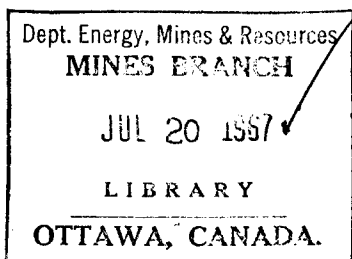




DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*THE COMPOSITION AND PROPERTIES
OF CERAMIC CLAYS AND SHALES
OF QUEBEC*



J. G. BRADY AND R. S. DEAN

MINERAL PROCESSING DIVISION

NOVEMBER 1966



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THE COMPOSITION AND PROPERTIES OF
CERAMIC CLAYS AND SHALES OF QUEBEC

by

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

ABSTRACT

Forty-one representative samples of clays and shales were investigated by various firing methods and by X-ray diffraction, differential thermal analysis and chemical analysis. In addition, thirteen of the samples were studied by thermogravimetric analysis, thermal expansion and plasticity measurements, to determine their processing problems.

The results show that, with the exception of some refractory kaolin-rich samples occurring on the Canadian Shield which have a white to brown fired colour, the ceramic clays and shales of Quebec are common, heterogeneous, mainly red-firing materials. Most of the clays are suitable only for making common brick and tile because they have short firing ranges and high fired shrinkages at temperatures where they become dense and very hard. As a rule the shales are more suitable than the clays for making dense facing brick, because they usually have longer firing ranges. The Quebec Group shales are more refractory and usually have more plasticity and fewer processing problems than the Utica, Lorraine, Rockcliffe and Queenston shales of the St. Lawrence Lowlands. Some of the Quebec Group shales are probably suitable for the manufacture of sewer pipe.

The majority of the kaolin-rich samples, as they occur, are not suitable for ceramic products; many are contaminated with minerals containing iron.

The principal clay minerals in the common clays and shales are illite and/or chlorite. The majority of these samples contain mixed layer systems involving combinations of illite, and/or chlorite, with an expandable phase. Kaolin is a principal component of the kaolin-rich samples only. The principal non-clay minerals are quartz, feldspar, calcite, dolomite and pyrite. The principal constituents in thirteen fired specimens are quartz and feldspar with lesser amounts of cristobalite, mullite, hematite and rutile.

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Direction des mines

Rapport de recherches R 187

COMPOSITION ET PROPRIÉTÉS DES ARGILES ET DES SCHISTES
À CÉRAMIQUE DU QUÉBEC

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

RÉSUMÉ

Les auteurs ont étudié quarante et un échantillons représentatifs d'argiles et de schistes à l'aide de diverses méthodes de cuisson, de la diffraction des rayons X, de l'analyse thermique différentielle et de l'analyse chimique. En outre, treize de ces échantillons ont été étudiés par analyse thermogravimétrique et soumis à des mesures d'expansion thermique et de plasticité afin de déterminer les difficultés de traitement que ces matériaux peuvent présenter.

Les résultats indiquent que, sauf certains matériaux réfractaires à forte teneur en kaolin qu'on retrouve dans le Bouclier canadien et qui prennent à la cuisson une couleur blanche à brune, les argiles et schistes à céramique du Québec sont des matériaux ordinaires, hétérogènes qui prennent habituellement à la cuisson une couleur rouge. La majeure partie des argiles ne conviennent qu'à la fabrication de tuyaux de drainage et de brique ordinaire, à cause de leurs courtes gammes de cuisson et de forts retraits aux températures nécessaires pour les amener à un état dense et dur. De façon générale, les schistes conviennent mieux que les argiles à la fabrication de brique de parement dense parce que leurs gammes de cuisson sont plus étendues. Les schistes du groupe de Québec sont plus réfractaires et ordinairement plus plastiques et présentent moins de difficultés lors du traitement que ceux des groupes Utica, Lorraine, Rockcliffe et Queenston des basses terres du Saint-Laurent. Quelques schistes du groupe de Québec pourraient probablement convenir à la fabrication de tuyaux d'égout.

La plupart des échantillons à forte teneur en kaolin ne peuvent servir seuls à la fabrication de produits céramiques. Plusieurs d'entre eux renferment des impuretés ferrifères.

Les principaux minéraux argileux dans les argiles et schistes ordinaires sont l'illite et la chlorite. La plupart de ces échantillons contiennent des systèmes à couches mixtes où l'on rencontre des combinaisons l'illite et (ou) de chlorite avec phase expansible. Le kaolin ne prédomine que dans les échantillons à forte teneur en kaolin. Les principaux minéraux non argileux sont le quartz, le feldspath, la calcite, la dolomie et la pyrite. Les principaux composants des treize échantillons soumis à la cuisson sont le quartz et le feldspath avec des quantités moindres de cristobalite, de mullite, d'hématite et de rutile.

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INTRODUCTION

Quebec lacks high-quality refractory clays such as fire clays, ball clays and stoneware clays. A few kaolin deposits have been investigated but to date they have not been developed as a source of kaolin. Common, red-firing clays and shales are abundant and are used for the manufacture of brick and tile.

In 1915, Keele (1, 2) contributed a major report on the ceramic properties of clays and shales from the province. Prior to that time, only scattered reports appear in the early literature, principally by Dr. Christian Hoffman, a chemist with the Geological Survey of Canada from about 1872 to 1907. In an unpublished report of 1907, entitled "The Clays and Clay Manufactures of Canada", Dr. Robert Chalmers discusses the clays of Quebec used for brick-making but makes no reference to shales. He lists eighty plants operating at that time, presumably many of them making hand-moulded bricks from surface clays and operating only during frost-free months.

After Keele's major contribution in 1915, a few smaller reports were published by Keele (3, 4, 5, 6) and Keele and Cole (7, 8). Wilson (9, 10), the Quebec Department of Mines (11, 12), Carnochan (13), Carnochan and Rogers (14) and Goodwin (15) published reports on the kaolin at St. Remi d'Amherst. McMahon (16) discussed the use of a few Quebec shales for the manufacture of roofing tile. Phillips (17) investigated the use of electrolytes

on the drying properties of a clay from Lakeside, and discussed briefly the clays and shales of Quebec (18). Wilson (19,20,21,22) investigated the use of Quebec clays and shales for lightweight aggregate. Brady (23) discussed some properties of a few clays from Quebec.

The mineralogy of some Quebec clays and shales has been discussed by Dean (24), Allan and Johns (25), Brydon and Patry (26), and others. The mineralogy and properties of some Ontario clays and shales that correspond to some of those in Quebec have been studied by Brady and Dean (27).

The purpose of this report is to show the ceramic properties and mineralogical composition of 13 shales and 28 clays taken mainly from the populated areas of Quebec. Thirteen of the samples were selected for special study. Many of the samples are typical of materials being used by the clay products industry or are representative of materials from certain areas. Although brief mention is made of the geology of each sample, a knowledge of the over-all geology of Quebec is essential for exploration. A good discussion of this has been prepared by staff members of the Geological Survey of Canada (28,29), and Dresser and Dennis (59,60). Of the five characteristic geological regions of Canada, only the Canadian Shield, the Plains (St. Lawrence Lowlands) and the Appalachian Region affect Quebec. The Canadian Shield covers most of Quebec and accounts for most of the area northwest of the St. Lawrence river and north of the Ottawa river. The St. Lawrence Lowlands extend

along the St. Lawrence river to Quebec City, with the Canadian Shield to the northwest and the Appalachian region to the southeast. They also extend in a narrow band along the Ottawa river for perhaps 100 miles northwest of Hull. Anticosti Island, the Mingan Islands, and a narrow strip of land on the north shore opposite the islands, are also part of the St. Lawrence Lowlands. The Appalachian region in Quebec occurs southeast of Logan's Line, a fault zone that runs from Lake Champlain northeast to Quebec City, and then down the St. Lawrence river and the Gulf of St. Lawrence.

The province has been subjected to severe glaciation and this has influenced the nature of the unconsolidated Pleistocene deposits that cover the bedrock. These deposits consist of sands, gravels, boulder clays and, in some instances, stoneless clays. It is the latter that are of interest to the ceramic industry. Most of these clays, both marine and non-marine, are common, low-fusion materials that generally are difficult to process into ceramic products. Many of them are suitable only for drain tile, structural tile and common brick. Some are being used for facing brick, but generally they are difficult to vitrify or fire to a dense, hard condition.

Of particular interest are the clays deposited by the Champlain Sea which flooded the St. Lawrence Lowlands in Quebec and extended up some of the tributaries of the Ottawa and St. Lawrence rivers. These deposits usually consist of stratified clay, sand and silt. Many of the beds consist of extremely fine sediments that offer some possibilities to the clay worker but also often present great difficulties in processing.

Investigations on the surficial geology, particularly in the thickly populated southeastern portions, have been made by Lasalle (30, 31), Lasalle and Elson (32, 33), Gadd (34, 35, 36, 37, 38), Gadd and Karrow (39), Karrow (40, 41), and MacClintock and Stewart (42).

The only known occurrences of refractory clays and kaolin are in the Canadian Shield. These are mainly isolated occurrences and, to date, no major development of the deposits has taken place, primarily because of the limited size of the deposits or because of beneficiation problems. Kaolinized rock deposits occur at St. Remi d'Amherst, Papineau County; Brebeuf, Terrebonne County; Point Comfort, on Thirtyone Mile Lake, Gatineau County; and Chateau Richer, Montmorency County. Refractory clays are present at Schefferville, New Quebec.

At the present time the Ordovician shales of the St. Lawrence Lowlands are the most important raw materials being used in Quebec. These are common, low-fusion materials suitable mainly for the manufacture of facing brick. The bedrock geology of the St. Lawrence Lowlands has been investigated by Foerste (43), Clark (44-55), Houde and Clark (56), Osborne (57), Wilson (58), and others. The most commonly used materials are Ordovician shales from the Utica and Lorraine Groups. Others in the St. Lawrence Lowlands that have possibilities are shales from the Queenston (Becancour River) Formation and shales of the Rockcliffe Formation.

The Ordovician and Cambrian shales of the Quebec Group, Appalachian Region, are another important raw material source for brick,

tile, and possibly sewer pipe. Their geology in the Quebec City area has been discussed by Osborne (57).

Further information on the general geology of Quebec, including information on the Quebec Group shales, is provided by Dresser and Denis (59, 60).

MATERIALS INVESTIGATED

The following list gives sample names (underlined, and in French) and numbers, the counties of origin, and, where available, the geological units from which the samples were collected. The samples are numbered from 1 to 41, grouped according to area and for type, with the numbers in brackets being the laboratory differential thermal analysis numbers.

The samples were arbitrarily divided into six divisions, five of which were formed according to areas and one according to clay type. All thirteen shales were placed in the first two divisions, one being the Quebec City area and north (Samples 1 to 5), the other being Southern Quebec (Samples 6 to 13). The dividing line for the shales was arbitrarily placed at Quebec City. All kaolins and fireclays were placed in division 6 (Samples 36-41). The remaining twenty-two samples (all clays) were divided into divisions designated as Gaspé and Eastern Quebec (Samples 14 to 21), Southeastern Quebec and Montreal area (Samples 22 to 28), and North Shore, Northwestern and Western Quebec (Samples 29 to 35).

Shales from Quebec City and Mont Joli

1. (U946), Lauzon (Q.G.), Levis County; a Quebec Group shale from a pit at Lauzon.
2. (U947), Ile d'Orléans (Q.G.), Montmorency County; a shale from the Quebec Group on Ile d'Orleans.
3. (U980), Beauport (U-L), Quebec County; a shale from the Utica-Lorraine Group at Beauport.
4. (U979), Boischatel (U-L), Montmorency County; a shale from the Utica-Lorraine Group at Boischatel.
5. (U1135), Mont-Joli (Q.G.), Matane County; a shale from the Quebec Group, northeast of Mont Joli at St. Octave de Metis.

Southern Quebec Shales

6. (U957), Delson (U), Laprairie County; a shale from the Utica Group at a Delson brick plant.
7. (U1169), St-Apollinaire (Q.G.), Lotbiniere County; a Quebec Group shale 2 miles southwest of St. Apollinaire, on southeast side of route 9 and of railroad.
8. (U1093), Lotbinière (U), Lotbiniere County; a shale from the Utica Group northeast of Lotbiniere on southeast side of route 3.
9. (U1048), Ste-Monique (Q), Nicolet County; a shale from the Queenston (Becancour River) Formation near the bridge over the Carmel River close to its junction with the southwest branch of the Nicolet River and near Ste. Monique.
10. (U1193), Boucherville (U-L), Chambly County; a shale from the Utica Group or lower part of the Lorraine Group occurring on a stream bank 3 miles east of Boucherville.
11. (U616), St-Grégoire (Q), Nicolet County; a weathered Queenston (Becancour River) Formation shale on high ground 1 1/2 miles east of St. Gregoire.

12. (U83), Laprairie (L), Laprairie County; a shale from the Lorraine Group at a Laprairie brick plant.
13. (U1126), Breckenridge (R), Gatineau County; a shale from the Rockcliffe Formation occurring south of the highway and 1 mile southeast of Breckenridge.

Clays from Gaspé and Eastern Quebec

14. (U1132), Douglastown, Gaspé East County; a common surface clay occurring near Douglastown.
15. (U1133), St-Alphonse, Bonaventure County; a common surface clay occurring near St. Alphonse.
16. (U1139), Estcourt, Temiscouata County; a common surface clay occurring near Estcourt.
17. (U693), Scott Junction, Dorchester County; a common surface clay, probably of glacial lake origin, occurring at the brick plant at Scott Junction.
18. (U1137), Ville St-Georges, Beauce County (Jersey Township); common surface clay, probably of glacial lake origin.
19. (U1136), Disraeli, Wolfe County; a common surface clay, probably of glacial lake origin, occurring on the stream bank west of route 1 and approximately 2 miles north of Disraeli at the brick plant.
20. (U685), Victoriaville, Arthabaska County; a common surface clay, probably marine, occurring just south of Victoriaville at the tile plant.
21. (U60), Deschaillons, Lotbinière County; a common glacial clay occurring just south of Deschaillons on the St. Lawrence River bank at the brick and tile plant.

Clays from Southeastern Quebec and Montreal Area

22. (U212), East Angus, Compton County; a common surface clay of glacial lake origin occurring at the brick plant at East Angus.

23. (U1129), Cowansville, Missisquoi County; a common surface clay occurring near Cowansville.
24. (U108), St-Jean, St. Jean County; a common surface clay, probably marine, at the sewer pipe plant at St. Jean.
25. (U741), Laprairie (Clay), Laprairie County; a common surface clay, probably marine, occurring 4 miles east of Laprairie.
26. (U56), Lakeside, Jacques Cartier County; a surface clay at the Lakeside tile plant, probably marine.
27. (U1130), Soulanges, Soulanges County; a common surface clay occurring near Soulanges.
28. (U630), Varenes, Vercheres County; a common surface clay 1/4 mile west of Varenes.

Clays from North Shore, Northwestern and Western Quebec

29. (U1134), Sept-Iles, Saguenay County; a common surface clay occurring on the outskirts of Sept-Iles.
30. (U504), Mistassini, Lac St. Jean Ouest County; a common surface clay, probably marine, occurring at Mistassini at the site of the brick plant.
31. (U1125), L'Assomption, L'Assomption County; a surface clay occurring 4 miles east of L'Assomption.
32. (U1219), Ste-Scholastique, Deux Montagnes County; a common surface clay occurring at Ste. Scholastique.
33. (U1128), Buckingham, Papineau County; a surface clay, probably marine, occurring adjacent to the river at Buckingham.
34. (U1127), Clerval, Abitibi County; a common surface glacial-lake clay near Clerval.
35. (U1223), Rouyn, Temiscamingue County, Laverlochere Township; a common surface glacial-lake clay occurring near Rouyn.

Kaolin Clays

36. (U542), Schefferville, New Quebec; unconsolidated fireclay from Redmond iron deposit, Schefferville, Section 251+00, 483' S. W.
37. (U1131), Château Richer, Montmorency County; kaolinized rock consisting mainly of about 80 per cent feldspar and 20 per cent kaolinite.
38. (U852), St-Rémi, Papineau County; a discoloured kaolinized rock similar to a low duty sandy fireclay occurring 2.5 miles from St. Remi d' Amherst on the road to Huberdeau.
39. (U1138), Brébeuf, Argenteuil County; a kaolinized rock, consisting mainly of quartz and a kaolin mineral, occurring 2.3 miles south of Brebeuf and 3/4 mile west of highway 57.
40. (U772), Labelle, Labelle County; a soft clay from the east side of Lac Labelle and about 7 miles from Labelle.
41. (U853), Point Comfort, Gatineau County; kaolinized rock from the east shore of Thirtyone Mile Lake, at Point Comfort, near the boundary of lots 21 and 22.

The following thirteen samples were chosen for special studies by temperature gradient firing, thermogravimetric analysis, and dilatometry: 1. Lauzon (Q.G.), 4. Boischatel (U-L), 5. Mont-Joli (Q.G.), 6. Delson (U), 7. St-Apollinaire (Q.G.), 8. Lotbinière (U), 9. Ste-Monique (Q), 12. Laprairie (L), 17. Scott Junction, 22. East Angus, 25. Laprairie (Clay), 30. Mistassini, 39. Brébeuf.

EXPERIMENTAL PROCEDURE

Routine Investigation of Physical Properties of Interest to the Ceramic Industry

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 Ste-Monique (Q) and Disraeli were obtained from 4 x 1 1/2 x 1 1/4 inch, hand-moulded specimens because of the small quantity of material required and the simplicity of the equipment used. De-aired specimens for routine investigation of Disraeli, Ste-Monique (Q) and Mont-Joli (Q.G.) (the latter hand-moulded also) were extruded by an International laboratory de-airing extruder. A comparison of the hand-moulded and extruded fired properties of Mont-Joli (Q.G.) was made.

The amount of water added to the dry samples to bring them to a plastic condition for moulding (water of plasticity) was measured. The plasticity of the samples was noted empirically by feel at the time the test specimens were prepared. A test specimen of each sample was subjected to rapid-drying conditions in a laboratory dryer at 85°C and any evidence of cracking was noted about 15 to 25 minutes after placing the specimen in the dryer. The remaining specimens were air-dried and then dried finally in an electric laboratory dryer overnight at 110°C. The drying shrinkage, based on the original length of the test specimen, was calculated.

All test specimens for routine investigation were fired in electric laboratory kilns at various appropriate temperatures. The firing shrinkage based on the original length, the 24-hour absorption in cold water, the colour, and the hardness were all noted. The total shrinkage, based on the original size, could then be obtained by adding 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 13 typical samples were investigated by temperature gradient firing. All test specimens were hand-moulded except those for Ste-Monique (Q), which were extruded and de-aired. Temperature gradient curves of a de-aired, extruded Queenstone shale sample from Georgetown, Ont., were also obtained to compare with the Queenston (Becancour River) sample from Ste. Monique.

The temperature gradient method has been described by Stone (61). The drying procedure for the specimens was the same as for the routine investigations. The 7 1/2-inch bars were marked at 1/2-inch intervals and duplicate samples were placed in a Stone temperature gradient furnace. The firing temperature at the central portion of the furnace was raised at the rate of 90 centigrade degrees per hour to 820°C, held there for 6 hours, then raised at the rate of 110 centigrade degrees per hour to the finishing temperature, which was held for one hour. Control was

automatic, with a cam-type controller. The gradient was approximately 450 to 550 centigrade degrees from the hot to the cold end of the bars, depending on the control temperature. The temperature and shrinkage at each mark on the bar were calculated. The absorptions of wafers cut from the test 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 chemical analysis methods is given by Charette et al. (62) with some modifications reported by Hole (63). All analyses were based on the dried condition at 105°C, and the totals of the constituents were derived from the sum of the oxide percentages and the per cent loss on ignition (L. O. I.).

Differential Thermal Analysis (DTA)

Some standard DTA reference clays and other materials have been discussed by Brady (23) and Brady et al. (64). Samples were placed in a nickel block and heated in an air atmosphere by a nichrome-wound furnace. Alundum was used for the inert reference material. The furnace and differential temperatures were recorded on a Leeds and Northrup X₁-X₂ Speedomax recorder equipped with a range expander for the differential scale. A Leeds and Northrup D. C. amplifier was used to amplify the differential temperature milli-voltage. The furnace temperature

was controlled by a Leeds and Northrup controller that raised the temperature at 12 centigrade degrees per minute. The amplifier was set at a scale sensitivity of 10 for all samples except the refractory clays or kaolins from Schefferville, Chateau Richer, St. Remi, Brebeuf, Labelle and Point Comfort, for which scale 40 was used. The peak amplitudes at scale 40 are reduced by a factor of 4 when compared to scale 10, in order to retain on the chart the curves caused by the intense reactions of kaolin-type minerals.

Plasticity Measurements

The relative plasticity of the 13 specially selected samples was determined by a Brabender plastograph. This method of determining relative plasticity (consistency) is more exact than the empirical method used during preparation of routine test specimens. The latter depends on the judgment and experience of the operator. The use of the Brabender plastograph with clays has been described by Marshall (65). Two hundred grams of dry sample were placed in the apparatus, with the pug knives revolving at the slowest speed. A continuous curve was obtained of the consistency while water was being added at the rate of 5 cc/min. A shale from the Dundas-Meaford Formation near Cooksville, Ont. (recently redefined as the Georgian Bay Formation by Liberty (66)) was used as a standard. This shale was labelled Cooksville (D-M) and has just sufficient plasticity to permit extrusion. The peak heights and the areas under the

plastograph curves were used to compare the plasticities of the samples; the higher the peak and the greater the area the greater is the plasticity.

Thermal Expansion

The thermal expansions of unfired specimens of the 13 specially selected samples were determined in a vertical, tube-type dilatometer and also, in some cases, in a horizontal Seger-type dilatometer. The principal components of the vertical dilatometer were a nichrome-wound furnace, a fused-quartz assembly, and an Ames dial. Specimens measuring 0.5 x 0.5 inch and about 2 inches long were prepared by hand-moulding, to avoid particle orientation effects. The sides parallel to the longitudinal axis were grooved with a 1/4-inch file to produce a final cross-section roughly X-shaped, with heavy central fillets. By thus reducing and equalizing thickness, the sensitivity of the apparatus to sudden changes in dimension was increased. The ends of the oven-dried specimens were sanded smooth and parallel, and the lengths measured to the nearest 0.0001 inch. The dilatometer furnace was manually controlled at a heating rate varying from 9 to 11 centigrade degrees per minute. Readings of length and temperature were made at two-minute intervals, except where sharp or extensive dimensional changes were anticipated or observed (as at the quartz inversion temperature, 573°C), when readings were made each minute. Maximum temperatures were limited to about 980°C because of the nature of the fused quartz assembly.

From these results, the changes in length with temperature were calculated in per cent of original length. No corrections were made for the expansion of the fused quartz, since this is very small and regular (0.585×10^{-6} inch per inch of length per degree Centigrade from 0 to 1200°C).

The vertical furnace was closed at the bottom and consequently the atmosphere was reducing in those cases where a large volume of H₂O, CO₂ or SO₂ was evolved from the unfired sample. Particularly for the shales, this reducing atmosphere affected the colour and might have affected their expansion characteristics. To check this effect, the expansion of the shale samples and one of the clays was determined in a Seger-type dilatometer with a platinum-wound horizontal furnace that had an oxidizing atmosphere. The temperature of this furnace was automatically controlled at a heating rate of about 3.3 centigrade degrees per minute. The temperature and the thermal expansion were automatically recorded. Hand-moulded specimens 25 mm in cross-section, with a central 7 mm hole, were filed to the same shape as the vertical furnace test specimens. The length was made to exactly 100 mm so that per cent expansion was recorded directly. The curves obtained were plotted to the same scale as those for the reduced specimens and were corrected to the true expansion by subtracting calibrated values of the apparatus from the recorded expansion values.

Tests were made on the effect of forming method (hand moulding, de-aired extruding, and isostatic pressing) on the thermal expansion of unfired specimens of Lauzon (Q. G.) in both reducing and oxidizing atmospheres. The long dimension of the de-aired extruded specimens was parallel to the direction of extrusion. It was assumed that particles were oriented in the direction of extrusion and that there was no particle orientation in the isostatically pressed or hand-moulded specimens. The isostatic pressure was 10,000 psi.

Fired test specimens were obtained for each of the 13 selected samples. Each sample was fired in an oxidizing atmosphere to the temperature which would normally be used in commercial production. After the ends were made smooth and parallel, the thermal expansion up to 700°C was obtained in the same manner as for the unfired samples in the vertical dilatometer. It was assumed, since the maximum test temperature was well below the initial firing temperature of the specimen, that no further reaction would take place and the cooling curve of the fired specimen would be the same as the heating curve. Thus the thermal expansion curves of the fired specimens were prepared and they represent changes in dimensions of the fired materials during the cooling period. The atmosphere in these tests appeared to be oxidizing to neutral. The sharp discontinuity in the curves between about 570 and 590°C was used to estimate the percentage quartz in the fired thermal expansion specimens. A line was drawn on the curve along the direction of the discontinuity and

the percentage expansion was noted between the upper and lower points of tangency (usually between 570 and 590°C). The expansion of a quartz rock (100% quartz) was obtained in a similar manner and the value was used as a reference standard.

Thermogravimetric Analysis (TGA)

Continuous plots of weight loss against temperature of the 13 selected samples were obtained by an automatically controlled, high-temperature Stanton thermobalance. A 2-gram, minus 100-mesh (Tyler) sample was dried to constant weight at 110°C and placed in the thermobalance crucible. A heating rate of 6 centigrade degrees per minute was used. This combination of sample weight and rate of temperature increase produced curves that can be related to DTA.

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

X-Ray Diffraction Analysis (XRD)

Representative portions of the various samples were finely ground in an agate mortar and analyzed with a Guinier-deWolff four-sample X-ray powder diffraction camera, to determine the non-clay constituents. A

similar procedure was followed with the plus 200-mesh fraction of the majority of the clays and some of the soft shales.

In order to concentrate the clay mineral fraction, about 2 grams of each clay or shale sample, which had been ground to minus 100 mesh, was dispersed in 100 ml of distilled water. All material coarser than 5 microns (equivalent settling diameter) was separated by centrifugation and removed. The minus 5-micron material was collected by centrifugation at 10,000 rpm in a Sorvall SS-3 Superspeed Centrifuge.

Free iron oxides were removed, by the method of Mehra and Jackson (67), from all minus 5-micron suspensions where the colour (red or brown) suggested their presence.

Oriented clay mineral mounts were prepared by drying small portions of the minus 5-micron suspension on borosilicate glass plates. The mounts were successively scanned with a North American Philips High-Angle X-Ray Diffractometer in atmospheres of approximately 0% and 100% relative humidity. These conditions were obtained by covering the sample chamber opening with polyethylene film and introducing a stream of nitrogen gas which had either been passed through a drying column or bubbled through hot (60°C) distilled water. Prior to being run, mounts were equilibrated for several hours in dry air or over warm water. Diffractometer scans were also made following saturation of the mounts with ethylene glycol and heat treatment for one-half hour at 580°C. Finally, mounts prepared from portions of the minus 5 micron suspensions which had been boiled in an excess of concentrated hydrochloric acid were examined

in the same manner.

Fired specimens of the 13 special samples were studied. The firing conditions were the same as those for the fired thermal expansion specimens, and each sample was fired to the maturing temperature that would normally be used in commercial production. The Guinier X-ray powder camera was used to identify crystalline phases within the heated samples.

RESULTS AND DISCUSSION

Ceramic Properties from Routine Investigations

The unfired and fired properties of representative shales from Quebec are shown in Tables 1 and 2. They are common shales and, with the exception of Boischatel (U-L), which fires to shades of cream and buff, all samples tend to fire salmon or light-brown at the lower firing temperatures and dark red or reddish-brown at the higher firing temperatures. The shales from the St. Lawrence Lowlands (Lorraine, Utica, Queenston, and Rockcliffe) have very low PCE's of about 01 to 6, while those from the Quebec Group have PCE's of 14 to 16. They have suitable firing ranges for the manufacture of facing brick, with the exception of the very calcareous material from Boischatel, where very careful control is required because of certain problems during firing. The plasticity of the shales is generally poor to fair, and consequently many require a plastic addition such as clay or bentonite,

TABLE 1

Properties of Shales from Quebec City Area and Mont Joli

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. **	Fired Shrinkage % *	Absorption %	Colour	Hardness	
Lauzon (Q.G.) (hand-moulded)	Brown, non-calcareous shale from a pit at Lauzon. Low plasticity; water of plasticity 15%; safe drying; drying shrinkage 4.2%.	14 (1388°C)	08	0.0	9.6	Salmon	Fairly hard	This material may require a plasticizer for extruding thin-section ware. Should be suitable for brick. Long firing range.
			06	0.7	9.5	Pale red	Fairly hard	
			02	2.5	5.7	Red	Hard	
			2	2.7	4.6	Dark red	Very hard	
Ile d'Orléans (Q.G.) (hand-moulded)	Light brown, non-calcareous shale from Ile d'Orléans. Good plasticity; water of plasticity 16.7%; safe drying; drying shrinkage 5.0%.	15 (1424°C)	08	0.2	12.1	Salmon	Fairly soft	Good-quality red-firing shale. Its properties are similar to the Mont-Joli sample. Suitable for brick and tile and possibly sewer pipe.
			06	2.0	9.3	Pale red	Fairly hard	
			04	3.0	7.0	Medium red	Hard	
			02	4.6	5.0	Red	Very hard	
			1	5.3	3.0	Dark red	Steel hard	
Beauport (U-L) (hand-moulded)	Grey, calcareous shale from a pit near Quebec at Beauport. Fairly plastic; water of plasticity 14%; safe drying; drying shrinkage 3.3%.	3 (1152°C)	06	0.0	11.0	Brown-salmon	Fairly hard	The test specimens were scummed. The material should extrude. Should be suitable for brick if care used in processing.
			04	0.3	11.0	Brown-salmon	Fairly hard	
			02	0.1	9.8	Dark brown-salmon	Hard	
			1	1.5	6.0	Red-brown	Very hard	
Boischatel (U-L) (hand-moulded)	Grey, very calcareous shale from a pit near Quebec at Boischatel. Fairly good plasticity; water of plasticity 15%; safe drying; drying shrinkage 4.1%.	4 (1165°C)	06	-0.3	16.1	Pink-cream	Fairly soft	Suitable for brick if extensive care taken in processing.
			04	-0.3	16.0	Pink-cream	Fairly soft	
			02	0.7	14.8	Pink-cream	Fairly hard	
			1	1.0	11.2	Green-buff	Hard	
			3	3.1	4.8	Brown-buff	Very hard	
Mont-Joli (Q.G.) (hand-moulded)	Red, non-calcareous shale from the Mont Joli area. Fairly plastic; water of plasticity 20.0%; safe drying; drying shrinkage 3.9%.	16 (1455°C)	08	0.3	12.7	Salmon	Fairly soft	Good-quality red-firing shale. Will extrude and should be suitable for brick and tile. Has a long firing range. May be suitable for sewer pipe.
			06	1.7	10.7	Dark salmon	Fairly hard	
			04	3.7	7.0	Red	Hard	
			02	4.3	5.4	Dark red	Very hard	
			2	5.1	4.6	Dark red	Very hard	
Mont-Joli (Q.G.) (de-aired, extruded)	Water of plasticity 18.5%, fairly weak before de-airing, good strong column after de-airing, drying shrinkage 4%.	16	06	2.5	8.6	Light red	Hard	When fired at the same temperatures the extruded and de-aired briquettes were denser and harder than the hand-moulded ones.
	04	4.8	3.8	Red	Steel hard			
	02	6.3	0.1	Dark red	Nearly vitrified			

* A minus sign indicates expansion.

** 08-945°C (1743°F); 06-991°C (1816°F); 04-1050°C (1922°F); 02-1101°C (2014°F); 1-1136°C (2077°F); 2-1142°C (2088°F); 3-1152°C (2106°F).

TABLE 2

Properties of Shales from Southern Quebec

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. **	Fired Shrinkage % *	Absorption %	Colour	Hardness	
Delson (U) (hand-moulded)	Grey, slightly calcareous common shale from pit at Delson. Hard; poor plasticity; water of plasticity 14%; safe drying; drying shrinkage 3.7%.	01 (1117°C)	08	0.7	8.5	Brown-buff	Fairly hard	Requires a plasticizer to extrude; satisfactory firing range for facing brick; tendency to scum.
			06	0.7	7.9	Brown-buff	Fairly hard	
			04	1.7	6.1	Brown-salmon	Hard	
			02	2.0	3.9	Light-brown	Very hard	
St. Apollinaire (Q.G.) (hand-moulded)	Red, non-calcareous common shale from St. Apollinaire. Fair plasticity; water of plasticity 15%; safe drying; drying shrinkage 3.4%.	14½ (1400°C)	08	0.7	9.3	Dark salmon	Hard	A plastic shale that should extrude well. It has a long firing range. It should be suitable for brick, tile and possibly sewer pipe.
			06	1.8	6.8	Light red	Hard	
			04	2.5	6.6	Red	Very hard	
			02	3.5	5.1	Red	Very hard	
			1	3.0	4.0	Dark red	Steel hard	
Lotbinière (U) (hand-moulded)	Grey, calcareous common shale from pit at Lotbinière. Fair plasticity; water of plasticity 15.6%; safe drying; drying shrinkage 4.3%	4+ (1170°C)	08	0.7	10.7	Light-brown salmon	Fairly hard	Should extrude but may require a plasticizer for difficult-to-extrude shapes. Should be suitable for facing brick and tile.
			06	2.0	9.0	Brown-salmon	Hard	
			04	2.0	7.9	Dark brown-salmon	Hard	
			02	3.8	4.2	Brown-red	Very hard	
			1	2.2	1.1	Dark brown-red	Steel hard	
St. Monique (Q) (de-aired, extruded)	Red, calcareous common shale from Ste. Monique area. Poor plasticity; water of plasticity 15%; safe drying; drying shrinkage 3.3%.	4- (1165°C)	Less than 08 see temperature gradient results				Probably difficult to extrude. Suitable for facing brick. Fires to a dense condition at a relatively low temperature.	
			08	3.3	4.9	Light red		Hard
			06	3.7	3.6	Red		Very hard
			04	4.7	0.5	Dark red		Steel hard
Boucherville (U.L.) (hand-moulded)	Buff, non-calcareous common shale from the Boucherville area. Low plasticity, but fairly workable; water of plasticity 21.7%; safe drying; drying shrinkage 3.6%.	4+ (1170°C)	06	2.8	12.4	Salmon	Fairly hard	Should extrude but may require a plasticizer for brick manufacture. Firing range is on the short side at about Cone 05.
			04	6.1	6.4	Medium red	Very hard	
			02	6.5	2.7	Red	Steel hard	
St. Grégoire (Q) (hand-moulded)	Red, weathered non-calcareous shale from St. Grégoire area. Good plasticity; water of plasticity 19.8%; very slight tendency to crack with rapid drying; drying shrinkage 6.5%.	6- (1198°C)	08	1.3	11.0	Light red	Fairly hard	Suitable for brick and tile.
			06	2.7	7.5	Medium red	Hard	
			04	4.1	4.5	Red	Very hard	
			02	6.3	1.1	Dark red	Steel hard	
Laprairie (L) (hand-moulded)	Grey, slightly calcareous common shale from pit at Laprairie. Very short; water of plasticity 14.5%; safe drying; drying shrinkage 2.8%.	1 (1136°C)	08	-0.7	11.2	Pale brown	Soft	This material requires a plastic additive for extrusion. It is suitable for facing brick.
			06	0	9.5	Light brown	Hard	
			03	-1.1	7.3	Brown	Hard	
			01	-0.7	5.7	Dark red-brown	Very hard	
Breckenridge (R) (hand-moulded)	Grey-green slightly calcareous common shale. Poor plasticity; water of plasticity 13%; safe drying; drying shrinkage 3.0%.	6 (1201°C)	06	-0.4	-	Tan	Very soft	This material probably requires a plastic addition for extrusion. Requires a relatively high firing temperature for brick.
			04	-0.3	13.0	Tan	Soft	
			02	2.3	11.8	Light red-brown	Fairly hard	
			1	4.1	7.2	Brown	Hard	

* A minus sign indicates expansion.

** 08-945°C (1743°F); 06-991°C (1816°F); 04-1050°C (1922°F); 03-1086°C (1987°F); 02-1101°C (2014°F); 01-1117°C (2043°F); 1-1136°C (2077°F).

or a chemical additive, before they will extrude. The samples from Ile d'Orlean, St. Apollinaire, Mont Joli and St. Gregoire should have sufficient plasticity for manufacturing building tile and drain tile, as well as facing brick. The Quebec Group samples, being more refractory and generally more plastic than those from the St. Lawrence Lowlands, in some cases should also be suitable for sewer pipe.

The effect of de-airing is illustrated by a comparison of the properties of the hand-moulded and de-aired extruded Mont-Joli (Q.G.) specimens in Table 1. When fired at the same temperature, de-aired specimens are generally harder and denser than hand-moulded specimens of the same material. Consequently, the fired results of the specimens from Ste. Monique and Disraeli would be slightly different had these been hand-moulded.

The properties of representative samples of clay are shown in Tables 3, 4 and 5. They are common, low-fusion materials having PCE's between 01 and 8. As with the shales, they fire salmon or light-brown at the lower firing temperatures and principally red at the higher firing temperatures. Many of the samples are very plastic and difficult to dry under fast-drying conditions. Most of them have very short firing ranges (a small increase in temperature produces a large change in shrinkage and absorption) at temperatures where the fired material becomes sufficiently dense and hard for facing brick or sewer pipe (usually less than 6 to 8 per cent absorption). Consequently, because of

TABLE 3

Properties of Clays from Gaspé and Eastern Quebec

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. **	Fired Shrinkage % *	Absorption %	Colour	Hardness	
Douglastown (hand-moulded)	Brown, non-calcareous clay from the Douglastown area. Fair plasticity; water of plasticity 25%; tendency to crack in rapid drying; drying shrinkage 5.1%. Contains some stones.	6	06	1.3	12.6	Dark salmon	Fairly hard	Common clay; care required in drying; has a satisfactory firing range. Presence of stones may make it difficult to manufacture such products as brick and tile
			04	3.8	8.5	Medium red	Hard	
			02	6.0	3.0	Good red	Steel hard	
St-Alphonse (hand-moulded)	Red, non-calcareous common clay from the St. Alphonse area. Good plasticity; water of plasticity 27.8%; slight tendency to crack with rapid drying; drying shrinkage 6.6%.	7 (1215°C)	06	3.3	11.1	Salmon	Hard	Combined drying and firing shrinkage high for dense products. Short firing range for dense products. Suitable for tile and common brick.
			04	6.3	7.0	Light red	Very hard	
			02	9.0	0.7	Dark red	Steel hard	
Estcourt (hand-moulded)	Buff, non-calcareous silty clay from near St. Francis river in the Estcourt area. Fairly plastic; water of plasticity 30.5%; safe drying; drying shrinkage 6.7%.	8+	06	2.5	13.9	Dark salmon	Fairly hard	Common clay. High combined drying and firing shrinkage for dense products. Short firing range. Probably suitable for drain tile and common brick.
			04	6.1	8.8	Medium red	Hard	
			02	10.1	2.3	Dark red	Steel hard	
Scott Junction (hand-moulded)	Grey, calcareous common clay from pit at Scott Junction. Fair plasticity (flabby); water of plasticity 26%; safe drying; drying shrinkage 6.8%.	5 (1177°C)	06	1.5	14.0	Salmon	Fairly hard	Tendency to scum. Short firing range for dense products. Suitable for brick and tile; care needed in firing brick.
			05	2.5	10.7	Salmon	Hard	
			03	9.0	0.9	Red	Steel hard	
			02	9.8	0.6	Red	Vitrified	
Ville St-Georges (hand-moulded)	Grey, silty, non-calcareous clay from Ville St. Georges area. Fair plasticity (flabby); water of plasticity 23.1%; safe drying; drying shrinkage 4.7%.	5+ (1180°C)	08	-0.3	17.0	Light red	Fairly hard	Short firing range for dense products. Suitable for tile and common brick.
			06	2.1	12.4	Light red	Fairly hard	
			04	3.1	10.5	Light red	Hard	
			02	7.5	1.2	Dark red	Steel hard	
Disraeli (de-aired, extruded)	Grey, non-calcareous clay from pit at Disraeli. Fairly plastic; water of plasticity 21.8%; safe drying; drying shrinkage 2.3%.	3 (1152°C)	05	2.0	12.2	Dark salmon	Fairly hard	Tendency to scum. Very short firing range for dense products. Suitable for tile and common brick.
			03	6.1	4.5	Red	Very hard	
			01	9.7	0.1	Dark red	Vitrified	
Victoria-ville (hand-moulded)	Brown, slightly calcareous common clay from pit at Victoria-ville. Very plastic and sticky; water of plasticity 29%; cracks in drying; drying shrinkage 7.2%.	3- (1150°C)	08	0.7	15.2	Light salmon	Fairly hard	Tendency to scum. Very short firing range for dense products. Difficult to dry. Suitable for drain tile if it can be dried.
			06	3.1	10.1	Brown-salmon	Hard	
			04	7.7	1.6	Red-brown	Very hard	
			02	8.0	0	Red	Vitrified	
Deschailons (hand-moulded)	Grey, non-calcareous clay from pit of brick and tile company, Deschailons. Fair plasticity (flabby); water of plasticity 29%; safe drying; drying shrinkage 6.9%.	2½ (1147°C)	06	2.0	15.6	Salmon	Fairly hard	Very short firing range. Very difficult to fire to a dense condition and achieve uniform properties.
			05	3.8	9.9	Light red	Hard	
			04	9.0	1.8	Light red	Very hard	
			02	10.0	0	Dark red	Vitrified	

* A minus sign indicates expansion.

** 08-94.5°C (174.3°F); 06-99.1°C (181.6°F); 05-103.1°C (188.8°F); 04-105.0°C (192.2°F); 03-108.6°C (198.7°F); 02-110.1°C (204.4°F); 01-111.7°C (204.3°F).

TABLE 4
Properties of Clays from Southeastern Quebec and Montreal Area

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. **	Fired Shrinkage % *	Absorption %	Colour	Hardness	
East Angus (hand-moulded)	Brown, slightly calcareous clay from pit at East Angus. Fairly good plasticity, (slightly flabby); water of plasticity 31.8%; safe drying; drying shrinkage 5.4%.	5½ (1190°C)	08	3.3	17.0	Light salmon	Fairly hard	Short firing range for dense products. High fired shrinkage.
			06	7.0	7.1	Light red	Very hard	
			04	9.2	3.0	Light red	Steel hard	
Cowansville (hand-moulded)	Grey, silty, very calcareous common clay from Cowansville. Poor plasticity (flabby); water of plasticity 27.2%; safe drying, drying shrinkage 3.3%.	2½ (1147°C)	06	0	29.6	Salmon	Soft	Will overfire quickly above cone 02 and so has a short firing range for dense products. Will be difficult to extrude. Scums.
			04	0.8	18.7	Salmon	Fairly soft	
			02	4.6	10.5	Light red	Hard	
St-Jean (hand-moulded)	Grey, non-calcareous clay from pit at St. Jean. Good plasticity; water of plasticity 28.7%; tendency to crack in drying; drying shrinkage 6.5%.	2- (1140°C)	08	1.3	16.4	Salmon	Fairly hard	High combined drying and fired shrinkage for dense products. Difficult to dry. Probably suitable for tile and common brick.
			06	4.1	10.2	Light red	Hard	
			04	7.1	5.8	Light red	Very hard	
			02	10.3	0.5	Dark red	Steel hard	
Laprairie (Clay) (hand-moulded)	Blue, common, slightly calcareous clay from Laprairie area. Very plastic; water of plasticity 40.0%; cracks badly on drying; drying shrinkage 9.7%.	1½ (1139°C)	06	0.3	19.3	Light red	Soft	Very difficult to dry. Very short firing range. Difficult to process for clay products.
			05	2.7	13.9	Brown-red	Hard	
			03	9.0	0.3	Brown-red	Steel hard	
Lakeside (hand-moulded)	Grey, calcareous clay from pit at Lakeside; very plastic; water of plasticity 32.8%; tendency to crack in drying; drying shrinkage 7.7%.	01 (1117°C)	06	0.8	20.8	Light salmon	Fairly soft	Tendency to scum. Difficult to dry. Short firing range for dense products. Difficult to process for clay products.
			04	2.8	14.7	Salmon	Fairly hard	
			02	11.6	0	Red	Vitrified	
Soulanges (hand-moulded)	Brown, calcareous clay from Soulanges area. Fair plasticity (inclined to be flabby); water of plasticity 22.5%; safe drying; drying shrinkage 4.0%.	5 (1177°C)	04	-0.1	18.3	Dark salmon	Fairly soft	The clay has a short firing range for dense products. Probably suitable for tile and common brick.
			02	1.0	14.8	Light red	Fairly hard	
			1	5.3	5.0	Brown-red	Very hard	
Varennes (hand-moulded)	Brown, non-calcareous common clay from 6 ft excavation in Varennes area. Good plasticity; water of plasticity 32%; cracks in drying, drying shrinkage 9.0%.	2 (1142°C)	08	2.7	13.9	Salmon	Hard	Very high drying shrinkage and difficult to dry. Short firing range for dense products. If it can be dried this material may be suitable for tile and common brick.
			06	4.1	10.4	Light red	Very hard	
			04	9.1	1.0	Red	Steel hard	

* A minus sign indicates expansion.

** 08-945°C (1743°F); 06-991°C (1816°F); 05-1031°C (1888°F); 04-1050°C (1922°F); 03-1086°C (1987°F); 02-1101°C (2014°F); 1-1136°C (2077°F).

TABLE 5
Properties of Clays from North Shore,
Northwestern and Western Quebec

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. **	Fired Shrinkage % *	Absorption %	Colour	Hardness	
Sept-iles (hand moulded)	Grey, non-calcareous common clay from Sept Iles area. Fair plasticity (silty); water of plasticity 23.0%; safe drying; drying shrinkage 4.6%.	2 (1142°C)	08	0.5	15.0	Light brown-salmon	Soft	Tendency to scum. Short firing range for dense products. Suitable for tile and common brick provided the material will extrude properly.
			06	0.5	14.8	Light brown-salmon	Soft	
			04	1.0	12.9	Salmon	Fairly hard	
			02	6.7	2.2	Dark red	Steel hard	
Mistassini (hand moulded)	Grey, non-calcareous common clay from 5 to 10 ft below surface in pit at Mistassini. Fair plasticity (flabby); water of plasticity 32.2%; cracks with rapid drying; drying shrinkage 6.6%.	2	06	1.3	17.4	Salmon	Fairly hard	Has only fair plastic characteristics. Difficult to dry and has a short firing range for dense products. Suitable for tile and common brick if above difficulties can be overcome.
			04	3.1	14.2	Dark salmon	Hard	
			02	10.5	0	Dark red	Overfired	
L'Assomption (hand moulded)	Grey, silty clay, slightly calcareous from 4 miles east of L'Assomption. Very plastic; water of plasticity 27.2%; cracks with rapid drying; drying shrinkage 7.4%.	2	06	-0.3	15.0	Light salmon	Fairly hard	Tendency to scum. Difficult to dry. Might be suitable for common brick and tile.
			04	0.5	12.8	Salmon	Hard	
			02	4.7	4.8	Red	Very hard	
Ste-Scholastique (hand moulded)	Grey, very calcareous common clay from Ste. Scholastique. Good plasticity; water of plasticity 34.1%; safe drying, drying shrinkage 6.0%.	2	08	1.0	23.3	Light salmon	Soft	Tendency to scum. Very short firing range for dense products. May be suitable for tile and common brick.
			06	1.2	23.0	Salmon	Soft	
			04	3.0	18.9	Salmon	Fairly hard	
			02	11.0	2.1	Red	Very hard	
Buckingham (hand moulded)	Grey, non-calcareous clay from near river at Buckingham. Good plasticity; water of plasticity 32.2%; safe drying; drying shrinkage 7.1%.	1 (1136°C)	06	2.0	16.1	Dark salmon	Fairly hard	High combined shrinkage and short firing range for dense products. May be suitable for tile and common brick.
			04	2.3	13.5	Dark salmon	Hard	
			03	8.3	2.7	Red	Steel hard	
Clerval (hand moulded)	Grey, highly calcareous clay from Clerval area. Very plastic; water of plasticity 34.5%; cracks with rapid drying; drying shrinkage 9.9%.	01 (1117°C)	06	-0.3	26.6	Light salmon	Fairly soft	Tendency to scum. Difficult to dry. Short firing range for dense products. Unsatisfactory material for clay products.
			04	3.5	15.6	Salmon	Fairly hard	
			03	10.0	1.9	Salmon	Steel hard	
Rouyn (hand moulded)	Grey, non-calcareous clay from Rouyn area. Good plasticity; water of plasticity 27.7%; safe drying; drying shrinkage 7.2%.	2	08	0.6	15.6	Salmon buff	Fairly soft	Drying shrinkage is high. Short firing range for dense products such as facing brick. Probably suitable for tile and common brick.
			06	0.9	15.4	Pink salmon	Fairly hard	
			04	2.3	12.3	Salmon	Hard	
			02	7.4	0.4	Medium red	Steel hard	

* A minus sign indicates expansion.

** 08-945°C (1743°F); 06-991°C (1816°F); 04-1050°C (1922°F); 03-1086°C (1987°F); 02-1101°C (2014°F).

the above processing problems, many of the samples are suitable only for common brick, drain tile and building tile, provided they will extrude and dry satisfactorily.

The properties of kaolin clays are shown in Table 6. This type of clay is only known to occur on the Canadian Shield in Quebec. With the exception of Schefferville, the samples may be referred to as kaolinized rocks and are not suitable for ceramic products as they occur. The sample from Schefferville is a refractory clay suitable only for medium-duty refractories, unless a more refractory material is added to it.

Chemical Analyses

The chemical analyses of the samples are shown in Table 7. The total of the elemental and organic carbon, about one third of the sulphur (S), carbon dioxide (CO_2), and H_2O ($+105^\circ\text{C}$) should be about equal to the L.O.I. The L.O.I. for clays high in FeO tends to be low. The H_2O (-105°C) represents moisture in the air-dried samples. The organic and elemental carbon plus the sulphur indicate roughly the quantity of oxidizable material present. Most of the sulphur probably occurs in pyrite (FeS_2).

Except for the kaolin clays and the Quebec Group shales, the analyses are typical of low-fusion, heterogeneous common clays and shales. In this respect they are generally similar to the Ontario samples examined previously (27), except that clays high in CaO and MgO (high

TABLE 6
Kaolin Clays

Sample	DESCRIPTION AND UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					REMARKS
			Cone No. **	Fired Shrinkage % *	Absorption %	Colour	Hardness	
Schefferville (hand-moulded)	Dark brown clay from Redmond deposit near Schefferville. Very plastic and sticky; water of plasticity 37.5%; slight tendency to crack in drying; drying shrinkage 6.0%.	31- (1458°C)	02	4.5	25.5	Light salmon	Soft	Suitable for use in the manufacture of medium duty refractories and if mixed with a refractory clay for high duty refractories.
			3	9.3	16.8	Pink-brown	Fairly hard	
			6	14.3	7.7	Brown-buff	Very hard	
Château Richer (hand-moulded)	White, gritty material, containing about 80% feldspar and 20% kaolinite from Château Richer. Very poor plasticity (sandy texture); water of plasticity 22%; safe drying; drying shrinkage 1.0%.	19 (1520°C)	8	1.8	17.4	Grey-white	Very soft	Clay can be separated from feldspar; some iron staining. Unwashed fired samples have specks. Difficult to vitrify.
			10	2.8	14.4	Pink-white	Soft	
			12	4.1	12.7	Pink-white	Fairly soft	
St-Rémi (hand-moulded)	Light red-brown clay-quartz mixture from St. Rémi d'Amherst area. Fairly good plasticity (contains some gritty material); water of plasticity 22.3%; safe drying; drying shrinkage 3.7%.	28 (1614°C)	10	2.5	15.6	Light grey	Soft	Difficult to vitrify because of quartz and kaolinite. Fired specimens contain specks. May be suitable for low duty refractory products if added to a dense-firing clay.
			12	2.8	14.5	Grey-buff	Soft	
			15	4.8	9.5	Red-brown	Hard	
Brébeuf (hand-moulded)	Buff clay-quartz mixture (sandy texture) from Brébeuf area. Fair plasticity; water of plasticity 16.2%; safe drying; drying shrinkage 3.3%.	31½ (1683°C)	10	0.7	14.9	Off-white	Very soft	Fired specimens are speckled. Quartz can be separated from clay but clay fraction fires off-white. Difficult to vitrify because of high quartz content. Suitable for refractories if mixed with other clays.
			12	0.9	14.1	Off-white	Very soft	
			15	1.2	13.2	Off-white	Very soft	
Labelle (hand-moulded)	Brown, sandy, non-calcareous clay from east side of Labelle Lake. Fairly plastic; water of plasticity 34.4%; safe drying, drying shrinkage 6.0%.	14+ (1395°C)	02	4.0	20.2	Light brown-red	Soft	Fired specimens are speckled at higher temperatures. Difficult to vitrify because of high quartz. Not suitable for clay products by itself.
			2	4.5	19.0	Light brown-red	Soft	
			5	5.0	18.1	Brown-red	Fairly soft	
			10	7.2	9.5	Dark brown-red	Hard	
Point Comfort (hand-moulded)	Buff clay-quartz mixture from Point Comfort. Fair plasticity (gritty), lacks consistency; water of plasticity 20.3%; safe drying; drying shrinkage 3.0%.	30½ (1648°C)	10	1.8	14.7	Cream	Soft	Specimens have specks when fired. Clay, when separated from quartz, fired off-white. Very difficult to vitrify. Possibly suitable for medium or low duty refractories.
			12	2.8	14.2	Cream	Fairly soft	
			15	3.3	11.8	Cream	Fairly hard	

* 02-1101°C (2014°F); 2-1142°C (2088°F); 3-1152°C (2156°F); 5-1177°C (2151°F); 6-1201°C (2194°F); 8-1236°C (2257°F); 10-1285°C (2345°F); 12-1306°C (2383°F); 15-1424°C (2595°F).

TABLE 7

Chemical Analyses*

(%)

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 **	S	H ₂ O +105 °C	H ₂ O -105 °C	CO ₂	Quartz %
1. Lauzon (Q.G.)	59.18	4.15	2.97	1.14	19.85	0.53	1.94	1.47	3.56	4.61	99.40	0.13	0.11	0.063	4.77	1.27	0.09	25.20
2. Ile d'Orléans (Q.G.)	57.29	3.86	3.52	1.13	21.03	0.45	1.91	1.27	3.70	5.66	99.82	0.39	0.36	0.028	5.60	1.29	0.10	22.49
3. Beauport (U-L)	55.15	3.45	1.72	0.67	13.39	6.84	3.53	1.03	3.08	11.12	99.98	2.21	0.58	0.73	3.81	1.14	5.98	28.30
4. Boischatal (U-L)	51.53	3.05	1.72	0.59	8.75	11.05	3.55	0.86	2.71	15.76	99.57	3.39	0.45	0.81	3.56	1.02	10.77	25.82
5. Mont-Joli (Q.G.)	54.20	1.81	6.15	1.05	24.55	0.49	1.82	1.20	3.40	5.43	100.10	0.14	0.13	0.028	5.62	1.35	0.05	20.30
6. Delson (U)	59.57	3.84	2.34	0.77	16.36	1.62	3.93	0.82	3.69	6.75	99.69	0.88	0.50	1.09	5.08	0.89	1.33	23.73
7. St-Apollinaire (Q.G.)	58.74	1.72	6.05	0.85	20.77	0.31	2.26	1.14	3.18	4.67	99.69	0.02	0.02	0.02	4.82	1.65	0.01	25.32
8. Lotbinière (U)	59.02	3.10	2.39	0.63	15.03	3.39	3.62	0.90	3.40	7.89	99.37	1.40	0.62	1.05	4.82	0.85	2.86	28.26
9. Ste-Monique (Q)	59.91	2.61	3.68	0.67	15.42	3.10	3.65	0.99	3.60	6.77	100.40	0.67	0.044	0.018	4.25	0.79	2.28	27.67
10. Boucherville (U-L)	61.83	1.37	6.38	0.73	16.41	0.26	3.54	0.90	3.69	5.10	100.21	0.36	0.34	0.034	4.93	1.50	0.06	27.83
11. St-Grégoire (Q)	64.50	1.67	4.77	0.75	15.12	0.48	3.10	1.37	3.17	4.41	99.34	0.29	0.09	0.009	3.88	0.95	0.74	36.87
12. Laprairie (L)	59.14	4.23	2.10	0.64	16.37	2.54	3.72	0.96	3.80	6.14	99.64	0.79	0.15	0.484	4.78	0.64	2.34	24.80
13. Breckenridge (R)	64.91	2.48	1.10	0.63	14.21	3.29	2.27	0.93	5.48	4.73	100.03	0.73	0.18	0.142	3.13	0.23	2.01	39.67
14. Douglstown	66.99	2.00	3.70	0.83	14.41	0.49	2.31	1.73	2.61	4.78	99.85	0.50	0.47	0.017	4.44	0.64	0.11	37.02
15. St-Alphonse	64.03	0.94	5.53	0.77	15.47	0.33	3.75	0.11	3.40	5.81	100.14	0.45	0.44	0.022	5.46	1.19	0.04	35.86
16. Estcourt	64.46	2.72	5.20	0.92	15.07	0.30	2.50	1.71	2.69	4.25	99.82	0.30	0.29	0.022	4.27	0.62	0.03	34.34
17. Scott Junction	60.37	3.69	3.30	0.87	16.86	1.81	3.14	1.84	3.51	4.34	99.73	0.37	0.16	0.120	4.02	0.55	0.78	22.20
18. Ville St-Georges	69.40	2.13	3.15	0.79	13.71	1.19	2.08	2.01	2.77	2.79	100.02	0.13	0.07	0.02	2.75	0.49	0.22	38.69
19. Disraeli	57.10	4.10	3.75	0.92	20.34	0.72	3.62	1.62	3.93	4.13	100.23	0.16	0.15	0.02	4.15	0.63	0.05	21.07
20. Victoriaville	59.08	2.97	3.90	0.98	17.21	2.29	3.16	2.14	3.44	4.20	99.37	0.47	0.35	0.063	4.22	1.09	0.43	23.19
21. Deschailons	58.41	3.76	3.84	0.94	17.37	2.02	2.85	2.30	3.42	4.71	99.62	0.43	0.32	0.051	4.30	0.95	0.40	18.40

TABLE 7 (continued)

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**	S	H ₂ O +105 °C	H ₂ O -105 °C	CO ₂	Quartz %
22. East Angus	55.19	3.46	4.44	0.88	20.48	0.72	3.74	1.43	4.22	5.11	99.67	0.19	0.10	0.035	5.40	0.65	0.34	17.90
23. Cowansville	62.89	3.11	2.95	1.04	15.25	2.50	2.89	2.26	3.04	4.07	100.00	0.51	0.17	0.063	2.68	0.14	1.26	29.63
24. St-Jean	58.16	2.09	6.75	0.68	17.01	1.62	3.33	2.52	3.13	4.81	100.10	0.41	0.15	0.024	4.03	1.64	0.95	19.63
25. Laprairie (Clay)	54.19	2.83	4.82	0.67	17.20	3.88	4.21	2.46	3.32	6.85	100.43	0.66	0.23	0.023	4.36	-	1.57	-
26. Lakeside	53.95	3.78	3.67	0.72	16.29	4.63	4.81	2.84	3.06	5.84	99.59	0.77	0.11	0.065	3.99	1.11	2.42	11.30
27. Soulanges	62.49	1.64	3.42	0.69	14.16	5.17	2.76	3.05	2.64	4.32	100.34	0.77	0.12	0.020	2.07	0.34	2.38	24.51
28. Varennes	56.12	1.29	6.81	-	16.50	2.10	2.93	2.49	2.75	8.61	-	-	0.21	0.012	-	-	0.29	-
29. Sept-Îles	58.76	3.88	2.89	0.89	16.84	4.04	3.73	3.45	3.56	1.66	99.70	0.13	0.10	0.108	1.78	0.28	0.11	20.38
30. Mistassini	62.23	2.42	3.97	0.69	15.95	3.22	2.68	3.24	3.03	2.52	98.95	0.10	0.06	0.039	2.75	0.68	0.12	16.40
31. L'Assomption	59.55	2.87	3.07	0.66	15.57	3.85	3.71	2.84	2.90	5.18	100.20	0.80	0.41	0.213	3.49	0.73	1.39	25.10
32. Ste-Scholastique	55.91	3.26	3.83	0.72	15.91	4.76	4.53	2.69	2.72	5.47	99.80	0.69	0.11	0.039	3.34	1.16	2.14	9.60
33. Buckingham	56.35	2.27	5.76	1.08	16.40	3.08	4.27	2.49	3.80	5.03	100.53	0.53	0.50	0.033	4.09	1.49	0.13	30.41
34. Clerval	53.48	3.00	2.82	0.58	15.70	6.17	4.39	2.68	3.15	8.13	100.10	1.51	0.47	0.036	3.87	0.76	3.81	12.62
35. Rouyn	62.14	3.40	2.76	0.66	15.37	3.04	3.57	3.19	2.55	2.89	99.57	0.26	0.16	0.038	3.00	0.79	0.36	16.40
36. Schefferville	39.09	0.46	8.19	2.50	33.09	0.37	0.44	0.01	0.09	15.90	100.14	1.62	1.60	0.028	14.68	1.38	0.10	7.38
37. Château Richer	54.83	0.28	0.46	0.29	28.72	6.14	0.34	4.50	1.11	3.46	100.11	0.03	0.02	0.01	3.44	0.58	0.04	1.40
38. St-Rémi	67.20	0.14	5.09	0.80	19.19	0.36	0.08	0.09	0.27	7.25	100.47	0.08	0.06	0.01	7.15	0.30	0.09	41.80
39. Brébeuf	73.93	0.09	0.05	0.10	18.57	n.d.	0.03	0.03	0.33	6.53	99.66	0.08	0.07	0.02	6.60	0.09	0.02	50.47
40. Labelle	43.93	0.82	14.68	1.98	22.95	1.13	1.79	0.30	0.48	11.58	99.64	0.94	0.92	0.028	10.73	1.89	0.07	14.75
41. Point Comfort	72.16	0.36	0.76	1.35	18.03	0.50	0.12	0.16	0.63	6.25	100.32	0.10	0.09	0.01	6.03	0.28	0.05	45.70

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

** Organic and elemental carbon.

- Not determined.

n.d. Not detected.

values usually indicate the presence of calcite and/or dolomite) are not as common in Quebec as in Ontario. The Al_2O_3 (usually a rough indication of clay content) of the common clays from all regions and of the shales from the St. Lawrence Lowlands varies from about 14 to 17 per cent. The alumina content of the Quebec Group shales runs about 20 to 24 per cent, while the kaolin-type samples have alumina contents running as high as about 35 per cent. The silica content of the majority of the common clays and shales varies from about 50 to 65 per cent, including 12 to 35 per cent free quartz (silica sand). In general, these common materials also contain appreciable quantities of FeO , Fe_2O_3 , CaO , MgO , Na_2O and K_2O . The CaO and MgO contents of the Quebec Group shales are generally lower than the other shales and this, coupled with their higher alumina contents, makes them more refractory than the St. Lawrence Lowlands or the Ontario shales.

Differential Thermal Analysis

The DTA curves of the samples are shown in Figures 1 to 6. Exothermic peaks point up and endothermic ones point down. In general, the clay mineral reactions cause the endothermic peaks at about 150°C and 590°C , and also the endothermic-exothermic doublets above 900°C that are observed when little or no carbonate is present. A double endothermic peak in the 750 to 850°C temperature range indicates dolomite is present, and possibly calcite; while a single, intense

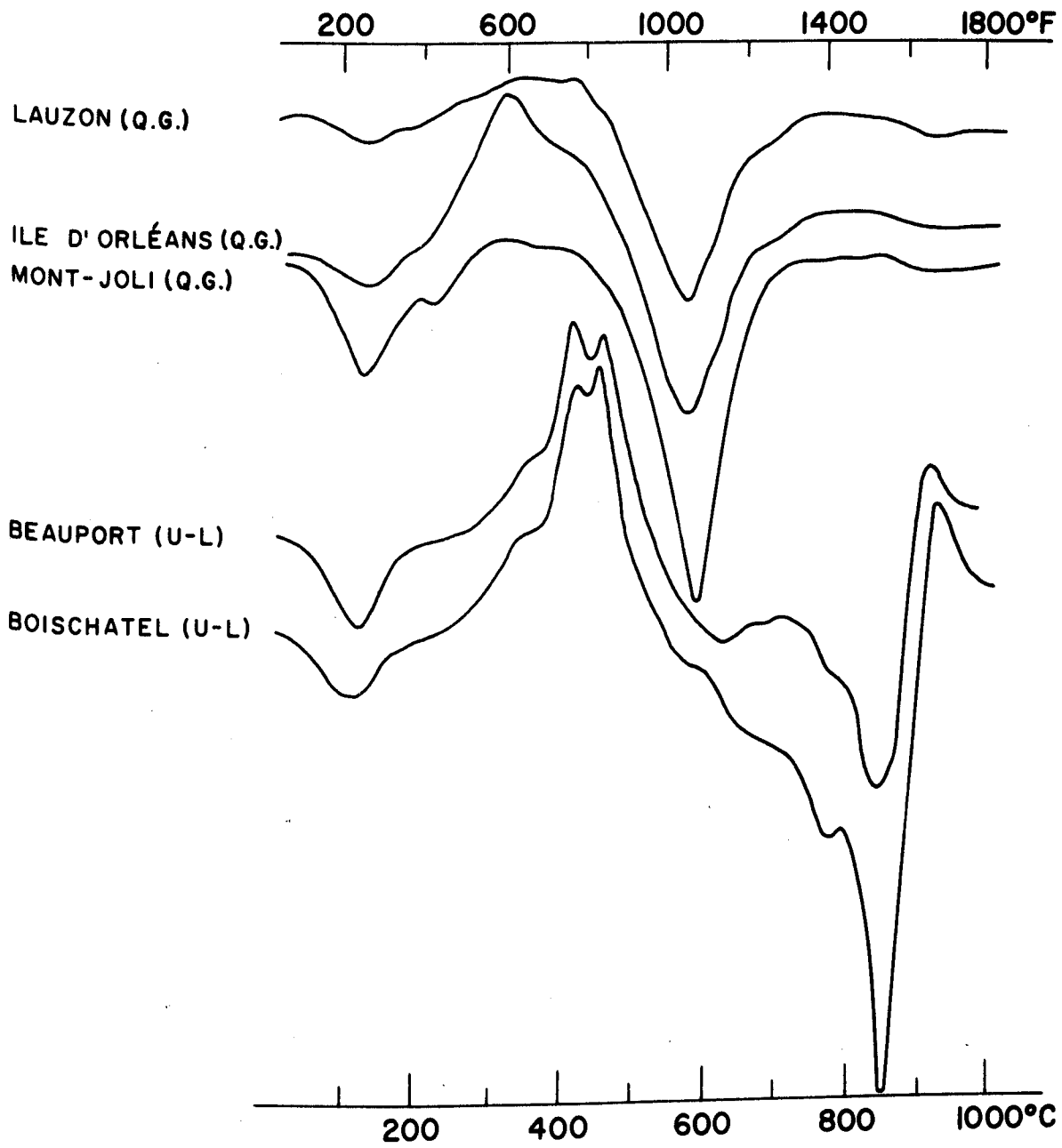


Figure 1. DTA curves of shales from Quebec City and Mont Joli.

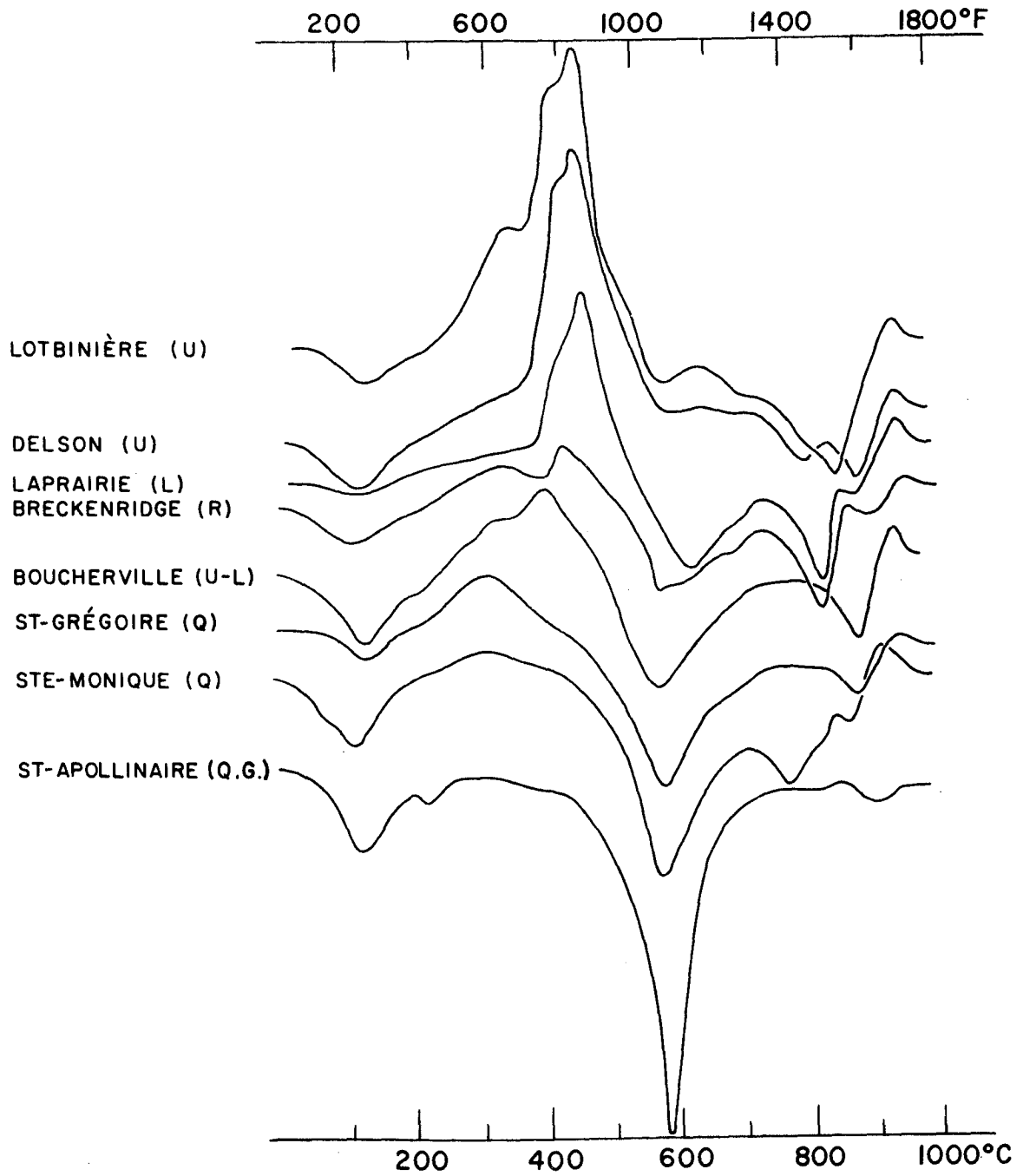


Figure 2. DTA curves of Southern Quebec shales.

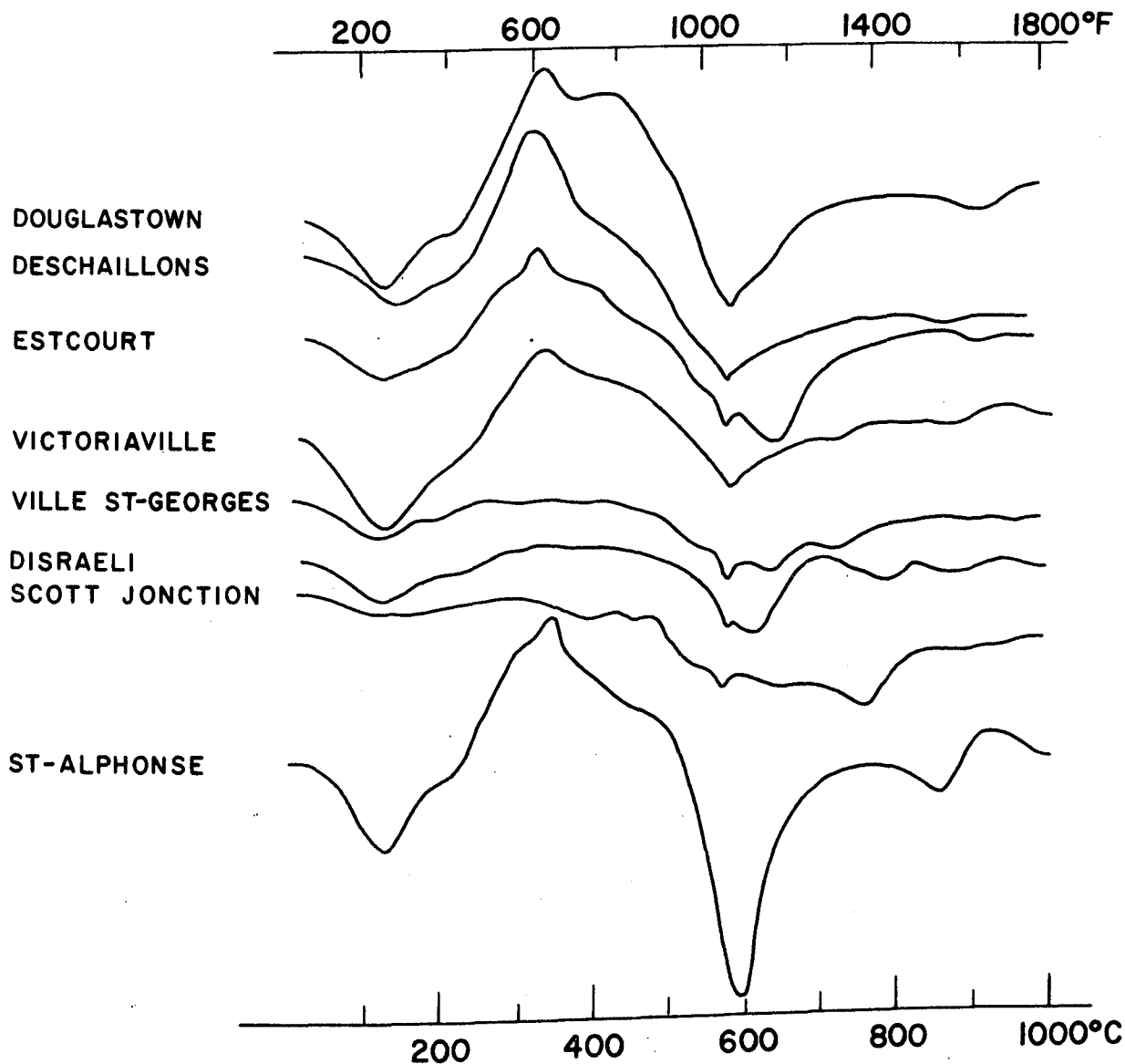


Figure 3. DTA curves of clays from Gaspe and Eastern Quebec.

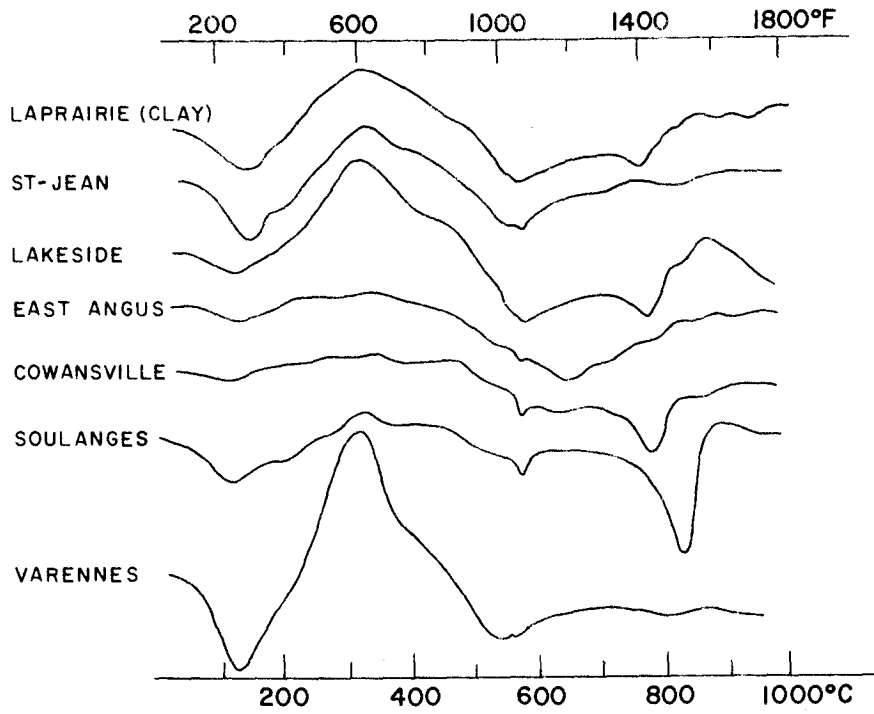


Figure 4. DTA curves of clays from the Montreal area and Southeastern Quebec.

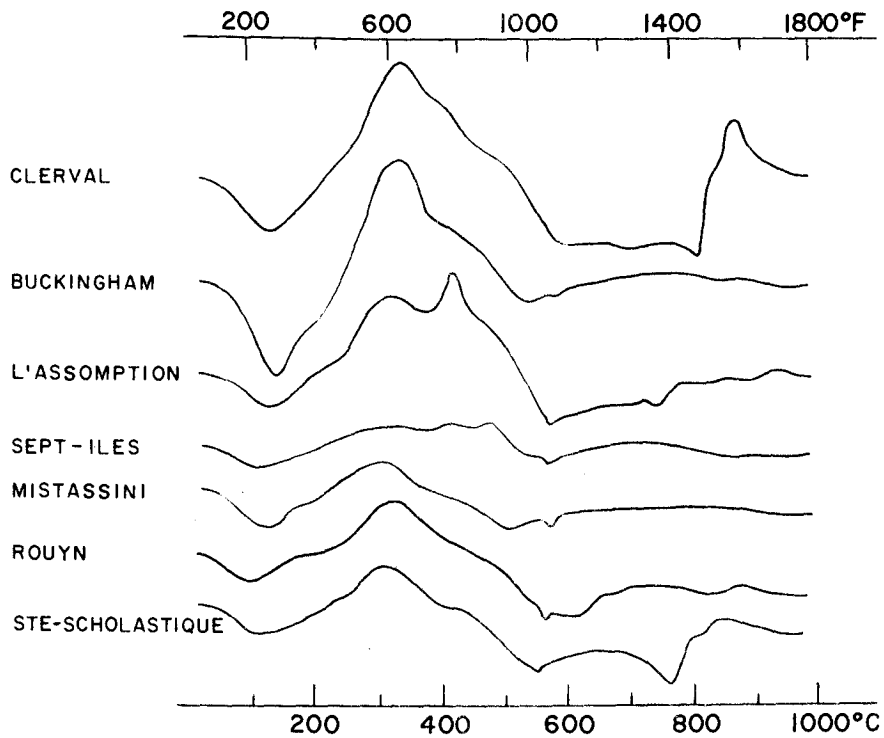


Figure 5. DTA curves of clays from North Shore, Northwestern Quebec and Western Quebec

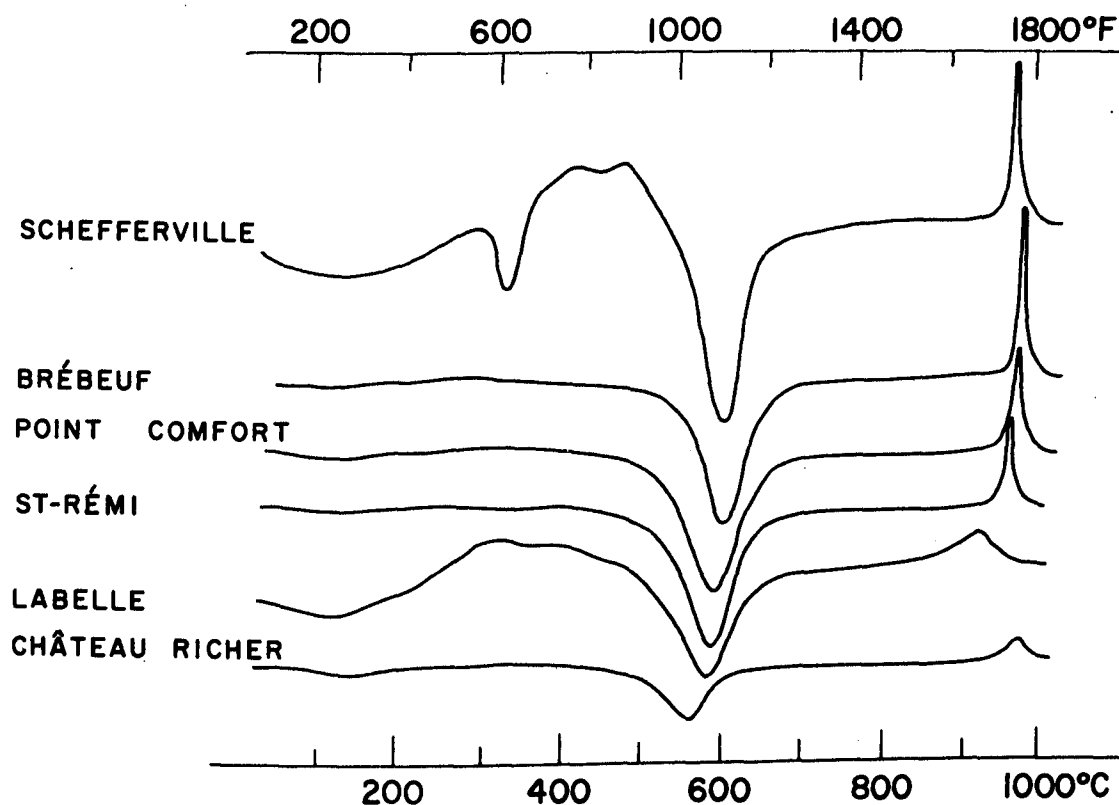


Figure 6. DTA curves of kaolin clays.

endothermic peak at 765 to 900°C indicates the presence of calcite. When about 5 per cent or less of carbonates are present and the peak at about 720 to 780°C is broad and dull, the samples may contain dolomite and calcite, or calcite only. Many of the clay and shale curves have broad exothermic peaks at about 320°C which indicate the presence of readily burned-out organic material. The combination of two exothermic peaks with an endothermic peak between them, at about 400 to 500°C, indicates the presence of organic material and probably pyrite. A small sharp peak at 575°C is caused by the inversion of quartz from the

low to the high form.

The curves in Figures 1 and 2 are typical of those produced by common shales containing illite and chlorite as the principal clay minerals. In some cases they are greatly influenced by reactions caused by carbonates and oxidizable material. The curves of the Quebec Group shales indicate that they contain no calcite or dolomite, very little pyrite, and moderate quantities of organic material. They have large endothermic peaks at about 590°C, indicating that the samples contain a substantial proportion of clay minerals. The curve of the Queenston (Becancour river) sample from Ste. Monique shows that it is calcareous, a feature common to the Queenston shales of Ontario. The weathered shale from St. Gregoire contains very little carbonate, an unusual feature for a Queenston shale. Except for Boucherville (U), the DTA curves of Figures 1 and 2 show that the Utica and Lorraine shales contain calcite and/or dolomite, sometimes in large quantities (Boischatel (U-L) and Beauport (U-L)). These figures also indicate that the Utica-Lorraine shales generally contain organic material and pyrite; sometimes in excessive amounts. The Rockcliffe Formation sample from Breckenridge contains moderate quantities of carbonates, pyrite and carbonaceous material.

The DTA curves of the common clays in Figures 3, 4 and 5 are typical of heterogeneous, low-fusion clays of the illitic-chloritic type. Most of them have ill-defined peaks at about 580°C and at 850 to 950°C as the result of clay mineral decomposition or reaction. The one for

St-Alphonse is an exception and has well-defined clay mineral peaks. A small sharp peak at 575°C, caused by the inversion of quartz, occurs on many curves. The majority of the curves have a broad exothermic peak at about 320°C, indicating they contain some readily burned out organic material. These peaks for Douglastown, St-Alphonse, Clerval and Buckingham show that their organic material is high, and double peaks at 325°C and 415°C indicate that L' Assomption contains excessive organic material and pyrite. Endothermic peaks between 765° and 830° indicate that some of the clays contain moderate quantities of calcite, with a few, such as Clerval, possibly also containing dolomite. These curves indicate that the calcite and dolomite content is much less than in many of the buff-firing Ontario clays (27).

The clay mineral peaks (scale 40) at 580°C and 950°C in Figure 6 indicate that the principal clay mineral in these samples is a kaolin type. The endothermic peak at 325°C on the Schefferville curve indicates that it contains gibbsite. Schefferville and Labelle contain a large amount of organic material, as shown by the large exothermic peaks at about 425°C and by chemical analyses.

X-Ray Diffraction Analysis

In the summary of mineralogical data in Table 8, the indicated relative abundances are only approximate because of frequent variation in the crystallinity of layer silicates.

St. Lawrence Lowland shales consist essentially of illite, quartz,

TABLE 8

X-Ray Diffraction Analyses of Quebec Clays and Shales*

Sample and Per Cent Plus 200 Mesh**	Illite	Chlorite	Kaolin	Montmorillonoid	Vermiculite	Mixed Layer Clays and Other Minerals	Quartz			Plagioclase			K Feldspar			Calcite			Dolomite			Amphibole		
							Wh.	F.F.	C.F.	Wh.	F.F.	C.F.	Wh.	F.F.	C.F.	Wh.	F.F.	C.F.	Wh.	F.F.	C.F.	Wh.	F.F.	C.F.
Lauzon (Q. G.)	B	B	D(?)			Illite-Verm. (C) Illite-Verm. (C); Anatase (G)	B	D	B	C	E	C												
Ile d'Orléans(Q. G.)	B	B	D(?)			Illite-Verm. (C); Pyrite (F); Anatase (G)	B	D	B	C	F	C												
Beauport (U-L)	B	C				Illite-Mont. (C); Pyrite (F); Anatase (G)	B	C		C	G		G			D	D			F				
Boischatel (U-L)	B	C				Illite-Mont. (A); Anatase (G); Hematite (E)	B	C		C	G					C	C			D				
Mont-Joli (Q. G.)	C	C				Illite-Verm. (D); Pyrite (E); Anatase (G)	C	G	C															
Delson (U)	B	C				Illite-Mont. (B); Anatase (C); Hematite (E)	B	C	B	C	F	C			G	F	G	F	F		F			
St-Apollinaire (Q. G.)	C	C	D(?)			Illite-Verm. (A); Pyrite (E)	B	B		D	D													
Lotbinière (U)	D	C				Illite-Mont. (D); Hematite (G)	B	C		C	G		G			E	F			E				
Ste-Monique (Q)	B	B				Anatase (G) Illite-Verm. (B) Hematite (G)	B	C		C	E													
St-Grégoire (Q)	B	C			D	Illite-Verm. (D); Pyrite (F); Anatase (G)	B	C	B	C	G	B	G			D								
Laprairie (L)	B	B				Chlorite-Verm. (D); Anatase (G)	B	C	B	C	E	C	G			E	F	D	F		E			
Breckenridge (R)	A	B					B	D					B	C		E	E							
Douglstown 9.2	B	B	D(?)		D	Chlorite-Verm. (C)	B	C	B	B	F	C	F			E								
St-Alphonse 0.9	B	B			D	Illite-Verm. (D); Hematite (G)	B	C	A	G														
Estcourt 6.8	B	B				Chlorite-Verm. (D); Illite-Verm. (D)	B	D	A	B	E	E	G											
Scott Junction 0.2	B	B				Pyrite (G?)	B	C	B	B	C	B	F	G	F	G			G				G	G
Ville St-Georges 5.3	B	B				Chlorite-Mont. (D)	B			B			F										G	G
Israell 0.2	B	B				Chlorite-Mont. (D)	C	D	B	C	C	B	G	G	G								G	G
Victoriaville 5.5	B	B				Chlorite-Mont. (D)	C	D	B	B	C	B	E	E	E								F	F
Deschallons 0.1	B	B				Illite-Mont. (D); Chlorite-Mont. (D)	C	D	B	B	B	B	E	D	E								F	F
East Angus 0.5	B	B				Chlorite-Verm. (D)	B	D	B	B	C	B	F	G	F			C					G	
Cowansville 0.3	B	B					C	D	B	C	C	C	F	F	F								G	G
St-Jean 2.4	B	C			B		C	E	C	B	C	B	E	F	E								F	F
Laprairie (Clay) 0.6	B	B				Mont.-Verm. (C)	D	D	C	B	B	B	E	E	F								F	E
Lakeside 0.4	B	C				Illite-Verm. (C)	D	E	D	B	B	B	E	F	E			F			F		F	E
Soulanges 1.1	B					Verm.-Mont. (B)	D	D	B	B	B	B	E	E	E	G	F			F	F		F	E
Varennes 6.1	D				A		D	D	C	B	B	B	E	E	E			G	G	G			E	E
Sept-Iles 2.8	A					Chlorite-Verm. (C)	D	E	C	B	B	B	E	D	E								D	E
Mistassini 2.1	A				D		C	D	B	A	B	A	D	D	E								F	E
L'Assomption 12.1	B					Chlorite-Mont. (B); Pyrite (G?)	D	D	B	B	B	B	F	E	F	G	G						F	E
Ste-Scholastique 0.4	B	C				Chlorite-Mont. (C)	D	E	B	B	B	C	E	E	E	F	G			F	G		E	E
Buckingham 3.7	B					Mont.-Verm. (B)	D	E	B	B	B	C	E	E	E								E	E
Clerval 0.2	C	B				Illite-Verm. (C)	D	E	B	B	B	C	E	F	F	E	F		F	E	F	G	E	F
Rouyn 0.1	C	A				Verm.-Mont. (C)	D	D	B	B	B	B	F	E	E								E	E
Schefferville 4.8	D		A			Gibbsite (C); Anatase (E); Hematite (E); Rutile (G)	D		A															
Château Richer 49.0	D		A							A	B	A												
St-Rémi 44.5	D		A			Anatase (C); Hematite (G); Rutile (G)	A	D	A	G														
Brébeuf 53.7	Tr		A				A	E	A															
Labelle 19.1			A		D		C	F	A	F		F												D
Point Comfort 45.1	D		A			Anatase (F)	A	D	A	G	G													

*Mineralogy determined by R.S. Dean. Clay minerals determined in minus 5 micron fraction. Non-clay minerals determined in (a) whole sample (W); (b) fine fraction (F.F.); (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.

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

chlorite, plagioclase, and more-or-less randomly interstratified mixed-layer systems composed of illite and an expandable phase. Variable, but often significant, quantities of carbonate minerals were also identified. Although expandable phases associated with hydrous mica had previously been recognized with these rocks (24), reliable detection of these was found to be possible only through the use of controlled, variable humidity in conjunction with the X-ray diffractometer studies.

The Boucherville sample was notable in that it contained no layer silicates other than highly disordered illite, whereas Utica-Lorraine shales within this region are known to contain a fairly uniform, well crystallized illite-chlorite mixture. This feature may possibly be a very local effect resulting from the alteration of the shale by a nearby igneous intrusion.

The Breckenridge sample, which was taken from what may be considered as the western extension of the St. Lawrence Lowland, differs from the younger Utica-Lorraine-Queenston samples in that it contains very abundant K-feldspar and is totally lacking in plagioclase. This change in feldspar species has been previously recognized (24) and correlated with changes in sediment source areas.

The Quebec Group shales were similar in bulk composition to those from the St. Lawrence Lowland, but differed in several significant aspects. With the notable exception of the St. Apollinaire sample, the single outstanding characteristic of the Quebec Group samples was the extremely high intensity ratio of the $7\overset{\circ}{\text{A}}/14\overset{\circ}{\text{A}}$ X-ray diffraction peaks, which exceeded even that commonly observed among iron-rich chlorites. This, together with

the fact that only very weak, modified, first-order basal reflections were recorded following the 580°C heat treatments, suggests that the bulk of the Quebec Group shale chlorite may be "septechlorite" (68), i. e., possess a structure similar to that of chamosite. The Mont-Joli sample, which was collected far to the northeast of the other Quebec Group samples, was also unique with regard to its exceptionally low content of non-clay detrital minerals.

The common clays tended to be, mineralogically, somewhat more variable than the shales, but some generalizations are possible. The common non-clay mineral constituents were plagioclase, quartz, K-feldspar and amphibole, in order of decreasing general abundance. The clays occurring within the folded Appalachian belt (including Gaspé) invariably contained roughly equivalent amounts of illite and chlorite. These minerals may be extremely well crystallized, as was shown by the "illite" within the minus 5 micron fraction of the Disraeli clay, which yielded a strong sharp pattern of 2M₁ muscovite. A similar mica was also recognized within the Cowansville sample. Most of the mixed-layer systems identified in the Appalachian clays appear to result from the development of expandable layers within chlorite, which is more readily attacked by weathering than are dioctahedral micas.

The common clays from areas underlain by the Canadian Shield generally are rich in plagioclase and somewhat deficient in quartz in comparison to the shales or the Appalachian clays. The clay mineralogy of these samples appears to be highly variable, and was probably determined

by the composition of local, glacially derived material.

The clay samples occurring within the St. Lawrence Lowland might be expected to reflect the mineralogical composition of both the underlying Palaeozoic shales and the Shield rocks to the north. Although the influence of the former is difficult to evaluate, that of the latter is manifest, as evidenced by the high plagioclase/quartz ratio and the persistent occurrence of amphibole, which has never been identified as a constituent of the shale.

The principal clay minerals within the kaolin clays all appear to belong to the kaolinite-metahalloysite series of the kaolin mineral group. The extremely high degree of layer stacking disorder and the evidence of changes in profile of the basal reflections with varying humidity indicate that the Château Richer kaolin lies close to, or at, the metahalloysite-halloysite end of the series. At the other crystallinity extreme, Brébeuf and (especially) Schefferville contained kaolinites which exhibited exceptionally high degrees of structural ordering. The latter sample is also worthy of note in that the quartz content of the minus 5 micron size fraction was below the minimum detection limit of the Guinier camera (approximately 0.05% quartz).

The mineralogical composition of the 13 selected samples (unfired and fired) is given in Table 9. Of particular interest is the presence of mullite in the fired specimens of Lauzon (Q. G.) and Mont-Joli (Q. G.), both of which are common shales high in alumina. Mullite also is contained in the fired specimen of Brébeuf because of the quartz-kaolinite composition and the high firing temperature.

TABLE 9

Mineralogical Composition of Selected Samples

Sample and PCE	*Unfired Composition+		Fired Properties		
			Firing Temp. °C	Absorption %	**Fired Composition
Lauzon (Q. G.) 14	Quartz Illite Chlorite	Plagioclase Illite-Verm. Kaolin (?)	1055	6.4	Quartz K-Feldspar Rutile Mullite (minor) Hematite (minor)
Bolschatel (U-L) 3	Quartz Illite Plagioclase Calcite Chlorite Illite-Mont.	Dolomite Pyrite K-Feldspar Anatase Organic Material (DTA)	1095	11.3	Quartz Plagioclase Pyroxene
Mont-Joli (Q. G.) 16	Illite-Mont. Illite Chlorite	Quartz Hematite Anatase	1065	4.8	Quartz Mullite Hematite
Delson (U) 01	Quartz Illite Chlorite Plagioclase Illite-Verm. Calcite	Dolomite K-Feldspar Pyrite Anatase Organic Material (DTA)	1005	6.7	Quartz K-Feldspar Hematite
St-Apollinaire (Q. G.) 14 1/2	Illite-Mont. Quartz Illite Chlorite	Plagioclase Kaolin (?) Hematite Anatase	1050	5.1	Quartz Hematite
Lotbinière (U) 4	Illite-Verm. Quartz Plagioclase Chlorite Illite	Calcite Dolomite Pyrite K-Feldspar Organic Material (DTA)	1060	4.7	Quartz Plagioclase K-Feldspar (minor) Hematite (minor)
Ste-Monique (Q) 4	Illite Chlorite Quartz Plagioclase	Illite-Mont. Calcite Hematite	980	5.0	Quartz K-Feldspar Plagioclase
Laprairie (L) 1	Quartz Illite Chlorite Plagioclase Illite-Verm. Calcite	Dolomite Pyrite K-Feldspar Anatase Organic Material (DTA)	1045	8.1	Quartz Plagioclase K-Feldspar Hematite (minor)
Scott Junction 5	Plagioclase Quartz Illite Chlorite	K-Feldspar Calcite Amphibole Pyrite (?)	1025	7.2	Quartz Plagioclase K-Feldspar Hematite (minor)
East Angus 5 1/2	Plagioclase Quartz Illite Chlorite	Chlorite-Verm. K-Feldspar Amphibole Calcite	990	5.3	Quartz Plagioclase K-Feldspar Hematite
Laprairie (Clay) 1 1/2	Plagioclase Illite Chlorite Quartz	Mont-Verm. K-Feldspar Amphibole	995	6.9	Quartz Feldspar Hematite (minor)
Mistassin 2	Plagioclase Illite Quartz	K-Feldspar Vermiculite Amphibole	1000	16.7	Quartz Feldspar Hematite (minor)
Brébeuf 31 1/2	Quartz Kaolinite	Illite (Trace)	1315	16.0	Quartz Mullite Cristobalite

* Mineralogy determined by R. S. Dean (DTA notes by J. G. Brady).
Major constituents listed first and start in upper left.

+ Abbreviations: Verm. - Vermiculite; Mont. - Montmorillonoid.

** Constituents determined by R. M. Buchanan. A few minor constituents not identified.

Processing Problems Associated with
Typical Clays and Shales from Quebec

Plasticity

The plasticity curves of the 13 special samples, where consistency is plotted against tempering water, are shown in Figures 7 and 8. In general, the higher the peaks and the larger the area under the peak, the greater the plasticity. The mixtures have a stiff plastic condition at water percentages corresponding to about the highest consistency. The clays are more plastic than the shales but some of the clay curves have sharp peaks indicating that they are sensitive to small additions of water at the stiff-plastic stage. The Mont-Joli and St- Apollinaire curves indicate that these materials have good plasticities for the manufacture of extruded products. The peak areas of Delson (U), Laprairie (L), Ste-Monique (Q), Lauzon (Q. G.) and Brebeuf indicate these samples are less plastic than the standard Cooksville (D-M). Consequently, they might not extrude satisfactorily unless an addition is made to increase the plasticity. All other samples should have sufficient plasticity for extrusion. The Laprairie (Clay) curve indicates that this material probably has too much plasticity for use by itself in the manufacture of clay products.

Thermogravimetric Analysis

The weight loss curves of the 13 selected samples are shown in Figures 9 and 10. The losses up to about 450°C are from adsorbed moisture and oxidizable material. The principal weight losses are caused by the loss of hydroxyl groups from the clay minerals (the clay minerals in the Quebec samples give small losses) between about 450°C

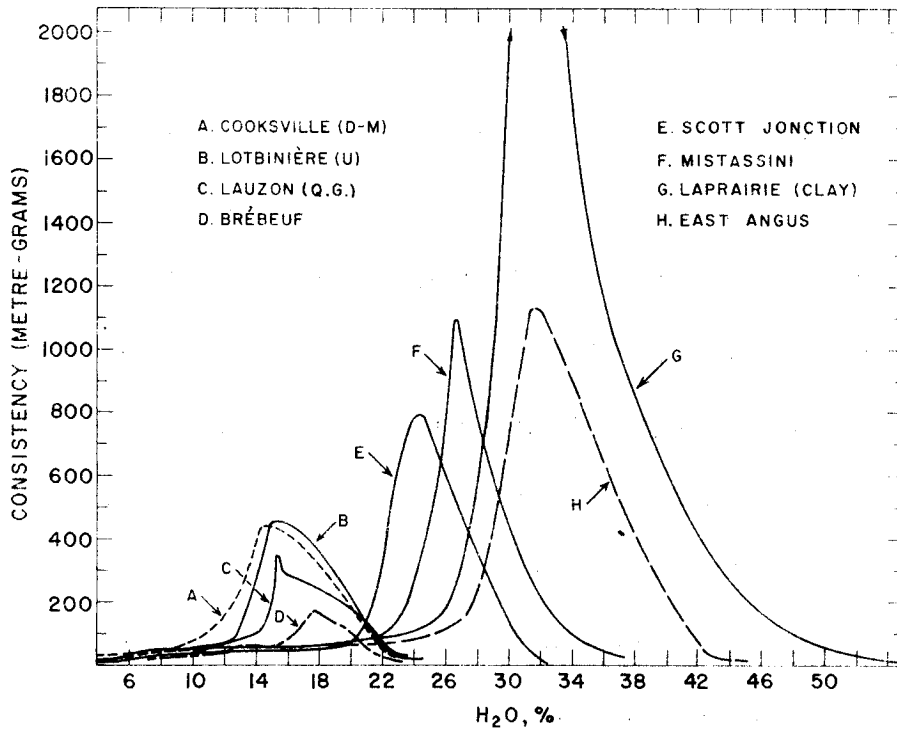


Figure 7. Plasticity of some clays and shales.

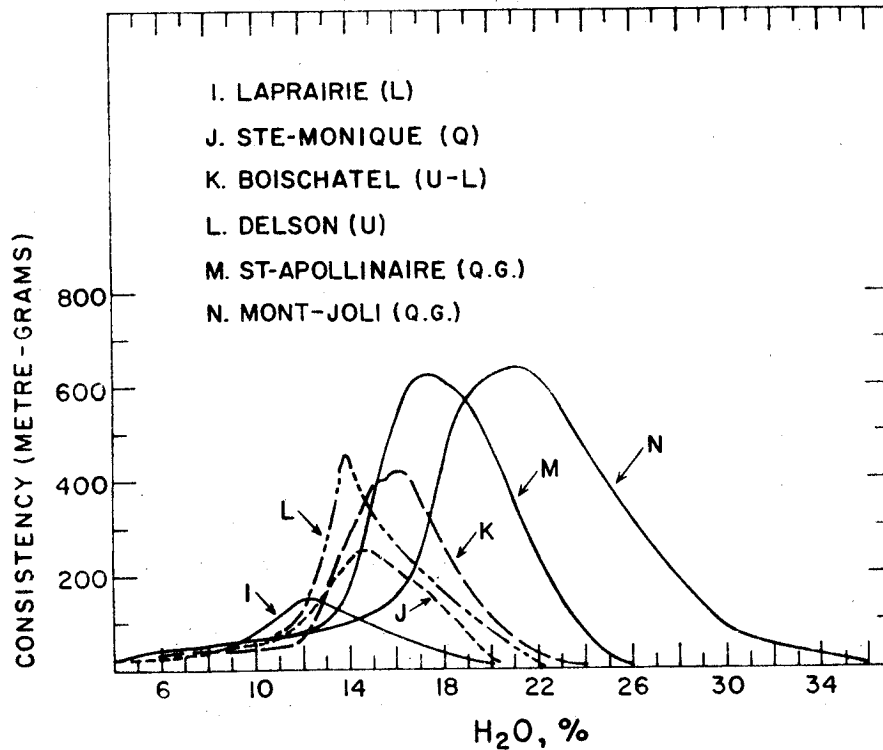


Figure 8. Plasticity of some shales

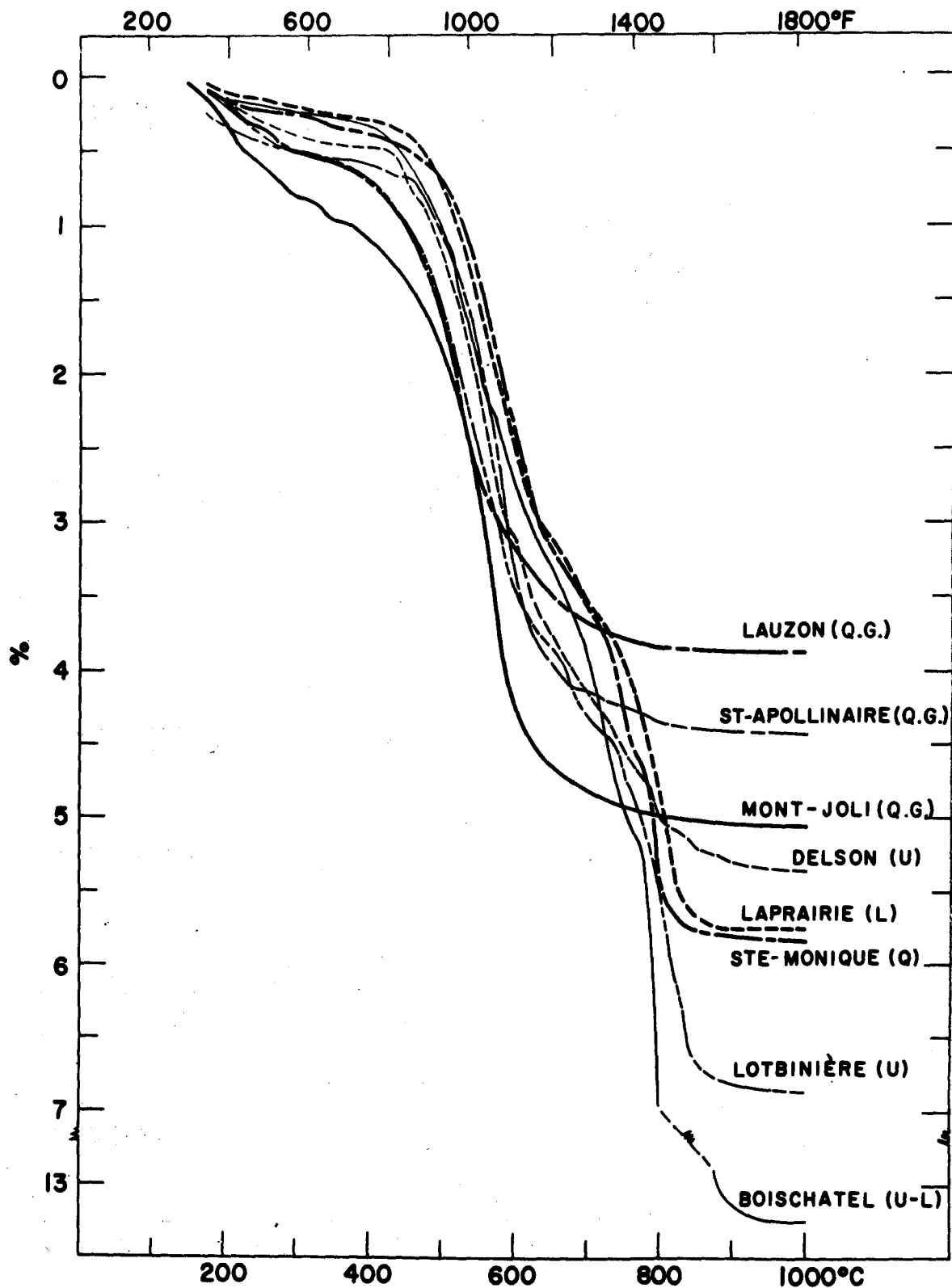


Figure 9. Percent weight loss of some shales.

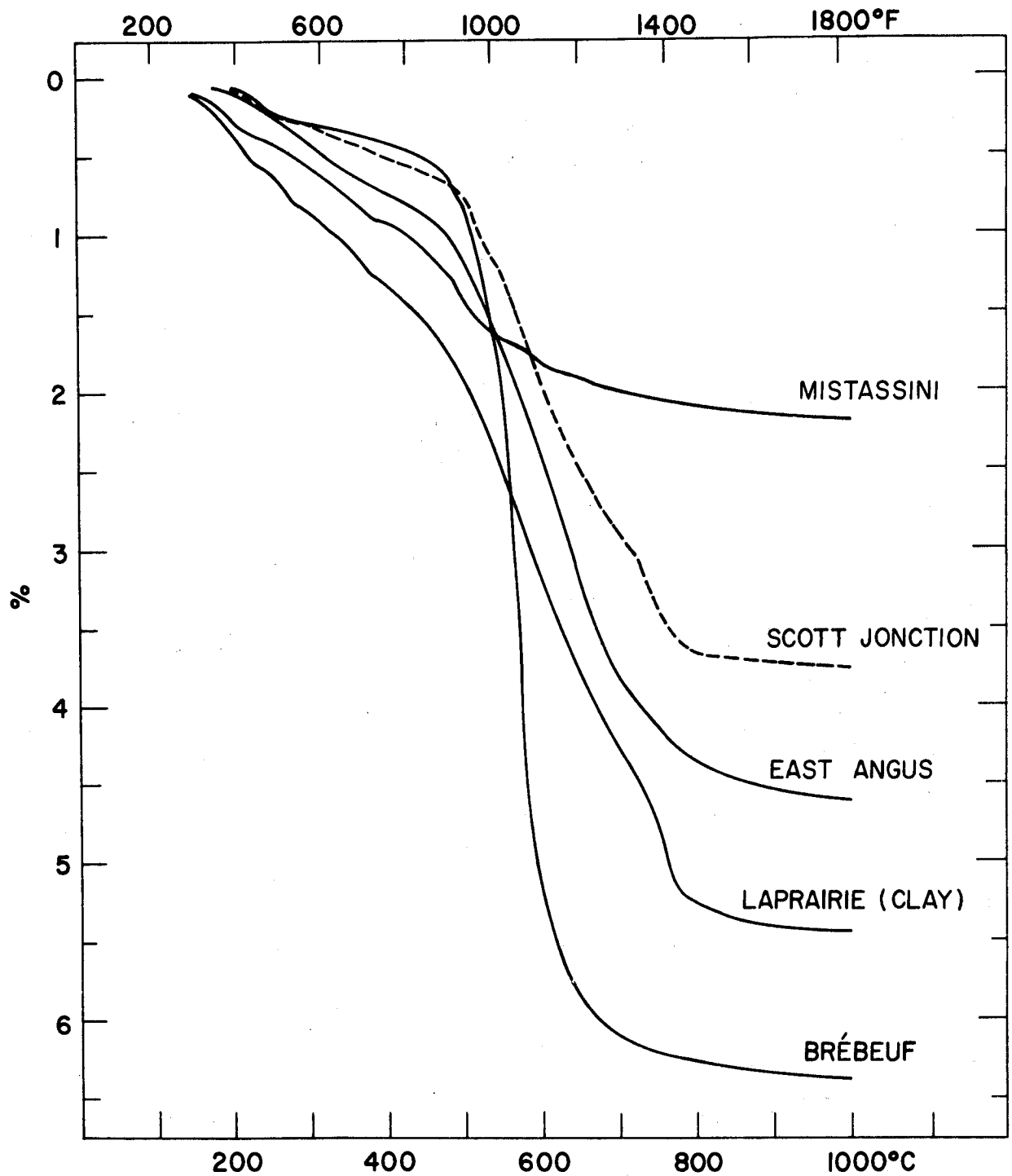


Figure 10. Percent weight loss of some clays.

and 700°C, and the decomposition of carbonates between about 700°C and 900°C. A minor weight loss also occurs at about 900°C, from the final breakdown of the clay minerals. The above reactions result in the release of various gases into the kiln atmosphere and as a result may cause some problems during firing. The non-calcareous common shales or clays from Lauzon, St. Apollinaire, Mont Joli, Mistassini and East Angus have very low weight losses. The non-calcareous kaolin rock from Brebeuf has a substantial loss and its curve is typical of kaolin minerals. The highly calcareous sample from Boischatel has a very large weight loss, resulting from the decomposition of dolomite and calcite. The curves for Boischatel (U-L) and Lotbinière (U) in particular, and for Delson (U) and Laprairie (L), indicate the presence of dolomite as well as calcite.

Firing Behaviour

The firing behaviours of the 13 selected samples are illustrated by curves for temperature gradient (absorption and shrinkage), DTA, rate of weight loss, and thermal expansion, in Figures 11 to 23. Negative values on the temperature gradient shrinkage scale represent expansion, and negative values on the thermal expansion curves indicate a decrease in size from the original length. In general, because of the 1-hour soaking period, the temperature gradient firing produced dense bodies at a lower temperature than did the routine hand-moulded specimens fired in electric kilns where no soaking time was allowed.

The heating rates used to obtain the curves in Figures 9 to 24 are more rapid than in industrial practice. West (69) has discussed the significance of heating rates and laboratory procedures in the application of DTA, of linear change on heating, and of TGA, to the firing of bricks in a tunnel kiln. West showed, for example, that the dehydration of the clay minerals at about 600°C is spread over a wider range when the heating rate is 1 centigrade degree per minute than when it is 12 centigrade degrees per minute.

Thermal Expansion

In Figures 11 to 18 the thermal expansion curves of the unfired samples, both in reducing and in oxidizing atmospheres, are shown as 'linear thermal expansion before firing'. In Figures 19 to 23, only the thermal expansion curves that were obtained in the vertical dilatometer are shown, because atmosphere did not affect the results appreciably. In addition, the thermal expansion curves of the fired specimens are shown in Figures 11 to 23 and labelled 'linear thermal expansion after firing'. These latter curves are equivalent to those that would be obtained by cooling the once-fired specimens from the maturing temperature; they are mainly linear, except for the quartz expansion at the inversion temperature of 573°C.

Initially the unfired specimens expand gradually to about 500°C and then more rapidly to about 650°C. The curves obtained with the slow heating rate of 3.3 centigrade degrees per minute have a much broader

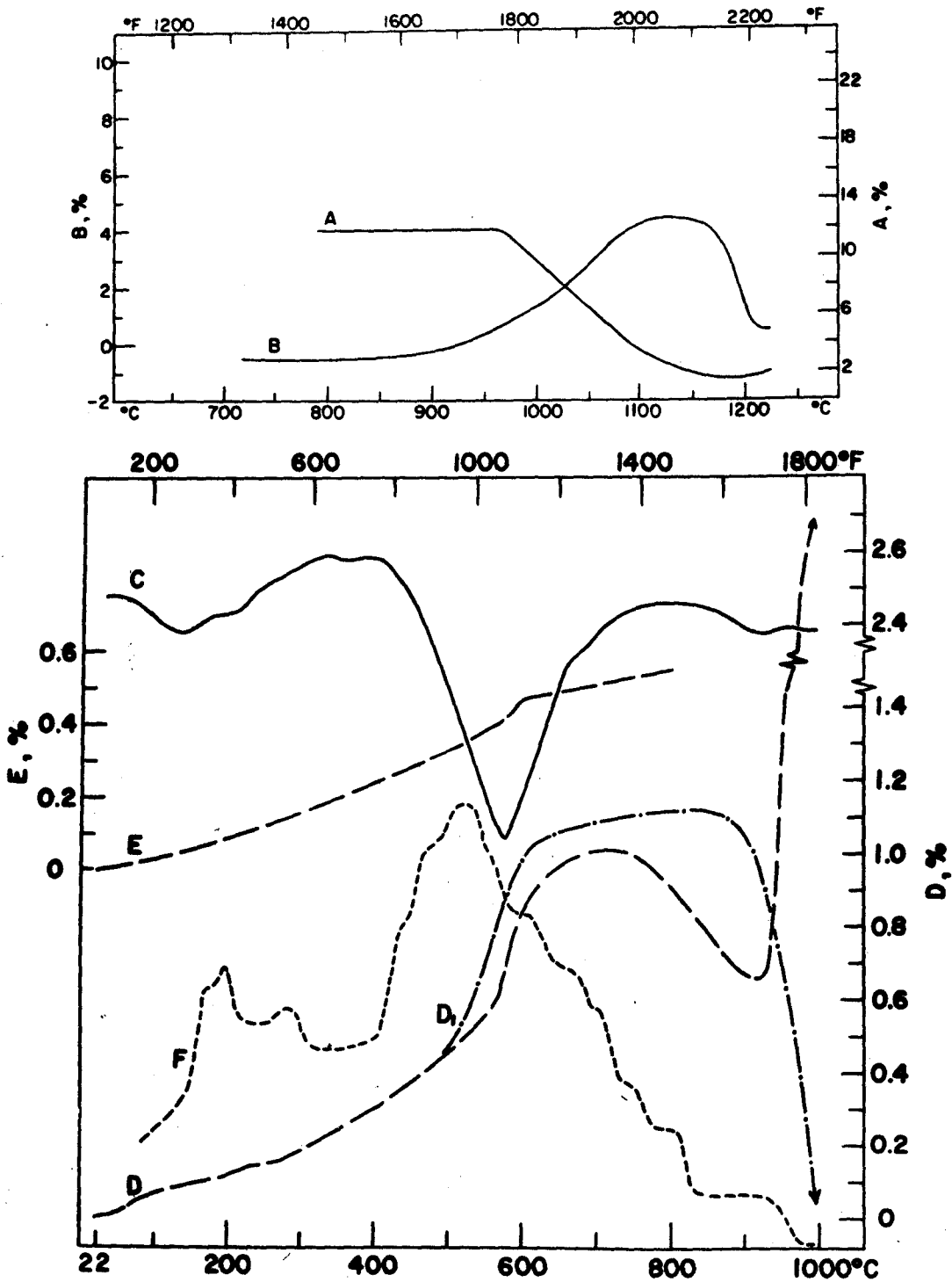


Figure 11. Firing Behaviour of Lauzon (Q.G.).

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing (reduction)
- D₁. Linear thermal expansion before firing (oxidation)
- E. Linear thermal expansion after firing
- F. Rate of weight loss

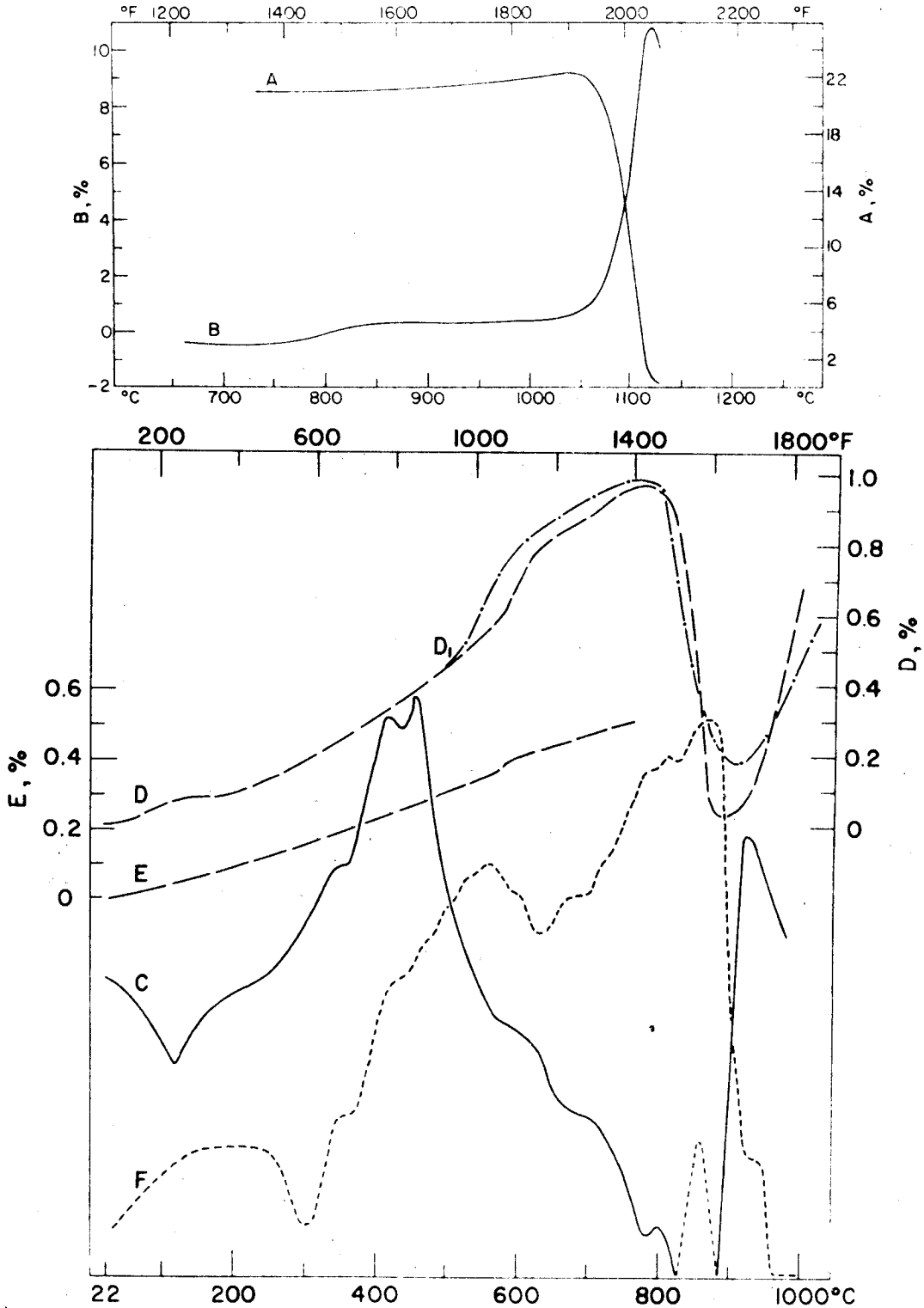


Figure 12. Firing Behaviour of Boischatel (U-L).

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing (reduction)
- D₁. Linear thermal expansion before firing (oxidation)
- E. Linear thermal expansion after firing
- F. Rate of weight loss

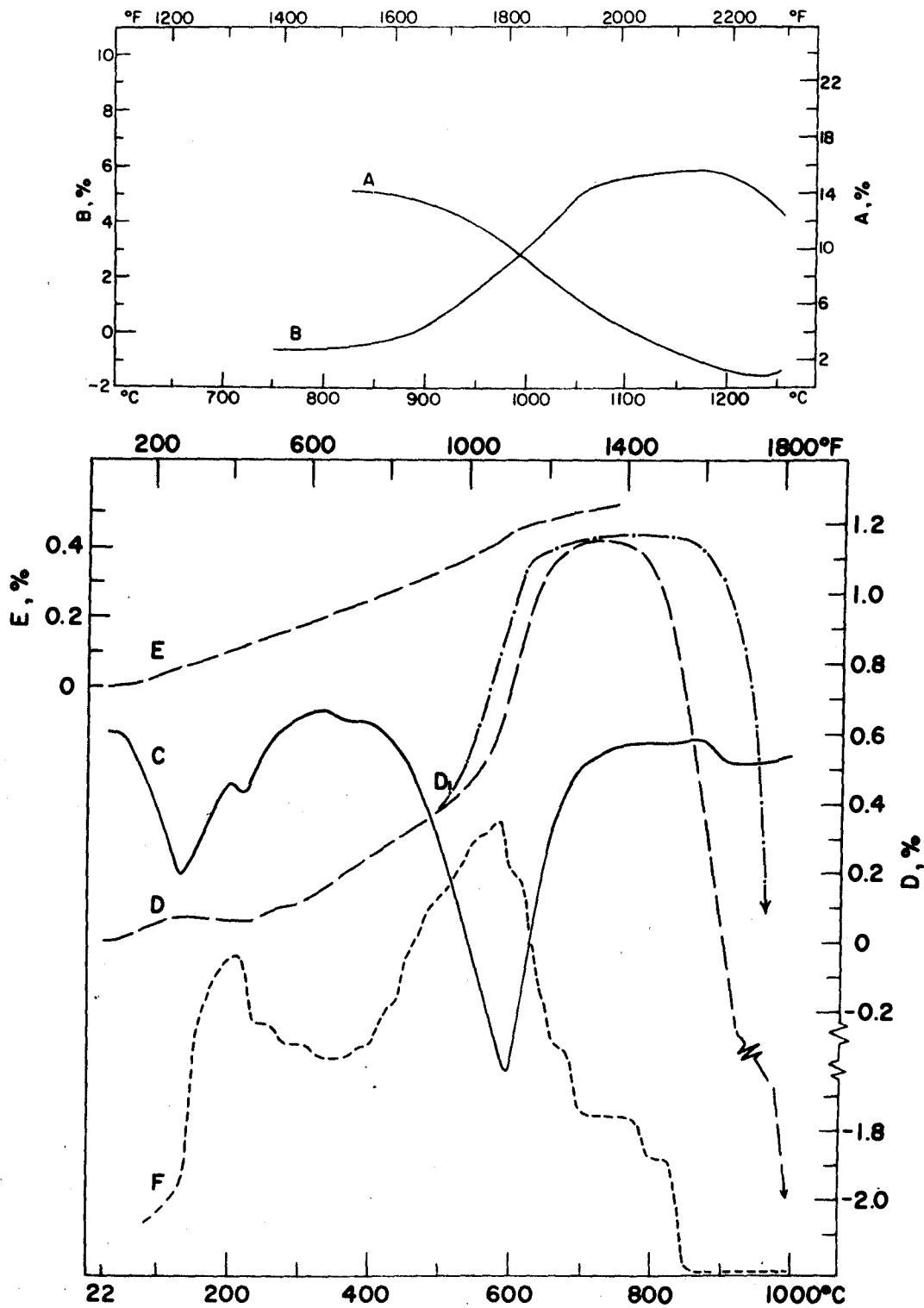


Figure 13. Firing Behaviour of Mont-Joli (Q.G.).

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing (reduction)
- D₁. Linear thermal expansion before firing (oxidation)
- E. Linear thermal expansion after firing
- F. Rate of weight loss

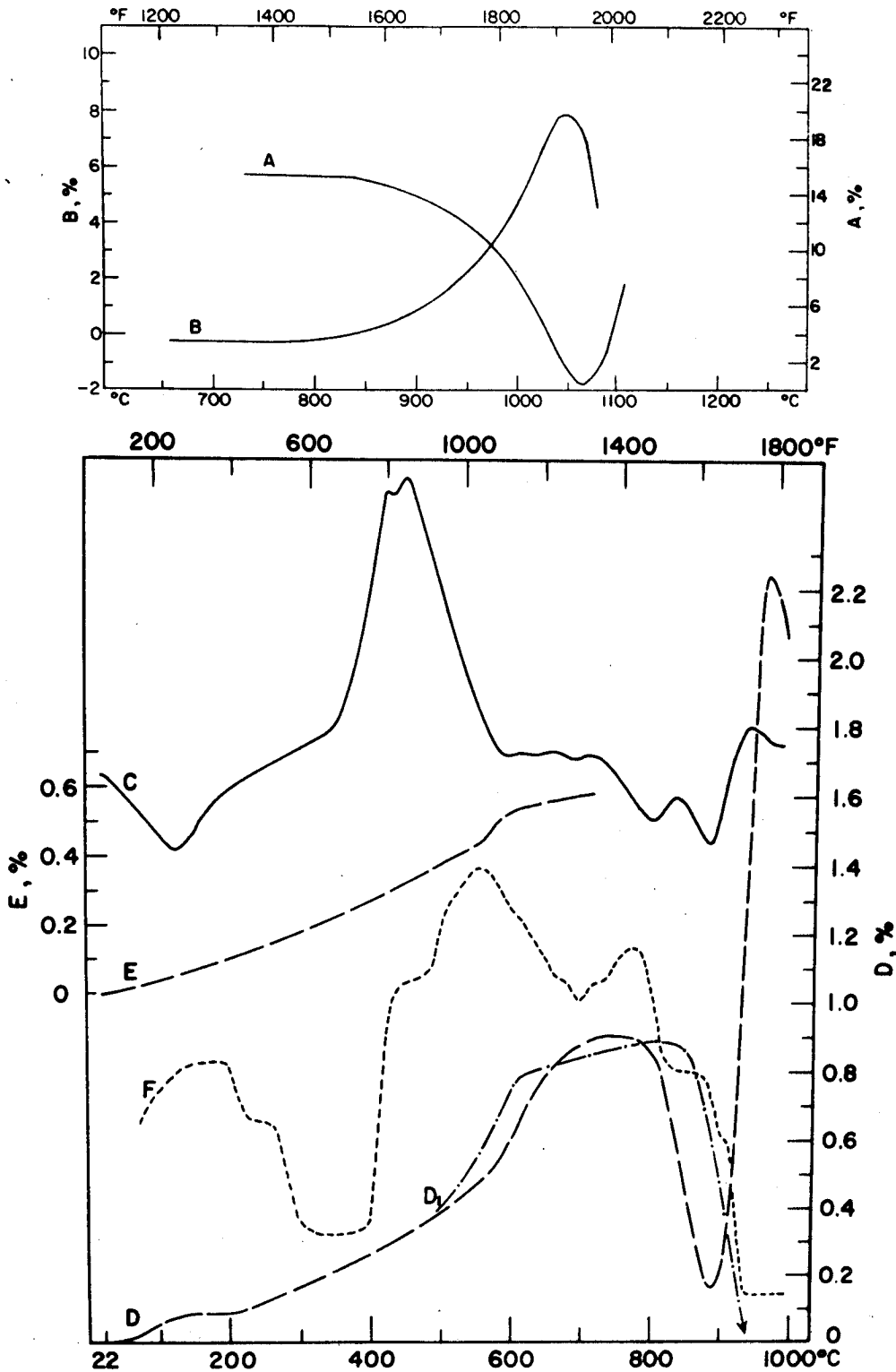


Figure 14. Firing Behaviour of Delson (U).

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing (reduction)
- D₁. Linear thermal expansion before firing (oxidation)
- E. Linear thermal expansion after firing
- F. Data of weight loss

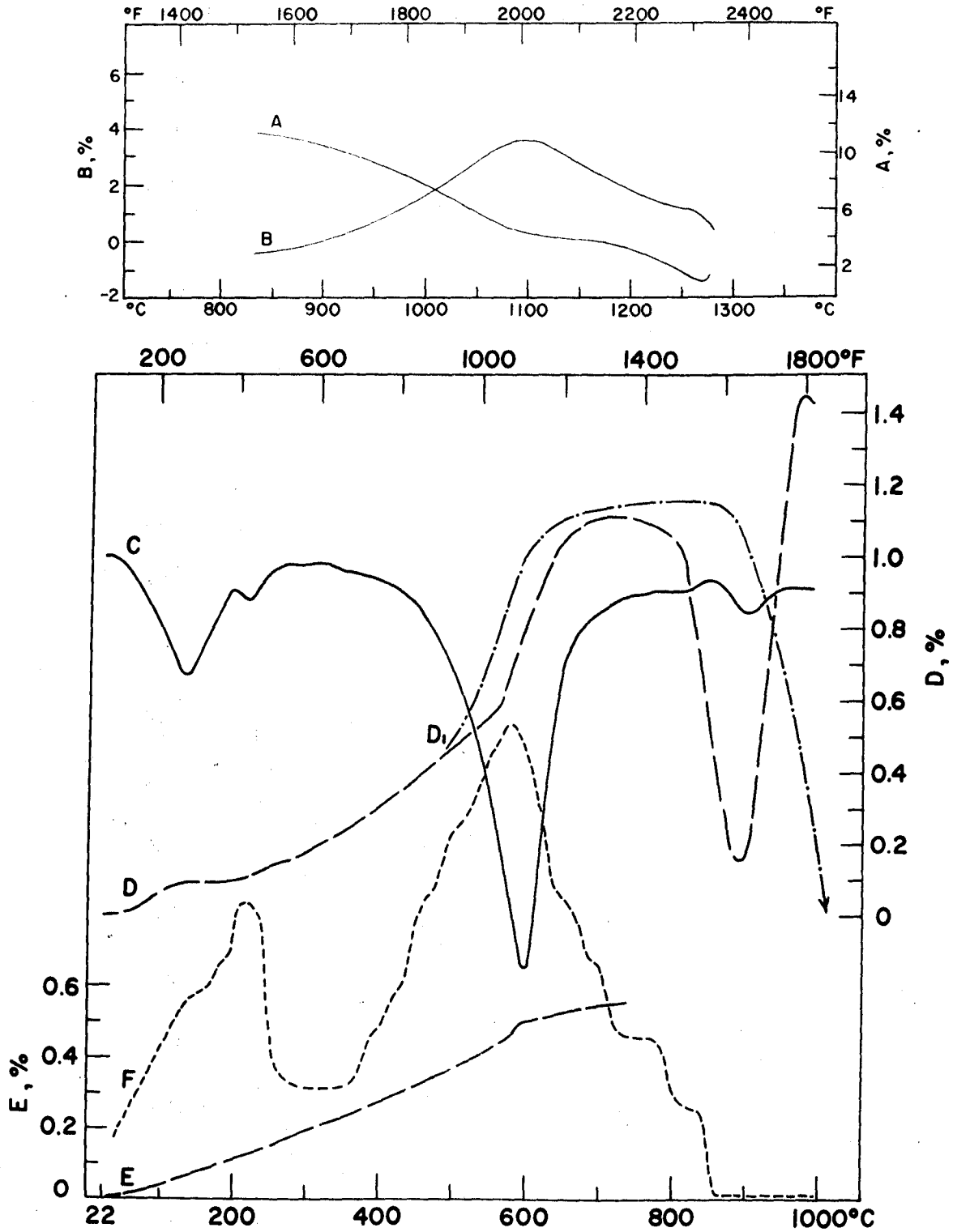


Figure 15. Firing Behaviour of St-Apollinaire (Q.G.).

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing (reduction)
- D₁. Linear thermal expansion before firing (oxidation)
- E. Linear thermal expansion after firing
- F. Rate of weight loss

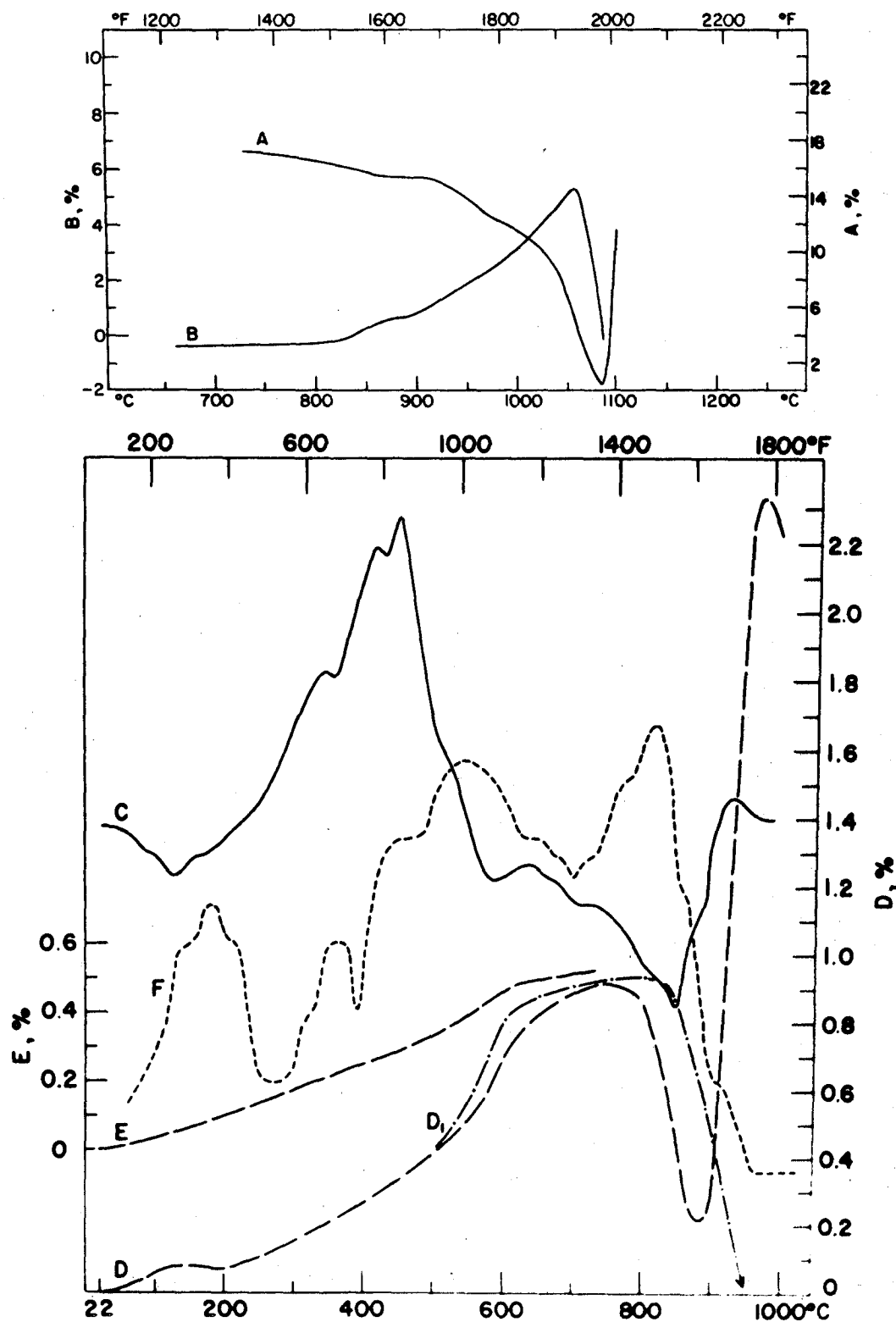


Figure 16. Firing Behaviour of Lotbinière (U).

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing (reduction)
- D₁. Linear thermal expansion before firing (oxidation)
- E. Linear thermal expansion after firing

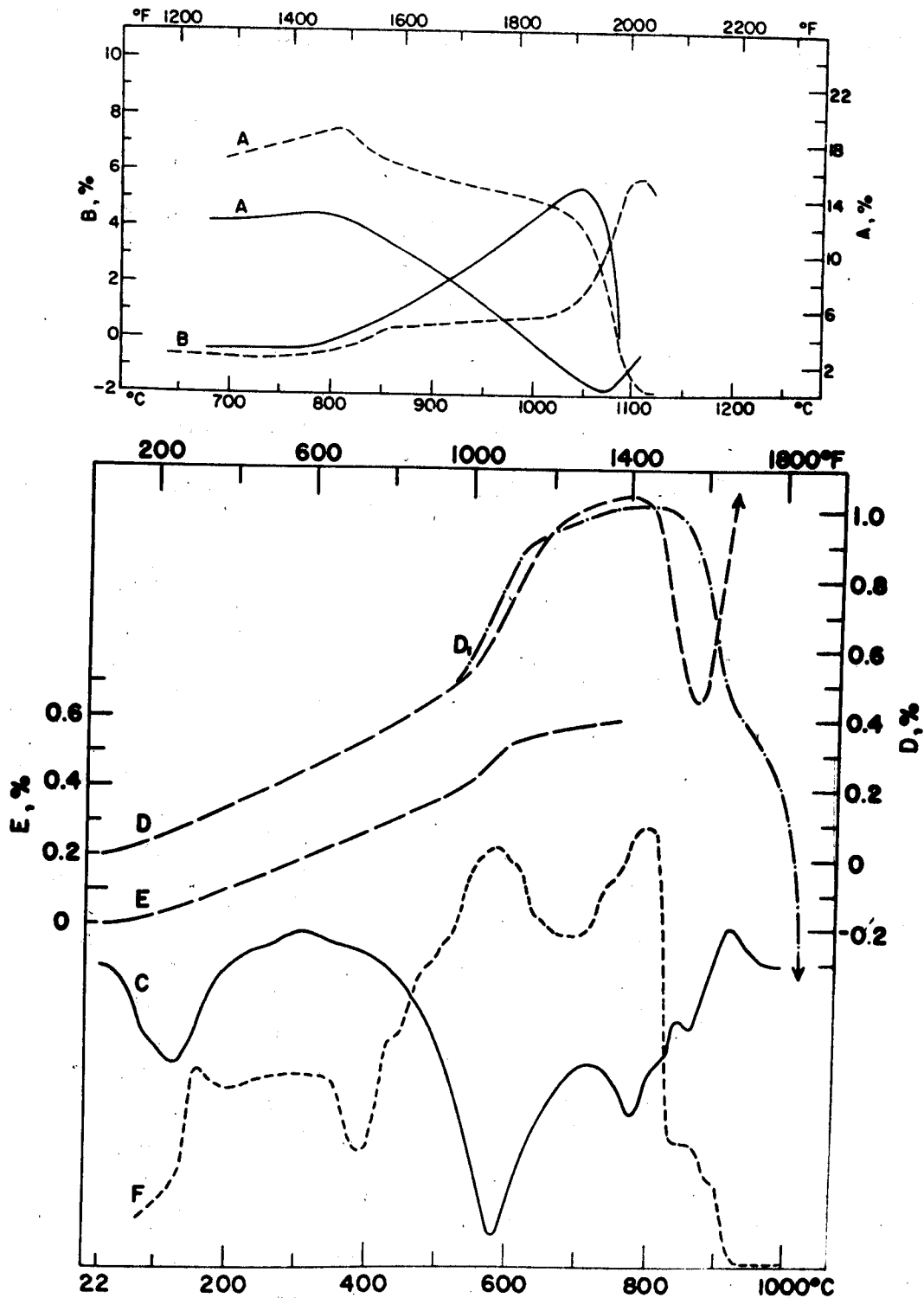


Figure 17. Firing Behaviour of Ste-Monique (Q).

- A.— Absorption Ste-Monique (Q)
- B.— Linear shrinkage Ste-Monique (Q)
- A.--- Absorption Georgetown, Ont. (Q)
- B.--- Linear shrinkage Georgetown, Ont. (Q)
- C. Differential thermal analysis
- D. Linear thermal expansion before firing (reduction)
- D₁. Linear thermal expansion before firing (oxidation)
- E. Linear thermal expansion after firing
- F. Rate of weight loss

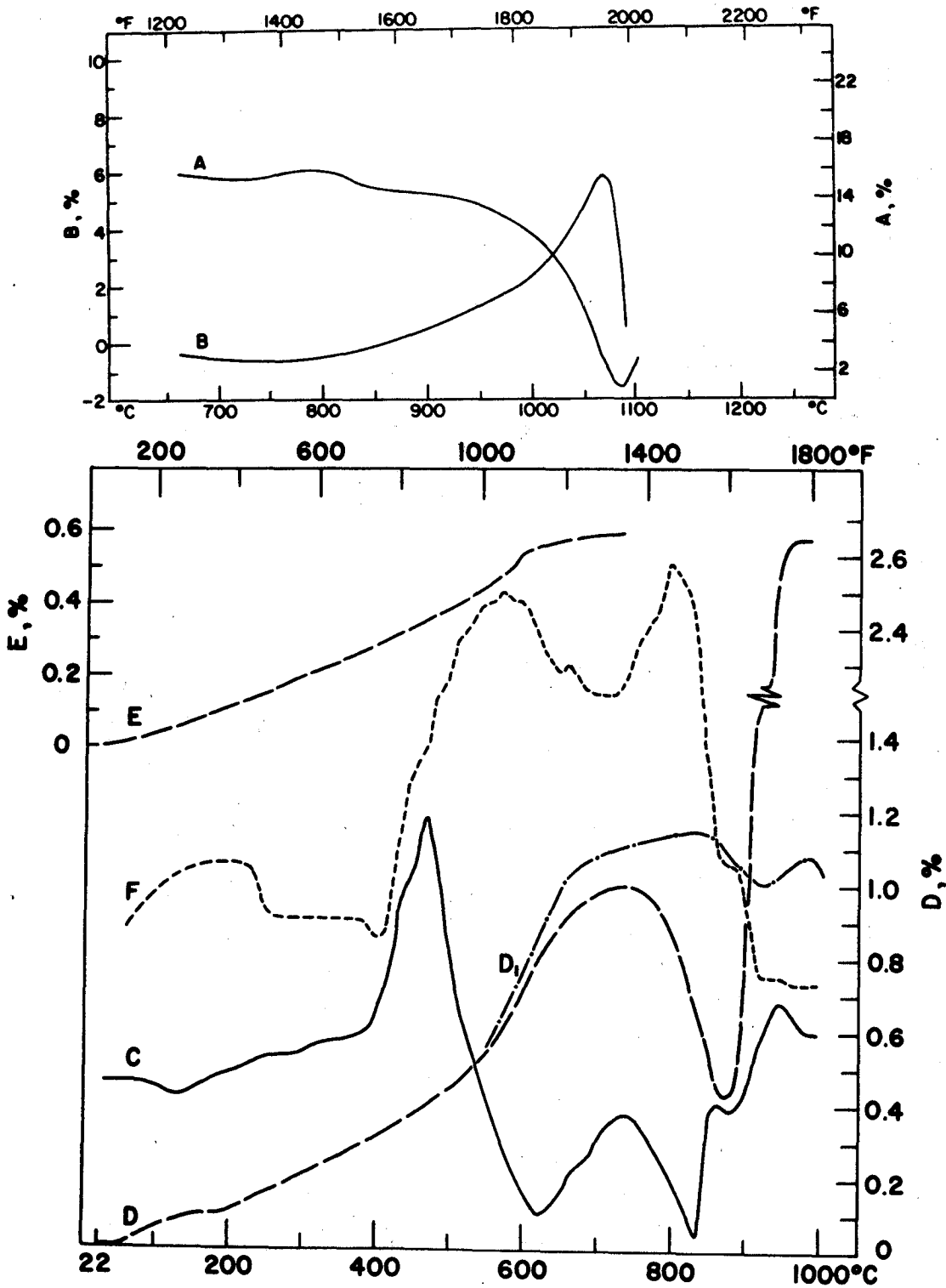


Figure 18. Firing Behaviour of Laprairie (L).

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing (reduction)
- D₁. Linear thermal expansion before firing (oxidation)
- E. Linear thermal expansion after firing
- F. Rate of weight loss

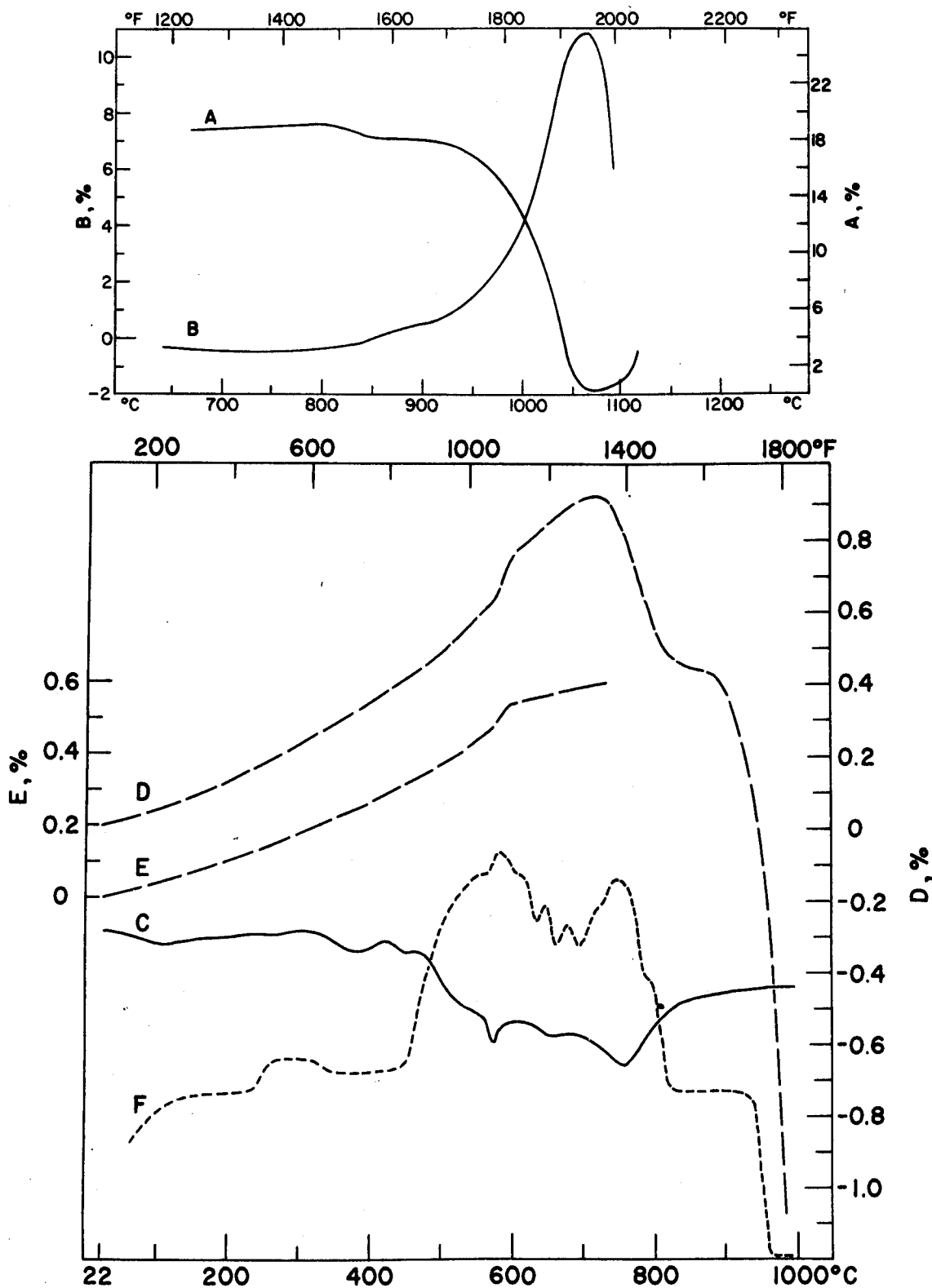


Figure 19. Firing Behaviour of Scott Junction.

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing
- E. Linear thermal expansion after firing
- F. Rate of weight loss

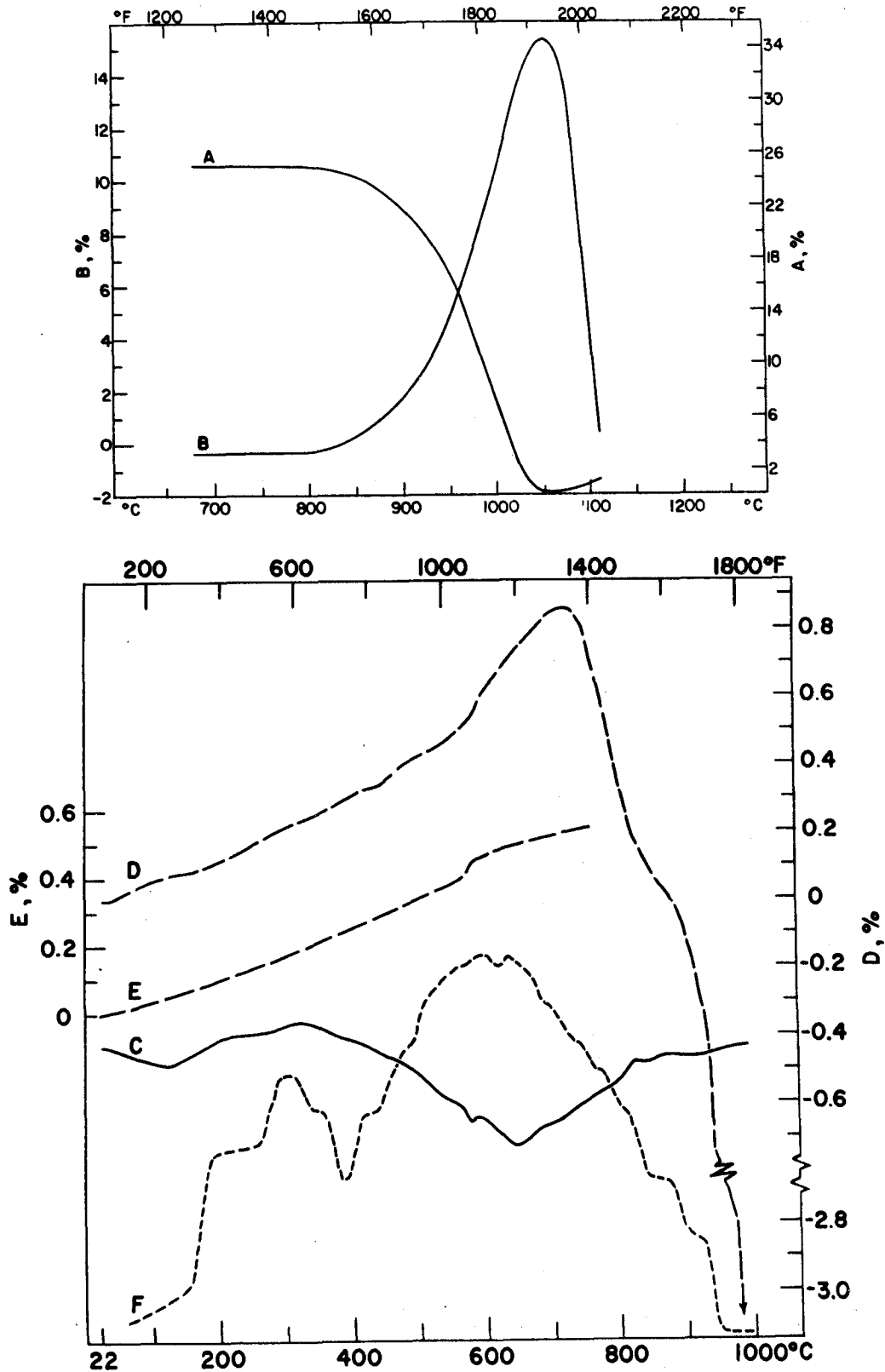


Figure 20. Firing Behaviour of East Angus.

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing
- E. Linear thermal expansion after firing
- F. Rate of firing

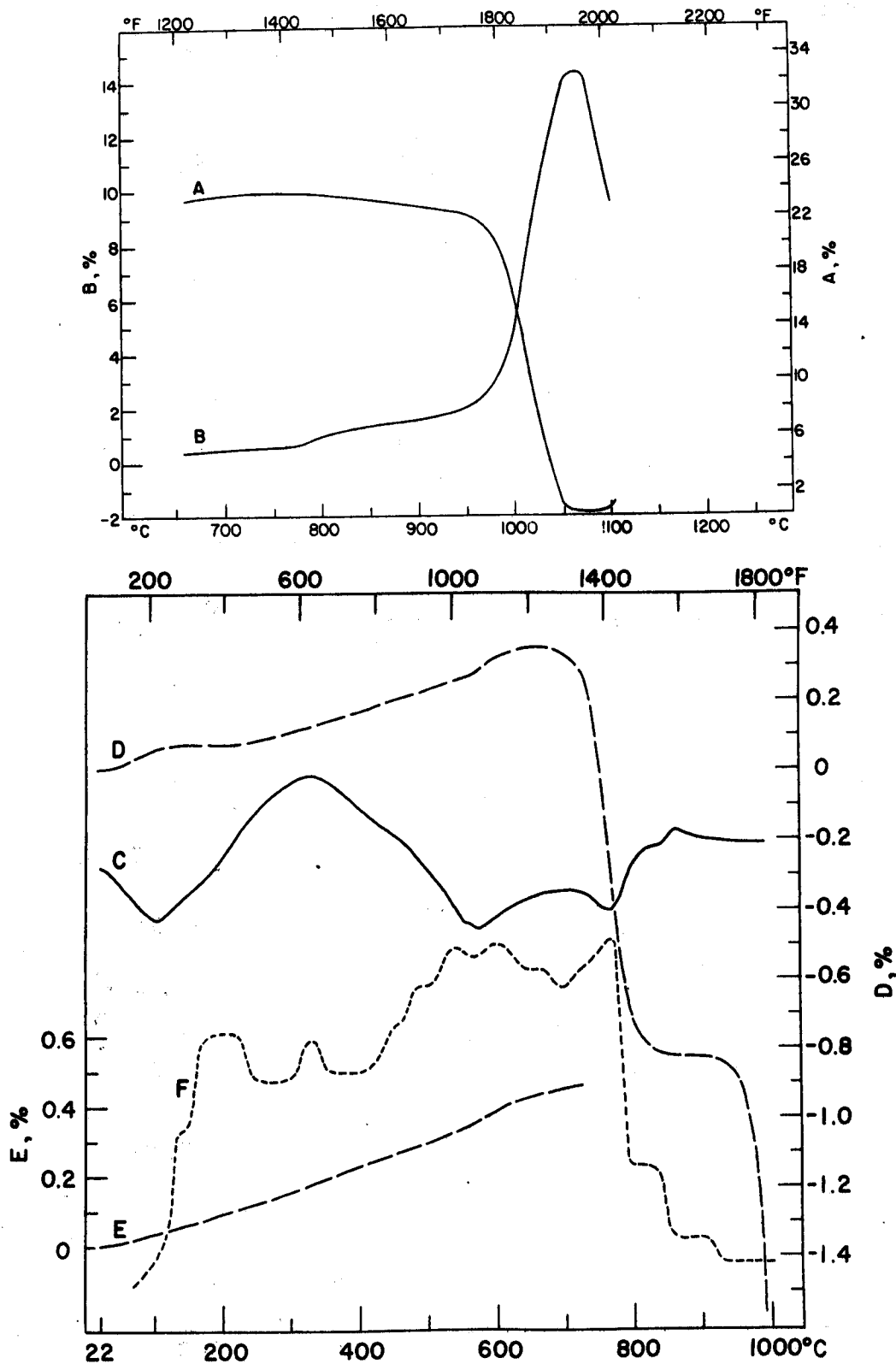


Figure 21. Firing Behaviour of Laprairie (Clay).

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing
- E. Linear thermal expansion after firing
- F. Rate of weight loss

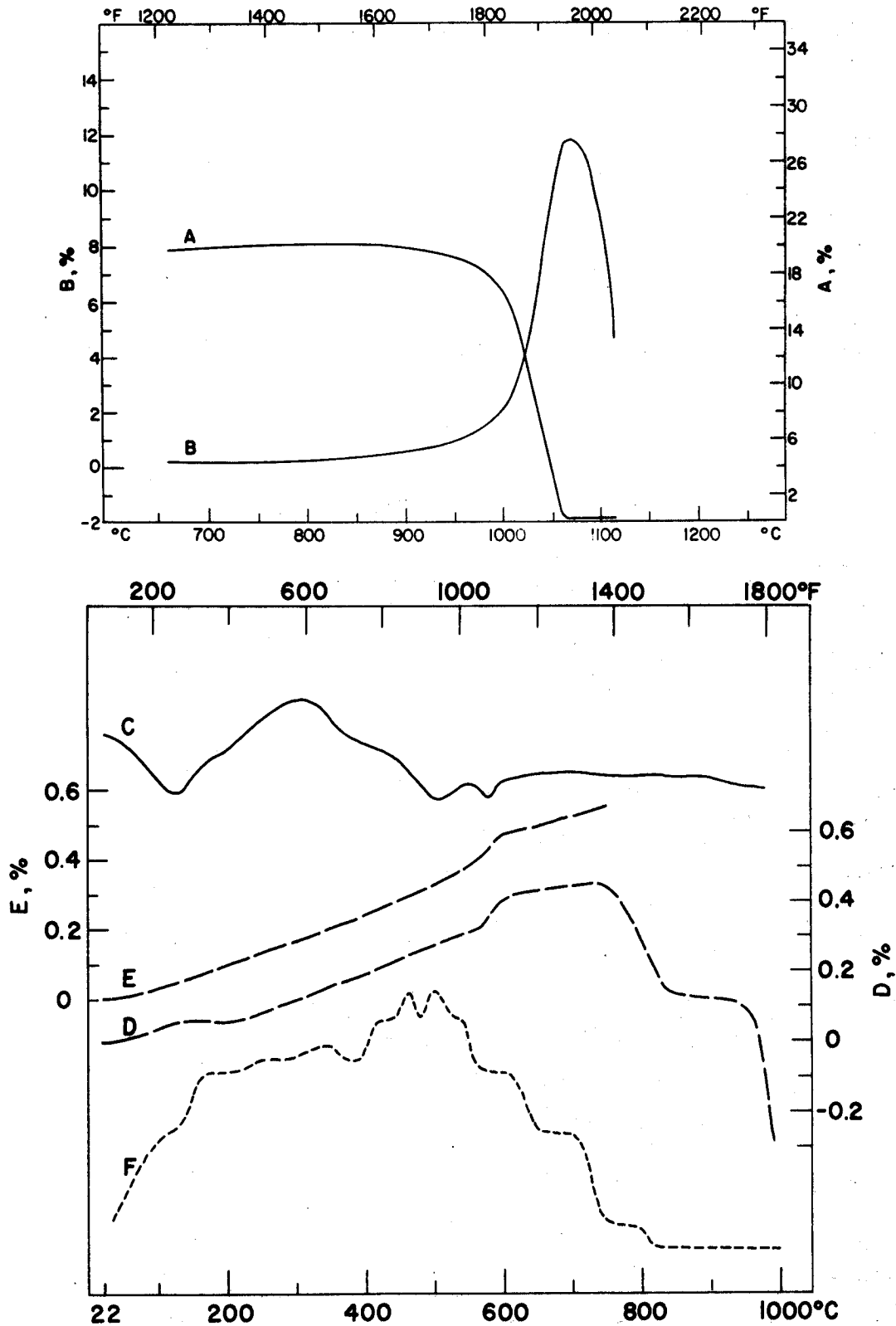


Figure 22. Firing Behaviour of Mistassini.

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing
- E. Linear thermal expansion after firing
- F. Rate of weight loss

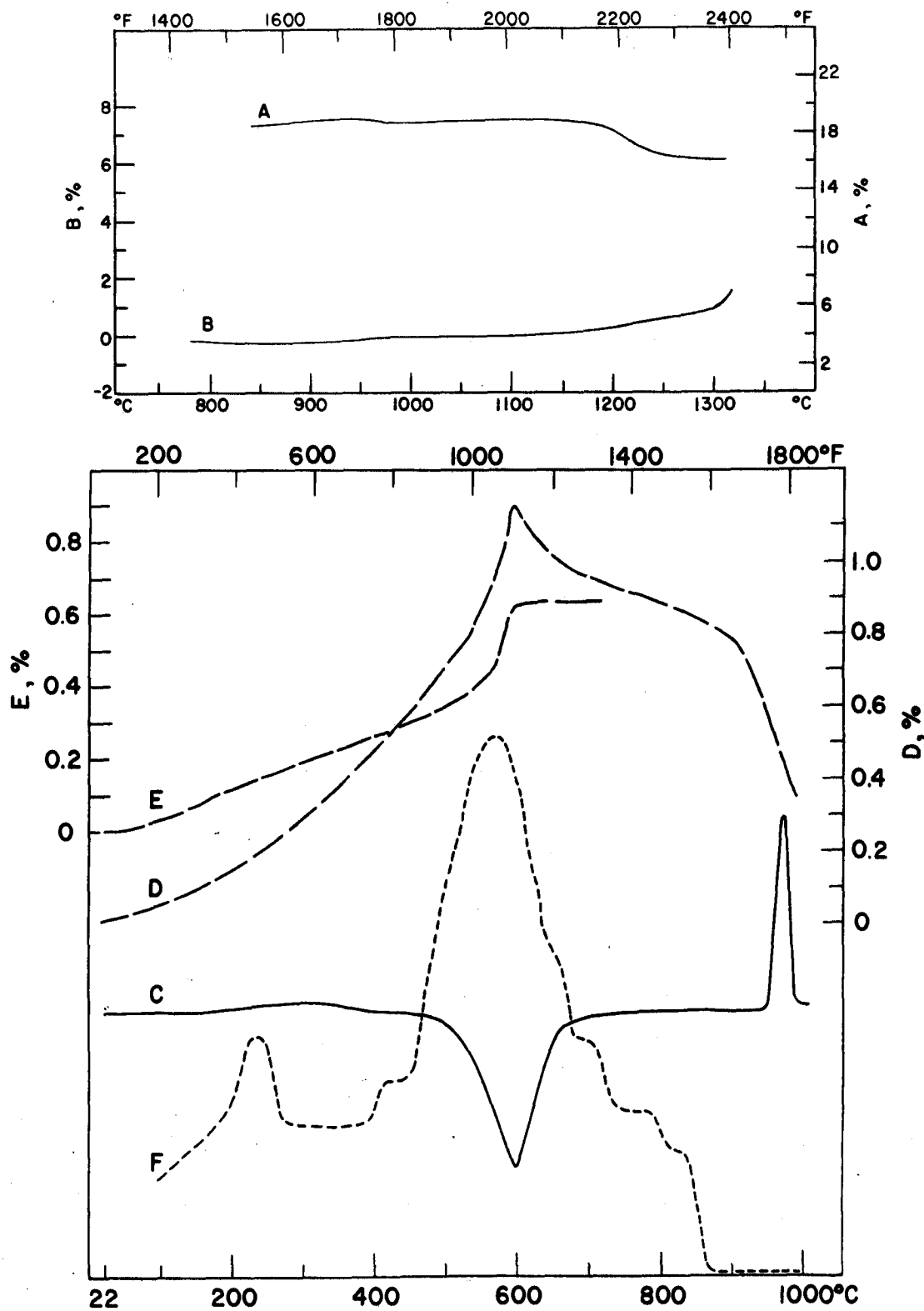


Figure 23. Firing Behaviour of Brébeuf.

- A. Absorption
- B. Linear shrinkage
- C. Differential thermal analysis
- D. Linear thermal expansion before firing
- E. Linear thermal expansion after firing
- F. Rate of weight loss

peak between about 600 to 800°C than do the curves obtained with the heating rate of about 10 centigrade degrees per minute. Shrinkage commences at about 700 to 800°C and, in some cases, proceeds above 1000°C until the material overfires, and, in other cases, reverses from shrinkage to expansion at about 850 to 900°C.

The reversal from shrinkage to expansion results from the expansion of a material high in calcite and/or dolomite, or from bloating induced by reducing conditions. West (69) has discussed this type of expansion curve for a Canadian Queenston shale made up principally of illite, chlorite and mica (all micaceous minerals), quartz, and dolomite. He noted that the expansion between 600 and 700°C resulted from the exfoliation of illite, chlorite, and mica in that order while they were dehydrating. He also noted that a sudden change from shrinkage to expansion at about 850°C coincided with the solid state reaction of magnesia and calcia from the decomposing dolomite with silica and alumina. Bell (70) has discussed the influence of lime on the thermal expansion of clay and has described the thermal expansion of some highly calcareous Canadian clays and shales of the illitic and chloritic type that have reversals from expansion to shrinkage and then shrinkage to expansion. The specimens from Boischatel and Laprairie have curves of the above type. Sharp reversals from shrinkage to expansion or visa versa could cause cracking during firing.

The curves of the unfired specimens from Lauzon, Delson, St. Apollinaire, Lotbiniere, and Ste. Monique showed reversals from shrinkage

to expansion at about 900°C, probably because of bloating induced by the reducing conditions in the vertical dilatometer. The curves produced under oxidizing conditions show continued shrinkage through 900°C instead of the reversal from shrinkage to expansion.

Paquin (71) has discussed the thermal expansion curves of mixtures of kaolin, muscovite and quartz. The sample from Brebeuf is of this type.

A summary of the quartz percentages in the unfired samples and in the fired thermal expansion samples is shown in Table 10. The percentages for fired specimens of Boischatel (U-L), St-Apollinaire (Q. G.) and Brébeuf were also determined by DTA and chemical analysis.

Discussions of Selected Samples

Lauzon (Q. G.)

The Lauzon (Q. G.) sample lacks plasticity (Figure 7) for the manufacture of extruded brick and probably requires fine grinding, a long pugging period, or the addition of a chemical or clay to increase plasticity. It is the least plastic of the Quebec Group shales studied. Because of the lack of fine-grained, plastic ingredients, this sample can be dried easily and has a small drying shrinkage. This shale is being used as a raw material for facing brick.

The curves in Figure 11 indicate that the Lauzon shale should not present many problems during firing. The absorption and shrinkage show that it has a greater firing range than the satisfactory minimum of about

TABLE 10

Summary of the Quartz Contents of
Selected Samples**

SAMPLE	UNFIRED		FIRED	
	Approx. Quartz from Chem. Anal., %	Approx. Quartz from DTA, %	Firing Temp., °C	Approx. Quartz from Thermal Expansion, %*
Lauzon (Q. G.)	25	19	1055	12
Boischatel (U-L)	25	12	1090	8 6 (DTA) 6.6 (Chem. Analysis)
Mont-Joli (Q. G.)	20	13	1060	9
Delson (U)	23	15	1000	11
St-Apollinaire (Q. G.)	25	16	1050	11 9 (DTA) 14.2 (Chem. Analysis)
Lotbinière (U)	28	17	1060	10
Ste-Monique (Q)	27	16	980	12
Laprairie (L)	24	19	1050	11
Scott Junction	22	21	1020	15
East Angus	18	15	990	10
Laprairie (Clay)	-	7	990	5
Mistassini	16	15	1000	13
Brébeuf	50	50	1315	43 46 (DTA) 35.5 (Chem. Analysis)

*Percentages based on discontinuity on thermal expansion curve of fired specimens at about 570 to 590°C. A rock containing 100% quartz (No. 179 in Mines Branch Jet Piercing Research Project Report IR 62-27) had 0.4 per cent linear expansion at the point of sharp discontinuity and this figure was used as a standard reference.

**There is little agreement in the quartz percentages obtained by the various methods employed. The amounts are approximate, and further work remains to be done in this field.

35°C necessary for face brick production, where 8 per cent or less absorption is desirable. With its firing range of about 70°C for absorptions of 8 to 4 per cent, hard dense face brick having fairly uniform properties such as colour, hardness, shrinkage and absorption can be obtained. This is a typical non-plastic shale from the Quebec Group that has good firing properties.

The DTA curve shows that the reactions during heating are relatively simple. There is a prominent peak at 580°C, indicating that the sample contains a substantial proportion of illitic and chloritic clay minerals. The very small, dull peaks at about 900°C are typical of a combination of chlorite and illite. There are no large quantities of oxidizable materials or carbonates to complicate the firing schedule. The broad peak at about 200°C suggests that the sample contains a substantial amount of adsorbed water for a shale.

The peak at 200°C on the rate of weight loss curve indicates a rapid loss of absorbed water. Another small peak at about 300°C shows that the organic material burns out rapidly at this temperature. The very large peak on this curve at 580°C indicates that the clay mineral structures are breaking down rapidly, with illite probably being the main one. A small shoulder at about 600°C is caused by the breakdown of a second clay mineral, probably chlorite. Other shoulders at temperatures beyond 650°C suggest that other small reactions are occurring.

The sample has a relatively small weight loss, of about 3.9 per cent, of which about 2.9 per cent is produced by the loss of hydroxyls from the clay minerals (Figure 9). The removal of water vapour produced by this reaction should not be a serious problem but draft must be provided.

The shape of the thermal expansion curves of the unfired Lauzon specimens to about 700°C is initially similar to most expansion curves for illitic and chloritic shales. In addition, these curves for reducing and oxidizing conditions coincide until about 500°C, where D_1 diverges slightly from D for the remainder of the test as shown on Figure 11 (this situation applied also to Figures 12 to 18 inclusive). The material expands on a gently upward sloping curve until the combination of the quartz inversion with the effect of the rapid exfoliation of the micaceous minerals results in an accelerated rate of expansion. The curves then reverse gently from expansion to shrinkage, with the curve obtained at the slow heating rate in the Seger dilatometer (oxidizing conditions) having a very broad peak and continuing downward. Under reducing conditions in the vertical dilatometer the test specimen apparently bloated, and the curve changes abruptly from shrinkage to a very rapid rate of expansion at 920°C. The rapid reversal at this temperature, coupled with the high rate of expansion, may cause firing cracks under reducing conditions unless close temperature control and a slow temperature increase are maintained.

The linear thermal expansion curve of the fired sample (Figure 11) shows a small sudden expansion at about 573°C, caused by quartz. The quantity is small (Table 10) when compared to the large amount in the fired Brebeuf specimen, and cracking during cooling is not likely to occur at the quartz inversion temperature.

Boischatel (U-L)

The Boischatel sample (Figure 8) has about the same plasticity as the standard Cooksville (D-M) (Figure 7), and consequently has just sufficient plasticity for extruding brick and possibly tile. This material has been used as a brick raw material for many years. The sample has more plasticity than the Lorraine and Utica samples from Laprairie and Delson in the Montreal area. As in the case with shales, it dries readily and has a small drying shrinkage.

The curves in Figure 12 indicate that the Boischatel shale has several problems during firing. This is a highly calcareous material and the shrinkage and absorption curves show that, typical of highly calcareous materials, it has a very short firing range for the production of dense products such as facing brick. Small increases of temperature produce large changes in shrinkage and absorption. Vitrification begins abruptly at about 1050°C and proceeds rapidly, resulting in difficulty in firing any product with less than about 15 per cent absorption. The

sample is a typical plastic one from the Utica-Lorraine Group that is highly calcareous and has excessive oxidizable material.

The DTA curve shows that the sample has major reactions from carbonaceous materials and pyrite at about 400°C and from dolomite and calcite between about 750 and 875°C. The clay reactions are obscured by these very intense reactions.

A broad peak at about 200°C on the rate of weight loss curve indicates a gradual loss of adsorbed water. A rising peak with shoulders at 350°C and 400°C indicates the rapid oxidation of organic material and pyrite respectively. Peaks at 550°C and 625°C indicate the breakdown of illitic and chloritic clay minerals. The peaks at 775°C and 850°C show the maximum points of decomposition of dolomite and calcite.

The sample has a large weight loss of 13.3 per cent, of which about 2.50 per cent is from clay minerals, 9.5 per cent from dolomite and calcite, and the balance from a substantial amount of oxidizable material and some adsorbed water.

Chemical analyses show that the sample contains a sufficient amount of organic material (0.45%), and of sulphur (0.81%) from pyrite, to cause bloating and black-coring unless a long oxidation period is provided when they decompose. Further, the decomposition of pyrite produces sulphurous gases, which will likely contribute to scumming and efflorescence unless they are removed from the kiln (Brownell 72, 73). The water

vapour produced by the breakdown of the clay minerals is not excessive, but it also adds to the volume of gases evolved by the carbonaceous material and pyrite. A very large volume of carbon dioxide is released into the kiln when the carbonates decompose. This CO_2 affects the pressure and drafts and may possibly cause a misinterpretation of flue-gas analysis, which could result in fuel wastage. In addition, the evolution of carbon dioxide from the material could prevent the penetration of the kiln atmosphere and thus have a serious effect on the final colour, since products fired from this material will probably be faint pink in an oxidizing atmosphere and buff in a neutral or reducing atmosphere.

The expansion characteristics of this shale during firing are much the same in an oxidizing or a reducing atmosphere. The raw material expands about 1.0 per cent up to about 775°C and then quickly reverses to shrinkage. It shrinks back to about its original length and suddenly reverses again at about 890°C . Although the reversals are not as sudden as for the very calcareous samples from Nelson (27) and Estevan (74), the thermal expansion curves during firing are similar. Because of the reversals from expansion to shrinkage and then from shrinkage to expansion, this shale may have a cracking problem during firing in either oxidizing or reducing conditions. A product, such as a brick heated rapidly through 775°C , could be shrinking at the surface and expanding in the interior, thus creating severe tensile stresses at the surface. When these stresses exceed the cohesive strength of the material, cracking

occurs -- the "heating-up" cracks referred to by Groskaufmanis (75). Robinson (76) has suggested that firing schedules should be programmed to provide a uniform rate of expansion throughout the burn. Such a procedure seems particularly suitable for materials of this type. The same argument applies at 890°C, where the exterior of a rapidly heated product could be expanding while the interior is shrinking.

According to Table 10, there is about half the original amount of quartz remaining in the fired sample, and its small expansion (Figure 12) should cause no difficulty in cooling.

Judging from the DTA and X-ray diffraction data for the Beauport (U-L) sample, it will have problems during firing somewhat similar to those encountered with Boischatel (U-L).

Mont-Joli (Q.G.)

The curve for Mont-Joli (Q.G.) (Figure 8) indicates that this material has sufficient plasticity for extruding brick, tile, and possibly sewer pipe. The sample dries readily and has a fairly small drying shrinkage. The very prominent adsorbed water peaks on the DTA curve (Figure 1 and Figure 13) suggest that there may have been some weathered shale in the sample. The sample extruded exceptionally well in the laboratory.

The absorption and shrinkage curves in Figure 13 indicate that, like Lauzon (Q.G.), the Mont Joli sample should be relatively easy to fire

to a hard, dense condition. This shale has a long firing range that, coupled with its unfired properties, indicates that it should be suitable for production of brick, tile, and possibly sewer pipe. The de-aired shale (Table 1) vitrifies at a much lower temperature than does the hand-moulded specimens (Table 1 and Figure 13). It fires to a hard dense condition at about 1030°C, a very low temperature for a shale having a PCE of 16. It is likely that de-aired specimens from Lauzon, St. Apollinaire and Ile d'Orleans, all common shales from the Appalachian region (Quebec Group) that have PCE's of 14 to 16, would also have relatively low maturing temperatures, well below their melting temperatures. This is in contrast to the Utica and Lorraine shales, whose PCE's are about 1 to 4 (Tables 1 and 2) and which fire to a hard dense condition very close to their melting temperatures. The Mont Joli sample is a typical plastic shale from the Quebec Group, with few firing problems.

The rate of weight loss curve and the DTA curve in Figure 13 are similar to those for Lauzon (Q. G.). The shale loses a small amount of weight from adsorbed water very rapidly at 200°C. It loses a further 3.75 per cent of its weight, out of a total loss of 5.05 per cent, from the breakdown of the clay minerals (Figure 9) at about 600°C. This loss in the form of water vapour is not excessive, but it must be removed to prevent a possibility of condensation and resultant scumming or kiln marking.

The thermal expansion curves of the unfired specimens (Figure 13) in oxidizing and reducing conditions are alike. They show a large and rapid rate of expansion from about 550°C to 600°C, due to the inversion of quartz and exfoliation of the micaceous clay minerals. West (69) points out that, fortunately, normal heating rates are low in this temperature range, preventing the development in the ware of steep temperature gradients that would cause differential expansion stresses that could result in rupture. As firing proceeds, the curves reach a maximum at about 1.1 per cent expansion at 800°C; then rapid shrinkage takes place, reaching a value of about 2.0 per cent at 1000°C, and continues.

The expansion curve of the fired specimen is mainly linear and the small quartz expansion at 573°C should not cause any cooling cracks.

The results in Table 1 and the DTA curves in Figure 1 indicate that Ile d'Orléans(Q.G.) has properties similar to Mont-Joli (Q.G.) and, except for the presence of more oxidizable material in the former, they probably behave the same during firing.

Delson (U)

The area under the plasticity curve for Delson (U) (Figure 8) is less than that for the standard Cooksville (D-M). Consequently, this sample probably requires a combination of fine grinding and an additive to increase plasticity before it will extrude. The shale has been used for many years for production of stiff-mud brick in combination with a plastic surface clay.

The temperature gradient curves for shrinkage and absorption in Figure 14 indicate that this material has a satisfactory firing range for production of hard, dense facing brick.

The DTA curve shows that the sample has a major reaction at about 450°C, from the oxidation of carbon and pyrite, which obscures the reaction caused by the breakdown of the clay minerals. The chemical analyses in Table 7 show that it contains 0.50 per cent organic and elemental carbon and 1.09 per cent sulphur, quantities sufficient to cause bloating or black coring under rapid firing conditions. The large volume of sulphurous gases must also be removed to prevent them from contributing to scumming and efflorescence. The rate of weight loss curve has a broad peak from 400 to 650°C where the evolution of CO₂, SO₂ and H₂O occurs. Out of a moderate weight loss of 5.35 per cent, about 4 per cent occurs in this temperature region. A further 1 per cent is lost from the breakdown of carbonates, with the maximum loss from this source occurring at about 775°C.

The rate of weight loss and the DTA curves for Delson (U) are very similar to those for the Billings shale from the Ottawa area (27), indicating that they probably behave alike during firing. Exfoliation of the micaceous minerals in Delson (U) starts at a slightly higher temperature than for the Quebec Group shales from Lauzon, Mont Joli and St. Apollinaire. The thermal expansion curve for reducing conditions has a very sharp peak at about 890°C, where shrinkage changes to rapid expansion.

There is a possibility of firing cracks or bloating occurring if the rate of temperature increase is too great at this point. Under oxidizing conditions the material continues to shrink instead of expanding again at 890°C. In view of the serious bloating problem under reducing conditions, it is likely that oxidizing conditions should be maintained during firing.

According to Table 10, the fired Delson (U) sample has about half the amount of quartz contained in the original sample. Inasmuch as the original amount was about 20 per cent, there should be no problem in cooling products fired from this shale under normal cooling conditions.

St-Apollinaire (Q. G.)

St-Apollinaire (Q. G.) has about the same plasticity (Figure 8) as Mont-Joli (Q. G.) and consequently it, too, should be suitable for extruded ware such as brick and tile and possibly sewer pipe. The adsorbed water peak on the DTA curve (Figure 15) is prominent and suggests that the sample, as with Mont-Joli (Q. G.), may contain some weathered shale. The sample is safe drying and the drying shrinkage is low.

The absorption and shrinkage curves (Figure 15) show that it has a very long firing range. The shrinkage curve indicates that the material reverts from shrinkage to expansion at a relatively low temperature of 1100°C, indicating that the temperature gradient bar may have bloated slightly. In addition to its plasticity, the fired properties also suggest that this shale should be suitable for brick, tile, and possibly sewer

pipe. De-airing would produce denser bodies and probably is required to produce close to zero absorption.

Typical of the Quebec Group shales that were examined, there appear to be no major problems in firing, particularly under oxidizing conditions. The DTA and rate of weight loss curves (Figure 15) are similar to those for Lauzon (Q. G.) and Mont-Joli (Q.G.). Out of a total weight loss of 4.40 per cent, about 3.5 is produced by the breakdown of the clay minerals. The thermal expansion curves of the unfired specimens have the same general shape as those for Lauzon. Under reducing conditions the unfired sample bloats, and under oxidizing conditions the sample continues to shrink beyond 900°C.

The curve of the fired material indicates there should be no problem in cooling, since the amount of quartz is about 11 per cent (Table 10).

Lotbinière (U)

The Lotbinière sample has about the same plasticity as Cooksville (D-M) (Figure 7), and consequently it should be possible to extrude such products as brick and tile. Its plasticity is less than that of the Mont Joli and St. Apollinaire samples. The material dries safely and it has a low drying shrinkage, properties common to most shales.

The absorption and shrinkage curves (Figure 16) of Lotbinière (U) show that it has a short but probably manageable firing range if close

control of temperature is maintained. It has a shorter firing range than the Delson sample, which is a Utica shale from the Montreal area.

The DTA curve shows that the sample has a large quantity of oxidizable material and a substantial quantity of dolomite and calcite. The problems of gas removal, and bloating and black coring, are similar to those described for Delson (U). The Lotbiniere sample contains more dolomite and calcite than does Delson (U) but much less than Boischatel (U-L). However, sufficient draft is necessary to remove the CO₂ from the kiln atmosphere; otherwise, reducing conditions could prevail.

The weight loss is a moderate 6.85 per cent, 3.30 per cent of which is produced by the breakdown of the clay minerals and 2.45 per cent by the decomposition of the carbonates (Figure 9). The rate of weight loss curve is similar to the one for Delson (U), although the various peaks are generally larger because of the greater weight loss from adsorbed water and carbonates.

The thermal expansion curve of the unfired specimen, like Delson (U), has a very sharp reversal from shrinkage to expansion at about 890°C under reducing conditions, where a slow heating rate is probably desirable to prevent cracking or bloating. Under oxidizing conditions the test specimen, like Delson (U), expands initially and then reverses to rapid shrinkage without any expansion beyond 890°C. Considering the composition and the bloating characteristics, it is likely that oxidizing conditions should be maintained during firing.

The expansion caused by quartz in the fired specimen is about 10 per cent (Table 10), an amount that should not cause cooling difficulties.

Ste-Monique (Q)

The Ste. Monique sample has poor plasticity (Figure 8), and consequently requires fine grinding and probably the addition of some substance to increase plasticity. Its plasticity is probably better than that of the Queenston shale from the Ottawa area, but it is less plastic than many of the shales used in the Toronto area (85).

The absorption and shrinkage curves in Figure 17 show that this material has a very long firing range and that it becomes dense before 1000°C. The curves may be compared in the same Figure with those of a Queenston shale from Georgetown, Ont. (27). The latter has an average carbonate content for a Queenston shale and its absorption and shrinkage curves are typical. The firing range of Georgetown (Q) is short, a feature encountered in many Queenston shales from Ontario. Both samples in Figure 17 were extruded and de-aired. The de-airing has probably helped contribute to the low firing temperatures for Ste-Monique (Q), but it nevertheless matures at a temperature about 100°C lower than does Georgetown (Q).

In spite of the sample being non-plastic, the DTA and rates of weight loss curves of Ste-Monique (Q) show that the sample contains a substantial amount of adsorbed moisture which is given off at a rapid rate at about 150°C. The intense sharp peak on the DTA curve at about 580°C

suggests that the clay minerals break down over a narrower temperature range than the Ontario Queenston shales (27). It is also apparent, from the peak at 775°C, that this sample contains less carbonate than the Ontario Queenston shales. The sample has a small amount of organic material which should burn out with ease.

Under reducing conditions Ste. Monique (Q) has an expansion curve similar to that of Boischatel (U-L) and the typical high-lime Queenston shales of the Toronto area. The sharp reversal from shrinkage to expansion indicates that a slow rate of temperature increase is necessary at about 860°C if the atmosphere is reducing. Under oxidizing conditions the specimen continues shrinking from about 800°C, with a decrease in rate between about 900 and 975°C.

Like Delson (U), about half of the original quartz percentage remains unreacted in the fired specimen (Table 10), but this should not cause difficulty during cooling.

Laprairie (L)

The Laprairie (L) shale is exceedingly non-plastic (Figure 8), and requires fine grinding and the addition of some material to increase plasticity for the manufacture of extruded ware. This material has been used for many years for the production of dry-pressed facing brick.

The adsorption and shrinkage curves are similar to those of Lotbinière (U) and feature a short firing range (Figure 18).

The DTA curve and the chemical analysis (Table 7) show that the sample contains less organic material and pyrite but more carbonates than Delson (U). The amount of oxidizable material is sufficiently high to cause bloating, unless the material is fired slowly while oxidation is taking place. Out of a weight loss of 5.75 per cent, 3.20 per cent is produced by clay minerals, 1.00 per cent by carbonates, and the balance by adsorbed water and oxidizable material. The volume of gases is not nearly so great as for Boischatel (U-L), but proper draft is required to eliminate them.

The thermal expansion curves of unfired Laprairie (L) specimens are typical of high-lime materials. The one obtained under reducing conditions suggests that bloating occurred beyond 875°C as well as "high-lime" expansion. A slow heating rate is probably necessary at the temperature where the curves change from shrinkage to expansion.

The thermal expansion curve of the fired specimen indicates that no difficulty should be experienced during cooling.

The Breckenridge (R) sample has properties somewhat similar to those of Laprairie (L) (Table 2) and the Rockcliffe sample from Ottawa (27). The DTA curves (Figure 2) indicate that Breckenridge (R) contains smaller amounts of oxidizable material and carbonates than Laprairie (L), so that less trouble may be encountered with bloating, black coring, and gas removal.

Scott Junction

The sample from Scott Junction is only moderately plastic for a clay but more plastic than most of the shales (Figure 7). As is common with clays that contain a substantial proportion of fine, non-plastic ingredients, it extrudes readily; but the column may be weak. The consistency is very responsive to small variations of water content. It dries safely, although it has a moderately high drying shrinkage. This clay is used for the production of facing brick and building tile.

The shrinkage and absorption curves (Figure 19) show that this clay has a very short firing range, particularly for production of dense products having less than 8 per cent absorption, as well as a large fired shrinkage. This material has a shorter firing range than Laprairie (L) or Lotbinière (U), shales that also have short firing ranges but whose shrinkages are not nearly as large when they are fired to a hard dense condition. Additions of sand or some type of more refractory clay or grog would probably increase the firing range and decrease the firing shrinkage. Production of such products as drain tile and building tile, where a higher absorption is allowable, would present less problems than brick production. The rate of weight loss curve has several peaks in the 600°C area, indicating the breakdown of clay minerals and mica. The weight loss is very low and the material contains little oxidizable material or carbonates. As a result, little difficulty should be experienced from problems associated with elimination of evolved gases.

The thermal expansion curve of the unfired specimen obtained under slightly reducing conditions is similar to that of Haney Brown (74) and shows no areas that should cause cracking during firing. The curve obtained under oxidizing conditions is similar except that the minor plateau at about 875°C does not appear. The same relationships were found for all the Quebec common clays studied; for this reason, their linear thermal expansion curves that were obtained under oxidizing conditions on the Seger dilatometer are not shown (Figures 19-22).

The expansion caused by quartz is small, and little difficulty should be experienced in cooling.

East Angus

The consistency curve in Figure 7 indicates that this is a fairly plastic clay. The peak is moderately sharp, indicating that the consistency will vary with small variations of water content. The drying characteristics are satisfactory. This material is being used for production of facing brick and building tile.

The absorption and shrinkage curves (Figure 20) indicate that this material has a short firing range which is about the same as Laprairie (L) and Lotbinière (U). However, the fired shrinkage is excessively high at temperatures where the material is hard and dense. An addition of some material such as sand would reduce the fired shrinkage and lengthen the firing range. Firing of drain tile and building tile would present less difficulty than would the firing of facing brick.

The DTA curves of East Angus and Scott Junction are somewhat alike, although the latter has a more distinct calcite peak at 760°C than East Angus. These curves, as is the case with many of the Quebec clays, have very small and indefinite peaks.

The rate of weight loss curve shows a rapid evolution of gases from oxidizable material at 300°C and also the breakdown of at least two clay minerals at about 600°C.

The thermal expansion curves, which are somewhat like those of Scott Junction, indicate there should be no cracking problems during heating or cooling.

Laprairie (Clay)

The consistency curve in Figure 7 shows that this is an extremely plastic clay: the consistency exceeded a torque of 2000 metre-grams. Owing to its very plastic nature, the clay cracks badly under rapid drying conditions and has a very high drying shrinkage. Because of these factors, it would be very difficult to use this clay by itself in the production of clay products. A substantial amount of grog or sand is necessary to reduce the shrinkage and aid drying; even then it may be impossible to produce a suitable body. A clay of this type is useful mainly as a plastic additive to non-plastic shale. The unfired properties of this clay are typical of the fine-grained clay portions of the Champlain Sea deposits that occur in Quebec and Ontario.

The shrinkage and absorption curves in Figure 21 show that this clay has an exceedingly short firing range and a very high firing shrinkage at temperatures where the material becomes hard and dense. In view of the difficulty in drying and the very short firing range, it is not possible to utilize this clay satisfactorily for the manufacture of clay products unless a more refractory non-plastic material, such as calcined clay or grog, is added to it.

The thermal expansion characteristics are similar to those of the Scott Junction sample.

Other clays that have similar properties and similar compositions are St-Jean and Lakeside.

Mistassini

The sharp-peaked consistency curve of this sample (Figure 7) indicates that this is a silty material which is sensitive to water additions. Clays of this type will extrude, but it is difficult to maintain a column of uniform consistency. The sample cracks with rapid drying and like most clays has a high drying shrinkage. This material has been used for brick and tile production. The plasticity curve of the sample is similar to Bracebridge (85), an Ontario material whose plastic characteristics are readily altered by electrolytes. It is possible that Mistassini may also be affected in somewhat the same manner.

The firing range of Mistassini is very short (Figure 22), about the same as Scott Junction. It has a very high fired shrinkage when fired to a dense condition and in this respect it is similar to East Angus and Laprairie (Clay). Because of these factors it is most difficult to fire to a hard dense condition unless an additive such as sand is added to lengthen the firing range and reduce the firing shrinkage. However, judging from the amount of quartz present in the pre-fired specimen (an estimated 13 per cent - Table 10), there is a limit to the quantity that can be added before plasticity and cooling properties are adversely affected. There would be less difficulty in firing more porous products, such as drain tile and building tile.

The DTA curve and the rate of weight loss curve are very similar to those of Bracebridge, and suggest their compositions are much the same. Both are non-calcareous and have low clay mineral contents. The Bracebridge sample has a larger amount of adsorbed water than Mistassini and consequently has a greater rehydration problem.

The thermal expansion curves of the unfired and fired Mistassini specimens are similar to those of Bracebridge and suggest that there should be no difficulty with cracking during firing and cooling under normal conditions.

Brébeuf

The Brébeuf sample is a kaolinized rock composed of about 50 per cent kaolin and 50 per cent quartz. Although the kaolin imparts a fair

plasticity to the mixture, the material will not vitrify, because of its composition; and the absorption and shrinkage curves (Figure 23) differ from those of the other samples. Consequently, if it is used for refractories, a plastic, vitrifying type of refractory clay must be added to it. If the clay is separated from the coarse quartz, the clay fraction fires to a buff colour.

The DTA curve is typical of one produced by a kaolin group clay mineral and has prominent peaks at 600°C and 960°C. The weight loss curve (Figure 10) is typical of kaolinite. The rate of weight loss curve shows a rapid loss of adsorbed moisture at about 200°C (not apparent on the DTA curve because of the low sensitivity of 40), and a very rapid loss of water vapour at 600°C. Small shoulders on this curve at temperatures higher than 600°C indicate that some minor reactions are taking place. The weight loss from the breakdown of the kaolin mineral is about 5.75 per cent, so that good draft is necessary at 600°C to remove the water vapour.

The thermal expansion curve of the unfired sample is similar to that of Cactus Hills Sandy Fire Clay (74) from Saskatchewan. The curve rises to a steep peak at 600°C and then shrinkage proceeds sharply at first and then very slowly to 900°C, from which point the rate increases again.

The thermal expansion curve of the fired sample shows that there is sufficient quartz (about 42 per cent - Table 10) present to cause cooling

cracks, and a minor expansion at 200°C from a small amount of cristobalite.

Effect of Forming Method on Thermal Expansion of Unfired Specimens

In Figures 11 to 18 it was shown that atmosphere may or may not affect the thermal expansion of unfired shale specimens. Another factor that affects thermal expansion is the method of forming. In Figures 11 to 23 all thermal expansion test specimens were hand-moulded to avoid particle orientation effects. The thermal expansion curves of hand-moulded, isostatic-pressed and de-aired-extruded specimens (unfired) of Lauzon (Q.G.) are shown in Figure 24 under reducing and oxidizing conditions.

Under reducing conditions the isostatic-pressed and the hand-moulded specimens show a reversal from shrinkage to expansion at about 925°C, whereas the de-aired-extruded specimen continues to shrink through and beyond this temperature. The latter also has a high initial expansion, which suggests that there is orientation of the micaceous particles.

Under oxidizing conditions all curves are similar (Figure 24) and after the initial expansion they show that shrinkage continues beyond 1000°C. The de-aired-extruded specimen has the greatest rate of shrinkage and the hand-moulded the least. The broad peak between 650 to 900°C is typical of the slow heating rate in the Seger dilatometer.

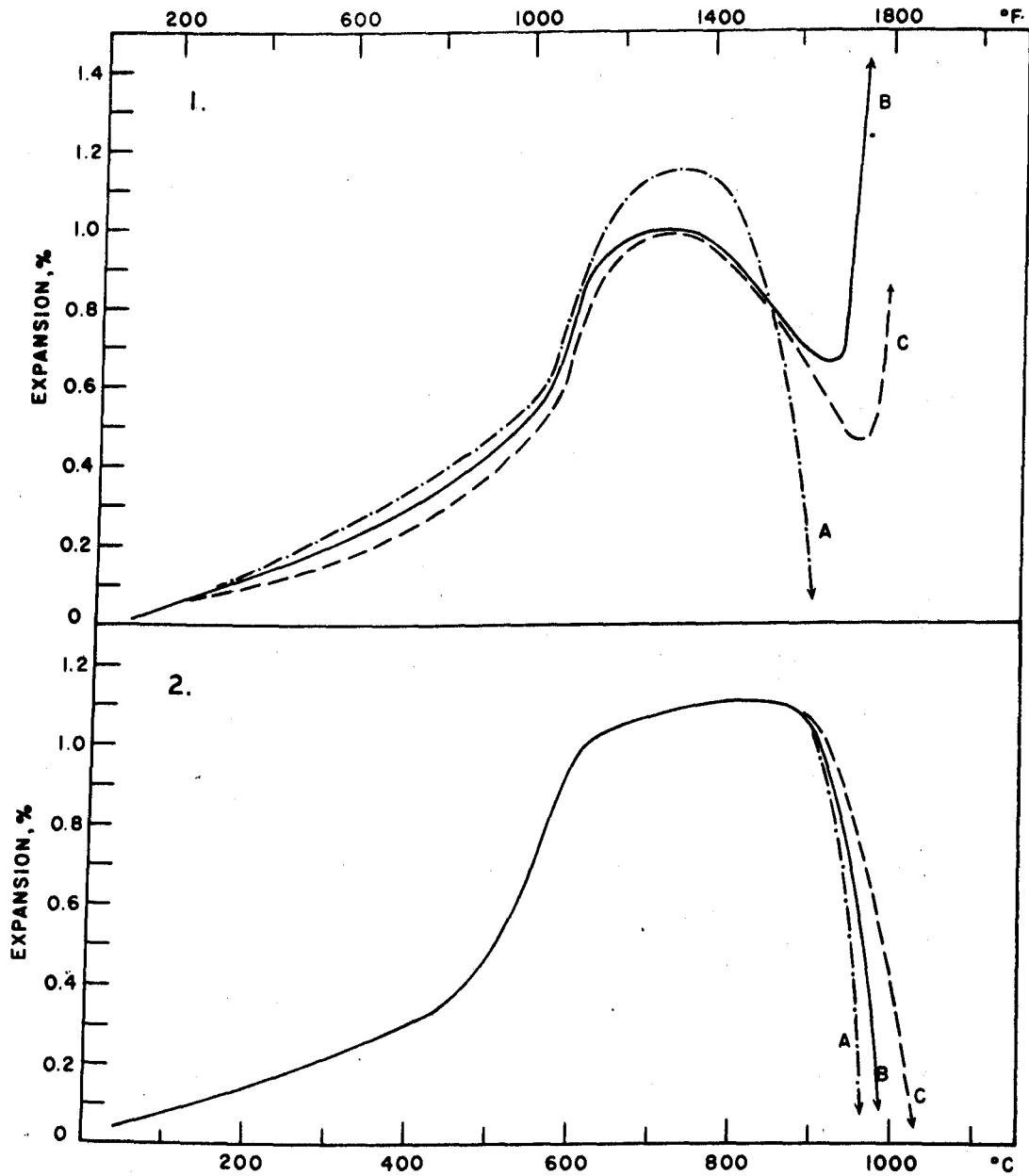


Figure 24. Effect of Method of Forming on Thermal Expansion of Lauzon (Q.G.) in 1. reducing atmosphere, 2. oxidizing atmosphere.

- A. Extrusion
- B. Hand-moulding
- C. Isostatic-pressing

It is interesting to note that a de-aired-extruded specimen of Ste-Monique (Q) in reducing conditions (not shown in any of the figures) behaved in the same manner as did the de-aired-extruded specimen of Lauzon (Q.G.) under similar conditions. In the Lauzon (Q.G.) case, apparently the densest specimens formed by de-aired extrusion (2.25 g/cm^3) do not have the same tendency to start expanding (or bloating) at about 900°C as do the less dense isostatically-pressed (2.18 g/cm^3) or hand-moulded (2.04 g/cm^3) specimens. High-lime materials are a likely exception to the above statement.

Although the curves are not reproduced here, it was found that hand-moulded and isostatically-pressed specimens of Lotbinière (U) had similar thermal expansion curves in reducing conditions and showed a change from shrinkage to expansion at about 875°C . However, the curves of Lotbinière (U) obtained in oxidizing conditions differed. The hand-moulded specimen expanded initially and then continued to shrink as did the Lauzon sample. The isostatically-pressed specimen changed very sharply to rapid expansion at about 850°C . No tests were conducted on extruded specimens of Lotbinière (U).

Although only limited data are available, it appears from the above that method of forming does have an influence on thermal expansion under the conditions encountered in this laboratory investigation. Further work should be carried out on examination of the structure of the specimens believed to have bloated, and on the initial density of the test specimens.

Summary of the Effects of Mineralogical Composition
on Properties of Ceramic Clays and Shales of Quebec

The effect of a constituent mineral upon the properties of a clay or a shale may depend on many factors such as abundance, particle size, composition, degree of crystallinity, cation exchange capacity, exchangeable ions, and drying and firing conditions. The subject has been discussed by Grim (77), Brady and Dean (27,28), Brady (79), and many others, and reference to the effect of some minerals has already been made in this report.

Montmorillonoids, and mixed-layer systems involving them, have a great influence on plasticity, and clays containing them usually have high drying shrinkages and are difficult to dry. Chlorite, illite and kaolins generally have less plasticity but they, too, are very plastic when their particle size is very small. A mixed-layer system tends to have higher plasticity than the individual mineral phases making up the unit (Grim, 77). The effect of clay-size vermiculite on plasticity has not been thoroughly examined.

The shales are generally consolidated, and thus the clay minerals have little chance of exerting maximum influence on plasticity. The Quebec Group shales and some of the shales from the St. Lawrence Lowlands contain a large proportion of clay minerals. Hence, plasticity is readily developed in some of the softer ones, particularly Mont-Joli (Q.G.), St-Apollinaire (Q.G.), Ile d'Orléans(Q.G.), Lotbinière (U), and St-Grégoire (Q), all of which contain substantial amounts of mixed-layer systems which include expandable phases. Conversely, the less plastic samples, such as Ste-

Monique (Q), Delson (U), Breckenridge (R) and Laprairie (L), are either deficient or lacking in such systems and, hence, may require special treatment to make them plastic (Bell, 80).

Plasticity is readily developed in the loosely consolidated common clays but, in general, these are not as plastic and sticky as are many of the clays from the prairies. Many samples contain small proportions of clay minerals (St-Alphonse is a notable exception) and a large proportion of non-clay minerals such as feldspar and quartz. This situation adversely affects plasticity and in extreme cases, when large amounts of non-plastic constituents are present, the clays are very sensitive to small additions of water at the stiff plastic stage. With clays of this type it is difficult to extrude a uniformly firm column.

Because of the uncertain proportion of each clay mineral in the total sample, only general conclusions can be drawn on the effect of the clay minerals on the drying properties of the common clays. The samples that were designated as glacial-lake clays (Scott Junction, Ville St-Georges, Disraeli, Deschailions, East Angus, Clerval and Rouyn) all dry safely except Clerval. The clays that were designated as marine (Victoriaville, St-Jean, Laprairie (Clay), Lakeside and Mistassini) crack in drying. A comparison of the compositions of the above samples (Table 8), and of their properties (Tables 3, 4 and 5), suggests that clays having a low chlorite-to-illite ratio, with appreciable amounts of (a) mixed-layer systems which include expandable phases, (b) montmorillonoid, or (c) vermiculite, have high drying shrinkages and are difficult to dry. Of the remaining clays,

Varenes, Douglstown and St-Alphonse are difficult to dry and contain vermiculite (the latter two also contain appreciable amounts of a mixed-layer system). This suggests that vermiculite causes drying difficulties. Estcourt, Cowansville and L'Assomption are safe drying and their clay mineral compositions conform with the foregoing generalizations. On the other hand, Buckingham, Ste-Scholastique, Sept-Iles and Soulanges are safe drying, although their clay mineral composition suggests that they should crack.

Except for Schefferville and Labelle, the kaolin-rich samples from the Canadian Shield contain a very large proportion of non-plastic constituents. Nevertheless, the small proportion of kaolin which they contain makes them fairly plastic. Schefferville contains an estimated 70 per cent kaolin, which results in the sample's being very plastic and sticky.

The crystalline structure of the chlorite, illite, montmorillonoid, vermiculite and mixed-layer systems contained in the Quebec common clays and shales breaks down with the evolution of a small amount of water vapour between 450°C and 700°C. The water vapour should be relatively easy to remove by moderate draft (when compared to kaolin clays), and, in most cases, slumping, kiln marking or scumming should not occur.

Some of the clays (Varenes and Lakeside, for example) and a few of the Quebec Group shales contain clay minerals such as montmorillonoid, vermiculite and mixed-layer systems which include expandable phases that have a substantial amount of adsorbed moisture. Samples of this type, the

clays particularly, may be subject to moisture regain after drying. This may lead, under certain conditions, to kiln marking or fracture of the ware during the early stages of firing if it is dried improperly or allowed to cool and take up moisture again.

Most of the kaolin-group samples are refractory, because the principal chemical constituents are silica and alumina. Schefferville also contains the refractory aluminous mineral, gibbsite. Château Richer has a relatively low melting temperature because it contains a very large amount of plagioclase feldspar. The refractoriness of Labelle is lowered by its high iron content (Table 7). Château Richer has been discussed elsewhere by Bell (81, 82), and Schefferville by Brady and Buchanan (83).

Illite, chlorite, montmorillonoid and vermiculite -- and mixed-layer systems containing them -- are not refractory, because they contain iron, alkalis and/or alkaline earths in addition to SiO_2 and Al_2O_3 . Thus, the refractoriness of the common clays and shales is limited by their clay mineral content as well as by their fluxes such as feldspar, dolomite, calcite and iron minerals. The Quebec Group shales are more refractory than the St. Lawrence Lowlands shales and the common clays, because they contain a larger proportion of clay minerals and a smaller amount of fluxes; nevertheless, they also vitrify at relatively low temperatures.

Quartz is a refractory, non-plastic ingredient that occurs to a moderate degree in the common clays and shales and extensively in some of the kaolin-rich samples. This mineral is generally desirable in quantities up to about 25 per cent. Being non-plastic, it assists drying, but in

large amounts it adversely affects plasticity. In the fired body it imparts strength, toughness and hardness and is sometimes added to lengthen the firing range. During firing, quartz helps to keep the product porous, thus allowing gases to escape. It undergoes a rapid change in dimension at 573°C and, because of this factor, in excessive amounts it is apt to cause heating or cooling cracks (particularly the latter). In addition, materials -- such as some of the kaolin-rich clays -- that contain a great deal of quartz are difficult to vitrify.

Plagioclase feldspar and, to a much lesser extent, K-feldspar are the principal fluxes occurring in the common clays and shales of Quebec. Like quartz, feldspar aids drying but it adversely affects plasticity if too large a proportion is present. It reacts vigorously with clay minerals, quartz, and other ingredients at the higher firing temperatures. Feldspar is the major ingredient of many of the common clays and is the cause of their short firing ranges and high fired shrinkages at the temperatures required for production of hard, dense products.

Dolomite and calcite occur in some of the Quebec samples, usually in small amounts. They generally are undesirable in large quantities, because they adversely affect the plasticity, evolve a large volume of gas and, being active fluxes, cause short firing ranges in common clays and shales. The short firing range of Boischatel (U-L) is the result of these minerals. Generally, with increasing additions of calcite and dolomite to a red-firing clay, the porosity increases, the shrinkage and hardness decrease, and the colour changes from red to buff. These minerals may

cause heating cracks, because some calcareous materials show rapid reversals in their expansion curve between about 775°C and 900°C . The fired colour of buff-firing clays containing dolomite and calcite is usually very sensitive to kiln atmosphere (Bell, 84). Clay products made from calcareous materials may be subject to scumming and efflorescence.

Pyrite and organic material occur in most of the St. Lawrence Lowlands shales. These substances, especially when they occur together, may cause bloating and black-coring unless a long oxidation is provided during firing. The sulphur dioxide or sulphur trioxide evolved from pyrite must be removed by good draft; otherwise, scumming and efflorescence may be caused. Organic material occurs in all samples, usually in minor amounts.

Such minerals as anatase, rutile and amphibole occur in insignificant quantities in the common clays and shales and have little effect on properties. They may, however, be detrimental to the kaolin clays.

The iron associated with the clay minerals and such iron minerals as hematite and pyrite causes clays and shales to burn red in oxidizing atmospheres.

CONCLUSIONS

The shales of Quebec are heterogeneous materials with fair to poor plasticity. The majority of them fire to salmon or light brown at low temperatures and dark red or reddish-brown at the higher temperatures. In some localities in the St. Lawrence Lowlands they are highly calcareous, have

short firing ranges, and fire to shades of cream or buff. In general, their firing ranges are sufficiently long for production of dense products such as facing brick, this being particularly true of the Quebec Group samples. The shales from the St. Lawrence Lowlands (Lorraine, Utica, Queenston, and Rockcliffe) have very low PCE's of about 01 to 6, whilst those from the Quebec Group have PCE's of 14 to 16. In addition to being more refractory, the Quebec Group shales are generally more plastic than the St. Lawrence Lowlands materials, and consequently some of them may also be suitable for sewer pipe. All of these shales are suitable for building tile and drain tile, provided they can be extruded.

Most of the surface clays of Quebec are common, low-fusion materials having PCE's between 01 and 8. As do the shales, they fire salmon or light brown at the low temperatures and red at higher temperatures, except for a few very calcareous samples that fire to lighter colours. Many of the samples have firing ranges that are too short for production of dense products. Consequently, the majority of the clays are suitable only for common brick, drain tile and building tile, provided they can be extruded and dried satisfactorily.

The kaolin-rich clays that occur on the Canadian Shield are generally not satisfactory for ceramic uses unless beneficiated, because they contain excessive quantities of non-clay minerals such as quartz or feldspar. Many are also contaminated with iron-bearing minerals. Beneficiation is difficult, particularly if a good-quality kaolin is required. In some cases the deposits are limited in extent or variable in composition.

The St. Lawrence Lowlands shales consist, principally of illite, quartz, chlorite, plagioclase, mixed-layer systems composed of illite and an expandable phase, and variable but often significant quantities of dolomite and calcite. The Quebec Group samples contain a high proportion of the same clay mineral groups as the St. Lawrence Lowlands shales, but a lesser amount and variety of non-clay minerals (mainly quartz and feldspar). The bulk of the chlorite in the Quebec Group shales may be septechlorite. Anatase and hematite may occur within both units, whereas pyrite is a minor constituent of the St. Lawrence Lowlands shales.

The common clays have a more variable composition than the shales. Their clay mineral constituents are chlorite, illite, montmorillonoid, vermiculite, and mixed-layer systems containing these phases. They contain abundant non-clay constituents which consist principally of plagioclase feldspar, quartz, K-feldspar, occasionally carbonates, and amphibole in decreasing order of abundance.

A wide variety of problems occur in the processing of the common clays and shales of Quebec, because of their heterogeneous nature. The Quebec Group shales, being the least heterogeneous, have the fewest difficulties in processing.

The refractoriness of the St. Lawrence Lowlands shales and the common clays is low, because of the large amounts of fluxing ingredients and the types of clay mineral they contain. Although the Quebec Group shales contain the same types of clay minerals as do the former set, they are more refractory because they contain small amounts of fluxes. Samples

composed of kaolin and quartz minerals are inherently refractory.

Some of the non-plastic shales require fine grinding, an additive to increase plasticity, and extensive mixing with water, before they can be extruded. Plasticity is readily developed in the loosely consolidated common clays but, in general, they are not as plastic and sticky as many of the clays and soft shales from the Prairies. Some of the common clays contain an abundance of non-plastic ingredients, such as quartz and feldspar, that makes them sensitive to small additions of water at the stiff plastic stage. Examination of their drying properties suggests that clays having a low chlorite-to-illite ratio, with appreciable amounts of mixed-layer systems, montmorillonoid and vermiculite, have high drying shrinkage and are difficult to dry. The kaolin-rich samples generally have a low clay content but are made fairly plastic by the kaolin clay mineral.

The major non-plastic ingredients have a considerable influence on properties other than plasticity. In general, the Quebec common clays and shales contain a moderate amount of quartz which aids drying and imparts strength, toughness and hardness to the fired body. Feldspar is a fluxing ingredient in these materials and, because it is a major ingredient in many of the common clays, these have high fired shrinkages and short firing ranges at temperatures suitable for production of dense, hard products.

The St. Lawrence Lowlands shales commonly contain pyrite, organic material, dolomite, and calcite, all of which may potentially cause difficulties. The first two cause bloating and black-coring unless a prolonged oxidation period is provided in the firing schedule. When dolomite and calcite occur

in substantial quantities, they evolve large volumes of gas (CO_2), reduce firing shrinkage, shorten the firing range, decrease hardness, and increase absorption. Pyrite, dolomite and calcite may cause scumming and efflorescence.

Composition, atmosphere, and method of forming influence the thermal expansion of clays and shales during firing. The effect of atmosphere depends on the composition of the materials and is an important factor in shales from the Lorraine and Utica Groups of the St. Lawrence Lowlands that contain pyrite, organic material, and carbonates. Heating-up cracks may appear in high-lime materials, whilst bloating or cracking may occur in the materials high in pyrite and organic material under reducing conditions. Most of the common shales and clays have moderate to small quartz content; cooling cracks should not arise from this.

Great significance has been attached to the plasticity of the samples because, at the present time, clay products made from the common clays and shales are extruded. Some of the non-plastic shales are being used at present for dry-pressed brick. In the future, such methods as isostatic pressing of sewer pipe, and the use of a large proportion of calcine in the manufacture of clay products, may be adopted. It is possible that, by using these new methods, and new combinations of raw materials, adjustment or elimination of some of the current processing problems may be achieved.

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