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CERAMIC CLAYS AND SHALES OF ONTARIO

J.G. BRADY AND R.S. DEAN

MINERAL PROCESSING DIVISION

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CERAMIC CLAYS AND SHALES OF ONTARIO

by

J.G. Brady* and R.S. Dean**

ABSTRACT

Forty-nine representative samples of Ontario clays and shales, mostly from well populated areas, were investigated by X-ray diffraction, differential thermal analysis, drying and firing techniques, and chemical analysis. With the exception of the kaolinitic Cretaceous clays of the Missinaibi valley of northern Ontario, all samples were found to be low-fusion, heterogeneous materials. The shales have the most favourable properties for brick making, whereas many of the surface clays are suitable only for the manufacture of partition and drain tile.

Nine typical samples were selected for special study by plastography, thermogravimetry, dilatometry, and temperature-gradient firing. Processing problems, such as short firing ranges, heating and cooling cracks and kiln atmosphere, are discussed in relation to mineralogical composition.

The mineralogical investigation revealed that the Palaeozoic shale samples of Ontario contained a clay mineral suite consisting essentially of illite and chlorite. Common non-clay shale constituents included quartz, carbonates, and plagioclase.

A study of the differences between clay mineral suites derived from the Canadian Shield and the Palaeozoic sedimentary rocks led to the discovery of mineralogical criteria whereby the origin of the clay minerals within individual Pleistocene clay deposits could be recognized.

Clays containing the Palaeozoic clay mineral suite occurred throughout southern Ontario west of Toronto. Weathering alteration of these usually resulted in the formation of "frayed edge" clay mineral structures which often consisted of multicomponent mixed-layer systems. In several instances both chlorite and illite were thus affected, although the alteration of the more labile trioctahedral chlorite was generally greater.

The Shield-derived clays contained highly varied, structurally disordered, clay mineral assemblages which were invariably rich in expandable phases, some of which occurred as unmixed minerals. A characteristic suite of non-clay constituents, rich in plagioclase, amphibole and K-feldspar, was also associated with the Shield-derived material.

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Direction des mines

Rapport de recherches R 175

LES ARGILES ET SCHISTES ARGILEUX À CÉRAMIQUE DE L'ONTARIO

par

J.G. Brady* et R.S. Dean**

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RÉSUMÉ

Quarante-neuf échantillons représentatifs des argiles et des schistes d'Ontario, la plupart provenant de régions densément peuplées, ont été analysés par les procédés suivants: diffraction des rayons X, analyse thermique différentielle, séchage et cuisson, et analyse chimique. À l'exception des argiles de kaolin du Crétacé, qu'on trouve dans la vallée Missinaibi, Nord de l'Ontario, tous les échantillons sont constitués de matériaux hétérogènes et à basse température de fusion. Les schistes constituent d'excellentes matières premières pour la fabrication de la brique, alors qu'une bonne partie des argiles de surface ne peuvent servir qu'à la fabrication de blocs de cloisons et de tuyaux de drainage.

Neuf échantillons représentatifs furent mis à part pour une étude plus poussée: plastographie, thermogravimétrie, dilatométrie, et gradient de températures de cuisson. Des difficultés de traitement: courtes gammes de cuisson, fissures de cuisson et de refroidissement, et atmosphère du four, sont étudiées en fonction de la composition minéralogique.

L'examen minéralogique a démontré que les échantillons de schistes paléozoïques d'Ontario contiennent un groupe de minéraux argileux apparentés constitués essentiellement d'illite et de chlorite. Les composants non argileux des schistes comprennent le quartz, les carbonates et le plagioclase.

Une étude comparative entre les éléments minéraux argileux en provenance du Bouclier canadien et des roches sédimentaires du paléozoïque a fourni quelques critères minéralogiques qui permettraient de déterminer le lieu d'origine de minéraux argileux contenus dans un gisement donné d'argile du pléistocène.

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Les argiles contenant le groupe de minéraux argileux du paléozoïque se rencontrent dans tout le sud de l'Ontario, à l'ouest de Toronto. L'atmosphérisation de ces minéraux leur donne ordinairement une structure "à bords frangés" et ils sont souvent organisés en systèmes à couches mixtes interstratifiés sans ordre. Dans plusieurs cas, la chlorite et l'illite ont été tous deux altérés, bien que l'altération de la chlorite trioctaédrique, plus instable, soit plus prononcée.

Les argiles constitués d'éléments provenant du Bouclier contiennent des assemblages de minéraux argileux très variés et mal structurés, qui sont tous riches en phases expansibles; quelques-uns de ces assemblages se présentent sous forme de minéraux purs. Un groupe caractéristique de composants non argileux, riches en plagioclase, amphibole et feldspath potassique, était associé aux matériaux rocheux provenant du Bouclier.

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INTRODUCTION

This report is intended, first of all, to outline the characteristics of typical Ontario ceramic clays and shales and to discuss the relationship between chemical and mineralogical composition and the processing problems and properties of these ceramic raw materials. Secondly, a detailed examination of the clay and shale mineralogy has been made in order to discover local and regional variations in the abundance of various minerals. Whenever possible, a geological interpretation of the mineralogical data has been offered.

The clays and shales of Ontario useful to the ceramic industry are mainly of the low-fusion "common" types. They vary from non-calcareous, red-firing to highly calcareous, buff-firing materials. In general, the shales are used locally for brick-making, and the clays for the manufacture of drain tile. There are no known clay deposits in Ontario suitable for refractories, or whitewares, or paper clays, except in the James Bay watershed of northern Ontario, along the Abitibi, Mattagami and Missinaibi rivers, where fire clays, stoneware clays and mixtures of kaolin and quartz are found. The latter mixtures are possible sources of good-quality china clay as well as glass sand. The fire clays and stoneware clays are probably suitable for refractories, sewer pipe, brick, and tile, depending mainly on their refractoriness and plasticity.

Many reports dealing with Ontario clays and shales of interest to the ceramic industry have been published. Hewitt (1) and Guillet (2) have discussed the principal clay and shale occurrences of Ontario. The latter author has briefly described the typical properties of the various shale formations and surface clays, and has discussed the geology and origin of certain deposits.* Allen and Johns (3), Brydon and Patry (4) and Sadler (5), among others, have investigated the mineralogical composition of some Ontario specimens. Sadler's samples have been included in the present study.

The ceramic properties of a large number of Ontario clays and shales have been reported by Baker (6) and Keele (7). Montgomery (8) has described the clay products industry of Ontario in a publication in which he refers briefly to the type of raw material used at each plant.

Special mention should be made of the northern Ontario kaolins and fire clays, which have been the subject of continued interest over the years. According to Keele (7, 9), E.B. Borron discovered the extensive deposits of white sand and clay along the Missinaibi river in 1880 and C.M. McCarthy reported the occurrence of fire clays on the Mattagami river in 1916. Bell (10) visited the Missinaibi deposits in 1904. Keele (7, 9, 11, 12, 13, 14, 15, 16) wrote numerous reports describing the properties of these and other northern Ontario clays. Baker (17), McLearn (18), Montgomery and

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*As this report goes to press, a bulletin entitled "The Clay Products Industry of Ontario", by G.R. Guillet, has been published by the Ontario Department of Mines as Industrial Mineral Report 22 (1967).

Watson (19), Dyer and Montgomery (20), Montgomery (21), Dyer (22), Davey (23), Dyer and Crozier (24), Crozier (25), Hilder (26), Hancock (27) and Guillet (2) have also contributed to this literature.

Special ceramic problems involving Ontario clays and shales have been discussed by Montgomery (28), Hewitt and Montgomery (29), Naish (30, 31, 32, 33), Corbett (34), McRitchie (35), Groskaufmanis (36), Bell (37), Matthews (38), Wilson (39), and others.

The geological map of southwestern Ontario compiled by Sanford (40), the guidebook entitled "Geology of Central Ontario" (41), the paper by Sanford (42), and the report by Wilson (43) provide convenient sources of information regarding the bedrock geology within the areas from which the shale samples were taken. The classic study by Chapman and Putnam (44) is an indispensable guide to the geology of the Pleistocene clays of southern Ontario.

The portion of this report which is concerned with the evaluation of the ceramic properties of the clays and shales was prepared by J.G. Brady. R.S. Dean was responsible for carrying out the X-ray diffraction analyses of the unfired samples, the reporting of the results of this phase of the investigation, and the discussion of the geological-mineralogical relationships.

MATERIALS INVESTIGATED

Typical clays and shales were chosen for study from all well-populated areas of Ontario. Most of the materials are being used, or have been used, in the production of brick and tile. The most notable exceptions to this are the two samples from the Missinaibi valley of northern Ontario, which were chosen because of their composition and the interest being shown at present in these northern deposits.

The samples studied are listed in Table 1, and approximate sampling localities are indicated in Figure 1. Only forty-nine of the fifty-three samples in Table 1 were fully investigated, as no tests other than the mineralogical analysis were carried out on the Kingsville clay and the three Arkona shales were replaced by the composite Parkhill sample for purposes of ceramic testing.

The mineralogy of seven of the shale samples had previously been investigated by Sadler (5). In the same order as listed in Table 2 of Sadler's report (p. 8), these are: Streetsville (Q), Ottawa (Q), Nelson (Q), Booth (D-M), Carlsbad, Billings, and Rockcliffe.

The Rockcliffe and Kettle Point samples were collected by A.G. Sadler and R.S. Dean respectively. Thirteen samples were submitted by industry for investigation, and the remainder were collected by J.G. Brady in 1956 and 1957.

TABLE 1

Materials Investigated

PART I - SHALES AND REWORKED SHALES			
Sample	Company	Nature of Deposit	Pit or Sample Location
1.* Kettle Point	-	Kettle Point shale outcrop 12 ft section	Lake Huron shore at Kettle Point, Lambton Co.
2. Arkona (552)	Parkhill Brick Co. Limited	Hamilton shale "upper brownish shale"	N. bank of Ausable River, Middlesex Co., 2 miles ENE. of Arkona
3. Arkona (553)	"	Hamilton shale "middle bluish shale"	"
4. Arkona (554)	"	Hamilton shale "lower blue shale"	"
5. Parkhill (Hamilton)	"	Composite of Arkona 552-554. Total section 35 ft	"
6. Thedford (Hamilton)	George Coultis & Son Limited	Hamilton shale. Uppermost 8 ft of shale section	Lot 23, Con. III, Bosanquet Twp., Lambton Co.
7. Ottawa (Q)	Domtar Construction Materials Limited	Queenston shale	Lot 18, Con. III, Russell Twp., Russell Co.
8. Nelson (Q)	Diamond Clay Products Limited	Queenston shale	Lots 3 and 4, Con. I, N. D. S., Nelson Twp., Halton Co.
9. Owen Sound (Q)	-	Queenston shale outcrop	Hillside adjacent to 3rd Ave. East, Owen Sound
10. Streetsville (Q)	F.B. McFarren Limited	Queenston shale	Lot 3, Con. V, W.H.S., Toronto Twp., Peel Co.

*Numbers refer to localities shown in Figure 1.

(Table 1, cont'd)

Sample	Company	Nature of Deposit	Pit or Sample Location
11. Milton (Q)	Milton Brick Co. Limited	Uppermost 50 ft of unweathered Queenston shale	Lot 1, Con. I, Esquesing Twp., Halton Co.
12. Georgetown (Q)	-	Queenston shale. Shallow pit	Earlesmere Farms, R.R. 1, Georgetown
13. Grimsby (weathered Q)	Grimsby Tile Limited	10 ft section, weathered Queenston shale	Lot 23, Con. I, Clinton Twp., Lincoln Co.
14. Aldershot (weathered Q)	National Sewer Pipe Limited	Near-surface weathered Queenston shale	Lots 1 and 2, Con. II, East Flamborough Twp., Wentworth Co.
15. Aldershot (Iroquois)	National Sewer Pipe Limited	Reworked Queenston shale from Lake Iroquois lagoon	Lot 2, Con. I, East Flamborough Twp., Wentworth Co.
16. Carlsbad	-	Carlsbad shale. Shallow pit	Lot 7, Con. V, Gloucester Twp., Carleton Co.
17. Toronto Brick (D-M)	Toronto Brick Co. Limited	Dundas-Meaford shale	Don River valley, 3/4 mile N. of Bloor St., Toronto
18. Booth (D-M)	Booth Brick Limited	Dundas-Meaford shale	320 Horner Ave., Toronto
19. Cooksville (D-M)	Domtar Construction Materials Limited	Dundas-Meaford shale	Lots 19 and 20, Con. IS, Toronto Twp., Peel Co.
20. Reformatory (D-M)	Government of Ontario	Dundas-Meaford shale	Ontario Reformatory, Horner Ave., Toronto
21. Toronto (Reformatory)	Government of Ontario	Highly weathered or reworked Dundas-Meaford shale	Ontario Reformatory, Horner Ave., Toronto
22. Billings	-	Billings shale outcrop	E. bank of Rideau River at Smyth Road, Ottawa
23. Rockcliffe	-	Rockcliffe shale outcrop	S. bank of Ottawa River at Rockcliffe Park, Ottawa

(Table 1, cont'd)

PART II - CLAYS

Sample	Company	Nature of Deposit	Pit or Sample Location
24. Essex (blue)	Essex Brick and Tile	Blue-grey clay 15-20 ft below surface	Immediately N. of Essex, Essex Co.
25. Kingsville	B. Broadwell and Son	Reworked till. Sampling interval 4-30 in. below surface	Lot 12, Con. V, South Gosfield Twp., Essex Co.
26. Stevenson	Hill Tile Limited	Reworked till. Sampling interval 1-3 ft below surface	Lots 14 and 15, Con. XIII, Tilbury East Twp., Kent Co.
27. Fletcher	Fletcher Tile Limited	Reworked till. Sampling interval 0-36 in. below surface	Lot 2, Con. VIII, Tilbury East Twp., Kent Co.
28. Tilbury	Central Tile and Brick Corporation Limited	Reworked till. Sampling interval 1-3 ft below surface	1 mi. N. of Tilbury, Kent Co.
29. Forest	W.J. McFarlane & Sons Limited	Partially reworked till. Sampling interval 0-30 in. below surface	1/2 mi. N. of Forest, Lambton Co.
30. Dresden (brown)	Dresden Tile Yard Limited	Probably lacustrine clay. Sampling interval 1-6 ft below surface	Lot 8, Con. V, Gore of Camden Twp., Kent Co.
31. Dresden (blue)	Dresden Tile Yard Limited	Highly plastic grey clay. Sampling interval 1-6 ft below surface	Lot 11, Con. IV, Dawn Twp., Lambton Co.
32. Tupperville	Earl Lindsay and Sons, Limited	Lacustrine clay. Sampling interval 1-10 ft below surface	Lot 23, Con. III, Gore of Chatham Twp., Kent Co.
33. Wilkesport	Wilkesport Tile & Brick Co.	Lacustrine clay. Sampling interval 1-10 ft below surface	N. bank of North Sydenham River 1/2 mi. E. of Wilkesport, Lambton Co.

(Table 1, cont'd)

Sample	Company	Nature of Deposit	Pit or Sample Location
34. Petrolia	F.W. Howlett and Sons, Limited	Floodplain deposit. Sampling interval 1-6 ft below surface	Lot 12, Con. IX, Enniskillen Twp., Lambton Co.
35. Elginfield (brown)	Rydall Brick and Tile Limited	Lacustrine clay. Sampling interval 2-6 ft below surface	Lot 17, Con. XVI, London Twp., Middlesex Co.
36. Elginfield (blue)	Rydall Brick and Tile Limited	Lacustrine clay, sampled at point 12 ft below surface	Lot 17, Con. XVI, London Twp., Middlesex Co.
37. Paisley	Paisley Brick and Tile Yard	Lacustrine clay. Sampling interval 1-10 ft below surface	Lot 4, Con. V, Elderslie Twp., Bruce Co.
38. Wallenstein	N.S. Bauman Limited	Clay till underlain by lacustrine clay. Sampling interval 1-10 ft below surface	Lot 20, Con. XIV, Wellesley Twp., Waterloo Co.
39. Brownsville	Deller's Tile Limited	Brown clay, probably lacustrine. Sampling interval 2-7 ft below surface; underlain by blue clay	Lot 21, Con. XI, Dereham Twp., Oxford Co.
40. Norwich	Norwich Brick and Tile Limited	Lacustrine clay. Sampling interval 2-10 ft below surface	Otter Creek valley, 2 mi. NW. of Norwich, Oxford Co.
41. St. George	Kitchener Brick Company Limited	"Surface clay". Sampling interval not known	Vicinity of St. George, Brant Co. Exact location unknown.
42. Beaverton	Beaverton Brick and Tile	Plastic lacustrine clay. Sampling interval 1-12 ft below surface	Lot 12, Con. V, Thorah Twp., Ontario Co.
43. Napanee	Napanee Brick and Tile Works Limited	Lacustrine clay. Sampling interval 6-16 ft below surface	Lot 13, Con. VI, North Fredericksburg Twp., Lennox and Addington Co.
44. Manotick	Ottawa Brick and Terra Cotta Company Limited	Test pit in marine clay. Sampling interval 1-12 ft below surface	3/4 mi. due W. of Rideau River bridge at Manotick, Carleton Co.

(Table 1, concluded)

Sample	Company	Nature of Deposit	Pit or Sample Location
45. Arnprior	Dochart Brick and Tile Company Limited	Marine clay. Sampling interval 1-15 ft below surface	Lots 7 and 8, Con. XIII, McNab Twp., Renfrew Co.
46. Bracebridge	Home Brick Limited	Lacustrine clay, sampled at point 12 ft below surface	Lots 4 and 5, Con. XIII, Draper Twp., Muskoka Dist.
47. North Bay	Gravell Brick Company Limited	Lacustrine clay. Sampling interval not known	Lot 16, Con. C, Widdifield Twp., Nipissing Dist.
48. Sudbury	-	"Surface clay". Sampling interval not known	Lot 9, Con. 3, Graham Twp., Sudbury Dist.
49. Dorion	Superior Brick and Tile Company Limited	Lacustrine clay. Sampling interval not known	3 mi. due N. of Canadian National Railways bridge over Wolf River near Dorion Sta., Thunder Bay Dist.
50. Fort William	Superior Brick and Tile Company Limited	Lacustrine and fluvial clay. Sampling interval not known	Lots 11 and 12, Con. I, N.R., Paipoonge Twp., Thunder Bay Dist.
51. Kenora	-	No information available	Patent Claim 286, Con. II, Jaffray Twp., Kenora Dist.
52. Missinaibi (1323)	-	Kaolinitic Cretaceous clay	Along Missinaibi River, Burstall Twp., Cochrane Dist.
53. Missinaibi (1326)	-	Kaolinitic Cretaceous clay	Along Coal Creek, Burstall Twp., Cochrane Dist.

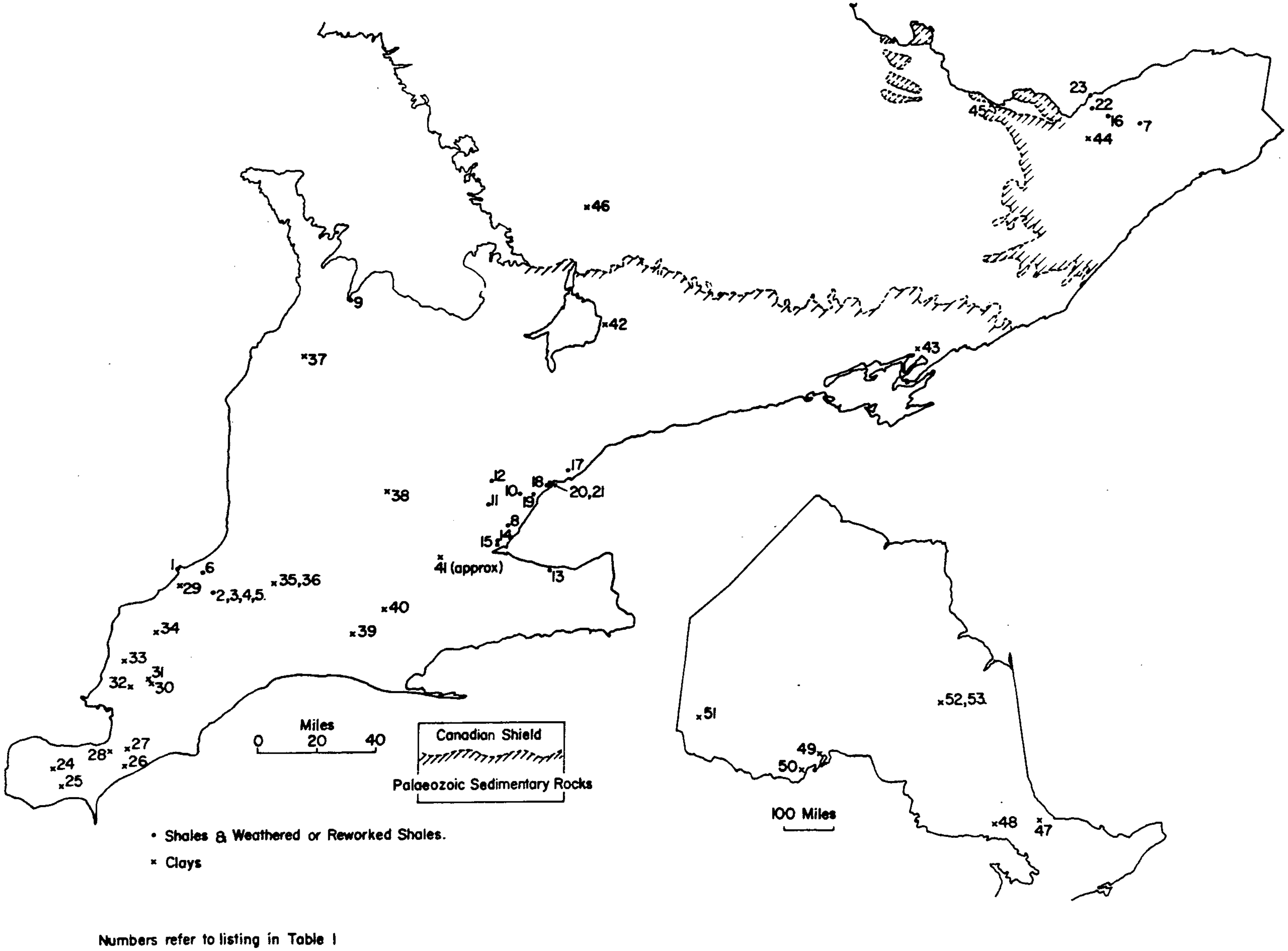


Figure 1. Locations of samples.

In the course of the investigation of the ceramic properties of the Ontario samples, it was found to be advantageous to group these according to the following scheme:

Queenston (Q) Shales and Related Materials

*Ottawa (Q), Grimsby (weathered Q), Streetsville (Q), Georgetown (Q), Milton (Q), *Nelson (Q), Owen Sound (Q), Aldershot (Iroquois), Aldershot (weathered Q).

Dundas - Meaford (D-M) and Miscellaneous Shales

Reformatory (D-M), Toronto Brick (D-M), Booth (D-M), *Cooksville (D-M), *Parkhill (Hamilton), Thedford (Hamilton), *Billings, Carlsbad, Rockcliffe, Kettle Point.

Southwestern Clays

*Stevenson, Tilbury, Tupperville, Wilkesport, Dresden (brown), Essex (blue), Fletcher, Dresden (blue).

Southern Clays

Elginfield (brown), Brownsville, Forest, St. George, Norwich, *Wallenstein, Elginfield (blue), Petrolia, Toronto (Reformatory).

North-Central Clays

Arnprior, *Bracebridge, Napanee, Manotick, Beaverton, North Bay, Paisley.

Northwestern and Northern Clays

Fort William, Dorion, Kenora, Sudbury, *Missinaibi (1323), Missinaibi (1326).

The above subdivisions bear no definite relationship to the surficial or bedrock geology or to the grouping employed by Guillet (2). The highly weathered or reworked Toronto (Reformatory) Dundas-Meaford shale is herein classified as a clay, owing to its relatively high plasticity. The nine samples marked with an asterisk were selected for special study as described in the following section.

METHODS AND PROCEDURES

The fired properties of the 49 samples were determined by routine methods and/or the temperature gradient method. Differential thermal analysis (DTA), X-ray diffraction analysis (XRD) of the unfired samples, and chemical analysis of the majority of the samples were carried out. In addition, temperature gradient curves, thermogravimetric analyses (TGA), thermal expansion curves, and the fired-specimen mineralogy of nine selected samples were obtained. The nine samples illustrate typical processing problems which may occur with Ontario clays and shales; the methods for investigating these problems have been discussed by Brady et al.(45).

The nine special samples are (1) Ottawa (Q), (2) Nelson (Q), (3) Cooksville (D-M), (4) Parkhill (Hamilton), (5) Billings, (6) Stevenson, (7) Wallenstein, (8) Bracebridge, and (9) Missinaibi (1323).

Properties of Unfired and Fired Specimens, and Temperature Gradient Investigation

All samples were ground to pass a 16-mesh Tyler laboratory screen. Any effervescence with hydrochloric acid was noted. The unfired and fired properties of the samples were obtained from hand-moulded test specimens and, in a few cases, from de-aired, extruded ones. Hand-moulded test specimens measuring 4 x 1 1/2 x 1 1/4 inches, prepared from all samples in steel moulds because of the small quantity of material required and the simplicity of equipment and measurements, were used for routine investigation. Hand-moulded test specimens measuring 8 1/2 x 1 x 1/2 inch, prepared from the nine selected samples (except Ottawa (Q)), were used in determining fired properties by the temperature gradient method.

Several samples were extruded by an International laboratory de-airing extruder. Specimens measuring about 4 x 1 x 1 inch were cut from the extruded columns for routine investigation. Longer bars were cut from the extruded Ottawa (Q) and Cooksville (D-M) samples for temperature gradient tests.

Dry-pressed specimens measuring 3 1/4 x 1 3/4 x 1 inch were prepared from the Owen Sound (Q) sample.

The plasticity of the samples was noted empirically at the time the test specimens were prepared. The water of plasticity and the drying shrinkage were measured. A test specimen of each sample was subjected to rapid drying conditions in a laboratory dryer at 85°C, and any evidence of cracking was noted. The remaining specimens were air-dried for at least 24 hours and then dried finally in an electric laboratory dryer overnight at 110°C.

All test specimens except those utilized for temperature gradient studies were fired in laboratory electric furnaces at various appropriate temperatures. The fired shrinkage (based on the unfired length), 24-hour absorption in cold water, colour, and hardness were noted. The pyrometric cone equivalents (PCE) were determined.

The temperature gradient method has been described by Stone (46). The firing temperature at the central portion of the furnace was raised at the rate of 90 centigrade degrees per hour to 820°C, held there for 6 hours, then raised at the rate of 110 centigrade degrees per hour to the finishing temperature, which was held for one hour. Control was automatic with a cam-type controller. The gradient was approximately 450 to 550 centigrade degrees from the hot to the cold end of the bars, depending on the central temperature. The temperature and shrinkage at each mark on the bars were calculated. The absorption of wafers cut from the test bars was determined after a 24-hour soak in cold water. The colour and hardness at each bar mark were noted.

Chemical Analysis

A brief explanation of the chemical analysis methods used has been given by Charette et al. (47). All analyses were based on dried weight at 105°C, and the totals of the constituents were derived from the sum of the oxide per cent plus the per cent loss on ignition (L.O.I.).

Differential Thermal Analysis (DTA)

The DTA standards utilized in the present investigation were those which have previously been discussed by Brady (48) and Brady and Dean (49). The samples were placed in a nickel block and heated in an air atmosphere by a nichrome-wound furnace. The furnace and the differential temperatures were recorded on a Leeds and Northrup X_1 - X_2 Speedomax recorder equipped with a range expander for the differential scale. A Leeds and Northrup D.C. Amplifier was used to amplify the differential temperature millivoltage. The furnace temperature was controlled by a Leeds and Northrup controller which raised the temperature at 12 centigrade degrees per minute. The amplifier was set at a scale sensitivity of 10 for all samples except for Missinaibi (1323), where the sensitivity at about 400°C was changed to 40, and for Kettle Point, where 40 was used throughout. In these two instances, peak amplitudes were reduced by a factor of four (at scale 40) so as to retain the curves on the chart.

The quartz content of each of the nine selected samples was estimated by DTA. Because the endothermic reactions of the clay minerals obscure the small peak produced by the reversible reaction from the low to the high form of quartz at 573°C, a special procedure was necessary to obtain these percentages. The sample was heated to about 750°C to eliminate the non-reversible endothermic reactions of the clay minerals, cooled to about 350°C, and then heated again through 573°C. The peak area was measured by a planimeter and compared with the area produced by a sample consisting of 100 per cent quartz.

X-ray Diffraction Analysis (XRD)

Representative portions of the various samples were finely ground in an agate mortar and subsequently examined with a Guinier-de Wolff four-sample X-ray powder diffraction camera (50) in order to determine the non-clay constituents. A similar procedure was followed with the plus 200-mesh fraction of the majority of the clays and some of the soft shales.

In order to concentrate the clay mineral fraction, roughly 3 grams of each clay or shale sample, which had been ground previously to minus 100 mesh, was dispersed in 200 ml of distilled water. All material coarser than approximately 5 microns equivalent settling diameter was separated by centrifugation and removed. Glacial acetic acid was subsequently added to the suspension so that a total acid concentration of 2 per cent was obtained. The minus 5-micron material, which was flocculated by this treatment, was collected by centrifugation.

Free iron oxides were removed by the method of Mehra and Jackson (51) from all minus 5-micron suspensions where the colouration (red, brown, or buff) suggested their presence.

Oriented clay mineral mounts were prepared by drying small portions of the minus 5-micron suspension on borosilicate glass slides. These were scanned with a North American Philips High-Angle X-ray Diffractometer before and after saturation with ethylene glycol and after heating for one-half hour at 580°C. A small portion of each minus 5-micron suspension was boiled for 15 minutes in an excess of concentrated hydrochloric acid. The residue was collected by centrifugation and washed twice with 2 per cent acetic acid solution. An oriented mount of the acid-treated material was prepared and subsequently scanned with the diffractometer.

The minus 5-micron fraction of each sample which had been found to contain chlorite, either as an unmixed phase or as part of a mixed-layer system, was investigated by means of the differential dissolution technique of Hashimoto and Jackson (52). The purpose of this study was to verify the composition of the chlorite interlayer as being ferro-magnesian rather than aluminous, as is sometimes the case in certain soils and sediments.

Representative portions of the seven shale samples which had previously been studied by Sadler (5) were examined with the Guinier X-ray powder camera. This procedure allowed the identities of the non-clay constituents of these specimens to be verified and their relative abundances estimated according to the scheme utilized in the present investigation.

Specimens of fired material were obtained from each of the nine selected samples. The firing conditions were the same as those for the fired thermal expansion specimens, and each sample was fired to the temperature which would normally be used in commercial production. The Guinier X-ray powder camera was used to identify crystalline phases within the heated samples.

Plasticity by the Brabender Plastograph

The relative plasticity of the nine specially selected samples was determined by a Brabender plastograph. This method of determining relative plasticity (consistency) is more exact than the empirical method used during preparation of routine test specimens, which is dependent upon the judgment and experience of the operator. The use of the Brabender plastograph with clays has been described by Marshall (53). Two hundred grams of dry sample was placed in the apparatus, with the pug knives revolving at the slowest speed. A continuous curve, which was an expression of the consistency, was obtained while water was being added at the rate of 5 cc/min. The Cooksville (D-M) sample served as a convenient standard in this study, as the plasticity of the Dundas-Meaford shale from this locality is just sufficient to permit extrusion. The peak heights and the areas under the plastograph curves were used to compare the plasticities of the samples: the higher the peak and the greater the area, the greater is the plasticity.

Thermogravimetric Analysis (TGA)

Continuous curves of total weight loss vs. temperature for the nine selected samples were obtained by an automatically controlled, high-temperature Stanton thermobalance. A two-gram, minus 100-mesh (Tyler) sample was dried to constant weight at 110°C and placed in the thermobalance crucible. A heating rate of 6 centigrade degrees per minute was used. This particular combination of sample weight and rate of temperature increase was chosen when it was found that under these conditions the recorded weight-loss deflections occurred at the same temperature as did the DTA peaks produced by the same reactions. This arrangement simplified the interpretation of these results.

The weight-loss curves were replotted differentially, to show rate of weight loss for each 2.5 minutes (this interval representing a temperature change of 15 centigrade degrees). Furthermore, the vertical scale was plotted logarithmically, so that the effect of reactions accompanied by very small changes in weight could be more clearly observed when these occurred individually or were superimposed upon a reaction involving a larger weight change.

Dilatometry

The thermal expansions of unfired specimens of the nine specially selected samples were determined in a vertical tube-type dilatometer and in a horizontal Seger-type dilatometer. The principal components of the vertical dilatometer were a nichrome-wound furnace, a fused-quartz assembly, and an Ames dial (Brady et al. (45)). Specimens measuring 0.5 x 0.5 inch and about 2 inches long were prepared by hand-moulding, to avoid particle orientation effects. The sides parallel to the longitudinal axis were grooved with a 1/4-inch file to produce a final cross-section roughly X-shaped, with heavy central fillets. By thus reducing and equalizing thickness, the sensitivity of the apparatus to sudden changes in dimension was increased. The ends of the oven-dried specimens were sanded smooth and parallel, and the lengths measured to the nearest 0.0001 inch. The dilatometer furnace was manually controlled at a heating rate varying from 9 to 11 centigrade degrees per minute. Readings of length and temperature were made at two-minute intervals, except where sharp or extensive dimensional changes were anticipated or observed (as at the quartz inversion temperature, 573°C), when readings were made each minute. Maximum temperatures were limited to about 980°C because of the nature of the fused quartz assembly. From these results, the changes in length with temperature were calculated in per cent of original length. No corrections were made for the expansion of the fused quartz, since this is very small and regular (0.585×10^{-6} inch per inch of length per degree centigrade from 0 to 1200°C).

The verticle furnace was closed at the bottom and consequently the atmosphere was reducing in those cases where a large volume of H_2O, CO_2 or SO_2 was evolved from the unfired sample. Particularly for the shales, this reducing atmosphere affected the colour and might have affected their expansion characteristics. In order to examine this effect, the expansion of the samples was determined in a Seger-type dilatometer having a platinum-wound horizontal furnace with an oxidizing atmosphere. The heating rate of this furnace was automatically controlled at about 3.3 centigrade degrees per minute. The temperature and the thermal expansion were automatically recorded. Hand-moulded specimens 25 mm in cross-section, with a central 7-mm hole, were filed to the same shape as the vertical furnace test specimens. The length was made exactly 100 mm so that per cent expansion could be recorded directly. The curves obtained were plotted to the same scale as were those obtained in the vertical dilatometer, and were corrected to the true expansion by subtracting calibrated values of the apparatus from the recorded expansion values.

Fired test specimens were obtained for each of the nine selected samples. Each sample was fired in an oxidizing atmosphere to the temperature which would normally be used in commercial production. After the ends were made smooth and parallel, the thermal expansion up to 700°C was determined in the vertical dilatometer in the same manner as for the unfired samples. It was assumed, since the maximum test temperature was well below the initial firing temperature of the specimen, that no further reaction would take place and the cooling curve of the fired specimen would be the same as the heating curve. Thus, the thermal expansion curves of the fired specimens were prepared as representing changes in dimensions of the fired materials during the cooling period. The atmosphere in these tests appeared to be oxidizing to neutral. The sharp discontinuity in the curves between 570 and 590°C was used to estimate the percentage of quartz in the fired thermal expansion specimens. For this purpose, a line was drawn on the curve along the direction of the discontinuity and the percentage expansion was noted between the upper and lower points of tangency (usually between 570 and 590°C). The expansion of a quartz rock (100% quartz) was obtained in a similar manner and this value was used as a reference standard.

RESULTS

Properties of Unfired and Fired Specimens

The unfired and fired properties of the 49 representative Ontario clays and shales are shown in Tables 2 to 7. It is evident that the majority of Ontario clays and shales are low-fusion, heterogeneous materials, suitable for brick and/or tile but not suitable for refractory or whiteware products. One exception is the fire clay from the Missinaibi valley of northern Ontario, which has a PCE of 31 1/2.

Chemical Analysis

The chemical analyses are shown in Table 8, where columns to the right of the total show additional information. The total elemental and organic carbon, sulphur, carbon dioxide (CO_2), and $H_2O + 105^{\circ}C$ should be about equal to the L.O.I. (dry basis). The $H_2O - 105^{\circ}C$ represents the moisture in the samples and shows the condition of the well air-dried sample prior to drying at 105°C. Most of the analyses indicate that the Ontario materials are common clays and shales, because their Al_2O_3 content is low (generally 14 to 17 per cent), their silica content is high (50 to 65 per cent, except for high carbonate clays), and their CaO, MgO, Na_2O, K_2O, FeO and Fe_2O_3 percentages are generally high. Only one sample, Missinaibi (1323), has a high per cent Al_2O_3 (27.54) and a low CaO, MgO, Na_2O and K_2O content, which indicates that this is a refractory clay. Non-hydrated members of the kaolinite-metahalloysite series, the principal mineral constituent of the latter sample, have a composition approximating SiO_2 46.5 per cent, Al_2O_3 39.5 per cent, and combined water 14.0 per cent.

Samples having relatively high MgO and CaO percentages of greater than a total of 10 to 12 per cent, and correspondingly high CO_2 contents of greater than about 7 per cent, fall into the category of common low-fusion clays that contain excessive calcite and/or dolomite. These materials fire to a salmon-buff-green colour and have a short firing range.

Those clays having a high combined FeO and Fe_2O_3 content, and low Al_2O_3 and CO_2 percentages, are common salmon to red-firing materials. The clays with the higher K_2O percentages contain a relatively high proportion of illite and/or K-feldspar. Samples, such as Billings, which have a relatively high organic carbon content plus a high sulphur content are difficult to fire during the oxidation period.

The quartz column lists a figure for the percentage of crystalline silica, which was obtained with some difficulty by the Trostel and Wynn method (54). The values generally appear to be in the order of 5 per cent high for many of the low-fusion clays and shales, particularly those with higher contents of quartz. An empirical method currently under development by the chemical laboratories of the Mineral Sciences Division, Mines Branch, was used to evaluate the quartz content of a few samples. These have been noted in Table 8.

TABLE 2

Physical Properties of Queenston (Q) Shales and Related Materials

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No.+	Fired Shrinkage*, %	Absorption, %	Colour	Hardness	
Ottawa (Q), deaired extruded **	Red, calcareous shale from pit at Russell, Ontario. Hard; poor plasticity, extruded with difficulty under vacuum; 14% water of plasticity; dried safely; 1.7% drying shrinkage.	3½ 1160°C (2120°F)	04	-0.8	10.9	Medium red	Hard	Does not have sufficient plasticity for extruding without a plasticizer; short firing range, may crack with rapid firing; suitable for face brick.
			02	0.5	5.5	Dark red	Very hard	
			1	1.5	1.2	Dark red	Steel hard	
Ottawa (Q), hand-moulded	Same comments as above, except water of plasticity and drying shrinkage.		04	-1.7	11.0	Light red	Fairly hard	Less dense than deaired extruded specimens for equivalent heat treatment.
			02	-2.0	9.3	Medium red	Hard	
			1	-1.1	3.6	Brown-red	Very hard	
Ottawa (Q), temp. gradient deaired extruded	See above.		1828°F	-1.02	11.9	-	-	Temperature gradient schedule used produces denser products than deaired extruded specimens and much denser than hand-moulded.
			1898	-1.10	11.2	-	-	
			1957	0.57	7.1	-	-	
			2000	-0.45	2.1	-	-	
Grimsby, (weathered Q), hand-moulded	Red, weathered calcareous shale from pit at Grimsby. Good plasticity; water of plasticity 20.4%; safe drying; drying shrinkage 5.4%.	5 1177°C (2151°F)	06	0.7	11.3	Light red	Fairly hard	Will extrude satisfactorily; short firing range for dense products; suitable for brick and tile.
			04	3.0	8.3	Light red	Hard	
			02	3.8	3.9	Brownish red	Very hard	
Streetsville (Q)	Red, calcareous shale from McFarren pit. Poor plasticity; water of plasticity 15%; safe drying; drying shrinkage 3.4%.	4 1168°C (2134°F)	06	-0.1	12.8	Light red	Fairly hard	Will extrude; suitable for manufacture of face brick.
			04	-0.3	12.8	Light red	Fairly hard	
			02	-0.1	10.5	Brown-red	Hard	
			1	2.7	5.1	Brown-red	Very hard	
Georgetown (Q), deaired extruded	Red, very calcareous shale from Georgetown. Good plasticity, extruded well; water of plasticity 16.6%; safe drying; drying shrinkage 3.3%.	3½	06	0	12.0	Light red	Fairly hard	Extrudes well; suitable for stiff mud products such as brick and tile.
			04	0.7	11.0	Light red	Fairly hard	
			02	1.3	7.6	Brown-red	Hard	
			1	2.0	5.0	Red-brown	Very hard	
Milton (Q), hand-moulded	Red, very calcareous shale from pit at Milton. Good plasticity, water of plasticity 17.5%; safe drying; drying shrinkage 4.0%.	4½ 1173°C (2143°F)	06	0	12.4	Dark salmon	Fairly hard	Extrudes well; suitable for stiff mud products such as brick and tile; short firing range for dense products.
			04	0	11.4	Dark salmon	Hard	
			02	0.3	8.6	Light red-brown	Hard	

TABLE 2 (continued)

Nelson (Q), deaired extruded **	Red, very calcareous shale from Diamond clay pit between Tansley and Nelson. Fair plasticity; water of plasticity 14.2%; safe drying; drying shrinkage 3.5%.	$2\frac{1}{2}$ 1148°C (2098°F)	06	-0.1	12.3	Light red	Fairly hard	Extrudes well; suitable for brick and tile; short firing range, may crack with rapid firing.
			04	-0.1	11.5	Dark salmon	Fairly hard	
			02	0.7	8.9	Brown-salmon	Hard	
			01	0.8	7.0	Brown-salmon	Hard	
			1	4.3	4.5	Dark buff	Steel hard	
Nelson (Q), temp. gradient hand-moulded	Same comments as above except slight difference in water of plasticity and drying shrinkage.		1837°F	-0.45	20.62	Pinkish-buff	Fairly soft	The schedule for the hand-moulded temp. gradient produces earlier vitrification. These specimens are more porous at lower temperature than deaired samples.
			1899	-0.36	20.25	Greyish-buff	Fairly soft	
			1951	0.44	17.95	Greyish-buff	Fairly hard	
			1995	3.37	10.91	Greenish-buff	Hard	
			2017	7.47	2.00	Greenish-buff	Steel hard	
Owen-Sound (Q), hand-moulded and dry pressed	Red, highly calcareous shale from outcrop at Owen Sound; contains green bands; presses satisfactorily; dries safely after hand-moulding; water of plasticity 21%; drying shrinkage 5%.	6 1201°C (2194°F)	02	0	17.5	Light buff	Soft	First series is hand-moulded and the second dry-pressed. The carbonate content is too high for clay products. Hand-moulded samples are less porous than dry-pressed ones.
			1	0	17.5	Light buff	Soft	
			3	0	17.5	Light buff	Soft	
			02	0	24.0	Light buff	Soft	
			1	0	22.6	Light buff	Soft	
			3	0	22.6	Light buff	Soft	
Aldershot (Iroquois), hand-moulded	Red-brown clay, from near Aldershot, silty, probably from Lake Iroquois. Non-calcareous; good plasticity; water of plasticity 21.7%; very slight tendency to crack with rapid drying; drying shrinkage 5.6%.	$5\frac{1}{2}$ 1187°C (2170°F)	06	2.5	10.0	Light red	Fairly hard	Good plasticity; short firing range; suitable for difficult-to-extrude products such as tile or brick.
			04	5.5	4.7	Red	Very hard	
			02	7.5	0.8	Dark red	Steel hard	
Aldershot (weathered Q), hand-moulded	Red-brown slightly calcareous, weathered Queenston shale, from Aldershot. Good plasticity; water of plasticity 22.8%; safe drying, drying shrinkage 6%.	$4\frac{1}{2}$	06	1.1	13.5	Light red	Fairly hard	Good plasticity; short firing range; suitable for difficult-to-extrude products such as tile or brick.
			04	3.1	8.4	Red	Hard	
			02	5.6	3.0	Dark red	Very hard	

* A minus sign indicates expansion.

\+ 06-991°C (1816°F); 04-1050°C (1922°F); 02-1101°C (2014°F); 01-1117°C (2043°F); 1-1130°C (2077°F); 3-1152°C (2106°F).

** One of the nine selected samples.

TABLE 3

Physical Properties of Dundas-Meaford (D-M) and Miscellaneous Shales

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No.+	Fired Shrinkage*, %	Absorption, %	Colour	Hardness	
Reformatory (D-M), hand-moulded	Grey, calcareous shale from pit on Horner Ave., Etobicoke. Fairly plastic; water of plasticity 17.5% ; safe drying ; drying shrinkage 3.8%.	4½ 1173°C (2143°F)	06	0.8	10.7	Salmon	Fairly hard	Will extrude for brick; satisfactory firing range for red face brick and tile; scums.
			04	2.1	7.8	Pale red	Hard	
			02	3.7	4.3	Light red	Very hard	
Toronto Brick (D-M), hand-moulded	Hard, grey, calcareous shale, from pit in Don Valley, Toronto, inclined to be short ; water of plasticity 15.7% ; safe drying ; drying shrinkage 3.0%.	3½ 1160°C (2120°F)	06	0.3	9.4	Brown-red	Fairly hard	Same comments as above.
			04	0.7	8.8	Brown-red	Fairly hard	
			02	-0.2	6.7	Brown-red	Hard	
Booth (D-M), hand-moulded	Hard, grey calcareous shale from pit on Horner Ave., Etobicoke. Fairly plastic; water of plasticity 19.2%, safe drying ; drying shrinkage 3.3%.	3½	04	0.8	9.3	Light red	Fairly hard	This shale is suitable for the manufacture of face brick. Scums.
			02	2.0	6.5	Red-brown	Very hard	
			1	0.3	1.7	Brown-red	Vitrified	
Cooksville (D-M), de-aired extruded temp. gradient **	Grey, calcareous shale from pit near Cooksville. Fairly plastic; extrudes well; water of plasticity 14% ; safe drying; drying shrinkage 2%.	4 1168°C (2134°F)	1865°F	2.03	10.38	Brown-red	Fairly hard	Extrudes well; suitable for brick and tile. Some additives required for difficult-to-extrude shapes.
			1924	3.60	6.78	Brown-red	Hard	
			1974	4.76	2.18	Brown-red	Very hard	
			2016	2.70	1.14	Brown-red	Nearly vitrified	
Cooksville (D-M), temp. gradient hand-moulded	Same comments as above except water of plasticity 17.5% and drying shrinkage slightly higher.		1799°F	1.10	14.16	Dark salmon	Fairly hard	The deaired temp. gradient specimens vitrify at a lower temperature than this sample.
			1865	1.72	12.85	Light red	Hard	
			1924	2.11	10.69	Red	Hard	
			1974	3.35	5.39	Reddish brown	Very hard	
			2016	1.56	2.54	Dark brown	nearly vitrified	
Cooksville (D-M), hand-moulded	Water of plasticity 14.2%, safe drying; drying shrinkage 3.0%.		08	0.0	11.3	Pale brown	Fairly hard	The temp. gradient specimens vitrify at a lower temperature than the hand-moulded specimens.
			06	0.3	11.1	Pale brown	Fairly hard	
			04	0.7	9.4	Red-brown	Hard	
			02	1.7	7.1	Red-brown	Very hard	
Parkhill (Hamilton), hand-moulded **	Soft, grey, calcareous shale from the Ausable river, south of Sylvan; sample from 35 ft pit face. Fair plasticity; water of plasticity 27.9%; safe drying; drying shrinkage 6.1%.	4½	06	2.0	13.4	Light salmon	Fairly hard	Will extrude; suitable for tile and salmon brick.
			04	4.1	10.0	Salmon	Hard	
			02	5.1	6.0	Salmon-brown	Very hard	
Parkhill (Hamilton), temp. gradient hand-moulded	Same as above		1765°F	2.32	17.40	Salmon	Fairly hard	Temperature gradient specimens vitrify at a lower temperature than routine hand-moulded, because of difference in firing schedule.
			1844	3.67	14.00	Dark salmon	Fairly hard	
			1912	4.58	11.30	Light red	Hard	
			1974	6.24	4.65	Brown-red	Very hard	
			2024	8.82	0.35	Red-brown	Steel hard	

TABLE 3 (continued)

Thedford (Hamilton), hand-moulded	Top 8 ft soft, grey high calcareous shale from pit at Thedford. Partly weathered; good plasticity; water of plasticity 22.9%; safe drying; drying shrinkage 5.1%.	3 1152°C (2106°F)	06	-0.7	20.3	Light cream	Soft	Will extrude well; suitable for drain tile and partition tile; scums badly.
			04	-1.0	16.9	Cream	Fairly soft	
			02	-0.5	14.4	Buff	Fairly hard	
			1	-0.3	14.7	Dark buff	Fairly hard	
Billings, hand-moulded **	Black, very slightly calcareous shale from outcrop at Ottawa. Very short; poor plasticity; water of plasticity 12.6%; drying shrinkage 2.3%.	1 1136°C (2077°F)	08	-1.3	11.8	Pale salmon	Fairly soft	Probably requires a plastic additive to extrude; contains excessive organic material; suitable for brick if fired properly.
			06	-2.1	11.3	Pale red	Fairly hard	
			04	-2.8	14.7	Red	Hard	
			02	-3.1	10.5	Dark red	Hard	
Billings, temp. gradient hand-moulded	Same as above		1664°F	0.10	11.86	Dark salmon	Fairly hard	Longer firing and soaking time on temperature gradient specimens produces much greater shrinkage and less adsorption than on hand-moulded.
			1744	0.85	10.13	Light red	Hard	
			1814	2.55	7.48	Medium red	Very hard	
			1872	4.20	4.24	Red	Steel hard	
			1922	4.72	1.95	Dark red	Nearly vitrified	
Carlsbad, hand-moulded	Dark grey, calcareous shale from Haley pit at Ottawa. Very short, poor plasticity; water of plasticity 16.1%; safe drying; drying shrinkage 3.0%.	3½	08	-0.3	11.3	Salmon	Fairly soft	Probably requires a plastic additive to extrude; requires care to oxidize; suitable for brick and has been used for expanded lightweight aggregate.
			06	0.3	10.0	Pale red	Fairly hard	
			04	0.7	9.3	Red	Hard	
			02	1.7	7.4	Dark red	Very hard	
Rockcliffe, hand-moulded	Grey, calcareous shale from Ottawa outcrop. Poor plasticity; water of plasticity 15.3%; safe drying; drying shrinkage 1.9%.	5½ 1187°C (2170°F)	06	-1.3	17.0	Light brown	Very soft	Scums; requires a plasticizer for extrusion; difficult to vitrify; not suitable for dense extruded products.
			04	-1.3	16.3	Light brown	Very soft	
			02	0.7	12.2	Brown	Hard	
			1	0.1	13.7	Brown	Hard	
Kettle Point, hand-moulded	Black, non-calcareous shale, composite sample of 12 ft section on shore at Kettle Point. Poor plasticity; water of plasticity 21.4%; safe drying; drying shrinkage 3.0%; scums badly.	8 1236°C (2257°F)	06	1.7	23.9	Light red	Very soft	Badly scummed; difficult to vitrify; extremely high in oxidizable material. Not suitable in raw state for brick and tile.
			04	4.3	19.1	Light red	Fairly soft	
			02	8.3	10.4	Dark red	Hard	
			1	8.8	8.2	Dark red	Very hard	

* A minus sign indicates expansion.

\+ 08-945°C (1743°F); 06-991°C (1816°F); 04-1050°C (1922°F); 02-1101°C (2014°F); 1-1136°C (2077°F).

** One of the nine selected samples.

TABLE 4

Physical Properties of Southwestern Clays

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No.+	Fired Shrinkage*, %	Absorption, %	Colour	Hardness	
Stevenson, hand-moulded **	Brown, slightly calcareous surface clay above lime pebbles from pit at Stevenson . Plastic;cracks with rapid drying; water of plasticity 30.6%; drying shrinkage 8.8%.	3½ 1160°C (2120°F)	06	2.3	10.4	Salmon	Hard	Difficult to dry; lime pebbles are a problem for face brick; suitable for common brick and tile.
			04	4.3	6.3	Light red	Very hard	
			01	7.8	0	Good red	Vitrified	
Stevenson, temp. gradient hand-moulded	Same comments as above		1645°F	1.60	16.32	Salmon	Fairly hard	The temp. gradient hand-moulded specimens have higher shrinkage and lower absorption than the routine hand-moulded ones, particularly at the higher temperatures.
			1730	2.70	14.23	Dark salmon	Hard	
			1808	4.19	11.84	Dark salmon	Hard	
			1875	6.61	6.99	Light red	Very hard	
			1935	9.25	1.96	Red	Steel hard	
Tilbury	Brown,slightly calcareous surface clay (1 to 3 ft) above lime pebbles from pit at Tilbury. Plastic; slightly gritty; water of plasticity 27.3% ; cracks slightly with rapid drying; drying shrinkage 7.5%.	10 1285°C (2345°F)	06	2.5	13.0	Dark salmon	Fairly hard	Care required in drying; lime pebbles are a problem for face brick; suitable for common brick and drain tile.
			04	4.8	8.0	Light red	Hard	
			02	7.1	2.3	Red	Very hard	
			1	9.0	0.4	Dark red	Vitrified	
Tupperville, hand-moulded	Brown, calcareous clay, from pit at Tupperville. Plastic; water of plasticity 27.2%; cracke slightly on rapid drying; drying shrinkage 8.2%.	4 1168°C (2134°F)	06	0.5	15.1	Dark salmon	Fairly hard	Care required in drying; firing range inclined to be short for dense products; suitable for brick and tile.
			04	1.3	14.0	Salmon	Fairly hard	
			02	3.7	6.0	Brown-red	Very hard	
Wilkesport, hand-moulded	Brown, very calcareous surface clay from pit near river. Plastic; water of plasticity 27%; cracks slightly on rapid drying; drying shrinkage 7.0%; some lime pebbles.	4½ 1173°C (2143°F)	06	0.3	17.6	Salmon	Fairly hard	Care required in drying; short firing range for dense products; suitable for drain tile.
			02	1.1	12.0	Salmon	Hard	
			1	6.1	0.5	Red-brown	Nearly vitrified	
Dresden , (brown), hand-moulded	Brown surface clay (6 ft) from pit south of plant. Very calcareous; plastic; water of plasticity 27.5%; tendency to crack in rapid drying; drying shrinkage 8.2% ; some lime pebbles.	3 1152°C (2106°F)	06	0.5	18.9	Salmon	Fairly soft	Care required in drying; difficult to make dense products; suitable for drain tile.
			04	0.7	17.6	Salmon	Fairly hard	
			02	2.5	8.2	Salmon-buff	Hard	
Essex (blue), hand-moulded	Grey, very calcareous clay taken from 15 ft level of pit. Plastic; gritty; has some stones and lime pebbles; water of plasticity 24.2%; safe drying; drying shrinkage 5.7%.	3+ 1154°C (2110°F)	06	-0.1	17.5	Cream	Fairly soft	Short firing range for dense products; suitable for drain tile.
			04	0.7	17.1	Cream	Fairly soft	
			02	2.0	13.2	Pale salmon	Fairly hard	
			1	6.7	1.8	Red-buff	Very hard	
Fletcher, hand-moulded	Brown, non-calcareous surface clay (3 ft) from pit near Fletcher. Plastic; water of plasticity 30.8%; tendency to crack in drying; drying shrinkage 7.8%; some lime pebbles.	9½ 1270°C (2320°F)	06	3.1	12.8	Dark salmon	Fairly hard	Care required in drying; short firing range for dense products; suitable for drain tile.
			04	5.0	9.0	Light red	Hard	
			02	8.8	1.4	Red	Steel hard	
Dresden (blue)	Brown surface clay (6 ft) from north of plant. Calcareous; plastic; water of plasticity 30.7%; slight tendency to crack with rapid drying; drying shrinkage 7.7%; some lime pebbles.	5+ 1182°C (2160°F)	06	0.8	17.1	Dark salmon	Fairly hard	Care required in drying; short firing range for dense products.
			04	4.0	9.3	Light red	Very hard	
			02	6.5	4.2	Red	Steel hard	

* A minus sign indicates expansion.

\+ 06-991°C(1816°F); 04-1050°C(1922°F); 02-1101°C(2014°F); 1-1136°C(2077°F).

** One of the nine selected samples.

TABLE 5

Physical Properties of Southern Clays

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No.+	Fired Shrinkage, % *	Absorption, %	Colour	Hardness	
Elginfield (brown), hand-moulded	Brown, slightly calcareous clay, top 2-5 ft from tile pit at Elginfield. Plastic; water of plasticity 26.1%; cracks badly with rapid drying ; drying shrinkago 7.3% ; some lime pebbles.	5+ 1182°C (2160°F)	06	0.7	13.3	Light red	Fairly hard	Care required in drying; short firing range for dense products; suitable for tile and perhaps brick.
			04	2.8	7.3	Dark red	Very hard	
			02	6.1	3.0	Dark red	Steel hard	
Brownsville, hand-moulded	Brown, calcareous clay, about 5 ft surface clay below 2 ft soil from tile pit at Brownsville. Plastic; water of plasticity 28.7% ; tendency to crack in drying; drying shrinkage 6.5%.	3+ 1154°C (2110°F)	06	0.5	16.8	Salmon	Fairly hard	Short firing range for dense products; suitable for drain tile and partition tile.
			04	0.7	14.5	Dark salmon	Fairly hard	
			02	3.0	4.1	Medium red	(Warped) Very hard	
Forest, hand-moulded	Brown, calcareous surfacs clay from tile pit at Forest (surface 30 inches). Good plasticity; gritty; water of plasticity of 26.5% ; cracks in rapid drying; drying shrinkage 7.9% ; some lime pebbles.	4½ 1173°C (2143°F)	06	0.1	15.5	Salmon	Fairly hard	Care required in drying; and some lime pebbles below about 30 inches; very short firing range for dense products.
			04	0.3	13.7	Salmon	Fairly hard	
			02	5.5	2.7	Dark brown-red	Nearly Vitrified	
St. George, hand-moulded	Brown surface clay from pit at St. George and used in Kitchener. Highly calcareous ; fairly plastic; water of plasticity 22.5%; tendency to crack in rapid drying; drying shrinkage 5.0%.	2 1142°C (2088°F)	06	-0.8	23.5	Cream	Very soft	Some care required in drying ; very short firing range for dense products.
			04	0	21.7	Cream	Very soft	
			02	-0.3	21.4	Cream-buff	Soft	
			1	2.0	14.5	Buff	Fairly hard	
Norwich, hand-moulded	Brown surface clay (10 ft) from tils pit at Norwich . Highly calcareous ; good plasticity ; water of plasticity 28.6% ; slight tendency to crack in drying ; drying shrinkage 7.3%; some lime pebbles.	2	06	1.2	20.9	Cream	Fairly soft	Some care required in drying; very short firing range for dense products; suitable for drain tile.
			04	2.3	20.5	Cream	Fairly soft	
			02	3.8	17.1	Yellow-buff	Fairly hard	
			1	9.0	9.6	Yellow-buff	Hard	
Wallenstein, hand-moulded **	Brown highly calcareous surface clay from Bauman pit at Wallenstein. Good plasticity; water of plasticity 24.6% ; slight tendency to crack in drying; drying ahrinkage 6.7%; a few lime pebbles.	2½ 1148°C (2098°F)	06	0.1	19.7	Dark cream	Fairly soft	Very short firing range, suitable for drain tile but not for dense clay products.
			04	0.3	17.6	Dark cream	Fairly hard	
			02	1.7	16.4	Yellow-buff	Fairly hard	
			1	6.3	0.4	Green-buff	Steel hard	
Wallenstein, temp. gradient hand-moulded	Same as above.		1804°F	0.38	24.00	Salmon-buff	Fairly soft	Temperature gradient hand-moulded specimens vitrified at a lower temperature than routine hand-moulded specimens.
			1874	0.65	23.80	Light buff	Fairly hard	
			1933	1.28	21.60	Light buff	Fairly hard	
			1985	4.31	10.81	Green-buff	Hard	
			2025	8.45	0.75	Green-buff	Steel hard	
Elginfield (blue), hand-moulded	Highly calcareous clay below surface brown; sampled at 12 ft mark. Fair plasticity; water of plasticity 18.1%; safe drying; drying shrinkage 5.6%; some lime pebbles.	7 1215°C (2219°F)	06	-3.1	32.0	Cream	Very soft	Extremely calcaraous, with a very short firing range; will not vitrify.
			02	-4.0	31.0	Cream	Very soft	
			1	-3.8	30.5	Dark cream	Very soft	
			2	-4.5	31.5	Dark cream	Very soft	
Petrolia, hand-moulded	Surface, very slightly calcareous clay from tile pit about 6 feet in depth at Petrolia. Good plasticity; water of plasticity 33.4% ; drying shrinkage 7.8% ; safe drying ; some lime pebbles.	6+ 1204°C (2200°F)	06	2.3	16.8	Salmon	Fairly hard	Very plastic clay, with a short firing range. Suitable for drain tile but not for dense products.
			04	4.7	11.1	Light red	Hard	
			02	10.0	0.2	Dark red	Vitrified	
Toronto (Reformatory)	Clay-like reworked Dundas Senford shale from pit on Horner Ave., Toronto. Good plasticity; calcareous; water of plasticity 23.4% ; safe drying; drying shrinkage 5.2%.	5 1176°C (2151°F)	06	1.3	13.4	Salmon	Fairly hard	Tendency to scum; suitable for extruded brick and tile.
			04	2.3	10.2	Dark salmon	Hard	
			02	3.8	5.3	Light red	Very hard	

* A minus sign indicates expansion.

\+ 06-991°C(1816°F); 04-1050°C(1422°F); 02-1101°C(2014°F); 1-1136°C(2077°F); 2-1142°C(2088°F).

** One of the nine selected samples.

TABLE 6

Physical Properties of North-Central Clays

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. +	Fired Shrinkage*, %	Absorption, %	Colour	Hardness	
Arnprior, hand-moulded	Grey, non-calcareous surface clay from Dochart pit at Arnprior. Very plastic (sticky); water of plasticity 32.2%; cracks badly with rapid drying; drying shrinkage 8.7%.	01^{+} 1120°C (2050°F)	06	1.0	17.9	Salmon	Fairly hard	Care required in drying; very short firing range; probably requires a non-plastic addition for drain tile manufacture.
			04	3.7	11.1	Dark salmon	Hard	
			02	9.1	0	Good red	Vitrified	
Bracebridge, hand-moulded **	Grey, non-calcareous surface clay from Home Brick pit at Bracebridge. Very plastic; water of plasticity 25.3%; tendency to crack with drying; plasticity decreased and drying improved with small $Ca(OH)_2$ addition; safe drying; drying shrinkage 6.4%.	2 1142°C (2088°F)	06	0.3	15.9	Salmon	Fairly hard	Difficult to dry; very short firing range for dense products; suitable for drain tile if processed properly.
			04	1.8	12.5	Dark salmon	Hard	
			02	8.0	1.2	Dark red	Steel hard	
Bracebridge, temp. gradient hand-moulded	Same as above.		1759°F	0.73	16.61	Salmon	Fairly soft	Temperature gradient hand-moulded specimens vitrify at lower temperatures than routine hand-moulded specimens.
			1829	1.41	15.21	Dark salmon	Fairly hard	
			1890	3.64	11.04	Pale red	Hard	
			1938	8.68	1.52	Red	Steel hard	
Napanee, hand-moulded	Brown, non-calcareous surface clay from pit of Napanee Brick and Tile. Plastic; gritty; water of plasticity 38.1%; cracks in drying; drying shrinkage 8.0%.	2½ 1203°C (2098°F)	010	2.7	19.3	Salmon	Fairly hard	Care required in drying; very short firing range for dense products; probably suitable for drain tile with careful processing.
			06	7.1	10.3	Pale red	Hard	
			04	12.7	0.5	Brown-red	Steel hard	
			02	7.6	0	Red	Overfired	
Manotick, hand-moulded	Grey, calcareous surface clay about 1 mile northwest of Manotick. Very plastic; tendency to be sticky; water of plasticity 25.3%; cracks badly, with rapid drying; drying shrinkage 8.5%.	1½ 1194°C (2082°F)	04	1.1	11.4	Dark salmon	Fairly hard	Very difficult to dry; high drying shrinkage; short firing range.
			02	6.6	1.8	Brown-red	Very hard	
Beaverton, hand-moulded	Grey, highly calcareous clay, from pit near river at Beaverton tile plant. Plastic; water of plasticity 20.0%; tendency to crack with rapid drying; drying shrinkage 5.9%.	3 1152°C (2106°F)	06	-1.0	20.8	Cream	Very soft	Difficult to dry; very short firing rangs; not suitable for dense products; probably suitable fer drain tile.
			04	-1.5	20.0	Cream	Soft	
			02	-1.0	16.5	Cream	Soft	
			1	0.7	10.1	Dark buff	Hard	
North Bay, deaired extruded	Non-calcareous surface clay near plant at North Bay. Mixture of brown, fine-grained clay, and grey, silty material; tendency to crack in drying; drying shrinkage 3.3%; extruded well with about 20% water.	4 1168°C (2134°F)	06	1.8	10.7	Light red	Fairly hard	Care required in drying; firing range for dense products short; should be suitable for brick and tile.
			04	5.2	3.2	Dark red	Steel hard	
			02	7.0	0.7	Very dark red	Vitrified	
Paisley	Brown, highly calcareous clay from tile pit at Paisley. Very plastic; water of plasticity 28.8%; tendency to crack in drying; drying shrinkage 7.2%.	4½ 1173°C (2143°F)	06	1.8	19.2	Cream	Fairly soft	Care required in drying; very short firing range for dense products; probably suitable for drain tile.
			04	2.3	18.8	Dark cream	Fairly soft	
			02	3.3	17.3	Yellow-buff	Fairly hard	
			1	7.7	2.3	Dark buff	Steel hard	

* A minus sign indicates expansion.

\+ 010-887°C(1629°F); 06-991°C(1816°F); 04-1050°C(1922°F); 02-1101°C(2014°F); 1-1136°C(2077°F).

** One of the nine selected samples.

TABLE 7

Physical Properties of Northwestern and Northern Clays

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No.+	Fired Shrinkage*, %	Absorption, %	Colour	Hardness	
Fort William, hand-moulded	Brown surface clay, very slightly calcareous, from pit of Superior Brick and Tile. Good plasticity; gritty; water of plasticity 26.5%; slight tendency to crack with rapid drying; drying shrinkage 6.3%.	2+ 1145°C (2094°F)	06	0.1	15.0	Salmon	Fairly soft	Requires care in drying; suitable for brick and tile.
			04	1.1	12.6	Light red	Fairly hard	
			02	3.3	7.9	Good red	Hard	
Dorion, hand-moulded	Brown, very calcareous clay from pit of Superior Brick and Tile. Good plasticity; water of plasticity 22.8%; safe drying; drying shrinage 4.4%.	5 1177°C (2151°F)	04	-0.1	20.0	Cream-buff	Soft	Short firing range; difficult to make dense clay products.
			02	0.7	17.0	Cream-buff	Fairly soft	
Kenora, hand-moulded	Brown, non-calcareous clay from Jaffray Township, near Kenora. Good plasticity; water of plasticity 24.8%; slight tendency to crack with rapid drying; drying shrinkage 7.6%.	5	06	1.7	11.6	Dark salmon	Fairly hard	Care required in drying; should be suitable for brick and tile.
			04	3.1	6.5	Red	Hard	
			02	8.3	0.1	Dark red	Nearly vitrified	
Sudbury, hand-moulded	Buff, non-calcareous clay from 18 miles west of Sudbury. Plastic; water of plasticity 26.2%; slight tendency to crack with drying; drying shrinkage 7.0%.	3 1152°C (2106°F)	06	1.0	14.1	Salmon	Fairly hard	Care required in drying; suitable for back-up brick or tile; addition of non-plastic would help drying.
			04	4.0	7.8	Pale red	Hard	
			02	8.8	0.0	Brown-red	Vitrified	
Missinaibi, (1323), hand-moulded **	Salmon, non-calcareous clay from Missinaibi river, Burstall Township. Plastic (greasy); water of plasticity 29.4%; safe drying; drying shrinkage 5.4%.	30½ 1674°C (3045°F)	02	2.3	21.8	Light salmon	Very soft	Slight vanadium scum; fire clay suitable for medium-duty refractories open firing.
			5	5.0	14.2	Light salmon	Fairly hard	
			10	7.4	10.9	Light buff	Hard	
			15	9.0	5.6	Speckled brown	Very hard	
Missinaibi, (1323), temp. gradient hand-moulded	Same as above		2018°F	4.43	19.22	Pale salmon	Fairly soft	The temperature gradient firing program results in lower absorption and higher shrinkages than the hand-moulded method.
			2170	9.64	11.44	Pinkish salmon	Hard	
			2288	10.50	9.59	Greyish cream	Hard	
			2370	11.83	7.69	Creamy buff	Very hard	
			2395	12.27	6.88	Creamy buff	Very hard	
Missinaibi, (1326), hand-moulded	Brown, non-calcareous clay. Good workability and plasticity (greasy); water of plasticity 29.2%; tendency to crack in rapid drying; drying shrinkage 6.7%. From same area as Missinaibi (1323).	13 1349°C (2460°F)	06	3.7	12.5	Dark salmon	Hard	Care required in drying; high drying and fired shrinkage; suitable for common brick and tile.
			04	6.3	7.2	Light red	Very hard	
			02	9.2	2.2	Red	Steel hard	
			6	7.7	0.4	Dark red	Overfired	

* A minus sign indicates expansion.

\+ 06-991°C(1816°F); 04-1050°C(1922°F); 02-1101°C(2014°F); 5-1177°C(2151°F); 6-1201°C(2194°F); 10-1285°C(2345°F); 15-1424°C(2595°F).

** One of the nine selected samples.

TABLE 8

Chemical Analysis**

SAMPLE	SiO_2	FeO	Fe_2O_3	TiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	LOI	Total	Tot. C	Org. & El. C***	S	H_2O +105 °C	H_2O -105 °C	CO_2	Quartz
1. Ottawa (Q)	56.56	2.73	3.57	0.87	15.96	4.81	3.41	1.00	3.81	7.59	100.31	*	*	*	3.89	0.16	3.71	26.4^{+}
2. Grimsby (weathered Q)	57.63	1.80	4.47	0.87	15.32	4.69	2.41	0.63	3.98	7.84	99.64	1.12	.10	0.022	3.90	0.68	3.75	29.4
3. Streetsville (Q)	56.59	1.99	3.63	0.80	13.83	6.79	2.75	0.71	3.71	9.11	99.91	*	*	*	3.82	0.16	5.30	29.2
4. Georgetown (Q)	48.36	1.95	4.38	0.78	14.28	9.29	4.07	0.12	4.30	12.10	99.63	*	*	0.023	3.59	0.58	8.52	19.6
5. Milton (Q)	50.49	2.34	4.65	0.77	15.32	7.31	3.77	0.24	4.56	10.22	99.67	1.85	.02	.017	4.16	0.42	6.71	21.5
6. Nelson (Q)	49.00	1.43	3.74	0.58	14.09	11.52	2.14	0.62	3.50	12.86	99.48	*	*	*	3.06	0.50	9.81	26.7
7. Owen Sound (Q)	38.52	1.83	3.85	0.63	13.08	15.10	5.33	0.12	3.89	18.01	100.36	*	*	0.028	3.47	0.39	14.44	9.9
8. Aldershot (Iroquois)	65.39	1.43	4.62	0.93	15.01	0.61	2.69	0.86	3.59	5.55	100.68	0.28	0.24	0.032	4.90	0.84	0.14	38.3
9. Aldershot (weathered Q)	64.44	1.49	4.26	0.93	14.49	1.64	2.51	0.90	3.43	6.45	100.54	0.59	0.42	0.028	5.03	0.84	0.61	38.7
10. Reformatory (D-M)	56.59	4.81	2.24	0.95	16.99	2.26	3.84	0.77	4.39	6.29	99.13	0.92	0.19	0.078	4.60	0.55	2.65	26.5
11. Toronto Brick (D-M)	58.16	5.11	1.78	0.88	16.76	2.87	3.29	0.94	3.92	6.37	100.08	0.99	0.21	0.27	4.11	0.46	2.42	27.5
12. Booth (D-M)	55.96	4.49	1.97	0.86	16.44	3.75	3.31	0.89	4.07	7.33	99.07	*	0.19	*	4.03	0.38	3.11	29.9
13. Cooksville (D-M)	56.66	4.33	1.80	.87	15.21	4.50	3.68	1.03	3.79	7.97	99.84	1.29	0.10	0.63	3.86	0.46	4.30	25.9^{+}
14. Parkhill (Hamilton)	52.33	4.46	1.70	0.97	17.70	5.54	3.12	0.24	4.12	9.71	99.87	1.53	0.23	.154	4.60	0.35	4.78	19.0
15. Thedford (Hamilton)	43.25	3.87	1.14	0.76	14.14	14.20	2.95	0.19	3.47	15.63	99.60	3.45	0.11	0.130	3.81	0.30	12.24	12.9
16. Billings	56.67	4.65	2.30	0.86	17.66	1.49	3.44	0.78	4.04	8.59	100.47	1.13	0.82	1.15	5.57	0.48	1.10	25.1^{+}
17. Carlsbad	56.74	4.77	1.29	0.84	15.10	5.13	2.95	1.16	3.07	8.07	99.12	*	0.18	0.16	4.64	0.25	3.90	34.4
18. Rockcliffe	61.17	2.38	1.07	0.66	12.76	6.52	0.89	0.81	4.67	8.74	99.67	*	0.05	*	2.30	0.28	6.40	42.9
19. Kettle Point ⌿	56.76	2.06	4.05	0.81	13.80	0.52	1.57	0.52	3.26	15.70	99.05	7.48	7.36	2.75	9.20	0.71	0.44	31.4
20. Stevenson	64.98	1.11	4.56	0.78	14.93	0.95	1.81	0.78	3.33	6.22	99.45	0.65	0.55	0.022	5.32	1.57	0.37	33.1^{+}
21. Tillbury	67.60	1.06	4.50	0.76	14.72	0.81	1.60	0.68	3.16	5.52	100.41	0.85	0.74	0.033	4.32	1.52	0.42	38.6
22. Tupperville	58.26	1.30	4.47	0.69	13.88	5.30	2.84	0.74	3.17	9.44	100.09	1.61	0.33	0.008	3.88	1.47	4.67	32.2
23. Wilkesport	54.32	1.43	3.46	0.73	12.24	7.70	3.69	0.58	2.76	12.32	99.23	2.35	0.44	0.028	5.45	0.81	7.00	33.4
24. Dresden (brown)	52.43	2.40	3.67	0.68	10.93	9.46	3.60	0.79	2.83	13.29	100.08	2.47	0.22	0.025	3.67	0.67	8.29	30.9
25. Essex (blue)	52.52	2.85	1.65	0.63	12.68	8.73	4.04	0.70	2.92	13.03	99.75	3.20	0.84	0.25	3.71	0.61	8.65	27.9

TABLE 8 (continued)

Sample	SiO_2	FeO	Fe_2O_3	TiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	LOI	Total	Tot. C	Org. & El. C***	S	H_2O +105 °C	H_2O -105 °C	CO_2	Quartz
26. Fletcher	64.61	1.10	4.22	0.73	15.76	0.68	1.63	0.72	3.25	6.87	99.57	0.81	0.81	0.024	5.17	1.61	N.D.	36.4+
27. Dresden (blue)	59.27	1.17	3.38	0.72	15.21	3.76	2.39	0.59	3.38	10.14	100.01	2.36	1.04	0.048	5.12	0.51	3.03	33.6
28. Elginfield (brown)	66.52	1.18	3.98	0.78	13.51	2.13	2.17	1.40	2.88	5.52	100.07	0.48	0.24	0.013	4.16	1.38	0.83	33.5+
29. Brownsville	58.20	1.37	4.65	0.86	14.64	5.71	2.53	1.14	3.05	8.86	101.01	1.10	0.25	0.012	4.06	1.52	3.42	31.2
30. Forest	58.28	1.37	3.62	0.67	13.21	5.65	3.45	0.84	3.26	10.21	100.56	1.70	0.30	.050	4.13	1.30	5.13	33.3
31. St. George	45.45	1.14	3.03	0.52	10.50	16.87	3.11	1.20	2.30	16.03	100.15	3.81	0.11	0.045	2.32	0.55	13.57	26.5
32. Norwich	38.33	1.62	2.95	0.58	11.00	18.34	4.31	0.77	2.59	19.40	99.88	4.69	0.18	0.029	2.84	0.76	16.53	22.0
33. Wallenstein	47.58	1.17	3.16	0.61	10.81	13.18	4.18	1.08	2.51	16.08	100.36	3.29	0.14	0.020	4.01	0.47	11.55	23.1
34. Elginfield (blue)	31.53	1.30	1.44	0.36	7.09	24.96	5.96	0.78	1.65	25.61	100.68	7.03	0.18	0.058	N.D.	0.40	25.10	18.3
35. Petrolia	62.72	1.70	4.47	0.83	15.11	1.65	2.11	0.63	3.44	7.78	100.44	1.24	0.94	0.028	4.83	1.53	1.06	34.7
36. Toronto (Reformatory)	56.95	3.13	4.03	0.87	15.24	3.77	3.31	0.76	4.05	7.69	99.80	0.80	0.20	0.013	4.25	0.92	2.82	26.3
37. Arnprior	58.31	2.62	4.52	0.86	16.92	3.48	3.64	3.10	3.35	2.88	99.68	0.14	0.06	0.023	2.80	1.63	0.26	18.4
38. Bracebridge	63.16	2.44	3.70	0.78	16.09	2.80	2.62	3.21	3.44	2.25	100.49	0.17	0.07	0.022	2.31	0.69	0.34	31.2
39. Napanee	56.76	1.91	5.76	0.95	18.23	2.28	3.87	1.78	4.15	4.77	100.46	0.21	0.14	0.018	3.70	2.47	0.21	16.6
40. Manotick	59.92	1.77	4.06	0.76	15.02	4.94	3.41	2.60	3.15	4.70	100.33	0.75	0.10	0.019	2.08	1.42	2.40	32.9
41. Beaverton	41.73	1.27	2.56	0.40	9.54	21.31	2.31	1.78	2.11	17.34	100.35	4.35	0.08	0.035	1.60	0.59	15.63	23.8
42. North Bay	63.72	1.16	4.52	0.67	16.08	1.58	2.28	2.40	3.30	4.60	100.31	0.60	0.55	0.019	3.30	1.38	0.17	36.1
43. Paisley	41.06	1.75	2.87	0.60	12.15	14.81	5.28	0.62	3.16	18.16	100.46	3.99	0.12	0.030	3.71	0.45	14.16	19.4
44. Fort William	60.40	2.02	6.47	0.80	13.88	3.73	4.03	2.19	2.11	4.34	99.97	0.35	0.20	0.021	3.01	1.46	0.51	33.1
45. Dorion	51.06	1.30	3.46	0.49	11.59	12.27	5.10	2.16	1.91	10.59	99.97	2.46	0.12	0.017	1.88	0.74	8.54	23.4
46. Kenora	64.00	1.25	4.14	0.52	16.18	2.23	2.07	2.65	2.60	4.61	100.25	0.95	(a)	(a)	3.96	1.69	(a)	34.9
47. Sudbury	65.12	1.77	3.60	0.63	15.12	1.75	2.72	2.33	2.97	3.57	99.58	0.22	0.21	<0.015	3.03	1.19	0.01	39.1
48. Missinaibi (1323)	55.56	0.15	4.22	1.23	27.54	0.26	0.20	0.04	0.16	10.50	100.19	0.14	0.08	<0.015	10.61	0.50	0.22	22.4
49. Missinaibi (1326)	62.72	2.18	9.32	0.83	15.00	0.12	1.25	0.09	2.22	6.76	100.47	0.48	0.17	0.029	5.50	0.75	1.16	23.8

(a) Insufficient sample.

* Not available but amount is negligible.

** Chemical analysis by D.J. Charette, F.W. Brethour, F.E. Piercy, E.M. Penner, R. Craig, J.C. Hole, and E. Mark, and L.McCorriston, Mineral Sciences Division, Mines Branch.

† Kettle Point total Fe as Fe_2O_3 = 6.33 per cent.

*** Organic and elemental carbon.

\+ Values obtained by difference after volatilizing silicate silica with calcium fluoride (instead of using Trostel and Wynn method).

Differential Thermal Analysis

The DTA curves of the samples are shown in Figures 2 to 7. Exothermic peaks point up and endothermic ones down. In general, reactions involving clay minerals are represented by endothermic peaks at about 150°C and 590°C, and the endothermic-exothermic doublets above 900°C which are observed when little or no carbonate is present. A double endothermic peak in the 750 to 850°C temperature range indicates that dolomite is present, possibly together with calcite, while a single, intense endothermic peak at 800 to 900°C is characteristic of calcite alone. Many of the clay and shale curves have broad exothermic peaks at about 300°C. These indicate the presence of readily combustible organic material. A second peak or an exothermic-endothermic peak at about 400°C is present when a sample contains pyrite. Frequently, the combined organic material-pyrite peaks consisting of two sharp exothermic peaks and one small endothermic peak are very intense.

The shale curves in Figures 2 and 3 are typical of those produced by low-fusion shales containing illite and chlorite as the principal clay minerals, calcite and/or dolomite as the carbonates, and organic material and possibly pyrite as the oxidizable material. In a comparison of the Queenston and Dundas-Meaford shales, the former have a much wider variation in carbonate content.

The DTA curves of the clays in Figures 4, 5, 6 and 7 show more variation than those of the shales. Some of the clays from the Ontario

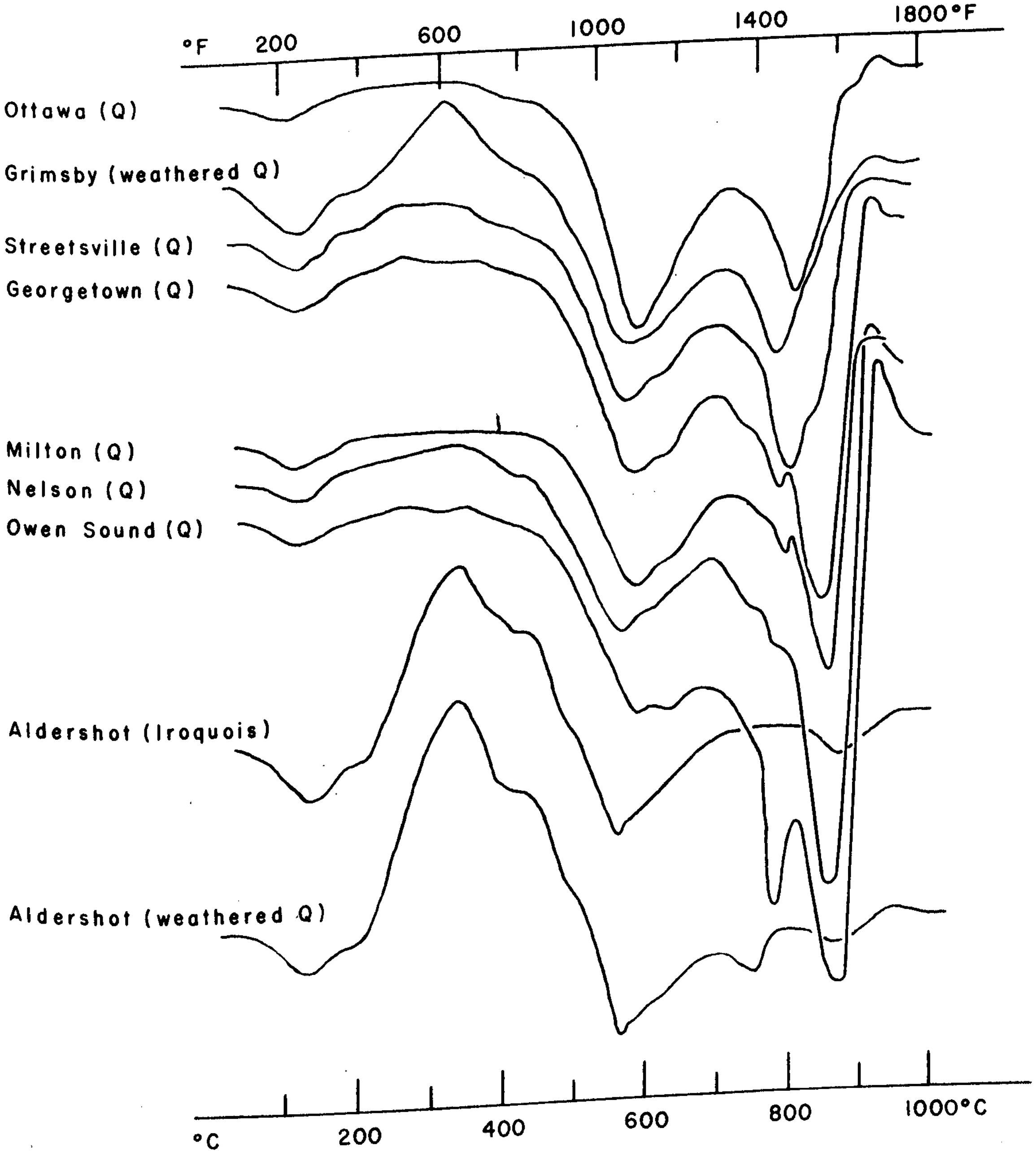


Figure 2. DTA curves of Queenston (Q) shales and related materials.

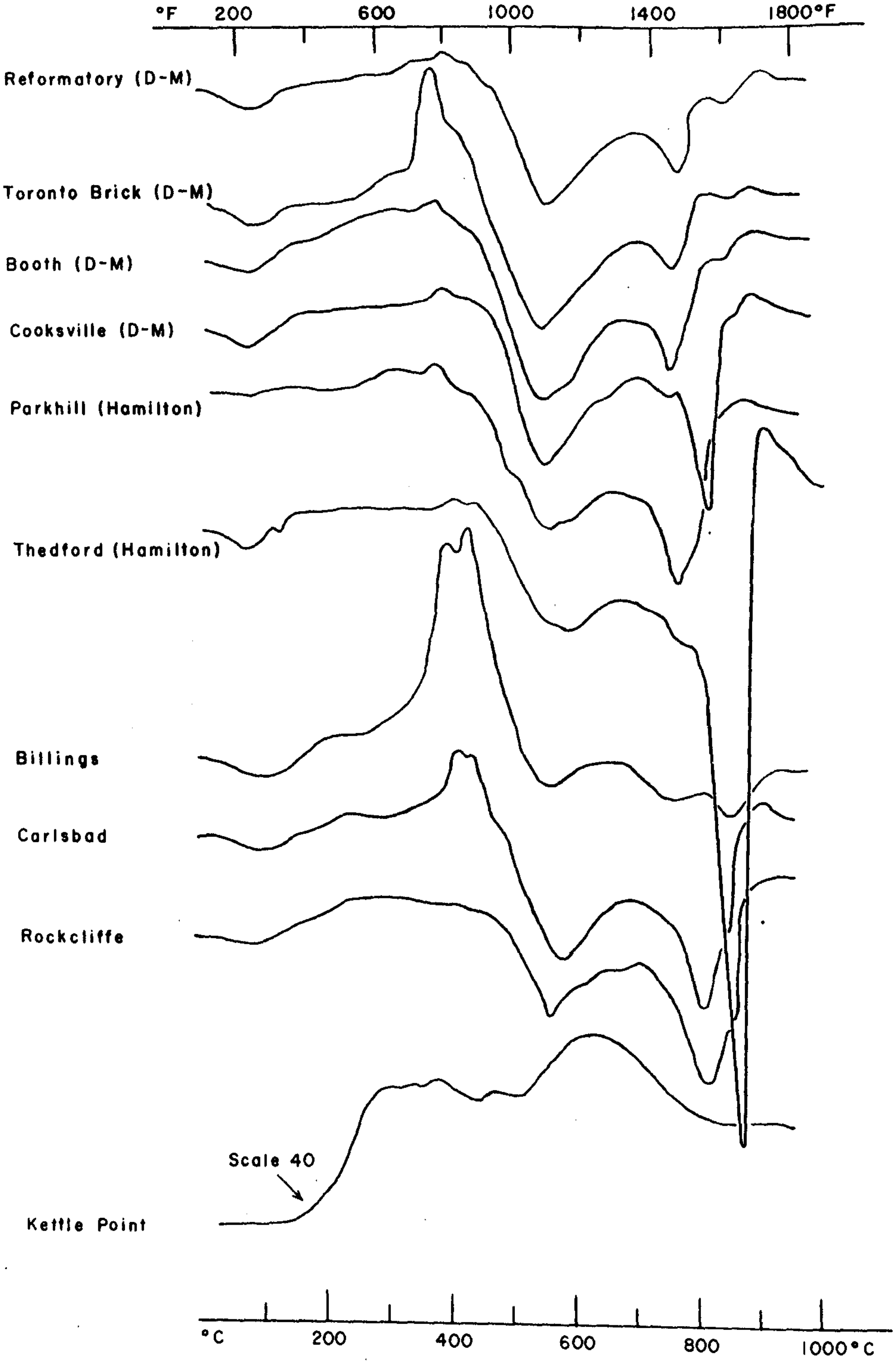


Figure 3. DTA curves of Dundas-Meaford (D-M) and miscellaneous shales.

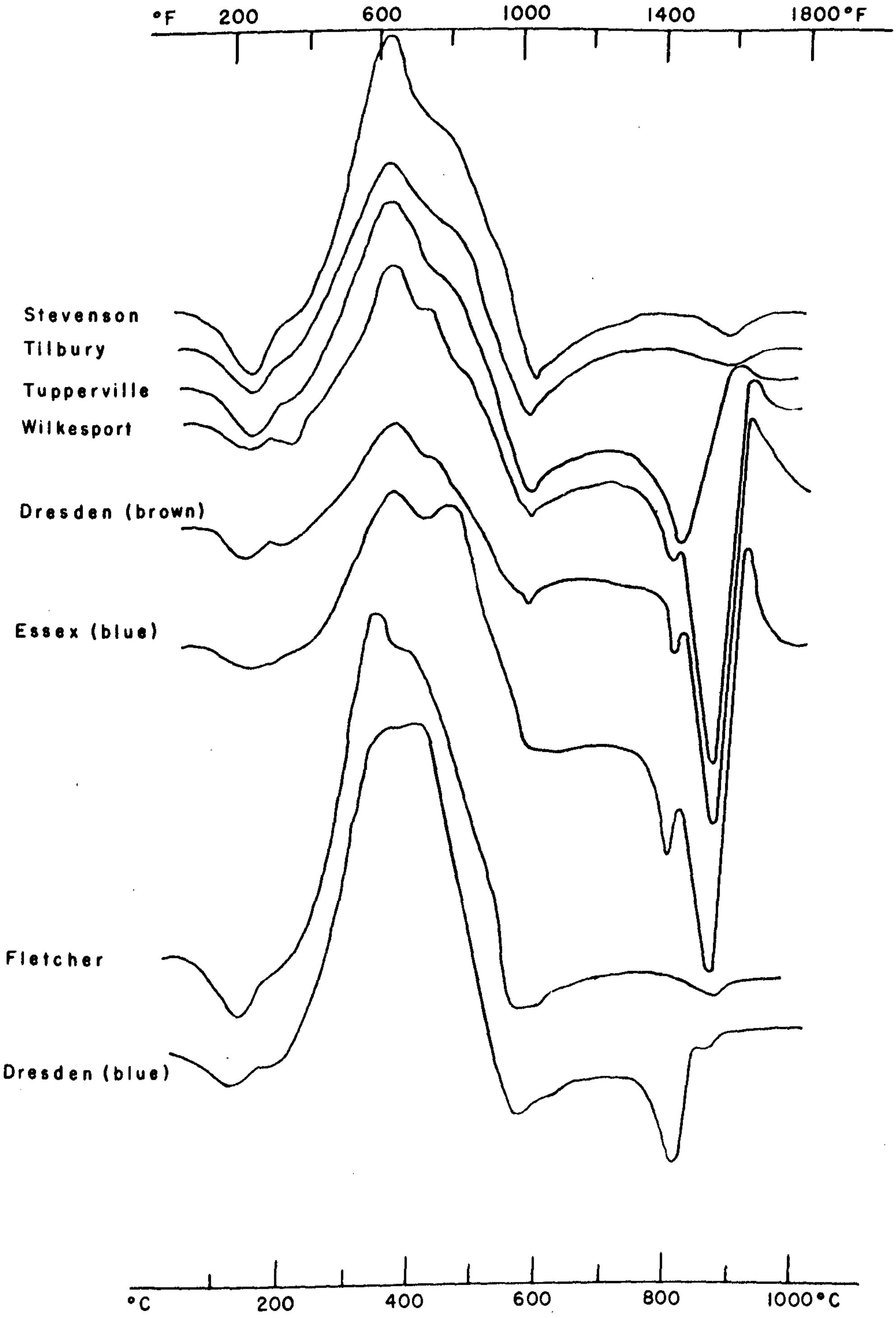


Figure 4. DTA curves of southwestern clays.

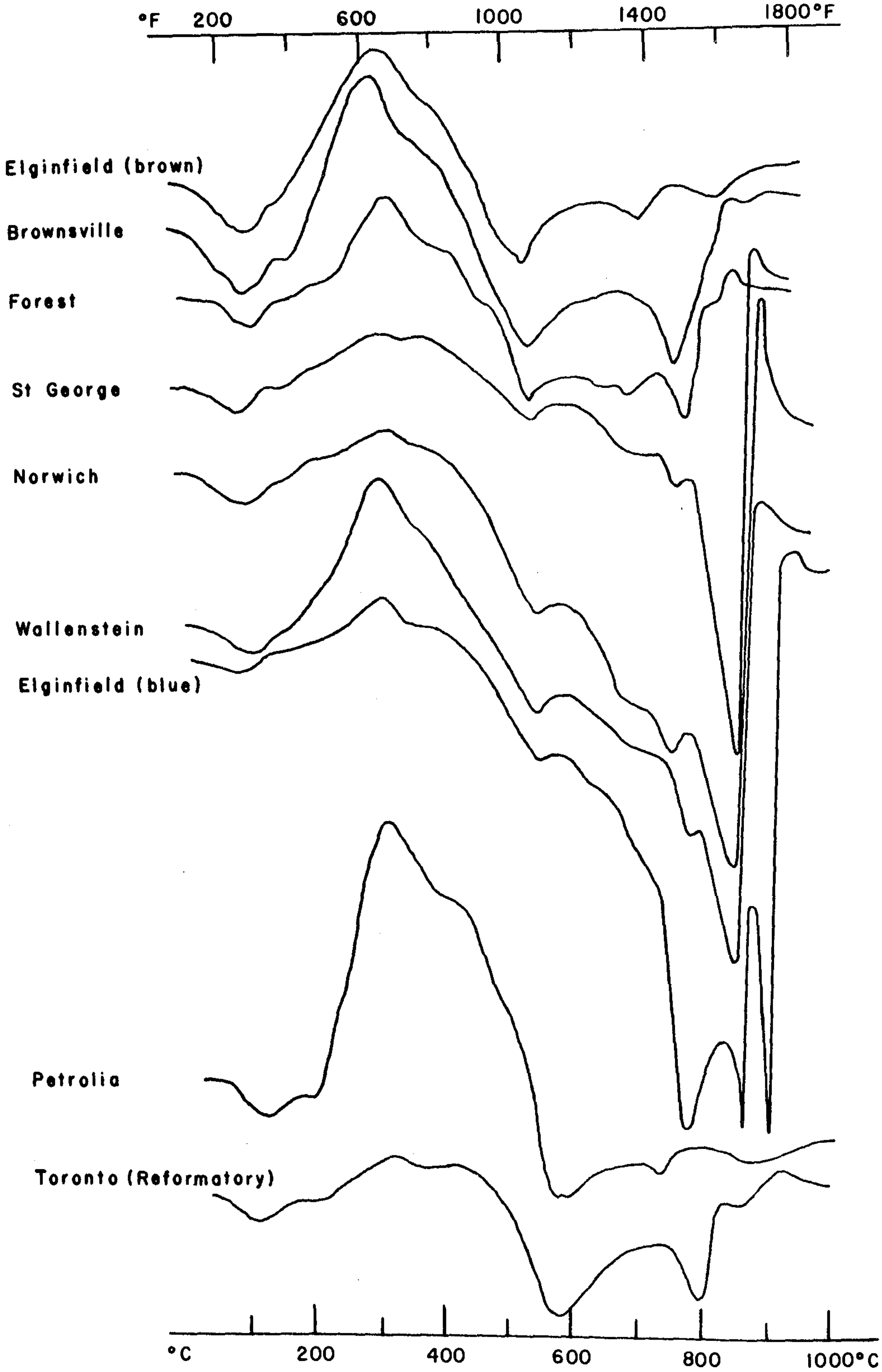


Figure 5. DTA curves of southern clays.

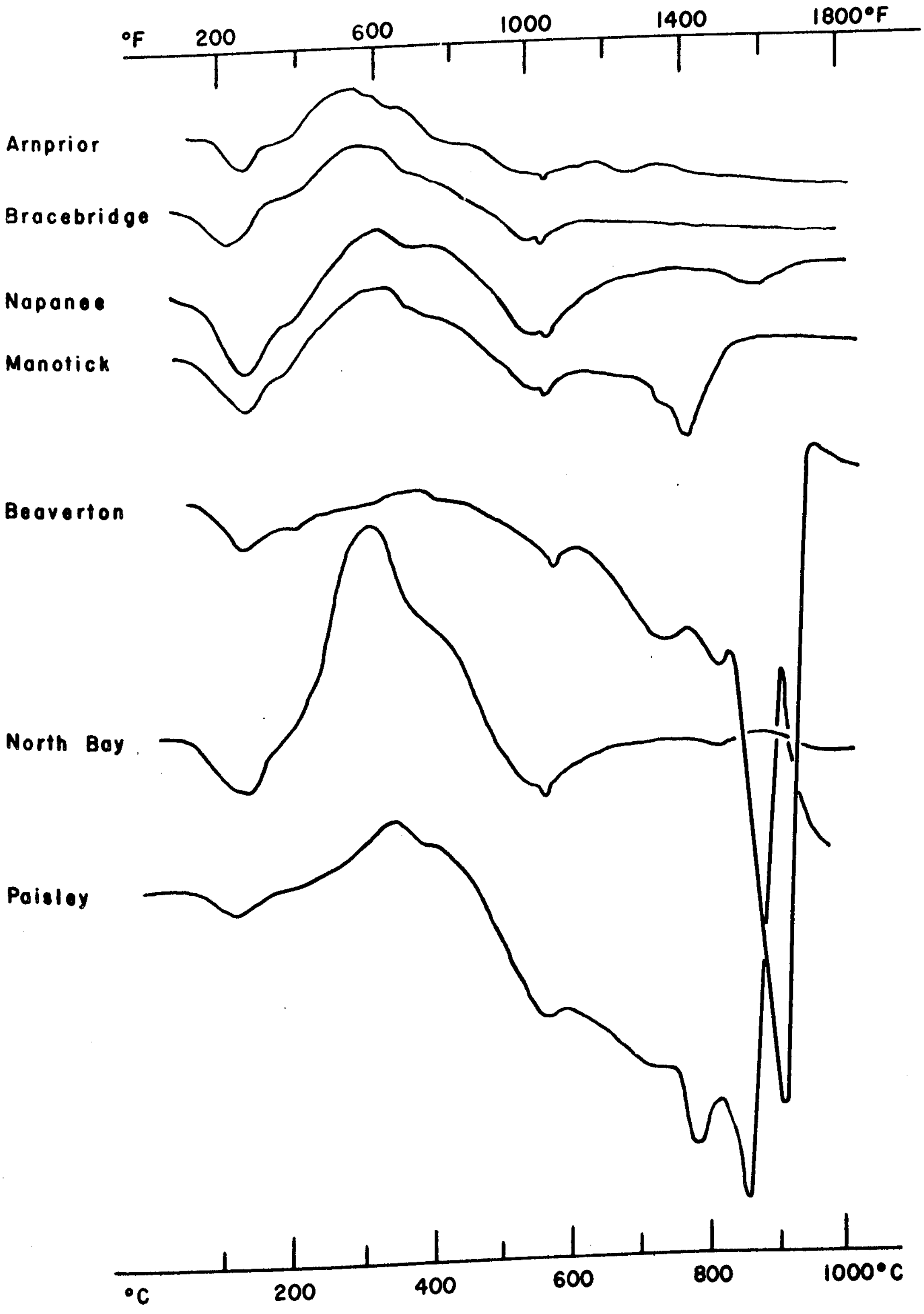


Figure 6. DTA curves of north-central clays.

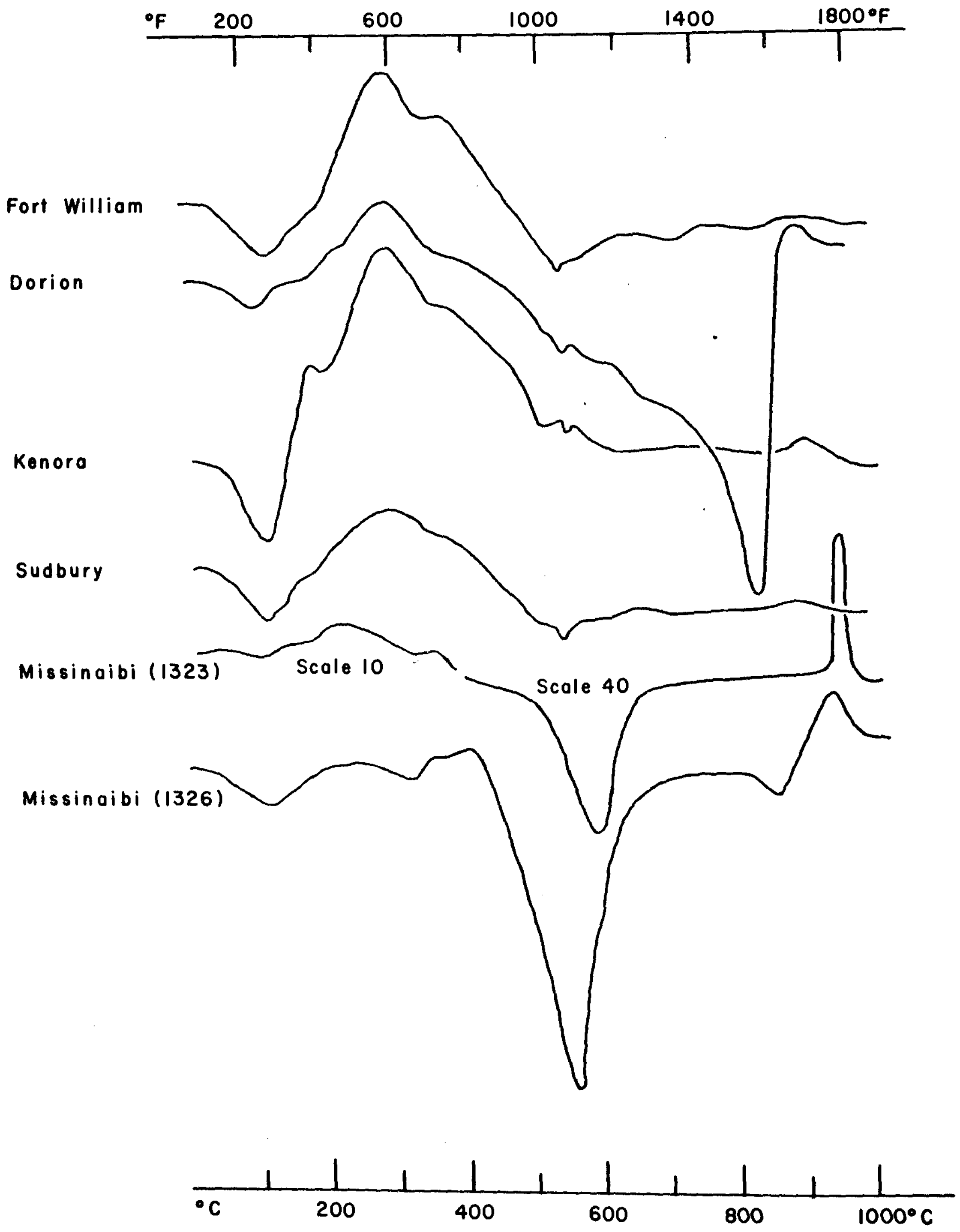


Figure 7. DTA curves of northwestern and northern clays.

"Highlands" are quite rich in carbonate minerals. The carbonate peaks for Elginfield (blue) in Figure 5 are extremely large and indicate that it contains a large amount of dolomite and calcite. In this curve, the lowermost portion of the 900°C endothermic peak caused by the decomposition of $CaCO_3$ has been inverted in order to retain it on the diagram. The adsorbed water peaks for the clays are larger on the average than those for the shales, indicating that water is adsorbed more readily by the former. The curves also show that the clays contain more oxidizable material than the shales and that it is usually of the type which is readily burnt out at low temperatures.

The clays from northern and northwestern Ontario exhibit curves that generally have small, broad clay reaction peaks at about 600°C, and carbonate peaks which are small or lacking entirely (Figures 6 and 7). The minute peak caused by the inversion of the low to the high form of quartz at 573°C appears on some of the curves. The Missinaibi clays differ from other samples in that the principal DTA reactions at approximately 600°C (endothermic) and 950°C (exothermic) are produced mainly by the kaolin group constituents.

X-Ray Diffraction Analysis

The general principles underlying the identification and characterization of the major clay mineral groups by X-ray diffraction have been outlined by Brindley (55), Warshaw and Roy (56), and various other workers. The results of the application of these techniques to the Ontario clay and shale samples are given in Tables 9 to 12. The relative abundance of the various clay minerals, as shown by the lettering system, must be considered to be, at best, a rough approximation because of the variation in crystallinity which is commonly encountered among these layer silicates.

Table 9 indicates that the principle clay mineral constituents of the unaltered Dundas-Meaford, Queenston and Hamilton shales are illite (dioctahedral) and chlorite (trioctahedral). The diffractograms illustrated in Figure 8 are typical of those obtained from all Hamilton shale samples and suggest that the clay mineral fraction of this formation consists entirely of illite and chlorite crystallites having relatively thick, uninterrupted sequences of 10 and 14 Å layers respectively. Similar results have been obtained by Towe (57) in New York state. On the other hand, Allen and Johns (3) have reported that one of their Hamilton formation samples from Thedford, Ontario, contained illite which yielded a 10 Å reflection which was asymmetrically broadened toward low Bragg angles, indicating the presence of a significant proportion of expandable layers.

The latter situation was, however, much more common among the older shales. Mixed-layer systems containing expandable phases were identified in seven of ten samples of Queenston and Dundas-Meaford shales or reworked shales. In the case of the weathered and reworked Queenston shales from Aldershot the development of mixed-layer systems by weathering has proceeded to the point where the entire trioctahedral clay

TABLE 9

X-ray Diffraction Analysis of Palaeozoic Shales and Reworked Shales

Sample and Per Cent Plus 200 Mesh	Illite	Chlorite	Kaolin	Mixed-Layer Clay Minerals and Miscellaneous Constituents	Quartz		Plagioclase		K-Feldspar		Calcite		Dolomite		Hematite
					Wh.	C.F.	Wh.	C.F.	Wh.	C.F.	Wh.	C.F.	Wh.	C.F.	Wh.
Ottawa (Q) +	A	B			B		D				D				F*
Grimsby (weathered Q) 3.2% (o)	A	B			C		G				D				
Streetsville (Q) +	A	B		Anatase (G)*	B		E		G*		D				F*
Georgetown (Q)	B	C		Illite-Verm. (D) Anatase (G)	B		F		G		C		E		G
Milton (Q) (o)	A	B		Illite-Verm. (D)	C						D		G		G
Nelson (Q) +	A	B			B		G				C		G		G*
Owen Sound (Q)	A	C		F. E. Verm.-Illite (D)	C						C		D		G
Aldershot (Iroquois) 9.95% (x)	A			F. E. Chlorite-Verm. (C)	B	B	D	B	G	F					G
Aldershot (weathered Q) 7.75% (x)	A			F.E. Chlorite-Mont.-Verm.(B)	B	B	D	B	G	F	F	C			G
Reformatory (D-M)	A	B			C		E				E		G		
Toronto (Reformatory) 4.95% (o)	B	C		Chlorite-Verm. (D) Anatase (G)	C	B	E	C		G	E	D			
Toronto Brick (D-M)	A	B		F. E. Chlorite-Mont. (D)	C		F				F				
Booth (D-M) +	B	B		Anatase (G)* Pyrite (G)*	B		D		G*		E		F		
Cooksville (D-M)	A	B		Pyrite (DTA) Organic Material (DTA)	C		E				D		G		
Arkona (552) (o)	A	B		Pyrite (G)	C	D	G				C	A	G		
Arkona (553)	A	B		Pyrite (G) Anatase (G)	C	D	G	G			E	B	G	G	
Arkona (554)	A	B		Anatase (G)	B		G				D		E		
Parkhill (Hamilton)	A	B		Pyrite (G) Anatase (G) Organic Material (DTA)	C	D	G				D	B	F		
Thedford (Hamilton) (o)	A	B			C		G				C		G		
Billings +	B	B		Pyrite (E) Organic Material (DTA)	B		D				E				
Carlsbad +	B	B		Pyrite (F) Anatase (G)* Organic Material (DTA)	B		D		G*		D		F*		
Rockcliffe +	B	B			B		F*		B		D		F*		
Kettle Point	C	C	D	Pyrite (D) Marcasite (E) Jarosite (G) Organic Material (DTA)	B		F								

Samples previously studied by Sadler (5) designated by (+); additions to Sadler's data by R. S. Dean designated by asterisk. Remainder of table by R. S. Dean with exception of differential thermal analysis (DTA) notes by J. G. Brady.

Clay minerals determined in minus 5-micron fraction. Other minerals determined in whole sample (Wh.) and, where shale disaggregation was complete , in plus 200 mesh coarse fraction (C.F.). Mineral abundances in each size range estimated from A (very abundant) to G (trace).

Abbreviations: Verm.- vermiculite; Mont. - montmorillonoid; F. E. - "frayed edge" type mixed-layer clay mineral.

Abundance of mica flakes within plus 200 mesh fraction indicated as follows: (xxx) fairly common; (xx) rare; (x) trace; (o) not detected.

TABLE 10

X-Ray Diffraction Analysis of Southern Ontario Clays

Sample and Per Cent Plus 200 Mesh	Illite	Chlorite	Kaolin	Mixed-Layer Clay Minerals and Miscellaneous Constituents	Quartz		Plagioclase		K-Feldspar		Calcite		Dolomite		Amphibole	
					Wh.	C.F.	Wh.	C.F.	Wh.	C.F.	Wh.	C.F.	Wh.	C.F.	Wh.	C.F
Kingsville 10.45% (o)	B		D	F. E. Mont.-Chlorite (C) Mont.-Illite (C)	B		F		G							
Stevenson 10.35% (o)	A		D	F. E. Mont.-Chlorite-Illite (C) Organic Material (DTA)	C	A	F	C	G	F						G
Tilbury	B			F. E. Verm.-Chlorite (C)	A		F		F							
Tupperville 2.05% (x)	B	D		F. E. Chlorite-Verm.-Mont. (B)	B	A	E	D	G	E	E	D	E	F		
Wilkesport 2.20% (o)	B	D		F. E. Chlorite-Verm.-Illite (C)	B	B	F	D	G	F	D	D	D	E		
Dresden (brown) 4.0% (x)	A	D		F. E. Chlorite-Mont. (C)	B	B	E	C	G	E	C	C	D	F		
Essex (blue) 14.15% (o)	A	B	D	Pyrite (DTA) Organic Material (DTA)	B	B	D	D	G	F	C	D	C	D	G	
Fletcher 10.10% (o)	A		D	F. E. Chlorite-Illite-Verm. (B) Organic Material (DTA)	C	A	F	C	G	F						
Dresden (blue) 12.0 (o)	A			F. E. Chlorite-Verm.-Mont. (C) Organic Material (DTA)	B	B	F	E			E	D	E			
Elginfield (brown) 0.7% (x)	C	D		F. E. Mont.-Verm. (C) F. E. Chlorite-Mont. (C)	B	A	C	B	E	F	G	G			G	
Brownsville 2.25% (xxx)	C	D		F. E. Verm.-Chlorite-Mont. (C) Illite-Verm. (C)	C	A	E	B	G	E	D		G		G	G
Forest 10.15% (x)	B	C		F. E. Verm.-Illite (C) F. E. Chlorite-Mont.-Verm. (C)	C	A	F	C	G	E	D	D	D	E		
St. George 0.85% (xx)	C	D		F. E. Chlorite-Verm. (C) F. E. Illite-Verm. (D)	C	B	E	D	G	F	C	D	F	E		
Norwich 0.15%	A	B		F. E. Chlorite-Mont. (D)	C	B	D	C	F	F	B	C	C	D	G	
Wallenstein 1.0% (x)	C	D		F. E. Mont.-Verm. (C) F. E. Mont.-Chlorite (C) Organic Material (DTA)	B	B	E	C	F	E	C	E	D	D		G
Elginfield (blue) 1.45% (xx)	B	B		F. E. Verm.-Mont. (D)	C	C	D	D	G	G	B	B	B	D	G	
Petrolia 0.9% (o)	C	C		F. E. Illite-Verm. (C) Chlorite-Mont. (D) Organic Material (DTA)	B	B	G	E		G		F		G		
Paisley 0.35% (x)	B	C		F. E. Chlorite-Verm.-Illite (C) Illite-Mont. (D)	C	B	F	C	G	G	C	D	D	B		

Mineralogy by R. S. Dean with exception of differential thermal analysis (DTA) notes by J. G. Brady.

Clay minerals determined in minus 5-micron fraction. Other minerals determined in whole sample (Wh.) and in plus 200 mesh coarse fraction (C.F.). Mineral abundances in each size range estimated from A (very abundant) to G (trace).

Abbreviations: Verm. - vermiculite; Mont. - montmorillonoid; F. E. - "frayed edge" type mixed-layer clay mineral.

Abundance of mica flakes within plus 200 mesh fraction indicated as follows: (xxx) fairly common; (xx) rare; (x) trace; (o) not detected.

TABLE 11

X-ray Diffraction Analysis of Clays Occurring Upon or Near the Canadian Shield

Sample and Per Cent Plus 200 Mesh	Illite	Chlorite	Verm.	Mont.	Mixed-Layer Clay Minerals	Quartz		Plagioclase		K-Feldspar		Calcite		Dolomite		Amphibole	
						Wh.	C.F.	Wh.	C.F.	Wh.	C.F.	Wh.	C.F.	Wh.	C.F.	Wh.	C.F.
Arnprior	C				Mont.-Verm. (B) Illite-Verm. (D)	D		B		E						E	
Bracebridge 2.35% (x)	B			C	Verm.-Mont. (D) Illite-Mont. (D)	D	B	B	A	F	E					F	G
Napanee 4.15% (xx)	D				F. E. Mont.-Chlorite (C) Illite-Verm. (C) Illite-Mont. (D)	E	A	E	B	G	E					G	G
Manotick	C			C	Verm.-Chlorite (D)	B		B		D		G				F	
Beaverton 3.55% (x)	C	D			Mont.-Verm. (B) Mont.-Chlorite (C) Illite-Verm. (D)	E	B	D	B	G	E	B	D	F (DTA)		G	
North Bay	C				Verm.-Illite (C) F. E. Chlorite-Verm. (C)	B		B		D						G	
Fort William 14.4% (xxx)	D	D	B	C	Mont.-Verm. (C)	C	B	C	B	G	G	F (DTA)				G	G
Dorion	D	D			Mont.-Verm. (B) Chlorite-Verm. (C)	C		B		G		D		D		G	
Kenora	D			A	Chlorite-Verm. (D)	D		C		E						G	
Sudbury	C	D			Illite-Mont. (C) F. E. Chlorite-Verm. (C)	B		B		F						G	

Mineralogy by R. S. Dean with exception of differential thermal analysis (DTA) notes by J. G. Brady.

Clay minerals determined in minus 5-micron fraction. Other minerals determined in whole sample (Wh.) and in plus 200 mesh coarse fraction (C.F.). Mineral abundances in each size range estimated from A (very abundant) to G (trace).

Abbreviations: Verm. - vermiculite; Mont. - montmorillonoid; F. E. - "frayed edge" type mixed-layer clay mineral.

Abundance of mica flakes within plus 200 mesh fraction indicated as follows: (xxx) fairly common; (xx) rare; (x) trace; (o) not detected.

TABLE 12

X-ray Diffraction Analysis of Cretaceous Kaolinitic Clays From the Missinaibi River Valley

Sample and Per Cent Plus 200 Mesh	Illite	Kaolin	Quartz	Anatase	Hematite	Siderite	Rutile	Alunite
Missinaibi (1323) 9.7% (o)		A	C	F	G			
Missinaibi (1326) 5.9% (o)	B	B	B	F	G	E	G	F

Mineralogy by R. S. Dean. All minerals determined in whole sample. Mineral abundancee estimated from A (very abundant) to G (trace).

Abundance of mica flakes within plus 200 mesh fraction indicated as follows: (xxx) fairly common; (xx) rare; (x) trace; (o) not detected.

Figure 8. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Arkona (552) shale.

Co/Fe radiation; recorder scale factor - 1; time constant - 16; scanning speed 1° 2θ/minute; 1° slits; Geiger counter detector.

Scan 1 - Untreated (air dry)
Scan 2 - Heated for 1/2 hour at 580°C
Scan 3 - Boiled in concentrated HCl

Mineral constituents listed in Table 9.

mineral (chlorite) fraction has been affected.

The effects of shale chlorite alteration may be illustrated by the diffractograms of the weathered or reworked Dundas-Meaford Toronto (Reformatory) shale. The 13.5 Å reflection recorded from the heat-treated mount (Figure 9, Scan 2) represents the unweathered portion of the chlorite. The remainder of the original shale chlorite, which has been altered to a mixed-layer chlorite-vermiculite, contributes to the asymmetrical diffraction band which extends from the 13.5 Å position toward larger Bragg angles. The effect of similar heat treatment upon unaltered Hamilton shale chlorite is shown in Figure 8, Scan 2.

All trioctahedral phases (chlorite and its alteration products) were completely decomposed by the hydrochloric acid treatment. The absence of 7.1 and 3.57 Å reflections from the acid-treated material (Figures 8 and 9, Scan 3) indicates that kaolin group clay minerals were not present in detectable quantities.

The minus 5-micron fraction of samples collected from the various shale units invariably yielded X-ray powder patterns characteristic of both $2M_1$ and IM muscovite polymorphs (58). These were most readily recognizable among the younger (Devonian) shales. The widespread occurrence of this mixture is in accord with the observations of Towe (57) and Dean (59) in New York State and Quebec respectively.

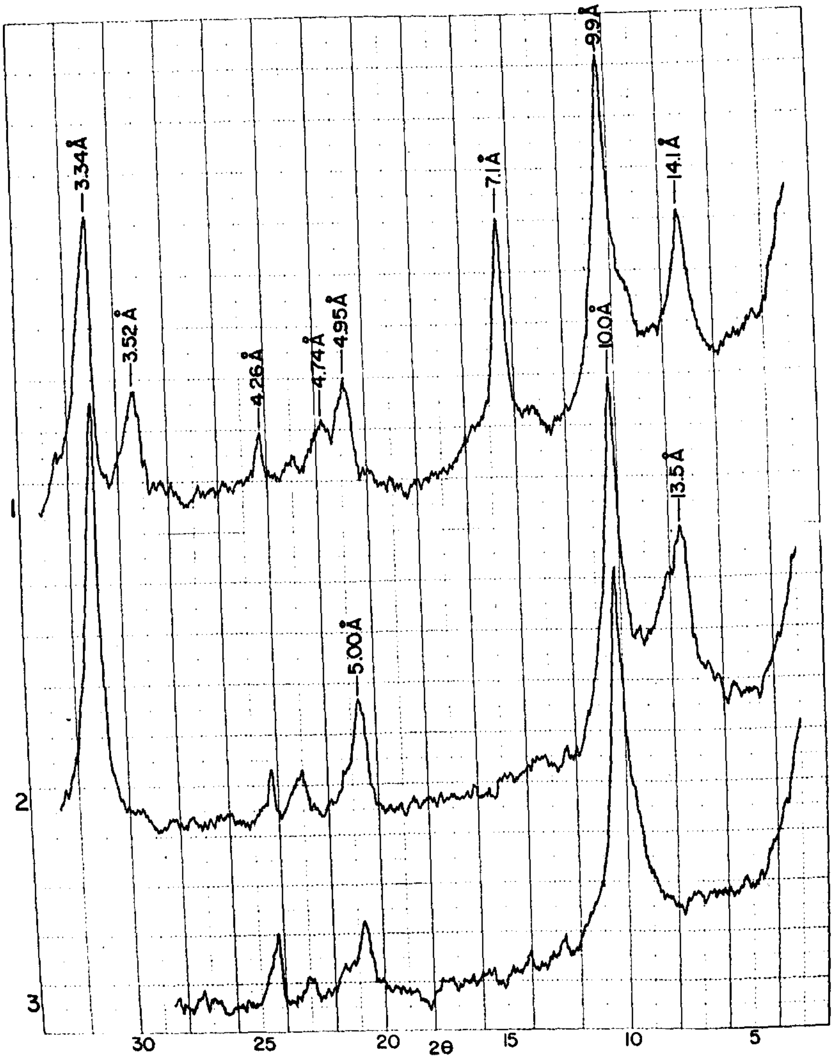


Figure 9. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Toronto (Reformatory) weathered or reworked shale.

Co/Fe radiation; recorder scale factor - 1; time constant - 16; scanning speed 1° 2θ/minute; 1° slits; Geiger counter detector.

Scan 1 - Untreated (air-dry)
Scan 2 - Heated for 1/2 hour at 580°C
Scan 3 - Boiled in concentrated HCl

Mineral constituents listed in Table 9.

The Kettle Point sample is distinctive in that it contains a mixture of illite and chlorite which is apparently accompanied by minor kaolin. Moreover, the total clay mineral content appears to be less than that of the older shales. Finally, the Kettle Point chlorite is quite poorly crystallized and seems to respond partially to the differential dissolution test for interlayer alumina (52). This phenomenon is responsible for any uncertainty attached to the identification of kaolin within the Kettle Point sample, since this is based upon the assumption that chloritic phases are invariably decomposed by boiling concentrated hydrochloric acid.

The subdivision of the Pleistocene clays of Ontario into the groups listed in Tables 10 and 11 is of genetic, as well as areal, significance. Gravenor (60) has noted that the clay content of tills increased rapidly beyond the point where the Wisconsin ice sheet had first come into contact with the Palaeozoic shales. This evidence, together with the recognition of certain mineralogical similarities between the clays and shales, indicates that the major portion of the clay mineral fraction of the southern Ontario clay samples listed in Table 10 has been derived from the underlying Palaeozoic strata, whereas the remaining clays (Table 11) have been derived from the rocks of the Canadian Shield.

The clay minerals within the southern Ontario clays exhibit ample evidence of both their Palaeozoic sedimentary rock origin and the effects of weathering alteration. Three of the samples (Elginfield (blue), Essex (blue), and Norwich) which were collected from the greatest depth below the surface bear a striking mineralogical resemblance to the Palaeozoic shales. In these cases, the alteration of illite and chlorite is comparable to that observed within the weathered or reworked Dundas-Meaford shale from the Ontario Reformatory at Toronto (Figure 9) and certainly less than that noted within the weathered and reworked Queenston shale samples from Aldershot (Table 9).

X-ray diffractograms of the Norwich clay are illustrated in Figure 10. Partial alteration of chlorite has, apparently, led to the development of the mixed-layer chlorite-montmorillonoid which yields a 17.0 - 14.1 Å diffraction band following glycol saturation (Figure 10, Scan 2).

The lower stability of trioctahedral clay minerals relative to the dioctahedral varieties during weathering has been noted by many workers, including Jackson et al. (61) and Droste (62). The diffractograms of the Wilkesport clay (Figure 11), which is a composite sample from the pit working face down to a depth of about 10 feet, illustrate a typical case where the alteration of trioctahedral chlorite is fairly well advanced while dioctahedral illite remains apparently unaffected. The development, following glycol saturation, of a 14 Å reflection with a band extension toward larger Bragg angles (Figure 11, Scan 2) suggests the presence of a mixed-layer vermiculite-illite. The presence of a chlorite phase is indicated by the 13.8 - 10 Å band which was observed following heat treatment (Figure 11, Scan 3), while the association of the previously

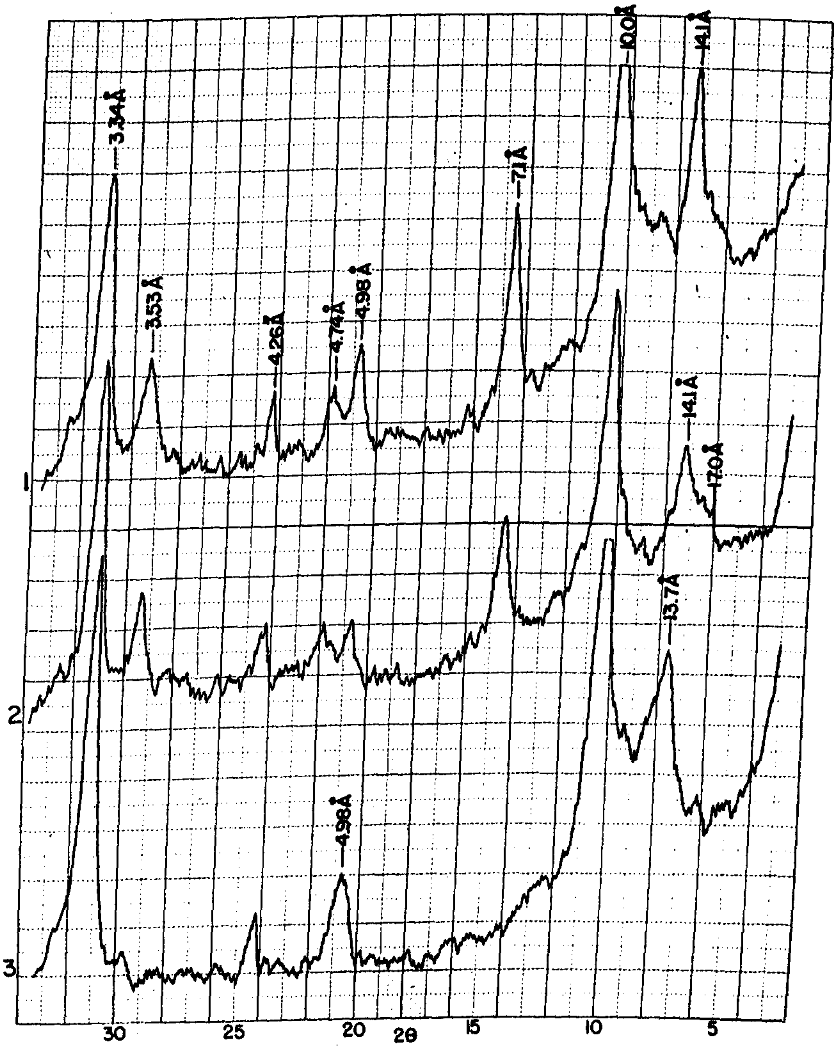


Figure 10. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Norwich clay.

Co/Fe radiation; recorder scale factor - 1; time constant - 16; scanning speed 1° 2θ/minute; 1° slits; Geiger counter detector.

Scan 1 - Untreated (air-dry)
Scan 2 - Ethylene glycol saturated
Scan 3 - Heated for 1/2 hour at 580°C

Mineral constituents listed in Table 10.

Figure 11. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Wilkesport clay.

Co/Fe radiation; recorder scale factor - 1; time constant - 16; scanning speed 1° 2θ/minute; 1° slits; Geiger counter detector.

Scan 1 - Untreated (air-dry)
Scan 2 - Ethylene glycol saturated
Scan 3 - Heated for 1/2 hour at 580°C
Scan 4 - Boiled in concentrated HCl

Mineral constituents listed in Table 10.

recognized vermiculite-illite with the chlorite is suggested by the apparent failure of the heat treatment to increase, significantly, the intensity of the 10 Å reflection and by the demonstration that the chlorite was part of a system containing a phase (or phases) which would collapse toward 10 Å when heated. The results of the hydrochloric acid treatment (Figure 11, Scan 4) support the view that the chlorite-vermiculite-illite system is trioctahedral and indicate the absence of kaolin.

Reference to Tables 9 and 10 indicates that 3-component mixed-layer systems, such as that described above, are common weathering alteration products of the Palaeozoic rock chlorite. In general, it would appear that, during the alteration process, individual layers (or portions of these) within the chlorite crystallites tended to assume varied states of hydration and thus gave rise to mixed-layer systems such as chlorite-vermiculite-montmorillonoid or, in cases where a tendency existed toward interlayer dehydration and collapse to 10 Å, to chlorite-vermiculite-illite. This postulated transformation of chlorite to trioctahedral expandable phases is in agreement with previous observations that the metal-hydroxyl complex (usually referred to as the 'brucite' layer) which occurs as a unit separate from the talc-like silicate layer (63, p. 245) is selectively attacked during weathering (64).

Early studies of the weathering of layer silicates revealed that, in many instances, the alteration generally first affected the outer edges of the crystallites and subsequently proceeded inward parallel to the basal cleavage planes toward the central, or "core", region (65). The selective attack in this manner upon the 'brucite' layer of chlorites and the interlayer cation (K^+) of mica results in what is commonly referred to as a "frayed edge" structure (66, p. 30).

The diffraction of X-rays by a "frayed edge" layer silicate has been described by MacEwan (67, p. 98) who considered a partially hydrated mica having:

> " .... a more or less unaltered core, and a gradually increasing hydration towards the outside of the particle. Such a structure would give a sharp 10 Å reflection due to the core, with a series of overlapping satellite bands of increasing mean spacing due to the hydrated shells."

The X-ray diffractometer studies indicate frequent occurrences of "frayed edge" structures among the Ontario clays. An excellent example is furnished by the mixed-layer chlorite-vermiculite-illite within the Wilkesport sample which, when heated (Figure 11, Scan 3), yielded a continuous band extending between 10 and 13.8 Å rather than the distinct 001/001 intensity maximum which would be expected from a uniform, randomly interstratified mixture of 14 Å chlorite and 10 Å illite and collapsed vermiculite layers (68, p. 414).

In accordance with the "frayed edge" concept, selective destruction of the 'brucite' layer within the Wilkesport chlorite by weathering has proceeded in such a way as to produce a lateral gradational zoning within each crystallite. The unaltered 'brucite' occurs as patches or "islands" (69, p. 87) which are most abundant in the vicinity of the crystallite "core".

Heat treatment collapsed all 'brucite' - free interlayer space and caused the chlorite phase to make a stronger intensity contribution to its "pure state" 14 Å line (70, p. 26). Each heated crystallite therefore contains a series of random mixed-layer systems, with the relative proportions of the two phases varying continuously and progressively from the (13.8 Å) "core" to the outer (10 Å) limit of the "frayed edge". The relative contribution to the various parts of the 13.8 - 10 Å band will vary among individual crystallites of weathered chlorite, according to their stage of alteration.

The reflections obtained at 7.04 and 3.51 Å from the untreated Wilkesport clay (Figure 11, Scan 1) correspond to the higher basal orders of chlorite and are most probably due to the occurrence of the residual 'brucite' patches within layer sequences in which the basal spacing has remained close to that of the original chlorite (approximately 14 Å).

The chlorite-montmorillonoid within the Norwich clay is probably also a "frayed edge" mixed-layer. In this instance, some or all of the chlorite crystallites have, presumably, been marginally altered to the interstratified system, with the montmorillonoid patches concentrated along the crystallite margins.

The degree of clay mineral alteration was found to vary widely among the shallower southern Ontario clays. X-ray diffractograms of the near-surface Fletcher sample (Figure 12) indicate that weathering has resulted in the alteration of chlorite to a "frayed edge" chlorite-illite-vermiculite without noticeable effects upon illite. The degree of clay

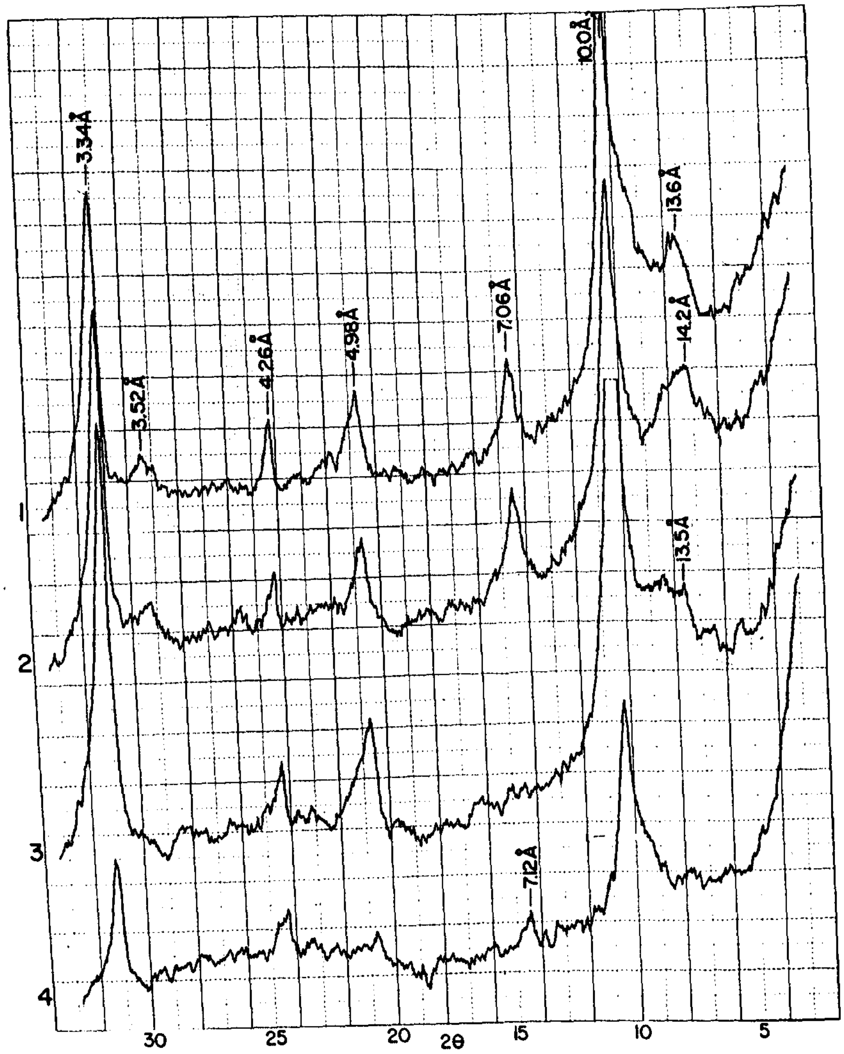


Figure 12. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Fletcher clay.

Co/Fe radiation; recorder scale factor - 1; time constant - 16; scanning speed 1° 2θ/minute; 1° slits; Geiger counter detector.

Scan 1 - Untreated (air-dry)
Scan 2 - Ethylene glycol saturated
Scan 3 - Heated for 1/2 hour at 580°C
Scan 4 - Boiled in concentrated HCl

Mineral constituents listed in Table 10.

mineral alteration in this sample is generally comparable to that observed within the Wilkesport clay (Figure 11).

In the case of the Kingsville shallow clay, weathering alteration appears to have affected both illite and chlorite components. The 14-10 Å band which was recorded from the heated clay (Figure 13, Scan 3) suggests that the more extensively altered chlorite has been transformed into a "frayed edge" mixed-layer. The expandable phase within the latter system was tentatively identified as montmorillonoid rather than vermiculite when no appreciable intensity re-enforcement of the 14 Å "pure state" line was noted following glycol saturation (Figure 13, Scan 2). However, in the presence of a second major mixed-layer system, the possibility that the altered chlorite might contain undetected layer types in addition to chlorite and montmorillonoid cannot be excluded.

The diffractograms of the Kingsville clay also show that the 14 - 10 Å band obtained from the heated sample (Figure 13, Scan 3) is quite similar in intensity and profile to that recorded from the same powder which had also been subjected to the treatment described by Hashimoto and Jackson (52) for the removal of aluminous interlayer material (Figure 13, Scan 4). This result is typical of those obtained from the Ontario clays, and served to confirm the ferro-magnesian composition of the chlorite phase interlayer.

The second mixed-layer system within the Kingsville clay is listed in Table 10 as a montmorillonoid-illite and is thought to represent the

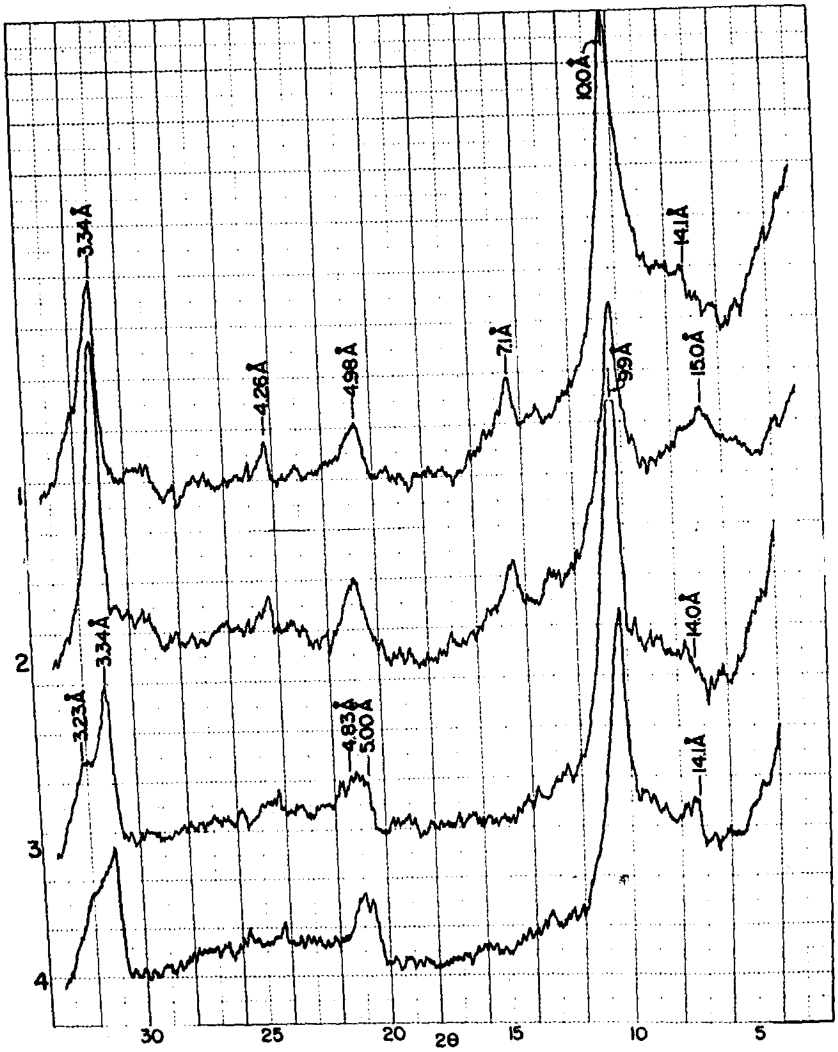


Figure 13. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Kingsville clay.

Co/Fe radiation; recorder scale factor - 1; time constant - 16; scanning speed 1° 2θ/minute; 1° slits; Geiger counter detector.

Scan 1 - Untreated (air-dry)
Scan 2 - Ethylene glycol saturated
Scan 3 - Heated for 1/2 hour at 580°C
Scan 4 - 4 hours at 420°C, 2.5 minutes 0.5N NaOH boil (52) followed by heating for 1/2 hour at 580°C

Mineral constituents listed in Table 10.

weathering alteration product of the (dioctahedral) illite. The interstratification of these two layer types is indicated by the sharp increase in the intensity of the 3.34 Å reflection from the glycol-saturated clay (Figure 13, Scan 2) relative to that obtained from the air-dry material. The enhancement of this particular reflection is due to the coincidence of the 003 reflection from 10 Å illite with the 005 reflection from 16.7 Å glycol-montmorillonoid layers within the same mixed-layer system. The broad 15 Å peak obtained from the glycol-saturated Kingsville clay represents the 001/001 montmorillonoid-illite reflection as well as a 001/001 contribution of unknown intensity and spacing from the montmorillonoid-chlorite system. The 10 Å peak from the glycol-saturated mount (Figure 13, Scan 2) represents the Kingsville clay illite which was not involved in the montmorillonoid-illite mixed-layer system. The broad reflections occurring at 5.00-4.83 and 3.34-3.23 Å which were recorded from the heated clay (Figure 13, Scan 3) are due to the collapse of montmorillonoid layers of the montmorillonoid-illite to variable basal spacings between 10.0 and 9.7 Å as a result of the partial replacement of interlayer K^+ by smaller cations.

The Kingsville, Essex (blue), Stevenson and Fletcher clays are also interesting in that they contain minor quantities of kaolin. The weak 7.12 Å reflection obtained from the Fletcher sample was apparently unaffected by several successive treatments with boiling concentrated hydrochloric acid (Figure 12, Scan 4). Similar quantities of kaolin were detected within the three other samples, all of which had been collected from a flat clay plain within the extreme southwestern corner of the province. According to Guillet (2, p. 19), these extensive clay deposits were formed when the uppermost few feet of local glacial tills were reworked to a stone-free clay by the waters of proglacial lakes.

The clay mineral assemblages within the more highly altered southern Ontario samples (such as Kingsville) resemble more closely those within the Shield-derived clays than the illite-chlorite mixture within the presumed parent material. A seemingly reliable indication of clay mineral provenance was, however, provided by the X-ray powder patterns of the clay micas. In the case of each sample listed in Table 10, regardless of the apparent degree of weathering alteration, the sharpness (or definition) of the mica reflections at 4.49 and 1.50 Å and of the doublet or band at 2.59-2.57 Å was comparable to that which, invariably, has been observed among the Palaeozoic shales of both Quebec (59) and Ontario. It would appear that these reflections are largely contributed by the portion of the shale illite which is more resistant to weathering alteration.

Several of the clays occurring within the area of the Canadian Shield yielded diffractograms which are not unlike those obtained from the more highly weathered southern Ontario samples. The Guinier X-ray powder patterns reveal, however, that among Shield-derived samples the clay mineral crystallites appear to be highly disordered as a result of random layer displacements parallel to the *ab* crystallographic plane and structural discontinuities within individual silicate layers. In most instances, only weak diffuse bands were observed in the vicinity of 4.49 and 2.59-2.57 Å and the 1.50 Å reflection was either very weak or absent. The presence of these characteristics in the clay minerals of the Beaverton, Napanee and Manotick samples suggests that these are Shield-derived clays, and therefore belong in Table 11 in spite of the fact that they occur within areas underlain by Palaeozoic rocks.

The clays which were derived from the Canadian Shield are mineralogically more diversified than those derived from Palaeozoic strata. The Shield clay samples listed in Table 11 are generally deficient in illite and chlorite and rich in expandable clay minerals, the latter occurring either as constituents of mixed-layer systems or as separate crystallites.

The X-ray diffractograms obtained from the untreated Dorion clay (Figure 14, Scan 1) revealed a prominent 14.2 Å reflection which represents, as suggested by subsequent tests, a mixture of montmorillonoid-vermiculite, chlorite-vermiculite and chlorite. The Kenora sample (Figure 15) contains an even greater proportion of expandable layers, most of which occur as unmixed montmorillonoid.

Diffuse basal reflections were obtained from the layer silicates within some of the Shield clay samples, such as Kenora (Figure 15). This broadening indicates an effective thinning of the clay mineral crystallites, i.e. a reduction in the average number of silicate layers within the individual diffracting units.

The poor crystallinity and highly varied types of interlayering among the Shield clay minerals raise many doubts in connection with the

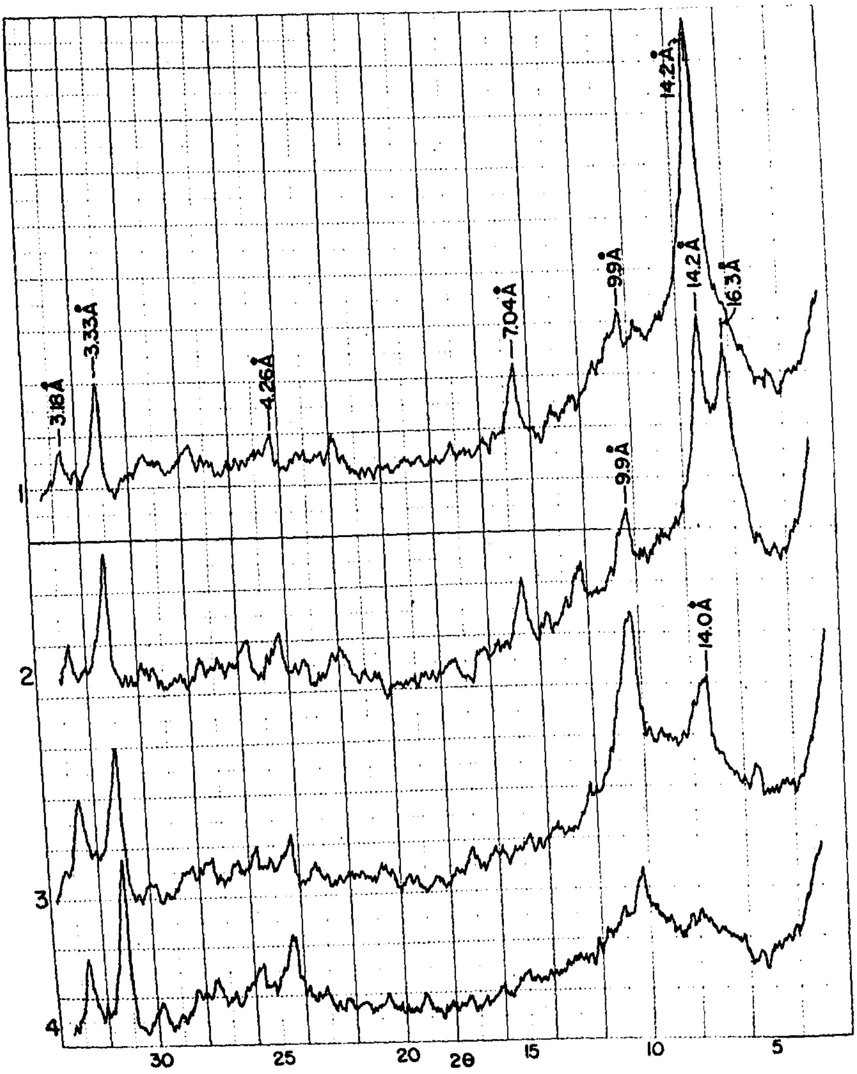


Figure 14. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Dorion clay.

Co/Fe radiation; recorder scale factor - 1; time constant - 16; scanning speed 1° 2θ/minute; 1° slits; Geiger counter detector.

Scan 1 - Untreated (air-dry)
Scan 2 - Ethylene glycol saturated
Scan 3 - Heated for 1/2 hour at 580°C
Scan 4 - Boiled in concentrated HCl

Mineral constituents listed in Table 11.

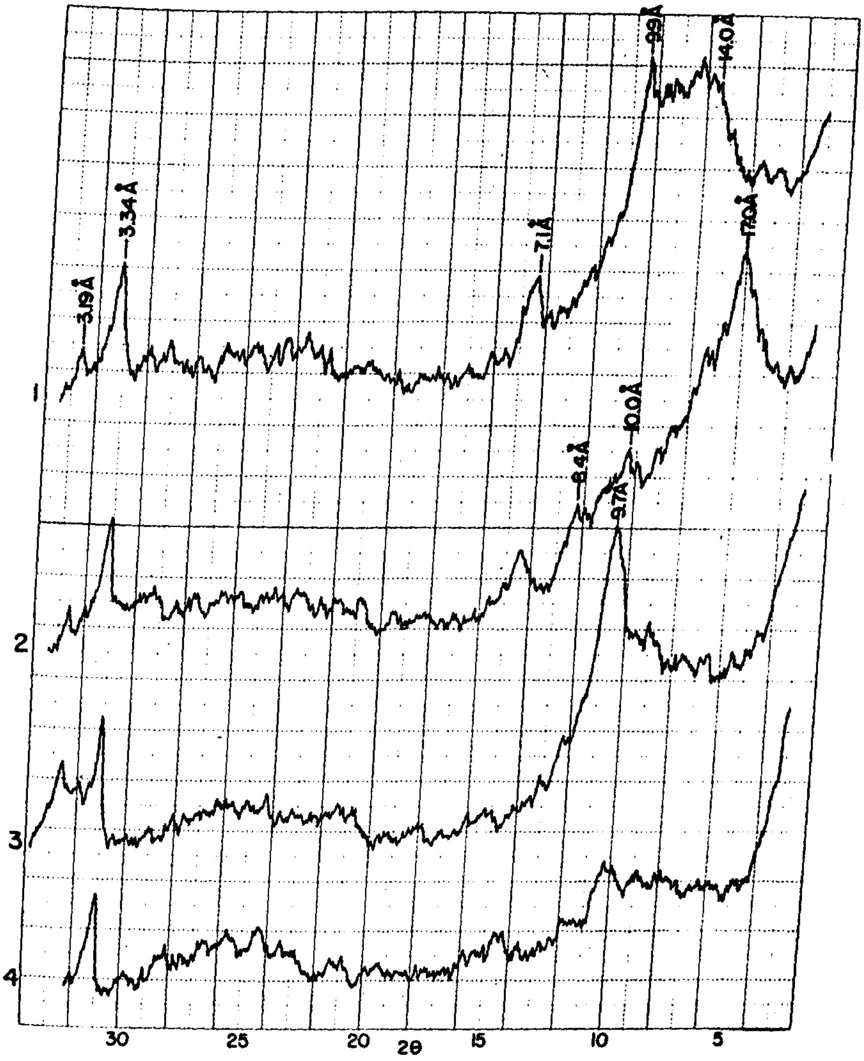


Figure 15. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Kenora clay.

Co/Fe radiation; recorder scale factor - 1; time constant - 16; scanning speed 1° 2θ/minute; 1° slits; Geiger counter detector.

Scan 1 - Untreated (air-dry)
Scan 2 - Ethylene glycol saturated
Scan 3 - Heated for 1/2 hour at 580°C
Scan 4 - Boiled in concentrated HCl

Mineral constituents listed in Table 11.

identification and characterization of particular phases or mixed-layer systems. As an example, considerable uncertainty is involved in the identification of the expandable phase or phases which are interlayered with chlorite in the Dorion clay (Figure 14) and interpretations other than that given in Table 11 are certainly possible, although the writers consider this to be the most likely arrangement. Again, in the case of the Arnprior clay (Figure 16), the nature of the interstratification between the montmorillonoid and vermiculite is difficult to deduce.

Most troublesome, however, is the general susceptibility of all Shield-derived clay minerals to decomposition by the hydrochloric acid treatment (Scan 4 of Figures 14, 15 and 16) and the poor quality of their transmission X-ray powder patterns. With the exception of the chlorite, or mixed-layer systems containing chlorite, no basis was found whereby dioctahedral and trioctahedral clay minerals could be distinguished.

Examination of Tables 9 to 11 indicates the existence of systematic variations in the distribution of certain non-clay minerals among the various groups of samples. K-feldspar and amphibole are most abundant within the Shield-derived clays, and the latter is entirely absent from the unweathered Palaeozoic shales. The occurrence of plagioclase is quite similar although, with the possible exception of the Queenston formation samples from Owen Sound and Milton, it is a minor constituent of all the Palaeozoic shale samples. The southern Ontario clays (Table 10) contain, as a group, intermediate quantities of these three minerals.

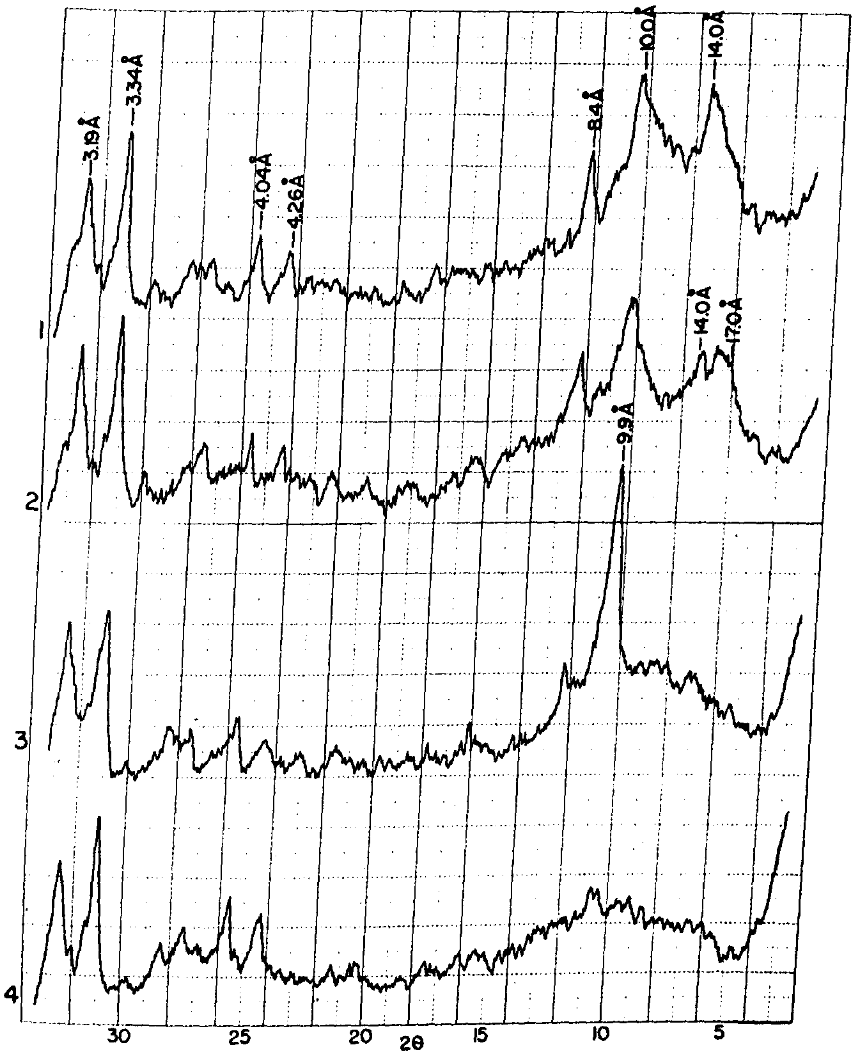


Figure 16. X-ray diffractograms of oriented mounts of minus 5-micron fraction of Arnprior clay.

Co/Fe radiation; recorder scale factor - 1; time constant - 16; scanning speed 1° 2θ/minute; 1° slits; Geiger counter detector.

Scan 1 - Untreated (air-dry)
Scan 2 - Ethylene glycol saturated
Scan 3 - Heated for 1/2 hour at 580°C
Scan 4 - Boiled in concentrated HCl

Mineral constituents listed in Table 11.

Quartz is generally less abundant and more erratically distributed within the Shield-derived clays than within the Palaeozoic shales or southern Ontario clays. The Napanee and Beaverton clays are notably deficient in quartz.

The results of the mineralogical analyses of the kaolinitic Cretaceous clays from the Missinaibi river valley are listed in Table 12. The major difference between the two samples is the presence, in Missinaibi (1326), of substantial quantities of illite. The X-ray powder photographs reveal that a considerable proportion of this illite consists of $2M_1$ muscovite. The kaolin within both samples is a fairly well crystallized member of the kaolinite-metahalloysite series.

DISCUSSION OF GEOLOGICAL-MINERALOGICAL RELATIONSHIPS

A previous mineralogical study of the Ordovician shales of the St. Lawrence Lowland of Quebec (59) has revealed that post-Trenton strata (which include nearly all of the important shale units) contain a uniform clay mineral suite consisting essentially of illite and chlorite together with plagioclase and considerable quartz within the fine (less than 2 micron) fraction. Geological evidence indicated that this suite was characteristic of the sediment which had been derived from the region of the Appalachian geosyncline to the southeast.

The results of the present investigation have extended the areal range of this distinctive post-Trenton Ordovician mineral suite westward to the vicinity of the Niagara escarpment and have revealed the essentially identical mineralogical constitution of the Devonian Hamilton shale. The mineralogy of the intervening strata remains to be determined.

Although any conclusions which are drawn with respect to the Upper Devonian Kettle Point shale must be based upon the single sample examined, the presence of kaolin suggests that the detrital constituents of this unit have been subjected to more prolonged and/or intense weathering than those of the underlying Hamilton formation. Stronger weathering may have also sharply reduced the quantity of mafic minerals reaching the basin of deposition and hence the ultimate abundance of ferro-magnesian chlorite (59, p. 184). It may be quite significant, moreover, that the NaOH differential dissolution procedure (52) did not unequivocally characterize the Kettle Point chlorite interlayer complex as entirely ferro-magnesian rather than aluminous.

It was found that the Pleistocene clays of Ontario could be subdivided into two groups on the basis of the origin of the major portion of their clay mineral fractions. The clays of the first group, which include all southern Ontario samples collected west of Toronto (Table 10), contain clay minerals which had largely been derived from Palaeozoic sedimentary rocks, whereas the clay minerals within the remaining samples (Table 11) were derived from the Canadian Shield. The principal basis of this subdivision was the identification, in the Guinier X-ray powder photographs, of certain reflections which were characteristic of the well crystallized fraction of the shale illite. Preliminary work in Quebec suggests, however, that these criteria may ultimately prove to be unreliable in areas where the Shield clay minerals have developed from glacial material containing appreciable quantities of mica.

It should be emphasized that the supposition of a Palaeozoic sedimentary rock origin is restricted to the bulk of the clay mineral fraction of the southern Ontario clays. Previous studies by Gravenor (60), Dreimanis et al. (71), and Dell (72) have indicated that, with the exception of sedimentary rock fragments, carbonates, sulphides, and gypsum, the bulk of the material coarser than fine sand within the glacial deposits of southern Ontario was derived from the Canadian Shield. In comparison with the clays of the Canadian Shield (Table 11), the unaltered Palaeozoic shales contained considerably less plagioclase and K-feldspar, and no detectable quantities of amphibole. It would therefore appear likely that the amphibole, and at least a portion of the plagioclase and K-feldspar, detected within the southern Ontario clays were derived from the Canadian Shield.

The presence of minor kaolin was noted in four clay samples which had been collected from the extreme southwestern portion of the province. Evidence that this kaolin had been derived from nearby Palaeozoic strata and was not a product of post-glacial weathering was provided by the Essex (blue) sample, which also contained an unaltered illite-chlorite clay mineral suite. Furthermore, the kaolin content of the four clays was very similar to that of the sample taken from the Kettle Point shale, which underlies extensive areas of the surficial deposits to the north and northeast of these sampling localities.

The diversity in the origins of the clay mineral and non-clay mineral fractions of the glacial deposits of southern Ontario is not entirely surprising, if consideration is given to the fact that the Palaeozoic rocks are, on the whole, deficient in coarser grained material whereas Shield-derived tills tend to be deficient in clay (60). It should be noted, however, that in any mixture of clays from both sources, detection of the Shield-derived clay minerals would be virtually impossible in the presence of appreciable quantities of Palaeozoic-type illite.

In considering the origin of the southern Ontario clays, it is also significant that, in the course of the final retreat of the Wisconsin ice sheet from this area, the direction of glacial movement was radially outward from the centres of two major ice lobes which occupied the Lake Huron and lower Great Lakes (Erie and Ontario) basins respectively (44, pp. 26-32). The restriction of these glaciation centres to areas underlain by sedimentary rocks, and their partial isolation from the main mass of the continental ice sheet, may have been important factors contributing to the predominance, within the latter-stage glacial deposits of southern Ontario, of clay minerals which had been derived from Palaeozoic strata. The influence of the direction of glacial transport on the mineralogy of the clays could be more positively evaluated by a study designed to reveal whether or not the change from Shield-derived to Palaeozoic sediment-derived clay minerals coincides with the boundary between the deposits laid down by the Huron or Erie ice lobes and the deposits of the Lake Simcoe-Kawartha Lakes ice sheet north of the Oak Ridges interlobate moraine. Similarly, it would be interesting to determine the approximate southwestern limit of the Shield-derived clay minerals within glacial tills that were laid down prior to the separation of the Wisconsin ice sheet into these lobes.

The degree of weathering alteration of the southern Ontario clay samples (Table 10) was highly variable, and was undoubtedly influenced by factors such as the conditions of local drainage, clay texture, and subsurface depth. The more labile trioctahedral chlorite was most readily attacked, with "frayed edge" mixed-layer systems of chlorite and expandable phases the usual product. Similar but less extensive alteration of illite was noted in many instances. These observations are in general agreement with those of Whittig and Jackson (73), Murray and Leininger (74), Droste (62), Droste and Tharin (75), and Droste et al. (76), who have studied the weathering of illite and chlorite in glacial deposits of the north-central United States. The present investigation did not, however, confirm the occurrence of the unmixed expandable clay minerals which were identified by these workers as the final products of weathering alteration. Nevertheless, it is entirely possible that these may occur within the highly weathered uppermost soil horizons which were generally not included in the ceramic clay samples.

The alteration of the highly unstable rock flour which had been produced by glacial erosion and grinding of the igneous and metamorphic rock assemblages of the Canadian Shield has resulted in the formation of the poorly crystallized layer silicates which are abundant within clays which were derived from this region. The reactions which have resulted in the formation of these clay minerals are considered by the writers to have taken place spontaneously within chemical systems consisting of rock flour and water. The effective spatial limits of the chemical system enclosing each individual particle would, presumably, have been restricted according to the permeability of the clay mass. If this were low, then local variations in rock flour composition would be reflected within the resultant clay mineral assemblage. Conceivably, this alteration may have begun during glacial transport. Leaching and oxidation are important in so much as they have affected the bulk composition of clays or have caused certain ions (such as Fe^{++}) to become inaccessible as oxides. In many respects, this process is analogous to that which was postulated in order to explain the origin of chlorite within the Ordovician shales of the St. Lawrence Lowland (59, pp. 180-188).

The two samples of Cretaceous Missinaibi clay were unique in view of their composition, genesis, and antiquity (2). Kaolin-bearing sedimentary deposits of varying age occur at widely scattered points upon and marginal to the Canadian Shield. These clays, together with the illite-kaolin - K-feldspar suite which occurs within pre-Trenton shales of the

St. Lawrence Lowland of Quebec (59), are typical products of the deep-weathering conditions which apparently prevailed over much of the Shield area in pre-glacial time.

The mineralogical data obtained in the course of the present investigation are, with several notable exceptions, in agreement with the results of previous studies. The identification of illite and chlorite as the principal clay mineral constituents of the Dundas-Meaford, Queenston and Hamilton shales, or their stratigraphic equivalents in Quebec and New York state, has been made by Allen and Johns (3), Sadler (5), Towe (57), and Dean (59). The recognition by the present writers of illite and chlorite as the principal original clay mineral constituents of the glacial deposits of southern Ontario, and the subsequent progressive alteration of these to mixed-layer systems by weathering, is supported by the results of several mineralogical investigations of tills within the northern United States, most pertinent among which is that of Droste (62). The results of the present investigation are also in good agreement with the conclusions reached by Gravenor (60) and Dell (72) regarding the origins of the clay and non-clay fractions of southern Ontario glacial deposits. The results of the mineralogical examination of clay samples from five localities within the Ottawa area by Brydon and Patry (4) were consistent with the conclusions drawn by the present writers regarding the mineralogy of Shield-derived clays.

Following a study of seven samples taken from various depths within the glacial deposits of southern Ontario, Webber and Shivas (77) reported that the clay minerals within the parent material of the soils of this region consisted of illite and montmorillonite, a conclusion which must be reviewed in the light of the results of the present investigation. Certain of the mineralogical identifications performed by Allen and Johns (3) may also be open to question. Most notably, no trace has been found, either in Ontario or Quebec, of the interstratified mixture of mica and chlorite identified by these workers within the Queenston shale at Milton and Streetsville and a clay deposit at Ottawa (among other localities). Furthermore, the proportion of unmixed vermiculite reported by these writers appears to have been, in general, greatly overestimated, usually at the expense of mixed-layer clay minerals.

DISCUSSION OF CERAMIC PROPERTIES OF CLAYS AND SHALES

General Observations

Some interesting results arising from the different methods of forming and firing the nine special samples are listed as follows: Ottawa (Q) and Nelson (Q) in Table 2; Cooksville (D-M) and Parkhill (Hamilton) in Table 3; Stevenson in Table 4; Wallenstein in Table 5; Bracebridge in Table 6; Missinaibi (1323) in Table 7. For equivalent temperatures, the temperature-gradient hand-moulded specimens are denser than the routine hand-moulded specimens, probably because of the longer soaking time that is given to the smaller cross-section temperature-gradient bars at the final temperature. The deaired extruding method was not used as extensively as the hand-moulded method, so that not as many results are available for the former method. The deaired, extruded temperature-gradient bars, fired to a given temperature close to the maturing point, produced the hardest and densest specimens, followed, in order of decreasing density, by the hand-moulded temperature-gradient bars, the strong, deaired extruded routine samples, the hand-moulded routine ones, and the dry-pressed samples. All deaired specimens are very dense at the lower firing temperatures.

The Owen Sound (Q) dry-pressed specimens were much more porous than the hand-moulded ones for equivalent firing temperatures.

The relative proportions of the minerals in the samples are of great significance. The effect of various clay and non-clay minerals on the manufacturing of ceramics has been discussed by Grim (78). Brady and Dean (49) and Brady (79) have discussed variations in mineralogical composition in relation to the utilization of some Canadian clays in the ceramic industry.

The calcite and/or dolomite content has a major effect on the fired colour and other properties of Ontario clays and shales. As the carbonate content increases, porosity increases, shrinkage and hardness decrease, and the fired colour changes from red to buff. The high calcite and dolomite contents of Owen Sound (Q) (Table 9), Norwich, Paisley, and Elginfield (blue) (Table 10), and the high calcite contents of Thedford (Hamilton) (Table 9), St. George and Wallenstein (Table 10), and Beaverton

(Table 11), cause the fired briquettes to be porous close to the fusion point. The firing range of these materials for the manufacture of dense products is thus extremely short.

The Georgetown (Q), Milton (Q) and Nelson (Q) samples (Table 9), the Wilkesport, Dresden (brown) and Essex (blue) samples (Table 10), and the Dorion samples (Table 11), all contain less carbonates than the above-mentioned samples; nevertheless, they have enough to produce short firing ranges and cause difficulty in firing, unless very close control of temperature is maintained. The fired colours of this group vary from buff to light red-brown.

The red-firing surface clay samples from southwestern Ontario, and most of the northern and northwestern clay samples, contain little or no carbonates. As a result, they are easy to fire to a hard, dense condition. Other problems exist with these clays, however, such as drying difficulties and, in some of them, the presence of lime pebbles.

The Ontario shales are generally hard and non-plastic, and the clay minerals in them have little chance of breaking down to the very fine particle size common to clay-water mixtures. The principal clay minerals in the shales are illite and chlorite, which have moderate plasticities. As might be expected, the shales dry safely.

The degree of plasticity of the Ontario clays is related to the abundance of expandable clay mineral phases (vermiculite and montmorillonoid). Mixed-layer minerals tend to impart a higher plasticity to clays than do their unmixed constituent phases (78, p. 69). In general, however, the abundance of montmorillonoid and mixed-layer systems containing montmorillonoid phases is small in comparison to the low-fusion, common, red-firing clays from the Prairie Provinces and British Columbia.

The clay samples are difficult to dry, and have high drying shrinkages and high green strengths because of their expandable clay mineral content and their apparent deficiency in coarse non-plastic material (Tables 10, 11 and 12). Only four clays contain montmorillonoids which are not interstratified with other layer types and, as might be expected, these are plastic and difficult to dry. Bell (37) has discussed the effect of a small amount of bentonite (mainly montmorillonite) on the plasticity of Queenston shale. The Missinaibi (1323), Essex (blue), and Toronto (Reformatory) samples dry without cracking because they do not contain montmorillonoid, or mixed-layer systems which include montmorillonoid or vermiculite phases. Dorion and Elginfield (blue) dry without cracking because they contain large quantities of non-plastic ingredients, such as calcite, dolomite, quartz and feldspar, and only small quantities of plastic clay minerals. It is interesting to note that Missinaibi (1323) dries safely although it contains a large proportion of a kaolin mineral (about 62 per cent) which gives it good plasticity. It has been suggested in unpublished work with Quebec clays that vermiculite may contribute to drying difficulties. The occurrence of vermiculite as an expandable phase within many of the difficult-to-dry Ontario clays supports this view.

Being very heterogeneous, the majority of the Ontario clays and shales have low melting points and frequently require very close control in firing in order to obtain uniform, dense products. Again the Missinaibi (1323) clay is a notable exception, because it contains essentially only two minerals, kaolin and quartz, which is a refractory combination.

All samples contain a significant proportion of quartz (Table 8). This mineral aids drying and helps to reduce the plasticity of the clays. Most of the quartz in the clay samples passes through a 200 mesh (Tyler) laboratory screen (Tables 10, 11 and 12) and consequently it is fine enough to react during firing. In both the clays and the shales it combines with other ingredients to form silicates. Some quartz may remain unreacted if the sample contains an excessive amount (such as in some of the southwestern and northern clays, and a few of the shales). If abundant quartz remains in the fired ware, care is required in cooling through the quartz inversion point at 573°C.

The clays occurring upon or near the Canadian Shield (Table 11) have feldspar as a major constituent. It, too, is very fine and affects the unfired clays in much the same way as quartz. The feldspar serves as a flux, and where it is the principal constituent and the carbonate content is low, the samples have short firing ranges and high fired shrinkages (e.g. Bracebridge).

Most of the samples contain some readily combustible organic material and a small quantity of pyrite. These are eliminated by firing under oxidizing conditions. The Kettle Point shale is so rich in them that its use as a ceramic raw material would be impossible without prefiring. The Billings shale bloats easily if improperly fired. Other clays containing much organic material but little pyrite are: Petrolia, Fletcher, Dresden (blue), and Stevenson.

Processing Problems of the Selected Clays and Shales

The nine selected samples represent the most common materials readily available for use by the ceramic industry in Ontario. Ottawa (Q) and Nelson (Q) are samples of, respectively, a moderately calcareous and a highly calcareous Queenston shale, used for the manufacture of face brick. Ottawa (Q) fires to a red colour and Nelson (Q) fires to various shades of buff or light red. Cooksville (D-M), a typical red-firing Dundas-Meadord shale from the Toronto area, is used for face brick and tile. Parkhill (Hamilton) is a moderately calcareous material which is used in the manufacture of salmon-brown coloured brick and tile. The Billings shale was used at one time for the manufacture of red face brick in the Ottawa area. It contains a relatively high quantity of organic material and pyrite. Stevenson is a slightly calcareous surface clay typical of those used for drain tile in southwestern Ontario. Wallenstein is a buff-firing, highly calcareous clay which is successfully used for the manufacture of drain tile. Bracebridge is a common, non-calcareous, red-firing clay that is being used successfully in the manufacture of drain tile. Missinaibi (1323) is a buff-firing, very refractory fire clay; clays in northern Ontario of this type offer some possibilities for use in ceramics, but so far only exploration has taken place.

Plasticity

The plasticity curves of the nine selected samples in which comparative resistance to pugging action (a measure of consistency or plasticity) is plotted against per cent tempering water are shown in Figures 17 and 18. In general, the higher the peak and the larger the area under the peak, the greater the plasticity. The sample-water mixtures have a stiff plastic condition at water percentages corresponding to the highest consistency. The clays are more plastic than the shales, but some of the clay curves (Wallenstein and Bracebridge, for example) have sharp, narrow peaks indicating that they are sensitive to small additions of water at the stiff-plastic stage. The peak areas of Ottawa (Q), Nelson (Q) and Billings indicate that these samples are less plastic than the standard Cooksville (D-M). Consequently, they probably will not extrude satisfactorily unless an addition is made to increase plasticity. All other samples should have sufficient plasticity for extrusion. Missinaibi (1323) has a broad peak that suggests it has good plastic properties.

Thermogravimetric Analysis

The weight loss curves of the nine selected samples are shown in Figure 19. Wallenstein and Nelson (Q) have the highest weight losses because they contain a normal quantity of the type of clay minerals found in "common" clays and shales, and substantial amounts of carbonates. Missinaibi (1323)

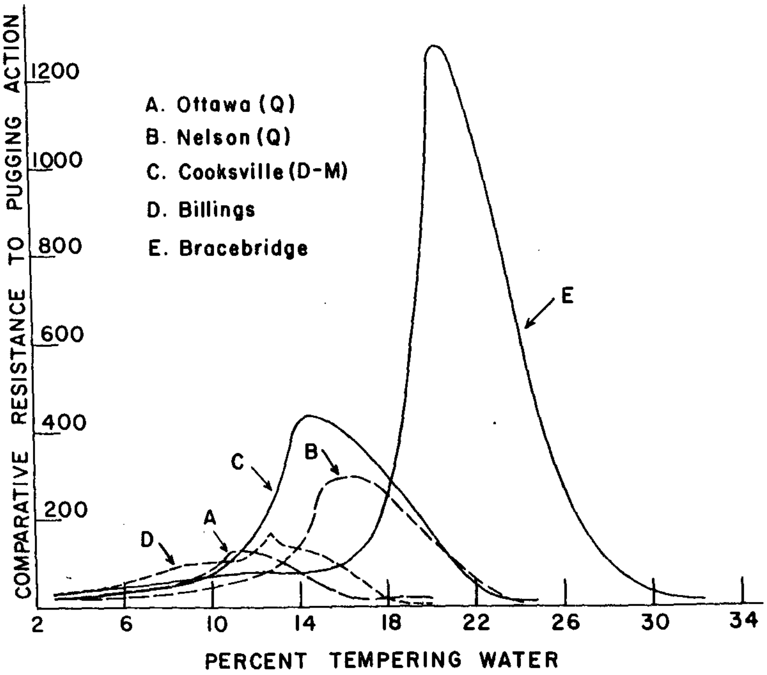


Figure 17. Plastograph curves of shales and a plastic clay.

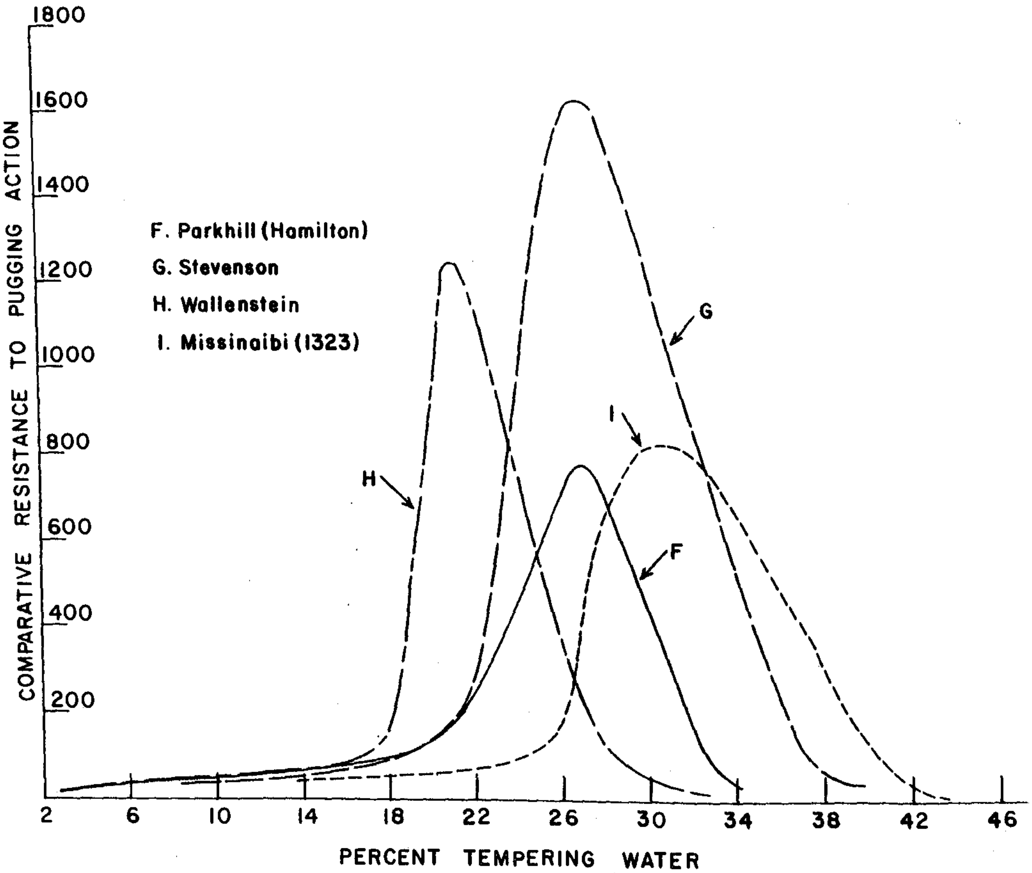


Figure 18. Plastograph curves of a plastic shale and plastic clays.

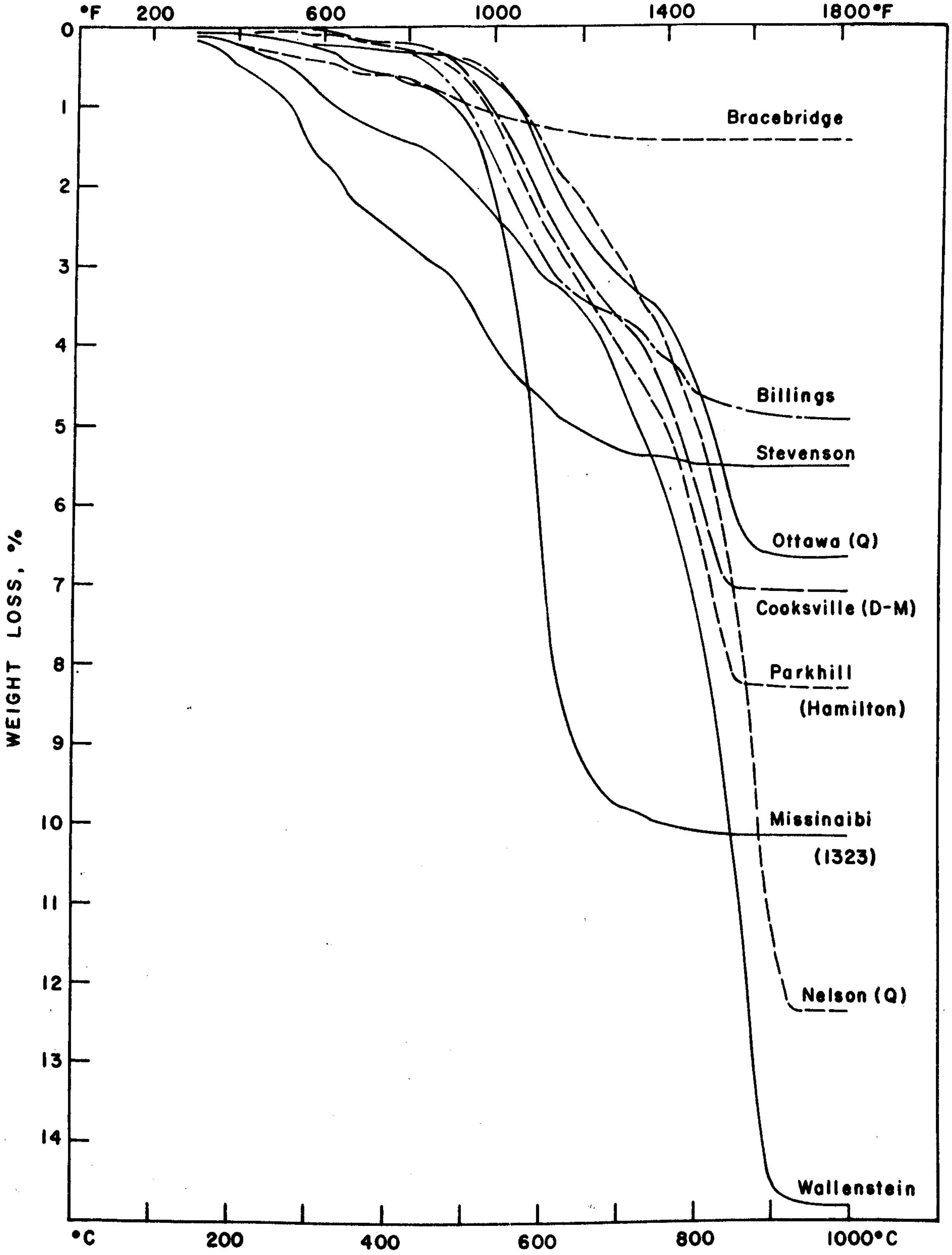


Figure 19. Weight loss of selected samples.

has a high weight loss, which is caused by the dehydroxylation of the large amount of kaolin-group clay mineral which it contains (about 62 per cent). Cooksville (D-M), Parkhill (Hamilton) and Ottawa (Q) have lower weight losses than Nelson (Q) or Wallenstein because they have lower carbonate contents. Billings and Stevenson contain very little carbonates; their weight loss is the result of the dehydroxylation of clay minerals. Bracebridge contains a high proportion of anhydrous silicates such as quartz and feldspar, and consequently has a very low weight loss. The rates of weight loss for the nine samples are shown in Figures 20 to 28.

Dilatometry

The thermal expansion curves of the raw (unfired) and fired selected samples are shown in Figures 20 to 28. They are discussed separately in conjunction with each sample in the following sections. Negative values on the raw thermal expansion curves indicate a decrease in size from the original lengths. The thermal expansion curves of Ottawa (Q), Nelson (Q), Cooksville (D-M) and Billings obtained from the vertical dilatometer were different to those obtained using the Seger dilatometer. Because of the evolution of gases from these samples and the design of the vertical furnace, reducing conditions were probably encountered in this (vertical) unit. Hence, for each of the above four samples, two thermal expansion curves are shown, one for oxidizing and the other for reducing conditions. Only the thermal expansion curves that were obtained in the vertical dilatometer are shown for Parkhill (Hamilton), Stevenson, Wallenstein, Bracebridge and Missinaibi (1323), because the results from both dilatometers were much the same.

The curves labelled 'thermal expansion (fired)' are equivalent to those that would be obtained by cooling the once-fired specimens from the maturing temperature; they are mainly linear, except for the expansion of quartz at the inversion temperature of 573°C.

Initially, the raw (unfired) specimens in the vertical furnace (tendency to reduction) and Seger furnace (oxidizing) expand gradually up to about 450°C and the thermal expansion curves are similar. Above this temperature the curves diverge, with the one obtained from the Seger furnace at a slow heating rate showing a greater rate of expansion. This effect has been discussed by West (80) in the case of a Queenston shale. In most instances, shrinkage commences at about 700 to 800°C and, in some cases, reverses to expansion at about 850 to 900°C. At the lower heating rate employed in the course of the investigations conducted under oxidizing conditions, the reversals from expansion to shrinkage and from shrinkage to expansion within the above temperature ranges occur about 50°C above those recorded for the samples fired more rapidly under reducing conditions.

The reversal from shrinkage to expansion results from the expansion of a material high in calcite and/or dolomite, or from bloating induced by reducing conditions. West (80) has discussed this type of expansion curve for a Canadian Queenston shale made up principally of illite, chlorite and (coarse) mica (all layer silicates), quartz, and dolomite. He noted that the expansion between 600 and 700°C resulted from the exfoliation of illite, chlorite, and mica in that order while they were dehydrating. He also noted that a sudden change from shrinkage to expansion at about 850°C coincided with the solid-state reaction of magnesia and calcia from the decomposing dolomite with silica and alumina. Bell (81) has discussed the influence of lime on the thermal expansion of clay and has described the thermal expansion of some highly calcareous Canadian clays and shales of the illitic and chloritic type that have reversals from expansion to shrinkage and then shrinkage to expansion. Nelson (Q) yields curves of the above type. Sharp reversals from shrinkage to expansion or vice versa could cause cracking during firing.

The curves of the unfired Cooksville (D-M) and Billings samples showed reversals from shrinkage to expansion at about 900°C, probably because of bloating induced by the reducing conditions in the vertical dilatometer. On the other hand, the curves representing samples heated under oxidizing conditions showed continued shrinkage through 900°C, rather than a reversal to expansion.

As pointed out in a preceding paragraph, the rate of heating has an effect on the shape of the thermal expansion curve. Further important factors affecting the shape of the curve are the unfired density and the method of forming the test specimen. Unpublished investigations at the Mines Branch have shown that the method of forming (which affects green density) is particularly important if reducing conditions are encountered during firing.

A summary of the quartz content of the unfired samples and the fired thermal expansion samples is given in Table 13. Examination of this table shows that the approximate quartz content is not excessive in any of the nine selected samples, although the values are somewhat high for Cooksville (D-M) and Stevenson. Quartz percentages remaining in the fired samples are low, well below the 25 to 35 per cent that may cause serious cracking problems (dunting) during firing.

Temperature Gradient

The temperature gradient curves of shrinkage and absorption are shown in Figures 20 to 28. These curves, along with those for DTA, rate of weight loss, and dilatometry, illustrate the firing behaviour of the selected samples. It should be noted that negative values on the temperature gradient shrinkage scale represent linear expansion and that different temperature scales are utilized for the two diagrams within each of Figures 20 to 28. With the exception of Ottawa (Q) and Cooksville (D-M), the temperature gradient curves were obtained from hand-moulded specimens.

Discussion of Selected Samples

Ottawa (Q)

The evaluation in Table 2 and a comparison of the Ottawa (Q) plastograph curve with the standard Cooksville (D-M) curve in Figure 17 indicate that this sample lacks plasticity and cannot be extruded satisfactorily.

TABLE 13

Summary of the Quartz Contents of Selected Samples*

SAMPLE	UNFIRED		FIRED	
	Approx. quartz-chemical analysis, %	Approx. quartz-DTA, %	Firing temperature, °C	Approx. quartz-thermal expansion, %**
Ottawa (Q)	26	21	1117	10
Nelson (Q)	26	21	1136	12
Cooksville (D-M)	26	21	1086	10
Parkhill (Hamilton)	19	19	1117	7
Billings	25	19	1031	10
Stevenson	33	28	1050	15
Wallenstein	23	20	1086	11
Bracebridge	31	28	1050	10
Missinaibi (1323)	22	21	1395	6

* There is little agreement in the quartz percentages obtained by DTA and chemical analysis. The amounts are approximate.

** Percentages based on discontinuity of thermal expansion curve of fired specimens at about 570 to 590°C. A rock containing 100 per cent quartz (No. 179 in Mines Branch Jet-Piercing Research Project Report IR-62-27) had 0.40 per cent linear expansion at the point of sharp discontinuity, and this figure was used as a standard reference.

The plasticity could probably be improved by fine grinding and/or the addition of a plasticizer. An addition of about one per cent (based on the dry weight of shale) of bentonite in the tempering water is effective for the manufacture of stiff mud brick. This lack of plasticity is common to Queenston shales, although Ottawa (Q) is harder and less plastic than the Queenston shales from the Toronto-Hamilton area. Because of the lack of fine-grained, plastic ingredients, this sample can be dried easily and has a small drying shrinkage.

The firing behaviour of Ottawa (Q) is shown in Table 2 and Figures 19 and 20. Of the nine samples this is one of two that were deaired and as a result the fired test specimens are denser at the lower firing temperatures than the non-deaired calcareous shales. The temperature gradient curves indicate that this material has a short but manageable firing range for brick production, where 8 per cent or less absorption is desirable.

The DTA curve shows a very small loss of water at about 130°C, and negligible carbon burn-out at about 300°C. According to the rate of weight loss and thermal expansion curves, there are no major reactions below the latter temperature.

The peak resulting from the inversion of quartz at 573°C is masked by an endothermic clay peak on the DTA curve, but the reaction is detectable on the raw clay thermal expansion curve as an expansion of about 0.05 per cent.

The first major peak on the rate of weight loss curve, which reaches a maximum at about 590°C, represents the dehydroxylation of illite and the 'brucite' layer of chlorite, whereas the broad shoulder extending from this temperature to approximately 650°C probably represents the second dehydroxylation stage of chlorite. The latter reaction is not readily apparent from the DTA curve. The weight loss due to the clay breakdown is about 3.3 per cent, out of a total of 6.70 per cent (Figure 19). The removal of water vapour caused by this reaction should not be a serious problem, but draft must be provided for its removal; otherwise, condensation, scumming, or kiln marking could result.

The dissociation of about 8 per cent calcite occurs near 820°C, where a peak on the rate of weight loss curve indicates a rapid decrease in weight. The weight loss due to this reaction is small and amounts to about 3.1 per cent. Provision must be made for eliminating the CO_2 evolved, but this should not be a serious problem. An unexplained minor peak occurs at about 700°C just prior to the start of the 820°C calcite decomposition peak. The minor shoulder on the rate of weight loss curve at 940°C probably corresponds to a recrystallization reaction which appears as a small exothermic peak on the DTA curve.

The general shape of the thermal expansion curves is the same under both oxidizing and reducing conditions (hand-moulded specimens). An inversion from shrinkage to expansion was recorded at about 840°C under reducing conditions but not under oxidizing conditions. This inversion did, however, appear on the temperature gradient shrinkage curve where the bars were deaired and extruded and where the firing conditions were oxidizing (it should be noted that the shrinkage or expansion of a temperature gradient bar is measured on the fired material after it is cooled to room temperature whereas thermal expansion values are obtained during heating). At about 870 to 930°C the material starts to expand very rapidly, with the final expansion being about 2.3 per cent during firing. This is a much higher value than those obtained for other samples from Ontario and Quebec.

The material may have a cracking problem because of the rapid inversion from shrinkage to expansion at about 850°C. Brady et al. (45) have previously discussed this problem for the Estevan Buff clay, but the explanation bears repeating. It can be seen that a brick heated rapidly through 800-850°C could be expanding at the surface and shrinking in the interior (due to a temperature lag), thus creating severe tensile stresses at the surface. When these stresses exceed the cohesive strength of the material, cracking occurs - the "heating-up" cracks referred to by Groskaufmanis (82). Robinson (83) has suggested that firing schedules should be programmed to provide a uniform rate of expansion throughout the burn. Such a procedure seems particularly appropriate for materials of this type. In any case, uniform heating of the product is essential in order to minimize the problem.

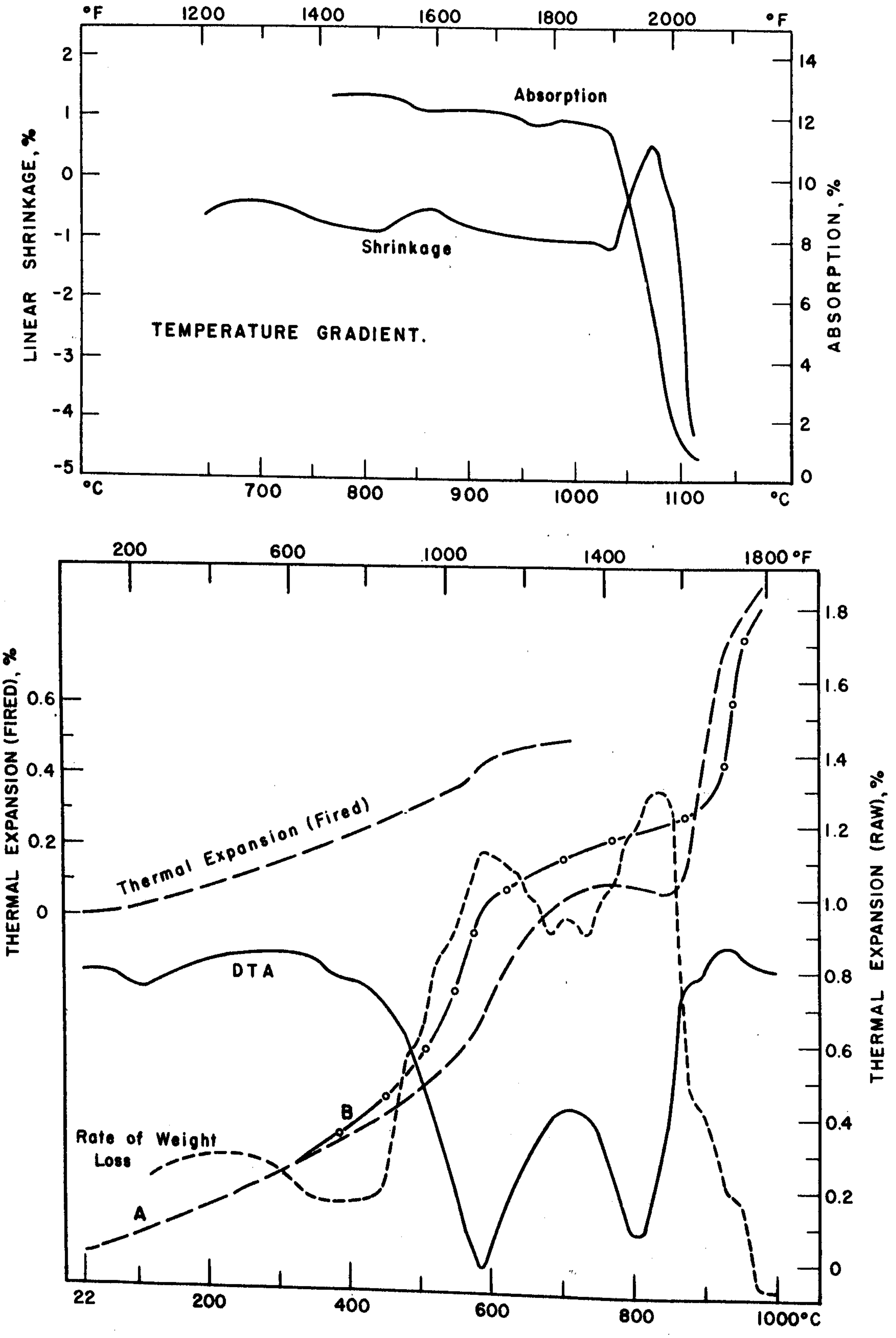


Figure 20. Firing behaviour of Ottawa (Q) shale.

A. Linear thermal expansion before firing (reduction)

B. Linear thermal expansion before firing (oxidation)

Nelson (Q)

This sample is a Queenston shale that contains more calcite and has more plasticity than Ottawa (Q). The sample can be extruded in the laboratory without a plasticizer and, if finely ground and given sufficient pugging, should be suitable, without additives, for the manufacture of thick sectioned ware such as extruded brick. The plastograph peak size (Figure 17), when compared with the Cooksville (D-M) standard, suggests that some difficulty might be experienced in extruding such products as thin-sectioned structural tile. Being relatively non-plastic, the material dries easily.

The firing behaviour of Nelson (Q) is shown in Figures 19 and 21. The temperature gradient curves indicate that this shale has the short firing range typical of high-lime clays. Vitrification begins at approximately 1050°C, where the absorption is about 20%, and proceeds fairly rapidly with increasing temperature. Control of size and absorption would thus be difficult if dense products were being fired.

There is nothing of significance on the initial part of the DTA curve, and the small reactions are similar to those for Ottawa (Q). The rate of weight loss curve has two peaks at about 590°C and 640°C, which coincide with two peaks on the DTA curve resulting from the breakdown of the clay minerals illite and chlorite. The high rate of weight loss peak at 875°C coincides with the decomposition of approximately 18 per cent calcite. The small shoulders on the curves at about 750°C indicate the dissociation of approximately 3 per cent dolomite.

The weight loss due to carbonate dissociation amounts to about 9.40 per cent out of a total of 12.40 per cent loss in weight between 110°C and 1000°C (Figure 19). Only a minor amount of this loss can result from the final decomposition of clay minerals between 750° and 900°C, and a large volume of CO_2 is therefore released into the kiln, affecting the pressure and drafts and causing a possible misinterpretation of flue-gas analysis, which could result in fuel wastage. In addition, the evolution of carbon dioxide from the brick could prevent the penetration of the kiln atmosphere. This could have a serious effect on the final colour, since bricks fired from this material will likely be faintly pink in an oxidizing atmosphere and buff in a neutral or reducing atmosphere. A further complication, arising just prior to carbonate decomposition, is caused by the release of about 2.6 per cent of water vapour from the clay minerals. This water must be removed in order to prevent condensation and to preserve the proper kiln atmosphere.

The thermal expansion curves for the Nelson (Q) shale are typical of high-lime clays and shales (81). The curves obtained under reducing and oxidizing conditions are similar up to about 800°C. Above this temperature, each shows a reversal from expansion to shrinkage at about 800°C and, subsequently, a reversal from shrinkage to expansion at about 900°C. The reversals are not as abrupt under oxidizing conditions, where a slower heating rate was utilized, nor does the oxidized sample shrink as much between 800 and 900°C. Because of the two reversals from shrinkage to expansion, this material may have a cracking problem similar to that of

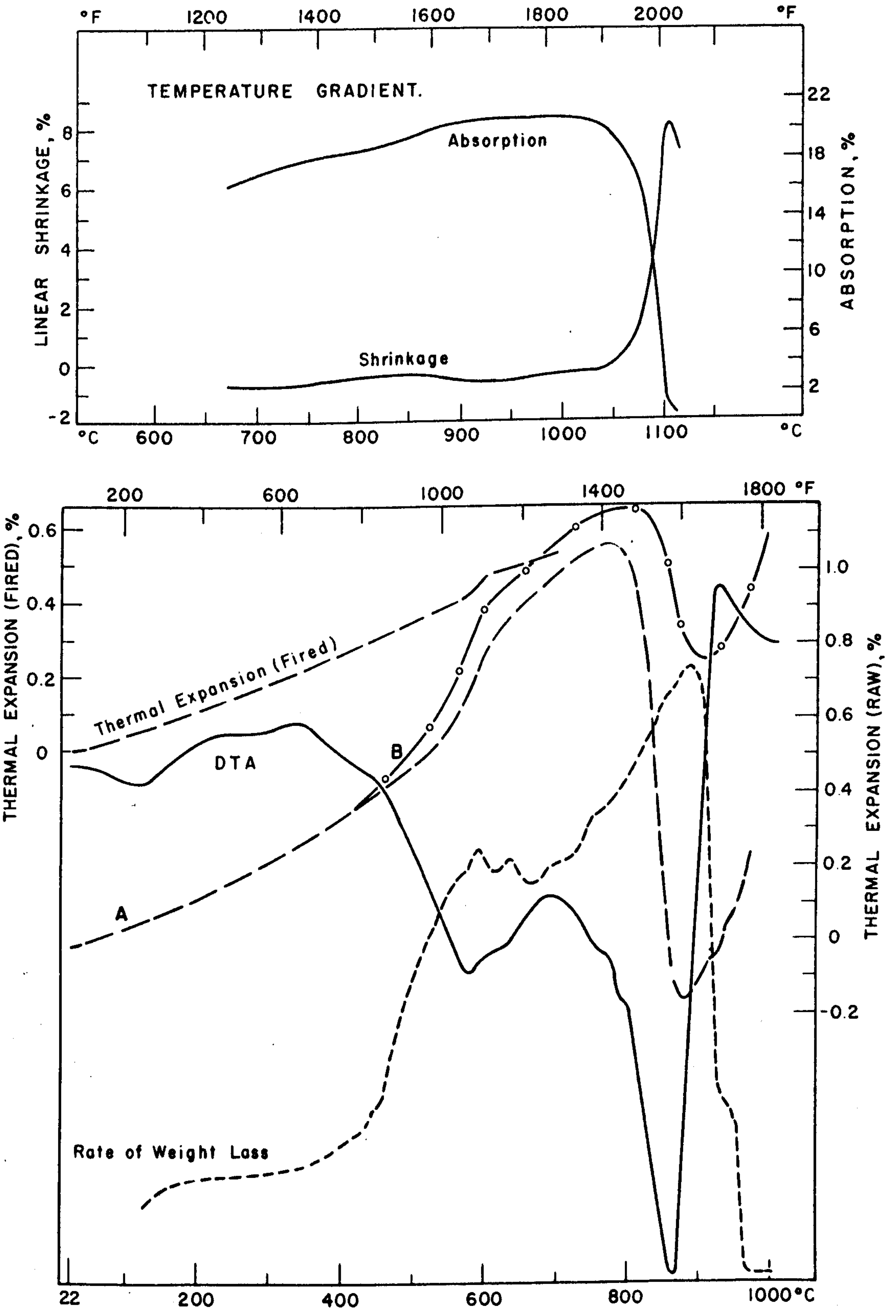


Figure 21. Firing behaviour of Nelson (Q) shale.
A. Linear thermal expansion before firing (reduction)
B. Linear thermal expansion before firing (oxidation)

the Ottawa (Q) sample, although it appears likely that it can be minimized by firing slowly and, preferentially, under oxidizing conditions in the critical temperature regions.

Cooksville (D-M)

The results in Table 3 indicate that Cooksville (D-M) is fairly plastic and with fine grinding should be suitable for extruded products. This shale is used commercially for brick and tile and is about on the border-line for the manufacture of these products in so far as plasticity is concerned. Consequently, the plastograph curve (Figure 17) of this material was selected as a standard to which other plastograph curves are compared. This sample, in common with most shales, dries safely. As a rule, materials having equal or less plasticity than Cooksville (D-M) are safe drying.

The curves of the effect of heat on the Cooksville (D-M) shale appear in Figures 19 and 22. They show that it has a longer firing range than Ottawa (Q) and a much longer one than Nelson (Q) (Figure 21). The shale is used locally for the manufacture of brick and tile. Temperature-gradient curves of hand-moulded and deaired extruded specimens show that a denser body is obtained by vacuum extrusion of the shale.

The DTA and rate of weight loss curves show that there are minor reactions up to about 400°C. Two slight shoulders at about 400°C on the rate of weight loss curve indicate the burnout of a small amount of organic material and pyrite, which also produced dull peaks on the DTA curve.

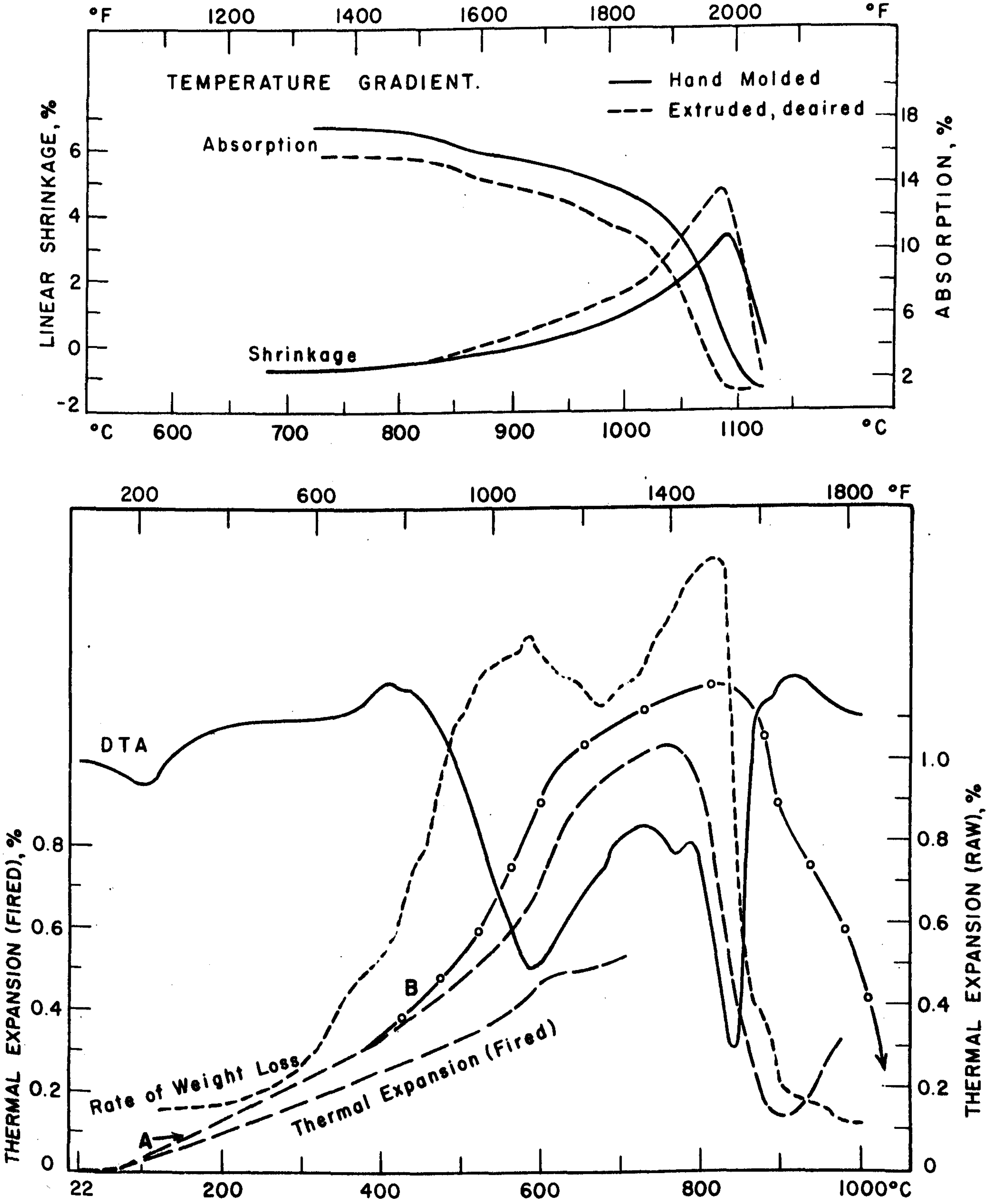


Figure 22. Firing behaviour of Cooksville (D-M) shale.
A. Linear thermal expansion before firing (reduction)
B. Linear thermal expansion before firing (oxidation)

Again, the rate of weight loss and the DTA curves indicate the breakdown of the illite and chlorite. The dissociation of a moderate quantity of calcite (perhaps 10 per cent) produces a major peak on the rate of weight loss and DTA curves between 810 and 840°C. The decomposition of a small amount of dolomite is indicated on both curves at about 750°C. The weight loss from the dehydrating clay minerals is about 3.2 per cent and that from the decomposing carbonates is 3.80 per cent out of a total weight loss of 7.15 per cent. Neither the water vapour nor the carbon dioxide from these reactions should prove difficult to remove.

The effect of atmosphere on thermal expansion is apparent from the curves for Cooksville (D-M). All unfired samples show an initial reversal from expansion to shrinkage. The material fired under reducing conditions, however, shrinks below 900°C and then expands slightly (probably from bloating) whereas the sample fired under oxidizing conditions continues to shrink above this temperature. Some care may be required in firing in order to prevent cracking, particularly if reducing conditions prevail at the critical reversal temperatures.

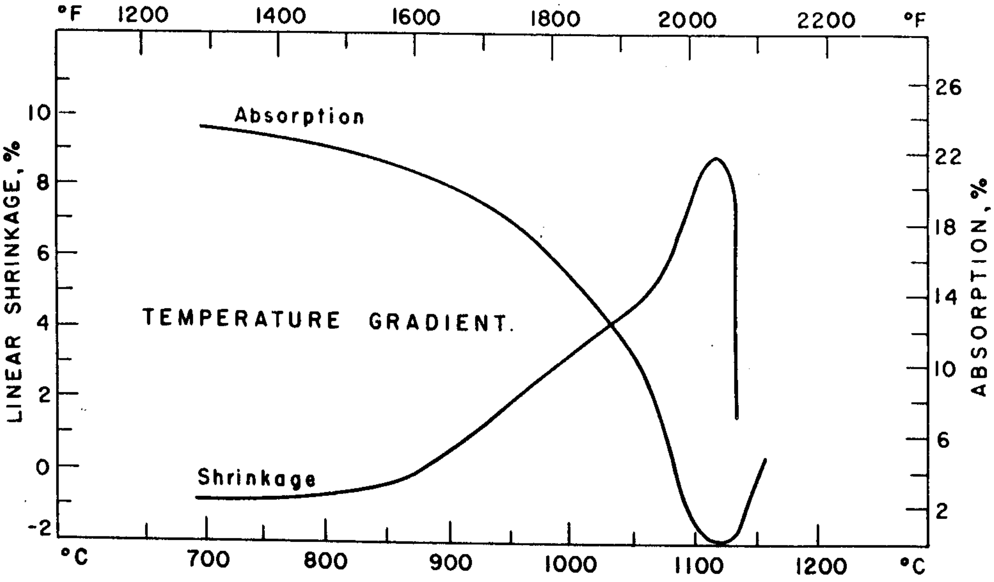
Parkhill (Hamilton)

This material is used by a plant at Parkhill for the manufacture of facing brick. The results in Table 3 and the curve in Figure 18 indicate that it is a very plastic shale. Its plasticity characteristics are, in fact, similar to those of an illitic clay that dries safely.

The firing characteristics of Parkhill (Hamilton) are shown in Table 3 and Figures 19 and 23. The temperature gradient curves indicate that it has a suitably long firing range for the manufacture of dense clay products. However, the firing shrinkage is inclined to be high and this may cause some problems unless firing conditions and temperatures are uniform. The high fired shrinkage may be due to the low percentage of free quartz and the correspondingly greater quantity of low melting materials and fluxes that allow shrinkage to proceed rapidly.

The rate of weight loss curve of Parkhill (Hamilton) is initially steeper than for any of the previous samples. The DTA and weight loss curves suggest that this is the result of adsorbed water removal and organic material oxidation (the latter at about 325°C). At about 400°C the DTA and rate of weight loss curves indicate that a small amount of pyrite is decomposing.

There is a rapid loss of weight between 500 and 600°C. The rate of weight loss curve again suggests that dehydroxylation of clay minerals is taking place. There is a loss of about 3.3 per cent water vapour from this reaction. The prominent peaks on the DTA and rate of weight loss curves at about 820°C are caused by carbonate decomposition, which amounts to 4.65 per cent out of a total of 8.35 per cent weight loss from 110 to 1000°C. The volume of gases produced by these reactions is not excessive and is only slightly greater than for Cooksville (D-M) but much less than for Nelson (Q).



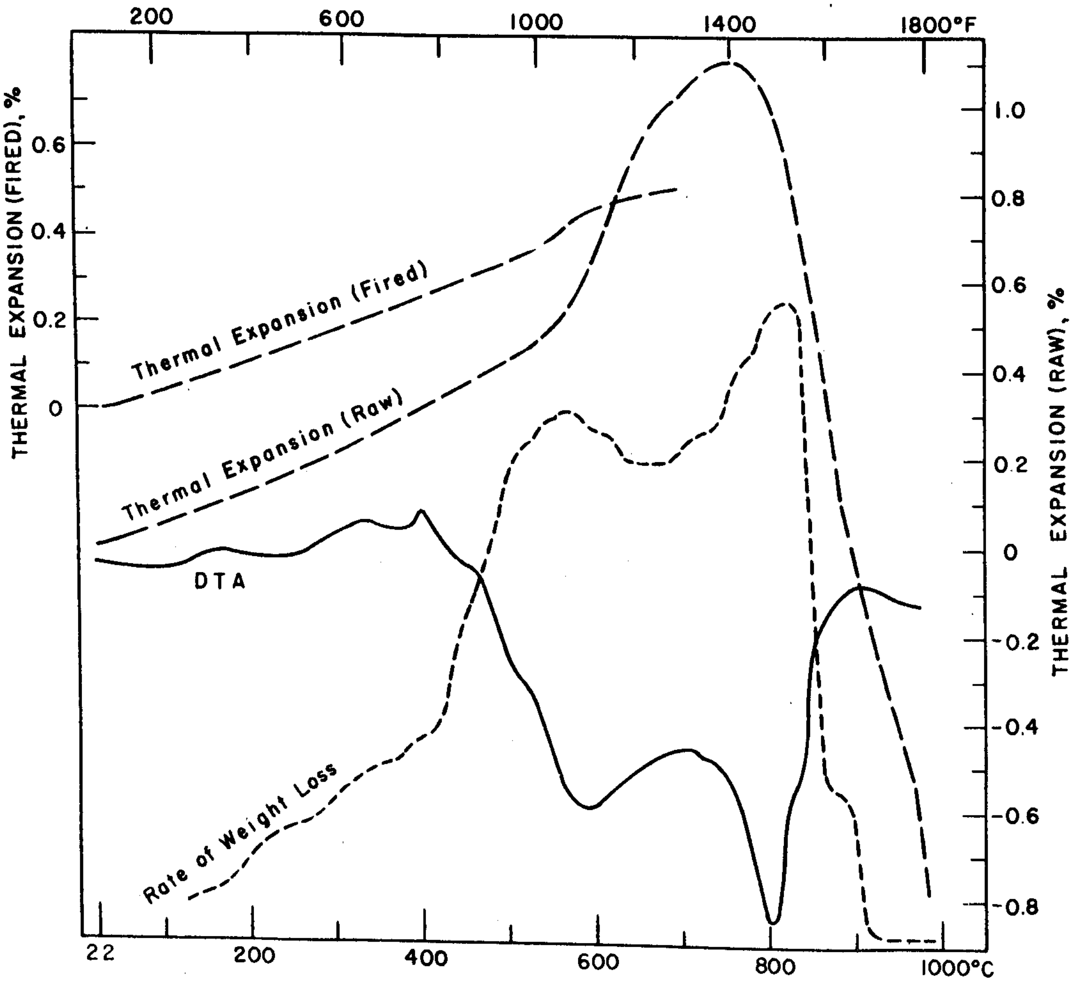


Figure 23. Firing behaviour of Parkhill (Hamilton) shale.

The thermal expansion curve for the raw shale rises to a peak at about 750°C, as in the previous samples, and subsequently inverts at a moderate rate and indicates continued shrinkage up to 980°C. The inversion probably will not cause firing cracks under well controlled firing conditions.

Billings

The evaluation in Table 3 and the curve in Figure 17 indicate that this shale lacks plasticity and will require fine grinding and the addition of a plasticizer for the manufacture of facing brick. The material behaves like Ottawa (Q) in so far as plasticity and drying are concerned.

The curves illustrating the firing behaviour of this shale from the Billings formation at Ottawa (Figures 19 and 24) show that it has a satisfactory firing range for production of dense clay products. The rate of weight loss curve has a small sharp peak at about 200°C, caused by the loss of adsorbed water. This effect is different than in the other shale samples studied and is more typical of a clay. The percentage weight loss at this temperature is very low, and the slope of the weight loss curve not great (Figure 19); consequently, no difficulty would likely result from the removal of adsorbed water.

A large double peak caused by the decomposition of organic material and pyrite on the DTA curve corresponds to a high rate of weight loss. Chemical analysis shows that this sample contains 0.52 per cent carbon from organic material and 1.14 per cent sulphur, probably from

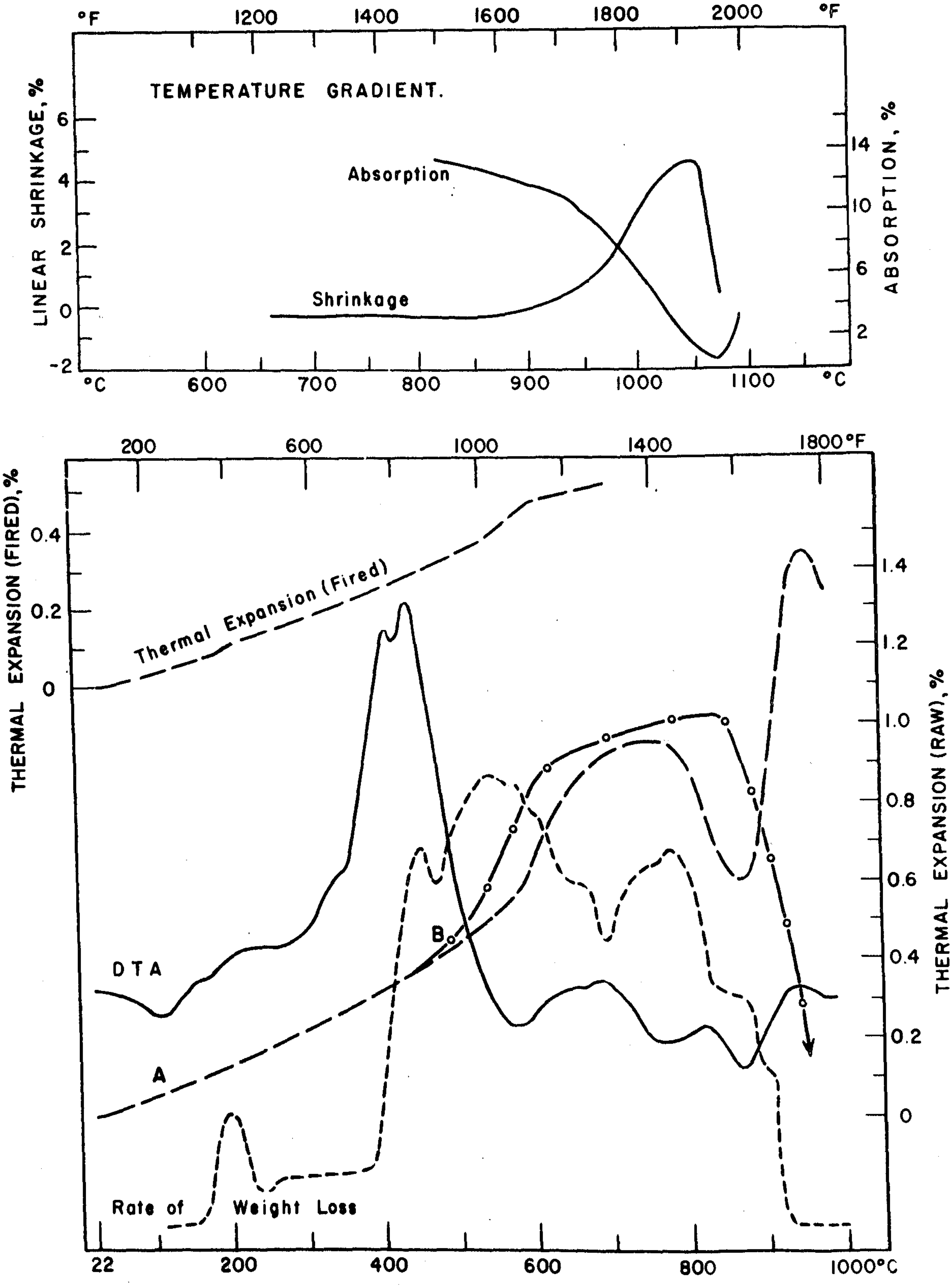


Figure 24. Firing behaviour of Billings shale.
A. Linear thermal expansion before firing (reduction)
B. Linear thermal expansion before firing (oxidation)

pyrite. The extremely large, sharp peaks on the DTA curve at about 400°C suggest that these materials are difficult to burn out unless provision is made for a long period of oxidation. Unless proper oxidizing conditions are provided, bloating and black coring will occur. The decomposition of pyrite produces sulphurous gases which, in this case, would likely contribute to scumming and efflorescence unless they were removed from the kiln (Brownell 84, 85). This observation applies also to the Parkhill (Hamilton) shale, where the problem is less severe. The breakdown of the illite and chlorite clay minerals at 550° to 650°C and the decomposition of the very small amount of calcite (about 2 per cent) are normal and should offer no serious problems during firing. Of the 4.95 per cent weight loss, about 2.8 per cent is water vapour from the clay mineral breakdown and about 1.0 per cent is carbon dioxide from carbonate decomposition.

The thermal expansion curves for the unfired Billings sample are somewhat similar to those for Cooksville (D-M). Under reducing conditions, the curve shows a change from expansion to shrinkage at about 775°C, and subsequently a rapid expansion at 875°C (probably from bloating). The oxidized sample, after its initial expansion, continues to shrink.

Stevenson

The curve in Figure 18 shows this to be a very plastic material. Likely, the montmorillonoid-chlorite-illite mixed layer system causes this, and undoubtedly contributes also to the drying problems and high drying shrinkage of the material (Table 4).

The initial portions of the DTA and rate of weight loss curves differ considerably from most of the other samples, because of the loss of adsorbed water and the oxidation of a large quantity of easily burned organic material. The low temperature weight loss of the Stevenson clay was greater than that recorded among the other selected samples. As shown in Figure 19, this amounted to approximately 1.0 per cent at 250°C, and indicates the presence of large quantities of loosely bound water within the clay minerals, notably the montmorillonoid-chlorite-illite. Table 10 indicates, furthermore, that the total clay mineral content of this sample is quite high.

The firing behaviour curves in Figures 19 and 25 and the results in Table 4 show that Stevenson has a satisfactory firing range for production of dense products. The fired shrinkage is excessive in the temperature region where the test specimens become vitrified.

This clay probably regains moisture readily after drying, and so is likely subject to kiln-marking during the early stages of firing. In tunnel kiln firing, ware formed from this clay could be exploded by steam forming within it. The problem is not nearly so severe here, however, as it is for Pipestone clay (45).

The DTA and rate of weight loss curves show weak clay mineral dehydroxylation reactions between approximately 550 and 650°C. The total weight loss is 5.55 per cent, about 2.3 per cent being from water vapour at 600°C.

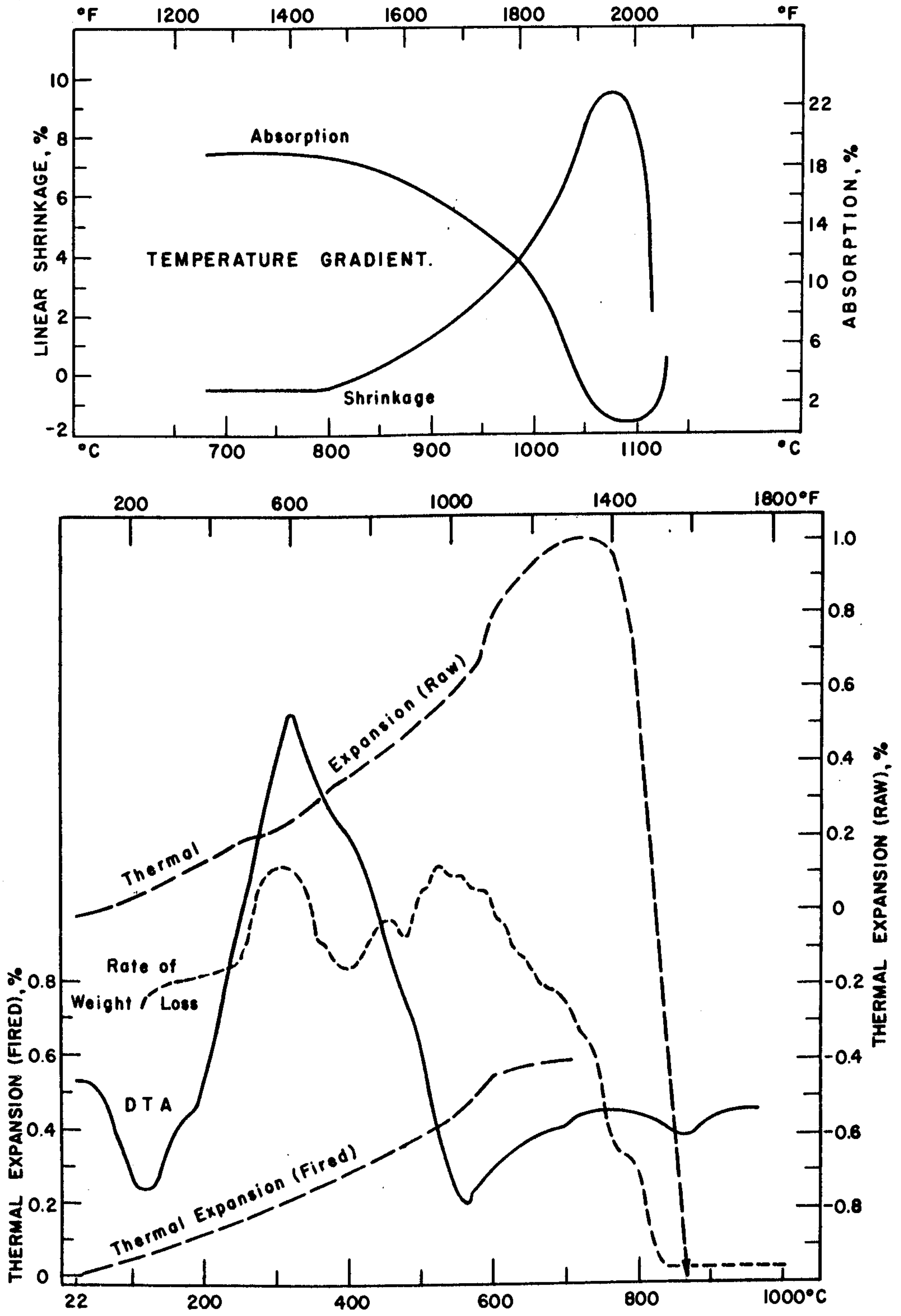


Figure 25. Firing behaviour of Stevenson clay.

The thermal expansion curve for the raw clay is similar to that for the Parkhill (Hamilton) shale. The curve rises gently towards a maximum expansion of about 1.0 per cent, reverses at 750°C, and continues to shrink up to 980°C at least. This material probably requires careful cooling through the quartz inversion temperature (573°C), although the fired curve indicates the problem is not serious.

Wallenstein

The plasticity of the Wallenstein clay (Table 5 and Figure 18) is less than that of Stevenson (Figure 18), but greatly exceeds that of the standard Cooksville (D-M) shale (Table 3 and Figure 17). The major causes of this high plasticity are the mixed-layer montmorillonoid-vermiculite and montmorillonoid-chlorite clay minerals (Table 10). Care is required in drying this material, in order to prevent cracking. The sharp, narrow peak on the plasticity curve (Figure 18) suggests that the sample is sensitive to small additions of water at the stiff plastic stage.

The firing behaviour curves in Figures 19 and 26 indicate that this material, in common with all highly calcareous clays and shales, has a very short firing range for production of hard, dense products. Like Stevenson, it contains a substantial quantity of readily oxidized organic material. The reactions produced by the various clay minerals between 550 and 625°C, as shown by the DTA and weight loss curves, are minor in comparison with those recorded from some of the shales within this temperature interval. The carbonate peaks are large and the problem

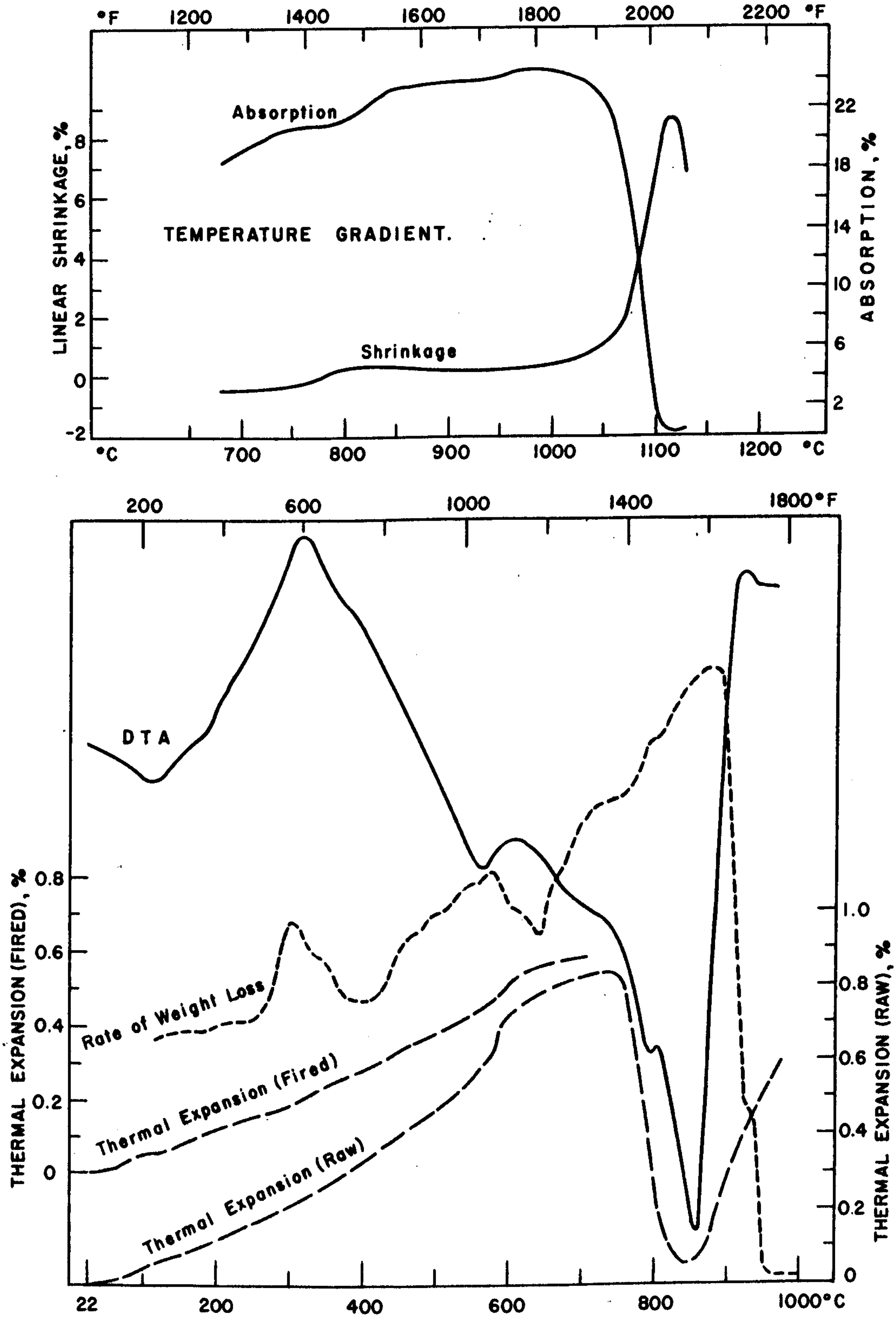


Figure 26. Firing behaviour of Wallenstein clay.

of carbon dioxide removal is much the same as that for Nelson (Q).

Out of a total weight loss of 14.80 per cent, the Wallenstein clay loses 11.10 from the decomposition of dolomite and calcite (Figure 19). The shape of the weight loss curve is similar to that obtained from Ottawa (Q), Nelson (Q), Cooksville (D-M) and Parkhill (Hamilton). All of the latter samples contain principally illite, chlorite, calcite, and/or dolomite, which are important constituents of Wallenstein.

The thermal expansion curve for the raw material is similar to that for Nelson (Q). An abrupt change from expansion to shrinkage was recorded at 750°C, and from shrinkage to expansion at 840°C. Undoubtedly, this material would be subject to the formation of heating cracks under certain conditions.

The sample contains a moderate amount of quartz, which should not cause difficulty during cooling.

Bracebridge

The Bracebridge clay (Table 6 and Figure 17) has about the same plasticity as Wallenstein (Figure 18) and consequently is somewhat sensitive to small additions of water. It is difficult to dry. Although, relative to the other selected samples, the clay mineral content of Bracebridge is low, the montmorillonoid and mixed-layer minerals containing a montmorillonoid or a vermiculite phase impart a high plasticity to the material. Of considerable interest is the ease with which the plasticity and drying characteristics are altered by electrolytes; for example, a very minor addition of hydrated lime ($Ca(OH)_2$) makes drying much easier.

The DTA curve shown in Figure 6 and the weight loss curve in Figure 19 indicate that the clay mineral content is quite low and that the sample is non-calcareous. Examination of Table 11 reveals that the principal non-clay constituents are quartz and feldspar.

The firing behaviour curves in Figure 27 show that the material has a very short firing range for production of dense products. The sample has a high rate of weight loss at 200°C, likely resulting from loss of the large amount of adsorbed water associated with the montmorillonoid, the illite-montmorillonoid, and the vermiculite-montmorillonoid. The material probably rehydrates readily, which could cause difficulty, particularly in tunnel kiln firing.

The thermal expansion curve for the unfired Bracebridge clay differs considerably from those for the remaining selected samples, although it, too, shows slight inversions at 750°C and 930°C. There are no abrupt changes such as those occurring among the calcareous shales and clays. The data shown in Table 13 indicate that no cooling cracks should be caused by quartz under normal firing conditions.

The weight loss of 1.45 per cent is very small and indicates that only minor quantities of gas will be evolved during firing.

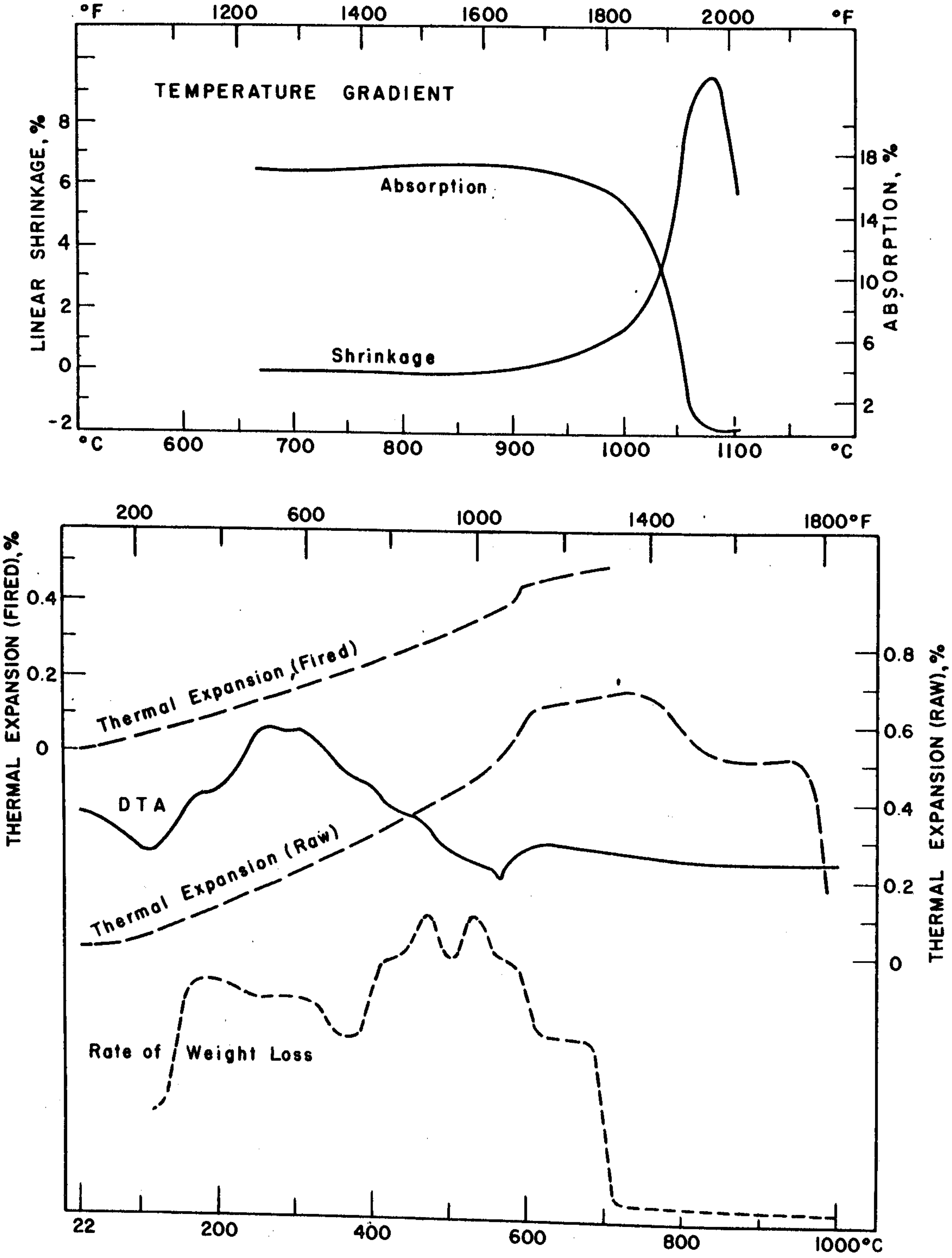


Figure 27. Firing behaviour of Bracebridge clay.

Missinaibi (1323)

The Missinaibi (1323) fireclay has properties much different from those of the calcareous clays and shales and the sample from Bracebridge. The evaluation in Table 7 and the curve in Figure 18 show that this is a plastic, greasy clay that is typical of a material whose principal constituent is kaolin. The plastograph curve is broad and similar to the one shown for kaolinite by Marshall (53). Regardless of its plasticity, the sample dries safely, a feature which is probably promoted by the high kaolin mineral content.

The temperature gradient curves (Figure 28) show that the clay is open firing and very difficult to vitrify. At 1300°C the absorption is 6 per cent and the shrinkage very high at 12 per cent. Thus, this clay could not be used successfully for clay products unless it was first mixed with another clay or a material which would counteract the above defects. It probably also could be made into a refractory grog by pre-firing.

The initial portion of the rate of weight loss curve has a moderately steep slope resulting from the loss of adsorbed water. The sharp peak at approximately 340°C probably represents the dehydration of poorly crystallized or amorphous iron oxides. Subsequently, the curve rises very sharply to a peak at 600°C, which represents the dehydroxylation of kaolin. The water vapour released by this reaction amounts to approximately 8.1 per cent, out of a total weight loss of 10.2 per cent (Figure 19). Strong draft is therefore necessary to prevent slumping, kiln marking, or possible scumming.

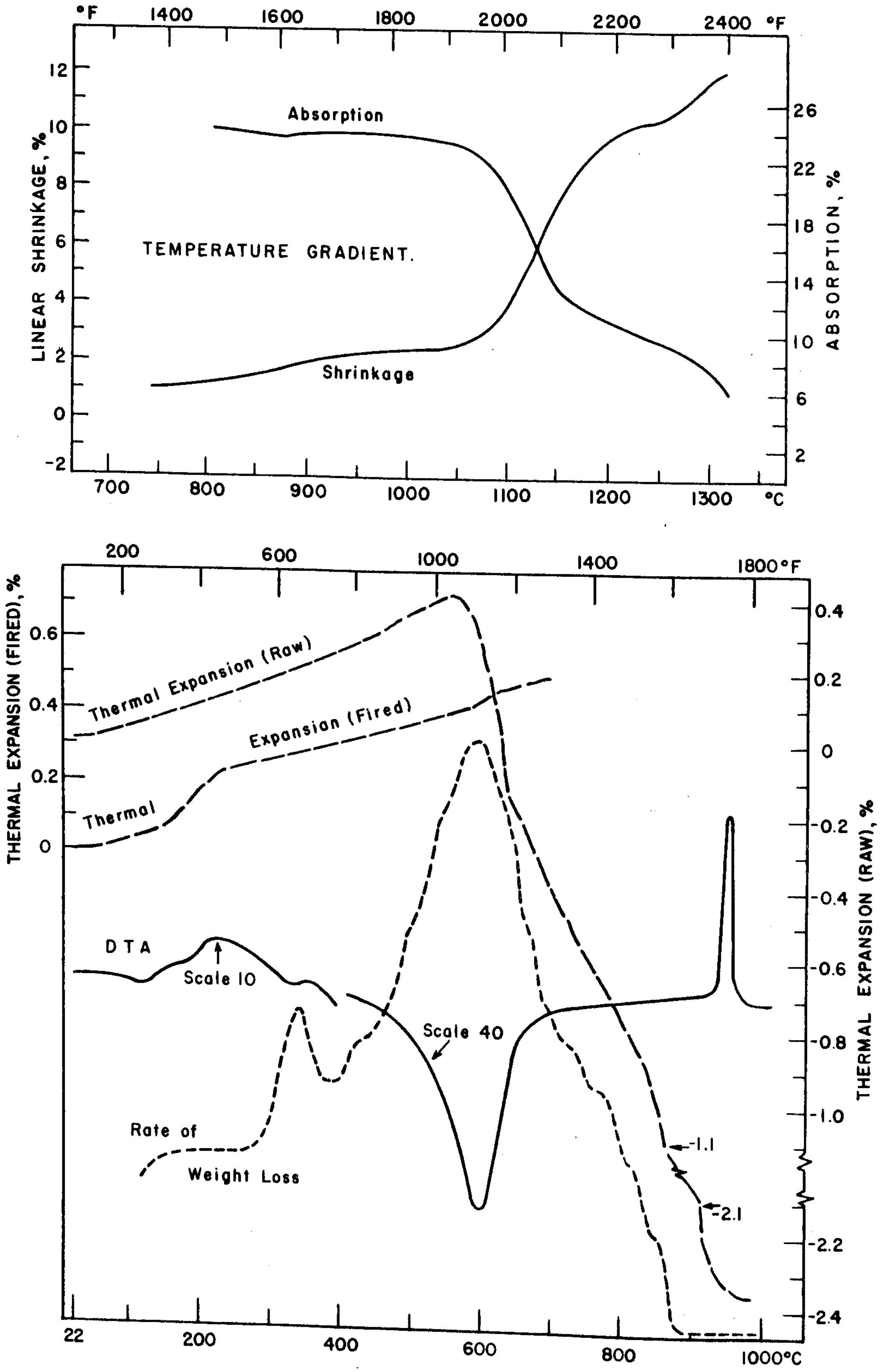


Figure 28. Firing behaviour of Missinaibi (1323) clay.

The thermal expansion curve of the raw clay is that of a typical kaolin-minor quartz type, as reported by Paquin (86). The curve shows a maximum expansion of 0.415 per cent at 560°C, followed by an abrupt decrease to a net total shrinkage of 2.36 per cent at 1000°C. The inflection at the top of the peak is moderately sharp; hence some cracking could occur during rapid heating of the clay.

The weight loss curve shown in Figure 19 is typical of a clay containing a high percentage of a kaolin group clay mineral, and therefore differs considerably from the other curves in this diagram.

Little difficulty should be expected from unreacted quartz during cooling (Figure 28). Care is probably required in cooling through 225°C, as the fired material contains cristobalite (Table 14), which causes a 0.175 per cent dimension change.

Summary of the Mineralogy of the Selected Samples

A summary of the mineralogical compositions of the unfired and fired selected samples is given in Table 14. The absorptions shown for the fired specimens serve as a measure of the heat treatment to which they have been subjected. With the exception of Missinaibi (1323), all samples listed in this table are common, heterogeneous materials that contain generally similar constituents, although in varying proportions. The principal constituents of the eight common clays and shales are quartz, illite, chlorite (except Stevenson and Bracebridge), calcite (except Bracebridge with none and Stevenson with a trace), and generally very small amounts of feldspar.

TABLE 14

Mineralogical Composition of Selected Samples

SAMPLE	* UNFIRED COMPOSITION	FIRED		
		Firing Temperature	Absorption, %	**Fired Composition
Ottawa (Q) PCE 3 1/2	Quartz - about 24% Illite Chlorite Calcite - about 8% Plagioclase - minor Hematite	Cone 01 (1117°C)	12.2	Quartz (D) K-feldspar (D) Plagioclase (C) Hematite (D)
Nelson (Q) PCE 2 1/2	Quartz - about 24% Illite Chlorite Calcite - about 18% Dolomite - about 3% Plagioclase - trace Hematite - trace	Cone 1 (1136°C)	13.0	Quartz (A) K-feldspar (B) Plagioclase (E) Hematite (B)
Cooksville (D-M) PCE 4	Quartz - about 24% Illite Chlorite Calcite - minor Plagioclase Dolomite - trace Organic material and pyrite-trace	Cone 03 (1086°C)	7.9	Quartz (A) K-feldspar (A) Plagioclase (C) Hematite (A)
Parkhill (Hamilton) PCE 4 1/2	Illite Chlorite Quartz - about 19% Calcite - minor Dolomite Plagioclase - trace Organic material and pyrite Anatase	Cone 01 (1117°C)	8.3	Quartz (B) K-feldspar (E) Plagioclase (B) Hematite (B)
Billings PCE 1	Quartz - about 22% Illite Chlorite Plagioclase Pyrite - about 2.5% Calcite - about 2% Organic material	Cone 05 (1031°C)	6.8	Quartz (E) K-feldspar (D) Plagioclase (C) Hematite (E)
Stevenson PCE 3 1/2	Quartz - about 31% Illite Montmorillonoid-Chlorite-Illite Kaolin - minor Plagioclase - trace K-feldspar Amphibole Calcite Organic material	Cone 04 (1050°C)	6.3	Quartz (A) K-feldspar (B) Plagioclase (E) Hematite (D)
Wallenstein PCE 2 1/2	Quartz - about 22% Illite Montmorillonoid-Vermiculite Montmorillonoid-Chlorite Chlorite Calcite - substantial Dolomite - minor Plagioclase - trace K-feldspar - trace Organic material Amphibole	Cone 03 (1086°C)	19.2	Quartz (C) K-feldspar (C) Plagioclase (D) Hematite (E)
Bracebridge PCE 2	Plagioclase Quartz - about 30% Illite Montmorillonoid Illite-Montmorillonoid Vermiculite-Montmorillonoid K-feldspar Amphibole	Cone 04 (1050°C)	12.3	Quartz (C) K-feldspar (A) Plagioclase (A) Hematite (A)
Missinaibi (1323) PCE 30 1/2	Kaolin - about 62% Quartz - about 22% Anatase - trace Hematite	Cone 14+ (1395°C)	5.4	Quartz (C) Mullite (A) Cristobalite (A)

* Constituents of unfired samples listed in approximate order of abundance.

** Fired composition determined by R. H. Buchanan. Letters indicate the abundance of each constituent relative to that of the same constituent in the other samples. With exception of Ottawa (Q), Nelson (Q), and Stevenson, fired specimens contain minor unidentified constituents.

Bracebridge, a clay which was entirely derived from the rocks of the Canadian Shield, differs from the other common clay samples because of its high feldspar and low clay mineral content. The common clays listed in Table 14 contain mixed-layer clay minerals, whereas the shales do not.

The eight common clays and shales were fired at approximately the same temperatures (1031°C to 1136°C, depending on the sample) and the same crystalline constituents (quartz, K-feldspar, plagioclase, and hematite) were identified in each fired specimen.

Missinaibi (1323) consists mainly of a kaolin mineral and quartz, constituents which are common to fireclays. Quartz, mullite, and cristobalite were identified in this material after firing to 1395°C.

CONCLUSIONS

The clay mineral fraction of the Palaeozoic shale samples from southern and eastern Ontario consists essentially of a mixture of illite and chlorite. Minor kaolin was identified within the Upper Devonian Kettle Point shale.

The surficial deposits of southern Ontario contain clay minerals which have been largely derived from the underlying Palaeozoic strata. Within these clays, chlorite and, to a lesser extent, illite have been progressively altered by weathering to "frayed edge" mixed-layer systems containing expandable phases. Four samples from the extreme southwestern portion of the province contain minor quantities of kaolin which, presumably, was derived from the Kettle Point shale.

The clay minerals within Pleistocene deposits which were derived from the rocks of the Canadian Shield are poorly crystallized and rich in expandable phases, some of which occur as unmixed montmorillonoid and vermiculite. The two Cretaceous samples from the Missinaibi river valley are unique because of their high kaolin content.

The Palaeozoic shales contain a non-clay mineral suite consisting of quartz, calcite, lesser amounts of dolomite and plagioclase and, with the notable exception of the Rockcliffe sample, little or no K-feldspar. In contrast to this, Pleistocene clays derived from the Canadian Shield invariably contain minor quantities of amphibole, are relatively rich in plagioclase and K-feldspar, but are generally lacking in carbonate minerals. The abundance of the latter mineral suite within surficial clays overlying the Palaeozoic strata of southern Ontario indicates an important contribution by the rocks of the Canadian Shield to the non-clay mineral fraction of these deposits.

Organic material and pyrite are common constituents of the clays and shales. The clays contain, on the whole, more organic material than do the shales, but it is generally of the type which is readily burned out. Some shales contain an extremely large amount of both organic material and pyrite, a combination which requires a prolonged oxidation period during firing, to prevent bloating or black coring. As a result of the decomposition and oxidation of these substances, carbon dioxide, sulphur dioxide and/or sulphur trioxide are released into the kiln atmosphere.

The presence of calcite and/or dolomite strongly affects the colour and properties of the Ontario clays and shales. As the carbonate content increases, porosity increases, fired shrinkage and hardness decrease, and the fired colour changes from red to buff. Samples containing a substantial amount of calcite and/or dolomite have very short firing ranges.

The red-firing surface clay samples from southwestern Ontario, and most of the northern and northwestern ones, contain little or no carbonate; as a result, these fire easily to a hard, dense condition. Other problems, such as the presence of lime pebbles in some of them, and drying difficulties, exist with these clays.

The Ontario shales are generally hard and non-plastic despite their high content of chlorite and illite. Most of the clays are plastic, probably because almost all of these contain expandable layer silicates, either as part of mixed-layer systems or as unmixed phases.

The illite-chlorite-quartz-calcite-dolomite-feldspar mixtures (and mixed-layer clay systems in the surface clays) common to the shales and clays yield quartz, plagioclase, K-feldspar and hematite as crystalline constituents when fired.

The majority of the samples investigated, being very heterogeneous mixtures, have low melting points and frequently require close control in firing to produce uniform, dense products. The northern Ontario fireclay is an exception because the principal mineral constituents are quartz and kaolin, a refractory combination.

It was shown that atmosphere has an effect on the thermal expansion characteristics of some Ontario samples, particularly at temperatures between approximately 700 and 900°C. It was further demonstrated that the rate of heating affects the critical temperature range wherein reversals from expansion to shrinkage and from shrinkage to expansion occur. Other factors that may assume importance to thermal expansion are the method of forming and the green density of the specimens. The calcareous, low-fusion shales and clays present cracking problems during heating because one or two reversals from expansion to shrinkage, and perhaps also from shrinkage to expansion, generally occur at temperatures between about 700 and 900°C. This is not a problem for the non-calcareous sample from Bracebridge, but is a source of difficulty with the kaolin-quartz mixture from the Missinaibi river valley.

The very calcareous Ontario clays and shales evolve a large amount of carbon dioxide and a relatively small amount of water vapour. The opposite holds true for the Missinaibi (1323) fireclay, where a large volume of water vapour is evolved from the clay mineral. A non-calcareous, rock-flour type of sample, such as Bracebridge which contains a relatively small proportion of clay minerals, evolves a very small volume of gas. All such gases influence the control of drafts, kiln atmospheres and kiln pressures.

Many of the clay samples contain substantial proportions of quartz and feldspar. The bulk of these ingredients are of minus 200 mesh size and are therefore sufficiently fine grained to react during firing.

The exact values for certain fired properties, such as shrinkage and absorption of a particular sample at a given temperature, are affected by such factors as the method of forming, size of specimen, and firing schedule. Thus, caution must be exercised in making exact comparisons between properties of the samples published in this report. Among procedures used in the laboratory, the results show that the deaired, extruded, temperature-gradient bars, fired to a temperature close to the maturing point, produce the densest specimens, followed in order of decreasing density by the hand-moulded temperature gradient bars, the deaired extruded routine samples, the hand-moulded routine ones, and the dry-pressed samples. All deaired specimens are very dense at the lower firing temperature.

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REFERENCES

1. D.F. Hewitt, "Ceramic Raw Materials in Ontario", Jour. Can. Ceram. Soc. 19, 14-26 (1950).

2. G.R. Guillet, "Clay and Shale in Ontario", Jour. Can. Ceram. Soc. 33, 15-24 (1964).

3. Victor T. Allen and W.D. Johns, "Clays and Clay Minerals of New England and Eastern Canada", Bull. Geol. Soc. Amer. 71, 75-86 (1960).

4. J.E. Brydon and L.M. Patry, "Mineralogy of Champlain Sea Sediments and a Rideau Clay Soil Profile", Can. Jour. of Soil Sci. 41 (No. 2), 169-181 (1961).

5. A.G. Sadler, "The Mineral Constitution of Some Ordovician Shales of Eastern and Southern Ontario", Mines Branch Research Report R-94, Department of Mines and Technical Surveys, Ottawa (March 1962).

6. M.B. Baker, "Clay and the Clay Industry of Ontario", Report of Ont. Bur. of Mines, Vol. XV, Part II (1906).

7. J. Keele, "Preliminary Report on the Clay and Shale Deposits of Ontario", Memoir 142, Geological Survey, Department of Mines, Ottawa (1924).

8. R.J. Montgomery, "Ceramic Industry of Ontario", Report of the Ont. Dept. of Mines, XXXIX, Part IV (1930).

9. J. Keele, "The Abitibi and Mattagami Rivers, Clay and Shale Deposits", Report of Ont. Bur. of Mines, Vol. XXIX, Part II, 31-55 (1920).

10. J.M. Bell, "Economic Resources of Moose River Basin", Report of Ont. Bur. of Mines, Vol. XIII, Part IV, 135-179 (1904).

11. J. Keele, "Investigation of Clay and Shale Resources, Northern Ontario", Summary Report 421, Mines Branch, Canada Dept. of Mines, Ottawa, 127-129 (1916).

12. J. Keele, "Investigation of Clay and Shale Resources; Clays in Northern Ontario", Summary Report 493, Mines Branch, Canada Dept. of Mines, Ottawa, 102-108 (1918).

13. J. Keele, "Investigations of Clay and Shale Resources; Northern Ontario", Summary Report 509, Mines Branch, Canada Dept. of Mines, Ottawa, 167-168 (1920).

14. J. Keele, "Clays and Shales in Vicinity of Fort William and Port Arthur", Summary Report 542, Mines Branch, Canada Dept. of Mines, Ottawa, 105-108 (1920).

15. J. Keele, "Testing of Brick and Fireclays from the Various Provinces: Northern Ontario", Summary Report 574, Mines Branch, Canada Dept. of Mines, Ottawa, 56-58 (1922).

16. J. Keele, "Notes on Clays of the Missinaibi River", Report of Ont. Dept. of Mines, Vol. XXX, Part I, 171-175 (1921).

17. M.B. Baker, "Iron and Lignite in the Mattagami Basin". Report of Ont. Bur. of Mines, Vol. XX, Part I (1911).

18. F.H. McLearn, "The Mesozoic and Pleistocene Deposits of the Lower Missinaibi, Opazatika and Mattagami Rivers, Ontario", Summary Report, 1926, Part C, 16-47, Geol. Sur., Department of Mines, Canada (1927).

19. R.J. Montgomery and R.J. Watson, "Fire Clay, Kaolin and Silica Sand Deposits of the Mattagami and Missinaibi Rivers", Report of Ont. Dept. of Mines, Vol. XXXVII, Part VI, 80-120 (1928).

20. W.S. Dyer and R.J. Montgomery, "Semi-Commercial Tests on Northern Ontario Fire Clays", Report of Ont. Dept. of Mines, Vol. XXXVIII, Part IV, 19-21 (1929).

21. R.J. Montgomery, "Laboratory Tests on Northern Ontario Fire Clays", Report of Ont. Dept. of Mines, Vol. XXXVIII, Part IV, 23-25 (1929).

22. W.S. Dyer, "Fire Clay Deposits of the Moose River Basin", Jour. Can. Ceram. Soc. 1, 32-39 (1932).

23. E.R. Davey, "Tests on Onakawana Fire Clays", Jour. Can. Ceram. Soc. 1, 40-46 (1932).

24. W.S. Dyer and A.R. Crozier, "Lignite and Refractory Clay Deposits of the Onakawana Lignite Field", Report of Ont. Dept. of Mines, Vol. XLII, Part III, 46-78 (1933).

25. A.R. Crozier, "Refractory Clay Deposits on the Missinaibi River", Report of Ont. Dept. of Mines, Vol. XLII, Part III, 88-101 (1933).

26. A.E. Hilder, "Mattagami River Refractory Clays, Recent Investigations and Future Development", Transactions of Canadian Institute of Mining and Metallurgy 38, 110-122 (1935).

27. Sidney Hancock Jr., "China Clay and Silica Sand in Kipling Township, Ontario", Canadian Mining Journal 46, 1149-1151 and 1178-1179 (1925).

28. R.J. Montgomery, "Some Fundamental Properties of Ontario Clays and Shales", Jour. Can. Ceram. Soc. 3, 28-32 (1934).

29. F.V.C. Hewett and R.J. Montgomery, "Assay Crucibles from Northern Ontario Fire Clays", Jour. Can. Ceram. Soc. 4, 39-41 (1935).

30. W.M. Naish, "Improving the Extrudability of a Queenston Shale by Experimentation on a Production Basis", Jour. Can. Ceram. Soc. 18, 57-59 (1949).

31. W.M. Naish, "A Further Report on the Queenston Shale", Jour. Can. Ceram. Soc. 19, 45-46 (1950).

32. W.M. Naish, "A Final Report on Improving the Extruding Properties of a Queenston Shale", Jour. Can. Ceram. Soc. 20, 41-43 (1951).

33. W.M. Naish, "Conditioning and Extruding a Low Plastic Shale", Jour. Can. Ceram. Soc. 22, 70-74 (1953).

34. Paul M. Corbett, "Methods of Affecting Fired Colours of Southern Ontario Brick Clays", Journ. Can. Ceram. Soc. 19, 47-54 (1950).

35. Frank H. McRitchie, "The Firing Behaviour of Three Canadian Pipe Clays", Jour. Can. Ceram. Soc. 22, 51-60 (1953).

36. E. Groskaufmanis, "Ceramic Glazes on Structural Clay Materials", Jour. Can. Ceram. Soc. 27, 108-111 (1958).

37. K.E. Bell, "Some Aspects of the Plastic and Related Properties of Queenston Shales", Jour. Can. Ceram. Soc. 31, 106-119 (1962).

38. J.G. Matthews, "Preliminary Report on Coated Lightweight Concrete Aggregate from Canadian Clays and Shales, Part III, Ontario", Memorandum Series No. 121, Mines Branch, Department of Mines and Technical Surveys, Ottawa (1952).

39. H.S. Wilson, "Lightweight Concrete Aggregates from Clays and Shales in Ontario", Mines Branch Technical Bulletin 51, Department of Mines and Technical Surveys, Ottawa (1963).

40. B.V. Sanford, "Geological Map of Southwestern Ontario Showing Oil and Natural Gas Producing Areas (1 in. = 6 mi.)", Geological Survey of Canada Map 1062A (1957).

41. B.A. Liberty et al., "Geology of Central Ontario", Amer. Assoc. Petrol. Geol. and Soc. Econ. Paleont. and Mineral. Guidebook (May, 1964).

42. B.V. Sanford, "Sources and Occurrences of Oil and Gas in the Sedimentary Basins of Ontario", Proc. Geol. Assoc. Can. 14, 59-89 (1962).

43. Alice E. Wilson, "Geology of the Ottawa-St. Lawrence Lowland, Ontario and Quebec", Memoir 241, Geological Survey of Canada (1946).

44. L.J. Chapman and D.F. Putnam, "The Physiography of Southern Ontario", Univ. of Toronto Press (1951).

45. J.G. Brady, K.E. Bell and L.K. Zemgals, "Some Methods of Invesitgation Firing Problems", Jour. Can. Ceram. Soc. 34, 9-20 (1965).

46. R.L. Stone, "Temperature Gradient Method for Determining Firing Range of Ceramic Bodies", Jour. Amer. Ceram. Soc. 36 (4), 140-142 (1953).

47. D.J. Charette, J.C. Hole and E. Mark, "Chemical Analysis of Ten Clays and Shales from Ontario", Internal Report MS-65-59, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa (June 22, 1965).

48. J.G. Brady, "Physical Properties and Differential Thermal Analysis of Some Canadian Clays and Shales", Jour. Can. Ceram. Soc. 26, 71-89 (1957).

49. J.G. Brady and R.S. Dean, "Ceramic Clays and Shales of British Columbia", Jour. Can. Ceram. Soc. 32, 46-70 (1963), and Mines Branch Technical Bulletin TB-54, Dept. of Mines and Tech. Surveys, Ottawa (January 1964).

50. P.M. deWolff, "Multiple Guinier Cameras", Acta Cryst. 1, 207-211 (1948).

51. O.P. Mehra and M.L. Jackson, "Iron Oxide Removal from Soils and Clays by a Dithionite-Citrate System Buffered with Sodium Bicarbonate", pp. 317-327, Clays and Clay Minerals, Proceedings of the Seventh National Conference on Clays and Clay Minerals, Pergamon Press, London (1960).

52. Isao Hashimoto and M. L. Jackson, "Rapid Dissolution of Allophane and Kaolinite-Halloysite after Dehydration", pp. 102-113, Clays and Clay Minerals, Proceedings of the Seventh National Conference on Clays and Clay Minerals, Pergamon Press, London (1960).

53. Claude L. Marshall, "A New Concept of Clay Plasticity", Bull. Amer. Ceram. Soc. 34 (2), 54-56 (1955).

54. L. J. Trostel and D. J. Wynn, "Determination of Quartz (Free Silica) in Refractory Clays", Jour. Amer. Ceram. Soc. 23 (1), 18-22 (1940).

55. George W. Brindley, "Identification of Clay Minerals by X-ray Diffraction Analysis", pp. 119-129, Clays and Clay Technology, Proceedings of the First National Conference on Clays and Clay Technology, California Div. of Mines Bull. 169 (1955).

56. C.M. Warshaw and R. Roy, "Classification and a Scheme for the Identification of Layer Silicates", Bull. Geol. Soc. Amer. 72, 1455-1492 (1961).

57. K.M. Towe, "Lateral Variations in Clay Mineralogy Across Major Facies Boundaries in the Middle Devonian (Ludlowville), New York", Ph. D. thesis, Graduate College, University of Illinois, Urbana (1961).

58. H.S. Yoder Jr. and H.P. Eugster, "Synthetic and Natural Muscovites", Geochim. et Cosmochim. Acta 8, 225-280 (1955).

59. R.S. Dean, "A Study of St. Lawrence Lowland Shales", Ph. D. thesis, Department of Geological Sciences, McGill University, Montreal (1962).

60. C.P. Gravenor, "Bedrock Source of Tills in Southwestern Ontario", Amer. Jour. Sci. 249, 66-71 (1951).

61. M.L. Jackson, S.A. Tyler, A.L. Willis, G.A. Bourbeau and R.P. Pennington, "Weathering Sequence of Clay-Size Minerals in Soils and Sediments", Jour. of Physical & Colloid Chem. 52, 1237-1260 (1948).

62. J.B. Droste, "Alteration of Clay Minerals by Weathering in Wisconsin Tills", Bull. Geol. Soc. Amer. 67, 911-918 (1956).

63. G.W. Brindley, "Chlorite Minerals", pp. 242-296, The X-ray Identification and Crystal Structures of Clay Minerals, Mineralogical Society, London (1961).

64. H. Steinfink, "The Crystal Structure of Chlorite. I: A monoclinic polymorph", Acta Cryst. 11, 191-195 (1958).

65. R.H. Bray, "Chemical and Physical Changes in Soil Colloids with Advancing Development in Illinois Soils", Soil Sci. 43, 1-14 (1937).

66. M.L. Jackson, "Interlayering of Expansible Layer Silicates in Soils by Chemical Weathering", pp. 29-46, Clays and Clay Minerals, Proceedings of the Eleventh National Conference on Clays and Clay Minerals, The MacMillan Company, New York (1963).

67. D.M.C. MacEwan, "Some Notes on the Recording and Interpretation of X-ray Diagrams of Soil Clays", Journ. of Soil Sci. 1, 90-103 (1949).

68. D.M.C. MacEwan, A. Ruiz Amil and G. Brown, "Interstratified Clay Minerals", pp. 393-445, The X-ray Identification and Crystal Structures of Clay Minerals, Mineralogical Society, London (1961).

69. Ralph E. Grim and William D. Johns, "Clay Mineral Investigation of Sediments in the Northern Gulf of Mexico", pp. 81-103, Clays and Clay Minerals, Proceedings of the Second National Conference on Clays and Clay Minerals, Nat. Acad. Sci.-Nat. Res. Coun. Pub. 327, Washington (1954).

70. G.W. Brindley and S.Z. Ali, "X-ray Study of Thermal Transformations in Some Magnesian Chlorite Minerals", Acta Cryst. 3, 25-30 (1950).

71. A. Dreimanis, G.H. Reavely, R.J.B. Cook, K.S. Knox and F.J. Moretti, "Heavy Mineral Studies in Tills of Ontario and Adjacent Areas", Jour. Sed. Petrol. 27, 148-161 (1957).

72. Carol I. Dell, "A Study of the Mineralogical Composition of Sand in Southern Ontario", Can. Jour. of Soil Sci. 39, 185-196 (1959).

73. L.D. Whittig and M.L. Jackson, "Mineral Content and Distribution as Indexes of Weathering in the Omega and Ahmeek Soils of Northern Wisconsin", pp. 362-371, Clays and Clay Minerals, Proceedings of the Fourth National Conference on Clays and Clay Minerals, Nat. Acad. Sci. - Nat. Res. Coun. Pub. 456, Washington (1956).

74. Haydn H. Murray and R.K. Leininger, "Effect of Weathering on Clay Minerals", pp. 340-347, Clays and Clay Minerals, Proceedings of the Fourth National Conference on Clays and Clay Minerals, Nat. Acad. Sci. - Nat. Res. Coun. Pub. 456, Washington (1956).

75. J.B. Droste and J.C. Tharin, "Alteration of Clay Minerals in Illinoian Till by Weathering", Bull. Geol. Soc. Amer. 69, 61-68 (1958).

76. John B. Droste, N. Bhattacharya and Jack A. Sunderman, "Clay Mineral Alteration in Some Indiana Soils", pp. 329-342, Clays and Clay Minerals, Proceedings of the Ninth National Conference on Clays and Clay Minerals, The MacMillan Company, New York (1962).

77. L.R. Webber and J.A. Shivas, "The Identification of Clay Minerals in Some Ontario Soils : 1. Parent Materials", Soil Sci. Soc. of Amer. Proc. 17, 96-99 (1953).

78. Ralph E. Grim, "Applied Clay Mineralogy", McGraw-Hill Book Company, Inc., New York, N.Y. (1962), Chap. 3, pp. 52-140.

79. J.G. Brady, "The Effect of the Mineralogical Composition of Whitemud Formation Clays on Their Utilization", Research Report R 99, Mines Branch, Dept. of Mines and Tech. Surveys, Ottawa (Aug. 1962).

80. Richard West, "Dilatometry of Structural Clay Products", Jour. Can. Ceram. Soc. 34, 29-33 (1965).

81. K.E. Bell, "The Influence of Lime on the Thermal Expansion of Clay", Jour. Can. Ceram. Soc. 34, 21-27 (1965).

82. E. Groskaufmanis, "Firing Face Brick in a Tunnel Kiln", Bull. Amer. Ceram. Soc. 41 (3), 151-155 (1962).

83. G.C. Robinson, "Planning a Kiln Schedule to Fit the Raw Material", presented at the Clay Plant Operators Forum, 1963, reported in Ceramic Age 79 (12), 56 (1963).

84. W.E. Brownell, "Efflorescence Resulting from Pyrite in Clay Raw Materials", Jour. Amer. Ceram. Soc. 41 (7), 261-266 (1958).

85. W.E. Brownell, "Efflorescence Resulting from Sulphates in Clay Raw Materials", Jour. Amer. Ceram. Soc. 41 (8), 310-314 (1958).

86. Pol Paquin, "Contribution à la Détermination de Certains Minéraux Argileux par Dilatométrie, Essais Quantitatifs", supplement to the Bulletin de la Société Française de Céramique, No. 58, January-March, 1963.

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