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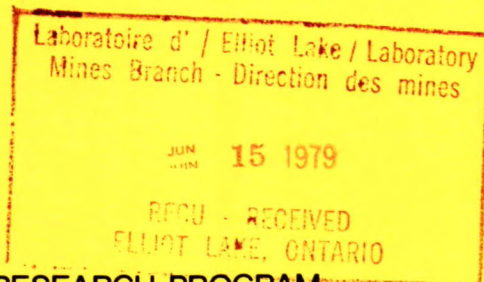
Canada Centre
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Centre canadien
de la technologie
des minéraux
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REPORT 78-21

CERAMIC CLAYS AND SHALES OF THE ATLANTIC PROVINCES

K.E. BELL, J.G. BRADY AND L.K. ZEMGALS



MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

JANUARY 1978

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Available by mail from:

Printing and Publishing
Supply and Services Canada,
Ottawa, Canada K1A 0S9

CANMET
Energy, Mines and Resources Canada,
555 Booth St.,
Ottawa, Canada K1A 0G1

or through your bookseller.

Catalogue No. M38-13/78-21 Price: Canada: \$3.00
ISBN 0-660-10214-5 Other countries: \$3.60

Price subject to change without notice.

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En vente par la poste:

Imprimerie et Édition
Approvisionnement et Services Canada,
Ottawa, Canada K1A 0S9

CANMET
Énergie, Mines et Ressources Canada,
555, rue Booth
Ottawa, Canada K1A 0G1

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Nº de catalogue M38-13/78-21 Prix: Canada: \$3.00
ISBN 0-660-10214-5 Autres pays: \$3.60

Prix sujet à changement sans avis préalable.

CERAMIC CLAYS AND SHALES OF THE ATLANTIC PROVINCES

by

K.E. Bell*, J.G. Brady** and L.K.Zemgals***

ABSTRACT

The work reported forms part of the Mineral Resource Determination Activity of the EMR Minerals Program. Previous reports have dealt with the clays and shales of British Columbia, Ontario and Quebec. The results constitute a contribution to the knowledge base necessary to ensure the orderly and efficient development of the ceramic industry in Canada, particularly in the clay products field. Twenty-nine samples, representative of a variety of typical clays and shales indigenous to the region, were examined to determine their composition and salient ceramic properties. In addition, the forming and firing characteristics of ten of the samples were studied in considerable detail. The results made it possible to evaluate suitability of the material for manufacturing ceramics, to determine processing problems that might be expected, and to make assumptions as to the most likely geological formations containing the best quality of ceramic material.

High-quality china clays, or kaolins, and ball clays are not found in the region. Two well-known deposits of kaolinitic material are classified as fire clays, owing to contamination with quartz, iron-bearing minerals and other impurities: although selected seams appear to meet requirements for medium-duty fireclay brick, the deposits as a whole are suitable only for low-duty application.

Good-quality red-firing shales are abundant throughout the region, particularly where associated with formations of Carboniferous age. These shales are notable for their substantial kaolin content, which imparts increased refractoriness and a wide firing range suitable for dense wares such as good-quality

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structural clay products and vitrified earthenware pottery.

The surface clays of the region are usually common, heterogenous, red-firing materials, with the expected low fusion temperatures and short firing ranges. Those that owe their origin to nearby bedrock shales may be suitable for use in the manufacture of porous products such as partition tiles, flower pots or low-grade earthenware, but they find their most useful application in mixtures with other material - shales or fire clays - where the better features of one material compensate for the shortcomings of another.

ARGILES ET SCHISTES ARGILEUX DE QUALITE CERAMIQUE DES
PROVINCES DE L'ATLANTIQUE

par

K.E. Bell*, J.G. Brady**, L.K. Zemgals***

RESUME

Le travail dont il est fait état dans ce rapport s'inscrit dans le cadre de l'activité du Programme des minéraux d'EMR qui a trait à l'évaluation des ressources minérales. D'autres rapports ont déjà été rédigés à propos des argiles et schistes argileux de la Colombie-Britannique, de l'Ontario et du Québec. Les résultats obtenus viennent enrichir les connaissances que nous devons avoir du domaine pour assurer l'essor de l'industrie de la céramique au Canada, particulièrement dans le secteur des produits argileux. Les auteurs ont examiné vingt-neuf (29) échantillons d'argiles et de schistes de divers types qui ont été recueillis dans la région à l'étude; ils en ont déterminé la composition et les propriétés du point de vue de la fabrication des céramiques. Ils ont également étudié dix d'entre eux dans le menu détail pour voir comment ils se comportent lors du façonnage et de la cuisson. Les résultats permettent d'évaluer la possibilité pour ces substances d'entrer dans la composition de produits céramiques, de déterminer la nature des problèmes de traitement aux-quels on peut s'attendre et d'émettre certaines hypothèses concernant les formations géologiques les plus susceptibles de renfermer les meilleures matières premières pour la fabrication des céramiques.

On ne trouve pas d'argile pour la fabrication de la porcelaine de haute qualité surnommée kaolin ni d'argile pour mise en boule (ball clay) dans la région. Deux gisements bien connus

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de matériaux kaolinitiques sont classés comme argiles réfractaires parce qu'ils renferment du quartz, des minéraux ferrifères et d'autres impuretés; quelques-unes des couches choisies semblent remplir les conditions nécessaires à la fabrication de briques réfractaires de résistance moyenne, mais, dans l'ensemble, ces argiles ne se prêtent qu'à des applications nécessitant une faible résistance.

Dans la majeure partie de la région, on trouve en abondance des schistes argileux rouges après cuisson de bonne qualité, associés pour la plupart à des formations d'âge carbonifère. Ces schistes se distinguent par leur forte teneur en kaolin qui améliore la résistance à la chaleur et élargit la gamme de températures de cuisson des produits denses, comme des produits à base d'argile de construction de bonne qualité ou des poteries en terre cuite vitrifiée.

Les argiles de surface que l'on trouve dans la région sont habituellement des matériaux communs, hétérogènes et rouges après cuisson, dont les températures de fusion sont basses et les gammes de températures de cuisson peu étendues. Ceux qui ont leur origine dans les schistes qui forment la roche de fond peuvent convenir à la fabrication de produits poreux, comme des tuiles de cloison, des pots à fleurs ou des articles en terre cuite de faible qualité. Habituellement, les mélanges avec d'autres matériaux (schistes ou argiles réfractaires) sont les plus utiles, car les meilleures propriétés de l'un suppléent aux défauts de l'autre.

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INTRODUCTION

A variety of clays and shales suitable for the manufacture of ceramic products occurs in all four Atlantic provinces. As in most parts of Canada, although there are no known deposits of high-grade kaolinitic clays, there are a few occurrences of low- to medium-duty plastic fire clays and stoneware clays in Nova Scotia. In all four there are also good-quality, red-burning common clays and shales suitable for such products as facing brick, sewer pipe, drain tile, building tile, and earthenware pottery.

Considering the geological background such variety is not surprising. With exception of the extreme northwest peninsula of Newfoundland, which is part of the relatively flat-lying St. Lawrence platform, the entire region under consideration forms the northeastern extension of the Appalachian orogenic zone. The geological record indicates alternating periods of regional uplifting accompanied by erosion -- e.g., much of the early Cretaceous Period is missing -- and periods of subsidence accompanied by sedimentation and volcanic outpouring. The geological history has been characterized by repeated folding, faulting, intrusion and metamorphism that has occurred on a relatively local scale, although at least two major disturbances of regional importance have been recognized. As a result of this tectonic activity, the bedrock may vary locally from early Precambrian rocks to lower Cretaceous clays. Physiographically, the region is

divided into a number of relatively small upland peneplains separated from lowland areas by mountain remnants. Thus the shale deposits are likely to be of limited areal extent, frequently occurring in folded belts, and may dip steeply in contrast to the extensive flat-lying deposits of central Canada and the prairies.

Similarly, clays derived from the bedrock are usually found in the channels of ancient rivers. The physiography of the region has precluded the formation of large bodies of water or seas, so that extensive lacustrine deposits are absent. The same applies to glacial and glaciofluvial deposits, which were not thickly deposited. It is believed there was no large-scale movement of ice-borne material but rather a relatively stable center of glaciation over central Newfoundland and possibly another in New Brunswick, from which glacial movement carried detritus to the Gulf of St. Lawrence and the continental shelf. With retreat of the glaciers, there was some inundation of the coastal areas, with sedimentation of marine clays and some deposition of fluvial material in the river valleys. Certain topographical features appear to have dominated for a considerable length of time, serving to channel rivers and streams in the same direction; many of the present rivers are believed to be flowing through the sediment-filled channels of pre-existing streams and it follows that existing clay outcrops may represent only lens-like deposits along the stream banks.

In the search for clays and shales for ceramic use,

it is therefore difficult to predict which areas have potential — diligent prospecting is necessary and the extent and uniformity of any deposit requires careful checking before proceeding with development.

In past years, as in most settled parts of Canada, the region saw the development and demise of numerous small clay product plants, using mostly surface clays of dubious character and satisfying strictly local needs. Of course, demands on the properties of clays and clay products at that time were less stringent than today. Fréchette ⁽¹⁾ reported the existence of brickworks in Nova Scotia at Avonport, Barney Brook, Lantz Siding, Pugwash, New Glasgow and Plymouth, and in New Brunswick at Bathurst West, Campbellton, Fredricton, Grafton, Nelson, St. John and St. Stephen. Sewer pipe was made at New Glasgow, N.S. Potteries were producing flower pots at Fairview and Middleton in Nova Scotia, and artware at St. Andrews and St. John in New Brunswick. Both silica brick and low-duty fireclay brick for ladles were manufactured at Sydney, N.S., and firebrick was made at New Glasgow, N.S. and St. John, N.B. Earlier still, it has been suggested that some of the bricks used to construct the original fortress at Louisbourg may have been made locally from surface clays at nearby Mira River where a brick plant flourished in the late 1800's. Today, the market for structural clay products is supplied by four plants manufacturing brick and tile — two in Nova Scotia, one in New Brunswick and one in Newfoundland — and one sewer pipe plant at New Glasgow, N.S. No such commercial enterprise

exists on Prince Edward Island, where, however, a small pottery industry has developed, principally comprising cottage and studio potters catering to the tourist trade and utilizing small local deposits of weathered shale, sometimes augmented with fire clay from the Musquodoboit valley in Nova Scotia. A number of studio potters are also active in Nova Scotia, New Brunswick and, more recently, Newfoundland. The only major pottery of the region, at St. John, N.B., was removed a few years ago to the province of Québec. Recently, small potteries have begun operations at Charlottetown, P.E.I., and Fredicton, N.B.

The first comprehensive study of promising deposits in Nova Scotia and New Brunswick was made just prior to World War 1 by Ries and Keele ^(2,3,4). More recently, Barnett and Abbot investigated some clays and shales from New Brunswick ⁽⁵⁾. Matthews investigated samples from Nova Scotia, New Brunswick and Prince Edward Island for light-weight aggregate production ⁽⁶⁾. An unusual white-firing material from Middleton, N.S., was described by Cameron ⁽⁷⁾. Some refractory clays of Nova Scotia and New Brunswick have received much attention, some aspects of which have been discussed by Ries, Keele, Fréchette, McMahon, Wright and Brady ^(2,3,8,9,10,11).

The clays and shales of Prince Edward Island have been described by Fréchette, McMahon, MacPherson, Milligan, Brady and Prest ^(12,13,14,15,16). This work has indicated there is no sizeable deposit of clay on the island having suitable properties for the manufacture of facing brick, according to

present standards. However, the bedrock formations include considerable shale, some of which has characteristics that permit the production of brick and tile. The clays and shales are red-firing and fuse at temperatures too low for firebrick manufacture.

Few detailed reports of the properties of Newfoundland clays and shales are available (17-21). According to Snelgrove there are large clay deposits along the coast and in the valleys of major rivers owing to glaciofluvial action (22). The clay samples examined at CANMET have not usually had properties suitable for good-quality facing brick. The red-firing bedrock shales that occur in some localities have more favourable properties (23).

The portion of this report dealing with evaluating ceramic properties of the clays and shales and their relationship to composition was prepared by K.E. Bell, J.G. Brady and L.K. Zengals. Mineralogy of the unfired samples was taken from Dean, who discussed the geological/mineralogical relationships (24). The mineralogy of the fired specimens was determined by R.M. Buchanan. Differential thermal analyses were interpreted by J.G. Brady and L.K. Zengals. K.E. Bell established methods for determining plasticity, differential thermogravimetric analyses and dilatometry in the Ceramic Section. Most of the samples were obtained by J.B. Brady, but some from New Brunswick were supplied by the New Brunswick Research and Productivity Council.

SCOPE OF INVESTIGATION

As with previous reports on the clays and shales of Ontario and Quebec, this report outlines the characteristics of typical clays and shales from the Atlantic Provinces that are suitable for the manufacture of clay products (25,26). The relationship between chemical and mineralogical composition and the processing properties of these ceramic raw materials is also discussed.

Twenty-nine samples of clay and shale are reported on. Many are from currently or formerly operated pits serving the clay products industry, others represent deposits considered potentially useful for clay products manufacture. The samples, classified according to province of origin, are identified in Table 1 and the approximate locations are shown in Fig. 1.

All of the samples were analyzed chemically. Mineralogical composition was determined by X-ray diffractometry (XRD) supplemented by differential thermal analysis (DTA). The salient ceramic properties, both fired and unfired, were determined, enabling an evaluation of their suitability for the manufacture of clay products.

Ten samples, generally representative of the various areas and varieties of material, were selected for more detailed studies of plasticity and extrudability. Also examined was the firing behaviour by temperature gradient firing, thermogravimetric

TABLE 1
Materials Investigated

Sample	Company	Nature of Deposit	Pit or Sample Location
NEWFOUNDLAND			
1. Random Island	Pelly-Shaw Newfoundland Limited	Lower Ordovician shale -upper 10-ft section; used for facing brick.	Pit on the northwest tip of Random Island on Trinity Bay and close to causeway.
2. Milton	C&M Pelly Ltd (now Pelly- Shaw Limited)	Several ft common surface clay; formerly used for common brick.	From pit at brick plant at Milton (near Clarenville on Trinity Bay).
3. Manuels River	--	Upper 15 ft of Cambrian shale.	From exposed section on east side of the Manuels River and north of the bridge over this river near Manuels, Conception Bay.
4. Summerside	--	Reddish Cambrian shale.	Taken from quarry at Summerside, Humber Arm.
PRINCE EDWARD ISLAND			
5. Howards Cove	--	Top 10 ft early Permian shale below about 4 ft overburden.	From cliffs at Howards Cove (near Cape Wolfe and 100 yds north of wharf) Queens Co.
6. Bacon Point	--	10 ft early Permian shale below about 10 ft glacial drift.	Taken from the cliffs at Bacon Point on Hillsborough Bay, Queens Co.
NOVA SCOTIA			
7. Sydney	Harris and Harris	4-ft section soft shale above sandstone, Upper Carboniferous (Point Edward).	From back of pit on Terrace Street just off Highway 4 and just inside city limits of Sydney, Cape Breton Co.
8. Cranton	--	Top few feet surface clay.	From farm of F. Timmons, (1958), Cranton P.O., Inverness Co., Cape Breton.
9. Antigonish	--	Red Upper Carboni- ferous shale (Canso Group).	From a 6-ft section on road cut at bridge over Pomquet River on trans-Canada Highway about 9 miles east of Antigonish, Antigonish Co.

TABLE 1 (Cont'd)

Sample	Company	Nature of Deposit	Pit or Sample Location
NOVA SCOTIA (Cont'd)			
10. New Glasgow "A"	Standard Clay Products, Limited	10 ft red plastic Carboniferous shale (Upper Stellarton) - may include a small amount of glacial drift; occurs above 1st oil shale seam; used for sewer pipe.	Taken as overburden at L.E. Shaw pit (see New Glasgow "C"), New Glasgow, Pictou Co.
11. New Glasgow "B"	Standard Clay Products, Limited	20 ft grey-blue soft Carboniferous shale (Stellarton Group); some surface clay probably admixed.	Representative sample from pit of Standard Clay Pro- ducts on the east bank of the river and just north of Highway 4 in New Glasgow, Pictou Co.
12. New Glasgow "C"	L.E. Shaw Limited	A 20-ft face dark blue-grey Carboni- ferous shale (Stellar- ton Group) below the oil shale seams; used for facing brick.	From L.E. Shaw pit 1/2 mile north of Highway 4 and about 1 1/2 miles east of the bridge on Highway 4 over the river in New Glasgow, Pictou Co.
13. Shubenaca- die	L.E. Shaw Limited	A borehole sample of a grey plastic fire clay, probably Creta- ceous.	From L.E. Shaw property (formerly Dominion Steel Company Limited), just east of Highway 2 and the rail- road, and on the southern outskirts of Shubenacadie, Hants Co.
14. Milford	L.E. Shaw Limited	A red Lower Carboni- ferous shale (Windsor Group); used for facing brick.	From pit between Highway 2 and the Shubenacadie River and 1/4 mile north of the river at Milford Station, Hants Co.
15. Lantz	L.E. Shaw Limited	An 8-ft section of red surface clay used for facing brick.	From pit on the east side of railroad and about 1 mile southwest of Lantz, Hants Co.
16. Musquodo- boit	--	Top 2 ft of a plastic, light-red fire clay below about 2 ft of overburden; Cretaceous; used for fire clay.	From pit area on Fenwick Foley farm in the valley and along the brook at the outskirts of Middle Musquo- doboit, Halifax Co.

TABLE 1 (Cont'd)

Sample	Company	Nature of Deposit	Pit or Sample Location
NOVA SCOTIA (Cont'd)			
17. Middleton	--	Light-buff clay or soft shale; probably altered Triassic shale.	On steep slope about $\frac{1}{3}$ mile northwest of Reg Neilly farm buildings (1950) and about $2\frac{3}{4}$ miles north of Middleton, Annapolis Co.
18. Parrsboro	--	Top few feet of red surface clay.	From about 1 mile north of the mouth of the Diligent River and some 6 miles west of Parrsboro, Cumberland Co.
NEW BRUNSWICK			
19. Alma	Sample No. 57, RPC* Research Note 6.	Grey, Carboniferous shale (Boss Point formation) on upper 6 ft of cliff.	From upper cliff on Bay of Fundy about $\frac{1}{4}$ mile east of Alma, Albert Co.
20. St. John	Formerly Atlantic Building Products Sample No. 8, RPC* Research Note 6.	6 ft red surface clay formerly used for building brick.	From a pit at Little River on Courtney Bay, near St. John, Saint John Co.; (plant and pit not now in operation).
21. Charlotte	Sample No. 1, RPC* Research Note 6.	4-ft section of grey surface clay.	From upper part of marine terrace on north bank of St. Croix River and $1\frac{1}{2}$ miles east of Highway 3 near St. Stephen, Charlotte Co.
22. Cornhill	Sample No. 37, RPC* Research Note 6.	Upper 2 ft of brown Carboniferous shale (Mississippian, Albert Formation).	From road cut $2\frac{1}{4}$ miles east-northeast of Cornhill, Kings Co.
23. Flowers Cove	Avon Coal Company, Limited	A 2-ft seam of soft Carboniferous shale (Lower Pennsylvanian, Minto Formation).	From near Minto, N.B.; coal stripping operation immediately below coal and below about 25 ft of overburden, 2 miles west of Flowers Cove (on Grande Lake), Queens Co.

TABLE 1 (Cont'd)

Sample	Company	Nature of Deposit	Pit or Sample Location
NEW BRUNSWICK (Cont'd)			
24. Chipman	L.E. Shaw Limited	A 25-ft face of red Carboniferous shale (Pennsylvanian, Hurley Creek formation); used for facing brick.	From a pit between the highway and railway near Redbank, N.B. and about 2 miles by road from the Shaw plant at Chipman, Queens Co.
25. Beersville	Michiels Pit; Sample No. 39, RPC* Research Note 6.	A 6-ft section of a grey Carboniferous shale (Pennsylvanian, Pictou Group).	From coal stripping operation on east bank of Coal Branch River and 1/2 mile south of the bridge, and 1 mile southeast of Beersville, Kent Co.
26. Upper Napan	--	6-ft section of brown, surface, marine clay overlying Carboniferous strata.	Sample from 13 auger holes at Upper and Centre Napan 1/4 mile southeast of the bridge over the Napan River and adjacent to Highway 11, at Upper Napan, Northumberland Co.
27. Ste. Anne	--	2-ft seam of grey, weathered shale (Carboniferous).	Sample from under thin coal seam and under about 10 ft overburden on south shore of Caraquet Bay at Ste. Anne-du-Bocage, Gloucester Co.
28. Stonehaven	--	15-ft section of red, Carboniferous shale (Pennsylvanian, Clifton formation).	Sample from below about 4 ft overburden on the cliff near the Government wharf, Stonehaven, Gloucester Co.
29. St. Leonard	Sample No. 5, RPC* Research Note 6.	2 ft of grey surface clay.	From the east bank of the St. John River and 1/4 mile south of bridge on Highway 17 at St. Leonard, Madawaska Co.

*New Brunswick Research and Productivity Council.

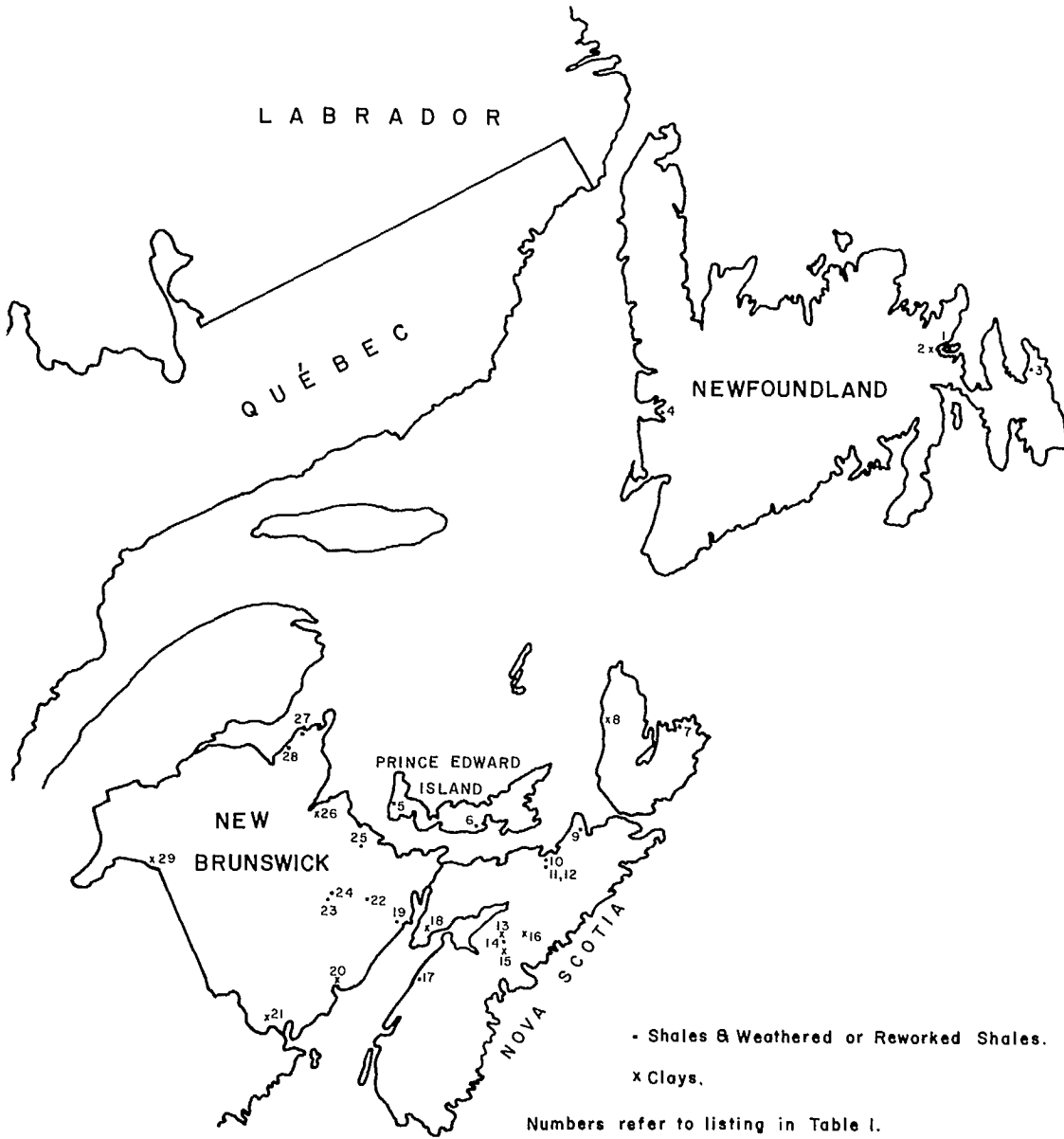


Figure 1. Locations of samples.

analysis (TGA) and thermal dilatometric analysis (TDA). This group of samples came from the following locations:

- | | |
|---------------------|------------------|
| 1. Random Island | 16. Musquodoboit |
| 6. Bacon Point | 17. Middleton |
| 12. New Glasgow "C" | 20. St. John |
| 13. Shubenacadie | 24. Chipman |
| 15. Lantz | 28. Stonehaven |

EXPERIMENTAL PROCEDURE

Investigation of Physical Properties

All samples were ground to pass a 16-mesh Tyler laboratory screen. Any effervescence with dilute hydrochloric acid was noted. The unfired and fired properties of all samples except Upper Napan were obtained from 10 x 4 x 3 cm, hand-moulded specimens because of the small quantity of material required and the simplicity of the equipment. Specimens for routine investigation of the Upper Napan sample, 10 cm by 2.5 cm square, were extruded under vacuum by a Midvale-Heppenstall extrusion press.

Similar de-aired, extruded specimens were prepared from the Random Island and New Glasgow "C" samples. Dry-pressed specimens, measuring 8 x 4 x 2.5 cm, were prepared from the Random Island sample. The fired properties of hand-moulded, extruded, and dry-pressed Random Island specimens were compared. A comparison was made of the firing behaviour and fired properties of extruded and hand-moulded New Glasgow "C" specimens.

The amount of water added to the dry samples to bring

them to a plastic condition for forming (water of plasticity) was measured. The plasticity of the samples was noted empirically by feel at the time the test specimens were prepared. A freshly formed specimen of each sample was placed in a laboratory dryer maintained at 85°C and any evidence of cracking under these severe conditions was noted after about 15 to 25 minutes. The remaining specimens were air-dried and then dried overnight in a laboratory dryer at 110°C. The drying shrinkage, based on the wet length of the specimen, was calculated.

All specimens for routine investigation were fired, in duplicate, in electrically heated laboratory kilns at various appropriate temperatures. The firing shrinkage based on wet length, 24-hour absorption in cold water, colour, and hardness were all noted. The total shrinkage, based on the original wet size, could then be obtained by direct addition of the drying and firing shrinkages. The pyrometric cone equivalent (PCE), which is approximately the heat-softening point, was determined.

Temperature Gradient Firing

The fired properties of the ten selected samples were investigated by temperature gradient firing of hand-moulded specimens. For purposes of comparison, de-aired extruded specimens of New Glasgow "C" were also examined.

The temperature gradient method has been described by Stone⁽²⁷⁾. The drying procedure was the same as for routine

investigations. The dry bars were marked at predetermined intervals and duplicate samples were placed in a Stone temperature gradient furnace. The firing temperature at the centre position of the furnace was raised at the rate of 90°C per hour to 820°C, held there for six hours, then raised at the rate of 110°C 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°C from hot to cold end of the bars, depending on the control temperature. The temperature and shrinkage at each mark on the bars were calculated. The adsorptions of wafers cut from the fired bars were determined after a 24-hour soak in cold water. The colour and hardness at each bar mark were noted. Temperature gradient curves of absorption and shrinkage were plotted from the results.

Chemical Analysis

A brief explanation of the analytical methods has been given by Charette *et al.* and some modifications have been reported by Hole ^(28,29). All analyses were based on the weights of the samples oven-dried at 105°C, the moisture loss below this temperature being reported separately as a measure of the adsorptive capacity of the samples under normal atmospheric conditions of temperature and humidity. Additional determinations were made of the major components of Loss on Ignition (LOI), viz. carbon in both combustible — organic and elemental — and mineral — as CO₂ — forms, sulphur, and chemically combined

moisture liberated at +105°C. Quartz estimates were obtained by a calcium fluoride-nitric acid-perchloric acid treatment currently employed in the Analytical Chemistry Section of the Mineral Sciences Laboratories of CANMET, as a replacement for the Trostel and Wynn method used in some earlier reports.

Mineralogical Analysis

The mineralogical compositions of the unfired samples were determined semi-quantitatively by XRD. The detailed procedures are given by Dean in a separate report, in which he also discusses possible relationships between regional geology and mineralogy of the samples⁽²⁴⁾. Over-all mineralogy was determined on representative aliquots of each sample as a whole. Detailed clay mineralogy was determined on a fine fraction — minus 5µm, equivalent spherical diameter — prepared to concentrate the clay minerals. Accessory minerals were determined in this fine fraction and in a coarse fraction of plus 200 mesh, Tyler, prepared by wet screening, thus giving an insight into their distribution and potential reactivity.

The mineralogy of the fired samples was determined by XRD in a quadruple focussing Guinier-deWolff powder camera. The order of abundance of identifiable constituents was estimated, although diffuse diffraction lines indicated the presence of unidentifiable, poorly crystallized constituents in all cases.

Differential Thermal Analysis

Some standard DTA reference clays and other materials have been discussed by Brady and Brady *et al*^(30,31). Samples were placed in a nickel block and heated in air in a nichrome-wound furnace. Alundum was used as the inert reference material. The furnace and differential temperatures were recorded on a two-pen recorder equipped with a range expander for the differential scale. A Leeds and Northrup dc amplifier was used to amplify the differential temperature milli-voltage. The rate of temperature rise of the furnace was automatically controlled at 12°C/min. The amplifier was set at scale sensitivity 10 for all samples except the kaolinitic clays from Musquodoboit and Shubenacadie, for which scale 40 was used. The peak amplitudes at scale 40 are reduced by a factor of 4 compared with scale 10, to retain on the chart curves caused by the intense reactions of kaolin-type minerals.

The quartz content of all samples was estimated by DTA. Because the endothermic reactions of the clay minerals obscure the small peak produced by the quartz inversion at 573°C, a special procedure was necessary. 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 with a planimeter and compared with the area produced by a sample consisting of 100% quartz.

Thermogravimetric Analysis

Continuous plots of weight loss vs temperature were obtained for the ten selected samples, using an automatically controlled, high-temperature Stanton thermobalance having a sensitivity of 1 mg. A 2-gram, minus 100-mesh (Tyler) sample, dried to constant weight at 110 °C, was placed in the thermobalance crucible and heated at the rate of 6 °C/min. This combination of sample weight and rate of temperature increase produced curves that can be related to DTA and TDA.

The weight-loss curves were re-plotted differentially, to show rate of weight loss for each 15 °C (2.5 min). Furthermore, the vertical or rate scale was plotted logarithmically, which served to de-emphasize the large peaks related to reactions accompanied by substantial weight losses, but to more clearly indicate the effects of reactions accompanied by very small changes in weight that appear as minor peaks or as shoulders superimposed upon a larger peak.

Thermal Dilatometric Analysis

The dilatometric behaviours of the ten selected samples were determined under both oxidizing and reducing conditions.

Oxygen-deficient atmospheres were usual when determinations were made in a vertical tube-type dilatometer. The principal components of the apparatus were a nichrome-wound furnace, a fused-quartz tube closed at the bottom to support the specimen,

and a fused-quartz push-rod to translate dimensional changes in the specimen to an Ames dial rigidly mounted on the upper end of the tube. Specimens, measuring about 1.5 cm square by 5 cm long, were prepared by hand-moulding to avoid particle orientation effects. The sides parallel to the longitudinal axis were grooved to produce a roughly X-shaped cross-section. By thus reducing and equalizing thicknesses, sensitivity to sudden changes in dimension was increased without significantly reducing the resistance of the specimen to warping or buckling. The ends of the oven-dried specimens were made plane and parallel, and their lengths were measured. Heating of the furnace was manually controlled at a rate varying between 9 and 11°C/min. Readings of temperature in °C and length to 0.0025 mm (0.0001 in.) were taken at 2-min intervals, except where sharp or extensive dimensional changes were anticipated or observed, as at the quartz inversion temperature at 573°C, when readings were made each minute. Maximum temperatures were limited to about 980 °C because of the nature of the fused-quartz components. From these results, the changes in length with temperature were calculated in per cent of original length. No corrections were made for expansion of the fused quartz because this is very small and regular, i.e., 0.585×10^{-6} cm/cm/°C from 0° to 1200°C. During heating, gases evolved from the specimens replaced the air in the tube, so that for the main part of each run the specimen was surrounded by water vapour and gaseous oxides of carbon and sulphur. This atmosphere can have a significant effect on the reactions

that take place during firing, in turn affecting the dilatometric behaviour.

The dilatometric behaviour of the samples in oxidizing atmospheres was determined in a horizontal, Seger-type dilatometer. An automatic recording unit was used, featuring a noble metal-wound tube furnace employing dense alumina media to transmit length changes to a linear variable differential transformer. Again, hand-moulded specimens of X-shaped configuration were prepared, measuring 25mm diagonally by 100 mm long. The rate of heating was automatically controlled at about 3.3°C/min. Calibration factors were used to correct the recorded curves to absolute values. Both ends of the furnace tube were open in this apparatus and convection effects ensured that the atmosphere surrounding the specimens was at least mildly oxidizing.

The reversible thermal expansion of the samples was shown by the dilatometric curves obtained during cooling in the Seger dilatometer, cooling being at the natural rate of the furnace. The sharp discontinuity in the curves between about 570° and 590°C was used to estimate the percentage of unreacted quartz in the fired body by comparing with that shown by a specimen of 100% quartz rock.

Plasticity Measurements

The relative plasticities of the ten selected samples were determined with the Brabender plastograph. This method of determining plasticity, or consistency, is more precise than

the empirical method used during routine testing, which depends on operator judgement and experience. The use of the plastograph with clays has been described by Marshall⁽³²⁾. The instrument was operated at normal sensitivity and slow speed. The mixer was charged with 200 g of dry sample and water was added at the rate of 1 mL/min to give a continuous curve when plotting consistency vs water content. This rate of water addition represents a decrease from that used in previous investigations of the clays of Ontario and Québec, viz., 5 mL/min^(25,26). The slower rate of addition has been shown by Bell to allow sufficient time for slower-slaking materials to more fully develop their potential consistency⁽³³⁾.

The curves obtained were compared with that of an arbitrarily selected standard: a shale of the Dundas-Meaford formation, recently re-defined as the Georgian Bay formation, from near Cooksville, Ontario. This shale, designated Cooksville (DM), is known to have just sufficient plasticity to permit satisfactory stiff extrusion of hollow tile shapes. Although plasticity is generally regarded as being proportional to the area under the plastograph curve, extrusion behaviour appears to correlate more closely with the height and configuration of the peak.

EXPERIMENTAL RESULTS AND DISCUSSION

Ceramic Properties from Routine Investigations

The unfired and fired ceramic properties of the samples are given in Tables 2 to 5, segregated according to

TABLE 2

Physical Properties of Newfoundland Clays and Shales

SAMPLE	DESCRIPTION AND UNFIRED CHARACTERISTICS	P. C. E.	FIRED CHARACTERISTICS					REMARKS
			Cone No.*	Fired Shrinkage, %	Absorption, %	Colour	Hardness	
Random Island, hand-moulded	Dark grey, non-calcareous Lower Ordovician shale from Random Island. Fairly plastic and good workability; water of plasticity 20.6%; safe drying; drying shrinkage 3.7%.	14 1388°C (2530°F)	06	1.3	13.4	Salmon	Fairly hard	Satisfactory for facing brick.
			04†	4.0	7.8	Medium red	Hard	
			02	4.8	6.2	Medium red	Very hard	
			1	5.7	4.2	Red	Very hard	
Random Island, temp. gradient hand-moulded	Same as above		1755°F	1.57	13.4	Salmon	Soft	Temperature gradient specimens vitrify at a lower temperature than routine hand-moulded because of difference in firing schedule.
			1838	3.04	11.0	Light red	Fairly soft	
			1925	5.56	6.9	Medium red	Fairly hard	
			1995	6.61	4.3	Medium red	Hard	
			2066	6.08	2.3	Red	Very hard	
Random Island, dry pressed	Water of plasticity 12.5%; safe drying; drying shrinkage 1.7%.		04	4.0	8.2	Medium red	Hard	Would likely make good quality red pressed bricks.
			02	4.8	6.4	Medium red	Very hard	
			1	5.3	5.2	Red	Very hard	
Random Island, de-aired extruded	Water of plasticity 20.0%; safe drying; drying shrinkage 3.1%.		06	1.7	11.4	Salmon	Fairly hard	The de-aired extruded specimens vitrify at a lower temperature than hand-moulded samples.
			04	2.8	8.9	Light red	Hard	
			02	5.7	2.9	Red	Very hard	
			1	6.0	1.4	Red	Steel hard	
Milton, hand-moulded	Pink, slightly calcareous surface clay from Milton. Good plasticity; water of plasticity 20.0%; slight tendency to crack in drying; drying shrinkage 5.3%.	6 1201°C (2194°F)	06	0	11.4	Brownish salmon	Fairly hard	Care required in drying; tendency to scum may make the manufacture of facing brick difficult; suitable for common brick and tile.
			04	0.7	9.2	Brownish salmon	Hard	
			02	2.8	6.5	Brownish red	Very hard	
			2	3.5	2.8	Dark brownish red	Steel hard	
Manuels River, hand-moulded	Brown, non-calcareous Cambrian shale from Manuels River. Rather poor plasticity; water of plasticity 18.9%; safe drying; drying shrinkage 3.0%.	11 1294°C (2361°F)	06	0.5	12.4	Light brown	Fairly soft	May be difficult to extrude; has a short firing range for dense products.
			04	2.5	8.0	Brown	Hard	
			02	4.5	3.2	Dark reddish brown	Steel hard	
Summerside, hand-moulded	Reddish violet, non-calcareous Cambrian shale from Summerside. Very low plasticity; water of plasticity 15.0%; safe drying; drying shrinkage 2.9%.	5† 1183°C (2162°F)	06	0.2	10.4	Medium brown	Fairly hard	Probably requires a plastic additive to extrude; low drying and firing shrinkages; fairly long firing range for dense products such as facing brick.
			04	2.3	5.9	Dark red	Very hard	
			02	3.7	4.5	Very dark red	Very hard	

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

** One of the ten selected samples.

TABLE 3

Physical Properties of Prince Edward Island Shales

SAMPLE	DESCRIPTION AND UNFIRED CHARACTERISTICS	P. C. E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. *	Fired Shrinkage, %	Absorption, %	Colour	Hardness	
Howards Cove, hand-moulded	Red, non-calcareous Permian shale from Howards Cove. Good plasticity; works well; water of plasticity 23.0%; safe drying; drying shrinkage 4.1%.	7 1/2 1225°C (2238°F)	06	2.3	12.7	Light red	Hard	Rather short firing range; it should be suitable for red facing brick, building tile and drain tile.
			04	5.0	7.5	Light red	Very hard	
			02	8.6	0.8	Dark red	Steel hard	
Bacon Point, hand-moulded **	Red, slightly calcareous Permian shale from Bacon Point. Good plasticity; water of plasticity 21.1%; very slight tendency to crack in rapid drying; drying shrinkage 5.3%.	7 1/2 1225°C (2238°F)	06	0.3	11.9	Dark salmon	Fairly hard	Good fired characteristics, although firing range is short. Should be suitable for red facing brick, building tile and drain tile.
			04	1.7	11.8	Light red	Hard	
			02	3.3	8.4	Red	Hard	
			1	5.5	3.9	Dark red	Steel hard	
Bacon Point, temp. gradient hand-moulded	Same as above.		1773°F	1.02	15.4	Dark salmon	Fairly hard	The temperature gradient hand-moulded specimens have higher shrinkages and lower absorptions than the routine hand-moulded ones, particularly at the higher temperatures.
			1856	2.30	13.4	Dark salmon	Fairly hard	
			1929	4.39	9.5	Light red	Hard	
			1990	7.64	3.6	Red	Steel hard	
			2043	8.72	1.1	Dark red	Nearly vitrified	
			2086	8.21	2.0	Very dark red	Slightly overfired	

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

** One of the ten selected samples.

TABLE 4
Physical Properties of Nova Scotia Clays and Shales

SAMPLE	DESCRIPTION AND UNFIRED CHARACTERISTICS	P. C. E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. *	Fired Shrinkage, %	Absorption, %	Colour	Hardness	
Sydney, hand-moulded	Red, non-calcareous Point Edward formation shale from Sydney. Good plasticity; water of plasticity 21.1%; safe drying; drying shrinkage 5.7%.	15 1/2 1440°C (2623°F)	06	0.3	12.5	Salmon	Fairly soft	Long firing range; should be suitable for facing brick, building tile and sewer pipe.
			04	1.4	10.0	Salmon	Fairly hard	
			02	3.3	7.0	Dark salmon	Hard	
			2	4.2	5.2	Light red	Steel hard	
			5	5.5	2.7	Red	Steel hard	
Cranton, hand-moulded	Brown, non-calcareous surface clay from Cranton. Good plasticity; water of plasticity 22.0%; cracks slightly in rapid drying; drying shrinkage 5.2%.	5 1177°C (2151°F)	08	1.3	12.4	Pale red	Soft	Fairly short firing range; requires care in drying; suitable for common brick and tile.
			06	2.0	10.7	Light red	Fairly hard	
			04	4.7	6.2	Medium red	Hard	
			01	8.7	0.3	Dark red	Nearly vitrified	
Antigonish, hand-moulded	Dark red, non-calcareous Canso Group shale from Antigonish. Good plasticity; water of plasticity 19.4%; safe drying; drying shrinkage 3.9%.	12 1306°C (2383°F)	06	0	12.4	Salmon	Fairly soft	Fairly short firing range; good raw and fired properties; should be suitable for facing brick, tile and sewer pipe.
			04	1.7	9.0	Light red	Hard	
			02	3.8	4.9	Red	Very hard	
			2	6.1	1.7	Red	Steel hard	
New Glasgow "A", hand-moulded	Dark brown, very slightly calcareous Upper Stellarton Group shale from New Glasgow. Good plasticity; slightly gritty; water of plasticity 19.4%; safe drying; drying shrinkage 5.0%.	8 1236°C (2257°F)	06	0.5	12.4	Dark salmon	Fairly hard	Long firing range; suitable for full range of dense structural products.
			04	3.0	6.5	Red	Hard	
			02	4.3	4.5	Red	Very hard	
			2	5.2	2.9	Red	Very hard	
New Glasgow "B", hand-moulded	Dark grey to blue, calcareous Stellarton Group shale from New Glasgow. Fair plasticity; water of plasticity 19.0%; safe drying; drying shrinkage 5.4%.	6 1201°C (2194°F)	06	1.0	12.9	Salmon	Fairly hard	Long firing range; suitable for full range of dense structural products.
			04	3.1	8.6	Brownish red	Hard	
			02	4.3	6.0	Brownish red	Very hard	
			2	5.0	4.8	Brownish red	Very hard	
New Glasgow "C", hand-moulded	Grey, non-calcareous Stellarton Group shale from New Glasgow. Fair plasticity; water of plasticity 17.7%; safe drying; drying shrinkage 4.4%.	14 1371°C (2500°F)	06	1.0	11.5	Pale pinkish buff	Soft	Long firing range; suitable for brick and tile.
			04	2.5	9.1	Pinkish buff	Fairly hard	
			01	5.0	4.7	Light brown	Very hard	
			2	5.5	3.5	Medium brown	Steel hard	
New Glasgow "C", temp. gradient hand-moulded	Same as above		1710°F	0.86	12.4	Pale brownish salmon	Fairly soft	Temperature gradient hand-moulded specimens vitrify at lower temperatures than routine specimens because of differences in firing program.
			1800	2.04	11.1	Pale brownish salmon	Fairly hard	
			1886	3.76	8.6	Pale brownish salmon	Hard	
			1961	5.59	5.8	Light reddish brown	Very hard	
			2031	6.88	3.2	Reddish brown	Steel hard	
			2093	7.00	1.0	Greyish brown	Steel hard	
			2148	6.36	0.6	Grey	Steel hard	
New Glasgow "C", deaired extruded	Grey, non-calcareous Stellarton Group shale from New Glasgow. Extrudes satisfactorily under vacuum with 14.0% water of plasticity; drying shrinkage 4.3%.		06	1.5	10.7	Pale pinkish buff	Fairly soft	Extruded-deaired specimens vitrify at lower temperatures than hand-moulded ones.
			04	1.9	8.0	Pinkish buff	Very hard	
			02	4.7	2.9	Light brown	Steel hard	
			2	5.3	0.8	Medium brown	Steel hard	

TABLE 4 (Continued)

SAMPLE	DESCRIPTION AND UNFIRED CHARACTERISTICS	P. C. E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. *	Fired Shrinkage, %	Absorption %	Colour	Hardness	
New Glasgow "C", temp. gradient desired extruded	Grey, non-calcareous Stellarton Group shale from New Glasgow. Extrudes satisfactorily under vacuum with 14.0% water of plasticity; drying shrinkage 4.3%.	14 1371°C (2500°F)	1705°F	0.30	12.9	Pale brownish salmon	Fairly soft	Extruded-deaired temperature gradient specimens vitrify at slightly lower temperatures than hand-moulded ones.
			1795	1.45	11.2	Pale brownish salmon	Fairly hard	
			1876	3.01	8.8	Pale brownish salmon	Hard	
			1951	4.68	6.0	Light reddish brown	Very hard	
			2025	5.72	3.3	Reddish brown	Steel hard	
			2085	6.96	1.3	Greyish brown	Steel hard	
			2140	6.44	0.7	Grey	Steel hard	
Shubenacadie, hand-moulded **	Grey, non-calcareous fireclay from Shubenacadie. Good plasticity; water of plasticity 25.8%; safe drying; drying shrinkage 6.7%.	28 1614°C (2937°F)	1	3.5	12.4	White	Fairly hard	Low-heat-duty fireclay; suitable for low-duty refractories. Requires an additive to flux the clay so that hardness and fairly low absorption can be obtained at firing temperatures, normal to structural clay product industry.
			5	4.4	10.5	White	Hard	
			10	5.5	6.7	Speckled cream	Very hard	
Shubenacadie, temp. gradient hand-moulded	Same as above		1812°F	1.17	22.5	Pinkish cream	Soft	Differences between temperature gradient specimens and routine specimens are attributed to differences in firing schedules.
			1903	2.67	20.1	Pinkish cream	Fairly soft	
			1992	4.07	17.4	Cream	Fairly hard	
			2075	4.85	15.6	Light cream	Fairly hard	
			2153	6.02	13.2	Light cream	Hard	
			2232	7.20	9.8	Light cream	Hard	
			2293	8.17	6.9	Light cream	Very hard	
			2339	8.88	4.9	Creamy grey	Steel hard	
Milford, hand-moulded	Red, calcareous Windsor Group shale from Milford. Inclined to be short; water of plasticity 21.9%; safe drying; drying shrinkage 3.9%.	6+ 1205°C (2200°F)	04	0.3	12.8	Light brownish red	Fairly soft	Good fired properties; used in conjunction with plastic Lantz clay for manufacture of brick and tile.
			02	0.3	12.5	Light brownish red	Fairly hard	
			01	1.3	9.8	Medium red	Fairly hard	
			2	2.8	5.3	Red	Very hard	
			5	5.5	0.8	Dark red	Nearly vitrified	
Lantz, hand-moulded **	Red, slightly calcareous surface clay from Lantz. Very plastic; water of plasticity 30.0%; safe drying; drying shrinkage 8.0%.	7 1215°C (2219°F)	06	2.8	11.4	Dark salmon	Fairly hard	Used to manufacture structural clay products in conjunction with Milford shale which reduces drying shrinkage and increases firing range.
			04	5.0	6.7	Light red	Very hard	
			02	8.0	0	Red	Vitrified	
Lantz, temp. gradient hand-moulded	Same as above		1670°F	1.83	15.5	Salmon	Fairly hard	Temperature gradient specimens have higher shrinkage and lower absorption than the routine hand-moulded ones because of differences in firing program.
			1753	3.08	12.9	Salmon	Hard	
			1831	4.81	8.7	Dark salmon	Very hard	
			1900	7.81	3.1	Light red	Steel hard	
			1954	8.90	0.5	Brownish red	Nearly vitrified	
Musquodoboit, hand-moulded **	Red, non-calcareous fireclay from Middle Musquodoboit. Good plasticity; water of plasticity 28.8%; safe drying; drying shrinkage 4.5%.	26+ 1595°C (2900°F)	06	1.2	22.1	Pinkish salmon	Fairly soft	Low-heat-duty fireclay; too refractory to be used alone for structural clay products.
			02	5.5	10.8	Light red	Hard	
			5	7.2	7.4	Light red	Very hard	
			10	8.0	1.9	Brown	Steel hard	

TABLE 4 (Continued)

SAMPLE	DESCRIPTION AND UNFIRED CHARACTERISTICS	P. C. E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. *	Fired Shrinkage, %	Absorption, %	Colour	Hardness	
Musquodoboit, temp. gradient hand-moulded	Red, non-calcareous fireclay from Middle Musquodoboit. Good plasticity; water of plasticity 28.8%; safe drying; drying shrinkage 4.5%.	26+ 1595°C (2900°F)	1735°F	1.41	24.1	Pinkish salmon	Very soft	Temperature gradient hand-moulded specimens vitrify at lower temperatures than routine specimens because of differences in firing program.
			1838	2.60	22.6	Pinkish salmon	Soft	
			1923	6.48	16.3	Light pinkish red	Fairly hard	
			2005	9.67	10.5	Light red	Hard	
			2082	11.01	7.7	Light brownish red	Very hard	
			2149	12.17	5.2	Brownish red	Very hard	
			2215	13.07	2.1	Pinkish grey	Steel hard	
			2272	14.22	0.5	Brownish grey	Steel hard	
Middleton, hand-moulded	Buff, non-calcareous shale from Middleton. Fair plasticity; water of plasticity 25.0%; slight tendency to crack in rapid drying; drying shrinkage 5.0%.	5 1/2 1189°C (2172°F)	04	3.5	15.0	Light creamy buff	Fairly hard	Care required in drying; short firing range; excessive fired shrinkage at low absorptions; suitable for drain tile.
			02	3.9	7.5	Light greyish buff	Hard	
			1	9.0	3.6	Greyish buff	Steel hard	
Middleton, temp. gradient hand-moulded	Same as above		1741°F	2.33	16.9	Light cream	Fairly soft	Temperature gradient hand-moulded specimens vitrify at lower temperatures than routine specimens because of differences in firing program.
			1820	3.34	14.9	Light cream	Fairly soft	
			1890	5.48	11.4	Cream	Fairly hard	
			1948	8.08	6.5	Creamish buff	Hard	
			1995	10.62	3.6	Light greyish buff	Very hard	
			2039	11.28	2.1	Greyish buff	Steel hard	
			2067	11.41	1.3	Greyish buff	Steel hard	
Parrsboro, hand-moulded	Red, non-calcareous surface clay from Parrsboro. Good plasticity; water of plasticity 24.4%; safe drying; drying shrinkage 6.6%.	13 1321°C (2410°F)	06	1.5	11.9	Pale red	Fairly hard	Excessive drying shrinkage; firing range too short for dense products; suitable for common brick, structural tile and drain tile.
			04	3.5	8.2	Medium red	Hard	
			02	6.7	2.4	Brownish red	Steel hard	
			2	7.7	0.2	Dark brownish red	Nearly vitrified	

* 08 - 945°C (1733°F); 06 - 991°C (1816°F); 04 - 1050°C (1922°F); 02 - 1101°C (2014°F); 01 - 1117°C (2043°F);

1 - 1136°C (2077°F); 2 - 1142°C (2088°F); 5 - 1177°C (2151°F); 10 - 1285°C (2345°F).

* One of the ten selected samples.

TABLE 5
Physical Properties of New Brunswick Clays and Shales

SAMPLE	DESCRIPTION AND UNFIRED CHARACTERISTICS	P. C. E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. #	Fired Shrinkage, %	Absorption, %	Colour	Hardness	
Alma, hand-moulded	Brown, non-calcareous Boss Point formation shale from Alma. Fairly plastic; water of plasticity 17.5%; safe drying; drying shrinkage 4.3%.	15 1/2 1440°C (2623°F)	06	0.5	13.5	Salmon	Fairly hard	Inclined to lack plasticity; fairly long firing range; suitable for brick and tile.
			04	3.3	8.7	Dark salmon	Hard	
			02	5.2	6.4	Medium red	Very hard	
			3	6.5	3.6	Red to dark red	Steel hard	
St. John, hand-moulded **	Reddish brown, non-calcareous surface clay from St. John. Good plasticity; water of plasticity 27.5%; safe drying; drying shrinkage 6.4%.	8 1236°C (2257°F)	08	0.9	16.9	Salmon	Fairly hard	Has a short firing range and too high a shrinkage for dense products such as facing brick; suitable for common brick and tile.
			06	3.3	11.7	Dark salmon	Hard	
			04	7.4	4.2	Medium red	Very hard	
			02	8.5	0.9	Red	Steel hard	
			1	9.2	0	Dark red	Nearly vitrified	
St. John, temp. gradient hand-moulded	Same as above.		1660°F	1.43	17.5	Brownish salmon	Fairly soft	Temperature gradient specimens vitrify at a lower temperature than routine hand-moulded because of differences in firing schedule.
			1748	3.19	14.8	Salmon	Fairly hard	
			1824	5.75	10.8	Pale red	Hard	
			1892	9.65	3.9	Light red	Steel hard	
			1952	11.76	0.1	Red	Nearly vitrified	
Charlotte, hand-moulded	Grey, calcareous surface clay from St. Stephen. Fairly plastic; somewhat silty; water of plasticity 30.6%; safe drying; drying shrinkage 6.3%.	2+ 1144°C (2092°F)	08	1.0	17.5	Light salmon	Fairly hard	Short firing range for dense products; suitable for common brick and tile.
			06	4.2	11.5	Light red	Hard	
			04	5.5	7.4	Medium red	Very hard	
			02	9.2	0.4	Dark red	Nearly vitrified	
Cornhill, hand-moulded	Dark brown, non-calcareous Mississippian shale from Cornhill. Fairly plastic; water of plasticity 17.8%; safe drying; drying shrinkage 4.0%.	8 1236°C (2257°F)	07 1/2	1.0	9.2	Dark salmon	Fairly hard	Long firing range; suitable for facing brick and tile, and possibly for sewer pipe.
			06	3.5	6.3	Medium red	Hard	
			04	3.8	4.8	Medium red	Very hard	
			02	5.5	0.6	Dark red	Nearly vitrified	
Flowers Cove, hand-moulded	Grey, non-calcareous Lower Pennsylvanian shale from Flowers Cove. Good plasticity; water of plasticity 15.2%; safe drying; drying shrinkage 3.7%.	15 1/2 1440°C (2623°F)	04	2.3	7.2	Brownish salmon	Hard	Long firing range; extrudes well; should be suitable for extruded clay products such as brick, tile and sewer pipe.
			02	2.8	5.7	Brownish salmon	Very hard	
			2	4.0	4.1	Light brownish red	Steel hard	
Chipman, hand-moulded **	Red, non-calcareous Pennsylvanian shale from Chipman. Good plasticity; water of plasticity 19.2%; safe drying, drying shrinkage 5.3%.	10 1/2 1290°C (2354°F)	06	0.5	11.2	Light red	Fairly hard	Long firing range, similar to some Quebec Group Shales. Difficult to vitrify unless fired to high temperature; suitable for brick and tile and sewer pipe.
			04	1.6	9.0	Light red	Rather hard	
			02	2.2	6.8	Red	Very hard	
			2	3.3	4.2	Dark red	Steel hard	
Chipman, temp. gradient hand-moulded	Same as above		1885°F	1.00	10.6	Pale reddish brown	Hard	The temperature gradient hand-moulded specimens have higher shrinkage and lower absorption than the routine hand-moulded ones, because of differences in firing schedule.
			1930	2.13	8.5	Light reddish brown	Hard	
			1993	3.40	6.0	Reddish brown	Very hard	
			2050	4.07	4.1	Dark reddish brown	Very hard	
			2092	4.50	2.6	Very dark reddish brown	Steel hard	
			2124	4.66	1.9	Very dark reddish brown	Steel hard	
			2143	4.53	1.7	Very dark reddish brown	Steel hard	

TABLE 4 (Continued)

SAMPLE	DESCRIPTION AND UNFIRED CHARACTERISTICS	P. C. E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. *	Fired Shrinkage, %	Absorption, %	Colour	Hardness	
Musquodoboit, temp. gradient hand-moulded	Red, non-calcareous fireclay from Middle Musquodoboit. Good plasticity; water of plasticity 28.8%; safe drying; drying shrinkage 4.5%.	26+ 1595°C (2900°F)	1735°F	1.41	24.1	Pinkish salmon	Very soft	Temperature gradient hand-moulded specimens vitrify at lower temperatures than routine specimens because of differences in firing program.
			1838	2.60	22.6	Pinkish salmon	Soft	
			1923	6.48	16.3	Light pinkish red	Fairly hard	
			2005	9.67	10.5	Light red	Hard	
			2082	11.01	7.7	Light brownish red	Very hard	
			2149	12.17	5.2	Brownish red	Very hard	
			2215	13.07	2.1	Pinkish grey	Steel hard	
			2272	14.22	0.5	Brownish grey	Steel hard	
			2361	12.93	0.4	Brownish grey	Steel hard	
Middleton, hand-moulded	Buff, non-calcareous shale from Middleton. Fair plasticity; water of plasticity 25.0%; slight tendency to crack in rapid drying; drying shrinkage 5.0%.	5 1/2 1189°C (2172°F)	04	3.5	15.0	Light creamy buff	Fairly hard	Care required in drying; short firing range; excessive fired shrinkage at low absorptions; suitable for drain tile.
			02	3.9	7.5	Light greyish buff	Hard	
			1	9.0	3.6	Greyish buff	Steel hard	
Middleton, temp. gradient hand-moulded	Same as above		1741°F	2.33	16.9	Light cream	Fairly soft	Temperature gradient hand-moulded specimens vitrify at lower temperatures than routine specimens because of differences in firing program.
			1820	3.34	14.9	Light cream	Fairly soft	
			1890	5.48	11.4	Cream	Fairly hard	
			1948	8.08	6.5	Creamish buff	Hard	
			1995	10.62	3.6	Light greyish buff	Very hard	
			2039	11.28	2.1	Greyish buff	Steel hard	
			2067	11.41	1.3	Greyish buff	Steel hard	
2085	10.00	1.0	Greyish buff	Steel hard				
Parrsboro, hand-moulded	Red, non-calcareous surface clay from Parrsboro. Good plasticity; water of plasticity 24.4%; safe drying; drying shrinkage 6.6%.	13 1321°C (2410°F)	06	1.5	11.9	Pale red	Fairly hard	Excessive drying shrinkage; firing range too short for dense products; suitable for common brick, structural tile and drain tile.
			04	3.5	8.2	Medium red	Hard	
			02	6.7	2.4	Brownish red	Steel hard	
			2	7.7	0.2	Dark brownish red	Nearly vitrified	

* 08 - 945°C (1733°F); 06 - 991°C (1816°F); 04 - 1050°C (1922°F); 02 - 1101°C (2014°F); 01 - 1117°C (2043°F);
1 - 1136°C (2077°F); 2 - 1142°C (2088°F); 5 - 1177°C (2151°F); 10 - 1285°C (2345°F).

* One of the ten selected samples.

TABLE 5
Physical Properties of New Brunswick Clays and Shales

SAMPLE	DESCRIPTION AND UNFIRED CHARACTERISTICS	P. C. E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. *	Fired Shrinkage, %	Absorption, %	Colour	Hardness	
Alma, hand-moulded	Brown, non-calcareous Boss Point formation shale from Alma. Fairly plastic; water of plasticity 17.5%; safe drying; drying shrinkage 4.3%.	15 1/2 1440°C (2623°F)	06	0.5	13.5	Salmon	Fairly hard	Inclined to lack plasticity; fairly long firing range; suitable for brick and tile.
			04	3.3	8.7	Dark salmon	Hard	
			02	5.2	6.4	Medium red	Very hard	
			3	6.5	3.6	Red to dark red	Steel hard	
St. John, hand-moulded **	Reddish brown, non-calcareous surface clay from St. John. Good plasticity; water of plasticity 27.5%; safe drying; drying shrinkage 6.4%.	8 1236°C (2257°F)	08	0.9	16.9	Salmon	Fairly hard	Has a short firing range and too high a shrinkage for dense products such as facing brick; suitable for common brick and tile.
			06	3.3	11.7	Dark salmon	Hard	
			04	7.4	4.2	Medium red	Very hard	
			02	8.5	0.9	Red	Steel hard	
			1	9.2	0	Dark red	Nearly vitrified	
St. John, temp. gradient hand-moulded	Same as above.		1660°F	1.43	17.5	Brownish salmon	Fairly soft	Temperature gradient specimens vitrify at a lower temperature than routine hand-moulded because of differences in firing schedule.
			1748	3.19	14.8	Salmon	Fairly hard	
			1824	5.75	10.8	Pale red	Hard	
			1892	9.65	3.9	Light red	Steel hard	
			1952	11.76	0.1	Red	Nearly vitrified	
Charlotte, hand-moulded	Grey, calcareous surface clay from St. Stephen. Fairly plastic; somewhat silty; water of plasticity 30.6%; safe drying; drying shrinkage 6.3%.	2+ 1144°C (2092°F)	08	1.0	17.5	Light salmon	Fairly hard	Short firing range for dense products; suitable for common brick and tile.
			06	4.2	11.5	Light red	Hard	
			04	5.5	7.4	Medium red	Very hard	
			02	9.2	0.4	Dark red	Nearly vitrified	
Cornhill, hand-moulded	Dark brown, non-calcareous Mississippian shale from Cornhill. Fairly plastic; water of plasticity 17.8%; safe drying; drying shrinkage 4.0%.	8 1236°C (2257°F)	07 1/2	1.0	9.2	Dark salmon	Fairly hard	Long firing range; suitable for facing brick and tile, and possibly for sewer pipe.
			06	3.5	6.3	Medium red	Hard	
			04	3.8	4.8	Medium red	Very hard	
			02	5.5	0.6	Dark red	Nearly vitrified	
Flowers Cove, hand-moulded	Grey, non-calcareous Lower Pennsylvanian shale from Flowers Cove. Good plasticity; water of plasticity 15.2%; safe drying; drying shrinkage 3.7%.	15 1/2 1440°C (2623°F)	04	2.3	7.2	Brownish salmon	Hard	Long firing range; extrudes well; should be suitable for extruded clay products such as brick, tile and sewer pipe.
			02	2.8	5.7	Brownish salmon	Very hard	
			2	4.0	4.1	Light brownish red	Steel hard	
Chipman, hand-moulded ***	Red, non-calcareous Pennsylvanian shale from Chipman. Good plasticity; water of plasticity 19.2%; safe drying, drying shrinkage 5.3%.	10 1/2 1290°C (2354°F)	06	0.5	11.2	Light red	Fairly hard	Long firing range, similar to some Quebec Group Shales. Difficult to vitrify unless fired to high temperature; suitable for brick and tile and sewer pipe.
			04	1.6	9.0	Light red	Rather hard	
			02	2.2	6.8	Red	Very hard	
			2	3.3	4.2	Dark red	Steel hard	
Chipman, temp. gradient hand-moulded	Same as above		1885°F	1.00	10.6	Pale reddish brown	Hard	The temperature gradient hand-moulded specimens have higher shrinkage and lower absorption than the routine hand-moulded ones, because of differences in firing schedule.
			1930	2.13	8.5	Light reddish brown	Hard	
			1993	3.40	6.0	Reddish brown	Very hard	
			2050	4.07	4.1	Dark reddish brown	Very hard	
			2092	4.50	2.6	Very dark reddish brown	Steel hard	
			2124	4.66	1.9	Very dark reddish brown	Steel hard	
			2143	4.53	1.7	Very dark reddish brown	Steel hard	

TABLE 5 (Continued)

SAMPLE	DESCRIPTION AND UNFIRED CHARACTERISTICS	P. C. E.	FIRED CHARACTERISTICS					REMARKS
			Cone No.*	Fired Shrinkage, %	Absorption, %	Colour	Hardness	
Beersville hand-moulded	Grey, non-calcareous Pennsylvanian shale from Beersville. Good plasticity; water of plasticity 19.2%; safe drying; drying shrinkage 5.8%.	12+ 1310°C (2392°F)	07 1/2	1.0	11.6	Brownish buff	Fairly hard	Long firing range; suitable for brick, tile and sewer pipe.
			06	2.3	8.4	Brownish salmon	Hard	
			04	2.5	7.5	Brownish salmon	Very hard	
			02	3.8	4.4	Reddish brown	Steel hard	
			3	4.3	2.9	Dark reddish brown	Steel hard	
Upper Napan de-aired extruded	Dark buff, non-calcareous marine surface clay from Upper Napan. Good plasticity; water of plasticity 22.3%; safe drying; drying shrinkage 3.6%.	8 1/2 1248°C (2279°F)	08	1.0	13.8	Pale red	Soft	Extrudes well and has a rather low drying shrinkage. Has a fairly short firing range; suitable for common brick and tile but not dense products.
			06	2.2	11.3	Light red	Fairly soft	
			04	5.0	5.6	Medium red	Steel hard	
			01	8.8	0.2	Dark red	Nearly vitrified	
Ste. Anne, hand-moulded	Light grey, non-calcareous weathered shale from Ste. Anne-du-Bocage. Good plasticity; water of plasticity 23.3%; safe drying; drying shrinkage 7.4%.	18 1500°C (2732°F)	06	0	11.6	Light buff	Medium hard	Has excessive drying shrinkage and fires to a dense condition at a relatively high temperature of about cone 5. May be suitable for very low grade refractories or brick and tile and possibly sewer pipe.
			04	0.8	10.8	Light buff	Medium hard	
			02	1.2	9.5	Light buff	Hard	
			2	2.2	7.6	Light buff	Hard	
			5	3.8	3.1	Pinkish buff	Steel hard	
Stonehaven hand-moulded **	Brown, non-calcareous Pennsylvanian shale from Stonehaven. Good plasticity; water of plasticity 22.5%; safe drying; drying shrinkage 4.7%.	12 1306°C (2383°F)	06	1.4	11.2	Light red	Fairly hard	Has a satisfactory firing range for dense products; should be suitable for facing brick, tile and possibly sewer pipe.
			04	4.3	5.8	Light red	Very hard	
			02	6.8	2.0	Red	Steel hard	
			1	7.1	0.3	Dark red	Nearly vitrified	
Stonehaven, temp. gradient hand-moulded	Same as above.		1656°F	0.57	13.3	Light red	Fairly soft	Temperature gradient bars vitrify at a lower temperature than routine specimens because of different firing schedule.
			1740	2.50	11.0	Light red	Fairly hard	
			1822	4.65	7.5	Medium red	Hard	
			1895	6.85	3.3	Red	Very hard	
			1957	8.50	0.8	Dark red	Steel hard	
			2018	8.44	0.5	Dark red	Overfired	
St. Leonard, hand-moulded	Grey, non-calcareous surface clay from St. Leonard. Fair plasticity; flabby; water of plasticity 29.4%; safe drying; drying shrinkage 3.5%.	6+ 1205°C (2200°F)	04	3.0	19.5	Pale red	Fairly soft	Short firing range and very high firing shrinkage makes it difficult to use for dense products. Suitable for drain tile, structural tile and common brick.
			02	7.5	8.1	Medium red	Hard to very hard	
			1	8.9	7.4	Red	Very hard	
			3	11.3	0.7	Very dark red	Nearly vitrified	

*08-945°C(1733°F); 07 1/2-959°C(1758°F); 06-991°C(1816°F); 04- 1050°C (1922°F); 02- 1101°C (2014°F); 01-1117°C(2043°F); 1- 1136°C(2077°F); 2-1142°C(2088°F); 3-1152°C(2106°F); 5-1177°C(2151°F).

** One of the ten selected samples.

province of origin. However, the types of material represented cannot be classified in an entirely satisfactory way along provincial lines because the geology of the region is not subject to such arbitrary boundaries and a number of formations extend from one province to another or reappear in another province as an equivalent series.

Good-quality china clays are not known with the possible exception of an occurrence reported at depth in a mine at Mount Pleasant, N.B. The minus 325-mesh fraction of a sample of this material showed a PCE of Cone 33. It fired clear white at low temperatures, but developed small dark specks at Cone 10. Similarly, there are no known deposits of high-grade fire clays, but there are a number of low-duty fire clays, which by ASTM definition has a PCE of Cone 15 to Cone 29. The highest grades and best-known of these are found along the valleys of the Musquodoboit and Shubenacadie Rivers in Nova Scotia. Some seams of these Cretaceous clays equal the upper limit for low-duty fire clays and have been used in the manufacture of fireclay brick. However, they have found their greatest use as admixtures to extend the firing ranges of easily vitrified surface clays used in the manufacture of structural clay products and pottery. They are two of the samples selected for detailed study and are reported upon later. Other refractory materials included the very low-duty shales at Sydney, N.S., and at Alma, Flowers Cove, and Ste. Anne-du-Bocage, N.B. The geology supports the possibility that high-grade clays may yet be discovered, as conditions for the

weathering of suitable parent rocks could have existed in times past in many areas. For example, minor occurrences of refractory, kaolinitic materials have been reported near Melford on Cape Breton and near Porters Lake east of Dartmouth, N.S. but neither deposit has been reported in sufficient detail to establish a commercial potential.

Among the common clay materials, the best ceramic properties are shown by the shales, which are generally more refractory and show wider firing ranges for dense products such as structural clay wares. Not surprisingly, their properties are similar to those of the Quebec Group shales of the Cambrian and Ordovician Periods from the adjacent western arm of the Appalachian orogenic zone. In the Atlantic Provinces, the shales suitable for ceramic purposes appear to be exclusively of Paleozoic age: at one extreme are the older Cambrian shales of Newfoundland and, at the other, the more recent Carboniferous and Permian shales reported from the three other provinces. Except for the Random Island sample, which is classified as Lower Ordovician and thus near-Cambrian, and an unusual white shale from Middleton, N.S., the Ordovician and other mid-Paleozoic Periods are not represented in this study, although these shales form the basis for the greatest part of the extensive structural clay products industry in Ontario and western Quebec. The major problem with the shales is their hardness and resultant low plasticity. In this respect, the Cambrian shales of Newfoundland are the worst. The samples from Manuels River and from Summerside would doubtless require fine grinding

or the addition of a plasticizing agent for satisfactory extrusion. The Random Island sample extruded well under vacuum, although the resulting denser body vitrified more rapidly. The properties of the dry-pressed specimens indicate that it should be possible to make good-quality red pressed bricks of excellent uniformity from this shale. On the other hand, the Permian shales from Howards Cove and Bacon Point, P.E.I., are probably the softest and most plastic of the shale samples. They are also among the least refractory, with identical PCE's of Cone 7½, and have rather short firing ranges for dense products. The bulk of the common shales from Nova Scotia and New Brunswick are of Carboniferous age, mostly attributed to the Pennsylvanian Period. They generally have PCE's in the Cone 10 to Cone 14 range, except for the calcareous samples from New Glasgow and Milford, N.S., which have PCE's of Cone 6 to Cone 8. Plasticities vary from fair to good: most appear to be adequately plastic for satisfactory extrusion of brick shapes, but some might require additions of plasticizing agents to extrude thin-shelled or multi-cored ware. For example, satisfactory extrusion was obtained in tests with the New Glasgow sample, which was judged to have only fair plasticity. The soft white shale from Middleton, N.S., is apparently the only non-Paleozoic sample among the group of shales. Its probable origins are discussed by Dean, who concludes that it is most likely the product of alteration and selective leaching, in situ, of shale of the Triassic Blomidon formation (24). It has a relatively low PCE of Cone 5½ and a short firing range. It

would probably be suitable only for the manufacture of porous ware such as drain tile or, as indicated previously, flower pots.

The variety of surface clays represented by the relatively few samples, coupled with uncertainties with regard to the geology of the bedrock from which they might be derived, makes it difficult to classify the clays according to origin. Major differences in ceramic behaviour and such properties as PCE exist between clays considered to have had similar origins, e.g., the marine clays from Charlotte and Upper Napan. They can, however, be loosely classified according to firing range. The samples from St. John, Charlotte and St. Leonard, N.B., and Parrsboro, N.S. show short firing ranges for absorptions below 7 or 8%, and could not be satisfactorily used for dense products. The samples from Milton, Nfld., Cranton and Lantz, N.S., and probably that from Upper Napan, N.B., show firing ranges for dense products that are adequate to allow for satisfactory control in commercial kilns. The high drying and firing shrinkages shown by most of the surface clays could cause cracking problems.

Sample Compositions and their Relationship to Processing Behaviour and Problems

The processing behaviour of ceramic raw materials is primarily dependent on their composition. In clay products, the mineralogical constitution is usually accorded more consideration than the chemical composition, because the nature of the mineral components govern the forming properties, drying

behaviour and, in large part, the nature and extent of the reactions that take place on firing. The effects of various clay and non-clay minerals on the manufacture of ceramics are discussed in detail by many authors such as Grimshaw, and Grim and, with respect to Canadian clays and shales, by Brady and Dean (34,35,25,26,36).

The chemical analyses of the samples are presented in Table 6. The mineralogical analyses, determined by XRD, are given in Table 7, and are supplemented by the data from DTA, the curves for which are shown in Fig. 2, 3 and 4.

With the exception of the fire clays from Shubenacadie and Musquodoboit, and of the anomalous sample from Middleton, the clays and shales are heterogeneous mineral assemblages of various chemical compositions, leading to their classification as common clays.

Kaolinitic clay minerals predominate in the Cretaceous clays from Shubenacadie and Musquodoboit, with accessory illite and mixed-layer micaceous minerals identified by XRD. The DTA curves are dominated by strong endothermic peaks at 580°C and exothermic peaks at about 960°C, characteristic of the dehydroxylation of kaolinite and subsequent re-crystallization of the amorphous materials so formed. The primary accessory minerals are quartz and small amounts of feldspars. In short, they are quite typical fire clays. The material from Middleton is principally mica, or illite, mixed with quartz and feldspar sands. It also contains a mixed-layer clay mineral assemblage that includes montmorillonoid as a component, indicated by the

TABLE 6
Chemical Analysis^a

Sample	SiO ₂	FeO	Fe ₂ O ₃	TiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	LOI	Total	Tot. C	Org. & El. C ^b	S	H ₂ O +105 °C	H ₂ O -105 °C	CO ₂	Quartz
1. Random Island	54.98	4.09	4.33	1.06	22.29	0.20	2.40	0.92	2.93	6.81	100.01	0.46	0.41	0.240	6.80	1.55	0.17	18.10
2. Milton	67.29	1.94	3.30	0.79	14.47	2.49	1.83	2.90	2.31	3.35	100.67	0.20	0.15	0.035	1.96	0.35	0.18	29.70
3. Manuels River	58.57	3.12	4.97	0.84	18.09	0.54	3.22	0.67	3.77	6.55	100.34	0.28	0.21	0.019	5.02	0.85	0.26	21.40
4. Summerside	62.11	1.70	5.61	0.90	17.07	n.d.	3.26	1.18	4.47	3.09	99.62	0.02	0.01	0.018	3.63	0.15	0.05	29.68
5. Howards Cove	56.25	1.26	6.75	1.01	19.76	1.11	3.18	0.97	3.76	6.02	100.07	0.26	0.02	0.010	4.77	0.51	0.89	19.10
6. Bacon Point	65.44	0.65	5.50	0.91	15.76	0.73	2.16	0.95	3.19	4.51	99.80	0.13	0.01	0.008	3.61	0.61	0.42	35.70
7. Sydney	65.60	0.39	4.83	0.97	18.72	0.40	1.07	0.25	2.80	5.22	100.12	0.07	0.06	0.046	4.37	1.28	0.04	32.10
8. Cranton	61.27	2.27	4.26	0.95	17.61	0.40	2.63	1.30	3.89	5.94	100.52	0.25	0.20	0.018	4.52	0.84	0.19	21.90
9. Antigonish	62.98	1.68	5.17	0.98	17.94	0.10	1.62	1.24	3.33	5.20	100.24	0.30	0.24	0.016	4.36	0.42	0.21	27.30
10. New Glasgow "A"	65.37	1.04	5.54	0.78	15.48	0.69	1.67	0.75	2.61	6.31	100.24	0.76	0.62	0.026	4.20	0.65	0.49	37.80
11. New Glasgow "B"	56.44	4.99	2.16	0.75	17.86	2.22	1.86	0.42	2.31	10.96	99.97	1.94	0.90	0.145	5.86	0.79	3.85	20.60
12. New Glasgow "C"	56.23	6.21	1.32	1.13	20.13	0.69	1.59	0.25	2.40	10.49	100.63	1.34	1.27	0.050	5.87	1.25	0.26	24.26
13. Shubenacadie	61.59	0.52	0.87	1.27	22.53	0.20	0.27	0.19	1.20	11.41	100.05	2.74	2.69	0.310	7.13	1.48	0.20	31.10
14. Milford	65.36	1.03	3.95	0.77	12.86	4.10	1.88	0.24	3.25	7.26	100.70	0.94	0.10	0.015	3.08	0.20	3.08	39.60
15. Lantz	56.94	2.20	4.61	0.89	20.51	1.61	2.83	0.80	3.70	6.12	100.21	0.51	0.21	0.043	5.31	1.28	1.11	20.60
16. Musquodoboit	50.37	0.46	6.85	1.22	28.50	0.08	1.03	0.28	1.33	10.04	100.19	0.61	0.60	0.04	9.47	1.03	0.03	13.70
17. Middleton	61.21	0.52	0.87	0.84	19.02	0.34	5.65	0.15	4.96	5.95	99.51	0.12	0.07	0.028	5.06	0.97	0.18	24.40
18. Parrsboro	63.43	2.24	4.96	1.07	17.94	n.d.	2.13	0.56	3.21	4.10	99.74	0.20	0.20	0.034	4.10	0.64	0.02	23.46
19. Alma	55.51	1.72	5.45	0.94	21.37	0.32	1.80	0.25	3.81	8.53	99.81	1.95	1.95	0.046	6.51	1.73	n.d.	21.59
20. St. John	59.16	2.19	5.64	1.04	18.52	0.77	2.58	1.08	3.48	5.70	100.16	0.25	0.16	0.018	4.91	0.89	0.30	23.30
21. Charlotte	58.11	3.76	3.96	1.03	18.25	1.74	3.12	1.48	3.39	5.16	100.27	0.51	0.51	0.026	4.20	0.84	n.d.	24.19
22. Cornhill	55.35	1.77	6.48	1.05	20.83	0.38	2.83	1.20	4.35	5.12	99.61	0.16	0.15	0.020	4.45	1.28	0.04	16.70
23. Flowers Cove	61.53	2.63	2.34	1.31	21.18	0.30	1.08	0.25	2.49	7.76	100.87	0.69	0.44	1.230	6.04	1.06	0.89	27.90
24. Chipman	62.46	0.88	6.96	1.14	17.85	0.18	1.66	0.24	3.09	6.07	100.53	0.09	0.06	0.012	4.97	1.05	0.10	35.40
25. Beersville	57.84	3.41	2.74	1.05	20.32	0.48	1.82	0.19	3.80	7.71	99.41	1.87	1.86	0.470	5.99	1.76	0.05	21.77
26. Upper Napan	59.89	1.73	6.05	1.09	18.51	0.26	2.64	1.35	3.37	4.60	99.76	0.20	0.18	0.015	4.50	1.76	0.08	23.60
27. Ste. Anne	73.49	0.65	1.43	1.09	15.32	0.02	0.71	0.13	2.03	4.67	99.55	0.09	0.07	0.430	4.30	1.01	0.04	46.86
28. Stonehaven	56.03	2.72	6.40	0.93	20.30	0.58	2.75	0.27	3.83	7.05	100.86	0.14	0.06	0.025	5.42	0.70	0.30	17.90
29. St. Leonard	68.43	3.39	1.61	1.00	13.63	0.60	2.03	1.92	2.04	4.92	99.78	1.25	1.25	0.050	3.64	0.68	n.d.	39.84

^aChemical Analysis by J. C. Hole, H. Lauder, E. Mark, D. Precious, R. Sabourin, Mineral Sciences Division, Mines Branch.

^bOrganic and elemental carbon.

n.d. Not detected.

TABLE 7

X-Ray Diffraction Analyses of Atlantic Provinces Clays and Shales

Sample and Per Cent Plus 200 mesh *	Illite	Chlorite	Kaolin	Mixed-Layer Clays and Other Minerals	Quartz			Feldspase			Calcite			Benatite	
					Wh.	F.F.	C.F.	Wh.	F.F.	C.F.	Wh.	F.F.	C.F.	Wh.	C.F.
1. Random Island Ordovician Shale (Nfld.) 7.0%	B	C	B	Chlorite-Verm.-Illite (C); Pyrite (C); Anatase (G)	C	D	B	C	E	C					
2. Milton Surface Clay (Nfld.) 30.8%	B	A		Amphibole (F)	B	C	B	B	C	B	D	D	D	G	
3. Manuela River Cambrian Shale (Nfld.) 5.3%	A	C		Chlorite-Verm.-Illite (C)	B	C	B	E	F	E	G				
4. Summerside Cambrian Shale (Nfld.)	A	C			B	C	-	C	D	-	G	G	-	-	D
5. Howards Cove Permian Shale (P.E.I.) 1.3%	A	B	C	Illite-Verm. (D); Chlorite-Mont. (D)	C	D	B	D	F	E	G	G	G	E	B
6. Bacon Point Permian Shale (P.E.I.) 1.4%	A	C	D	Chlorite-Verm. (D); Dolomite (G)	B	D	A	D	G	D	G	E	G	E	E
7. Sydney D.25%	C	B		Verm.-Illite (B); Illite-Mont. (C); Anatase (F); Barite (G)	B	D	B			F					E
8. Cranton Surface Clay (N.S.) 5.7%	A	B		Chlorite-Mont. (D);	C	D	B	D	E	B	D	G	B		G
9. Antignoiash 0.20%	A		B	Chlorite-Verm. (C); Anatase (G); Pyrite (G)	B	D	A	C	F	C	F	G	F		F
10. New Glasgow "A" 10.0%	A	C	B	Chlorite-Verm. (C); Anatase (G); Gypsum (G); Rutile (G)	A	C	A	D	F	D	G	G			F
11. New Glasgow "B" 8.1%	A	D	B	Verm.-Illite (D); Siderite (C); Pyrite (G); Gypsum (G); Anatase (G); Rutile (G)	B	C	A	E		E	G	G	D	P	
12. New Glasgow "C" 2.9%	A	D	B	Verm.-Illite (D); Siderite (C); Gypsum (G); Pyrite (G); Anatase (F); Rutile (G)	B	C	C	F					G	G	
13. Shubenacadie Cretaceous Clay (N.S.) 7.3%	C		A	Verm.-Diact.-Chlorite (D); Rutile (F); Anatase (F); Pyrite (G)	A	E	A			G				G	
14. Milford 2.35%	A	D		Illite-Verm. (C); Anatase (G)	A	C	A	G		E	F	G	C	G	A
15. Lentz Surface Clay (N.S.) 2.15%	A	B	C	Dolomite (E); Amphibole (G)	B	D	A	D	F	D	F	G	C	E	G
16. Musquodoboit Cretaceous Clay (N.S.) 5.25%	C		A	Verm.-Diact.-Chlorite-Illite (D); Anatase (F); Rutile (F)	B	E	A			E			F	F	
17. Middleton 3.75%	A			Chlorite-Mont.-Illite (C); Gypsum (G)	B	D	C				C	E	A		
18. Parrsboro Surface Clay (N.S.) 2.85%	A	C	C	Rutile (F); Anatase (G)	A	C	A	D	G	D	G	F	F		D
19. Alma -	A		C	Chlorite-Illite-Verm. (C); Rutile (G); Anatase (G); Zircon (G)	B	C	-			-			-		-
20. St. John Surface Clay (N.B.) 2.8%	A	B	D	Verm.-Mont. (C); Amphibole (G)	B	C	A	C	D	B	F	F	D		E
21. Charlotte Surface Clay (N.B.) 0.15%	B	B			B	C	B	C	D	B	E	F	E	E	F
22. Cornhill 0.45%	A	C		Chlorite-Verm.-Mont. (D)	C	D	B	C	E	C	F	G	E		D
23. Flowers Cove 0.8%	B	C	C	Chlorite-Verm.-Mont. (C); Pyrite (E); Marcasite (G); Anatase (F); Rutile (F)	A	C	D								
24. Chipman 1.9%	B	C	C	Mont.-Illite (B); Anatase (G); Rutile (F)	A	C	A			G					D
25. Beersville 1.6%	B	C	C	Illite-Verm. (C); Chlorite-Verm.-Illite (D); Pyrite (F); Marcasite (G); Anatase (F); Rutile (G)	B	C	C								
26. Upper Marine Clay (N.B.) 2.4%	A	C	C	Mont.-Chlorite (C)	B	C	A	C	D	C	D	E	D		G
27. Ste. Anne 2.7%	C		A	Verm.-Illite (B); Pyrite (F); Anatase (G)	A	C	A				E	F	E		
28. Stonehaven 0.45%	A	B	C	Illite-Verm. (C); Anatase (G)	B	C	B	G		F			G	A	D
29. St. Leonard Surface Clay (N.B.) 5.3%	B	B			A	C	A	B	D	B	G	G	G	E	

Mineralogy determined by R.S. Dean. Clay minerals determined in minus 5 micron fraction. Non-clay minerals determined in (a) whole sample (Wh); (b) fine fraction (F.F.), minus 5 microns; and (c) coarse fraction (C.F.), plus 200 mesh. Mineral abundances in each size range estimated from A (very abundant) to G (trace). Abbreviations; Verm. - vermiculite; Mont. - montmorillonoid; Diact. - Diactahedral.

*Disaggregation of shales was incomplete; only per cent plus 200 mesh (coarse fraction) for the clays is reported as being significant.

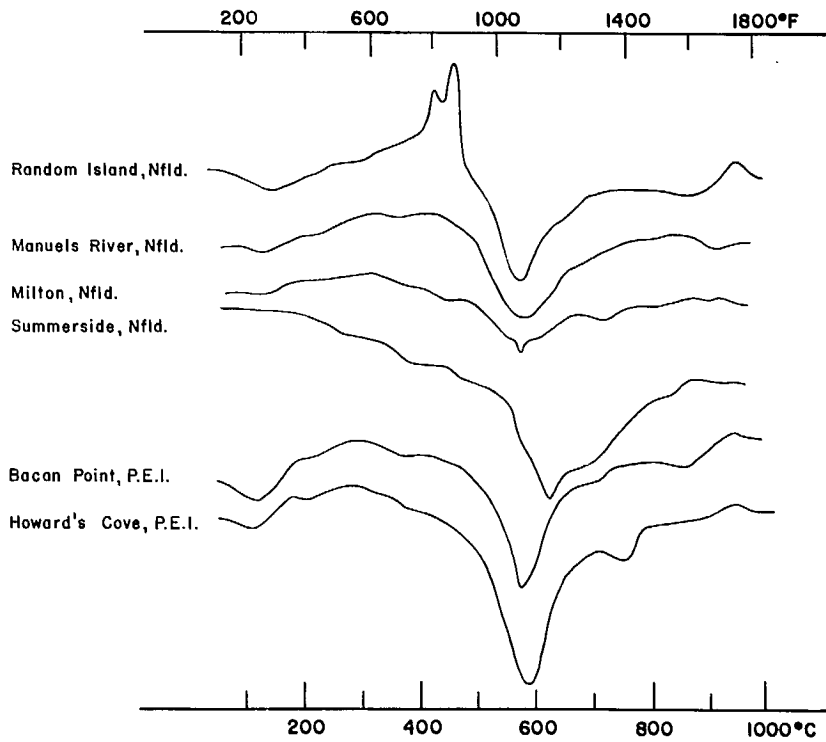


Figure 2. DTA curves of clays and shales from Newfoundland and Prince Edward Island.

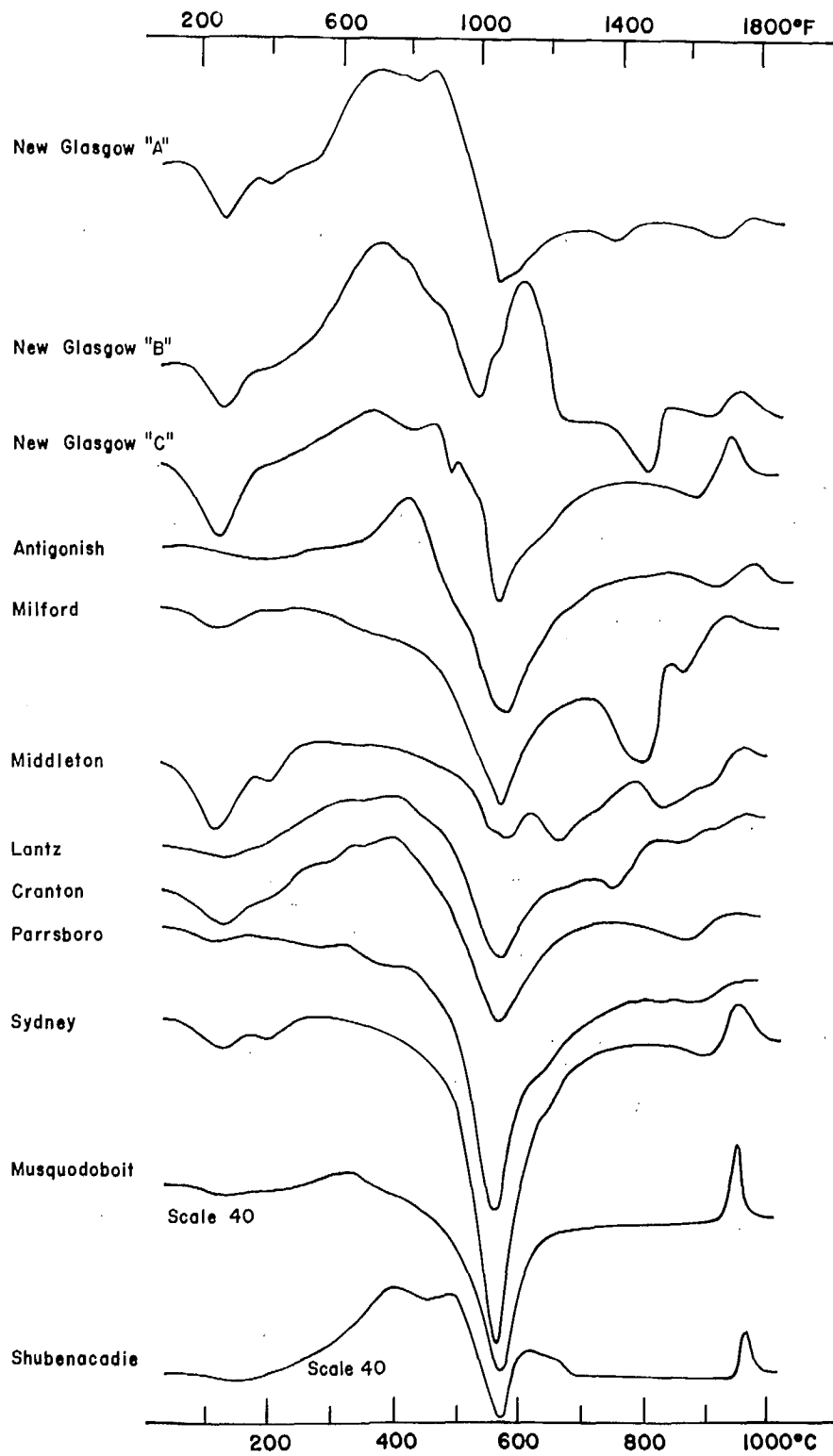


Figure 3. DTA curves of clays and shales from Nova Scotia.

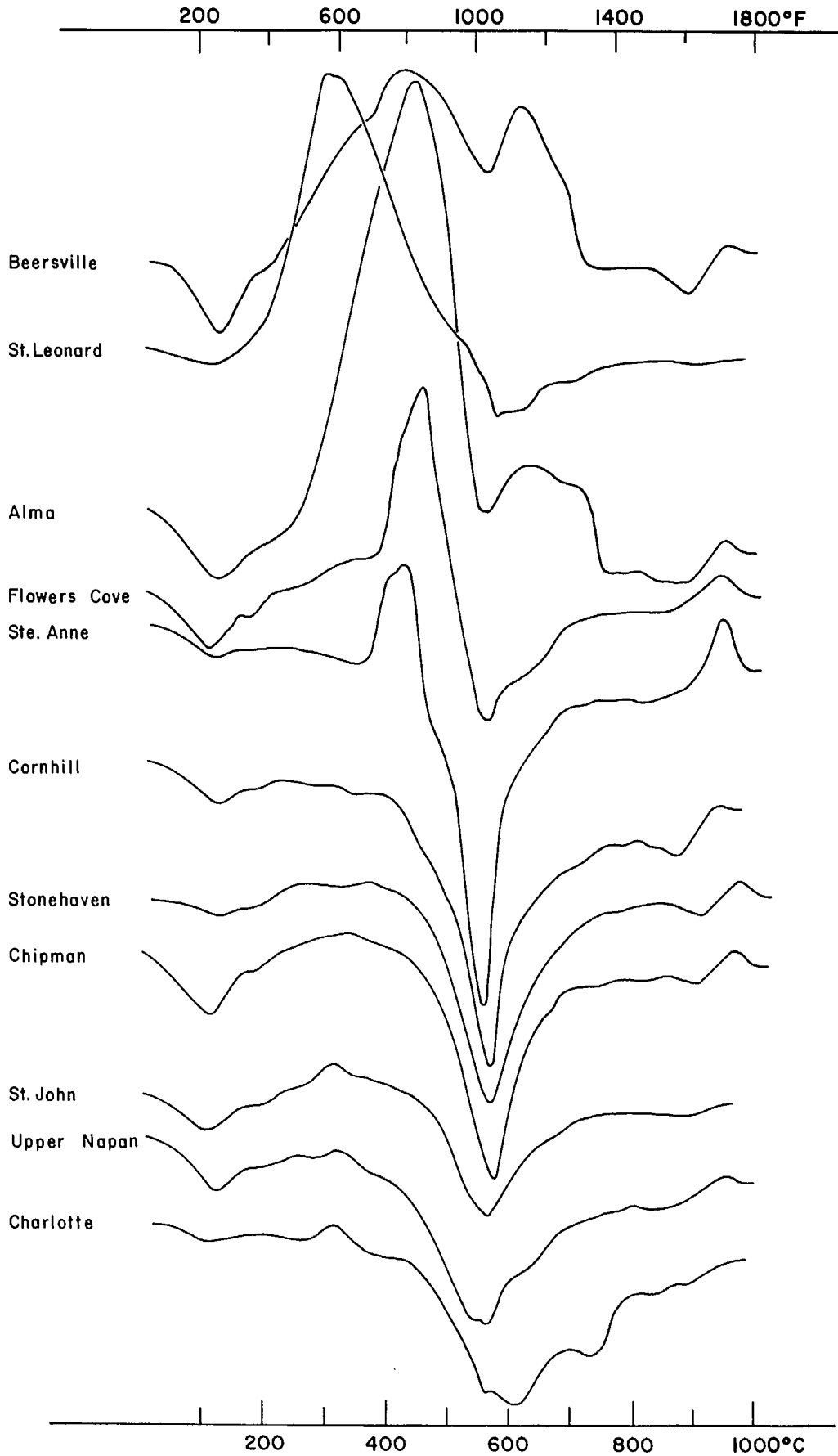


Figure 4. DTA curves of clays and shales from New Brunswick.

strong endothermic peak, at just over 100°C on the DTA curve, that reflects the strongly moisture-absorptive nature of the montmorillonoid layers. The multiple endothermic peaks above about 500°C probably represent the multi-stage dehydroxylation of the micaceous components of various compositions, degrees of crystallinity and particle size. The effects of composition on the ceramic behaviour of these materials is discussed in more detail later.

The common shales and clays, the latter being mostly derived from the former, are typical mixtures of multiple clay minerals, quartz and feldspars, with minor amounts of accessory minerals. XRD shows that most of them contain both kaolinitic and micaceous (illite, chlorite) clay minerals, as well as mixed-layer clay minerals containing expansible phases. The presence of the latter can impart useful plastic properties to the material but if in too great a proportion, they can lead to lamination during extrusion. Also, their hygroscopic characteristics can lead to drying problems and high drying shrinkages, as well as picking up moisture again if exposed to humid atmospheres after drying, with subsequent firing problems. The mixed clay mineral composition of a sample is often reflected in the DTA curves, where the endothermic peak between about 550 and 600°C, corresponding to dehydroxylation of the clay minerals, may appear as a doublet or bear shoulders indicative of the various minerals dehydroxylating at different temperatures. The widespread occurrence of kaolin as a component of the clays and shales of the Atlantic Provinces

distinguishes them from those of central Canada. Although kaolin has been identified as a minor component in the Quebec group shales, it is absent in the common materials found west of Quebec City⁽²⁶⁾. In the common clays and shales of Ontario, it occurs only in minor proportions in only a few deposits in the extreme south-west. The presence of kaolin is apparent in the higher Al_2O_3 contents of those materials of which it is a major constituent (Table 6). Higher alumina content generally results in increased refractoriness (PCE) to the point where some of these materials can be classified as very low-duty fire clays, and were, in fact, used to manufacture fireclay brick in earlier times. Such material usually displays a wider firing range, rendering it suitable for the manufacture of a wider variety of ceramic products.

All of the samples contain fine-grained non-clay minerals, principally quartz and feldspars. These are predominantly less than 200 mesh, as indicated in Table 7. These non-plastic materials reduce plasticity and hence affect the forming properties and reduce dry strengths. During firing, the quartz only partly reacts and thus forms a skeleton to reduce shrinkage and maintain shape. Quartz does, however, exhibit a reversible crystallographic phase change at $573^{\circ}C$ that is accompanied by expansion during heating and contraction during cooling: these volume changes in the quartz grains set up stresses in the ceramic body that can lead to rupture, commonly called "dunting". Dunting is less likely when the quartz is fine grained and represents less than about 35% of

the total composition. The quartz content of each sample, determined by a chemical method, is shown in the supplementary columns of Table 6. Dunting is unlikely to occur, except possibly in the Milford and New Glasgow "A" materials, where it has not been reported to be a problem commercially, and in those from Ste. Anne and St. Leonard. The feldspars, on the other hand, act as fluxes during firing, and promote vitrification. The plagioclase feldspars are more reactive than the K-feldspars, hence tend to reduce the vitrification range further, which may limit the potential of the material to porous, soft-fired, ceramic products only.

Nearly all of the samples contain sufficient quantities of iron—5 to 7% when calculated as Fe_2O_3 — to ensure that they fire to some shade of red. In many cases the iron is present as hematite, lending the raw material a characteristic reddish colouration. Combined iron is probably present in the chlorite clay minerals, and in the mixed-layer clay mineral assemblages containing chlorite and vermiculite. In the shales from Random Island, Nfld., from Flowers Cove, Ste. Anne, and Beersville, N.B., and to a lesser extent in those from New Glasgow and Antigonish, N.S., some of the iron is present as pyritic minerals or sulphides, as shown by XRD and by the strong exothermic peaks, usually doublets, around 400 to 425°C on the DTA curves. Sulphur was also determined by chemical analysis and is reported in the supplementary columns of Table 6. The presence of sulphides introduces a requirement for a careful oxidation period during firing to prevent black-coring or bloating,

particularly if elemental carbon is also present.

Organic and elemental carbon, determined chemically, is reported in the supplementary columns of Table 6, and is clearly shown as exothermic peaks on the DTA curves. In Fig. 4, for example, the St. Leonard sample contains a substantial amount of easily oxidized carbon, probably lignite, and shows a strong exothermic peak at about 300°C. Very small amounts of a similar type of oxidizable matter, possibly derived from rootlets, are shown in the lower three curves of the same figure. The material from Alma is more difficult to oxidize and is probably a higher ranking variety of coal, hence the maximum rate of burn-out is not reached until about 450°C. The material from Beersville contains about the same amount of organic and elemental carbon as that from Alma, but is still more difficult to oxidize and the exothermic peak on the DTA curve extends from about 300°C to 700°C. In this case, oxidation of the carbonaceous material is interrupted by the dehydroxylation of the clay minerals, shown by the interfering endothermic peak between about 400°C and 600°C: during this period the pores of the ware would be filled with water vapour, preventing the ingress of oxygen. The precise nature of the organic carbon in the Beersville sample has not been determined. The shape of the DTA curve is very similar to those for the Shubenacadie and New Glasgow "B" samples of Fig. 3. The carbon in the Shubenacadie material is known to be a fairly hard bituminous coal, whereas that in the New Glasgow "B" sample is believed to derive from associated seams of oil-shale. During firing, the volatiles

in the latter would distill off, leaving a residue of coke, which would be difficult to oxidize.

The difference between total carbon and organic and elemental carbon, shown in the supplementary columns of Table 6, represents the carbonate content, identified by XRD to be present usually as calcite, occasionally as dolomite and, in the New Glasgow samples, as siderite. Calcite in even minor amounts is readily identified in the raw materials by its effervescence when treated with dilute HCl. This procedure forms the basis for the classification of "calcareous" in Tables 2 to 5. Only the Milford shale contains an amount of lime approaching the levels common to the Ordovician high-lime shales that predominate in south-western Quebec and southern Ontario. The mineralogical analysis shows, however, that the lime, or calcite, in the Milford sample is concentrated in the coarse fraction rather than being finely disseminated throughout the mineral, hence the fired material is red rather than buff.

Sulphur in detectable quantities was found by chemical analysis in all samples. In many samples it occurred as a constituent of pyrite, and could be detected by XRD or DTA. In the three New Glasgow samples and the material from Middleton, gypsum (CaSO_4) was reported by XRD. Some soluble sulphates were probably present in all samples. In those with significant sulphur content, the addition of barium compounds would be required to control scumming and efflorescence.

The effect of composition on ceramic behaviour and

associated processing problems is examined in greater detail for a number of representative samples in the following section.

Properties of Selected Samples

Ten samples were selected for more detailed examination of their ceramic behaviour, either because they were considered typical of their geographical area or geological origins, or because they were considered to justify initial development for ceramic use or expansion of existing production facilities. These materials are treated individually below.

In addition to their previous characterization on the basis of composition and preliminary forming and firing tests, the forming and firing behaviour of the selected samples were examined in greater detail. Their plasticities were measured with the Bradender Plastograph; variations in consistency with water content are shown in Fig. 5 and 6. On the basis of experience, these curves can be related to extrusion behaviour. The firing behaviour of the selected samples was examined dynamically by DTA, TGA, and TDA. The DTA curves have been shown in Fig. 2, 3, and 4. The weight loss curves obtained by TGA are shown in Fig. 7 and 8. The linear dimensional changes occurring during firing in both oxidizing and oxygen-deficient atmospheres, determined by TDA, are shown later for the individual samples in Fig. 9 to 18, along with cooling curves that show the reversible thermal expansion of the fired materials through the temperature range covering the crystalline inversions of the silica minerals. For convenience, the data obtained by

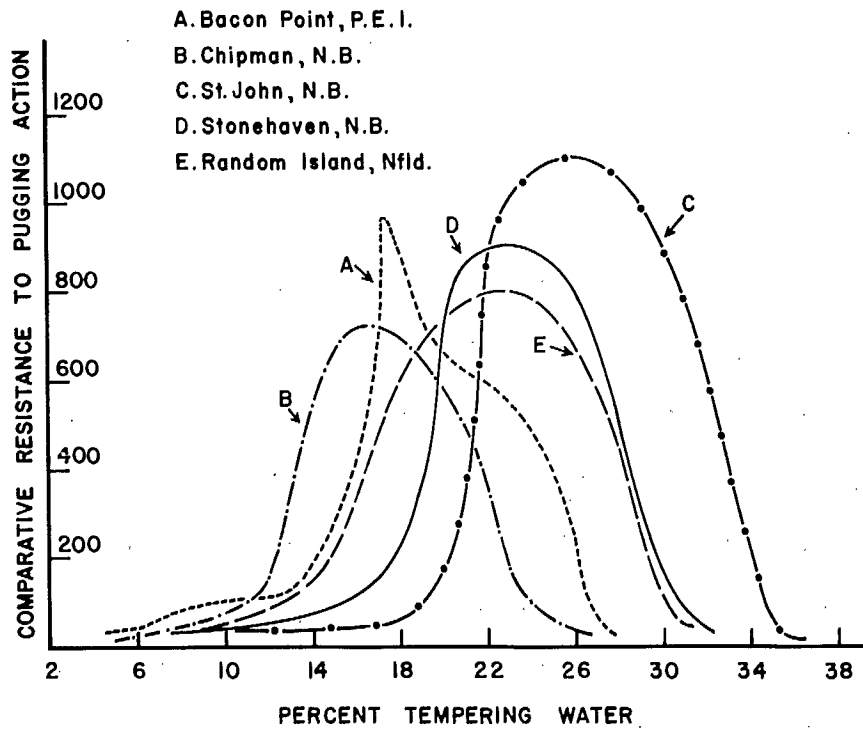


Figure 5. Plastograms of selected clays and shales from Atlantic Provinces.

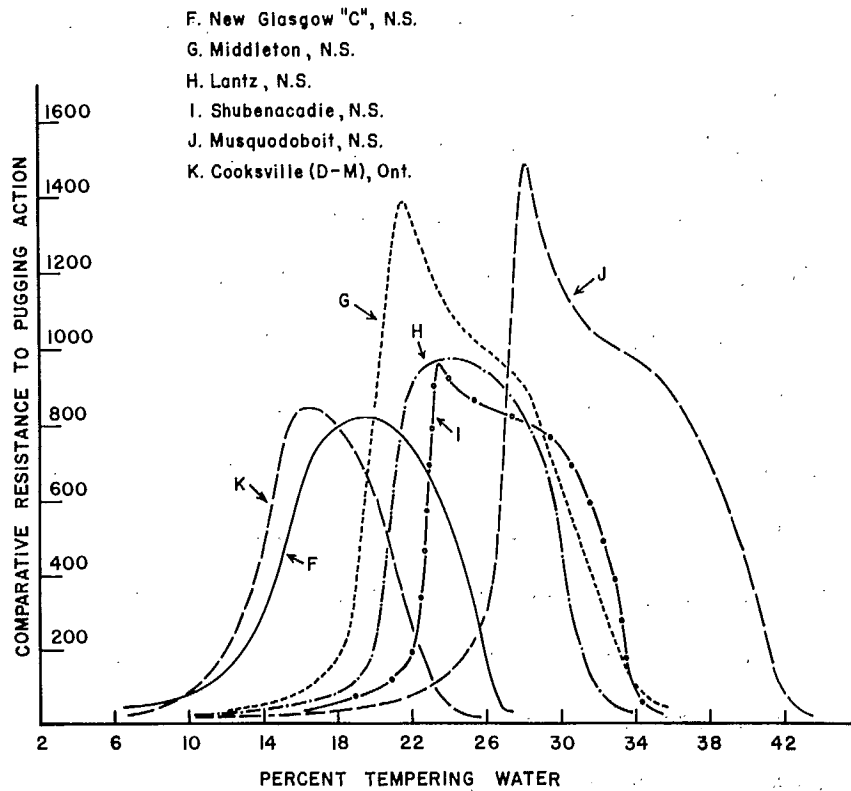


Figure 6. Plastograms of other selected clays and shales from Atlantic Provinces

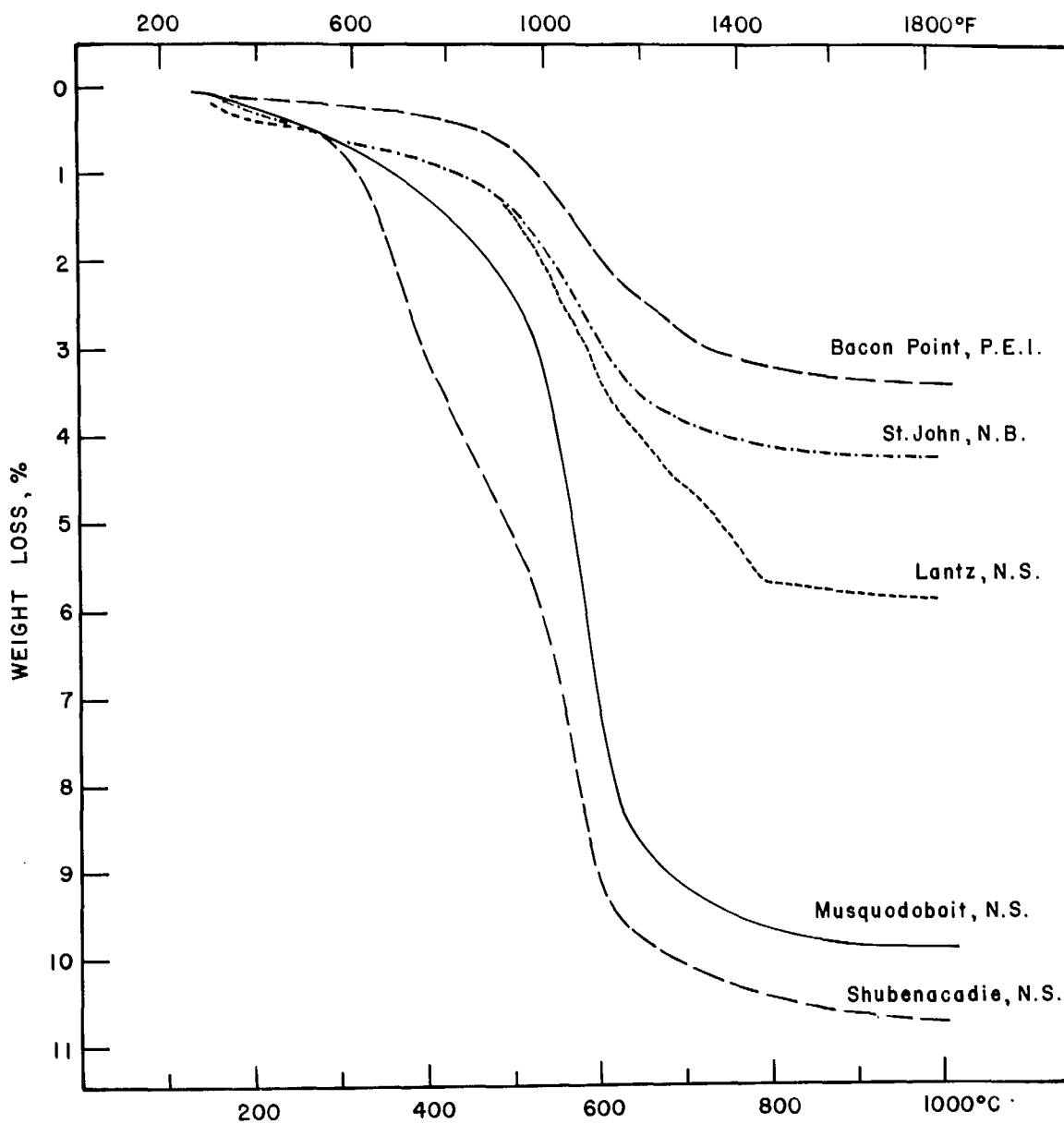


Figure 7. Weight loss of selected samples from the Atlantic Provinces.

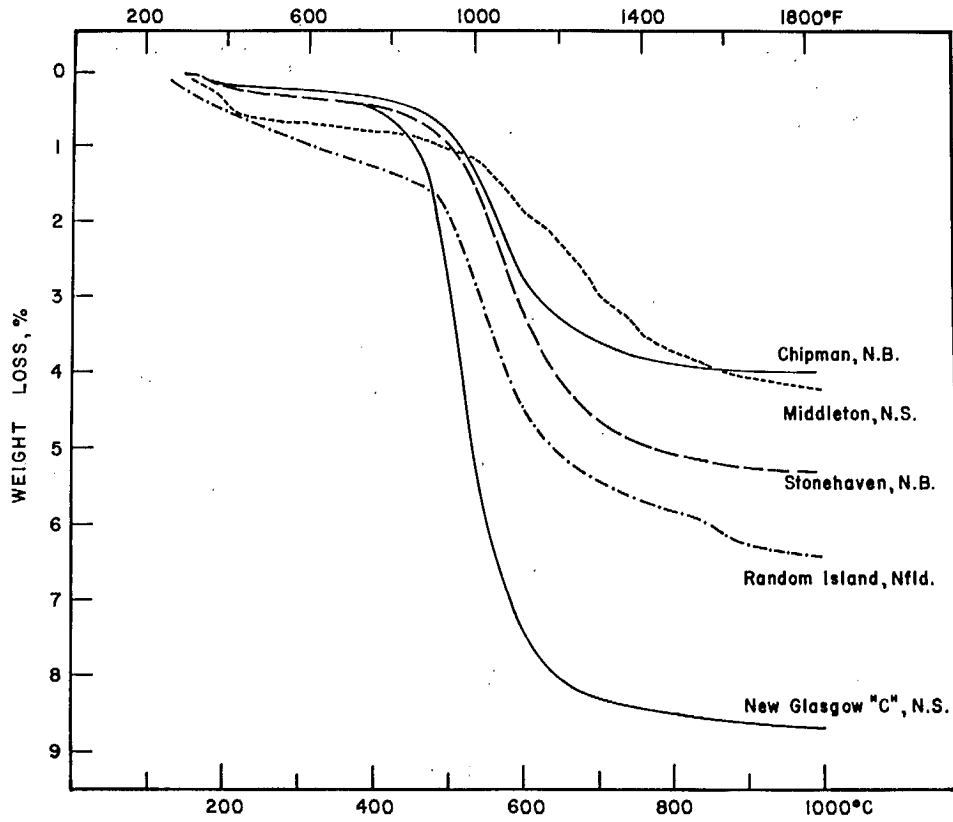


Figure 8. Weight loss of other selected samples from the Atlantic Provinces.

TABLE 8

Mineralogical Composition of Selected Samples *

SAMPLE	UNFIRED Composition **	FIRED PROPERTIES		
		Firing Temperature	Absorption %	Fired Composition ***
1. Random Island (PCE 14)	Quartz (about 18%), plagioclase, kaolin, illite, chlorite, chlorite-vermiculite-illite, anatase, pyrite, organic material.	Cone 02 (1101°C)	8.5	Quartz (about 9%), hematite, mullite (minor), rutile.
6. Bacon Point (PCE 7½)	Quartz (about 35%), illite, plagioclase, chlorite, kaolin, chlorite-vermiculite, hematite, K-feldspar, calcite, dolomite.	Cone 01 (1117°C)	15	Quartz (about 15%), hematite, K-feldspar (minor), rutile.
12. New Glasgow "C" (PCE 14-)	Quartz (about 24%), illite, siderite, kaolin, vermiculite-illite, chlorite, organic material, plagioclase, anatase, gypsum, calcite, pyrite, rutile.	Cone 01	10	Quartz (about 10%), spinel, K-feldspar, mullite.
13. Shubenacadie (PCE 28)	Quartz (about 31%), kaolin, illite, vermiculite-dioct chlorite, organic material, rutile, anatase, pyrite, calcite, plagioclase.	Cone 10 (1285°C)	10	Quartz (about 10%), mullite, K-feldspar, rutile, cristobalite.
15. Lantz (PCE 7)	Illite, quartz (about 20%), chlorite, kaolin, plagioclase, calcite, dolomite, organic material, hematite, K-feldspar, amphibole.	Cone 04 (1050°C)	9	Quartz (about 9%), hematite, K-feldspar, spinel, rutile.
16. Musquodoboit (PCE 26+)	Kaolin, quartz (about 14%), illite, vermiculite-dioct chlorite-illite, hematite, K-feldspar, anatase, rutile, organic material, plagioclase.	Cone 5 (1177°C)	8	Quartz (about 8%), mullite, hematite, K-feldspar, rutile, cristobalite.
17. Middleton, N.S. (PCE 5!)	Illite, quartz (about 24%), K-feldspar, chlorite-smectite-illite, gypsum.	Cone 01	10	Quartz (about 10%), spinel, K-feldspar, rutile.
20. St. John, N.B. (PCE 8)	Illite, quartz (about 23%), chlorite, plagioclase, vermiculite-smectite, kaolin, hematite, K-feldspar, organic material, amphibole.	Cone 04	10	Quartz (about 10%), hematite, K-feldspar (minor), rutile.
24. Chipman (PCE 10!)	Quartz (about 35%), illite, smectite-illite, chlorite, kaolin, hematite, rutile, anatase, plagioclase.	Cone 1 (1136 C)	13	Quartz (about 13%), hematite, mullite, K-feldspar, rutile, spinel.
28. Stonehaven (PCE 12)	Illite, quartz (about 18%), chlorite, illite-vermiculite, kaolin, hematite, calcite, plagioclase, anatase.	Cone 04	10	Quartz (about 9%), hematite, rutile.

* Constituents listed in decreasing order of estimated abundance.

** Crystalline materials determined by R. S. Dean, presence of significant amounts of organic material derived from DTA.

*** Fired compositions determined by R. M. Buchanan: diffuse diffraction lines indicated the presence of unidentifiable, poorly crystallized constituents in all cases.

DTA and TGA are included in these figures, but the TGA curves have been re-plotted differentially to show rate of weight loss. It should be noted that the rate of weight loss scale, vertical axis, is logarithmic, which de-emphasizes the height of the peaks representing substantial weight losses, but more clearly delineates the minor peaks or the shoulders superimposed on the larger peaks that result from simultaneous minor reactions. Supplementary to the data obtained in the preliminary tests reported in Tables 2 to 5, the effect of firing temperature on the fired properties of the selected samples was examined in greater detail by the temperature gradient method. The data for absorption and firing shrinkage vs firing temperature are also shown graphically for each sample in Fig. 9 to 18 respectively. In addition, the mineralogical composition of fired specimens of each selected sample was determined by XRD. The mineralogy of the unfired and fired materials is compared in Table 8. The percentage of unreacted quartz in the fired samples was estimated from the extent of the discontinuity at about 573°C in the thermal expansion curve for the fired sample, by direct linear comparison with a similar curve for a rock composed 100% of quartz.

Selected Shales

a) Random Island

Some of the oldest shales known occur in the province of Newfoundland. On Random Island in Trinity Bay is a deposit of dark grey, red-burning shale, currently considered to be of

lower Ordovician age. This material is being used for the manufacture of brick.

Analysis by XRD shows that the material contains substantial quantities of a mixture of clay minerals: illite, kaolinite, chlorite and a mixed-layer assemblage including vermiculite. The micaceous minerals are not well crystallized and their structures are disordered, which probably accounts for their hygroscopic nature. Release of a moderate amount of adsorbed water at just over 100°C is indicated on the DTA and Rate of Weight Loss curves of Fig. 9, and products made from this material would probably be subject to moisture regain if exposed to humid atmospheres between drying and firing. For the same reason, the clay minerals are not clearly defined by the DTA or DTGA curves, for which the mixture combines to give rather broad diffuse peaks at just under 600°C. Nor is the presence of kaolin clearly indicated by TDA, where the thermal expansion curve reflects the high content of micaceous clay minerals. Above about 400°C, when dehydroxylation of the clay minerals begins, the curve shows a sharp expansion demonstrated by West to be caused by exfoliation of the clay micas in concert with the expansion accompanying the quartz inversion at 573°C⁽³⁷⁾. Normally, the kaolinitic minerals begin to shrink above about 650°C, which is not apparent here because of the continuing expansion of the micas to about 800°C, when the exfoliated structure collapses. At a faster heating rate in an oxygen-deficient atmosphere, final shrinkage begins at a lower temperature and much more abruptly, which would cause stressing of the ware and

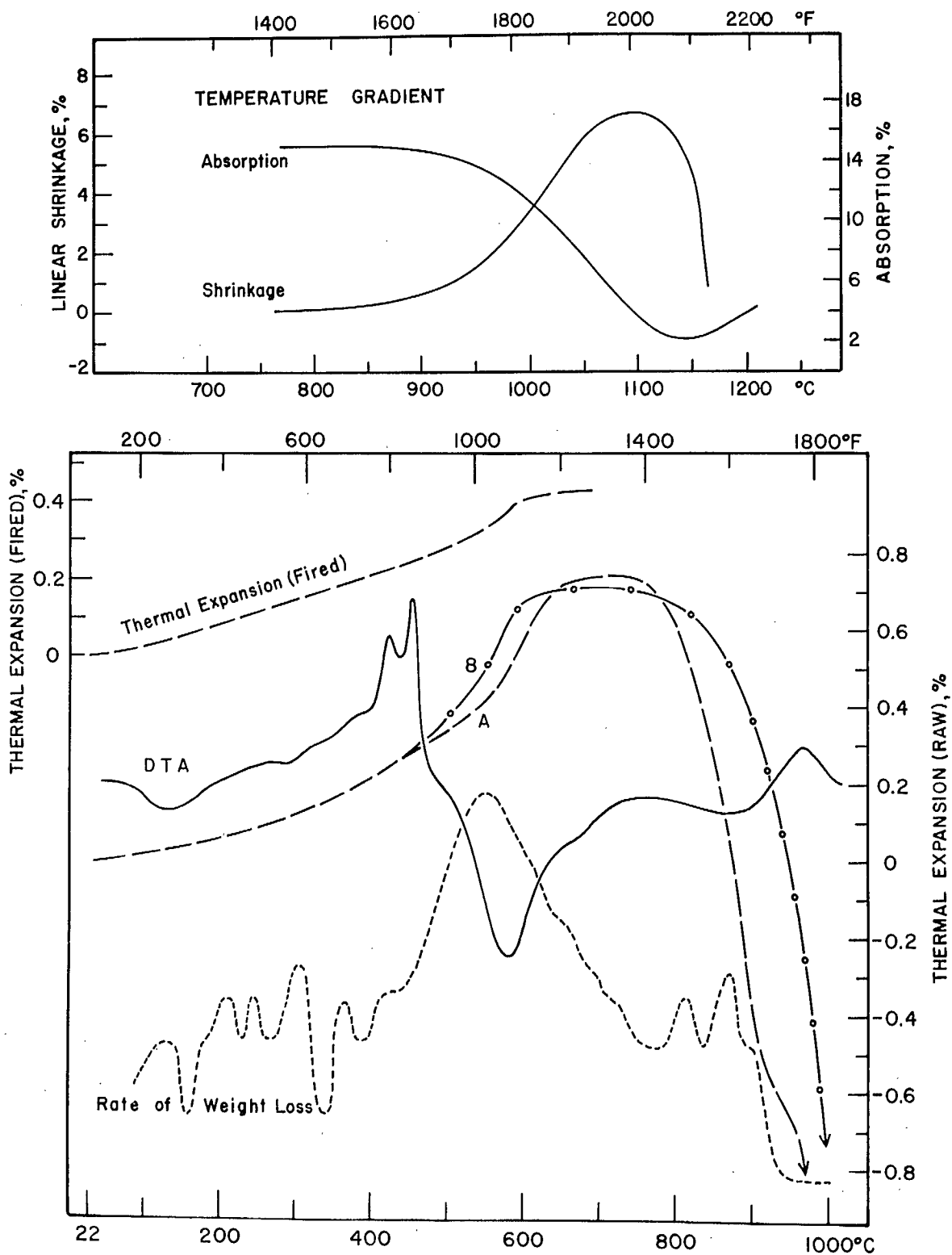


Figure 9. Firing behaviour of Random Island shale.
A. Linear thermal expansion (raw shale), reducing atmosphere.
B. Linear thermal expansion (raw shale), oxidizing atmosphere.

might initiate cracking if the strength were low.

The mixed clay mineral composition undoubtedly affects a number of ceramic properties of the material. For example, the plastogram of Fig. 5 shows a moderate consistency at a level more than adequate for satisfactory extrusion of brick, but thin-shelled, multi-cored ware would be difficult to extrude. Maximum consistency is reached with an addition of 23% water, but a good stiff-plastic condition is attained with 20%. The breadth of the Plastograph peak, a function of the mixed clay mineral composition, indicates relative ease of control of extrusion. Although of good dry strength, the material contains sufficient non-plastic components — quartz and feldspar — and less-plastic kaolin to control drying shrinkage to a reasonable level of 3.7% for hand-moulded specimens. Again, the mixed clay mineral composition affects the firing behaviour — the temperature gradient curves show that vitrification begins at low temperatures and proceeds quite uniformly through to above 1100°C, where the material overfires. Absorptions between 8 and 3%, the desirable range for brick, are obtained over a range of about 70°C, sufficient for commercial control. Within this range, firing shrinkages are relatively constant at a somewhat high 6 to 7%, promising good size uniformity of products.

DTA shows that the material contains a small amount of carbon and an appreciable amount of pyrite; chemically, 0.24% sulphur was reported in Table 6. Care would therefore be required to oxidize these components prior to the onset of

vittrification, to prevent black-coring or bloating of the products. DTA indicates that these oxidizable materials can be effectively burned out before the pores are blocked by the substantial amounts of water vapour emanating from the dehydroxylating clay minerals, which could otherwise delay their oxidation and cause problems.

The free silica in the raw material — chemically, 18.1% quartz — although concentrated in the coarse fraction, is largely reacted in a well-fired specimen: about 9% of unreacted quartz was estimated for a specimen fired at Cone 02. The thermal expansion curve of the fired specimen shows only a moderate dimensional change owing to the quartz inversion, which is unlikely to cause difficulty at normal cooling rates.

Two other Paleozoic samples, those from Manuels River and Summerside, although similar in many aspects of their behaviour to the Random Island sample, are somewhat older geologically, being attributed to the preceding Cambrian Period. Mineralogically, they contain essentially the same suite of micaceous clay minerals as does the Random Island sample, but neither contains kaolin. Both also contain more quartz and a wider variety of non-plastic minerals, particularly feldspars. As a result, both show adequate but poorer plastic properties. Because of their greater content of fluxes, i.e., feldspars, and lack of refractory kaolin, they show shorter firing ranges for dense products than does the Random Island material.

b) Bacon Point

Prince Edward Island, as previously noted, has only a limited indigenous ceramic industry beyond a fairly well developed craft movement catering to the tourist trade. Because of shortcomings in the local raw materials, they are frequently mixed with imported clays to improve their ceramic properties. The local potters usually extract their materials from weathered pockets of the red Pennsylvanian-Permian shales that are common throughout most of the Island. The similarity of composition of the two samples reported here and of others referenced by Dean, indicates that all would exhibit very similar ceramic properties⁽²⁴⁾. The material selected for detailed study is from the cliffs of red shale at Bacon Point on Hillsborough Bay. The sample represents the top 10 ft of shale and is overlain by 10 ft of glacial drift.

The mineralogical analysis shows a mixed clay mineral composition, including illite, chlorite and kaolin, with illite the dominant member. DTA and DTGA as shown in Fig. 10 do not clearly distinguish the mixed-mineral nature but the greater illite and lower kaolin content is reflected in a shift of the main endothermic peak to a lower temperature compared with the Random Island sample. Again, a mixed-layer mineral component containing an expansible phase, vermiculite, is indicated by the endothermic peak, related to the release of adsorbed water, at just over 100°C. The strongly micaceous character of the clay minerals is reflected in the dilatometric behaviour of the material: the TDA curve is typical of those for micaceous minerals, rising

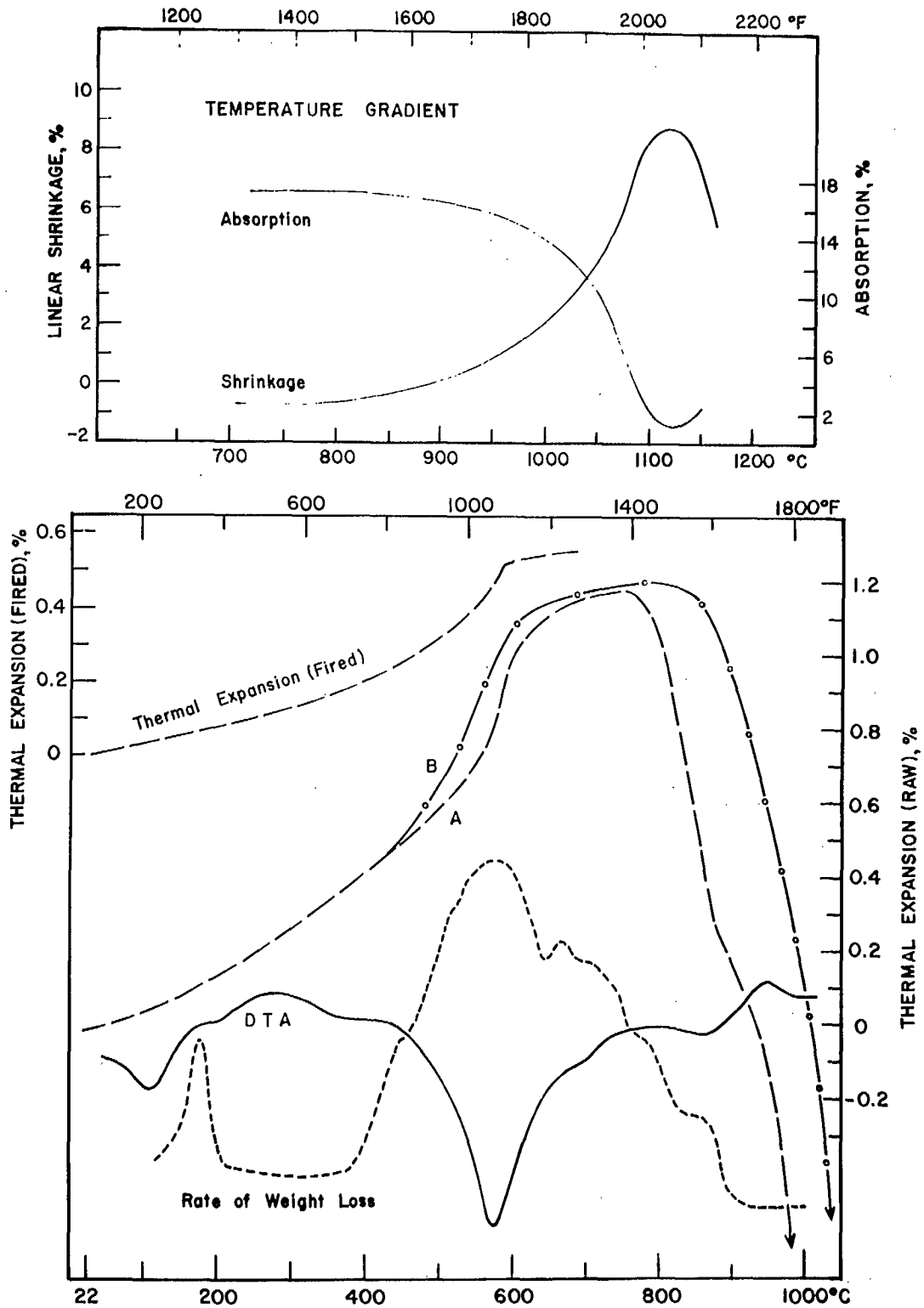


Figure 10. Firing behaviour of Bacon Point shale.
A. Linear thermal expansion (raw shale), reducing atmosphere.
B. Linear thermal expansion (raw shale), oxidizing atmosphere.

to above 1% expansion owing to exfoliation of the mica crystallites and remaining at that high level until the second stage of dehydroxylation is complete. In this case, the peak exceeds the usual height owing to the high percentage of quartz — 35.7% by chemical analysis — and the resultant expansion at 573°C. Shrinkage, once begun, is abrupt and extensive. At faster heating rates, shrinkage commences even more abruptly and could cause stressing and possibly fracture of the ware. This is probably due in part to reactions involving the feldspars and the substantial iron content of about 6% as Fe_2O_3 , which would be expected to be reduced to the more reactive form in the prevailing oxygen-deficient atmosphere in the test. Small amounts of calcite and dolomite are indicated by the endothermic peaks at about 700°C and 860°C on the DTA curve, but quantities are not so large as to significantly affect the firing behaviour.

The ground shale is moderately plastic, but the plastogram of Fig. 5 shows a broad basic peak upon which is superimposed a narrow sharply rising peak. This characteristic is attributed to the dilatant behaviour of the substantial content of fine-grained quartz, feldspars and hematite, which exhibit pseudo-plasticity because of their fine particle size. Materials showing this characteristic usually laminate during the forming process. A laminar structure subject to the strains imposed by the rather high drying shrinkage, above 5%, could account for the minor drying cracking observed with this material.

No unusual firing problems are evident. The small amount of organic material burns out readily by about 300°C.

The dimensional changes owing to the quartz inversion are of considerable magnitude and care would be required to prevent dunting, particularly when cooling semi-vitrified ware in which much of the quartz remains unreacted. Unfortunately, the production of dense, vitrified wares from this material is difficult, owing to the short vitrification range, evidenced in the temperature gradient curves. Handcrafted pottery made from Island shales has often been reported to be subject to warping when fired to an impermeable condition, and it has been common practice to counter the short firing range by adding refractory clay imported from Musquodoboit, N.S.

The mineralogical and chemical compositions of this sample and that from Howards Cove, toward the west end of the Island, show little significant difference except that the latter contains substantially less quartz. As a result, its forming properties are probably superior, but the vitrification range is further reduced (Table 3). The most evident difference in the DTA's of the two samples is in the carbonate peaks (Fig. 2). The Howards Cove sample shows a larger endothermic peak at 700°C, related to the dissociation of calcite, and shows no dolomite peak. In neither case is the carbonate content sufficient to significantly affect ceramic behaviour. The main endothermic clay mineral peak at around 600°C is larger for the Howards Cove sample, reflecting the greater clay content at the expense of quartz in the Bacon Point material, and is shifted to a higher temperature owing to the attendant increase in kaolin content. Nevertheless,

the similarities between the two samples far outweigh the differences.

c) Stonehaven

A shale strikingly similar to the Prince Edward Island deposit occurs about a hundred miles west on the New Brunswick mainland at Stonehaven on Baie des Chaleurs, the properties of which are illustrated in Fig. 11. Its origin is attributed to the Pennsylvanian period so that it is somewhat older than the shale at Bacon Point.

Although it contains essentially the same clay minerals in roughly the same relative proportions the Stonehaven shale has a considerably greater total clay content: e.g., free quartz is only 18% compared with 36% in the Bacon Point shale (Tables 6, 7). This difference in composition is primarily responsible for the differences in ceramic properties and behaviour.

The presence of an adsorptive mixed-layer clay mineral assemblage — illite-vermiculite — is indicated by the doublets on the DTA and DTGA curves between 100° and 200°C. Again, the dried products could be subject to moisture regain. Oxidation is no problem as the material contains little carbon and no pyrite is evident. The mixed clay mineral composition is not clearly delineated by the main endothermic clay-dehydroxylation peak just below 600°C where the overlapping reactions appear as barely perceptible shoulders, but the size of the peak is significantly greater than that for the Bacon Point shale, reflecting its greater clay content. The total water of crystallization released, 5.42% as shown in Table 6, is not excessive, and

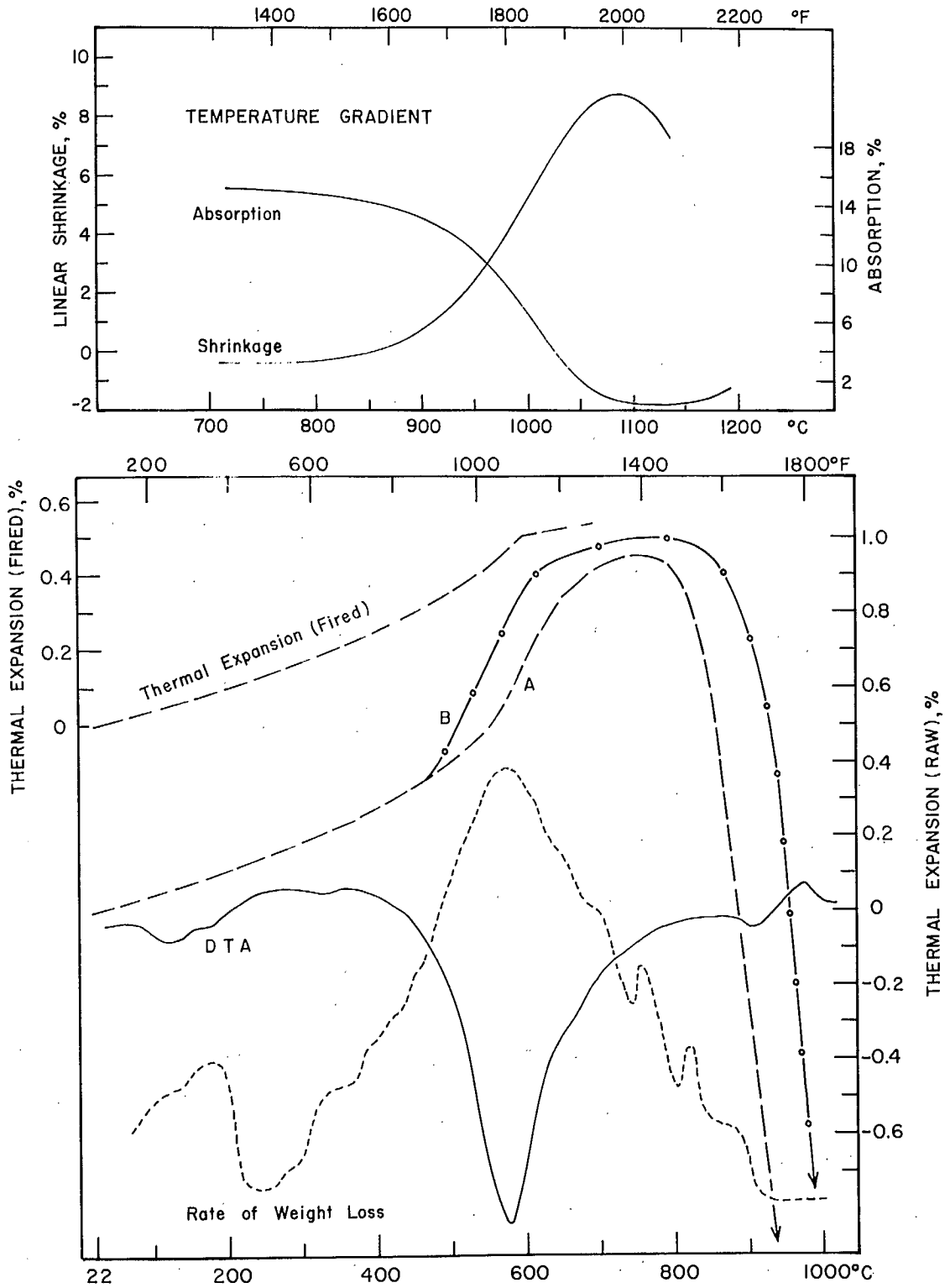


Figure 11. Firing behaviour of Stonehaven shale.

A. Linear thermal expansion (raw shale), reducing atmosphere.

B. Linear thermal expansion (raw shale), oxidizing atmosphere.

condensation problems would not be anticipated with normal drafts. The attendant exfoliation of the micaceous clay minerals causes a rather abrupt increase in the rate of thermal expansion: because the ware at this point would be porous and soft, it should readily absorb attendant stresses and heating-up cracks are unlikely. Between about 700° and 800°C, two small peaks on the rate of weight loss curve probably relate to dissociation of calcite as no dolomite was detected by XRD. The variation in temperature is probably a function of differing particle sizes of the calcite grains as calcite occurs primarily in the coarse fraction. The amounts are so small that the reactions are barely perceptible on the DTA curve and will have no significant effect on the ceramic behaviour of the material. The greater iron content, 9% vs 6% for Bacon Point shale, imparts to the fired body a clear red colour instead of the salmon to reddish brown.

Because it contains more kaolin and markedly less feldspar, and that of one type only (Table 7), this shale is more refractory than the Bacon Point shale — PCE Cone 12 vs Cone 7½. The temperature gradient curves show a firing range for dense products that is not only twice as wide as that for Bacon Point but occurs at lower temperatures, and overfiring takes place much less abruptly.

Because it contains more clay and less non-plastic quartz and feldspar, the plastic properties of the Stonehaven sample are much superior to those of the Bacon Point shale. The plastogram of Fig. 5 shows a broad rounded peak with an

optimum water addition of about 21%, indicative of easy, controllable extrusion of both heavy and thin-section ware. Nevertheless, the material dries safely with a shrinkage of less than 5%.

The Stonehaven shale should be useful for the manufacture of a full range of dense structural products such as brick, tile and sewer pipe, and probably pottery.

d) New Glasgow "C"

In New Glasgow, N.S., both a brick plant and a sewer pipe plant are utilizing deposits of dark grey Carboniferous shale, accessible over a fairly wide area. The preliminary evaluation of samples from two pits, designated New Glasgow "B" and "C", as reported in Table 4, are very similar except for fusion temperature. The similarities are also evident from the chemical and mineralogical analyses (Tables 6 and 7). The lower PCE of sample "B" is probably due to its greater content of alkalies and alkaline earth constituents, present as feldspars and as calcite, which would act as fluxes at the fusion temperature. From the viewpoint of ceramic processing, the most significant variable over the entire deposit is the carbon content, which is high in all cases and presents a requirement for long and careful oxidation during firing to prevent blackening or bloating. This is well illustrated in the DTA curves of Fig. 3, where oxidation of the carbon in sample "B" is not completed until about 700°C, after being interrupted by dehydroxylation of the clay minerals between about 400 and 600°C. The small endothermic peak at about 800°C on the same

curve indicates the presence of a moderate amount of calcite, barely evident on the curve for sample "C". The source of most of the organic material is probably the upper strata of the deposit, which is classified as an oil-shale and is stripped off and discarded during mining. Thus, the carbon content varies with depth and, because it is sensitive to weathering, it also varies horizontally throughout the deposit. The New Glasgow "C" sample was selected for detailed study because it is considered more representative of the material normally used for structural clay products manufacture.

The shale is only moderately plastic and thin-walled ware would thus probably be difficult to extrude. However, the plastogram of Fig. 6 shows a fairly wide, gently rounded peak reaching maximum consistency with an addition of about 18% water, and control of pugging is not a serious problem. Both green and dry strengths are rather low, and various additives have been employed to improve extrusion behaviour and to serve as binders. Additions of deflocculants are particularly useful in overcoming drying cracking encountered in large, heavy-section ware such as sewer pipe (38).

Chemical analysis indicates about 25% quartz, and XRD shows illite to be the dominant clay mineral, kaolin to be common, and chlorite and a mixed-layer vermiculite-illite phase to be present in minor amounts. The mixed clay mineral composition is reflected in the curves of Fig. 11. The main clay peak at 560°C on the DTA curve indicates dehydroxylation of illite but shows small shoulders at both higher and lower temperatures

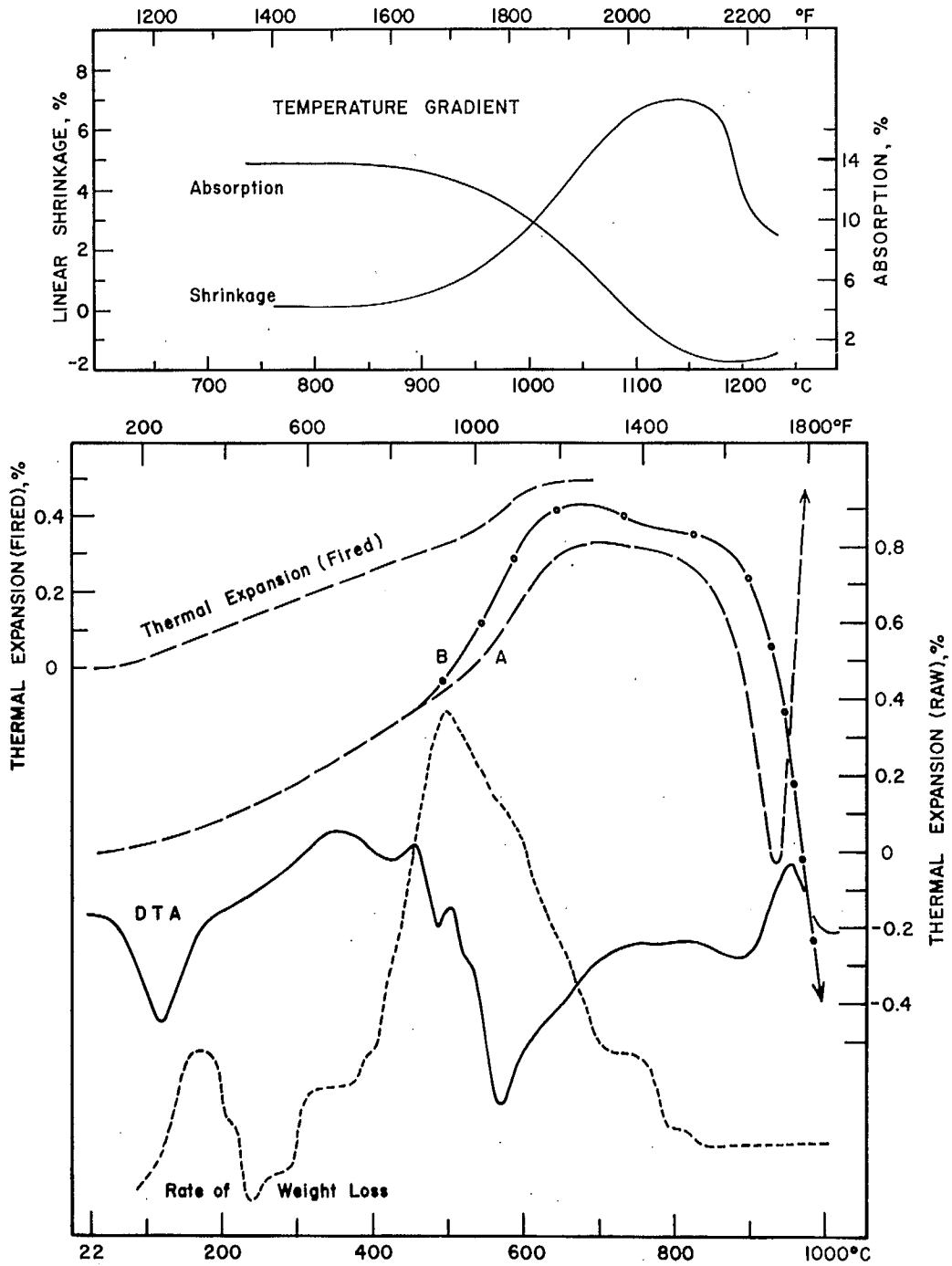


Figure 12. Firing behaviour of New Glasgow "C" shale.
A. Linear thermal expansion (raw shale), reducing atmosphere.
B. Linear thermal expansion (raw shale), oxidizing atmosphere.

owing to the other clay minerals. The TDA curve shows the typical thermal expansion behaviour of micaceous clay minerals, modified by a small shrinkage commencing just above 600°C owing to the kaolin component. The rather large dehydration peaks at just over 100°C on the DTA and DTGA curves possibly owe as much to the dehydration of colloidal organic matter as to that of the expansible clay mineral phase. Oxidation of carbon begins at a low temperature, consistent with this assumption, and is not complete until about 500°C. The resultant broad exothermic peak on the DTA curve is interrupted by an exothermic-endothermic doublet beginning at 425°C, indicative of a moderate amount of pyrite. Such combinations of carbon, sulphur and iron are conducive to black-coring and bloating if oxidation is not completed before incipient vitrification begins to close the pores. By way of example, the TDA curve, A, obtained at the faster heating rate in a oxygen-deficient atmosphere shows a sharp expansion at about 900°C, quite like that shown by the high-lime shales of Ontario and Quebec. However, this sample is comparatively low in calcite; microscopic examination of the expanded specimen revealed an extremely uniform and very finely vesiculated structure. The material has since been shown to be suitable for production of good-quality lightweight aggregate. Gypsum was also identified in this sample by XRD. Many weathered areas of the deposit show encrustations of white salts on outcrops, no doubt due to sulphur from weathered pyrite combining with lime from the calcite component. Additions of barium salts are required to prevent scumming and efflorescence

on products made from this shale.

Properly oxidized and well-fired, the material makes a high-quality facing brick of a pleasing shade of light reddish brown, with dark specks resulting from vitrification of small grains of siderite (FeCO_3), in which form much of the iron occurs. The temperature gradient curves show a wide firing range for dense products, at temperatures approaching the high end of the range normally employed for structural clay products.

In the manufacture of sewer pipe it has been found useful to add a proportion of New Glasgow "A", a reddish-brown mixture of Carboniferous shale and clay that, in this area, overlies the oil shale above New Glasgow "C". Such additions improve the plasticity and hence the green and dry strengths, as well as reducing the carbon content and easing the oxidation of heavy thick-section pipe.

Other Upper Carboniferous shales of the region with significant potential for the manufacture of clay products include samples from Sydney and Antigonish in Nova Scotia, and from Chipman, Alma, Flowers Cove, Beersville and Ste. Anne in New Brunswick. All are characterized by relatively high PCE's compared with the Devonian shales common in western Quebec and Ontario. The PCE's of a majority of the samples exceed Cone 15, established by the ASTM as the lower limit for refractory clays. This is undoubtedly due to their considerable content of kaolin and relative freedom from fluxes such as feldspar. The DTA curves of Fig. 4 show that the Alma and Beersville shales would present oxidation problems equal to or greater than New Glasgow "C" or "B".

e) Chipman

A deposit of red Upper Carboniferous (Pennsylvanian) shale at Chipman, N.B., has been shown over many years to be suitable for manufacture of the type of dense, durable facing brick required to withstand the elements in the Atlantic Provinces, where saturated masonry is frequently exposed to freezing and thawing. The temperature gradient curves in Fig. 13 show a wide firing range for dense products, the body maturing at about the same firing temperature as the New Glasgow shale but showing lower firing shrinkage. This material would probably also be suitable for the manufacture of sewer pipe and stoneware-type pottery, provided the required plasticity were developed.

Although the plastograph curve of Fig. 5 is of the desirable configuration — broad and rounded — the peak consistency at about 16% water addition is only slightly above that considered minimal for smooth, sound extrusion. Minor variations in pugging could easily result in feathering or dog-earing of the corners of the extruded column. Finer grinding or the addition of deflocculants or plasticizers would be required for forming complex shapes.

The low plasticity is primarily due to the high content of quartz, determined chemically to be about 35.5% (Table 6), along with minor amounts of other non-plastic minerals. Even a well-fired specimen shows a significant dimensional change at the quartz inversion temperature and care in cooling is recommended to prevent dunting (Fig. 13). The high quartz

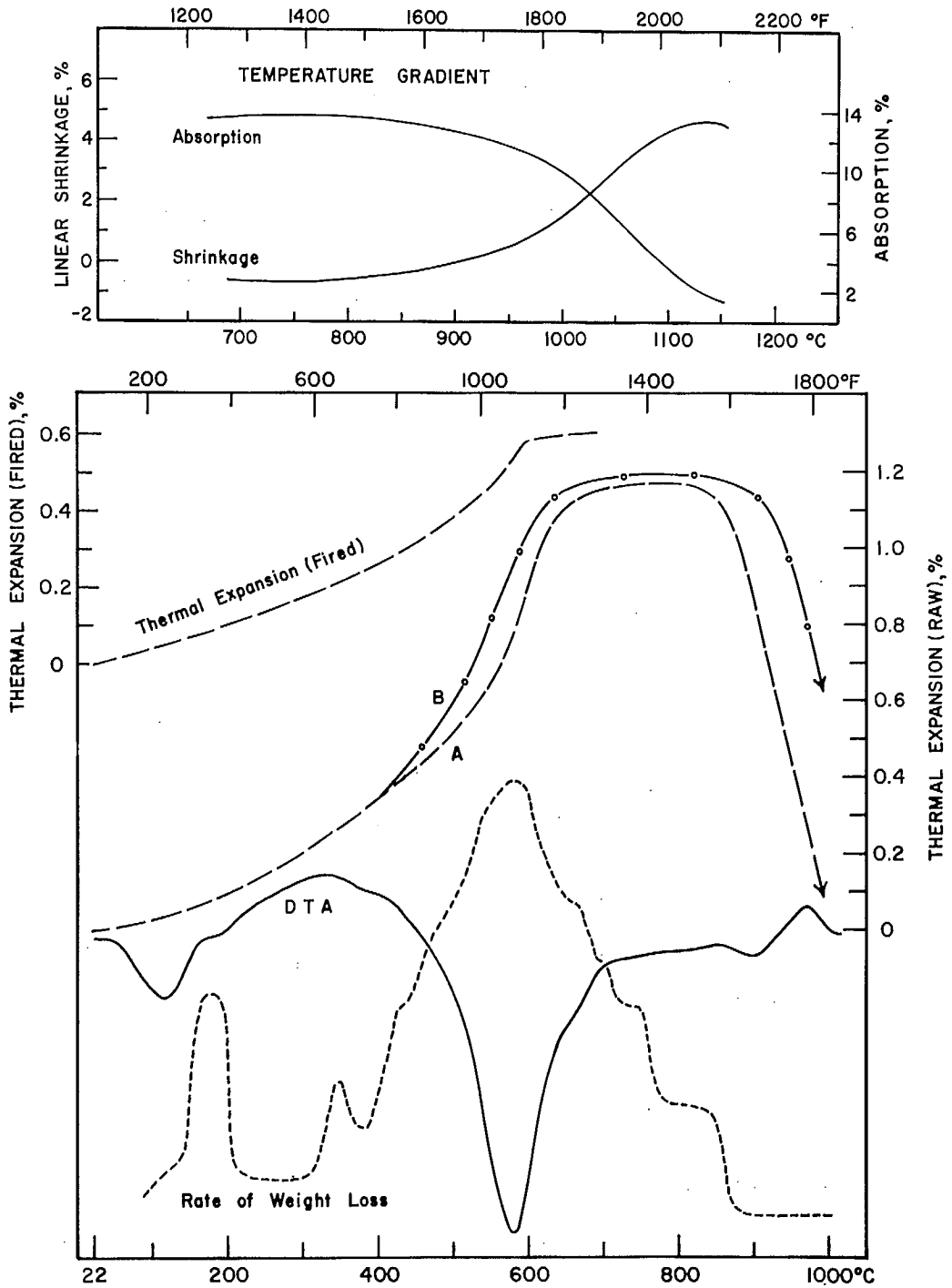


Figure 13. Firing behaviour of Chipman shale.

A. Linear thermal expansion (raw shale), reducing atmosphere.

B. Linear thermal expansion (raw shale), oxidizing atmosphere.

content is also reflected in the dynamic firing curves of Fig. 13, where it contributes to the sharp thermal expansion just below 600°C. However, the expansion of almost 1.2% is principally due to exfoliation of the micaceous clay mineral content, illite being the dominate component, both separately and in a mixed-layer clay mineral assemblage with montmorillonoid. The presence of the latter is evident from the peaks below 200°C on the DTA and DTGA curves, reflecting the loss of adsorbed water. Thus there is risk of dry products regaining moisture from the atmosphere. Again, the main clay dehydroxylation peaks just below 600°C fail to delineate the mixed nature of the clay mineral component except for some small shoulders on the curves. As seen in Table 7, XRD shows illite and montmorillonoid-illite to be the dominant minerals, with medium amounts of chlorite and kaolin. This mixture undoubtedly contributes to the wide firing range of the material — the montmorillonoid phase promotes early vitrification whereas the quartz and kaolin increase the refactoriness, preventing early overfiring. The sample contains over 7% iron oxides, distributed throughout as hematite, causing it to fire dark red.

Selected Surface Clays

f) Lantz

A deposit of smooth red surface clay of considerable depth and uniformity occurs at Lantz, Nova Scotia. Dean has postulated that the deposit has been derived primarily from the kaolinitic clays of the upper Shubenacadie valley, with

minor contributions from the underlying and adjacent shales (24). Although it exhibits the high shrinkages and short firing range typical of most common clays, it has long been used successfully in the manufacture of structural products in combination with the fire clays at Shubenacadie, where it serves to reduce the firing temperatures, and with the nearby Milford shale, where it provides the plasticity necessary for extrusion.

Although not excessively plastic, the plastogram peak is sufficiently high to indicate suitability for extrusion of complex thin-walled tile and shows a wide pugging range indicative of easy pugging control (Fig.7). The plastic characteristics and the safe drying behaviour, in spite of high drying shrinkage, reflect its composition (Table 4). It consists principally of the less-plastic clay minerals with significant amounts of non-plastics: about 20.5% quartz, considerable feldspar, and minor amounts of calcite, dolomite and amphibole.

The mixed clay mineral composition is indicated by the thermal analytical curves of Fig. 14, particularly the multiple peaks and shoulders on the DTGA curve at around 500 to 600°C. The primary clay minerals are well-crystallized illite and chlorite, with a lesser amount of kaolin, as shown by XRD in Table 7. The thermal analytical curves show a small amount of easily oxidized organic material that burns out around 300 to 350°C, and a small amount of pyrite that decomposes/oxidizes at about 425°C. The latter is present in too small an amount for identification by XRD and no oxidation problems are indicated. The peaks at about 700 to 750°C reflect the dissociation

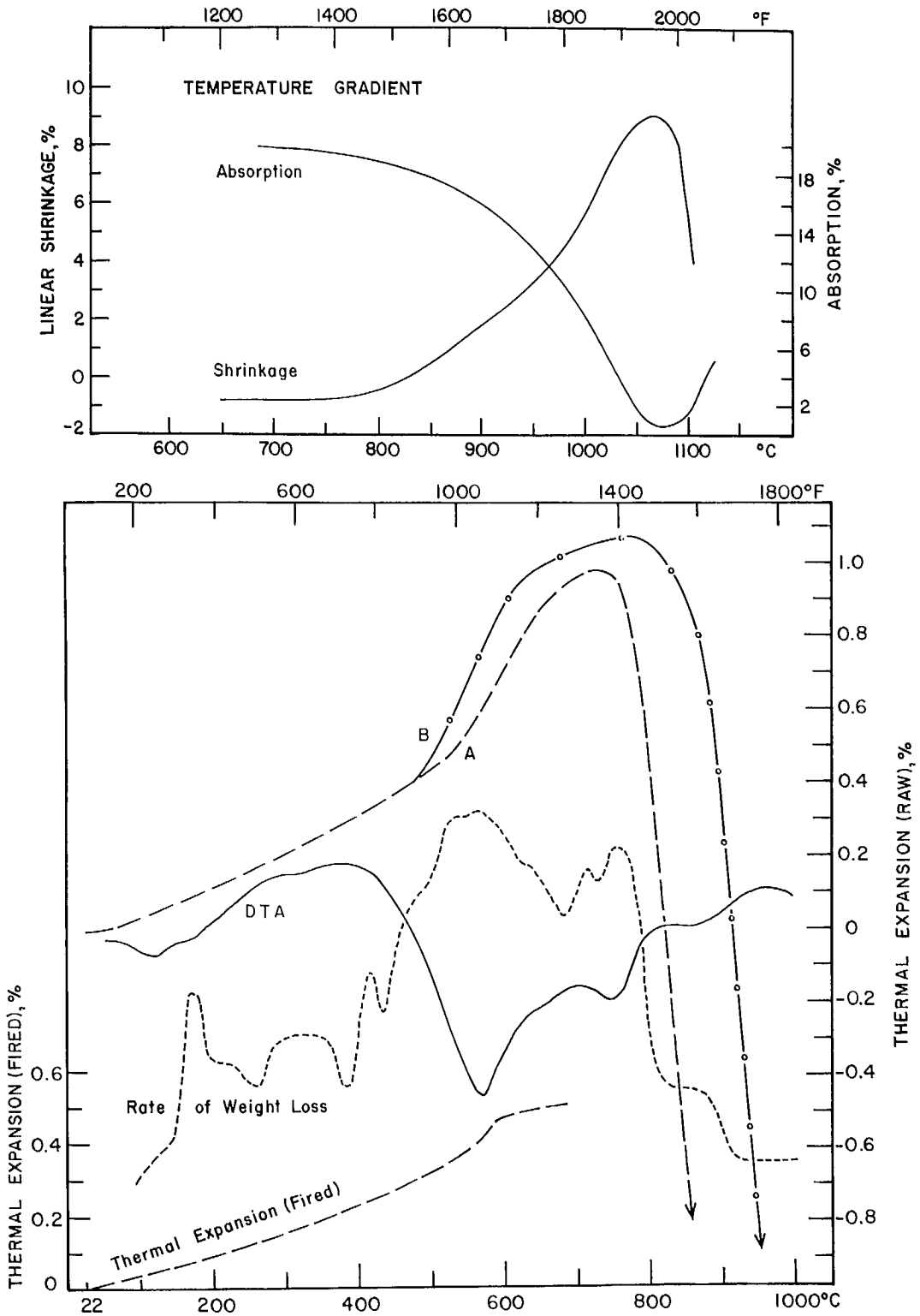


Figure 14. Firing behaviour of Lantz clay.
A. Linear thermal expansion (raw clay), reducing atmosphere.
B. Linear thermal expansion (raw clay), oxidizing atmosphere.

of calcite and dolomite. The lime-magnesia content, as seen in Table 6, is too small to cause firing problems similar to those demonstrated by high-lime clays and shales. The dilatometric curve is typical of materials composed primarily of micaceous clay minerals and quartz, although in reducing conditions shrinkage begins very abruptly and at a significantly lower temperature, probably due to the fluxing action of reduced iron oxides. If the clay were used alone, reducing conditions could pose risk of cracked ware or kiln-car wrecks -- the more refractory materials usually combined with this clay ameliorate the sharp dimensional change, and such problems are not normally encountered.

Similarly, the temperature gradient curves of Fig. 14 indicate a short firing range for dense products made from the clay alone, less than 50°C for products meeting the ASTM specifications for exposed brick, but the usual additions of refractory clay or shale serve to extend the firing range to a width more suitable to normal temperature control in commercial kilns.

g) St. John

A red surface clay strikingly similar to the foregoing deposit occurs at Little River, near St. John, N.B. The ceramic properties of the Lantz and St. John samples are nearly identical, as shown in Tables 4 and 5. Chemically, the major difference is the lack of carbonates in the St. John clay; mineralogically, the St. John clay contains a little more feldspar and a little less kaolin, plus a montmorillonoid-bearing mixed-layer clay mineral

assemblage. In earlier times, the St. John material was used for brick manufacture — in all probability for common brick as the firing technology of the time would not likely have been capable of the close temperature control required by the inherent short firing range for dense products such as facing brick. It also formed the basic raw material for a pottery located at St. John, although for this purpose it was modified by additions of clay from Musquodoboit or of talc, pyrophyllite and ball clays to improve its casting and firing behaviour.

The clay is smooth, fine-grained and plastic. The plastogram of Fig. 5 peaks at the same level of consistency as that for the Lantz material, but requires about 2% more water for maximum plasticity. The drying shrinkage, at 6.4%, is high, but specimens do not crack even under severe drying conditions.

As expected for materials of similar composition, there is little significant difference in the thermal analytical curves of the two clays. Those for the St. John clay, of course, show no carbonate peaks and, also, only the slightest indication of pyrite. A broader peak on the DTGA curve reflects the greater amount of water adsorbed by the expansile phases and indicates the possibility of moisture regain by ware not moved directly from the dryer to the kiln.

The temperature gradient curves of Fig. 15 show that vitrification takes place more rapidly than for the Lantz material, hence the firing range is even shorter. This is doubtless due to the lesser kaolin and greater feldspar contents

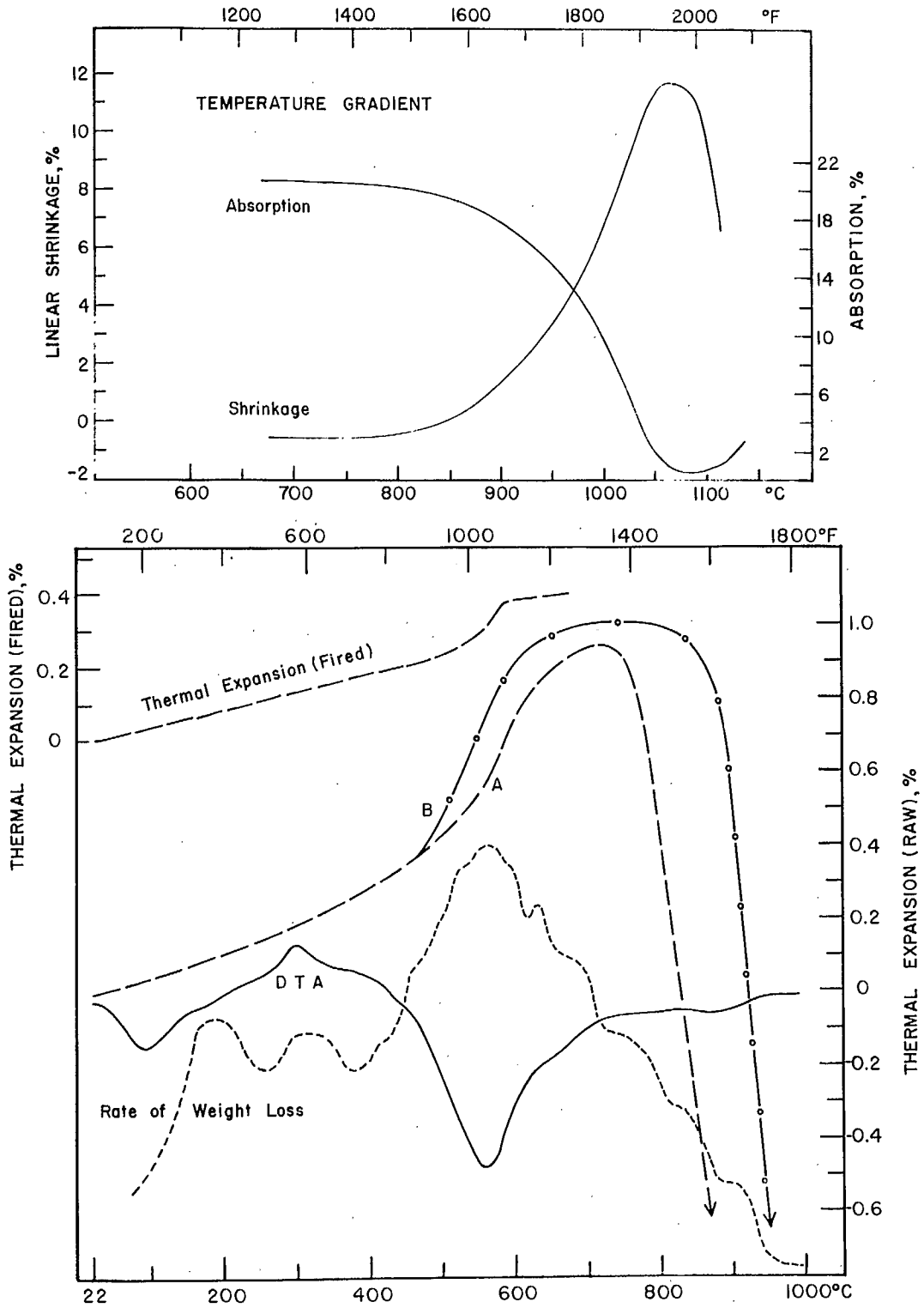


Figure 15. Firing behaviour of St. John clay.

- A. Linear thermal expansion (raw clay), reducing atmosphere.
- B. Linear thermal expansion (raw clay), oxidizing atmosphere.

of the St. John material. At equal firing temperatures, the thermal expansion curve for the fired St. John clay shows a moderately sharper dimensional change at the quartz inversion temperature of 573°C, indicative of the presence of a greater amount of unreacted quartz. Some care in cooling ware would be advisable to ensure that dunting does not occur.

h) Middleton

Patches of white or buff clay, or soft shale, that frequently has been remarked upon in the literature because of its light natural and fired colour, occur in the Annapolis Valley of Nova Scotia, just north of Middleton. Although the age and origin of the material have been subject to considerable speculation, Dean has recently postulated that it is a product of in situ alteration of the Triassic Blomidon shale (24). Doubtless, the material has received so much attention because of its superficial resemblance to china clay, for which it has been mistaken. In fact, its composition and ceramic properties render it suitable only for low-grade porous products such as farm drain tile and, perhaps, flower pots (39).

Analysis by XRD, as shown in Table 7, reveals that the major constituents are quartz and illite with substantial amounts of feldspar and an interstratified clay mineral assemblage comprising chlorite, montmorillonoid and illite. The thermal analytical curves of Fig. 16 reflect the mixed clay mineral composition in a series of endothermic peaks, each accompanied by weight loss. The peak at 125°C corresponds to removal of adsorbed water from the clay micas. The peaks just below 200

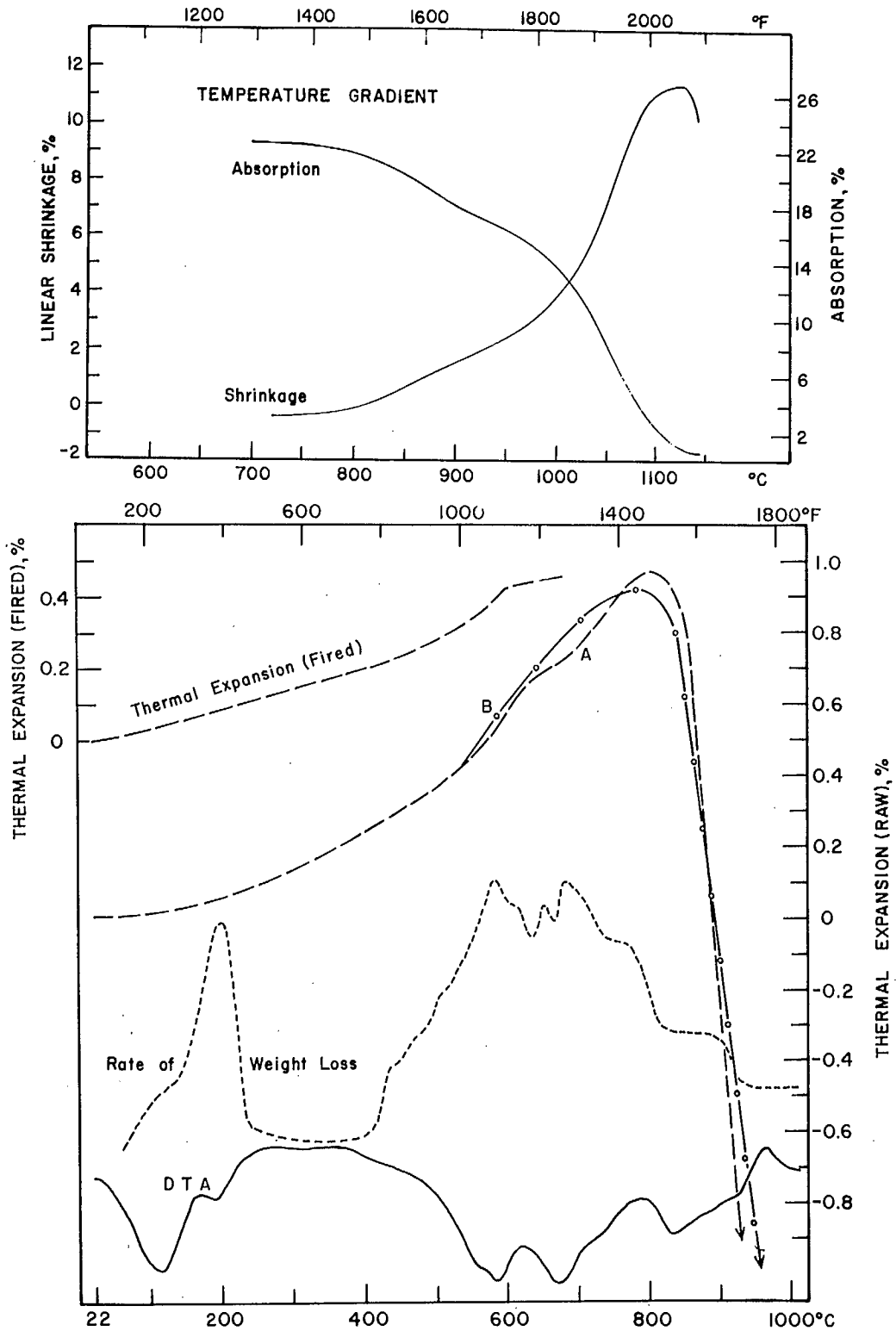


Figure 16. Firing behaviour of Middleton clay.

- A. Linear thermal expansion (raw shale), reducing atmosphere.
- B. Linear thermal expansion (raw shale), oxidizing atmosphere.

and 700°C represent the dehydration and dehydroxylation respectively of montmorillonoid; the doublet just below 600°C, the dehydroxylation of chlorite and illite; and the endothermic-exothermic peaks between 800 and 1000°C, the final dehydration and structural reorganization of the illite. The high quartz content of 24.4% by chemical analysis, shown in Table 6, is not strongly evident from the dilatometric curves, probably because the body is very porous and expansion of the individual quartz grains is absorbed internally.

The temperature gradient curves show that vitrification takes place very rapidly above 1000°C, hence production of uniform products with absorptions below about 14% would present serious problems in temperature control, effectively limiting applications of the material to porous products.

The plastogram of Fig. 6 shows a sharp high-rising peak typical of dilatant materials. This is not surprising considering the substantial content of fine-grained non-plastic or pseudo-plastic materials — quartz, feldspar, mica. This shape of curve is usually associated with lamination problems during extrusion and would be expected to cause similar problems when spinning flower pots.

Selected Fireclays

i) Shubenacadie

Although many clays and shales of the region contain substantial amounts of kaolin, rendering them moderately refractory, only two that approach the useful upper limit for low-duty

fireclay brick as defined by ASTM are readily accessible — at Shubenacadie and Musquodoboit, N.S. The deposit at Shubenacadie comprises seams and lenses of plastic and sandy materials. Thus, it varies both with depth and laterally in plasticity and in refractoriness, although the latter remains high because the principal variable component is quartz, a relatively refractory material. The sample chosen for detailed examination was the grey plastic portion of a core taken in the area of the operating pit. Its PCE was Cone 28.

The sample was amply plastic, attaining maximum consistency with the addition of about 25% water. The plastogram of Fig. 6 shows a broad basic peak upon which is superimposed a small abruptly rising sharp peak, attributed to dilatant behaviour of the fine-grained sand components and indicating a tendency to laminar flow behaviour. The material did not crack with rapid drying although the drying shrinkage was high at 6.7%. Again, the sand content probably contributed to an open pore structure and uniform shrinkage.

The mineralogical analysis in Table 7 shows the material to be a mixture of clay and quartz. The clay component is principally kaolin, which is responsible for the refractory nature of the sample, but includes a moderate illite content and a minor amount of a mixed-layer clay mineral assemblage. The chemical analysis seen in Table 6 shows the quartz content to be about 31%. As this sample represents only a plastic seam, the over-all quartz content of the deposit is undoubtedly considerably higher — sufficiently so that great care is

required during cooling of fired ware to prevent cracking, which takes the form of micro-cracks throughout the body resulting in loss of ring or a dead sound when two affected bricks are struck together. Even for this plastic sample, the thermal expansion curve of Fig. 17, for a moderately dense specimen pre-fired to about 10% absorption, shows a sharp dimensional change of about 1.5% at the quartz inversion temperature. Rapid cooling or re-firing would undoubtedly cause dunting. Minor components include feldspar and a very small amount of calcite, as well as the titania compounds usually associated with kaolinitic clays. The presence of pyrite is shown in XRD analysis and is evidenced by the high sulphur content determined chemically. Most of the iron in the sample is present as pyrite, visible in the deposit in association with narrow bands or lenses of coal: the fired material is off-white or cream with some dark specks. The coal is present in sufficient quantity and is of high enough rank that it is not completely oxidized until nearly 700°C, as shown on the DTA curve of Fig. 17. The large, broad exothermic peak from about 250° to 700°C, representing oxidation of the carbon, is interrupted by an inversion at 425°C related to the dissociation of pyrite and again by the main clay dehydroxlation peak at about 580°C. It must be borne in mind that this DTA curve was obtained at lower sensitivity than those previously discussed, and that the vertical scale is only one quarter of those previously shown, hence the extent of the indicated reactions is comparatively substantial. Thus it is evident that good drafts are

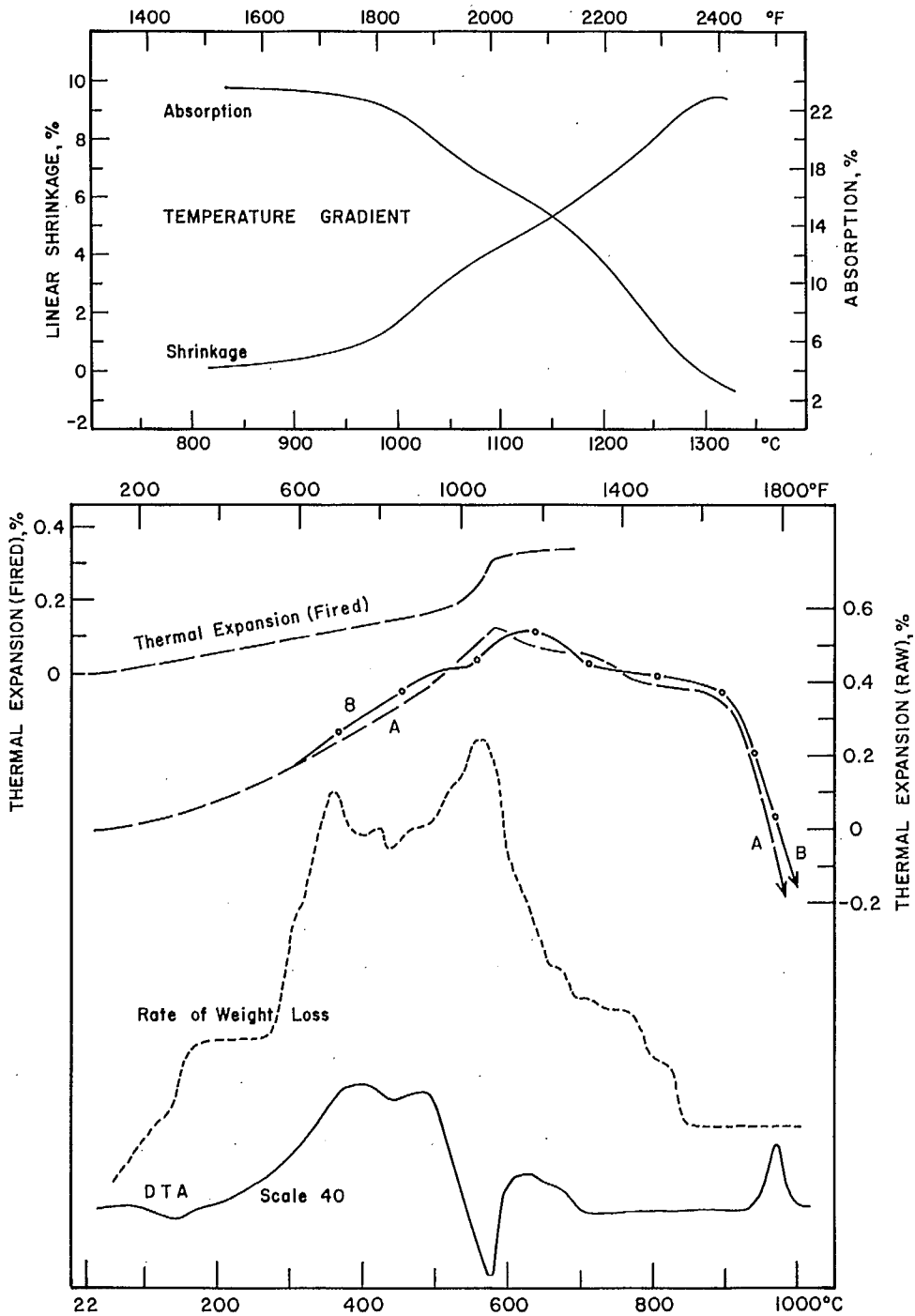


Figure 17. Firing behaviour of Shubenacadie fireclay.
A. Linear thermal expansion (raw clay), reducing atmosphere.
B. Linear thermal expansion (raw clay), oxidizing atmosphere.

required during the oxidation period both to provide oxygen and to carry away the considerable quantities of gaseous oxidation products of carbon and sulphur as well as the substantial amounts of steam generated by the clay mineral breakdown. Kaolin contains 14% water of crystallization, so that strong drafts will not only maintain oxidizing conditions and hasten the removal of combustible materials but will also sweep away the vapours of sulphur and water that might otherwise condense as acids either on cooler ware, where scumming would result, or on metallic components of the structure such as dampers and stacks, where they would cause corrosion problems. The inherent development of such a strongly reducing atmosphere does not markedly affect the dilatometric behaviour during firing. Similar curves were obtained in oxidizing and in oxygen-deficient atmospheres. Both curves are typical for kaolin-quartz mixtures, showing a total expansion of about 0.5% ; shrinkage of the kaolin component is indicated above about 600°C, but overall shrinkage is restrained by the quartz and micaceous minerals until about 900°C. In air, shrinkage accompanying burn-out of the combustible matter visibly reduces the rate of thermal expansion at around 500°C, but in the oxygen-deficient atmosphere this reaction appears to be delayed until about 700°C.

The temperature gradient curves showing fired shrinkage and absorption are typical of plastic fireclays. The firing temperatures required to develop dense products are above those normal for structural clay products manufacture. For brick-making, the Shubenacadie material is mixed with a less refractory

surface clay from nearby Lantz, N.S.

j) Musquodoboit

A series of occurrences of fire clay along the Musquodoboit valley between Paint Brook and Murphy Brook have been examined by Wright (10). The deposits consist of seams or, more probably, lenses of red, buff, and grey clays, or mottled combinations thereof, with variable quartz content. Depths vary from about 10 to 100 ft, and they are overlain by from a few to more than 100 ft of red boulder clay. They often occur under, over, or interbedded with seams of coarse silica sand. The materials are considered to be of Cretaceous age and, except for iron contents reported to range from about 1 to 10%, are similar to the Shubenacadie material. The iron probably derives from a ridge of ferruginous slate to the north of the valley and adversely affects the refractoriness of the contaminated seams. The least contaminated materials reach PCE's of Cone 31 or better, whereas those of the high-iron materials average around Cone 20 or lower. In previous years these materials have been used to manufacture low-duty fire brick, and, as previously noted, in combination with various clays and shales of the region used for pottery. A sample of red fire clay from the Murphy Brook area, near Middle Musquodoboit, was chosen for detailed examination. This sample had about median iron content at 6.85% Fe_2O_3 and a PCE of Cone 26⁺.

The plastograms of Fig. 6 show nearly identical curves for the Musquodoboit and Shubenacadie materials, although the former requires about 8% more water for any equivalent

degree of plasticity. The Musquodoboit material undoubtedly has a greater surface area to be wetted, owing to its greater clay and consequent lower quartz content shown in Table 6 to be 13.7% vs 31.1% for Shubenacadie. The sample shows an equally pronounced and sharp peak superimposed on the main rounded peak, probably due to the influence of the hematite component — fine-grained iron oxides show strongly dilatant behaviour. Laminar flow tendencies during plastic forming would be expected although such problems were not noted with the hand-moulded specimens of this investigation, which dried without cracking and showed a drying shrinkage of only 4.5%.

Table 7 shows that the primary clay mineral is kaolin, with lesser amounts of micaceous minerals — illite and a mixed-layer assemblage of micaceous clay minerals. The absence of a montmorillonoid phase, present in the Shubenacadie sample, results in less absorbed water as shown by the smaller peaks around 200°C in the thermal analytical curves of Fig. 18. It is unlikely that moisture regain would be a serious problem with dry ware from this material. The strong endothermic peak at 590°C and the exothermic peak at 950°C on the DTA curve are typical of kaolinitic materials. The presence of micaceous minerals is less evident but is indicated by the dilatometric curves, where shrinkage begins around 900°C after final dehydration of the micas. The effect of the iron oxide components is indicated by the dilatometric curve obtained under oxygen-deficient conditions, where the fluxing action of reduced iron oxides causes shrinkage to begin about 50 to 60°C

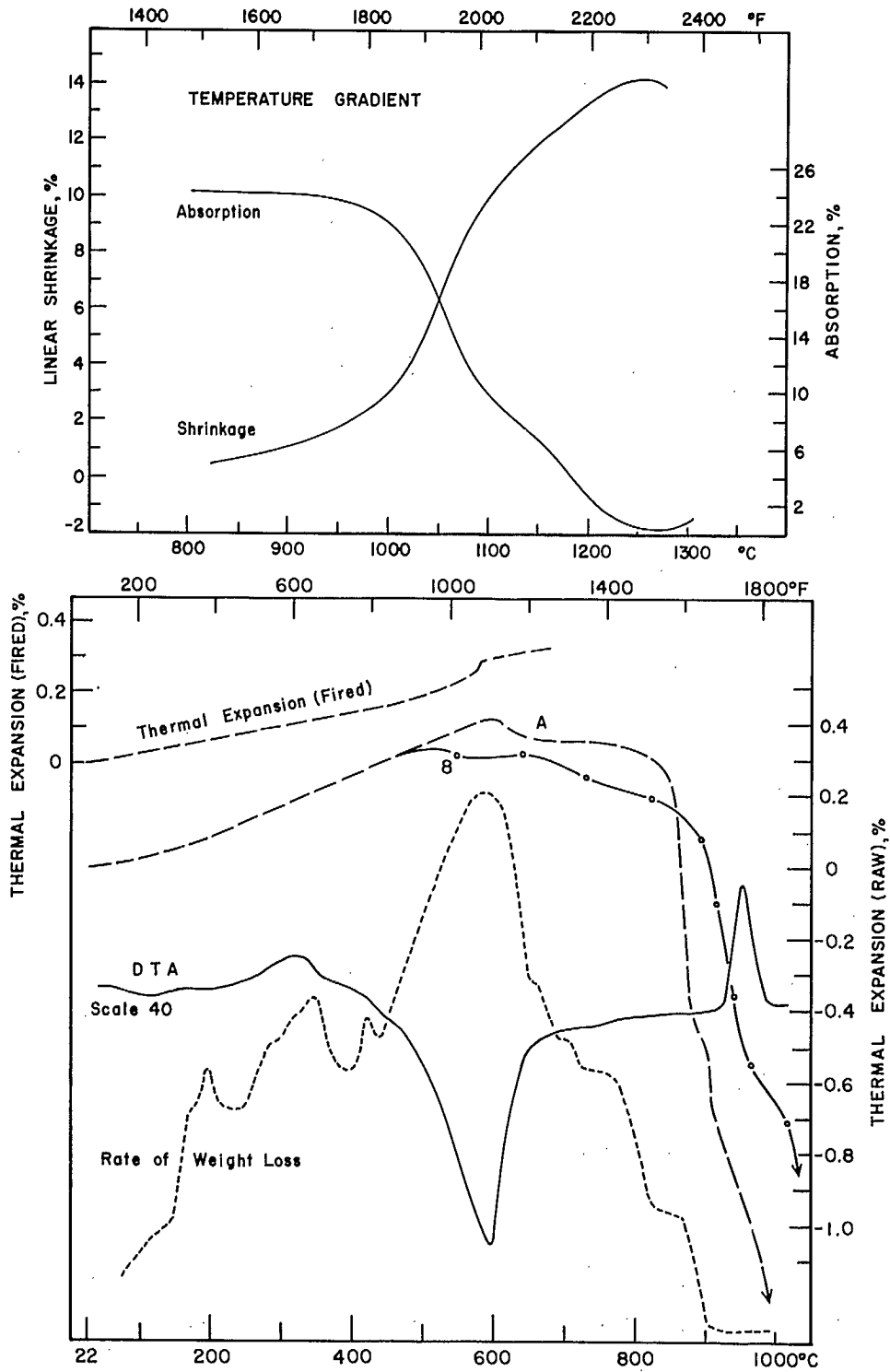


Figure 18. Firing behaviour of Musquodoboit fireclay.
A. Linear thermal expansion(raw clay), reducing atmosphere.
B. Linear thermal expansion(raw clay), oxidizing atmosphere.

lower than in an oxidizing atmosphere. A small amount of organic material, probably rootlets and easily oxidized, is indicated by the peaks at about 350°C on the DTA and DTGA curves. The peaks at 425°C indicate the presence of a very small amount of pyritic material, much too small a proportion for identification by XRD. Although it possibly contains more of the refractory clay mineral, kaolin, than the material from Shubenacadie, the Musquodoboit sample contains more feldspar and substantially more iron, which serve as fluxes at higher temperatures. As a result, the Musquodoboit clay is less refractory — Cone 26⁺ compared with Cone 28 for the Shubenacadie material. The temperature gradient curves also show a more rapid rate of vitrification and a substantially greater shrinkage than for the Shubenacadie clay.

The material of this sample has been used principally as a refractory addition to extend the firing ranges of low-PCE common clays and shales of the region. It has also been used for low-duty fireclay refractories although these have limited applications, medium-duty materials usually being preferred. The sample selected for examination is red-burning owing to its high iron content. However, Wright reported on some samples low in ferruginous material that showed PCE's in the medium-duty range (10). It is uncertain whether or not these low-iron seams contain sufficient quantities of material to justify their selective mining or whether such procedures are in fact possible. Most of the deposit appears to be mottled red and grey clay.

SUMMARY

The geology of the Atlantic Provinces region is such that a great variety of clays and shales of many ages are exposed or are readily available near the surface. Unfortunately, high-quality kaolinitic clays, the china clays or ball clays, are not known among this number. The fire clays at Shubenacadie and Musquodoboit, N.S. contain the most kaolin and are the most refractory of the known deposits. However, the impure nature of the latter materials and their mode of occurrence — non-uniform, cross-bedded, or lens-like seams interspersed with sands — makes it improbable they could be economically developed and beneficiated to produce china clays of Whiteware grade or better.

Much of the bedrock of the region consists of shale-bearing strata of various geological ages, often exposed or located conveniently near the surface. Shales of the Carboniferous period are particularly prevalent and many of these are particularly useful for the manufacture of dense structural clay products and, probably, pottery. Owing to their content of kaolin, they are more refractory and thus show wider firing ranges than the Ordovician and Devonian shales more common in the Prairies. Care in selecting a deposit for exploitation would be advisable to avoid those deposits that are particularly heavily contaminated with organic matter and pyritic material as these pose requirements for extended oxidation periods during

firing with attendant disadvantages of reduced output or higher capital costs, and reduced fuel efficiency.

The surface clays are of less interest for ceramics. Characteristically for this type of material, they usually contain substantial amounts of impurities and are of mixed mineral composition, which causes rapid vitrification and limits their application to porous ware such as farm drain tile and partition tile or low-grade earthenware pottery. Glacial clays are not thickly deposited over most of the region. These are usually of little interest because of their content of stone and other detritus, but where they have been sorted and re-deposited by wave, tide or stream action they may be of some ceramic use. Similarly, clay deposits of recent origin, derived from the bedrock shales, may occur either under or over the glacial material. Some surface clays have found useful applications as additions to nearby shales, to improve their plastic forming properties and to reduce their maturing temperatures and hence the fuel requirements for firing.

ACKNOWLEDGMENTS

The writers wish to express their appreciation to R.S. Dean and R.M. Buchanan of the Industrial Minerals Laboratory, for mineralogical analyses of the unfired and fired materials, respectively.

Thanks are also due to the staff of the Chemical Laboratory, particularly J.C. Hole, H. Lauder, E. Mark,

D. Precious and R. Sabourin, who performed the chemical analyses.

The cooperation of the New Brunswick Research and Productivity Council is also acknowledged for locating and collecting some of the samples.

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