerals with the 14 A and 7 A basal spacings. Iron-rich chlorites are readily attacked by warm hydrochloric acid and also give a strong X-ray reflection at 7 A. These chlorites may or may not have a first order line at 14 A depending on the distribution of the iron atoms in the crystal.

The changes in the X-ray patterns on heating the samples correspond to the changes observed by Brindley (7) in the chlorite mineral penninite where the intensity of the 001 (14 A) reflection became more intense and the 002 (7 A) became weaker within the temperature range 400-700° C. In the cases of the Streetsville and Nelson shales the higher spacing contracted on heating and the 7 A line disappeared.

TABLE 11

Mineral Balances of the Raw Queenston Shales

Material	Total %	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	K_2O	Na_2O	CO_2	H_2O
Sample 1 Streetsville Shale	99.76	56.50	13.81	3.62	1.99	0.80	6.78	2.75	3.70	0.71	5.29	3.81
Crystalline Silica	29.20	29.20										
Calcite	12.01						6.72				5.29	
Remainder	58.55	27.30	13.81	3.62	1.99	0.80	0.06	2.75	3.70	0.71	-	3.81
Calculated Chemical Analysis of Remainder	100.00 (approx)	46.5	23.6	6.2	3.4	1.4	0.1	4.7	6.3	1.2		6.5
Sample 2 Ottawa Shale	100.13	56.47	15.93	3.56	2.73	0.87	4.80	3.40	3.80	1.00	3.70	3.88
Crystalline Silica	32.48	32.48										
Calcite	8.41						4.71				3.70	
Remainder	59.24	23.99	15.93	3.56	2.73	0.87	0.09	3.40	3.80	1.00	-	3.88
Calculated Chemical Analysis of Remainder	100.00 (approx)	40.4	26.9	6.0	4.6	1.5	0.2	5.7	6.4	1.7		6.5
Sample 3 Nelson Shale	98.99	48.76	14.02	3.72	1.42	0.58	11.46	2.13	3.48	0.62	9.76	3.04
Crystalline Silica	26.64	26.64										
Calcite	18.75						10.57				8.18	
Dolomite	3.16						0.89	0.69			1.58	
Remainder	50.44	22.12	14.02	3.72	1.42	0.58	-	1.44	3.48	0.62	-	3.04
Calculated Chemical Analysis of Remainder	100.00 (approx)	43.8	27.8	7.4	2.8	1.2	-	2.9	6.9	1.2	-	6.0

TABLE 12

Mineral Balances of the Fine Fractions of the Queenston Shales

Material	Total %	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	K_2O	Na_2O	CO_2	H_2O
Sample 1c Streetsville Fraction	99.38	52.40	20.62	5.58	2.44	0.82	2.92	3.08	5.27	0.36	2.04	3.85
Crystalline Silica	17.64	17.64										
Calcite	4.64						2.60				2.04	
Remainder	77.10	34.76	20.62	5.58	2.44	0.82	0.32	3.08	5.27	0.36	-	3.85
Calculated Chemical Analysis of Remainder	100.00 (approx)	45.1	26.8	7.2	3.2	1.1	0.4	4.0	6.3	0.5		5.0
Sample 2b Ottawa Fraction	99.97	47.85	23.55	6.00	3.22	0.78	1.92	3.76	5.69	0.44	1.76	5.00
Crystalline Silica	9.72	9.72										
Calcite	2.86						1.62				1.24	
Dolomite	1.05						0.30	0.28			0.52	
Remainder	86.34	38.13	23.55	6.00	3.22	0.78	-	3.53	5.69	0.44	-	5.00
Calculated Chemical Analysis of Remainder	100.00 (approx)	44.0	27.1	6.9	3.7	0.9	-	4.2	6.6	0.5	-	5.8
Sample 3c Nelson Fraction	99.94	47.52	20.60	6.00	1.93	0.67	5.12	3.31	5.52	0.34	4.46	4.47
Crystalline Silica	12.92	12.92										
Calcite	8.05						4.55				3.50	
Dolomite	2.01						0.57	0.48			0.96	
Remainder	76.96	34.60	20.60	6.00	1.93	0.67	-	2.83	5.52	0.34	-	4.47
Calculated Chemical Analysis of Remainder	100.00 (approx)	45.0	26.8	7.8	2.5	0.9	-	3.7	7.2	0.4	-	5.8

Dundas and Carlsbad Shales of the Maysvillian Stage

Treatment of the Samples

Each shale was crushed to pass a 10 mesh sieve, then blunged and heated with distilled water for six hours. The resulting suspension was divided equally and placed in two containers. The depth of each was adjusted to 20 cm by the addition of distilled water. After a calculated period of time, the top 9 cm of each sample was carefully siphoned off and dried at 105° C. The size fractions collected are listed in Table 13.

TABLE 13

Size Fractions of the Dundas and Carlsbad Shales

Shale Sample			Observed Maximum Diameter in Microns (Optical Microscope)
No.	Name	Fraction	
4	Dundas	Raw shale	150
4a	"	Medium	2
4b	"	Fine	1
5	Carlsbad	Raw shale	150
5a	"	Medium	4
5b	"	Fine	Two types observed, one of 2-4 microns and one less than 1 micron

Examination of the Shales

Differential Thermal Analysis

DTA results of the Dundas and Carlsbad shale specimens are illustrated in Figure 6 and Figure 7. The curves show the following characteristics:

Dundas Raw Shale (Curve 4, Figure 6)

Endothermic peaks:

115° C - elimination of adsorbed water

590° - loss of structural water from a clay mineral or minerals

760° - may be due to loss of CO_2 from magnesium carbonate present in the form of dolomite

860° - final decomposition of the dolomite combined with the breakdown of calcite to CaO and CO_2

Exothermic peaks:

440° C - small broad peak probably due to the presence of organic material

Dundas Shale, Medium Fraction (Curve 4a, Figure 6)

Endothermic peaks:

115° C - elimination of adsorbed water

590° - loss of structural water from a clay mineral or minerals

620° - further loss of structural water from a clay mineral or minerals

910° - final breakdown of the structure in a clay mineral or minerals

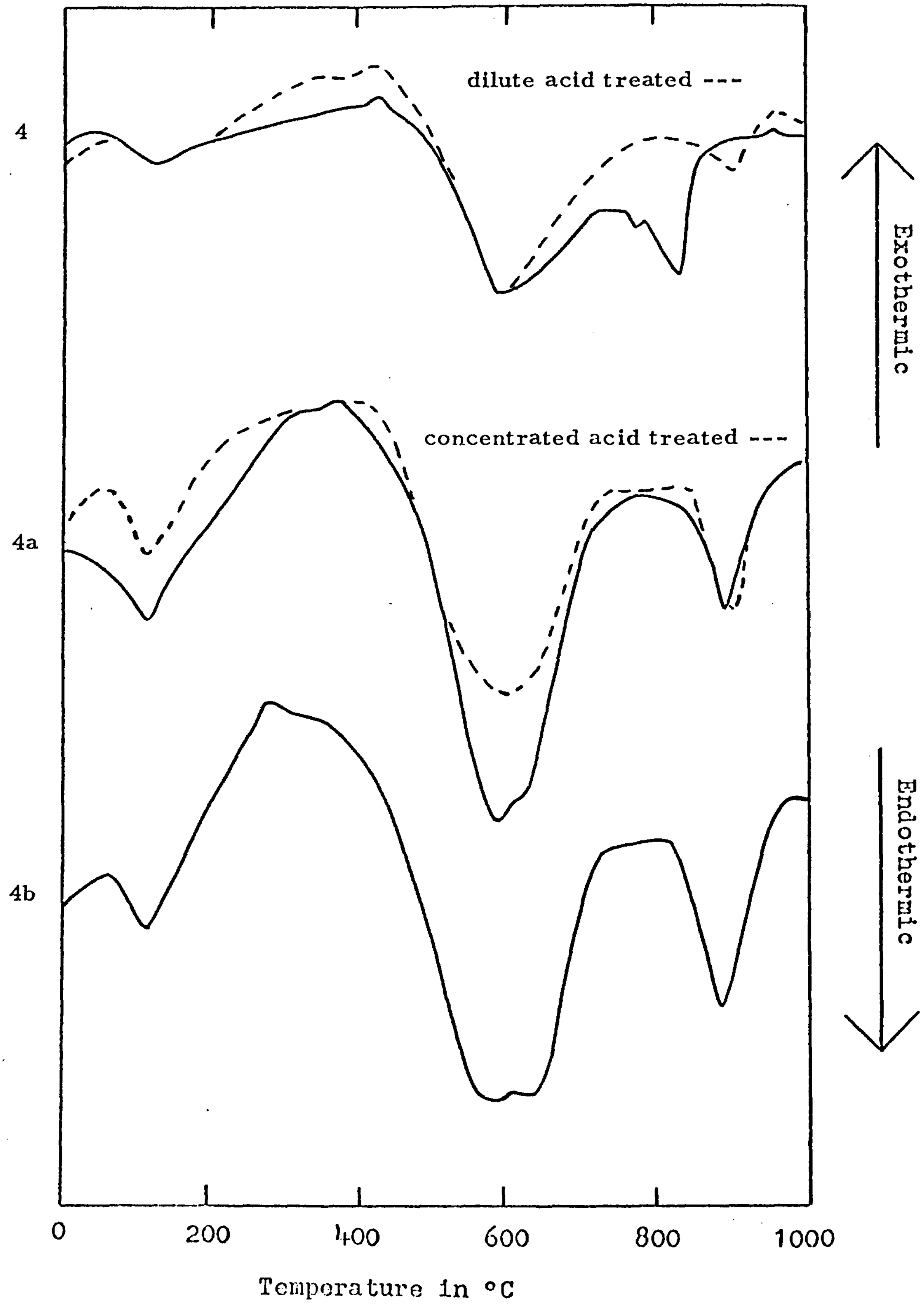

Figure 6. DTA curves of the Dundas shale fractions and the hydrochloric acid treated samples.

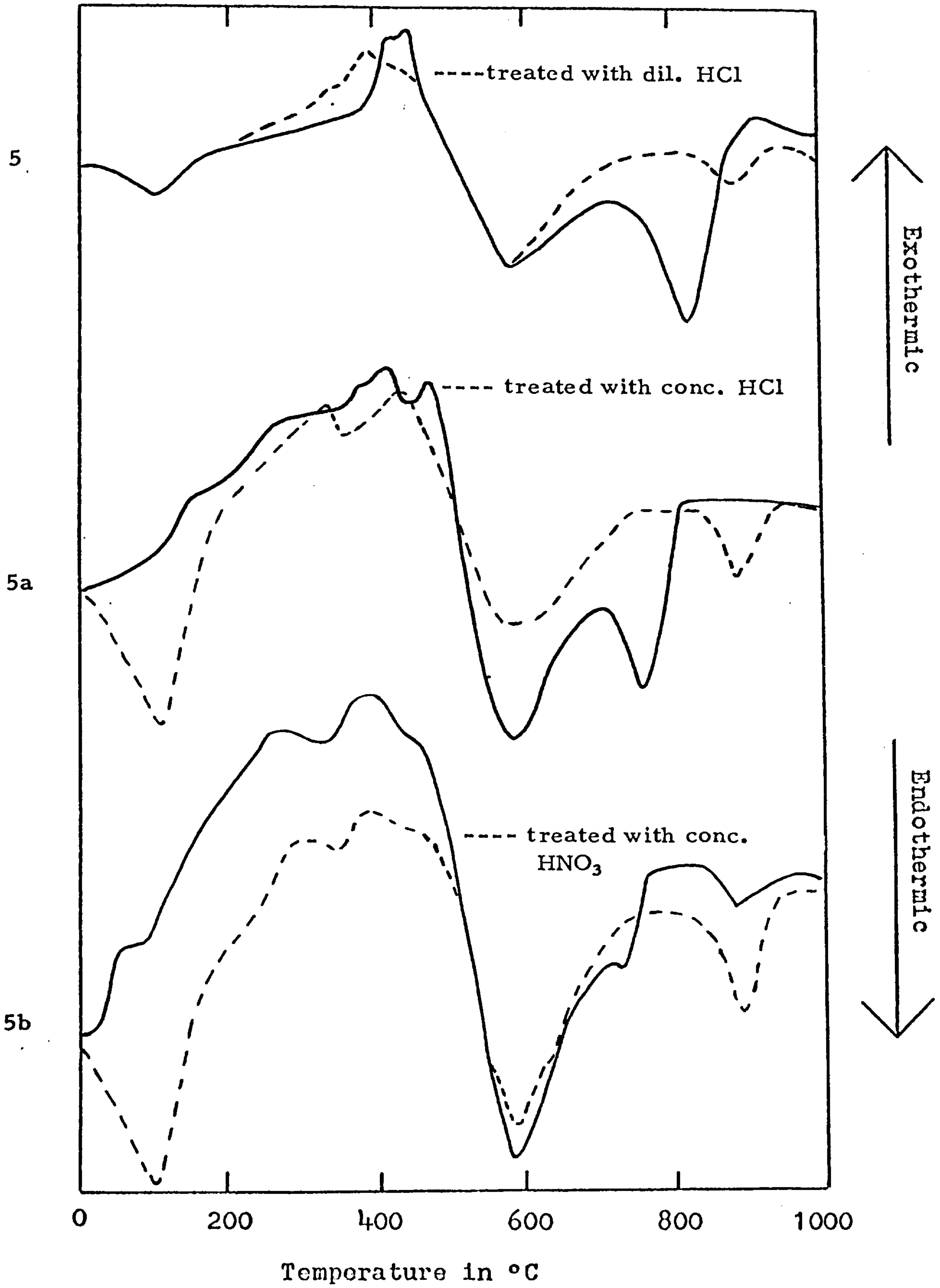

Figure 7. DTA curves of the Carlsbad shale fractions and the acid-treated samples.

Exothermic peaks:

350° C - broad effect probably due to the presence of organic material

Dundas Shale, Fine Fraction (Curve 4b, Figure 6)

Endothermic peaks:

130° C - elimination of adsorbed water

600° to 650° - double peak due to loss of structural water from a clay mineral or minerals

900° - final breakdown of the structure in a clay mineral or minerals

Exothermic peaks:

350° - broad effect probably due to the presence of organic material

Certain changes in the characteristic peaks can be observed in the DTA curves as the particle size decreases. The peaks due to adsorbed water, organic material, and the breakdown of clay mineral structures, all increase. The calcite and dolomite effects decrease and can only be identified in the raw shale sample. The peak caused by the breakdown of clay mineral structures, at approximately 600° C, also shows an increase in the relative amount of the material with a higher decomposition temperature. The DTA curve for the fine fraction shows a definite double peak at about 600° C.

The DTA curve of a sample of the raw shale treated with dilute hydrochloric acid is also shown in Figure 6. The form of the curve is similar to the ones obtained from the dilute acid treated Queenston shales (Figure 1). The dolomite and calcite peaks have been eliminated, and a high temperature endothermic clay mineral peak is in evidence. The curve is typical of the illite-type clay minerals.

The broken line superimposed on the curve of the medium fraction of Dundas Shale in Figure 6 represents the DTA of that sample after treatment with hot 50 per cent hydrochloric acid. A large part of the low-temperature endothermic clay mineral peak has been eliminated. The size of the high-temperature endothermic clay mineral peak appears to be unchanged. However, the maximum of the peak has been displaced to a slightly higher temperature.

Carlsbad Raw Shale (Curve 5, Figure 7)

Endothermic peaks:

110° C - elimination of adsorbed water

590° - loss of structural water from a clay mineral or minerals

830° - breakdown of calcite to CaO and CO_2

Exothermic peaks:

200° to 500° - probably due to the presence of organic material

425° to 450° - may be due to the oxidation of pyrite or siderite.

Carlsbad Shale, Medium Fraction (Curve 5a, Figure 7)

Endothermic peaks:

110° C - a large initial exothermic drift appears to have obscured this peak

590° - loss of structural water from a clay mineral or minerals

765° - breakdown of calcite to CaO and CO_2

Exothermic peaks:

100° to 530° - broad effect with multiple peaks may be due to the oxidation of organic material and iron compounds such as pyrite or siderite

Carlsbad Shale, Fine Fraction (Curve 5b, Figure 7)

Endothermic peaks:

590° C - loss of structural water from a clay mineral or minerals

735° - breakdown of calcite to CaO and CO_2

885° - final breakdown of the structure in a clay mineral or minerals

Exothermic peaks:

25° to 500° C - broad effect with multiple peaks may be due to the oxidation of organic material and iron compounds such as pyrite or siderite

The changes in the characteristic DTA curves as the particle size decreases follow the same trend as in the Dundas shale specimens. Clay mineral peaks increase, calcite peaks decrease, and the exothermic effects due to the oxidation of organic matter increase. One point of difference is that the endothermic clay mineral peak at approximately 600°C does not alter in shape appreciably. The appearance of the endothermic clay mineral peak at 885°C in curve 5b is most probably connected with the calcite content of the sample. In the DTA curves of samples which contain considerable amounts of calcite, the peak is absent. This suggests that a reaction between the calcite and the clay mineral occurs at a temperature lower than that at which the peak should normally be observed. In curve 5b, the calcite content of the fine fraction can be seen to be small and apparently not sufficient to react with all the particular clay mineral present.

Treatment of the shale samples with dilute hydrochloric acid shows the same changes in the DTA curves as reported previously for the Queenston shales. The calcite peak is eliminated and the specimens give typical illite DTA curves. The result for the dilute acid-treated raw Carlsbad shale is shown as a broken line superimposed on curve 5 in Figure 7.

Treatment with hot 50 percent hydrochloric or nitric acids produces samples which give very similar DTA curves. As with the Dundas shale, the main clay mineral breakdown peak is reduced, the calcite peak disappears, and a high-temperature endothermic clay mineral peak appears. Typical DTA curves are shown as broken lines in Figure 7 superimposed upon the respective untreated samples.

DTA examination of the Dundas and Carlsbad shales indicates the presence of a clay mineral showing characteristic endothermic peaks at 590° and 900° C, calcite, and organic matter. The presence of quartz was confirmed by DTA examination of samples precalcined at 750°C to remove interfering clay mineral effects. In addition, the Dundas sample shows evidence of the presence of dolomite; the Carlsbad shale appears to contain more organic matter than the Dundas, and in addition siderite ($FeCO_3$) or pyrite (FeS_2) may be present.

Chemical Analysis

The chemical analyses of the Dundas and Carlsbad shale samples are given in Table 14.

Several significant points can be noted in the chemical analyses. With decreasing particle size, the amounts of SiO_2, CaO, Na_2O, CO_2 and S decrease, the value for TiO_2 remains relatively constant, and the percentages of all the other constituents increase. The sulphur content of the Carlsbad samples suggests the presence of a small amount of pyrite.

TABLE 14

Chemical Analyses of the Dundas and Carlsbad Shale Fractions

Constituent	Dundas		Carlsbad		
	Sample 4 Raw Shale	Sample 4a Medium Fraction	Sample 5 Raw Shale	Sample 5a Medium Fraction	Sample 5b Fine Fraction
SiO_2	55.75%	47.33%	56.60%	51.08%	48.24%
Al_2O_3	16.38	23.42	15.06	18.08	20.20
Fe_2O_3	1.96	3.36	1.29	1.50	1.79
FeO	4.47	4.79	4.76	5.92	6.43
TiO_2	0.86	0.65	0.84	0.98	0.92
CaO	3.74	0.77	5.12	3.88	3.22
MgO	3.30	4.23	2.94	3.70	3.92
K_2O	4.05	6.49	3.06	4.10	4.80
Na_2O	0.89	0.43	1.16	0.69	0.55
CO_2	(3,10)	(1.35)	(3.89)	(2.97)	(1.97)
C (as organic matter)	(0.19)	(0.05)	(0.18)	(0.29)	(0.36)
S	n.d.	n.d.	(0.16)	(0.15)	(0.11)
Moisture	0.38	0.76	0.25	0.39	0.45
H_2O(+110°C)	n.d.	n.d.	(4.63)	(5.66)	(6.66)
LOI	7.30	7.50	8.05	8.54	8.44
Total	99.08	99.73	99.13	98.86	98.96

X-Ray Analysis

The d-spacings and relative intensities of the principal X-ray diffraction lines for the Dundas and Carlsbad shale samples are given in Table 15 and Table 16.

The Dundas shale fractions were examined by means of a 57.54 mm dia. Debye-Scherrer camera and also a Philips Diffractometer; in both cases Co K_{alpha} radiation with an Fe filter was used. The intensities of the diffraction lines obtained photographically were estimated visually, and for the diffractometer method peak heights were measured. The material in the packed mounts used in the latter technique had little or no preferred orientation.

The results are similar to those obtained with the Queenston shales and indicate the presence of clay minerals with basal spacings of approximately 14 A, 10 A, and 7 A. Other minerals which can be identified are calcite (3.03 A) and quartz (4.26 A and 3.35A). Treatment with 50 per cent hydrochloric acid tends to remove the lines corresponding to the 14 A and 7 A spacings in the Dundas shale; in the case of the Carlsbad shale, the 14 A line disappears but the 7 A line remains.

TABLE 15

d-Spacings and Relative Intensities of the Principal X-Ray Diffraction Lines Given by the Dundas Shale Samples

Sample 4 Raw Shale		Sample 4a Medium Fraction		Sample 4b Fine Fraction		Medium Fraction (4a) Treated with Concentrated HCl	
57.54.mmdia. Debye-Scherrer Camera, Co $\mathrm{K}_{\mathrm{alpha}}$ radiation, Fe Filter							
d(A)	Int.	d(A)	Int.	d(A)	Int.	d(A)	Int.
10.0	5	10.0	7	10.0	6	10.0	6
7.1	2	7.1	5	7.1	5	-	-
4.96	2	4.97	2	4.96	2	4.96	2
4.49	6	4.49	10	4.49	10	4.49	10
4.26	7	4.25	2	4.24	1	4.24	2
4.14	2	4.13	2	4.12	6	4.15	7
3.35	10	3.40	9	3.33	6	3.34	8
3.19	5	-	-	-	-	-	-
3.03	6	-	-	-	-	-	-
Philips Diffractometer, Co $\mathrm{K}_{\mathrm{alpha}}$ radiation, Fe filter							
		14.3	6	14.2	2	-	-
		10.1	19	10.1	13	10.1	24
		7.18	17	7.14	6	7.25	7
		4.99	4	5.03	4	5.02	4

TABLE 16

d-Spacings and Relative Intensities of the Principal X-Ray Diffraction Lines Given by the Carlsbad Shale Samples

Sample 5 Raw Shale		Sample 5a Medium Fraction		Sample 5b Fine Fraction		Medium Fraction (5a) Treated with Concentrated HCl	
d(A)	Int.	d(A)	Int.	d(A)	Int.	d(A)	Int.
13.8	6	14.1	4	14.2	4	-	-
9.9	6	10.0	5	10.0	5	9.9	5
7.1	7	7.1	5	6.8	5	7.1	4
4.98	3	4.96	3	4.99	2	4.99	3
4.47	8	4.48	5	4.50	7	4.48	5
4.25	8	4.26	5	4.26	5	4.25	6
4.03	4	4.03	2	-	-	-	-
3.85	3	3.86	2	-	-	-	-
3.66	3	-	-	-	-	3.65	4
3.53	3	3.53	4	-	-	3.51	4
3.35	10	3.34	10	3.35	10	3.34	10
3.20	4	3.19	4	3.19	2	3.20	2
3.04	6	3.03	6	3.03	5	-	-
2.57	5	2.58	5	2.60	6	2.57	5
2.46	6	2.46	5	-	-	2.45	5
2.39	4	2.38	4	-	-	2.39	2
2.28	6	2.28	5	-	-	2.28	5

The effects of heat treatment on the d-spacings and relative intensities of the principal X-ray diffraction peaks are shown in Table 17.

In the case of the Dundas shale sample (4a), the larger basal spacings shown by the specimen heated to 300° C appear as a somewhat diffuse band showing two maxima at 16.0A and 14.2A. With the sample heated to 600° C, a more defined band is evident and the maxima represent d-spacings of 14.2A and 13.5A. After heating to 700° C, the diffraction lines have contracted still further to 13.8A and 13.0A. The 7A spacing disappears after heat treatment at 600° C.

Similar results were obtained with the Carlsbad shale.

Discussion of the Results for the Dundas and Carlsbad Shales

The same general conclusions can be drawn as to the mineral constitutions of the Dundas and Carlsbad shales as for those of the Queenston shales.

The principal clay mineral constituents appear to be chlorite and illite and these predominate in the smaller grain-size fractions. The two major non-clay ingredients are quartz and calcite, and small amounts of organic matter are present. The Dundas shale contains dolomite and the Carlsbad contains pyrite.

Using the same principles as applied in the case of the Queenston shale samples, mineral balances can be drawn up and the results are given in Table 18 and Table 19.

In the case of the Dundas shale fraction 4a, the excess CO_2 after calculating the dolomite content, has been assigned arbitrarily to $MgCO_3$.

TABLE 17

Effect of Heat Treatment on the d-Spacings and Relative Heights of the Principal X-Ray Diffraction Peaks Given by the Medium Fractions of the Dundas and Carlsbad Shale Specimens

Shale	300°C		600° C		700° C	
	d(A)	Ht	d(A)	Ht	d(A)	Ht
Dundas 4a	16.0	5.0	14.2	10.1	13.8	7.5
	14.2	7.5	13.5		13.0	
	10.06	23.0	10.06	19.5	10.06	23.0
	7.06	16.3	-	-	-	-
	4.95	9.6	5.06	12.0	5.10	15.0
	4.48	8.7	4.52	12.5	4.48	13.0
Carlsbad 5a	14.1	5.0	13.5	6.6	13.5	7.8
	10.1	7.5	9.9	8.5	10.1	7.5
	7.04	8.0	-	-	-	-
	-	-	4.95	4.5	5.00	4.5
	4.50	5.5	4.50	7.0	4.48	7.8
	-	-	4.45	7.5	-	-
	4.26	10.0	4.25	9.5	4.24	8.5
	3.54	5.5	3.50	5.0	-	-
	3.19	4.6	?	-	3.19	4.0
	3.03	6.0	3.02	7.0	?	-
	2.57	6.3	2.56	6.5	-	-

TABLE 18

Mineral Balances of the Dundas Shale Samples

Material	Total %	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	K_2O	Na_2O	CO_2	H_2O (+110°C)	C (organic)	Moisture
Sample 4														
Dundas Shale	99.08	55.75	16.38	1.96	4.47	0.86	3.74	3.30	4.05	0.89	3.10	4.01	0.19	0.38
Crystalline Silica	29.88	29.88												
Calcite	6.28						3.50				2.78			
Dolomite	0.71						0.24	0.15			0.32			
Carbon as Organic Matter	0.19												0.19	
Moisture	0.38													0.38
Remainder	61.64	25.87	16.38	1.96	4.47	0.86	-	3.15	4.05	0.89	-	4.01	-	-
Calculated Chemical Analysis of Remainder	100.00 (approx)	42.0	26.6	3.2	7.3	1.4	-	5.1	6.6	1.4	-	6.5	-	-
Sample 4a														
Dundas Fraction	99.73	47.33	23.42	3.36	4.79	0.65	0.77	4.23	6.49	0.43	1.35	6.10	0.05	0.76
Crystalline Silica	3.28	3.28												
Dolomite	2.61						0.77	0.59			1.25			
Excess CO_2 as $MgCO_3$	0.19							0.09			0.10			
Carbon as Organic Matter	0.05												0.05	
Moisture	0.76													0.76
Remainder	92.84	44.05	23.42	3.36	4.79	0.65	-	3.55	6.49	0.43	-	-	-	-
Calculated Chemical Analysis of Remainder	100.00 (approx)	47.5	25.2	3.6	5.2	0.7	-	3.8	7.0	0.46	-	6.6	-	-

TABLE 19

Mineral Balances of the Carsbad Shale Samples

Material	Total %	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	K_2O	Na_2O	CO_2	H_2O (+110°C)	C (organic)	S	Moisture
Sample 5 Carlsbad Shale	99.94	56.60	15.06	1.29	4.76	0.84	5.12	2.94	3.06	1.16	3.89	4.63	0.18	0.16	0.25
Crystalline Silica	34.34	34.34													
Calcite	8.84						4.95				3.89				
Pyrite	0.34				0.18									0.16	
(Actual FeS_2)	(0.30)														
Carbon as Organic Matter	0.18												0.18		
Moisture	0.25														0.25
Remainder	55.99	22.26	15.06	1.29	4.58	0.84	0.17	2.94	3.06	1.16	-	4.63	-	-	-
Calculated Chemical Analysis of Remainder	100.00 (approx)	39.8	26.9	2.3	8.2	1.5	0.3	5.3	5.5	2.1	-	8.3	-	-	-
Sample 5a Carlsbad Fraction	99.39	51.08	18.08	1.50	5.92	0.98	3.88	3.70	4.10	0.69	2.97	5.66	0.29	0.15	0.39
Crystalline Silica	21.86	21.86													
Calcite	6.75						3.78				2.97				
Pyrite	0.32				0.17									0.15	
(Actual FeS_2)	(0.28)														
Carbon as Organic Matter	0.29												0.29		
Moisture	0.39														
Remainder	69.78	29.22	18.08	1.50	5.75	0.98	0.10	3.70	4.10	0.69	-	5.66	-	-	-
Calculated Chemical Analysis of Remainder	100.00 (approx)	41.1	25.9	2.5	8.3	1.4	0.1	5.3	5.9	1.0	-	8.1	-	-	-
Sample 5b Carlsbad Fraction	99.62	48.24	20.20	1.79	6.43	0.92	3.22	3.92	4.80	0.55	1.97	6.66	0.36	0.11	0.45
Crystalline Silica	13.98	13.98													
Calcite	4.48						2.51				1.97				
Pyrite	0.23				0.12									0.11	
(Actual FeS_2)	(0.21)														
Carbon as Organic Matter	0.36												0.36		
Moisture	0.45														0.45
Remainder	80.12	34.26	20.20	1.79	6.31	0.92	0.71	3.92	4.80	0.55	-	6.66	-	-	-
Calculated Chemical Analysis of Remainder	100.00 (approx)	42.7	25.2	2.2	7.9	1.2	0.9	4.9	6.0	0.7	-	8.3	-	-	-

Sulphur was detected in the Carlsbad shale by means of chemical analysis, and pyrite was suspected from the DTA results. This has been allowed for in the compilation of the mineral balances.

The crystalline silica was again determined by the chemical method of Trostel and Wynne (5).

Billings Shale of the Edenian Stage

Treatment of the Sample

The shale was treated in the same manner as the Dundas and Carlsbad samples and the resulting fractions were examined by means of an optical microscope to determine the approximate maximum grain size. The fractions collected are listed in Table 20.

TABLE 20

Size Fractions of the Billings Shale

Shale Sample		Observed Maximum Diameter in Microns (Optical Microscope)
No.	Fraction	
6	Raw shale	150
6a	Medium	A few particles larger than 20 microns but the majority smaller than 10 microns
6b	Fine	The majority less than 4 microns

Examination of the Shale

Differential Thermal Analysis

DTA results of the Billings shale specimens are illustrated in Figure 8. The curves show the following characteristics:

Billings Raw Shale (Curve 6, Figure 8)

Endothermic peaks:

115° C - elimination of adsorbed water

595° - loss of structural water from a clay mineral or minerals

690° to 800° - may be due to loss of CO_2 from carbonate minerals such as dolomite and calcite

890° - final breakdown of the structure in a clay mineral or minerals

Exothermic peaks:

450° C - large effect probably due to the presence of organic material and perhaps pyrite (FeS_2)

Billings Shale, Medium Fraction (Curve 6a, Figure 8)

Endothermic peaks:

100° C - elimination of adsorbed water

600° - loss of structural water from a clay mineral or minerals

760° - may be due to loss of CO_2 from carbonate minerals such as dolomite and calcite

900° - final breakdown of the structure in a clay mineral or minerals

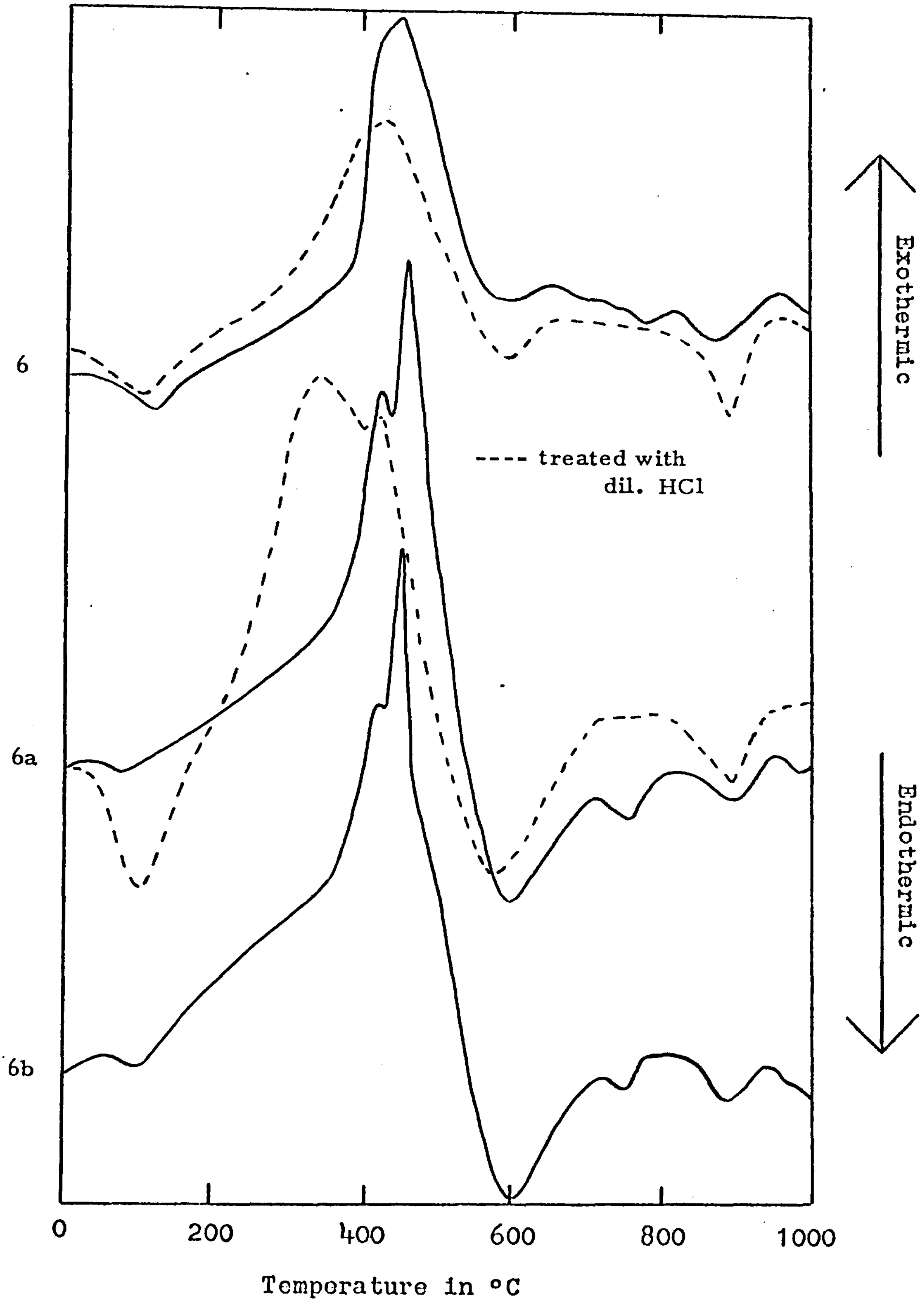

Figure 8. DTA curves of the Billings shale fractions and the dilute hydrochloric acid treated samples.

Exothermic peaks:

420° C	-	probably due to the presence of organic material
460°	-	probably caused by the oxidation of pyrite

Billings Shale, Fine Fraction (Curve 6b, Figure 8)

The form of the DTA curve is almost identical with the one given by the medium fraction (curve 5a).

The effects of dilute hydrochloric acid treatment on the raw shale and the medium fraction are illustrated by the DTA curves shown as broken lines in Figure 8. In both cases, the clay mineral endothermic peaks at 100°, 590°, and 900 °C have increased in size, and the endothermic peaks between 690° and 800° C, which were probably caused by the breakdown of alkaline earth carbonates, have disappeared.

The shale samples were heated to 380°C and held at that temperature for three days in order to remove the organic matter. Such treatment has been proved to be effective in certain instances (8), so enabling further examination by DTA. The DTA curves of the treated samples are shown in Figure 9. The principal changes, when compared with the DTA curves of the original samples in Figure 8, are an apparent increase in the clay mineral endothermic peak at 590° C and elimination of the organic matter exothermic peak at 420°C.

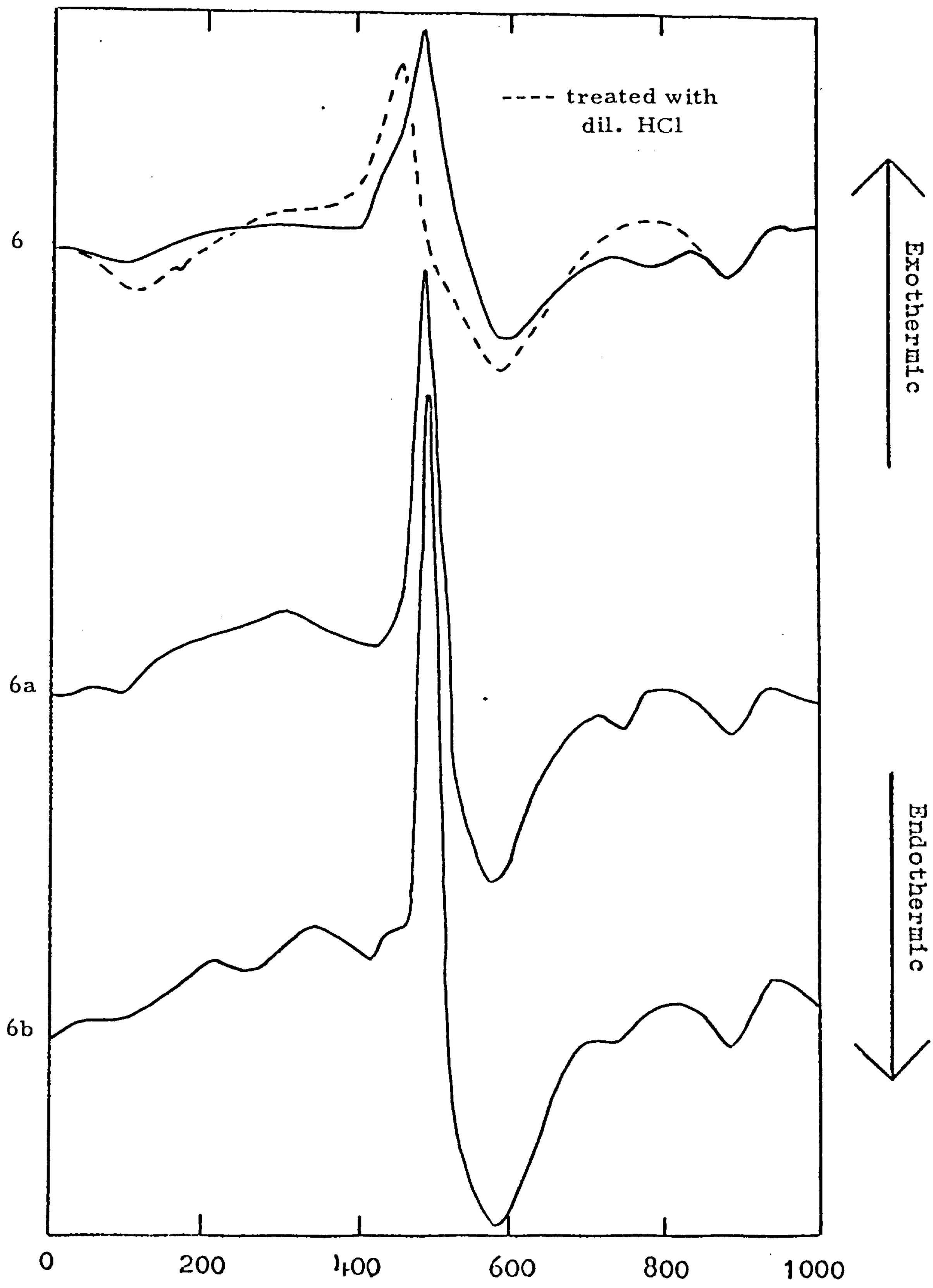

Figure 9. DTA curves of the Billings shale samples heated at 380°C.

The effects of various treatments of the Billings shale medium fraction are illustrated by the DTA curves shown in Figure 10.

Heating at 380° C removes the exothermic peak at 420° C which is most probably due to the presence of organic matter. The exothermic peak caused by the dissociation and oxidation of pyrite has been displaced from 460° to 490° C.

Hydrogen peroxide treatment of the sample which has been heated to 380° C to remove the coal macerals results in the elimination of the pyrite peak (420° C) and the endothermic carbonate mineral peak (750° C). The removal of this latter peak indicates that sulphuric acid may have been formed by reaction between the pyrite and hydrogen peroxide, with subsequent decomposition of any carbonates present. Normally hydrogen peroxide would not be expected to affect pyrite appreciably, but the fine particle size and previous heat treatment may have rendered the mineral more reactive.

Treatment of the medium fraction with 50% nitric acid results in the partial removal of the exothermic peaks due to pyrite and organic matter.

Heating at 380° C and subsequent treatment with 50% nitric acid result in the production of a DTA curve similar to the one produced by heating at 380° C followed by hydrogen peroxide treatment. In both cases the form of the curve is typical of an illitic type clay mineral.

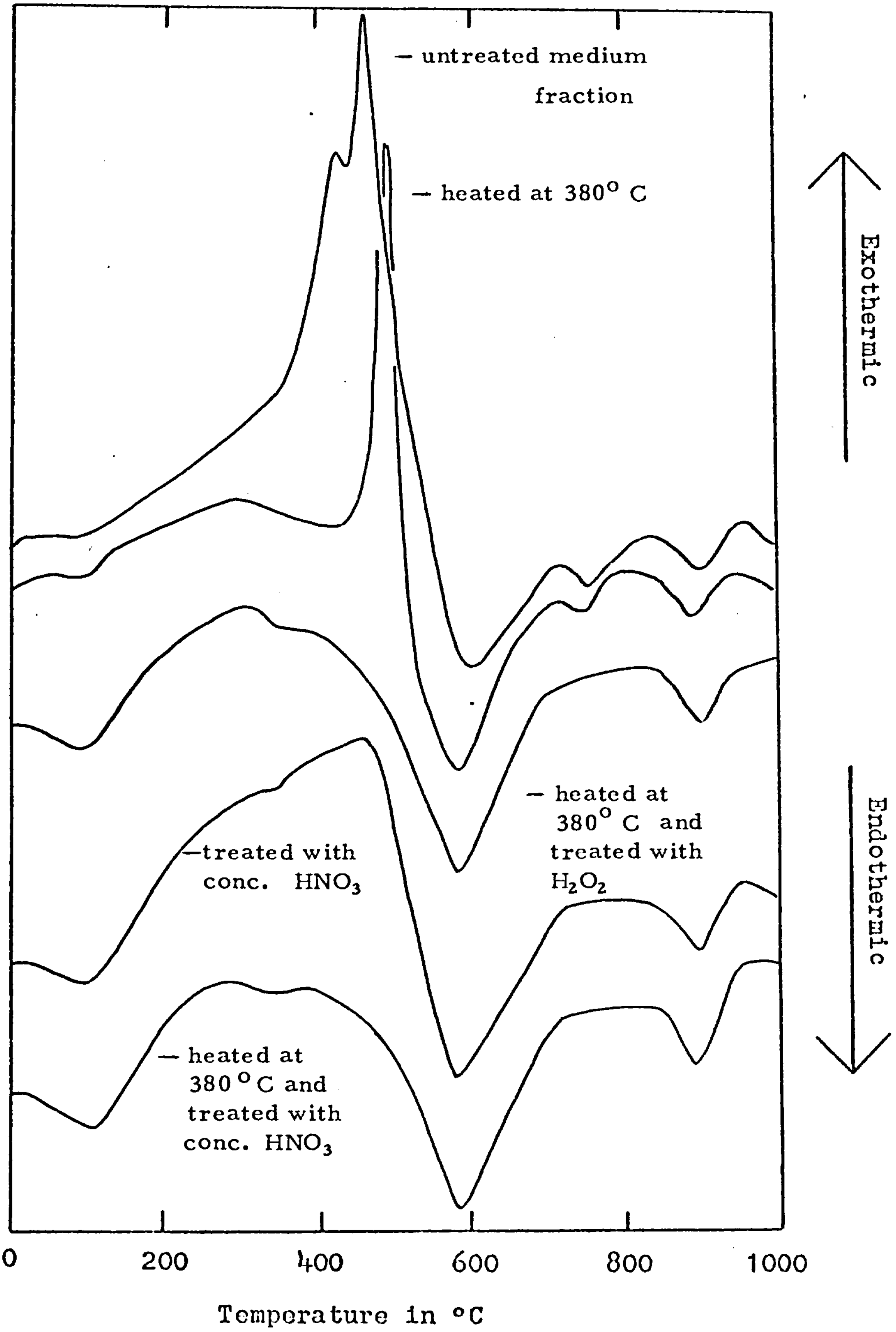

Figure 10. DTA curves of the Billings shale medium fraction after various treatments.

Chemical Analysis

The chemical analyses of the Billings shale samples are given in Table 21.

TABLE 21

Chemical Analyses of the Billings Shale Fractions

Constituent	Sample 6	Sample 6a	Sample 6b
	Raw Shale	Medium Fraction	Fine Fraction
SiO_2	56.40%	55.80%	54.96%
Al_2O_3	17.58	17.58	18.24
Fe_2O_3	2.29	2.14	2.22
FeO	4.63	4.76	4.95
TiO_2	0.86	0.91	0.92
CaO	1.48	1.40	1.28
MgO	3.42	3.36	3.36
K_2O	4.02	4.17	4.30
Na_2O	0.78	0.73	0.68
CO_2	(1.10)	(1.24)	(0.94)
C	(0.82)	(0.90)	(0.85)
S	1.14	0.95	0.83
Moisture	0.48	0.48	0.48
$H_2O(+110^{\circ} C)$	(5.49)	(5.54)	(6.07)
LOI	7.10	6.84	7.37
Total	100.18	99.12	99.59

The results for the Billings shale samples are very similar, and it is possible that the deposit in this area is of such a fine grain size that the sedimentation technique used is not drastic enough to effect any appreciable separation of the constituent minerals.

One point of interest lies in the presence of an appreciable quantity of sulphur, indicating sulphides and/or sulphate minerals.

X-Ray Analysis

X-ray analysis was carried out by means of the 114.83 mm dia. Debye-Scherrer camera as before. The d-spacings and relative intensities of the principal X-ray diffraction lines for the Billings shale samples are given in Table 22.

The presence of clay minerals with basal spacings of approximately 14A, 10A, and 7A is indicated. (Treatment with hot concentrated (50%) hydrochloric acid removes the mineral or minerals with 14A and 7A spacings).

Only a small amount of calcite (3.03A) is shown to be present, but strong diffraction lines representing spacings of about 4.26A and 3.34A indicate the presence of considerable quartz. Two diffraction lines, at 2.71A and 2.42A, may be due to pyrite (FeS_2). Heat treatment (380° C) of the medium fraction (6a) does not affect these particular diffraction lines, but they are removed by subsequent treatment with concentrated nitric acid.

TABLE 22

d-Spacings and Relative Intensities of the Principal X-Ray Diffraction Lines Given by the Billings Shale Samples

Sample 6 Raw Shale		Sample 6a Medium Fraction		Sample 6b Fine Fraction		Medium Fraction (6a) Heated at 380° C and Treated with Concentrated HNO_3	
d(A)	Ht	d(A)	Ht	d(A)	Ht	d(A)	Ht
14.2	5	14.0	3	14.5	4	14.1	4
9.9	5	9.9	4	10.1	5	10.0	5
7.1	6	7.1	4	7.1	5	7.1	4
4.97	3	4.96	2	-	-	-	-
4.49	7	4.48	5	4.48	5	4.48	5
4.25	7	4.24	5	4.26	5	4.24	5
3.52	4	3.52	4	3.52	2	3.53	10
3.35	10	3.33	10	3.34	10	3.34	10
3.19	3	3.19	3	3.21	4	3.20	5
-	-	3.02	2	3.03	3	-	-
2.71	3	2.70	2	2.72	4	-	-
2.57	5	2.57	4	2.57	6	2.55	6
2.45	2	2.44	3	2.46	5	2.46	6
2.43	2	2.42	3	-	-	-	-
2.38	2	2.38	3	2.38	4	2.38	4

The effects of heat treatment on the d-spacings and relative heights of the principal X-ray diffraction peaks as determined with the Philips Diffractometer are shown in Table 23.

TABLE 23

Effect of Heat Treatment on the d-Spacings and Relative Heights of the Principal X-Ray Diffraction Peaks Given by the Medium Fraction of the Billings Shale Sample

300° C		600° C		700° C	
d(A)	Ht	d(A)	Ht	d(A)	Ht
14.0	diffuse band	13.9	8.0	13.1	9.0
10.3	10.0	10.4	15.5	10.2	8.0
7.1	10.0	6.8) 6.3)	8.0	-	-
-	-	4.97	6.0	4.99	6.5
4.48	7.0	4.48	10.0	4.50	11.0
4.26	11.5	4.25	17.5	4.26	14.0
-	-	4.03	5.0	4.03	4.0
3.54	5.0	3.50	7.0	3.50	4.0
3.21	6.0	3.19	7.0	3.19	6.0

As in the case of the Dundas and Carlsbad shale samples, the larger basal spacings shown by the specimen heated to 300° C appear as a very indistinct and diffuse band representing about 14 A. The sample heated to 600° C shows a sharp well defined diffraction effect at about 14 A, but in this case the 7 A peak does not disappear. A series of diffraction peaks appears with the most prominent representing 6.8 A and 6.3 A. After heating to 700° C, the largest spacing appears to have contracted to 13.1 A and the diffraction effects at about 7 A have completely disappeared.

Discussion of the Results for the Billings Shale

As in the Queenston, Dundas and Carlsbad shales, the principal clay mineral constituents appear to be chlorite and illite. The major non-clay mineral is quartz and the minor minerals include calcite, dolomite, pyrite and organic matter.

Mineral balances of the Billings shale fractions are given in Table 24.

Rockcliffe Shale of the Chazyan Stage

Treatment of Sample

The shale was treated in the same manner as the Billings, Dundas and Carlsbad samples. Three size-fractions were obtained and these are listed in Table 25.

TABLE 25

Size Fractions of the Rockcliffe Shale

Shale Sample		Calculated E.S.D. in Microns
No.	Fraction	
7	Raw shale	150
7a	Medium	10
7b	Fine	1

TABLE 24

Mineral Balances of the Billings Shale Samples

Material	Total %	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	K_2O	Na_2O	CO_2	H_2O (+110°C)	C (organic)	S	Moisture
Sample 6 Billings Shale	100.19	56.40	17.58	2.29	4.63	0.86	1.48	3.42	4.02	0.78	1.10	5.49	0.52	1.14	0.48
Crystalline Silica	29.52	29.52													
Calcite	2.50						1.40				1.10				
Pyrite	2.42				1.28									1.14	
(Actual FeS_2)	(2.14)														
Carbon as Organic Matter	0.52												0.52		
Moisture	0.48														0.48
Remainder	64.75	26.88	17.58	2.29	3.35	0.86	0.08	3.42	4.02	0.78	-	5.49	-	-	-
Calculated Chemical Analysis of Remainder	100.00 (approx)	41.6	27.2	3.5	5.2	1.3	0.1	5.3	6.2	1.2	-	8.5	-	-	-
Sample 6a Billings Fraction	99.62	55.80	17.58	2.14	4.76	0.91	1.40	3.36	4.17	0.73	1.24	5.54	0.56	0.95	0.48
Crystalline Silica	25.96	25.96													
Calcite	2.18						1.22				0.96				
Dolomite	0.59						0.18	0.13			0.28				
Pyrite	2.02				1.07									0.95	
(Actual FeS_2)	(1.78)														
Carbon as Organic Matter	0.56												0.56		
Moisture	0.48														0.48
Remainder	67.83	29.84	17.58	2.14	3.69	0.91	-	3.23	4.17	0.73	-	5.54	-	-	-
Calculated Chemical Analysis of Remainder	100.00 (approx)	43.0	25.9	3.2	5.5	1.3	-	4.7	6.2	1.1	-	8.2	-	-	-
Sample 6b Billings Fraction	99.82	54.96	18.24	2.22	4.95	0.92	1.28	3.36	4.30	0.68	0.94	6.07	0.59	0.83	0.48
Crystalline Silica	25.00	25.00													
Calcite	2.14						1.20				0.94				
Pyrite	1.76				0.93									0.83	
(Actual FeS_2)	(1.55)														
Carbon as Organic Matter	0.59												0.59		
Moisture	0.48														0.48
Remainder	69.85	29.96	18.24	2.22	4.02	0.92	0.08	3.36	4.30	0.68	-	6.07	-	-	-
Calculated Chemical Analysis of Remainder	100.00 (approx)	42.4	26.1	3.2	5.8	1.3	0.1	4.8	6.2	1.0	-	8.7	-	-	-

Examination of the Shale

Differential Thermal Analysis

DTA results of the Rockcliffe shale specimens are illustrated in Figure 11. The curves show the following characteristics:

Rockcliffe Raw Shale (Curve 7, Figure 11)

Endothermic Peaks:

115° C - elimination of adsorbed water

585° - loss of structural water from a clay mineral or minerals. The sharpness of the effect indicates also the presence of a considerable amount of quartz which undergoes an alpha to beta crystal inversion at approximately this temperature

860° - breakdown of calcite to CaO and CO_2

Rockcliffe Shale, Medium Fraction (Curve 7a, Figure 11)

Endothermic peaks:

115° C - elimination of adsorbed water

590° - loss of structural water from a clay mineral or minerals

820° - breakdown of calcite to CaO and CO_2

925° - final breakdown of the structure in a clay mineral or minerals

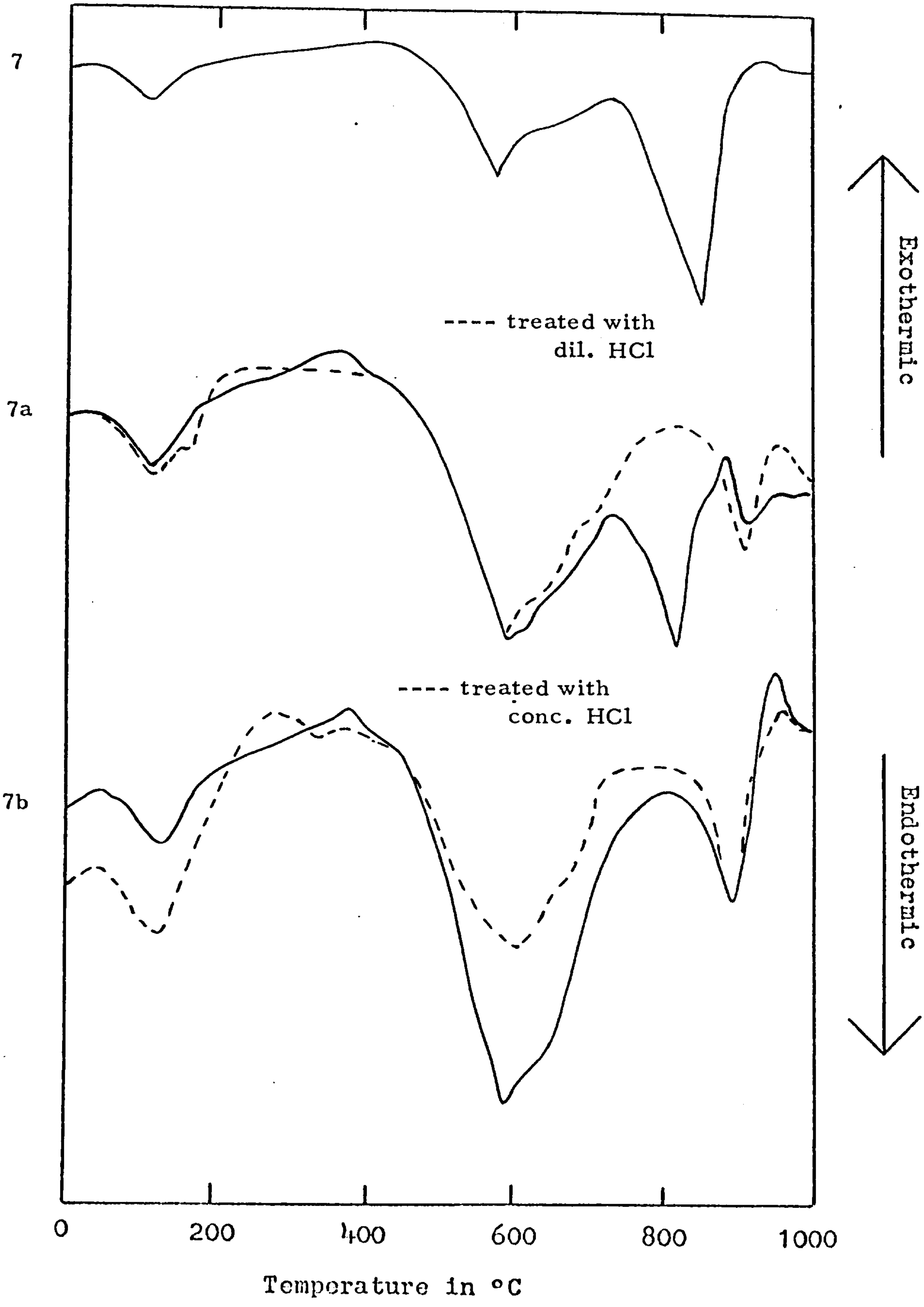

Figure 11. DTA curves of the Rockcliffe shale fractions and the acid-treated samples.

Exothermic peaks:

380° C - small amount of organic matter, siderite, or pyrite

890° - may be due to reaction between calcite and clay minerals

Rockcliffe Shale, Fine Fraction (Curve 7b, Figure 11)

Endothermic peaks:

125° C - loss of adsorbed water

585° - loss of structural water from a clay mineral or minerals

900° - final breakdown of the structure in a clay mineral or minerals

Exothermic peaks:

385° C - small amount of organic matter, siderite, or pyrite

955° - recrystallization of new minerals, such as olivine, after the final breakdown of a chlorite structure (9)

The effects of dilute hydrochloric acid treatment on the medium fraction are illustrated by the DTA curve shown as a broken line in Figure 11. An endothermic peak due to adsorbed water has appeared at 165° C. The peak at 820° C, due to the decomposition of carbonate minerals, has been eliminated and an endothermic peak at 900° C, due to the final breakdown of the structure in a clay mineral or minerals, has appeared.

The fine fraction was treated with concentrated (50%) hydrochloric acid in the manner described for the other shale samples. The DTA curve is shown in Figure 11 as a broken line superimposed on the curve of the original material. The peak at 585° C has been considerably reduced in area whilst the one at 900° C remains almost unchanged. The exothermic peak at 955° C, which may be due to the recrystallization of new minerals from a chlorite structure (9), has also been reduced, thus indicating that the acid treatment has removed a large proportion of the chlorite mineral. The shape of the curve after the acid treatment is similar to that of the illite-type clay minerals.

Chemical Analysis

The chemical analyses of the Rockcliffe shale samples are given in Table 26.

With decreasing grain size, similar trends can be noted in the amounts of the constituents as were observed in the previous shale samples examined; SiO_2, CaO, CO_2, and Na_2O decrease, TiO_2 remains relatively constant, and the remaining components increase.

TABLE 26

Chemical Analyses of the Rockcliffe Shale Fractions

Constituent	Sample 7 Raw Shale	Sample 7a Medium Fraction	Sample 7b Fine Fraction
SiO_2	61.00	51.00	45.60
Al_2O_3	12.72	17.26	23.18
Fe_2O_3	1.07	1.84	2.76
FeO	2.37	3.59	4.28
TiO_2	0.66	0.89	0.59
CaO	6.50	6.46	2.94
MgO	0.89	1.93	4.36
K_2O	4.66	5.60	6.55
Na_2O	0.81	0.76	0.27
CO_2	6.38	5.76	2.05
C (as organic matter)	0.05	0.03	0.18
S	neg	neg	neg
H_2O (+ 110° C)	2.29	3.92	6.36
Moisture	0.28	0.58	1.25
Total	99.68	99.62	100.37

X-Ray Analysis

The d-spacings and relative intensities of the principal X-ray diffraction lines for the Rockcliffe shale samples are given in Table 27. The results were obtained by using the 114.83 mm dia. Debye-Scherrer camera as described previously.

TABLE 27

d-Spacings and Relative Intensities of the Principal X-Ray Diffraction Lines Given by the Rockcliffe Shale Samples

7 Raw Shale		7a Medium Fraction		7b Fine Fraction	
d(A)	Int.	d(A)	Int.	d(A)	Int.
14.2	2	14.4	3	14.2	5
9.9	3	9.9	4	10.1	9
7.1	3	7.1	3	7.1	7
4.97	3	-	-	4.99	7
4.47	4	4.5?	5	4.50	10
4.26	9	4.26	7	4.25	3
4.13	6	4.14	5	4.16	8
-	-	-	-	3.73	5
-	-	-	-	3.36	6
3.33	10	3.34	10	3.34	9
3.26	4	3.25	3	-	-
3.18	4	3.19	3	-	-
3.03	4	3.03	9	3.03	7
2.86	4	-	-	-	-
2.57	7	2.58	7	2.57	10

The patterns are similar to those obtained for the shales previously examined and indicate the presence of chlorite (14A and 7A), illite (10A and 5A), quartz (4.26A and 3.34A), and calcite (3.03A). Atomic spacings of about 3.25A and 3.19A may be indicative of a potassium feldspar (10).

The effect of heat and concentrated hydrochloric acid treatment on the d-spacings and relative heights of the principal X-ray diffraction peaks, according to measurements with the Philips Diffractometer, are given in Table 28.

TABLE 28

Effects of Heat and Concentrated Hydrochloric Acid Treatment on the d-Spacings and Relative Heights of the Principal X-Ray Diffraction Peaks Given by the Fine Fraction of the Rockcliffe Shale

Fine Fraction		300° C		600° C		700° C		Treated with conc. HCl	
d(A)	Ht.	d(A)	Ht.	d(A)	Ht.	d(A)	Ht.	d(A)	Ht.
14.1	6.5	not definite		13.9	10.5	13.2	8.0	-	-
10.1	13.5	10.1	11.5	10.1	9.0	10.1	11.0	10.3	10.0
7.1	13.0	7.1	7.5	-	-	-	-	-	-
4.95	6.5	5.05	4.0	5.05	4.5	5.00	7.5	not definite	
4.48	10.0	4.49	7.0	4.49	16.0	4.50	11.0	4.48	12.0
						4.48	12.5		
3.52	10.0	3.52	6.0	not definite		not definite		not definite	
3.34	13.0	3.35	16.5	3.35	17.5	3.35	16.0	3.35	15.0
3.24	8.0	3.24	7.5	3.24	4.0	3.24	4.0	3.24	7.0
3.02	9.6	3.02	8.5	3.03	7.5	-	-	-	-
2.57	9.0	2.58	11.0	2.58	10.0	2.59	9.0	2.59	10.5

The changes observed are similar to those noted in the shale samples previously examined. The basal spacing at about 14 A becomes more definite and contracts on heating, the 10 A spacing appears unchanged, and the 7 A one disappears. Concentrated hydrochloric acid removes both the 14 A and 7 A peaks from the X-ray pattern.

The indications are that the clay minerals are principally illite and chlorite types.

Discussion of the Results for Rockcliffe Shale

The methods of analysis show that the principal clay mineral constituents of the shale are chlorite and illite types, and the major non-clay constituents are quartz, calcite, and potassium feldspar.

Mineral balances of the fractions have been drawn up on the principles used previously and the results are given in Table 29.

Dolomite was not identified in the tests carried out; but an exothermic DTA effect at about 380° C indicated the presence of organic matter, siderite, or pyrite in the Rockcliffe shale fractions 7 a and 7b. Therefore, in the cases where the chemical analyses show negligible amounts of organic matter and sulphur, any excess CO_2 remaining after all the CaO has been accounted for as calcium carbonate has been assigned to siderite.

TABLE 29

Mineral Balances of the Rockcliffe Shale Samples

Material	Total %	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	K_2O	Na_2O	CO_2	H_2O (+110° C)	C (organic)	S	Moisture
Sample 7 Rockcliffe Shale	99.68	61.00	12.72	1.07	2.37	0.66	6.50	0.89	4.66	0.81	6.38	2.29	0.05	neg	0.28
Crystalline Silica	42.78	42.78													
Calcite	9.40						6.50				5.11				
Siderite	3.36				2.09						1.27				
Carbon as Organic Matter	0.05												0.05		
Moisture	0.28														0.28
Remainder	41.60	18.22	12.72	1.07	0.2	0.66	-	0.89	4.66	0.81	-	2.29	-	-	-
Calculated Chemical Analysis of Remainder	100 (approx)	43.8	30.6	2.5	0.5	1.6	-	2.1	11.2	2.0	-	5.5	-	-	-
Sample 7a Rockcliffe Fraction	99.62	51.00	17.26	1.84	3.59	0.89	6.46	1.93	5.60	0.76	5.76	3.92	0.03	neg	0.58
Crystalline Silica	21.62	21.62													
Calcite	9.96						6.46				5.07				
Siderite	1.82				1.13						0.69				
Carbon as Organic Matter	0.03												0.03		
Moisture	0.58														0.58
Remainder	64.04	29.38	17.26	1.84	2.46	0.89	-	1.93	5.60	0.76	-	3.92	-	-	-
Calculated Chemical Analysis of Remainder	100 (approx)	45.9	27.0	2.9	3.8	1.4	-	3.0	8.8	1.6	-	6.1	-	-	-
Sample 7b Rockcliffe Fraction	100.37	45.60	23.18	2.76	4.28	0.59	2.94	4.36	6.55	0.27	2.05	6.36	0.18	neg	1.25
Crystalline Silica	3.20	3.20													
Calcite	4.66						2.61				2.05				
Carbon as Organic Matter	0.18												0.18		
Moisture	1.25														1.25
Remainder	91.08	42.40	23.18	2.76	4.28	0.59	0.33	4.36	6.55	0.27	-	6.36	-	-	-
Calculated Chemical Analysis of Remainder	100 (approx)	46.6	25.5	3.0	4.7	0.7	0.4	4.8	7.2	0.3	-	7.0	-	-	-

GENERAL DISCUSSION AND CONCLUSIONS

The combined evidence obtained from the analytical methods indicates that the major clay mineral constituents in all the shale samples consist of illitic and chloritic types, which, together with the principal non-clay materials, quartz, calcite, dolomite and perhaps feldspar, comprise more than 98 per cent of the raw shales. A summary of the mineral balance sheets for all the samples is given in Table 30. However, several reservations must be made concerning these results:

1. The presence of feldspar has been indicated in the mineral balances. X-ray measurements reveal that most of the shale specimens contain a constituent which gives a reflection corresponding to an atomic spacing of approximately 3.2 A. A single reflection, or two close together in this region, usually can be considered to be indicative of feldspar (10, 11); however, muscovite and many illitic materials also show a reflection for a spacing of about 3.2 A(12). The raw Rockcliffe shale and the Rockcliffe shale medium fraction are the only specimens to show two X-ray diffraction lines corresponding to atomic spacings of about 3.24 A and 3.19 A. According to the work of Bertrand and

Loisel (10), the double reflection is characteristic of potassium feldspar, and the single one of plagioclase.

2. The calculated percentages of the carbonate minerals are based on the assumption that the calcium is present primarily as calcite. This assumption is supported by DTA evidence, as the curves show large calcite peaks. However, this element must be associated with the various mineral constituents in a much more complicated manner. It is almost certain that some of the calcium is present in the illitic, chloritic and feldspathic structures, and that dolomite, and perhaps siderite, are more predominant minerals than is indicated by the mineral balance estimations.

With the exception of Rockcliffe shale, and keeping in mind the limitations of the methods of estimation, several general points of interest can be noted in the mineralogical compositions shown in Table 30:

1. The proportion of crystalline silica (mainly quartz) in the raw shale samples is relatively constant at about 30 per cent.

2. The proportion of the illite-chlorite (+ feldspar) fraction in the raw shale samples is roughly inversely proportional to the total amount of carbonate minerals.

3. For each shale sample, the proportions of clay mineral constituents increase, and the proportions of other minerals decrease with decreasing grain size.

On the basis of the mineralogical balance calculations shown in Table 30, the only qualitative distinguishing features between the shales examined is the presence of minor mineral constituents. As opposed to the Queenston shales the Dundas sample contains a small amount of organic matter, the Carlsbad contains slightly more organic material than the Dundas, plus a little pyrite, and the Billings shale contains even more organic material and pyrite than the Carlsbad.

A better differentiation becomes evident when the approximate chemical analyses of the remainder minerals are studied. These were calculated from the mineral balance estimations and represent mainly illitic, chloritic, and perhaps feldspathic constituents. The analyses are summarized in Table 31, where several major differences can be noted:

1. The ferrous to ferric ratio in the Queenston remainders is much smaller than the ratios for the Dundas, Carlsbad, Billings and Rockcliffe samples. It is probable that some of the ferric ion content of the Queenston shales is present as ferric oxide, thus giving them their characteristic red colour.

TABLE 30

Summary of the Mineralogical compositions of the Ordovician Shale Fractions

Stage	Richmondian						Maysvillian					Edenian			Chazyan		
Formation	Queenston						Dundas		Carlsbad			Billings			Rockcliffe		
Principal Locality	Streetsville		Ottawa		Nelson		New Toronto		Ottawa			Ottawa			Ottawa		
Sample No.	1	1c	2	2b	3	3c	4	4a	5	5a	5b	6	6a	6b	7	7a	7b
Illite-Chlorite (and Feldspar)	58.55	77.10	59.24	86.34	50.44	76.96	61.64	92.84	55.99	69.78	80.12	64.75	67.83	69.85	41.60	64.04	91.08
Crystalline Silica	29.20	17.64	32.48	9.72	26.64	12.92	29.88	3.28	34.34	21.86	13.98	29.52	25.96	25.00	42.78	21.62	3.20
Calcite	12.01	4.64	8.41	2.86	18.75	8.05	6.28	-	8.84	6.75	4.48	2.50	2.18	2.14	9.40	9.96	4.66
Dolomite	-	-	-	1.05	3.16	2.01	0.71	2.61	-	-	-	-	-	-			-
Siderite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.36	1.82	-
Pyrite	-	-	-	-	-	-	-	-	0.30	0.28	0.21	2.14	1.78	1.55	-	-	-
Carbon as Organic Matter	-	-	-	-	-	-	0.19	0.05	0.18	0.29	0.36	0.52	0.56	0.59	0.05	0.03	0.18
Totals	99.76	99.38	100.13	99.97	98.99	99.94	98.70	98.78	99.65	98.96	99.15	99.43	98.31	99.13	97.19	97.47	99.12

TABLE 31

Summary of the Calculated Chemical Analyses of the Remainder Minerals in the Ordovician Shale Fractions

Stage	Richmondian						Maysvillian					Edenian			Chazyan		
Formation	Queenston						Dundas		Carlsbad			Billings			Rockcliffe		
Principal Locality	Streetsville		Ottawa		Nelson		New Toronto		Ottawa			Ottawa			Ottawa		
Sample No.	1	1c	2	2b	3	3c	4	4a	5	5a	5b	6	6a	6b	7	7a	7b
SiO_2%	46.6	45.1	40.4	44.0	43.8	45.0	42.0	47.5	39.8	41.1	42.7	41.6	43.0	42.4	43.8	45.9	46.6
Al_2O_3	23.6	26.8	26.9	27.1	27.8	26.8	26.6	25.2	26.9	25.9	25.2	27.2	25.9	26.1	30.6	27.0	25.5
Fe_2O_3	6.2	7.2	6.0	6.9	7.4	7.8	3.2	3.6	2.3	2.5	2.2	3.5	3.2	3.2	2.5	2.9	3.0
FeO	3.4	3.2	4.6	3.7	2.8	2.5	7.3	5.2	8.3	8.3	7.9	5.2	5.5	5.8	0.5	3.8	4.7
TiO_2	1.4	1.1	1.5	0.9	1.2	0.9	1.4	0.7	1.5	1.4	1.2	1.3	1.3	1.3	1.6	1.4	0.7
CaO	0.1	0.4	0.2	-	-	-	-	-	0.3	0.1	0.9	0.1	-	0.1	-	-	0.4
MgO	4.7	4.0	5.7	4.1	2.9	3.7	5.1	3.9	5.3	5.3	4.9	5.3	4.7	4.8	2.1	3.0	4.8
K_2O	6.3	6.8	6.4	6.6	6.9	7.2	6.6	7.0	5.5	5.9	6.0	6.2	6.2	6.2	11.2	8.8	7.2
Na_2O	1.2	0.5	1.7	0.5	1.2	0.4	1.4	0.5	2.1	1.0	0.7	1.2	1.1	1.0	2.0	1.6	0.3
H_2O	6.5	5.0	6.5	5.8	6.0	5.8	6.5	6.6	8.3	8.1	8.3	8.5	8.2	8.7	5.5	6.1	7.0

2. The water content of the Billings and Carlsbad remainders is much higher than those of the other shale specimens.

3. The K_2O contents of the Rockcliffe remainders are high and decrease with decreasing grain size, thus indicating that a potash-containing mineral is present in the larger size fractions. This evidence fits with the X-ray results which indicate the presence of a potassium feldspar.

4. In each series of shale fractions, the Na_2O content decreases with decreasing particle size, while, with the exception of the Rockcliffe shale series, the K_2O content increases. This fact supports the X-ray evidence for the presence of a sodium (or sodium-calcium) feldspar in the larger grain sizes. The increase in K_2O content indicates an increasing illite content in the finer fractions of the shales.

The evidence from DTA, chemical, and X-ray diffraction tests showed that the major mineral constituents in the Queenston shale samples are illite, chlorite, quartz and calcite. Minor minerals include dolomite, a sodium (or sodium-calcium) feldspar, and probably free colloidal ferric oxide. The results provide further evidence for the belief that the isolated outcrops of red shale which occur in Russell county can be identified with the red

Queenston shale of the Toronto-Hamilton area. The mineralogical constituents of all three shale samples are almost identical and the specimens differ only in the relative amounts of each component.

The Dundas and Carlsbad shale samples have similar mineral constitutions to the Queenston samples. The grey colour of the raw material indicates that free ferric oxide is not present in appreciable quantities. Small amounts of organic matter were found in both specimens, and pyrite was identified in the Carlsbad shale. Mineral balance calculations show that the minerals in the remainder fraction (principally illite and chlorite) of the Carlsbad shale contain noticeably more water than those in the Dundas material. The Dundas and Carlsbad shales differ from the Queenston shales in having a much higher ratio of ferrous to ferric ion, although the total Fe content of all the samples is about 6.5 per cent.

Mineralogically the Billings shale resembles the Carlsbad sample; however, it was found to contain more organic matter and pyrite, and calcite was present only as a minor constituent. These two shales were obtained from the Ottawa area, while the Dundas was sampled from a locality near Toronto. It seems that, mineralogically, the Carlsbad shale more closely resembles the Billings shale, which it directly overlies, than it does the Dundas formation in the Toronto area and with which it has been geologically correlated.

The Rockcliffe shale was found to contain chlorite, quartz, potassium feldspar, calcite, and, perhaps, siderite.

It is not suggested in this report that the chloritic mineral found in the shales is the same for each formation. The chemical compositions of the remainder minerals indicate that this is not so. Other evidence can be noted in the DTA tests and in certain anomalies in the X-ray results.

SUGGESTED FUTURE WORK

This report is not presented as a comprehensive description of the mineralogy of the shales studied. Rather, it is intended as a framework, on which more detailed work may be based. The mineralogical balance sheets leave much to be desired, and outstanding points which require a more detailed study include:

1. The true nature of the illite-chlorite clay minerals and their association with one another.
2. The question of the feldspathic constituents.
3. The nature of the carbonate minerals.

Future work in this field should include more refined techniques for separating the dispersed shale suspensions. The use of a continuous-type super-centrifuge for such an operation, followed by careful analysis of the separated fractions, may reveal a separation or concentration of the clay-mineral constituents, and result in a positive identification of these components.

Electron micrograph studies of the fine fractions could reveal the shape of the ultimate particles and, as quite a considerable amount of work has been done on the morphology of clay minerals, certain deductions may be possible.

More precise X-ray and chemical analyses of the shale fractions are required. It is also necessary to examine heat-treated specimens and the action of organic liquids on the samples to help identify the minerals present.

The controlled action of mineral acids on the shales followed by analysis of the products could also prove useful in determining the nature of the mineral constituents.

Experiments should be carried out to ascertain the nature of the crystal and glass phases that form during the firing of the shales. A knowledge of the chemical and physical state of the starting materials would be invaluable in explaining why certain phases are formed. The information could then be used in determining methods for promoting certain desirable reactions or suppressing undesirable ones.

REFERENCES

1. A.E. Wilson. Geology of the Ottawa-St. Lawrence Lowland, Ontario and Quebec. Geological Survey Memoir 241 (1946).

2. J.F. Caley. Palaeozoic Geology of the Toronto-Hamilton Area, Ontario. Geological Survey of Canada Memoir 224 (1940).

3. A.B. Searle and R.W. Grimshaw. The Chemistry and Physics of Clays (Ernest Benn Limited, London, 1959), p. 274.

4. D.F. Hewitt. Ceramic Raw Materials in Ontario. J. Can. Ceram. Soc. 19, 14 (1950).

5. L.J. Trostel and D.J. Wynne. Determination of Quartz (Free Silica) in Refractory Clays. J. Am. Ceram. Soc. 23, 18 (1940).

6. G.W. Brindley. X-Ray Identification and Structures of Clay Minerals. Mineralogical Society of Great Britain Monograph. (Taylor and Francis Ltd., London, 1951), p. 169.

7. G.W. Brindley. Ibid, p. 193.

8. A.G. Sadler. Ph.D. Thesis, 1956 (Fuel Department, University of Leeds), p. 151.

9. Robert C. Mackenzie. The Differential Thermal Investigation of Clays (Mineralogical Society (Clay Minerals Group), London, 1957), p. 215.

10. A. Bertrand et M. Loisel. Note sur un essai d'identification des felspaths par diffraction des rayons X. Bull. Soc. Franc. Ceram. No. 51, 39 (1961).

11. G.W. Brindley. Ibid, opp. p. 312.

12. M.W. Molloy and P.F. Kerr. Diffractometer Patterns of API reference Clay Minerals. Amer. Minerals 46, 599 (1961).

AGS:lh

ACKNOWLEDGEMENTS

The author is indebted to the members of the Mineral Science Division who performed the chemical analyses used in this report, and especially to Mr. D. J. Charette, who was at all times most helpful and co-operative.

The X-ray data were supplied by the Mineralogical Section of the Mineral Processing Division and carried out under the supervision of Mr. R. M. Buchanan.

Information on the geological terms was kindly supplied by Dr. B.A. Liberty of the Geological Survey of Canada Branch.

Finally, the author would like to thank the members of the Ceramic Section for many hours of fruitful discussions, advice, and invaluable technical aid.

• • • • • •