NRRI/GMIN-TR-89/12A

LCMR CLAY PROJECT:
NRRI SUMMARY REPORT

By

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October 1990
Technical Report
NRRI/GMIN-TR-89/12A

Funded by the Legislative Commission
on Minnesota Resources

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Recommended Citation
Hauck, S., Heine, J., Zanko, L., Power, B., Geerts, S., Oreskovich, J., and Reichhoff, J., 1989, LCMR Clay Project: NRRI Summary Report: University of Minnesota Duluth, Natural Resources Research Institute, Technical Report NRRI/GMIN-TR-89/12A, 201 p.

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ABSTRACT

Minnesota has a variety of clays and shales that have potential as industrial clays. These clays are: 1) Precambrian clays; 2) Paleozoic shales; 3) pre-Late Cretaceous primary (residual) and secondary kaolins; 4) Late Cretaceous ball clays and marine shales; 5) Pleistocene glacial clays; and 6) Recent clays. Minnesota clays are currently used for brick and as a portland cement additive. Other potential uses include filler and coating grade kaolins, ceramic tile, refractory products, lightweight aggregate, sanitaryware, and livestock feed filler.

Precambrian clays occur in the 1.1 Ga Keweenawan interflow sediments of the North Shore Volcanic Group, the Middle Proterozoic Thomson Formation and in the Paint Rock member of the Biwabik Iron-Formation on the Mesabi Iron Range, all in northeastern Minnesota. The Paint Rock clays have potential as red coloring additives and glazes.

Paleozoic shales in southeastern Minnesota are primarily kaolinitic and illitic shales that are interbedded with limestones. The Ordovician Decorah and Glenwood Formations are marine shales that, in the past, have been used to make bricks, tile, and lightweight aggregate. The thickness of these shales ranges from 10-90 feet. The Decorah Shale has the lowest firing temperature with the best shrinkage and absorption characteristics of all the Minnesota clays.

The pre-Late Cretaceous primary and secondary kaolins are found in the western and central portions of Minnesota; the best exposures are located along the Minnesota River Valley from Mankato to the Redwood Falls area and in the St. Cloud area. The primary or residual kaolinitic clays are the result of intense weathering of

Precambrian granites and gneisses prior to the Late Cretaceous. Subsequent reworking of these residual clays led to the development of a paleosol and the formation of pisolitic kaolinite clays. Physical and chemical weathering of the saprolitic kaolinite-rich rocks produced fluvial/lacustrine (secondary) kaolinitic shales and sandstones. Recent exploration activity is concentrated in the Minnesota River Valley where the primary kaolin thickness ranges from 0 to 200+ feet, and the thickness of the secondary kaolins ranges from 0-45+ feet (Setterholm, *et al*, 1989). Similar kaolinitic clays occur in other areas of Minnesota, e.g., St. Cloud and Bowlus areas. However, less information is available on their thickness, quality, and areal distribution due to varying thicknesses of glacial overburden. Cement grade kaolin is extracted from two mines in the residual clays in the Minnesota River Valley, and a third mine there yields secondary kaolinite-rich clays that are mixed with Late Cretaceous shales to produce brick.

During the Late Cretaceous, Minnesota was flooded by the transgressing Western Interior Sea, which deposited both non-marine and marine sediments. These sediments are characterized by gray and black shales, siltstones, sandstones, and lignitic material. Significant occurrences of Late Cretaceous sediments are found throughout the western part of the state, with the best exposures located in Brown County, the Minnesota River Valley, and the St. Cloud area. In Brown County, the maximum thickness of the Late Cretaceous sediments is >100 feet. These sediments thicken to the west and can be covered by significant thicknesses (>300 ft.) of glacial overburden in many areas. Current brick production comes from the Late Cretaceous shales in Brown County. In the past, the Red Wing pottery in Red Wing, Minnesota, used Cretaceous and some Ordovician sediments to produce pottery, stoneware, and sewer pipe.

Glacial clays occur in glacial lake, till, loess, and outwash deposits, and these clay deposits range in thickness from 5 to 100+ feet. Much of the early brick and tile production (late 1800s and early 1900s) in Minnesota was from glacial clays. The last brickyards to produce from glacial lake clays, e.g., Wrenshall in northeastern Minnesota and Fertile in west-central Minnesota, closed in the 1950s and 1960s. There has also been some clay production from recent (Holocene) fluvial and lake clays that have thicknesses of 2-10+ feet. Both recent and glacial clays are composed of glacial rock flour with minor quantities of clay minerals. Carbonates can be a significant component of many of these clays. Glacial lake clays in northwestern Minnesota (Glacial Lake Agassiz - Brenna and Sherack Formations) begin to bloat at 1830° F due to the presence of dolomite and smectite clays. These clays are a potential lightweight aggregate resource.

Geochemistry, clay mineralogy, particle size, cation exchange capacity (CEC), raw and fired color, and firing characteristics are useful in distinguishing different potential industrial uses for Minnesota clays. These physical and chemical characteristics help to distinguish potentially useful clays from those with less desirable characteristics, e.g., high quartz or silica content, high shrinkage or absorption upon firing, undesirable fired color, too coarse-grained, CEC of <5 milliequivalents, etc. Certain clays, e.g., the bloating Decorah and Brenna Formation clays, and the high alumina, refractory, pisolitic clays of the Minnesota River Valley, have physical and chemical characteristics that indicate further exploration and product research are necessary to fully evaluate the potential of these clays.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF PLATES

LIST OF APPENDICES

INTRODUCTION

CLAY DISTRIBUTION

The purpose of the Natural Resources Research Institute's portion of this multi-agency clay project was to determine the geological, geochemical, mineralogical and physical characteristics of the different clays found throughout Minnesota. Four hundred and ninety-nine samples were collected during this program, which was funded by the Legislative Commission on Minnesota Resources and with additional funds from the Natural Resources Research Institute (Plate 1; Appendix A). Clay samples were collected in 65 of Minnesota's 87 counties (Table 1). A regional drilling program, kaolin processing research, and an assessment of the environmental and state regulations pertaining to clay mining were also conducted as a part of this program (Setterholm, *et al*, 1989; Prasad, *et al*, 1990; MDNR, 1989a, 1989b).

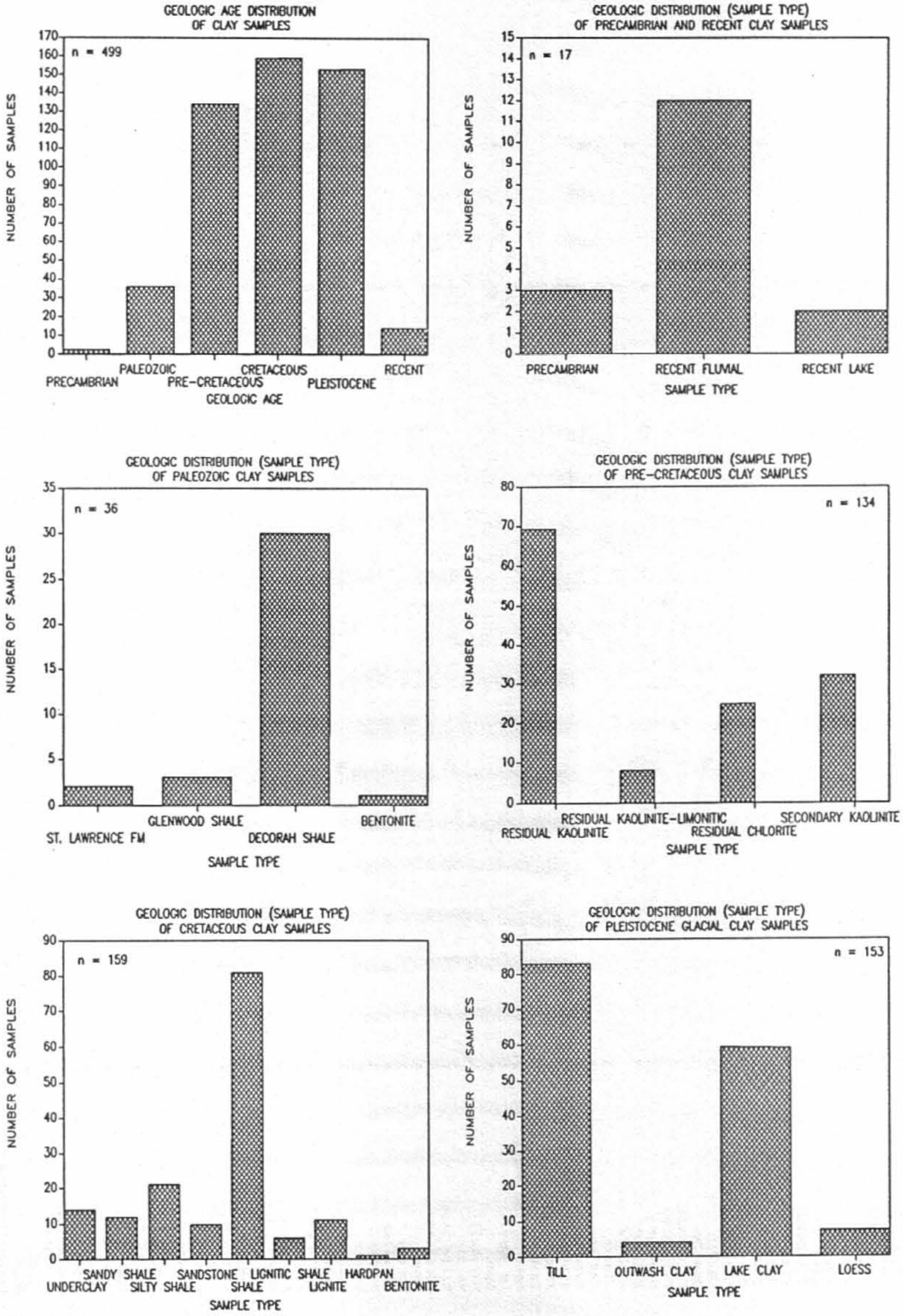
Geologic Distribution

The clay samples collected during this program have been divided into six geologic categories (Fig. 1; Table 2). Within these six geologic categories, the distribution of the clays was further subdivided to better assess the characteristics and relationships of the various types of clays (Fig. 1).

Clays in Minnesota occur in Precambrian to Pleistocene age rocks. Clays deposited during the last glacial epoch represent the largest surface exposure in Minnesota. These clays are represented by till, lake, outwash, and loess deposits.

Table I. Location of clay samples by county and clay type.

	No. of			Sample Type			
County	Samples	Precambrian	Paleozoic	Pre-Cretaceous	Cretaceous	Pleistocene	Recent
Aitkin	7					7	
Anoka	1					1	
Becker	1					1	
Beltrami	2					2	
Big Stone	1					1	
Blue Earth	4			1		3	
Brown	142			17	121	4	
Carlton	13	1				12	
Carver	1					1	
Cass	1					1	
Chippewa	1					1	
Chisago	1					1	
Clay	1						1
Cook	2	1				1	
Cottonwood	4					3	1
Crow Wing	4					3	1
Dakota	15		13			2	
Douglas	1						1
Faribault	1					1	
Fillmore	3			2		1	
Goodhue	14		11		1	2	
Houston	3		2				1
Hubbard	1					1	
Itasca	5					5	
Jackson	4				2		2
Kandiyohi	1					1	
Kittson	2					2	
Koochiching	7					7	
Lake	2					2	
Lake of the Woods	2					2	
Le Sueur	1						1
Lyon	5					5	
Marshall	1						1
Martin	1					1	
Mille Lacs	1					1	
Morrison	13			6	3	4	
Mower	5			1	4		
Murray	3					3	
Nicollet	6					6	
Nobles	3					2	1
Norman	1					1	
Olmsted	13		8			5	
Ottertail	1						1
Pennington	4					4	
Pine	3					3	
Pipestone	1					1	
Polk	3					3	
Red Lake	1					1	
Redwood	85			59	15	11	
Renville	28			18	8	2	
Rice	1					1	
Rock	1						1
Roseau	3					3	
Sibley	1					1	
Stearns	31			28	3		
St. Louis	19	1		1		17	
Todd	1					1	
Traverse	2				2		
Wabasha	1					1	
Wadena	2					2	
Washington	3		2			1	
Watonwan	1					1	
Winona	1			1			
Wright	1					1	
Yellow Medicine	4					4	
No.Counties	**65**	**No. Samples 3**	**36**	**134**	**159**	**153**	**13**



GEOLOGIC AGE DISTRIBUTION OF CLAY SAMPLES

GEOLOGIC DISTRIBUTION (SAMPLE TYPE) OF PRECAMBRIAN AND RECENT CLAY SAMPLES

GEOLOGIC DISTRIBUTION (SAMPLE TYPE) OF PALEOZOIC CLAY SAMPLES

GEOLOGIC DISTRIBUTION (SAMPLE TYPE) OF PRE-CRETACEOUS CLAY SAMPLES

GEOLOGIC DISTRIBUTION (SAMPLE TYPE) OF CRETACEOUS CLAY SAMPLES

GEOLOGIC DISTRIBUTION (SAMPLE TYPE) OF PLEISTOCENE GLACIAL CLAY SAMPLES

Figure 1. Age and sample type distribution of clay samples.

Table 2. Sample percentages of different types of clays.

- 1 % are Precambrian clays
- 8 % are Paleozoic clays
- 27 % are Pre-Cretaceous clays
- 31 % are Cretaceous clays
- 30 % are Pleistocene glacial clays
- 3 % are Recent river and lake clays

Glacial till, lake, and outwash deposits occur throughout the state while loess is concentrated in the southeast and southwestern corners of the state.

Underlying the glacial clays, particularly in the western and central portions of Minnesota, are Late Cretaceous shales of the Greenhorn stage of the Cretaceous Western Interior Seaway. Prior to the Late Cretaceous transgression, an intense period of weathering produced primary and secondary (fluvial/lacustrine) kaolinitic clays. While these clays have a wide distribution throughout Minnesota, they are minimally exposed. The best exposures are in the Minnesota River Valley in southwestern Minnesota and in the St. Cloud area in central Minnesota (Plate 1).

Paleozoic clays crop out only in southeastern Minnesota (Fig. 2). The Paleozoic clays in northwestern Minnesota are covered by several hundred of feet of Pleistocene and Cretaceous sediments. Of the Paleozoic clays, the shales in the Ordovician Decorah and Glenwood Formations have the best thicknesses and physical characteristics for industrial uses.

Only a few potentially useful Precambrian clays exist in Minnesota. These clays occur in the Paint Rock Member of the Biwabik Iron-Formation on the Mesabi Iron Range of northeastern Minnesota, in the argillaceous Thomson Formation, and in

Keweenawan sediments along the north shore of Lake Superior. However, very few usable Precambrian clays exist.

PHYSICAL AND GEOCHEMICAL TESTS

The clay samples were collected from outcrops and from mine faces in both closed and operating clay pits. The samples were collected using the protocols described in Appendix B. Additional samples were collected from samples donated by the U.S. Bureau of Mines (Haas, *et al*, 1987). These samples came from auger holes drilled during a regional survey of Minnesota clays to determine whether or not a suitable clay existed in Minnesota that could be used as a binder in taconite pellet production (Haas, *et al*, 1987). New data, in addition to the chemical and physical data in Haas, *et al* (1987), was also collected on some of these samples, e.g., firing data.

The physical tests conducted on the clays collected were X-ray mineralogy, cation exchange capacity, particle size analysis, Munsell color, and firing characteristics (firing range, shrinkage, absorption and color; Appendices C, and E-J). Major element geochemical analysis was also conducted to characterize the samples in terms of silica, alumina, iron, sulfur, and carbonate (Appendix D). These elements identify the potential impurities as well as help define the clay content of the sample. Table 3 shows the percentage of samples that were analyzed in each test.

The number of tests completed on each clay sample was determined by the amount of time and cost required to complete the tests within the time period of the project. The samples for each test were selected to best represent each particular type of clay within a geographic region or area. Analytical errors, standards, etc. for each of these tests are provided in Appendices D-F.

Table 3. Percentages of samples analyzed by various physical and chemical tests.

- Geochemistry (bulk sample - 14 major elements) - 65 %
- Cation Exchange Capacity (CEC) - 99 %
- Munsell Raw Color - 100 %
- X-ray Mineralogy (6 X-rays/sample - 2 micron fraction) - 58 %
- Particle Size Analysis (8000 determinations) - 96 %
- Firing Characteristics - (194 samples) - 39 %
    - 13 firings per sample from 1751-2450° F
    - 7 additional firings on 45 samples from 2460-2806° F
    - firing range, firing color, shrinkage, and absorption were determined on each fired sample

PREVIOUS WORK

The earliest work on potential commercial characteristics of clays in Minnesota was reported by Grout and Soper (1919). They principally described the location, type of clay product (if any), production figures, and firing characteristics of many clays in use in Minnesota prior to 1919. Follow up clay studies were conducted by Grout (1947), Bradley (1949), Riley (1950), Prokopovich and Schwartz (1957), Austin (1963), Parham and Hogberg (1964), Parham and Austin (1969), Parham (1970), Haas, *et al* (1987) and Heine and Hauck (1988). Riley (1950) and Prokopovich and

Schwartz (1957) specifically studied the bloating properties of the clays for use as lightweight aggregate.

PREVIOUS AND CURRENT CLAY PRODUCTION

Nearly every county in Minnesota, at least since 1860, had a clay production facility or tried to produce clays (Grout, 1947). Examination of the Minnesota Census records (1860-1890) and Minnesota Business Gazetteer (1860-1924) suggested that at the turn of the century there were more than 300 clay production or clay-related facilities, i.e., distribution centers, in Minnesota. Some of the largest non-brick clay users were the pottery, stoneware and sewer pipe companies that operated in Red Wing, Minnesota (Fig. 2) from 1855 (bricks were produced at first) until the last pottery closed in 1967 due to a labor dispute (Austin, 1963; Tefft and Tefft, 1981). With the closure of the Wrenshall brickyards (Carlton Co.) in 1953 (Heine and Hauck, 1988), the Ochs Brick and Tile Company in Springfield, Brown County, the Fertile brickyard in Polk County, and the Twin City brickyard in St. Paul were the last of the operating clay producers in the state. With the closure of the Twin City and Fertile brickyards in the early- to mid-1960's, only the Ochs Brick and Tile Company produced clay for industrial use. Recently (1986 and 1988), two new clay mines, i.e., the Northwest States Portland Cement Company of Mason City, Iowa and the Northern Con-Agg Company of Maple Grove, Minnesota, respectively, have produced residual kaolinitic clays as an additive to portland cement (Plate 2).

ACKNOWLEDGEMENTS

Data collection and support for this project was supplied by a grant from the Legislative Commission on Minnesota Resources. Access to mine facilities and other data were graciously provided by Mr. Rod Schutt of the Ochs Brick and Tile Company, Springfield, Minn., by Mr. Vern Stuessy of the Northwest States Portland Cement Company, Mason City, Iowa, Mr. Al Severson of Northern Con-Agg, Incorporated, Maple Grove, Minn., Messrs. MacDonald and Spillane of Nova Natural Resources Corporation, Denver, Colorado, Mr. Donald Vry of the Meridian Aggregate Company, St. Cloud, Minn., Mayor Hugh Line and the City of Wrenshall, Wrenshall, Minn., Mr. C. Firle of Fairfax, Minn., Mr. W. Munsell of Franklin, Minn., and Mr. G. Peterson and family, Zumbrota, Minn. We would like to thank Dr. Penelope Morton and the Department of Geology at the University of Minnesota, Duluth, and Mr. Dave Marklund and the Environmental Protection Agency in Duluth for their assistance and use of their X-ray diffractometer equipment. Messrs. Larry Haas and Roland Blake of the U.S. Bureau of Mines provided additional Minnesota clay samples from their taconite binder study, which greatly assisted the completeness of this study. Special thanks is also given to the many private property owners throughout the state who provided not only access to their property but frequently provided guidance to elusive sampling locations.

CLAY GEOLOGY

PRECAMBRIAN CLAYS

Precambrian clays in Minnesota are found in: 1) the interflow sediments (shales and siltstones) of the 1.1 Ga Keweenawan North Shore Volcanic Group; 2) the argillaceous rocks of the Middle Proterozoic Thomson Formation; and 3) the Lower Proterozoic Paint Rock Member of the Biwabik Iron-Formation. Of these three clays, the Paint Rock clays have the best potential as industrial clays. The mineralogy of the Paint Rock clays is kaolinite, illite, and hematite. The clays are considered waste material during the mining of iron ore. Due to the high iron content of these clays, these clays are being tested as possible color additives and as a glazing material (Toth, *et al*, 1990).

PALEOZOIC CLAYS

The Paleozoic rocks of Minnesota are largely confined to the southeastern portion of the state, although rocks of Ordovician age underlie thick glacial cover in the northwest corner of the state (Fig. 2). The Paleozoic rocks in southeastern Minnesota were deposited in a shallow marine sea about 550 million years ago. Their depositional extent was limited to the north and east by Precambrian rocks of the

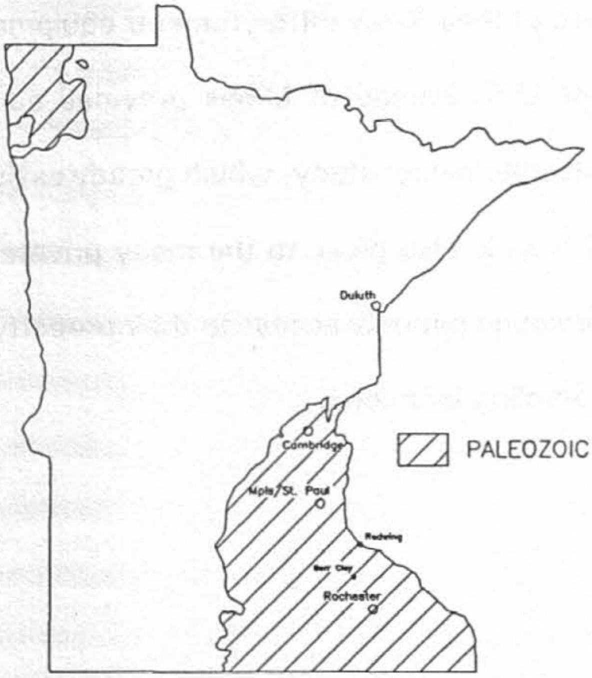


Figure 2. Distribution of Paleozoic rocks in southeastern Minnesota. (After Ojakangas and Matsch, 1982).

Wisconsin Arch and to the west by the Transcontinental Arch (Austin, 1972; Ojakangas and Matsch, 1982). Alternating transgressions and regressions of the sea were responsible for the Cambrian and Ordovician sandstone-shale-carbonate stratigraphy in this area (Fig. 3). Only three Paleozoic clay/shale units were investigated: the Late Cambrian St. Lawrence Formation and the Ordovician Glenwood Formation and Decorah Shale.

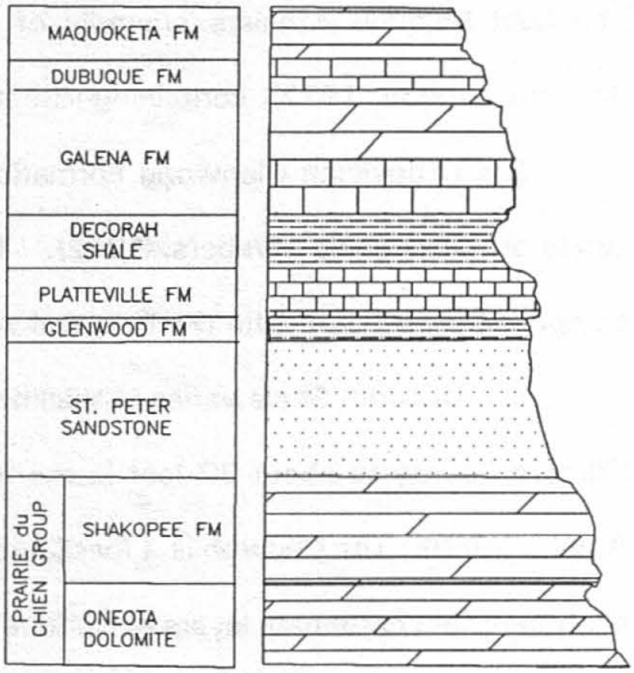


Figure 3. Stratigraphic section of Ordovician rocks in southeastern Minnesota. (Modified from Ojakangas and Matsch, 1982).

Of these three Paleozoic formations, the Ordovician Decorah Shale historically provided the largest volume and the best raw material for the manufacture of clay products (brick, tile, sewer pipe, etc.). The Twin City brickyard in St. Paul used shales from the Decorah Shale to produce brick and tile. The Glenwood Formation, because of its limited thickness (ave. 5 ft. versus 45-90 ft. for the Decorah), was used to a much lesser extent in ceramic applications. The only significant use of the St. Lawrence Formation occurred in Fillmore County, where it was quarried, primarily for its carbonate content; the shaly portions were mixed with quarry refuse and used as road material (Grout and Soper, 1919).

The Late Cambrian St. Lawrence Formation has two members, the Black Earth and the Lodi. Samples in this study come only from the more shaly Lodi Member.

The Lodi Member consists primarily of thin- to thick-bedded, argillaceous, silty dolomite (Austin, 1972), containing illite and mixed-layered clays.

The Ordovician Glenwood Formation is a thin (2-16 ft.) unit of argillaceous sandstone and shale (Webers, 1972). The Glenwood, like the St. Lawrence, is composed primarily of illite (Parham and Austin, 1967, 1969; this study).

The Decorah Shale varies in thickness from about 25 feet in the southeast in Fillmore County to about 90 feet in the north in the Twin Cities area (Parham and Austin, 1969). The Decorah is a fossiliferous, greenish-gray marine shale containing scattered, thin carbonate layers (limestone) in its lower portions, which increase both in thickness and frequency toward the top. A thin (0.75-1.5 in.) layer of potassium bentonite (the Millbrig K-bentonite) is also present within the basal portion of the Decorah at many localities (Parham and Austin, 1969). Illite and kaolinite are the major clay minerals. However, the kaolinite content decreases from the southwest toward the northeast where illite becomes the dominant clay mineral (Parham and Austin, 1969). This change in clay mineralogy, according to Parham and Austin (1969), is due to erosion of either pre-existing kaolinitic sedimentary rocks or a kaolinitic-rich saprolite.

Golden Hill Exposure, Rochester, Olmsted County, MN

The "Golden Hill" exposure has a complete stratigraphic section of the Decorah Shale and is located just south of Rochester, Minnesota, along U.S. Highway 52. At this locality the Decorah is approximately 43 feet thick and composed of fossiliferous shale interbedded with very thin layers of limestone. However, thicker beds of limestone (up to 4 inches thick) occur intermittently throughout the section but increase in frequency toward the top, reflecting the transition to a more quiescent, offshore (carbonate bank) depositional environment. The stratigraphy and associated sampling intervals are illustrated in Figure 4. Kaolinite is the dominant clay mineral, which suggests a close proximity to a kaolinitic source area (Parham and Austin, 1969).

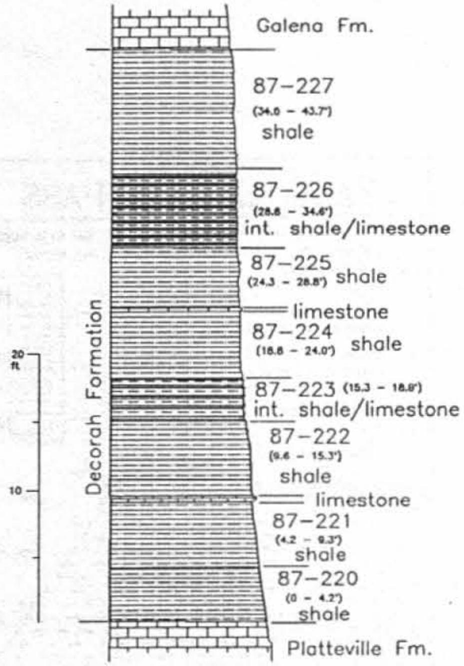


Figure 4. Stratigraphic column of the Decorah Shale at the Golden Hill outcrop.

Barr Clay Mine, Zumbrota, Goodhue County, MN

The Barr Clay mine is located near Zumbrota (Fig. 5). The geology and stratigraphy of the Barr Clay mine site is illustrated in Figures 6A, 6B, and 7. Nearly 60 feet of the Decorah

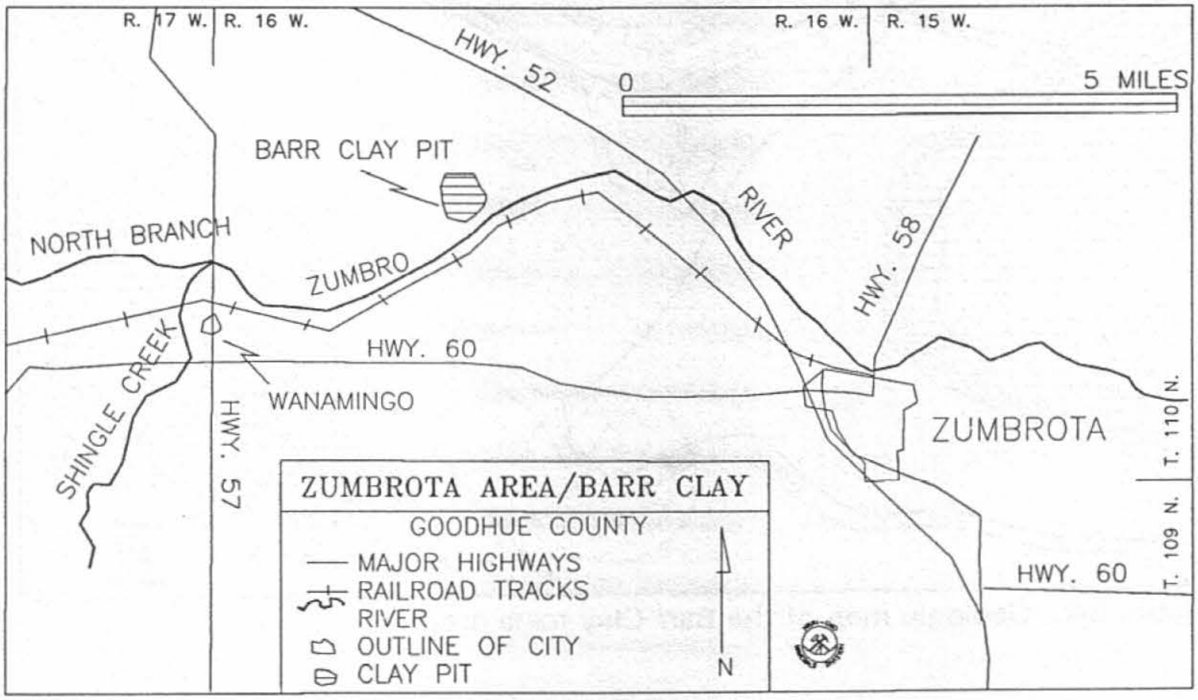


Figure 5. Location of the Barr Clay mine area.

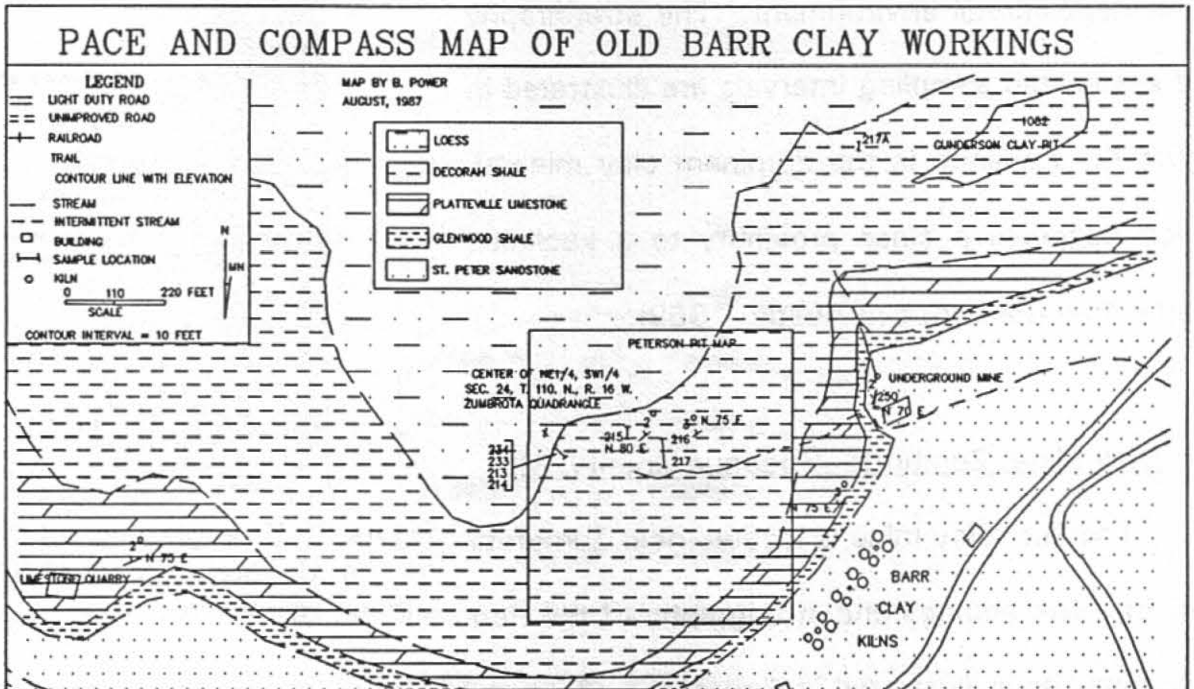


Figure 6A. Geologic map of the Barr Clay mine area.

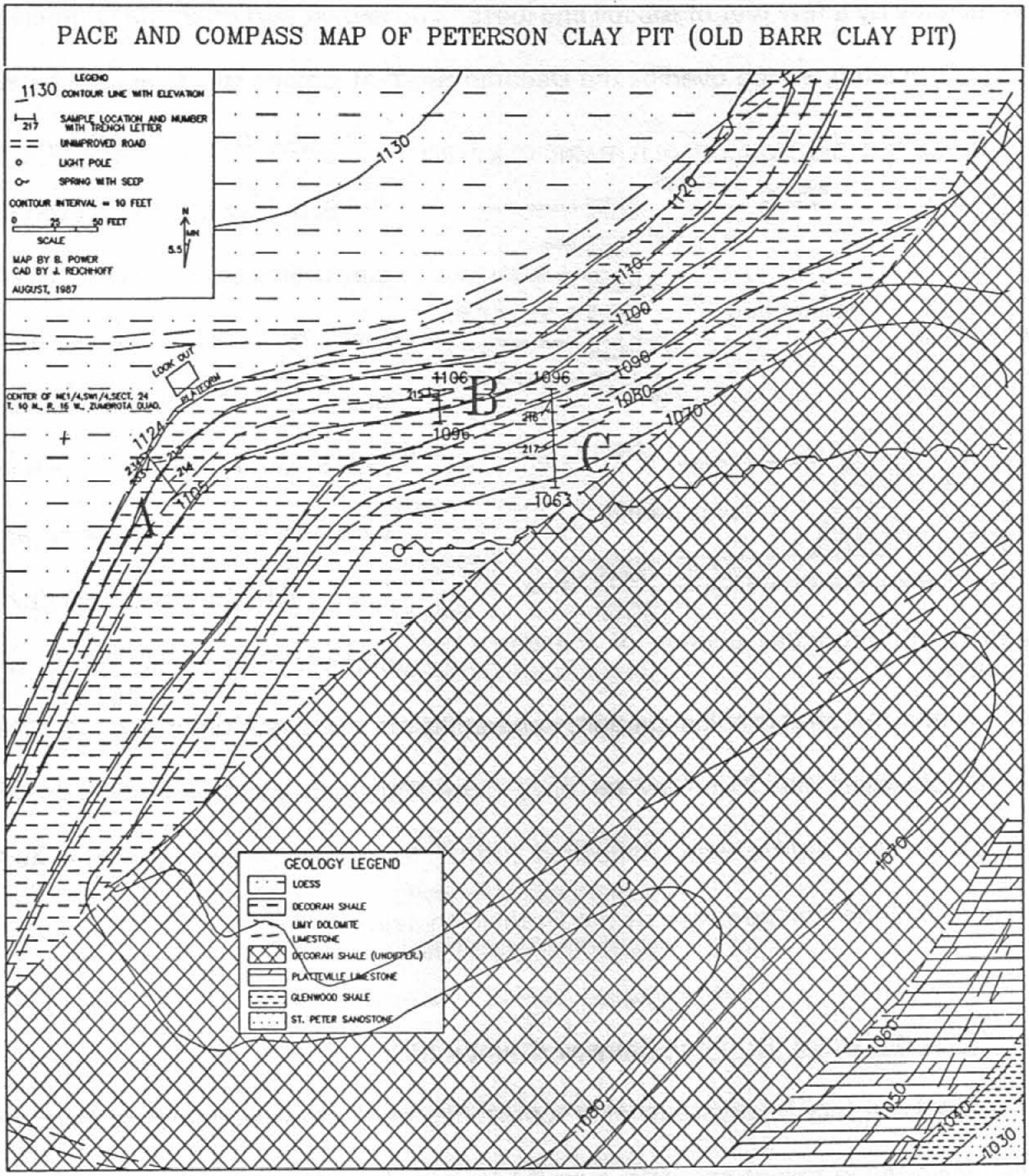


Figure 6B. Geologic map of the Peterson/Barr Clay pit.

Shale is present, with fossiliferous marine shale the predominating lithology. It is noteworthy that the Decorah at this location is completely exposed at the surface, covered only by a few feet of topsoil and loess. The lowest portion of the Ordovician Galena Formation, which overlies the Decorah Shale at Golden Hill, is absent here.

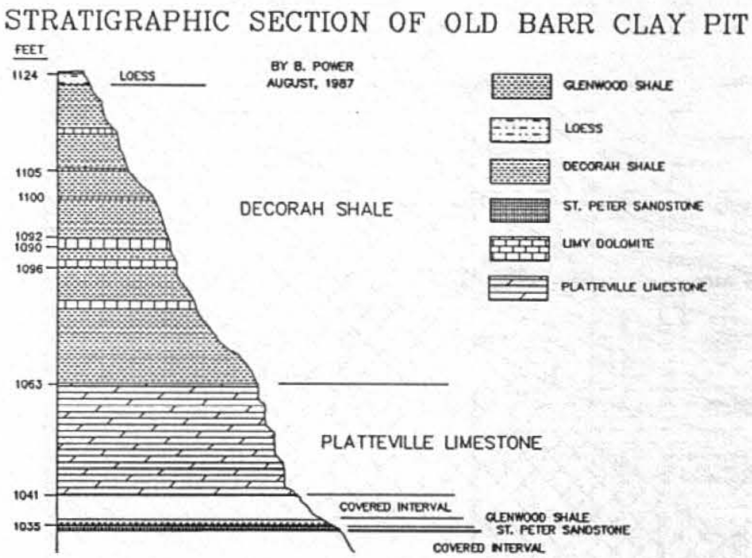


Figure 7. Stratigraphic column of the Barr Clay mine area.

The lowest shale unit at the Barr Clay mine was used for clay products to a greater extent than the higher shale units because of its thickness, uniformity, and minimal carbonate content (Grout and Soper, 1919). Moderately thick carbonate beds (up to 2 ft.) occur within the stratigraphic section, separating the shale-rich units (Fig. 7). The Decorah shales in the Barr Clay pit have more illite than the Golden Hill shales, suggesting these shales were deposited further from their Transcontinental Arch source during the transgression of the Ordovician sea.

Twin Cities Brickyard, St. Paul, Ramsey County, MN

The Twin City Brickyard locality represents the thickest sequence of Decorah Shale evaluated in this study, with over 90 feet of shale exposed in the pit (Figs. 8 and 9). Marine shales dominate the stratigraphic section. However, carbonate (limestone) beds occur throughout the section, varying from a fraction of an inch to two feet in thickness. The carbonate beds increase in frequency in the upper two-

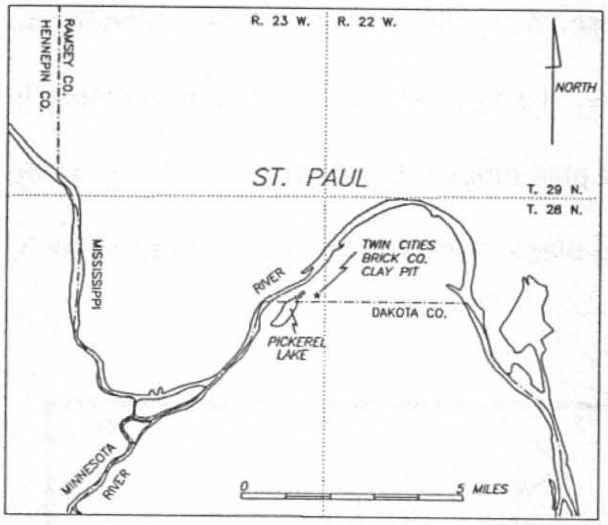


Figure 8. Location map of the Twin City Brickyard area.

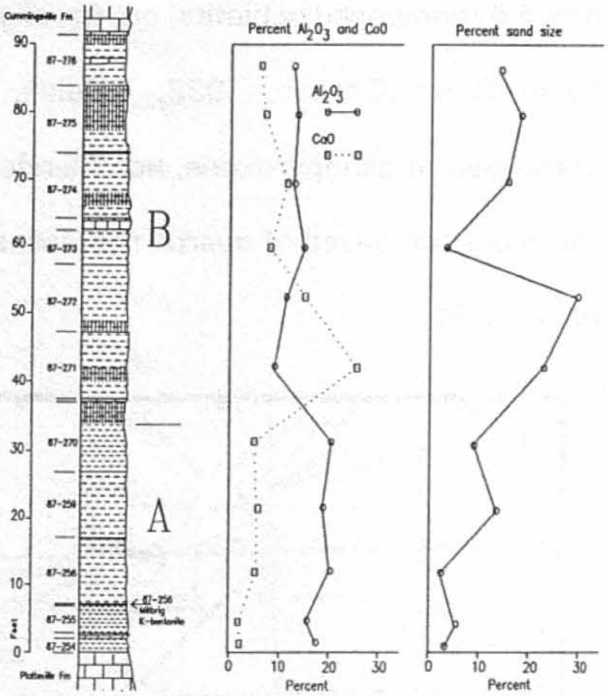


Figure 9. Stratigraphic column of the Decorah Shale in the Twin City Brickyard showing vertical changes in particle size and chemistry. (Stratigraphy modified from Sloan, *et al*, 1987).

thirds of the formation, which is reflected by both chemistry and particle size distribution (Fig. 9). Illite is the dominant clay mineral with minor kaolinite, and trace amounts of calcite and dolomite, which supports Parham and Austin's (1969) northward transgressing Ordovician sea.

PRIMARY AND SECONDARY KAOLINITE CLAYS

Underlying the Pleistocene and Late Cretaceous sediments in western and central Minnesota are pre-Late Cretaceous primary (residual) and secondary kaolinitic clays. The clay content of the saprolite or residual clays is dependent on the composition of the bedrock and the degree of weathering. The bedrock in the Redwood Falls (Fig. 10) area is the Archean (3.5 Ga) Morton Gneiss, which consists of granitic gneisses (adamellite to granite), tonalitic to granodioritic gneisses and amphibolites (Goldich, *et al*, 1980). The tonalitic to granodioritic gneisses are primarily composed of biotite, quartz, oligoclase, microcline with minor hornblende and hypersthene (Goldich, 1938; Goldich, *et al*, 1980), whereas the amphibolite is composed of clinopyroxene, hornblende and plagioclase (Lund, 1956). The granitic rocks are composed of quartz, microcline and plagioclase with minor biotite (Goldich, *et al*, 1980).

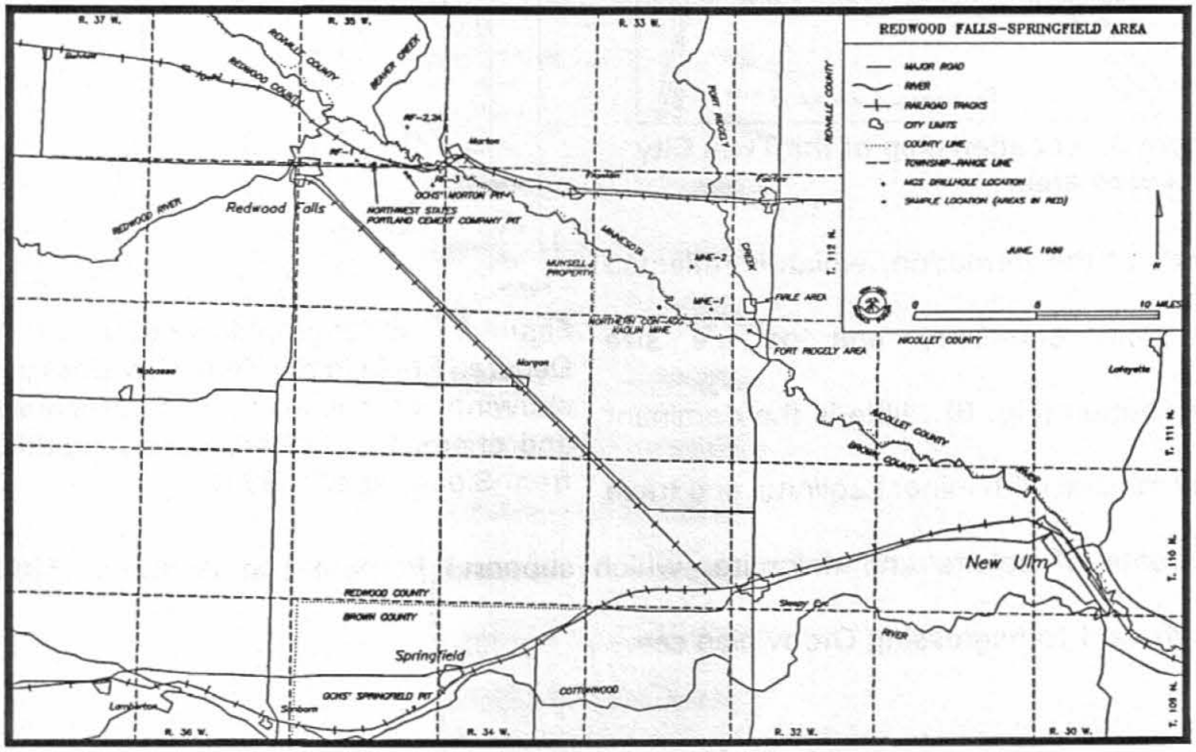


Figure 10. Location map of the Redwood Falls-Fairfax area, Minnesota River Valley.

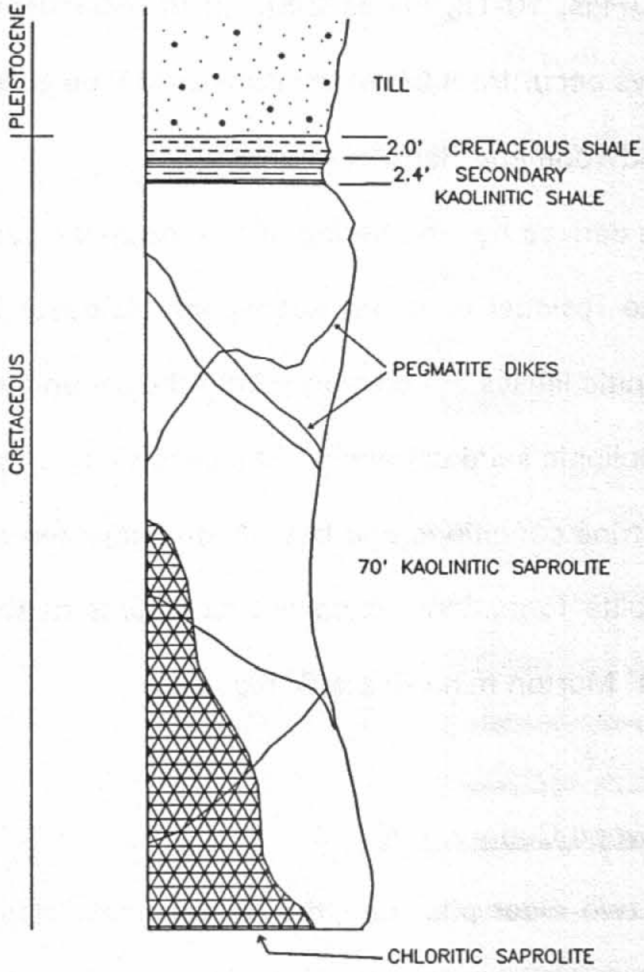
In general, the residual clays are composed of two types; a white to light greenish-yellow kaolinitic clay and a green, chlorite-rich clay. The kaolinitic saprolite is composed of kaolinite and quartz. Some feldspar may still be present near the unweathered bedrock contact. Residual gneissic textures or primary porphyritic textures may still be visible in the saprolite. In most areas, a 2-6 foot iron-stained zone occurs in the pre-Late Cretaceous clays below the Pleistocene contact. The iron-staining formed from groundwater precipitation of iron oxides moving along topographic/hydraulic gradients. Excellent exposures of the residual clays occur at the Northwest States Portland Cement mine (NWSPC), the Northern Con-Agg mine, the Firle and Munsell properties in the Minnesota River Valley (MRV), and the Meridian Aggregates mine in the St. Cloud area (Figs. 10-18; Plates 2-5). In the Minnesota River Valley, residual and secondary clays occur from the Mankato area in Blue Earth County to the Redwood Falls area in Redwood and Renville counties.

The secondary kaolinitic clays are derived by weathering of the residual clays. These clays are pisolitic at or near the residual or upper secondary (paleosol ?) contacts, or they are sandy or silty. Lignitic lenses are present within the secondary clays. Lignitic "trash" also occurs in kaolinitic sand channels. The secondary clays have been deposited under fluvial/lacustrine conditions and have been subjected to continued lateritic weathering, i.e., pisolite formation. Excellent exposures of the secondary clays are present in the Ochs' Morton mine (Plate 6; Fig. 19).

The NWSPC Mine, Redwood Falls, Redwood County, MN

The NWSPC mine now includes two older pits, i.e., the old and new Nova Natural Resources mines, which are on adjacent property (Plate 2). These mines are located on the south side of the Minnesota River Valley, east of Redwood Falls (Fig. 10). NWSPC mines the kaolin-rich saprolite for use in portland cement. The company mines approximately eighty feet of saprolite. The clays are shipped by truck and rail to Mason City, Iowa.

The stratigraphy in the mine is composed of Pleistocene, Late Cretaceous, and pre-Late Cretaceous sediments that overlie the residual kaolinitic clays (Fig. 11). The clay minerals in the mined residual clay are kaolinite with minor chlorite, illite and trace mixed-layered clays. The clay mineralogy of residual chloritic pods (biotite gneiss and amphibolite) within the weathered Morton Gneiss is chlorite and kaolinite with minor illite and mixed-layered clays.



CRETACEOUS SHALE
THIS SHALE IS LIGHT TO MEDIUM GRAY IN COLOR AND MASSIVE IN TEXTURE. OCCURRENCE OF THIS MATERIAL IS ERRATIC.

SECONDARY KAOLINITIC SHALE
THIS KAOLINITIC SHALE IS VERY PLASTIC AND CONTAINS MINOR WOOD FRAGMENTS. IT APPEARS TO BE A THIN DEPOSIT THAT OCCURS ERRATICALLY IN THIS AREA.

PEGMATITIC DIKE
THESE DIKES ARE COMPOSED OF QUARTZ AND FELDSPAR. THEY ARE 3 TO 9 INCHES IN THICKNESS AND CROSS-CUT ALL THE RELICT TEXTURES IN THE GNEISS.

KAOLINITIC SAPROLITE
THIS MATERIAL IS DOMINANTLY COMPOSED OF KAOLINITE WITH SOME CHLORITE AND STRINGERS OF QUARTZ AND FELDSPAR. RELICT GNEISSIC TEXTURES ARE PRESERVED BY THE QUARTZ-FELDSPAR STRINGERS.

CHLORITIC SAPROLITE
THIS MATERIAL IS COMPOSED OF CHLORITE, KAOLINITE AND BIOTITE. RELICT SCHISTOSE TEXTURES ARE PRESERVED BY THE BIOTITE. CONTACTS ARE MODERATELY SHARP TO GRADATIONAL BETWEEN THE CHLORITIC SAPROLITE AND THE KAOLINITIC SAPROLITE.

Figure 11. Stratigraphic section of the Northwest States Portland Cement Company kaolin mine, Redwood County.

Munsell Property, Franklin, Redwood County, MN

The Munsell property is located on the south side of the Minnesota River Valley, near Franklin, MN (Fig. 10). The Munsell property consists of two areas, the beanfield and the farmyard (Plates 3A and 3B).

The area referred to as the Munsell farmyard has exposures of bedrock, grus, and saprolite (Plate 3A). A drill road runs west from the farmyard, exposing saprolite, secondary kaolinite, glacially disturbed Late Cretaceous shale, and glacial tills, sands, and gravels. Outcrops in the farmyard expose a complete weathering sequence from bedrock to the deposition of secondary kaolinite.

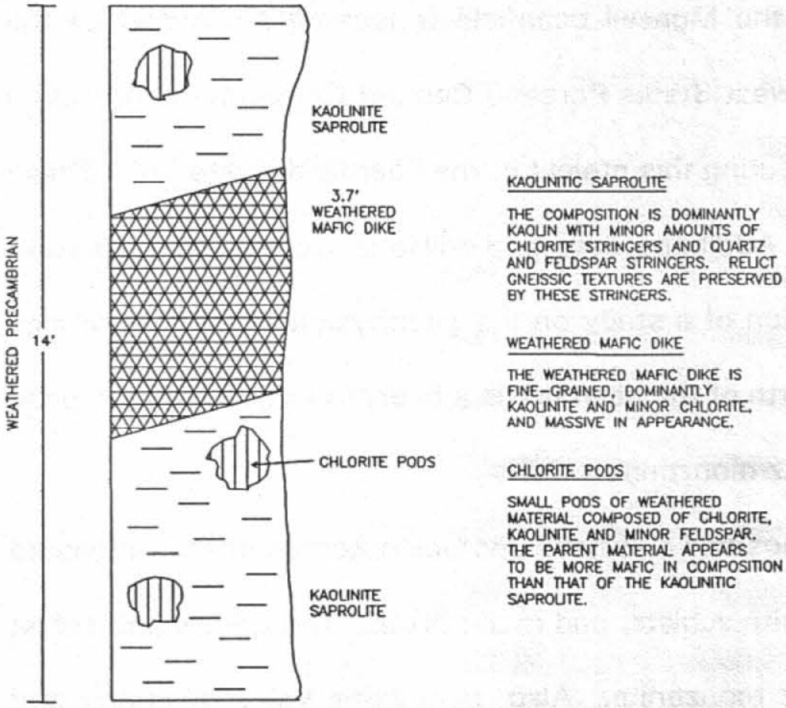
The area referred to as the Munsell beanfield is located northwest of the farmyard Plate 3B). The Northwest States Portland Cement Company completed a series of split core auger holes during this project in the beanfield (Plate 3B). These holes were logged and sampled. Additional data (and drill logs) from these holes were used to assist in the interpretation of a study on the geophysical responses of clay (Chandler, *et al*, 1990). Just north of the beanfield is a bedrock ridge of Precambrian mafic dikes and unfoliated quartz monzonite.

The Munsell farmyard exposures also have bedrock outcrops of the unfoliated quartz monzonite, gneisses, biotite schists, and mafic dikes. The gneiss and schist occur as xenoliths in the quartz monzonite. Also, pegmatitic veins of quartz and feldspar are present locally. The quartz monzonite outcrops become progressively more weathered from the eastern side of the farmyard toward the west. The outcrops grade from rock through grus to saprolite. There is an increase in clay content, at the expense of feldspar. The felsic rocks contain two types of feldspar, plagioclase and microcline, and the microcline is more resistant to weathering than the plagioclase.

The secondary clay along the drill road is not pisolitic, and no sedimentary features are observed. It is composed of kaolinite with very little fine-grained quartz. Further to the west along the road is a thin exposure of a convoluted, gray-black clay that is similar to the glacially disturbed Late Cretaceous sediments found at the Ochs' Morton mine. This material does not react with dilute HCl, whereas the glacial materials react strongly.

The Northern Con-Agg Mine, NW Brown County, MN

The stratigraphy in the mine is composed of recent (post-Pleistocene) fluvial sediments, saprolitic Morton Gneiss with xenoliths of amphibolite, and a saprolitic mafic dike (Plate 4; Fig. 12). The clays are kaolinite and minor illite. Very little chlorite is present. The clays have a yellow iron stain at the contact with the overlying Pleistocene fluvial sediments. The mine currently contains approxi-mately 40+ feet of saprolite, which is mined and shipped to Mason City, Iowa.



KAOLINITIC SAPROLITE

THE COMPOSITION IS DOMINANTLY KAOLIN WITH MINOR AMOUNTS OF CHLORITE STRINGERS AND QUARTZ AND FELDSPAR STRINGERS. RELICT GNEISSIC TEXTURES ARE PRESERVED BY THESE STRINGERS.

WEATHERED MAFIC DIKE

THE WEATHERED MAFIC DIKE IS FINE-GRAINED, DOMINANTLY KAOLINITE AND MINOR CHLORITE, AND MASSIVE IN APPEARANCE.

CHLORITE PODS

SMALL PODS OF WEATHERED MATERIAL COMPOSED OF CHLORITE, KAOLINITE AND MINOR FELDSPAR. THE PARENT MATERIAL APPEARS TO BE MORE MAFIC IN COMPOSITION THAN THAT OF THE KAOLINITIC SAPROLITE.

Figure 12. Generalized stratigraphic section of the Northern Con-Agg kaolin mine, Brown County.

Firle Property, Fairfax, Renville County, MN

The kaolinite occurrences on the Firle property (Figs. 10, 13, 14) are in saprolite of the Fort Ridgely Granite (Lund, 1950). Overlying the saprolitic Fort Ridgely Granite are glacial and Late Cretaceous sediments (Fig. 14). The Pleistocene sediments consist of sand and gravel. The Late Cretaceous shales and sandstones are similar to other Late Cretaceous sediments in the Minnesota River Valley. A pisolitic kaolinitic clay is interbedded with these shales and sandstones. This secondary kaolinitic clay is commonly found between the residual material and the Late Cretaceous shales in other parts of the Minnesota River Valley. The deposition of this pisolitic kaolinite is

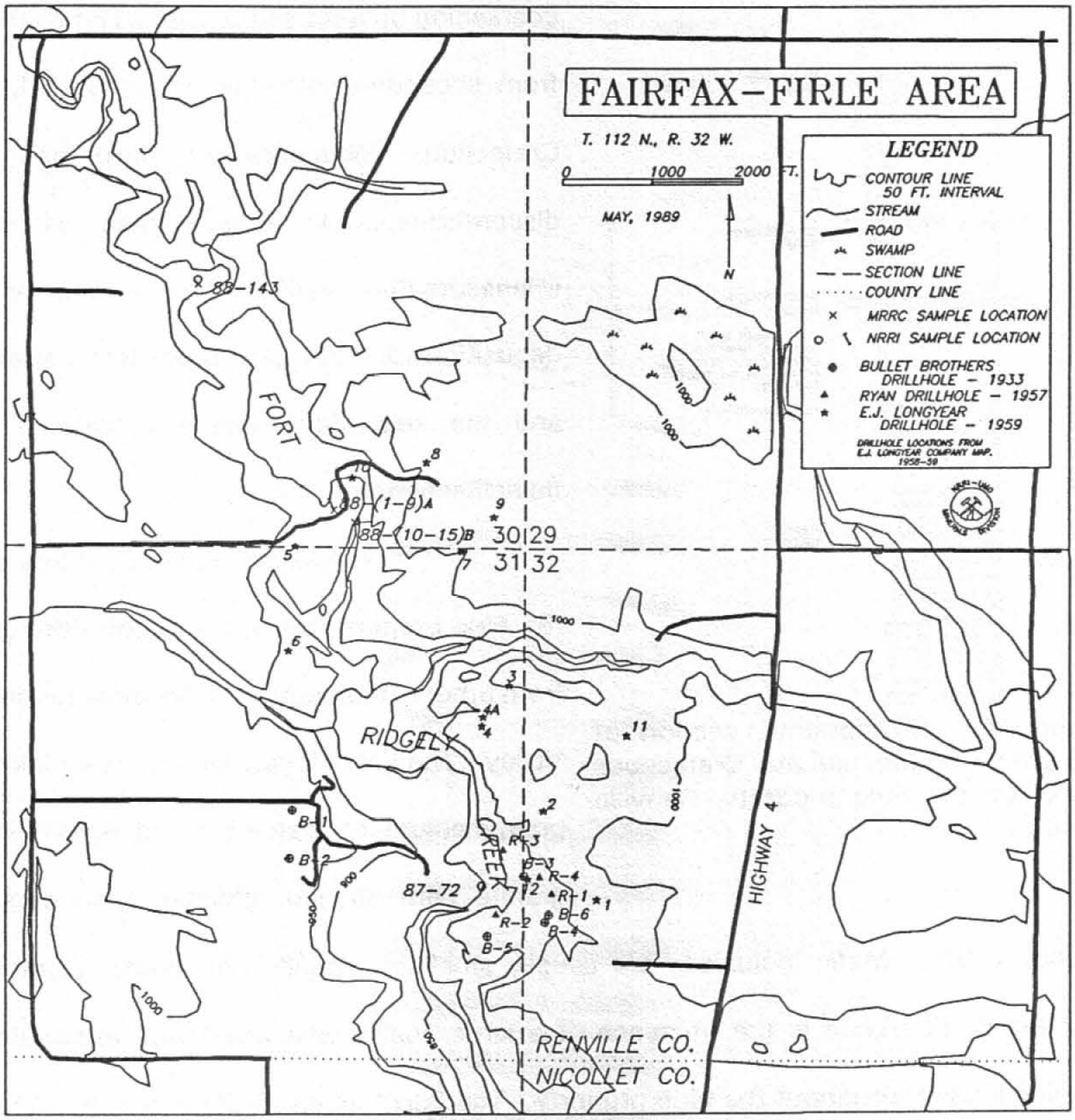


Figure 13. Location map of sample locations on the Firle property, Renville County.

probably the result of local variations in the source area, possibly the reworking of a pisolitic kaolinite, forming a stream lag deposit material.

Secondary kaolinites are absent on the Firle property but are found further to the west in Minnesota Geological Survey (MGS) drill hole MNE-1 (Fig. 10; Setterholm, *et al*, 1989). The kaolinitic shale and sandstones in this drill hole comprise several coarsening upward sequences. The change from secondary kaolinite deposits to Late Cretaceous sediments is sharp and is disconformable in most areas of the Minnesota River Valley. The environment of deposition for both Late Cretaceous shales and the secondary kaolinitic material is fluvial/lacustrine.

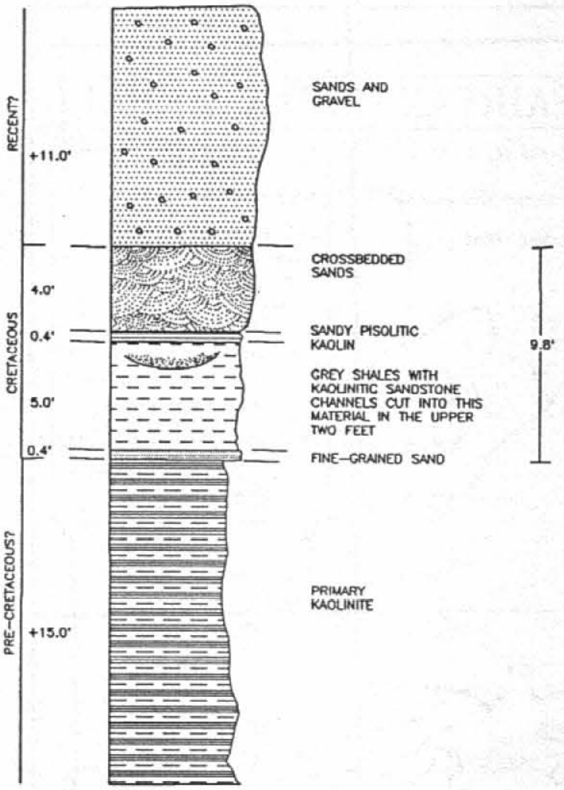


Figure 14. Stratigraphic section of pre-Late Cretaceous/Late Cretaceous rocks on the Firle property, Renville County.

The residual kaolinitic clays on the Firle property are significantly different from other exposures in the Minnesota River Valley. The Fort Ridgely Granite is a pink to gray, medium- to coarse-grained, porphyritic granite with aligned feldspar phenocrysts (Lund, 1950). Mafic inclusions are usually small and locally abundant. Another significant difference is the presence of a large quartz vein and many associated smaller veins throughout the Firle property. The Fort Ridgely Granite was fractured and hydrothermally altered during emplacement of the quartz veins. Some of the original kaolinite formation on the Firle property may be the result of hydrothermal alteration that occurred prior to weathering. The fracturing and hydrothermal alteration also made the subsequent chemical weathering more effective in the formation of kaolin. Processing of kaolin from the Firle property is reported in Prasad, *et al*, (1990)

Meridian Aggregates' Mine, St. Cloud, Stearns County, MN

The stratigraphy in the Meridian mine is composed of unweathered granite and mafic dikes, saprolite, and glacial sediments (Plate 5; Figs. 15, 16). The saprolite/granite contact is well exposed, vertically variable, and gradational. The saprolite is approximately 40-50 ft. thick and is removed as waste material so that the granite can be quarried for aggregate. The contact with the glacial sediments (gravel and till deposits) is sharp. Within the glacial sediments is a thin secondary kaolinitic-rich unit. Similar residual clays also are found over the granitic bedrock in the nearby Cold Springs Crystal quarry (Fig. 15).

The granitic bedrock is a part of the Stearns Granitic Complex (Goldich, 1968; Morey, *et al*, 1982; Dacre, *et al*, 1984). The "red" and "gray" granites that are, or have been, mined in the Meridian pit belong to the Stearns Granitic Complex. The "gray" granite is a granodiorite composed of quartz, plagioclase, microcline, biotite, and hornblende (Keighin, *et al*, 1972). The "red" granite is mainly composed of quartz, microcline, and plagioclase (Keighin, *et al*, 1972).

The compositional variability of the felsic and mafic parent rocks and the degree of weathering produces a variable clay assemblage in the saprolite. The whitest clay is associated with the most felsic composition of the granites, and the greenest clay is associated with the mafic dikes. The residual clays in some areas of the mine have been removed by glacial and pre-glacial processes. Slickenslides and other textures support the presence of faulting. These pre-weathering faults provided conduits for groundwater and therefore, allowed deep, variable weathering of the bedrock.

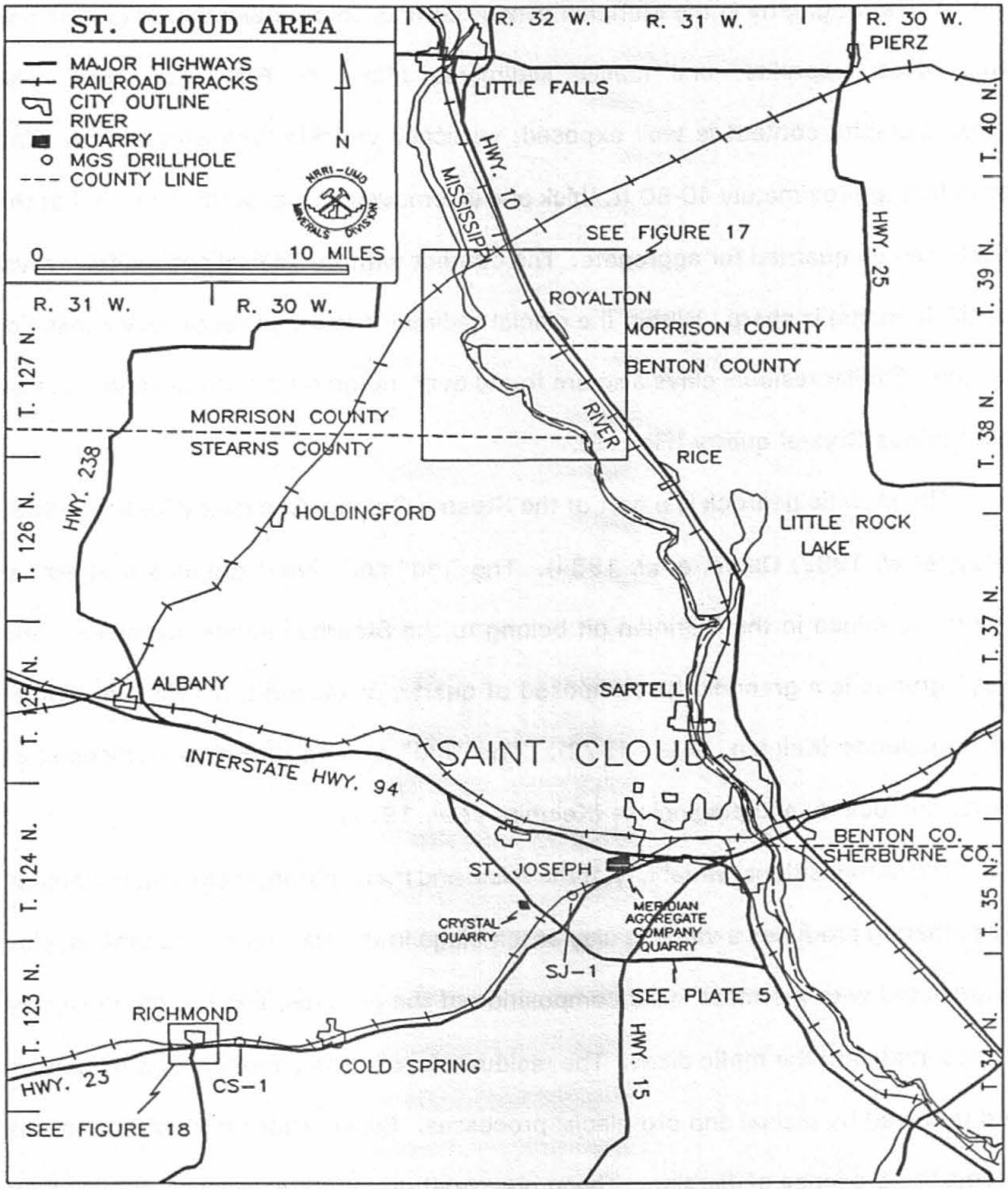


Figure 15. St. Cloud area location map, Stearns, Morrison, Benton, and Sherburne counties.

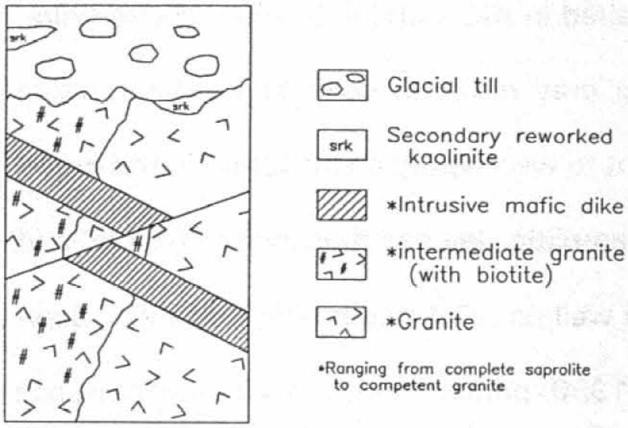


Figure 16. Generalized stratigraphic section of the Meridian Aggregates' St. Cloud mine.

Bowlus Occurrences, Bowlus, Morrison County, MN

The geology of the area along the Mississippi River between Bowlus and Royalton, Minnesota, is composed of glacial deposits, Late Cretaceous shales, secondary kaolinite, and primary clay deposits (Fig. 17). There are two types of primary clays present, a chloritic staurolite-bearing clay and a kaolinitic muscovite-bearing clay. Unweathered bedrock outcrops were not observed, and the full stratigraphy does not crop out in the area.

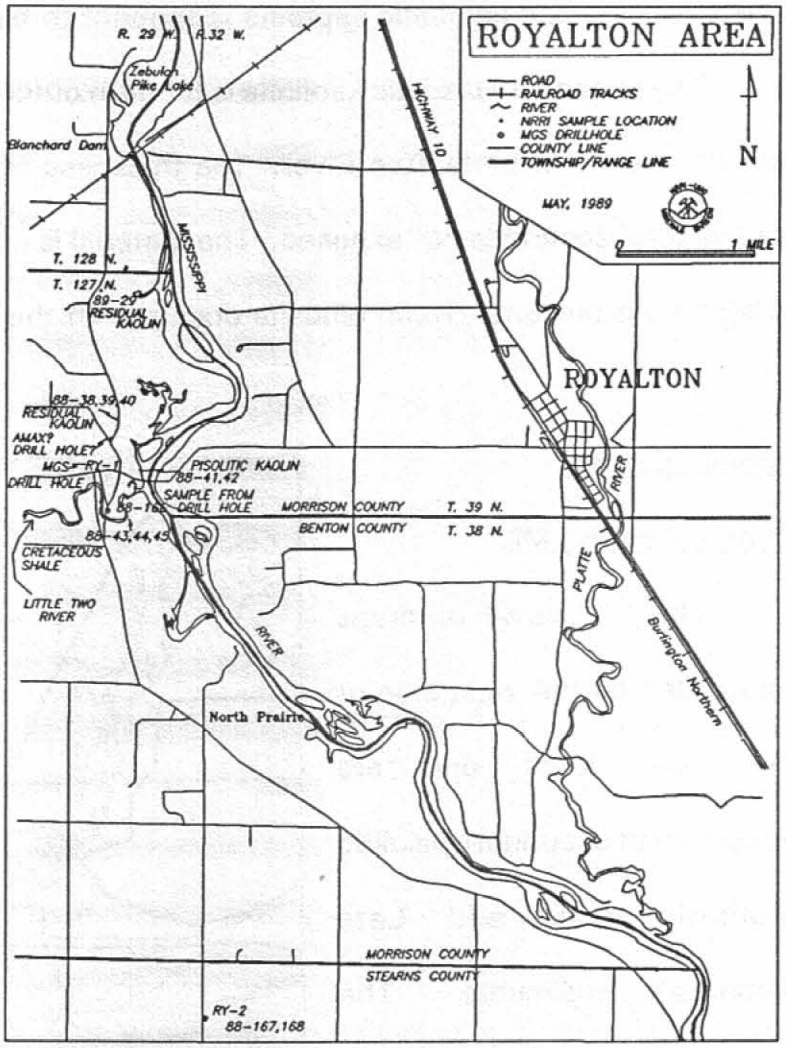


Figure 17. Bowlus - Royalton area location map.

The primary clays consist of both chloritic and kaolinitic residual materials. The chloritic residual clay crops out near Blanchard Dam on the Mississippi River, and the kaolinitic material is found along the bank of Little Two River. The parent rock for the chloritic material is a staurolite biotite schist and was encountered in MGS drill hole RY-1 (Setterholm, *et al*, 1989). The chloritic residual clay is gray green in color and exhibits relict schistose textures. The staurolite is resistant to weathering and is found in the gravel along the Mississippi River. The kaolinitic saprolitic clay has muscovite (1-5 cm) and quartz (0.5-2 cm) as accessory minerals as well as relict pegmatitic textures. Beryl has been found in the same area (J.D. Lehr, 1990, pers. comm.). Another occurrence was found in overgrown waste piles one mile north of Little Two River. This material is believed to be the waste from a former mine, but this could not be confirmed. The parent rock for the kaolinitic saprolite is thought to be a pegmatite.

The secondary pisolitic kaolinite is found in outcrops along the Mississippi River, near the mouth of Little Two River. The thickness of this material is over five feet, but the total section is not exposed. The material is iron-stained, and minor amounts of lignite are present. Trace gibbsite occurs with the pisolites.

Richmond Area,
Stearns County, MN

The Richmond outcrops are located on the west side of the Sauk River and are composed of secondary pisolitic kaolinitic clay and Late Cretaceous sediments. The pisolitic clay outcrop is located on the bank of the Sauk River,

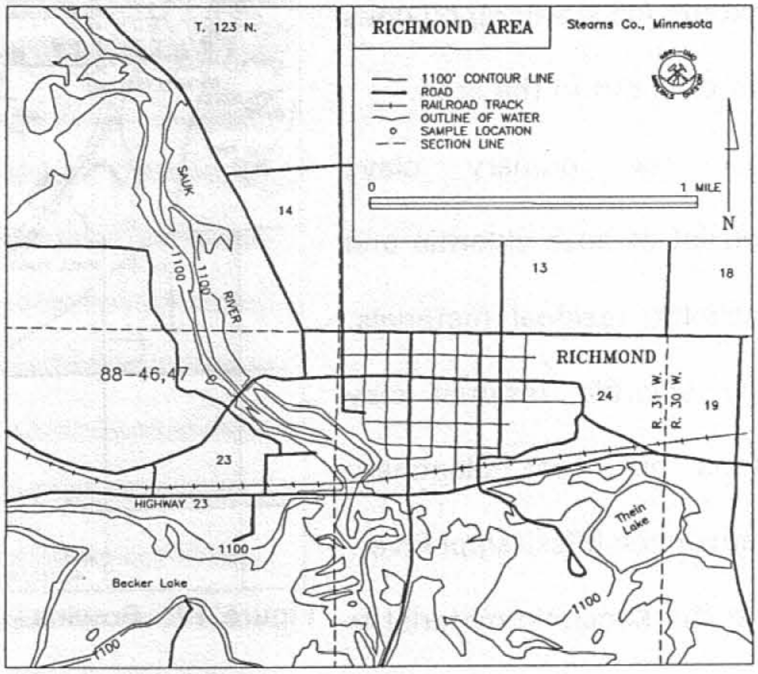


Figure 18. Richmond area location map.

and Late Cretaceous sediments are found along a hillside creek (Fig. 18). The Late Cretaceous sediments are described in Toth, *et al* (1990). The secondary kaolinite is an iron-stained pisolitic clay, with small amounts of lignite. The total thickness of this section is not known, and no exposures of primary clays were observed.

Och's' Morton Mine, Morton, Redwood County, MN

The Ochs' Morton mine has two pits, East and West (Fig. 10; Plate 6). The East pit is reclaimed. The stratigraphy in these pits includes Pleistocene, Late Cretaceous, pre-Cretaceous, and saprolitic Precambrian rocks (Fig. 19). More than 80

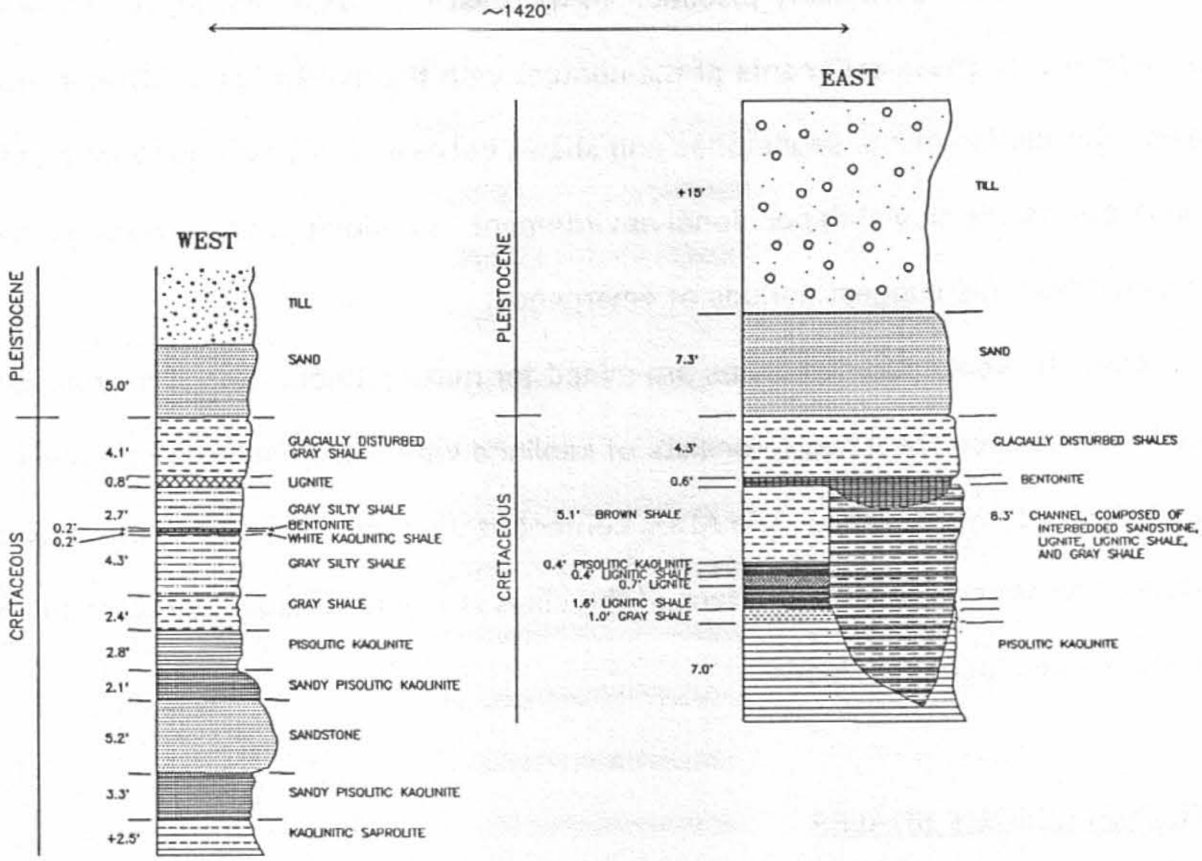


Figure 19. Ochs Brick and Tile Company's Morton mine, Redwood County - East and West pit stratigraphic sections (looking north).

feet of Pleistocene till and outwash sediments overlie the Late Cretaceous and pre-Cretaceous sediments. The Late Cretaceous shales and sandstone range from 10 to 20+ ft. thick and were eroded during glaciation.

The protolith of the kaolinitic saprolite is the Morton Gneiss. This saprolite is the same composition as the saprolite being mined at the NWSPC mine. In the West pit, some of the saprolite is pisolitic below the contact with the overlying secondary kaolinitic sediments. The pisolites in the saprolite are poorly formed and are found in the upper 6 to 10 inches when present.

The secondary kaolinitic sediments consist of interbedded kaolinitic shales and sandstones that are commonly pisolitic. In the East pit, lignite and lignitic shale is interbedded with these sediments at the contact with the overlying Late Cretaceous shales. Correlation of the sandstones and shales between the East and West pits is difficult due to the fluvial depositional environment. In addition, some pisolitic and brecciated textures suggest periods of emergence.

Only the secondary kaolinites are mined for making brick. The 2 micron size fraction of the secondary clays consists of kaolinite with trace amounts of gibbsite, illite, and mixed-layered clays. The Al_2O_3 content of the secondary clays ranges from 30-40%. However, the silica content of the clays is highly variable due to changes in fluvial depositional conditions.

LATE CRETACEOUS SHALES

During the Late Cretaceous most of western and central Minnesota was inundated by the Western Interior Sea (WIS; Austin, 1972). Both marine and non-marine sediments were deposited during the transgression and regression of the WIS (late Cenomanian - Greenhorn cycle, Unit 2; Shurr, *et al*, 1987).

The best exposures of these Late Cretaceous sediments are in and around the Minnesota River Valley. Clay is mined in the Ochs Brick and Tile mine near Springfield, Minnesota (Plate 7A; Fig. 10) to make bricks. The Late Cretaceous clays in this mine represent the thickest, contiguous section of currently exposed Late Cretaceous sediments in Minnesota, i.e., 60.5 feet.

Ochs' Springfield Mine, Springfield, Brown County, MN

The stratigraphy in the Springfield mine consists of Late Cretaceous shale, siltstone, sandstone, lignitic sediments, hardpan, and Pleistocene glacial drift (Plate 7A; Table 4 and Fig. 20). The Late Cretaceous sediments are subdivided into twenty-five subunits that are grouped into five major stratigraphic units (A, B, C, D, and E - Fig. 18; Plate 7A). The mine operates on two 30 foot benches. The upper bench contains units A, B, and the upper part of C. The lower bench contains units

Table 4. General stratigraphy of the Ochs Brick and Tile mine, Springfield, MN (Heine and Hauck, 1989).

Marine Sequence

Unit A - interbedded shales and sandstone - 7.0 ft.

Deltaic Sequence

Unit B - lignitic (coal) sequence - 2.1 ft.
Unit C - 3 upward coarsening sequences - 32.1 ft.
Unit D - 3 upward fining sequences - 14.6 ft.
Unit E - interbedded shale and sandstone (foreset beds) - 3.9 ft.

D, E, and the remainder of C. Units A and B are not currently mined due to their high sulfur content in the form of gypsum and pyrite.

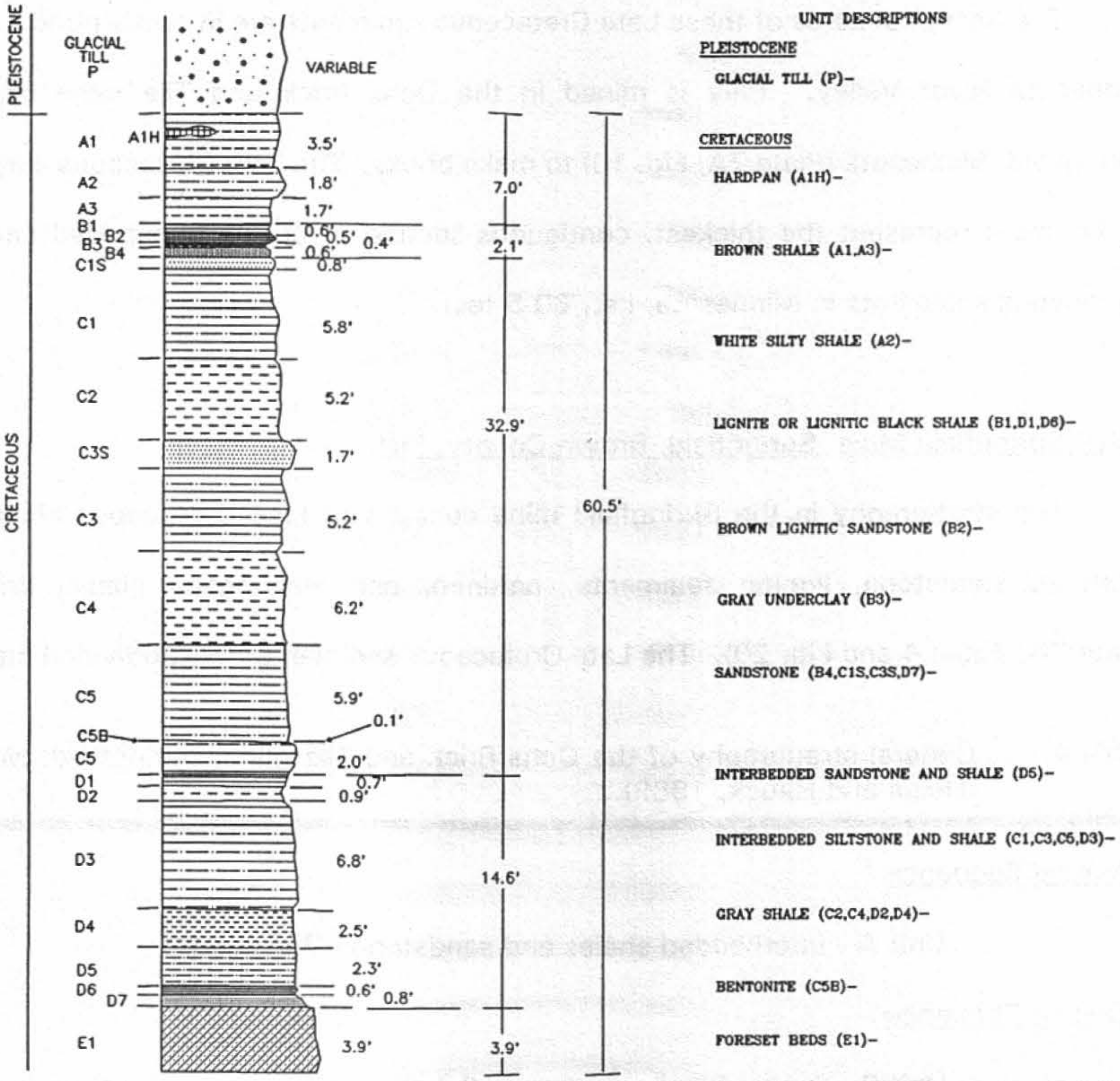


Figure 20. Stratigraphic section of the Late Cretaceous rocks in the Ochs Brick and Tile Springfield mine, Brown County.

The stratigraphy in the Springfield mine indicates that the sediments were deposited in a fluctuating and evolving nearshore environment. Unit E represents the upper portion of a prograding deltaic sequence. Within Unit D are three fining upward sequences; subunits D7 and D6, subunits D5 and D4, and subunits D3 through D1. The D7-D6 sequence represents a change from fluvial to more paludal conditions, based on the increase in lignitic material. These three fining upward sequences are produced by a migrating transportation source, such as a delta, that deposited these sediments into a standing body of water. Sloan (1964) originally proposed a deltaic-lacustrian origin for the upper units.

The basal subunits, C5 and C4, also represent a fining upward sequence that reverses in subunit C3 and C3S to an upward coarsening sequence. A second coarsening upward sequence occurs in subunits C2, C1, and C1S. These changes in style of deposition are also attributed to the same migration of the transporting source, i.e., a deltaic environment.

A major depositional change occurs in Unit B, with the formation of the lignite sequence. The presence of abundant lignitic material and broad, thin sands represent a paludal or estuarine environment. Unit A represents a nearshore marine environment. Sloan (1964) suggests that the units in the upper mine bench represent a transition from non-marine or estuarine into marine conditions. The stratigraphy represented in the lower mine bench is consistent with the continuation of a non-marine or estuarine depositional environment.

As indicated on the cross-sections on Plate 7B, there is a small domal structure near the center of the pit (Plate 7A). The long axis of the dome is northwest-southeast. Since the units do not thin over the dome, the minimum age of the dome is post-Late Cretaceous.

Other Cretaceous Clays

Other good exposures of Late Cretaceous sediments within the Minnesota River Valley crop out in the Ochs' Morton mine (Fig. 19) and on the Firle property (Figs. 13, 14), but these shales have no commercial value at the present. Within the Late Cretaceous sediments at the Ochs' Morton mine is a thin (avg. 2 in.) green to dark green bentonite (Ca-smectite - Parham and Hogberg, 1964; Fig. 19). This bentonite is mineralogically different from the C5B subunit in the Springfield mine, and this bentonite lies directly above the secondary kaolinite section. However, the regional extent and thickness of this unit has yet to be established.

Outcrops of Late Cretaceous Carlisle Shale occur in Traverse County on the shore of Lake Traverse. These shales generally fire white and at higher temperatures have a very high shrinkage and undergo a color change to yellow brown, which suggests a mineralogical phase change occurs at the higher temperature.

In the St. Cloud area, the Late Cretaceous section is presently exposed in the Richmond area (Fig. 18; see Toth, *et al*, 1990 for description of sediments). These shales are carbon-rich shales that contain gypsum and are similar to Unit B in the Ochs' Springfield mine, but the Richmond section is thicker and less sandy. However, like the Springfield shales, some of these shales have excellent firing characteristics and mining thicknesses (Toth, *et al*, 1990).

In southeastern Minnesota, the Cretaceous shales of the Austin area are composed of interbedded red, green, blue, and gray shales (Fig. 21). These shales are found in a circular depression in the Paleozoic bedrock (pers. com., V. Stuessy, 1988) and are interpreted to be lacustrine deposits.

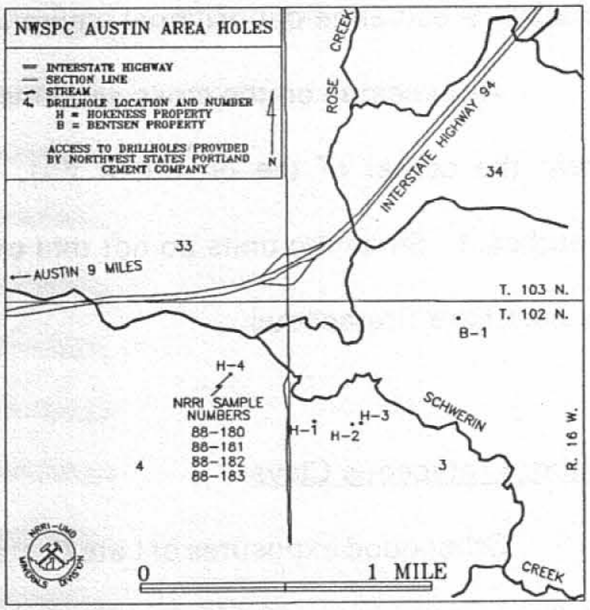


Figure 21. Austin area location map.

PLEISTOCENE GLACIAL CLAYS

The vast majority of Minnesota is covered by varying thicknesses of Pleistocene glacial deposits. These surficial deposits belong primarily to the Wisconsin glaciation, which overlies glacial debris of older glaciations. The surficial glacial deposits in much of Minnesota are primarily composed of material deposited by: 1) the Des Moines and Superior lobes; 2) in north-central and northeastern Minnesota, by the Wadena and Rainy lobes; and 3) various glacial lakes (Figs. 22, 23). Also, loess deposits that formed from fine-grained wind blown debris (Des Moines lobe) occur in the southeastern and southwestern portions of the state. These glacial deposits generally range from 5-100 ft., but can be up to 400 ft. in total thickness. The glacial lake clays (Fig. 23) were the primary source of brick making clays in the central and northern portions of Minnesota. Brickyards in Wrenshall in northeastern Minnesota produced bricks from Glacial Lake Duluth sediments while brickyards in the western and northwestern parts of Minnesota used Glacial Lake Agassiz sediments.

Bricks made from the glacial lake sediments generally fired to a cream or light red to salmon color. The glacial lake sediments are primarily composed of very fine-grained rock flour and a minimal amount of clay minerals. However, the offshore lacustrine clays of the Brenna and Sherack Formations in Glacial Lake Agassiz (Harris, *et al*, 1974; Arndt, 1977; Fenton, *et al*, 1983) bloat upon firing at 1830° F and may make excellent lightweight aggregate. The bloating of these clays may be due to dolomite and the presence of swelling clays. Carbonate is a major component of most glacial clays, especially those clays associated with the Des Moine Lobe, which contains a large percentage of Paleozoic carbonate-rich material.

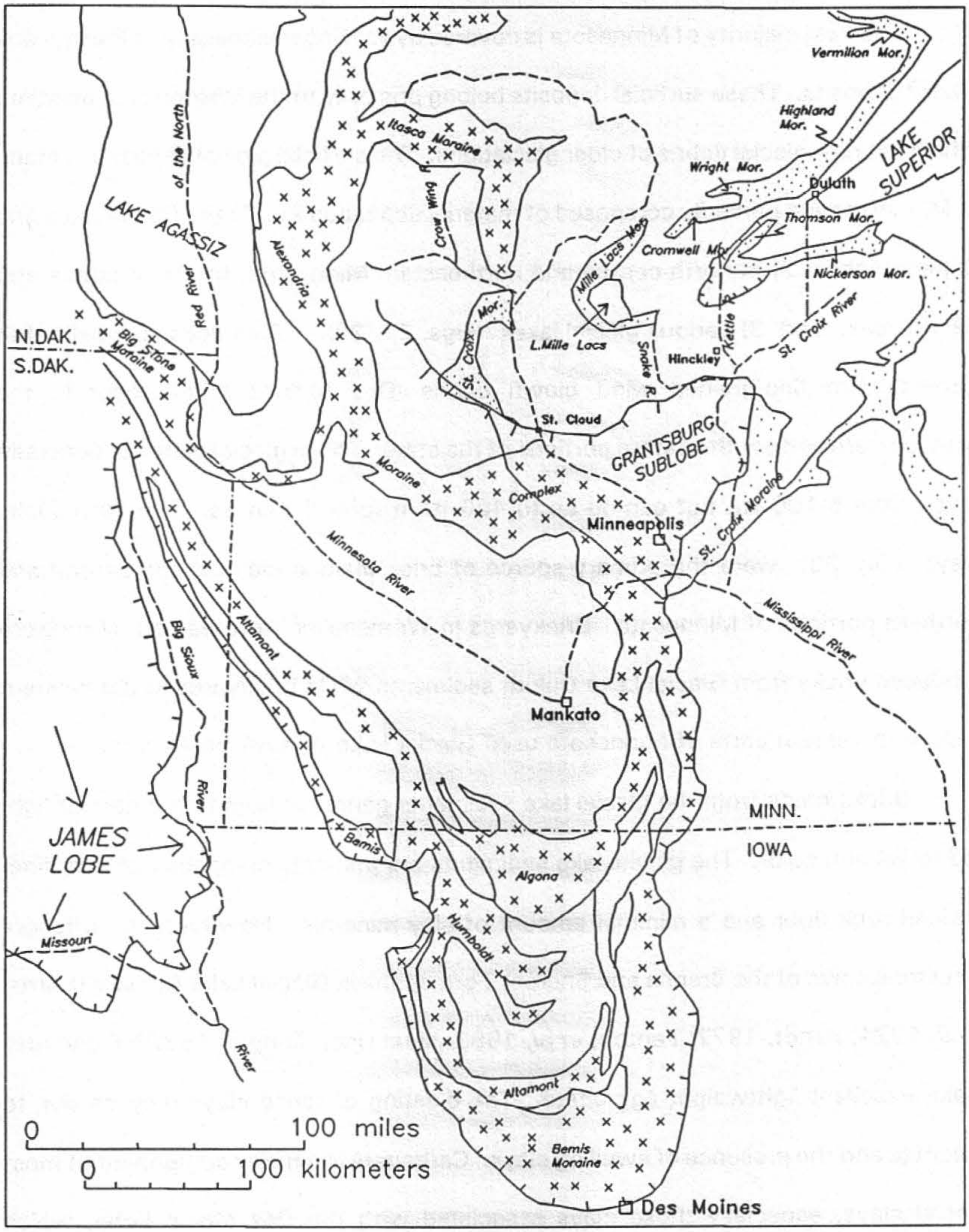


Figure 22. Distribution of Wisconsin tills (Des Moines and Superior lobes) in Minnesota (after Goldstein, *et al*, 1987).

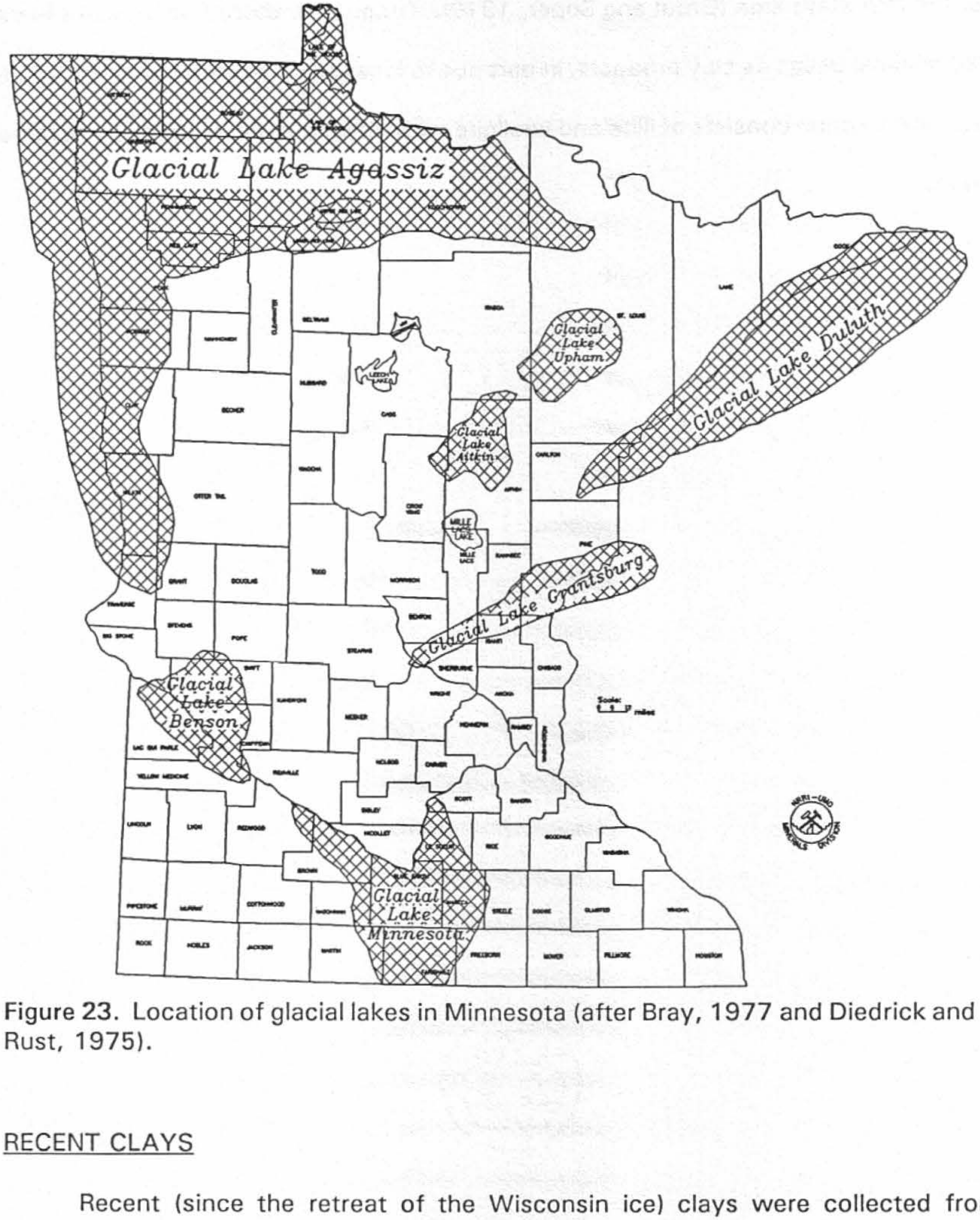


Figure 23. Location of glacial lakes in Minnesota (after Bray, 1977 and Diedrick and Rust, 1975).

RECENT CLAYS

Recent (since the retreat of the Wisconsin ice) clays were collected from lacustrine and river environments, in particular the Mississippi and Minnesota rivers (Plate 1). The largest use of Recent river clays was in the extreme southwest portion of Minnesota in Rock County, where the clays (ca. 1890) were used to produce bricks for the four state area (Grout and Soper, 1919). Otherwise, these Recent clays have had minimal usage as clay products, in part due to location on major waterways. The clay size fraction consists of illite and kaolinite with minor quantities of mixed-layered clays.

GEOCHEMISTRY

Major element (SiO_2, Al_2O_3, TiO_2, TFe_2O_3, FeO, CaO, MgO, MnO, Na_2O, K_2O, P_2O_5, CO_2, H_2O, and S) geochemical analysis is available on 65% of the samples collected (Appendix D). Total organic carbon (T.O.C.) is also analyzed for those samples that contained organic material. The SiO_2 and Al_2O_3 are major components in all Minnesota clays and are compared in Figure 24 for the various types of clays.

In the residual or saprolitic clays, the Al_2O_3, TiO_2, and total Fe_2O_3 values decrease with depth, while SiO_2 increases. MgO, Na_2O, and K_2O also increase slightly with depth. The aluminum and titanium are concentrated near the paleo-weathering surface due to their immobility during chemical weathering. TiO_2 is strongly correlated with Al_2O_3 suggesting that titanium is either retained in the kaolinite by substitution for Al or as discrete anatase and/or rutile particles (Newman and Brown, 1987).

These vertical changes in chemistry as well as the amount of weathering that a sample has undergone can be seen by comparing various geochemical "indices of weathering" (Fig. 25; Harnois, 1988 - CIW; Roaldset, 1972 - V; Vogel, 1975 - MWPI; Parker, 1970 - WI; Nesbitt and Young, 1982 - CIA) found in Appendix D-4 (floppy diskette). These indices were calculated as follows (all indices use molecular proportions):

$$\mathrm{CIW} = [Al_2O_3/(Al_2O_3 + CaO + Na_2O)] \times 100$$

$$\mathrm{CIA} = [Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)] \times 100$$

$$\mathrm{WI} = [(2Na_2O/0.35) + (MgO/0.9) + (2K_2O/0.25) + (CaO/0.7)] \times 100$$

$$\mathrm{MWPI} = [(Na_2O+K_2O+CaO+MgO)/(Na_2O+K_2O+CaO+MgO+SiO_2+Al_2O_3+Fe_2O_3)] \times 100$$

$$\mathrm{V} = (Al_2O_3 + K_2O)/(MgO + CaO + Na_2O)$$

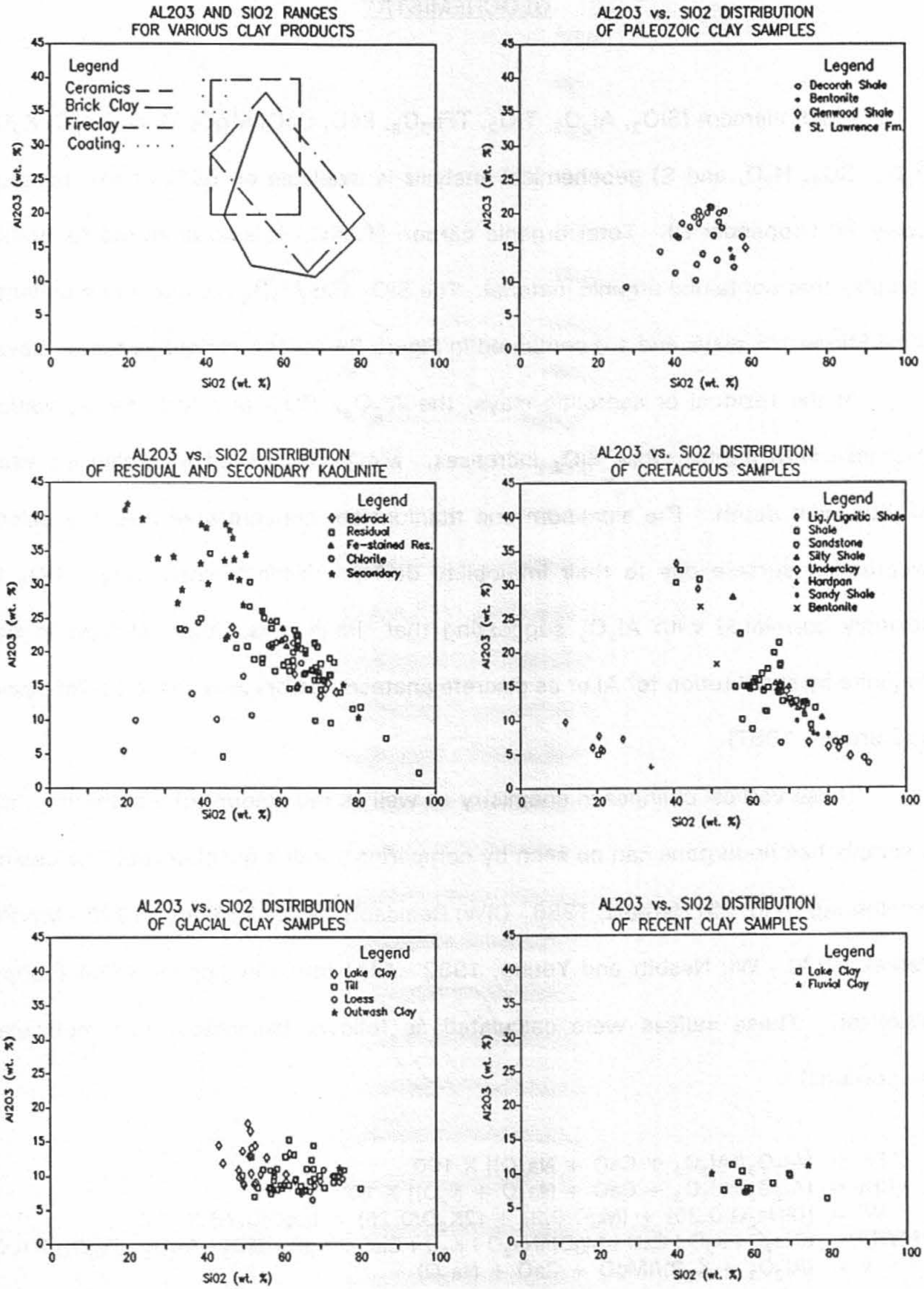


Figure 24. SiO_2 versus Al_2O_3 summary diagrams for each clay type.

Each index evaluates the mobile and immobile elements in the weathering profile differently. For this study, the CIA and CIW indices give the best indication of the degree of weathering that has affected the bedrock in Minnesota. The difference between the CIA and CIW indices is, as Harnois (1988) argues, that potassium can be easily leached during weathering. After potassium enters solution, new potassium minerals form that may adsorb on other clays by ion exchange. This adsorption of potassium would be greatest with clay minerals that had a high exchange capacity for potassium. Therefore, in soils where potassium has been leached, the CIA, WI and MWPI indices have limited use (Harnois, 1988). However, Setterholm, *et al* (1989) uses the CIA index effectively on drill hole samples to illustrate the degree of weathering over drill core intervals of 110-260 feet. When these indices are applied to a seventy foot thick vertical section in the NWSPC mine, all indices show a high degree of weathering for the saprolite in the NWSPC mine (Fig. 25). Comparison with data from Setterholm, *et al* (1989) shows that the full weathering profile is not exposed in the NWSPC pit and that a minimum of 30+ feet of weathered material may underlie the present pit floor (RF-1).

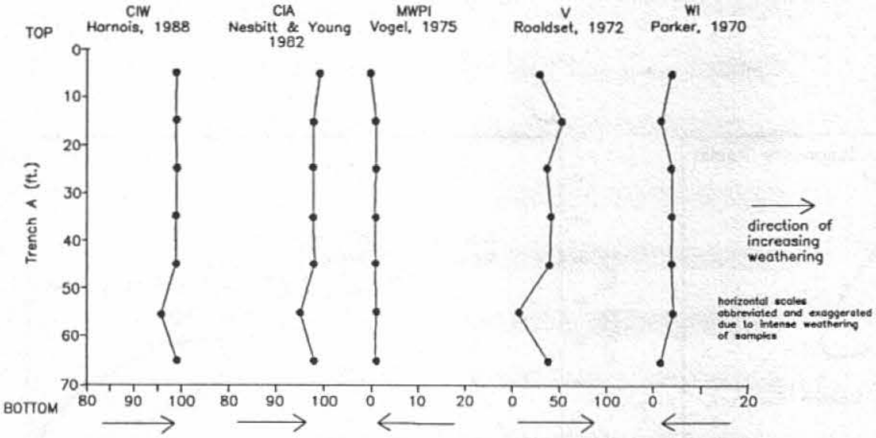


Figure 25. Comparison of various indices of weathering for Trench A in the NWSPC mine, Redwood Falls, Minnesota.

Figure 26-D illustrates the differences between the Al_2O_3 and SiO_2 content of the saprolitic clays being mined at the NWSPC mine in Redwood Falls and the

Northern Con-Agg kaolin mine in northwestern Brown County (Fig. 10). Clays from both of these mines are being used as additives in portland cement. The differences suggest there is either a difference in the composition of the protolith and/or the NWSPC clays have been more deeply weathered. Comparison of the CIA values for clays from these mines suggest that the NWSPC clays have been subjected to more weathering, but the differences in CIA values are minor.

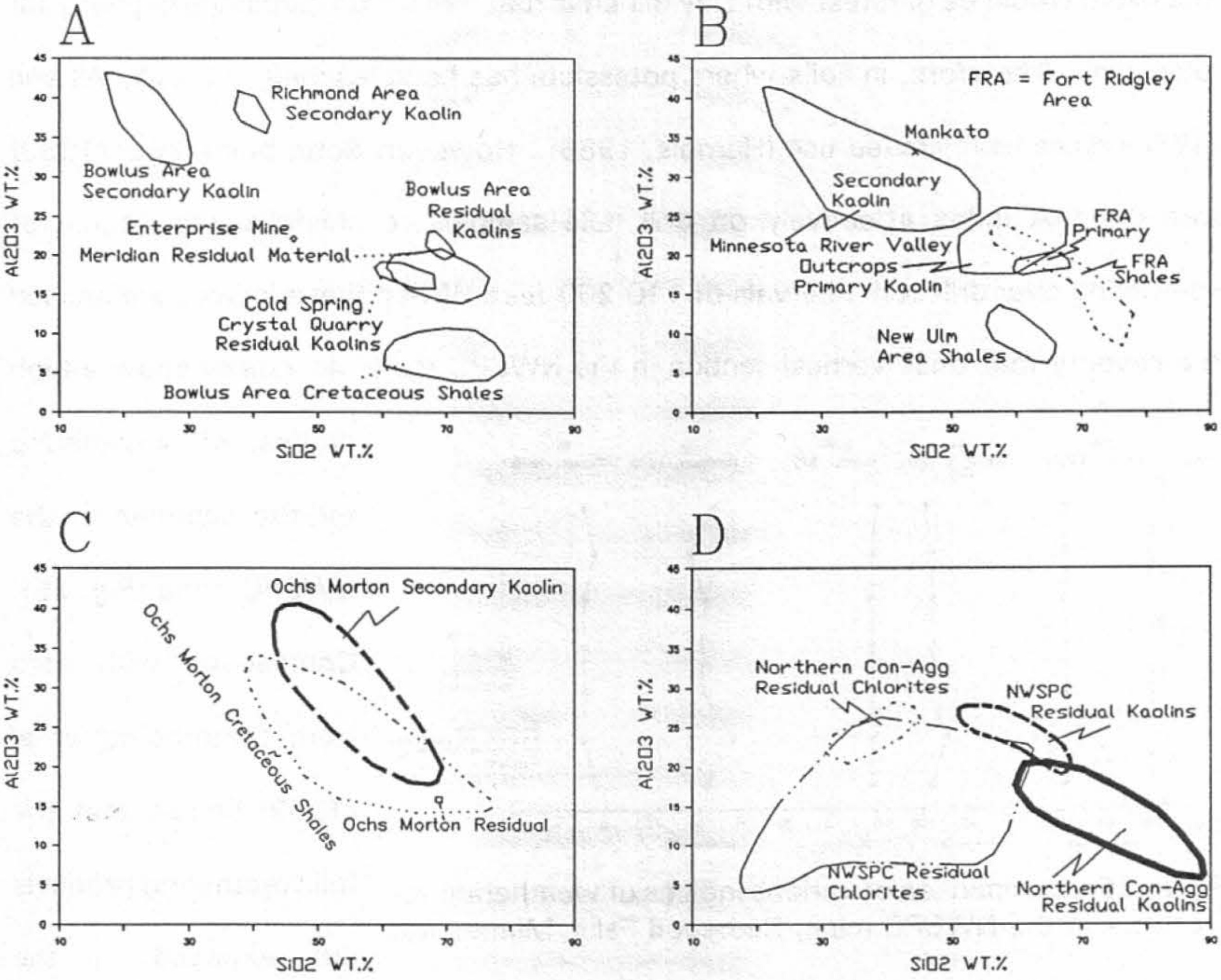


Figure 26. SiO_2- Al_2O_3 diagrams illustrating relationships between residual and secondary clays and Late Cretaceous clays.

The geochemistry of the secondary kaolinitic clays is controlled by the amount of quartz and kaolinite. With a decrease in the particle size, Al_2O_3 and TiO_2 increase and SiO_2 decreases (less quartz present). Figures 26-A and 26-B show this enrichment of Al_2O_3 and decrease in the amount of SiO_2 between the residual or saprolitic samples and the secondary kaolinitic clays. Again, TiO_2 has a strong correlation with Al_2O_3. MgO shows no change when compared to residual kaolinitic clays and does not appear to be dependent on, or related to, particle size. The secondary kaolinitic clays contain from 1.5-2 times as much Al_2O_3 as the saprolite or residual clays (Figs. 26-A, -B, -C). This relationship indicates that weathering and transportation of the residual clays have concentrated the kaolinite while removing other minerals, e.g., quartz, mica, etc. The K_2O and Na_2O content of the secondary kaolinite clays is less than in the residual clays, which also supports the weathering and reworking hypothesis.

One apparent problem with interpreting the geochemistry of outcrop samples is determining the possible effects that present day and "recent" paleo-weathering (limonite-stained zones) have had on the samples. As shown in Figure 27, samples collected from outcrops can have a higher Fe_2O_3 content (above the $Fe_2O_3 = FeO$ line) than fresher samples collected from drill core or on a mining face. The Fe_2O_3-FeO problem should be considered when evaluating or processing these clays.

The geochemistry of the Late Cretaceous sediments compared with the saprolitic and secondary kaolinitic clays is similar in many cases. Both the geochemistry and the X-ray mineralogy, i.e., presence of kaolinite in both types of samples, suggests a common genetic association between the two clay types, i.e., weathering and reworking of the residual and secondary kaolinitic clays contributed to the composition of the Late Cretaceous sediments. This relationship is apparent at the Ochs' Morton mine where white "porcelain" firing clays of one of the Late

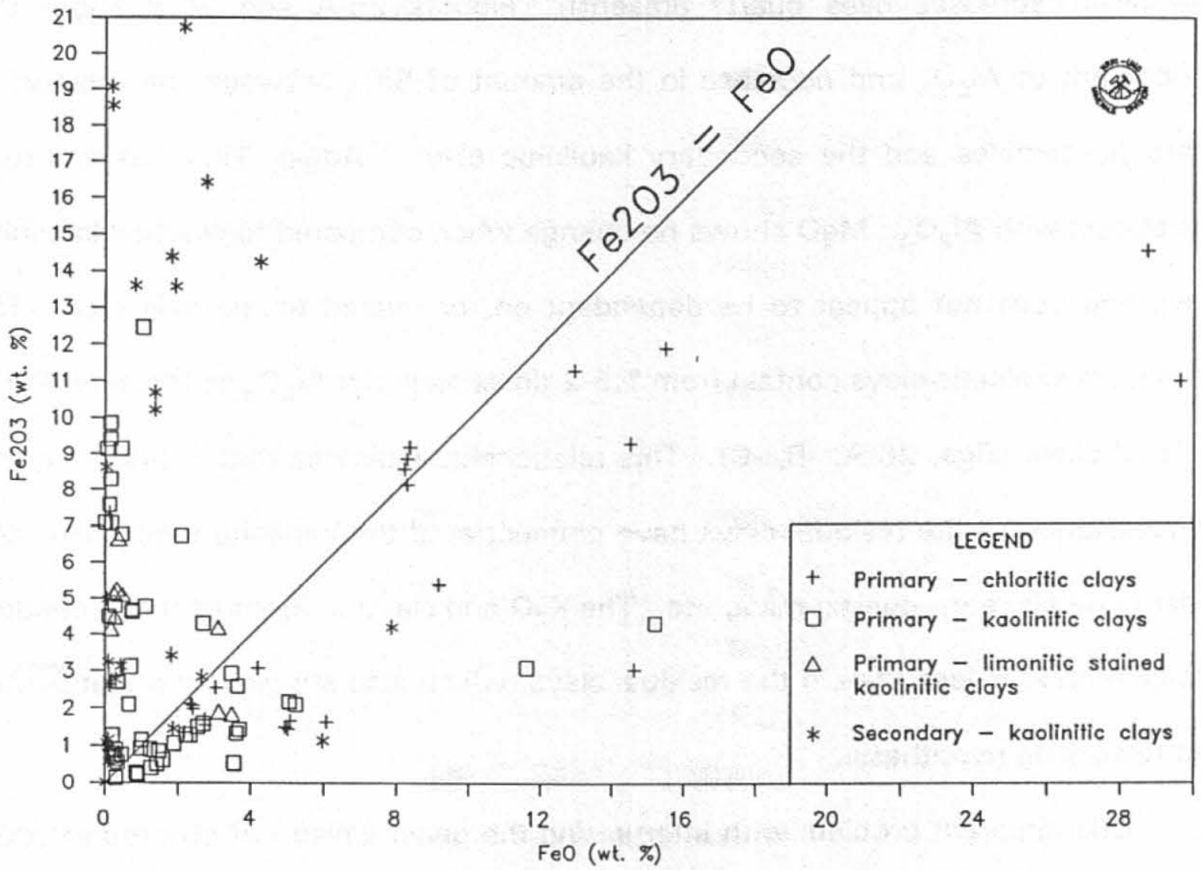


Figure 27. Fe_2O_3 versus FeO diagram for residual and secondary clays.

Cretaceous shales have about the same Al_2O_3 content as the secondary kaolinitic clays that directly underlie the shales (Fig. 24-C). However, this relationship is not apparent in the other areas, e.g., Bowlus (Fig. 24-A and 26-B). Yet, like many of the residual and secondary kaolin clays, the presence of secondary iron has contaminated many of the Late Cretaceous shales near the surface.

The geochemistry of the <10 mesh size fraction of the glacial tills reflects the source area of the major ice lobe, i.e., Des Moines, Superior, etc. (Fig. 28). Also, geochemical differences can be observed in the different moraine associations (Fig. 28). For example, the Culver moraine of the St. Louis sublobe generally has the highest SiO_2, TFe_2O_3, TiO_2, and alkalies. This not only represents the farthest distance from the source area, but may also indicate reworking of older tills, i.e.,

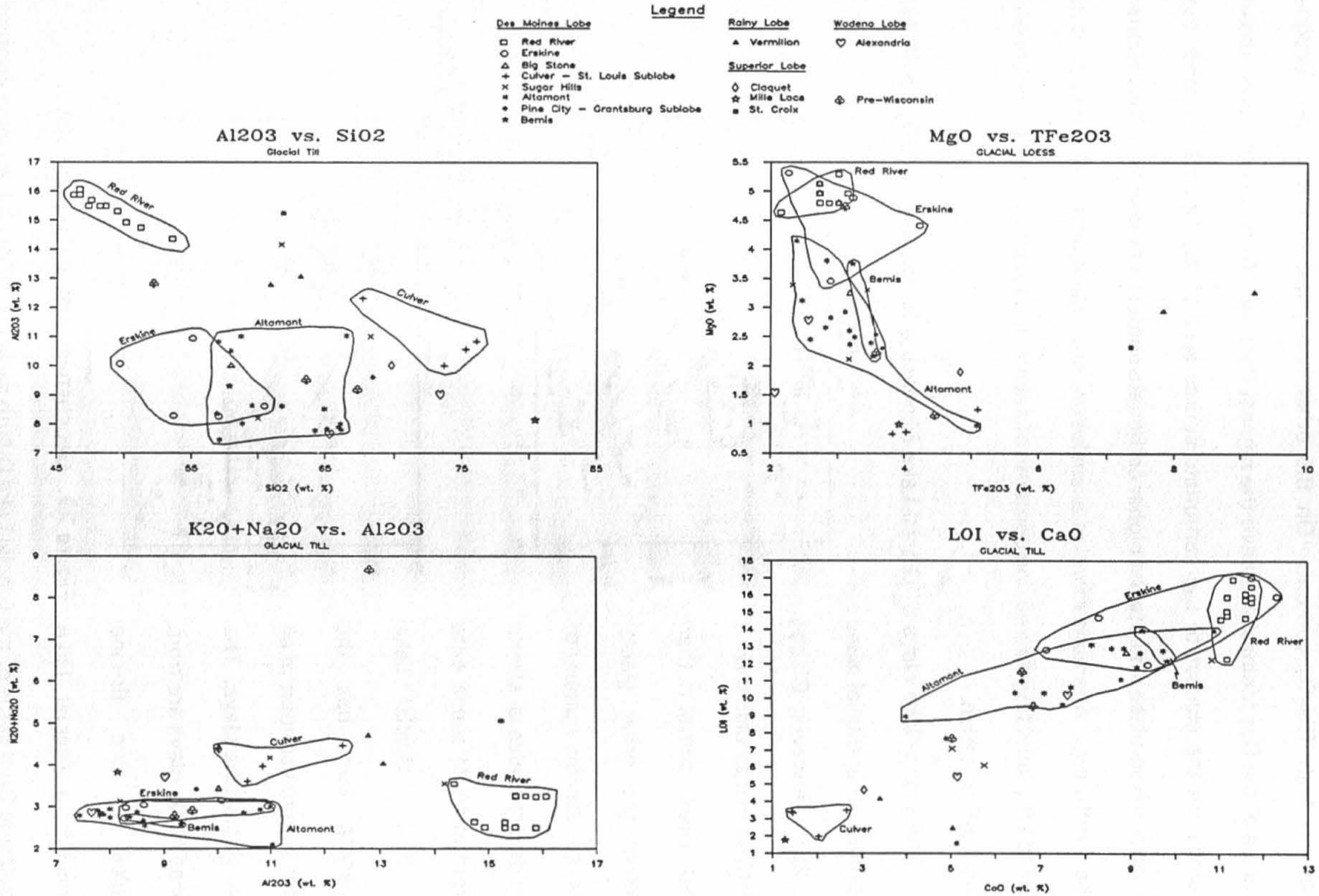


Figure 28. Geochemistry of <10 mesh size fraction of glacial tills.

Superior - high TFe_2O_3 content. On the other hand, the Red River and Erskine moraines of the Des Moines lobe have the highest CaO and LOI contents. Since these moraines are the closest to the carbonate source area of the Des Moine lobe, the chemistry of moraines reflects the higher carbonate content of these tills. Tills farther to the south, e.g., Altamont moraine association, etc., have decreasing contents of CaO and LOI, reflecting decreasing contents of calcite due to destruction of carbonate during transportation.

The glacial lake clays of Glacial Lake Minnesota have a higher SiO_2 (>58 %) than most other glacial lakes (Fig. 29). However, Glacial Lake Upham may also have a higher silica content than some of the other glacial lakes, but the low number of samples precludes a strong interpretation of these data (Fig. 29). Glacial Lake Minnesota also has the lowest alumina content of all of the glacial lake clays. The highest Al_2O_3 clays are from samples of the Brenna Formation in Glacial Lake Agassiz and from some of the Glacial Lake Duluth samples. This high alumina content

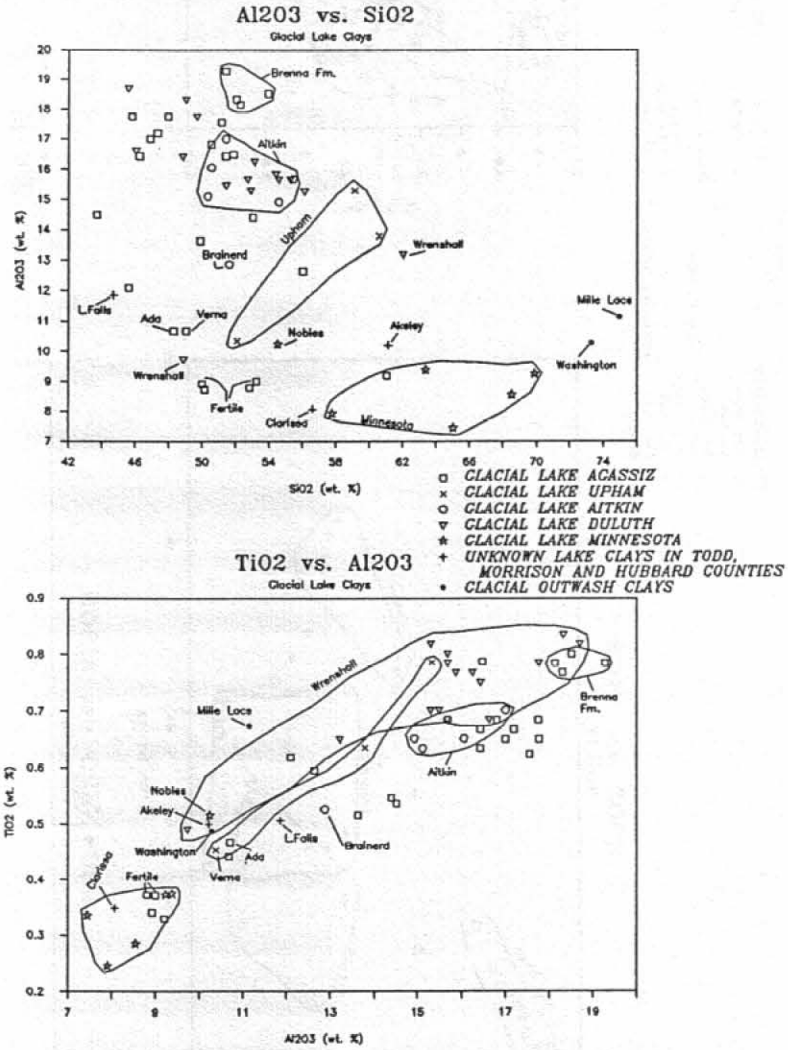


Figure 29. Geochemistry of glacial lake clays.

is again a reflection of the close proximity to their source area, e.g., Brenna Fm. - the Pierre Shale in North Dakota. Glacial Lake Duluth is also slightly more enriched in TiO_2 than the other glacial lake clays, which again may reflect a different source area for these clays. However, the wide range in chemical compositions of samples from glacial lakes Agassiz and Duluth indicate that more intensive sampling may illustrate that the differences in composition are minimal.

PHYSICAL CHARACTERISTICS

PARTICLE SIZE

Particle size analysis was conducted on 480 samples. The particle size distribution for each sample was determined by using Stoke's law for the silt and clay size fractions (1000 ml graduated cylinder with water, a deflocculant, and a 10-20 gm sample) and by sieving for the sand sized material. Analytical procedures and particle size data are given in Appendices C and E, respectively.

Figure 30 illustrates the <u>average</u> particle size range for the different types of clay collected during this investigation. The particle size distribution for some processed industrial clays is provided for reference (Fig. 30A). Comparison of the average particle size distribution for the various types of clays suggests that: 1) the secondary kaolinitic clays have potential as filler and coating grade clays; 2) some Late Cretaceous clays have potential as ball clays; 3) most glacial tills consist of sand and silt with minimal clay size material, while the glacial lake clays are either silt- or clay-rich with minimal sand; and 4) the Ordovician clays are generally ≥60 % clay.

Triangular sand-silt-clay plots are shown for each type of clay in Appendix E-1. By comparing the residual and secondary clay particle size distributions on these diagrams, the residual clays have a higher percentage of sand, whereas the secondary clays are more clay-rich, as would be expected. The effects of weathering on the particle size of the residual clays is not as evident in the vertical trench samples (Appendix E-1C; Figs. 39, 40), although Trench A at the NWSPC mine does show a progressive increase in the percentage of silt and clay at the expense of sand size particles (Appendix E-1C; Fig. 39). The particle size diagrams for the various strati-

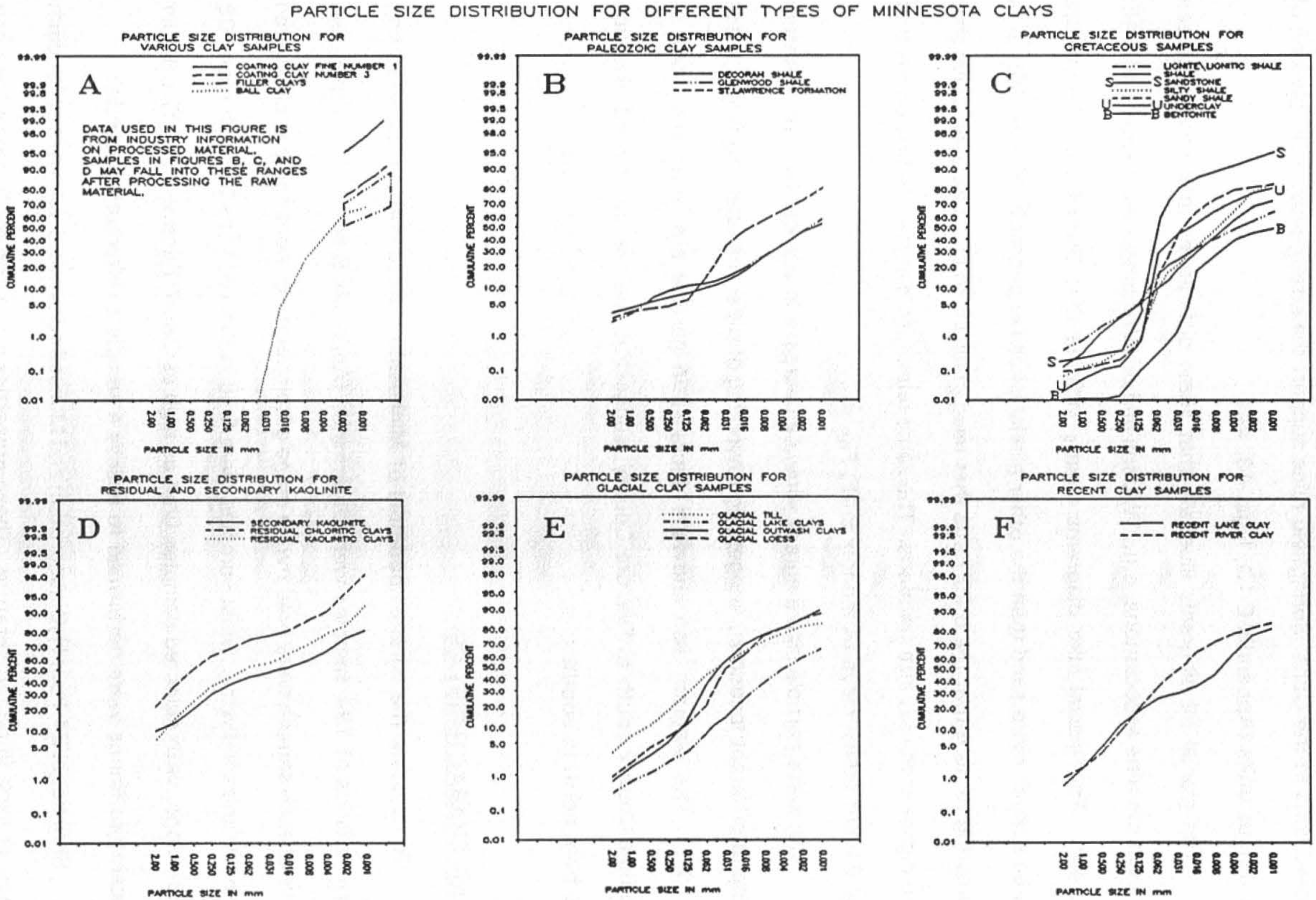


Figure 30. Cumulative particle size distribution diagram for the various types of Minnesota clays.

graphic units in the Ochs' Springfield mine support the stratigraphic sub division of the various units (Appendix E-1D; Figs. 43, 44).

The glacial till diagrams illustrate that some differences may exist between different moraine associations, e.g., Wadena and pre-Wisconsin tills (Appendix E-1E; Fig. 45). The glacial lake diagrams clearly indicate that Glacial Lake Minnesota contains much more sand than the other glacial lakes (Appendix E-1E; Fig. 46). It is interesting to note that the brickyards that used glacial lake clays all used clays that were higher in the silt size fractions. The same relationship applies to brickyards that used Recent fluvial clays (Appendix E-1E; Fig. 48).

The loess particle size diagram shows a decrease in particle size from bottom to top at different locations, suggesting reworking of older material (Appendix E-1E; Fig. 47). The diagram also shows a decrease in particle size from the north in Goodhue County south to Fillmore County, suggesting the prevalent wind direction was from north to south.

FIRING CHARACTERISTICS

To evaluate the ceramic potential of Minnesota's clays and shales, the firing characteristics of 194 samples were determined (Appendix B and F, G). Small test bricks of each sample were fired over a range of temperatures commonly encountered in the ceramics industry. Most samples were fired in the 1751° to 2381° F (cone 08 to 10) range, with selected samples fired as high as 2806° F (cone 19). The higher temperature firings were performed to assess a sample's refractory potential.

Shrinkage, 24-hour H_2O absorption and Munsell color were determined for each sample at each firing temperature. These properties are important because they can significantly influence a raw material's ceramic potential. The percent linear shrinkage (fired and total) and percent absorption were plotted against firing temperature for all fired samples. Plots for eight representative sample types are presented in Figure 31. The additional horizontal line at 8 percent on each plot marks the ASTM absorption standard for brick. Shrinkage-absorption diagrams for all fired samples are provided in Appendix G (Figs. 50-98).

By plotting shrinkage and absorption in this fashion, the degree of "maturing" that takes place during firing becomes apparent. For example, increasing firing temperature usually results in increasing shrinkage (except for samples that bloat, indicated by decreasing shrinkage) and decreasing absorption. An approximate, but by no means exclusive, indication of "maturity" is the point on the plot where percent shrinkage and absorption intersect.

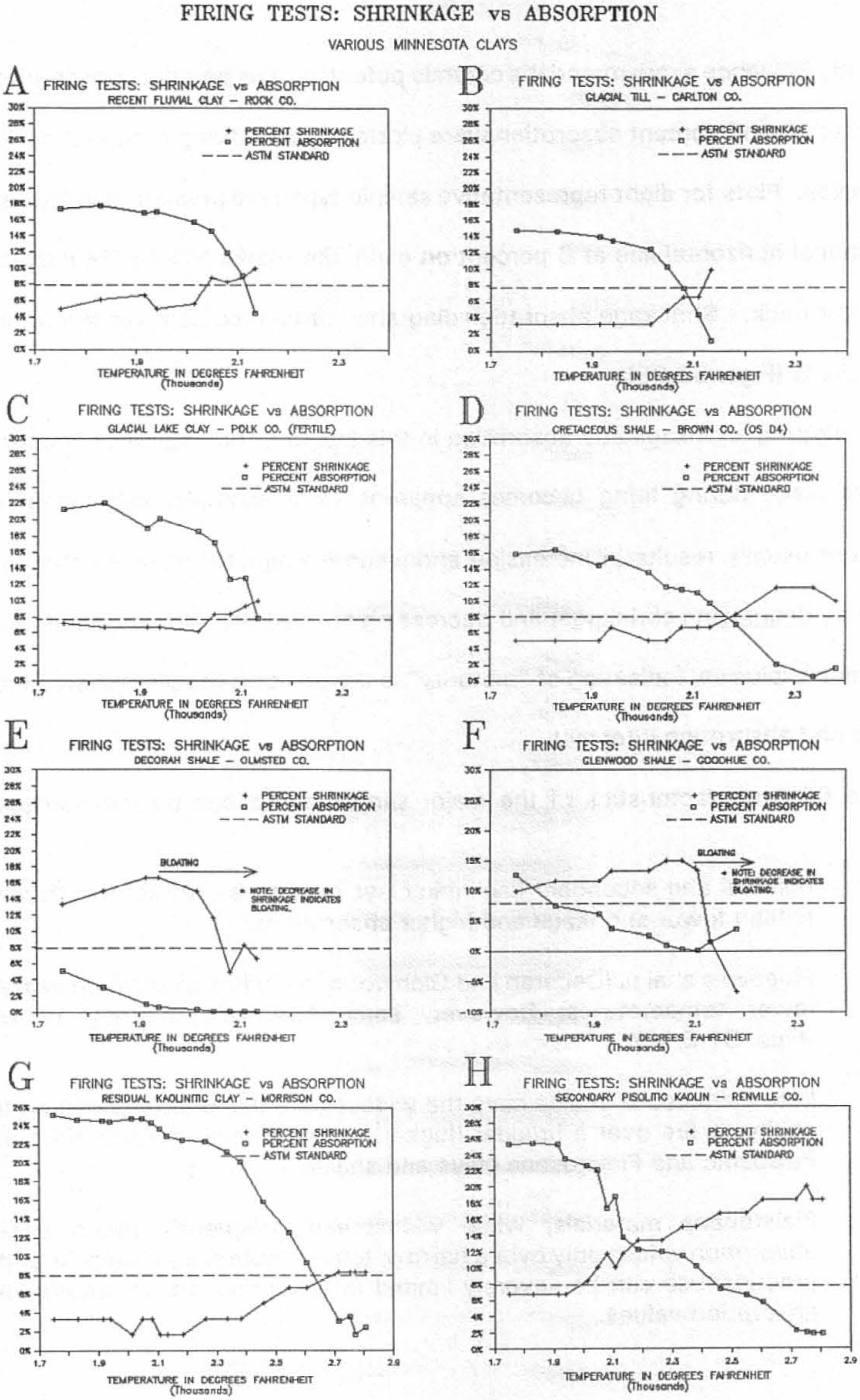
The firing characteristics of the major sample types can be summarized as follows:

1. residual and secondary kaolinitic clays tend to be refractory; they also exhibit lower shrinkage and higher absorption;

2. Paleozoic shales (Decorah and Glenwood) have low absorption values at lower temperatures; however, some have a tendency to bloat (Figs. 31-E, -F);

3. Late Cretaceous shales have the widest potential utility, based on their ability to fire over a broader (higher) range of temperatures than most Paleozoic and Pleistocene clays and shales;

4. Pleistocene materials, while widespread, frequently reach suitable absorption values only over a narrow temperature range; therefore, their practical use can be severely limited in applications that require lower absorption values.



A FIRING TESTS: SHRINKAGE vs ABSORPTION
RECENT FLUVIAL CLAY – ROCK CO.

B FIRING TESTS: SHRINKAGE vs ABSORPTION
GLACIAL TILL – CARLTON CO.

C FIRING TESTS: SHRINKAGE vs ABSORPTION
GLACIAL LAKE CLAY – POLK CO. (FERTILE)

D FIRING TESTS: SHRINKAGE vs ABSORPTION
CRETACEOUS SHALE – BROWN CO. (OS D4)

E FIRING TESTS: SHRINKAGE vs ABSORPTION
DECORAH SHALE – OLMSTED CO.

* NOTE: DECREASE IN SHRINKAGE INDICATES BLOATING.

F FIRING TESTS: SHRINKAGE vs ABSORPTION
GLENWOOD SHALE – GOODHUE CO.

+ NOTE: DECREASE IN SHRINKAGE INDICATES BLOATING.

G FIRING TESTS: SHRINKAGE vs ABSORPTION
RESIDUAL KAOLINITIC CLAY – MORRISON CO.

H FIRING TESTS: SHRINKAGE vs ABSORPTION
SECONDARY PISOLITIC KAOLIN – RENVILLE CO.

Figure 31. Representative shrinkage and absorption versus temperature diagrams for different types of clays.

X-RAY MINERALOGY

In order to determine the clay mineralogy, the <2 micron size fraction was examined on 65% of the samples. The analytical procedures are discussed in Appendix B, and X-ray data are given in Appendix H.

Paleozoic clays, as mentioned previously, are primarily composed of illite or kaolinite, depending on their location. Minor and trace amounts of carbonates and mixed-layered clays also occur in the 2 micron size fraction.

The residual/saprolitic clays were dominantly composed of kaolinite. Chlorite was either absent, or it comprised minor to dominant proportions of the sample depending on the protolith of the residual material. Illite was common and occurred in trace to minor amounts in most samples. Other trace and minor minerals in the residual clays include smectite, mixed-layered clays, quartz, hematite, and limonite. Calcite and/or dolomite were common in the residual clays in southeastern Minnesota, which formed from the dissolution of Paleozoic limestone and dolomite.

The secondary kaolinites are also dominantly composed of kaolinite. Common accessory minerals include quartz, gibbsite, and iron-oxides, with trace amounts of chlorite, mixed-layered clays and illite. The kaolinite X-ray diffraction peaks in the secondary clays commonly give evidence of a well-ordered clay mineral. In the residual clays, kaolinite is commonly disordered. In addition to the better developed kaolinite platelets, the secondary shales/clays contain a greater concentration of kaolinite compared to the residual clays.

The clay mineralogy of the Late Cretaceous sediments is similar to the residual and secondary kaolinitic clays, with kaolinite being the dominant mineral. The accessory minerals in the <2 micron size fraction include quartz, illite, chlorite, mixed-layered clays, and/or gypsum, with occasional iron-oxides.

The 2 micron fractions of glacial lake sediments, till, and loess are primarily composed of quartz, feldspar, and carbonates, i.e., rock flour. The carbonate content depends on the proximity of the sample to the northwestern portion of the state, particularly if the sample was associated with the Des Moines ice lobe and subsequent glacial lakes. Kaolinite, illite, mixed-layered clays, iron oxides, and micas comprise the lesser minerals present in the 2 micron size fraction. The recent clays collected contain illite, kaolinite, and calcite as the dominant clay-sized mineral fraction.

CATION EXCHANGE CAPACITY (CEC)

A potentially important characteristic of a particular clay, especially in landfill applications, is the clay's ability to adsorb or exchange ions. Cation exchange capacity (CEC) measures ability of a clay to adsorb or exchange ions. The higher the CEC of a clay, the greater its surface area, which promotes the sorption of cations, anions and organics (Dawson and Mercer, 1986).

The cation exchange capacity (CEC) was determined on 493 samples (Appendices C and I) using the methylene blue test (American Petroleum Institute, 1988) that was subsequently modified by the U.S. Bureau of Mines (Haas, *et al*, 1987). This test estimates the total cation exchange capacity of solids in solution, e.g., solids in drilling fluids.

The highest CEC was obtained on the green bentonitic shale in the Ochs' Morton East pit (CEC of 50; Fig. 19). Overall, the Paleozoic shales had the highest average CEC (12.5) followed by the glacial sediments (lake [12.4], loess [9.3], till

[8.9], respectively), recent clays [7.8] and the residual and secondary kaolinitic clays [4.6-6.9]).

COLOR

Both raw and fired color was determined on all samples collected and all fired samples (Appendices F and J, respectively). The Munsell Soil Color Chart, the Munsell Rock Color Chart, and the Munsell Book of Color were used to determine the fired color of every raw sample and fired brick. Both the Munsell color code and corresponding color name, e.g., 5YR 8/2 - very pale brown, were used to describe the samples. These data provide a general idea of the chemical composition of the sample.

SUMMARY AND CONCLUSIONS

Many of these clays have possible industrial uses, i.e., ceramic tile, lightweight aggregates, and livestock feed filler (Toth, *et al*, 1990). Also, exploration for paper and filler grade kaolinite is presently underway in the Minnesota River Valley. During this project, kaolinite clays from the Firle property and MGS drill hole MNE-1 were processed to at least filler grade (Prasad, *et al*, 1990). Residual clays are being used as environmentally safe (low alkali content of $\leq$ 1%) additives in portland cement.

Minnesota has a wide variety of clays that have not been, or are not presently being, used as industrial minerals. Many of these clays have sufficient thickness, grade and homogeneity to support an ongoing operation, besides also having favorable physical and chemical properties. Possible industrial uses for these clays are:

- ceramic tile (glazed and unglazed - Meridian and MRV clays)
- ceramic glazes (Precambrian iron-rich Paint Rock clays)
- lightweight aggregate (Decorah and Brenna Fm. and Unit A at Ochs' Springfield mine)
- refractory products (pisolitic and other alumina-rich secondary kaolinitic clays in the MRV and St. Cloud areas)
- sanitaryware (Springfield and Richmond ball clays mixed with kaolin-rich clays in the MRV and St. Cloud area)
- fillers (residual clays in the MRV) for livestock feed, plastics, etc.

Additional research on the occurrence of the clays and the geologic and geochemical controls on clay deposition and modification are needed to better understand where the better grade clays occur. Additional research on low value clay products is necessary to help encourage smaller industrial clay operations. The majority of the clays collected during this project are better suited for lower value clay products rather than the filler and paper grade clays. This does not mean that higher grade/value clays do not exist and that additional research should not be conducted, but the thick glacial overburden inhibits exploration and sampling for these clays because of potentially high stripping costs. At least equal emphasis should be placed on research and development for those medium to low grade clays that readily occur at or near the surface where industrial development, particularly in rural areas, would help diversify and enhance local economies.

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APPENDICES A THROUGH I

APPENDIX A

SAMPLE LOCATION DATA FILE

The sample location data for each sample analyzed are in a Lotus 1-2-3 file named SAMPLOC.WK1 on Disk 1. This file also indicates what tests were performed on each sample. The data available for each sample are listed under the following column headings:

Column A: Data sort number.
Column B: Sample number - 87 and 88 stand for year in which the sample was collected.
Column C: U. S. Bureau Mines (USBM) sample number for samples obtained from the USBM.
Column D: Sample type.
Column E: Rock type - this is an abbreviated designation for sorting the different sample types.
Column F: Geologic age.
Column G: Glacial ice lobe/moraine association name.
Column H: Glacial lake name.
Column I: Deposit name - designates mine name or outcrop.
Column J: County name.
Column K: 3rd section quarter.
Column L: 2nd section quarter.
Column M: 1st section quarter.
Column N: Section number.
Column O: Township number.
Column P: Range number.
Column Q: UTM northing coordinate.
Column R: UTM easting coordinate.
Column S: 2 degree sheet name.
Column T: 7.5' or 15' quadrangle name.
Column U: Station number - an alphanumeric designator for identifying which trench and channel sample was collected.
Column V: Unit name - an alphanumeric designator to identify a stratigraphic subunit, e.g., B4 at the Ochs' Springfield mine or 1 lower most sample in a trench.
Column W: Thickness in feet of the channel sample.
Column X: Chemistry - x indicates sample analyzed.
Column Y: Particle size - x indicates sample analyzed.
Column Z: Firing tests - x indicates sample that was fired.
Column AA: Cation exchange capacity - x indicates sample analyzed.
Column AB: Munsell color - x indicates Munsell color determined.
Column AC: X-ray mineralogy - x indicates 2 micron size fraction sample X-rayed.

APPENDIX B

FIELD SAMPLING METHODS

The sampling of clays in the field was divided into two categories: 1) outcrop sampling; and 2) mine pit sampling. Because of the industrial/economic emphasis of this project, the channel sampling method was chosen to give a general or more typical assessment of how a "run of the mill" clay sample might appear. Sufficient sample was collected at each sample point so that the following analytical tests could be conducted.

1. X-ray diffraction analysis
2. Particle size analysis
3. Whole rock geochemistry plus total organic carbon
4. Cation exchange
5. Firing characteristics
6. Munsell color

The sampling protocols discussed were chosen to: 1) provide sample location control, both in the mine pits and on an outcrop; 2) provide a representative sample of the clay within a given lithologic unit; and 3) allow the field geologists sufficient time to collect representative clay samples of all potential clay-bearing units over the southern one-third of the state in 1987 and the northern two-thirds of the state in 1988.

Outcrop Sampling

1. Property owners permission to sample was obtained, where necessary, prior to sampling.

2. The sample location was determined by pace and compass from the nearest known point on a 7 1/2-minute quadrangle map.

3. A three-foot wide channel, where possible, was cut approximately 0.5 feet into the outcrop unless there was a fresh face available (road construction, new basement, etc.). Other samples (from augered waste piles for new telephone poles, etc.) were collected as available.

4. Samples were collected and measured from the top of the outcrop to the bottom.

5. Sampling procedures were similar to steps 6 to 8 listed under mine pit sampling.

Mine Pit Sampling

The following procedures were followed during clay sampling in the various mine pits:

1. Most existing mine pits were mapped using theodolite, pace and compass, and/or tape and compass mapping methods for sample location control and geologic relationships. Sample locations are illustrated on the individual maps for each pit. A mine pit was mapped if sufficient exposure of the clay was available to document the geology in the pit.

2. Sample locations were chosen to provide the maximum information on the distribution and change in the clays.

3. Prior to sampling, the weathered surface was studied for textures, structure, etc.

4. Once the sample location on the pit wall or face was selected, a three-foot wide channel was cleaned on the working face or pit wall. If slump material was present, a three-foot wide trench was dug to the fresh clay material. The channel was dug approximately 0.5 feet deep or until the effects of weathering were not apparent.

5. The top of the channel was determined by the top of the pit wall, working face or the contact with the glacial overburden. The channel was then measured from top to bottom.

6. Within the prepared channel, the following steps were followed:

    a. The fresh surface was studied and divided into sample units. The sample units were determined based upon changes in lithology, texture, color, etc. If there were no changes within a given unit, a ten-foot channel sample was considered to be the maximum interval.

    b. Samples were collected beginning at the top of the channel and progressed to the bottom to avoid contamination.

7. Within a sample unit, a representative sample (representing approximately equal proportions of all the material within the unit) was collected using a chisel point rock hammer or a trowel.

8. For each sampling unit, the following were collected:

   a. Four clay samples for:
      1. X-ray analysis (approx. 0.5 kg). In the Ochs' Morton, Nova and NW States Portland Cement pit, two-foot channel samples were also collected for future work.
      2. Particle size analysis (approx. 0.5 kg).
      3. Whole rock geochemistry (approx. 0.5 kg).
      4. Firing characteristics and cation exchange (3-4 kg).

   b. Physical data:
      1. Weight of the sample.
      2. Munsell color.
      3. Lithological and structural data.

9. Bulk samples of the clay stockpiles ("run of the mill") in each pit were collected by taking random samples with a trowel, in approximately equal amounts, around the sides and over the top. Four sample bags were collected at each stockpile for the tests mentioned in 8a. Sample weight and Munsell color were also recorded.

APPENDIX C

PHYSICAL TESTING PROCEDURES

A series of analytical tests were performed to evaluate the physical and chemical characteristics of all 499 samples collected during the 1987 and 1988 field seasons. Those tests included the following:

1) Munsell Color - 493 samples (98.8 % of total)
2) Particle Size Analysis - 480 samples (96.2 % of total)
3) Cation Exchange Capacity - 493 samples (98.8 % of total)
4) Geochemistry - 334 samples (66.9 % of total)
5) Firing Characteristics - 194 samples (38.9 % of total)
6) Clay Mineralogy - 321 samples (64.3 % of total)

Every test was performed on each sample whenever possible. However, if a test was not appropriate for a particular sample, or time and/or budget constraints prevented complete testing (due to the number of samples involved), samples were prioritized and tested as conditions allowed. Still, all major clay classification categories were covered by all tests.

Testing results have been organized according to sample type. On the following pages brief descriptions of each test are presented.

Munsell Color

The Munsell system was used to assign colors (recorded as Raw Munsell Color) to 493 samples following their drying, homogenizing and pulverizing in the laboratory. Sample colors were determined by comparing raw, dried samples to the Munsell Soil Color Charts (1975), the Munsell Supplementary Chart for Gley (1975), or the Rock Color Chart (1984). Each sample was given the closest matching Munsell numerical and name designation, e.g., 10YR 8/1 - White.

Raw color is a particularly important property in non-ceramic applications like paper making, where a white or near-white color is required. On the other hand, the raw color of clay is less important in ceramic applications, where the final fired color is of primary importance. Finally, the identification of clay exposures in the field was occasionally expedited by referring to their color as described in previous studies.

Particle Size Analysis

Samples are split and blended using a sample splitter. All equipment is thoroughly cleaned between samples to prevent contamination. Two types of particle size analysis were conducted:

1. Sieve analysis - samples are sieved into four fractions:
    1. clay size (<0.06 mm)
    2. silt size (-230 mesh - >0.06 mm)
    3. sand size (-120 mesh - >1.25 mm)
    4. coarse (10 mesh - >2 mm)

    In the glacial tills, the type and percentage of the pebbles was noted even though the results would not be statistically valid. The glacial tills were also wet sieved to remove the finer material. A +10 mesh Tyler sieve was used to separate the different particle sizes.

2. Pipette method in a settling tube - procedures after R.L. Folk (1980) for silts and clays.

Cation Exchange Capacity

A potentially important characteristic of a particular clay type, particularly in landfill applications, is its ability to adsorb or exchange ions. Cation exchange capacity (CEC) is one measure of that ability. In general, the greater the CEC of a material, the greater its surface area, which promotes the sorption of sorbable wastes, including cations, anions and organics (Dawson and Mercer, 1986). Therefore, an evaluation of the cation exchange capacity of Minnesota's clays was performed.

Analytical Method The cation exchange capacity (CEC) of 493 samples was determined using the methylene blue test (MBT) as described in Section 6 of the American Petroleum Institute's (API) "Recommended Practice: Standard Procedures for Field Testing Drilling Fluids" (API, 1988) and modified by the Bureau of Mines (Haas, *et al*, 1987).

The methylene blue test provides an estimate of the total cation exchange capacity, or reactivity, of solids in drilling fluids. Since the solids of interest are generally clays, the test is applicable not only to drilling fluid clays (bentonites), but clays in general.

The API test calls for 2.0 cm^3 of drilling fluid to be used. Clay, however, rather than drilling fluid was of interest in this study. Therefore, the test, as modified by the Bureau of Mines (Haas, *et al*, 1987), was followed in which 0.200 grams of dried, pulverized (>90% passing 150 mesh) sample were used in place of drilling fluid. A description of the test follows.

Modified Methylene Blue Test Following weighing on an analytical balance, a 0.200 g ± 0.003 g sample was added to a 50 ml beaker containing 10 ml of distilled-deionized water (DD H_2O) and stirred with a magnetic stirrer for two minutes. Next, 15 ml of 3 percent hydrogen peroxide (H_2O_2), 0.5 ml of 5N sulfuric acid (H_2SO_4), and 10 ml of DD H_2O were added to the sample solution. The resulting solution, while being stirred continuously with the magnetic stirrer, was heated and boiled gently for 10 minutes, but not to dryness. Finally, the solution was diluted with DD H_2O to 50 ml and allowed to cool to room temperature.

After cooling, a 0.01 Normal methylene blue solution (made by dissolving 3.20 g dried reagent grade methylene blue in 1000 ml DD H_2O) was added to the sample solution in increments of 1 ml and stirred with the magnetic stirrer for 30 seconds. After each 1 ml addition and stirring, a glass stirring rod was dipped into the solution while the solids were still in suspension, and a drop of the suspension was transferred to a dry piece of filter paper (Fig. 32). The resulting spot was examined for any migration of the blue dye away from the central dyed solids to the surrounding moisture ring. If no dye migration was observed, this meant that all of the dye was adsorbed by the sample, and another 1 ml of methylene blue was required. The process continued until blue staining was detected, at which point the solution was stirred for an additional two minutes without further methylene blue addition. The suspension was then re-applied to the filter paper. If no dye staining was evident, the test continued, and another 1 ml was added. However, if blue dye was still visible in the moisture ring surrounding the dyed solids after the additional two-minute stirring, the endpoint had been reached, and the volume of methylene blue solution required to reach that point was recorded.

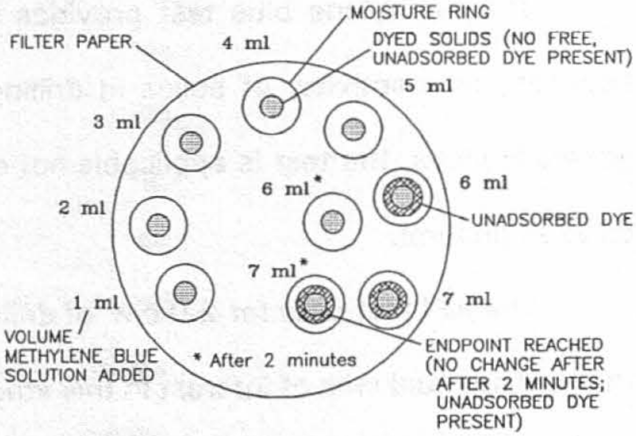


Figure 32. Cation Exchange Capacity Test (API, 1988).

Given that 1 ml of the 0.01 normal methylene blue solution equals 0.01 milliequivalent (meq), the cation exchange capacity was calculated as follows, and recorded as meq/100 g sample (Haas, *et al*, 1987):

The volume of methylene blue added to reach the MBT endpoint (in milliliters) was multiplied by 0.01 meq/ml, divided by the dry weight of the sample, and multiplied by 100. For example, if an endpoint was reached following the addition of 7 ml methylene blue solution to a sample, the cation exchange capacity of the sample equalled:

$$\frac{(7 \text{ ml}) \times (0.01 \text{ meq/ml})}{0.200 \text{ g}} \times 100, \text{ or } 35 \text{ meq/100 g}$$

More simply, the CEC could be calculated by multiplying the number of milliliters of methylene blue added by 5 (given an endpoint of 3 ml, the CEC would equal 15 meq/100 g).

Analytical Standard To check the accuracy of the CEC test, a Na-bentonite standard having a known CEC of 50 meq/100 g was used throughout the testing procedure. A CEC of 50 meq/100 g was determined consistently for each test of the standard.

Firing Characteristics

To evaluate the ceramic potential of Minnesota's clays and shales, the firing characteristics of 194 samples were determined using a synthesis of procedures and techniques developed by the American Society for Testing and Materials (ASTM; ASTM, 1986), the United States Bureau of Mines (USBM; Liles and Heystek, 1977; Klinefelter and Hamlin, 1957), and the United States Geological Survey (USGS; Grout and Soper, 1919). A numerical breakdown by sample type follows:

57	(29.4%)	Pre-Cretaceous (Primary & Secondary kaolinitic clays)
44	(22.7%)	Cretaceous
24	(12.4%)	Paleozoic
53	(27.3%)	Pleistocene
14	(7.2%)	Recent
2	(1.0%)	Precambrian
194	(100%)	TOTAL

These samples were believed to adequately represent the entire sample set collected during the 1987 and 1988 field seasons. Test firings of bricks made from each sample type were performed over a broad range of temperatures commonly encountered in the ceramics industry. This allowed for each sample's shrinkage, absorption and color characteristics to be quantified for a variety of potential applications (lower temperature construction bricks and tiles to higher temperature refractories).

Sample Preparation Thoroughly dried samples were pulverized to pass a -20 mesh screen. Glacial tills, however, were first wet-sieved on a 10 mesh screen to remove the finer material. The coarse fraction was saved and later used in identifying the particular glacial lobe from which the sample came. The remaining -10 mesh fraction was oven dried. Following drying, the -10 mesh fraction was prepared identically to the other non-glacial till samples.

Brickmaking Procedures Test bricks measuring 10 mm x 30 mm x 50 mm were used in all firing characteristic evaluations. These dimensions were very similar to those used by Liles and Heystek (1977) in their USBM clay and ceramic raw material test program. Bricks of this size were also much more practical to test given the following constraints:

1) the sheer numbers required for the production of useful data.
2) the physical limitations of both space and equipment.
3) the limited amount of sample with which to work.

A sufficient amount of raw, pulverized sample to make a minimum of 20 bricks was weighed and transferred to a large stainless steel mixing bowl. Usually, 1000 to 1500 grams of sample were adequate. Water from a 1000 ml graduated cylinder was added to the sample and worked by hand until the sample was completely moistened. The sample was then transferred from the bowl to a clean, flat surface for thorough hand-working and, if necessary, further additions of water. The sample was worked until it was "felt" to be of the proper consistency for extrusion, a physical state based largely on the experience and judgement of the person preparing the sample. Frequently, however, this could not be determined with any certainty until a minimum of one extrusion was attempted, at which point more sample or more water was added as needed.

The total amount of sample and water required for a successful extrusion was recorded, with the amount of water recorded as "percent water of plasticity", or:

$$(\text{grams } H_2O \text{ added/grams dry sample}) \times 100$$

In all cases, the weight of water was assumed to equal 1 g/ml.

Finally, all samples did not extrude equally, and some did not extrude at all. Consequently, samples were rated as "excellent, good, fair, poor, or non-workable (n/w)", based on their "extrudability". Generally, samples containing a high percentage of sand and/or silt-sized particles, and a low percentage of clay-sized particles were the poorest performers. It is possible, however, that many of the samples that exhibited poor extrusion characteristics could be successfully dry-pressed, a technique where very little water (5 to 6 percent) is added to a sample, the sample placed in a die, and pressed at approximately 1250 psi (Liles and Heystek, 1977). In this study, only those samples which were extruded successfully were fired; dry pressing was not performed.

Extrusion A hydraulic extruder built by the NRRI's machine shop was the key piece of equipment used in the brickmaking process. A prepared sample was placed in an opening near the back of the extruder and hydraulically advanced through the extruder cylinder via a piston. The front end of the extruder was fitted with a 10 mm x 30 mm die through which the sample was extruded. Speed controls allowed for fine adjustments to be made if the sample advanced too quickly or slowly.

Samples were extruded in the form of a plastic clay bar onto a cutting surface located in line with the extruder. When a suitable length of sample was extruded, the extrusion was halted. The sample was then positioned, and a wire cutter, fitted with 11 narrow-gage wires spaced 50 mm apart, was pulled downward, cutting 10 bricks simultaneously. The cutting apparatus was also fitted with metal points spaced 30 mm apart that embedded shrinkage marks in each brick's surface. All subsequent shrinkage measurements used these marks as a reference.

When 20 bricks were made, each brick was labeled with its corresponding sample number and a number from 1 to 20, e.g., 87-220-7. The numbers were stamped into the plastic brick's surface using metal type provided by a local newspaper. The numbers from 1 to 20 corresponded to each potential firing temperature, with "1" representing the lowest and "20" the highest.

Preparation of Bricks for Firing Following extrusion, cutting, and labeling, bricks were allowed to slowly air dry for approximately one week. The bricks were then placed in a drying oven and dried at 110° C for a minimum of 24 hours. Once cooled to room temperature, each brick was weighed (dry unfired weight), the distance between shrinkage marks measured, and the unfired Munsell color recorded. These and all subsequent measurements were entered and stored in Lotus 123 files (Appendix F).

Firing Method Up to twenty test firings were performed on each sample (one brick per firing). All firings took place in an oxidizing atmosphere. The first thirteen firings were performed in a Skutt Model 1070 electric kiln at the NRRI in Duluth. For those samples selected for high temperature firing (firings 14-20), a high temperature muffle furnace at the NRRI's Coleraine facility was used.

Because temperature alone does not adequately report the maturing or firing conditions of ceramic bodies or glazes (Fronk and Vukovich, 1974), Orton standard pyrometric cones and kiln sitter bars were used to control, respectively, the degree and the duration of each firing. Thus, firing temperatures reported in this study are really "temperature equivalents" and are based on the heating rate of the kiln (approximately 270° F, or 150° C, per hour) and the cone to which each test brick was fired. Each firing number (1-20) and its corresponding Orton cone and temperature equivalent are listed in Table 5.

For all firings, the dried test bricks were arranged in a specific order and laid flat on shelves inside the kiln. Recording the location of each brick was critical in the event a brick was destroyed or its label obliterated during a firing.

Table 5. Firing temperatures.

FIRING NUMBER	ORTON CONE	TEMPERATURE EQUIVALENT °F	°C
1	08	1751	955
2	06	1830	999
3	05	1915	1046
4	04	1940	1060
5	03	2014	1101
6	02	2048	1120
7	01	2079	1137
8	1	2109	1154
9	3	2134	1168
10	5	2185	1196
11	7	2264	1240
12	9	2336	1280
13	10	2381	1305
14 *	13	2460	1349
15 *	14	2548	1398
16 *	15	2606	1430
17 *	16	2716	1491
18 *	17	2754	1512
19 *	18	2772	1522
20 *	19	2806	1541

* DENOTES FIRING AT NRRI'S COLERAINE LABORATORY.

Three Orton standard self-supporting cones were placed on each shelf with the bricks during each firing. Proper deformation of the desired cone indicated a successful firing. For example, if the desired firing was Orton cone 04, the first cone (05) acted as the "Guide Cone", the second (04) as the "Firing Cone" and the third (03) as the "Guard Cone". Such an arrangement made it possible to tell if a particular firing proceeded too far (deformation of cone 03) or was incomplete (deformation of cone 05 but not of cone 04).

Each firing proceeded until the desired cone was reached. The kiln was then shut off and allowed to cool overnight to room temperature.

Standard Bricks To check the quality of the firing tests, bricks made from Kentucky-Tennessee Clay Co. ball clay (KT-9; #1 SGP) were fashioned and accompanied each batch of bricks during each firing session. Thirty-nine separate firings took place (three batches of bricks at 13 firings per batch) over a three month period. Therefore, triplicate data for the standard were produced for each of the 13 firings.

Seven of the samples selected for firing (87-001, 87-024, 87-177, 88-002, 88-064, 88-088, and 88-134) were also used to evaluate the quality of the firing tests. Three bricks, rather than one brick, were fired at each firing temperature. Their firing characteristics, as well as those of the aforementioned standard, are presented in Appendix F.

Tests Performed on Fired Bricks Each test brick in a particular sample's brick set was fired at successively higher temperatures until reaching vitrification. When a set of firings for a sample was complete, the fired color, linear shrinkage and weight of every brick in that set was recorded. Following weighing, absorption testing began.

Fired Color The Munsell Soil Color Chart (1975), the Rock Color Chart (1984), and the Munsell Book of Color (1976) were used to determine the fired color of every brick. Both the Munsell color code and corresponding color name, e.g., 5YR 8/2 - Very pale brown, were recorded and entered into the appropriate brick data file (Appendix J).

Linear Shrinkage As mentioned previously, shrinkage marks were set in each brick at a spacing of 30 mm when the bricks were in a plastic state. After drying, the distance between these marks was measured with calipers and recorded to the nearest 0.5 mm. "Percent dry linear shrinkage" was then calculated using the following formula:

$$\frac{30 - \text{Dry measurement}}{30} \times 100$$

Following firing, shrinkage was measured again. To determine "Percent fired linear shrinkage", the following formula was used:

$$\frac{\text{Dry measurement} - \text{Fired measurement}}{\text{Dry measurement}} \times 100$$

Finally, "Percent total linear shrinkage" (from plastic to fired state) was calculated and recorded:

$$\frac{30 - \text{Fired measurement}}{30} \times 100$$

Shrinkage is ultimately an important property in ceramic applications, for if a product of a specific size is required, then allowance for shrinkage must be considered. For example, it is desireable to use a clay for brickmaking that exhibits minimal change in shrinkage over a wide firing range (pers. com., R. Schutt, 1988). Not only does this give the manufacturer greater temperature flexibility during production, it also results in a product of uniform size and minimizes the need to modify the size of molds or extrusion dies.

Again, all shrinkage measurements made in this study were linear. Volumetric measurement could have also been used to determine shrinkage (Klinefelter and

Hamlin, 1957). While volumetric measurement might have been a more desireable method because it is not affected by warping or differential shrinkage, linear measurement was chosen for its simplicity and because it is a perfectly acceptable method to use when acquiring baseline data for a study of this magnitude, where approximately 8000 individual measurements were required. Future studies which address the firing characteristics of a limited number of samples may want to consider using the volume method of measurement.

Absorption Building brick, facing brick, hollow brick, pedestrian and light traffic paving brick, and structural clay tile must all meet certain standards established by the American Society of Testing and Materials. Water absorption (a measurement of durability) is but one of the many standards (others being efflorescence, modulus of rupture, compressive strength, freezing and thawing, etc.) outlined in ASTM Designations C 62, C 216, C 652, and C 902 (ASTM, 1986).

The water absorption properties of each test brick were evaluated using the techniques described in Section 7 of Methods C 67 (ASTM, 1986). First, previously weighed bricks were soaked in clean, 60 to 86°F (15.5 to 30° C) water for 24 hours (24-hour submersion test). After 24 hours, the bricks were removed, patted with a damp cloth to remove surface water, and weighed within 5 minutes. Percent absorption (24-hour) was then calculated as follows:

$$\frac{(W_s - W_d)}{W_d} \times 100$$

where:

W_d = dry weight of the brick, and
W_s = saturated weight of the brick after submersion for 24 hours

Immediately following the 24-hour submersion test, the test bricks were returned to their water bath and brought to a boil. Boiling continued for 5 hours (5-hour boiling test). After five hours, the bricks were slowly cooled by circulating 60 to 86° F (15.5 to 30° C) water through the bath continuously at a rate that allowed weighings to be made at the end of one hour. Again, the bricks were removed, patted with a damp cloth and weighed within 5 minutes. The percent absorption of each brick was then calculated as follows:

$$\frac{(W_b - W_d)}{W_d} \text{ X } 100$$

where:

W_d = dry weight of the brick, and
W_b = saturated weight of the brick after 5-hour boil

Whereas the 24-hour submersion test gives an indication of the open pore structure of the brick, the 5-hour boiling test gives an indication of its closed pore structure (pers. com., R. Schutt, 1989).

The percent absorption values calculated for both the 24-hour submersion and 5-hour boil tests are used for establishing the suitability of a brick or tile for its intended use. These values can be used individually or in combination. When used in combination, a value called the "saturation coefficient" results. The saturation coefficient is merely:

$$\frac{\text{24-hour submersion absorption}}{\text{5-hour boil absorption}}$$

For instance, in a random sample of five building or facing bricks intended for use where severe weathering occurs (Grade SW bricks), the average saturation coefficient cannot exceed 0.78, and the saturation coefficient of an individual brick in that group cannot exceed 0.80 (ASTM, 1986). However, the saturation coefficient requirement can be waived if: 1) the average 24-hour absorption does not exceed 8 percent; and 2) the 24-hour absorption of only one brick of the sample exceeds 10 percent (ASTM, 1986).

NOTE: Three grades of brick (SW, MW and NW) have been established by ASTM in Designation C 62-85a (ASTM, 1986). The grades are based on the weather conditions a brick is most likely to encounter when used. The SW grade, for instance, is required if a brick is subjected to the most severe weather conditions (frequent freezing while saturated), while the other two grades (MW and NW), can be used where the weather conditions are increasingly less severe.

It is possible that some bricks or tiles may not meet the ASTM-specified absorption/saturation coefficient requirements, yet still be suitable for use. For example, in Section 3.5 (Freezing and Thawing) of ASTM Designation C 62-85a (ASTM, 1986), ASTM states:

> "The requirements specified for water absorption (5-hour boiling) and saturation coefficient shall be waived provided a sample of five bricks, meeting all other requirements, complies with the following requirements when subjected to 50 cycles of the freezing-and-thawing test:
>
> | | |
> |---|---|
> | Grade SW | No breakage and not greater than 0.5% loss in dry weight of any individual brick." |

Freezing and thawing testing was not performed in this study due to time limitations (the testing is extremely time consuming). This testing method, and all other brick and structural clay tile testing methods, are described in detail in ASTM Designation C 67 (ASTM, 1986), and will therefore not be covered here.

Reporting of Brick Test Data Brick data for each sample were recorded in individual Lotus 123 files (Appendix F). All test calculations were performed within these files. From these data, graphs plotting percent shrinkage and percent 24-hour absorption versus firing temperature (cone temperature equivalent) in °F were produced.

Clay Mineralogy

1. Six X-ray diffractograms were run for each sample. The X-ray analysis was run on the clay size (2 micron) fraction of the X-ray sample collected in the field. The clay size fraction, as well as the silt, sand, and coarse fractions obtained from the sieve analysis, are being retained for future X-ray analysis on each size fraction.

2. Each X-ray sample was blended and split using a Carpco sample splitter. The splitter and other equipment used were thoroughly cleaned between samples to avoid contamination. The clay size fraction was then separated by centrifuging and used in the X-ray analysis.

3. For each clay fraction, the following chemical treatment and/or procedure was conducted to determine the clay mineralogy:

   a. Untreated raw sample (clay fraction)
   b. Magnesium saturated sample
   c. Potassium saturated sample

d. Glycolate magnesium saturated sample
e. Heat potassium saturated sample to 400° C
f. Heat potassium saturated sample to 550° C

Clay standard reference samples were run for comparison purposes. Clay X-ray preparation procedures were after Starkey, *et al* (1984), J. Pastor and S. Hauck (pers. com., 1987), and T. Toth (pers. com., 1989).

Sample Preparation Approximately 30 grams of dried, <1/4 inch sample were soaked in 400 ml beakers containing distilled water for a minimum of 48 hours (to soften and disaggregate the sample). Following soaking, the sample/water mixture was put into suspension by transferring to a laboratory blender and mixing thoroughly for two to three minutes. After allowing to set for approximately one hour, the suspension was examined for flocculation. If flocculation was evident, calgon (an anti-flocculant) would be added in 1 ml increments, and the sample would be re-blended and re-examined for flocculation. The process was repeated until flocculation was eliminated.

The sample/water mixture was then resuspended by mixing, and the time at which the mixing ceased was recorded. Since the objective was to withdraw only the clay-sized (-2 micron) fraction of each suspension, it was necessary to know the maximum depth at which a withdrawal could be made. This determination was made using principles of sedimentation, by which the distance (depth) a particle of known diameter and density travels in a fluid (water) in a given time can be calculated. The following formula was used:

$$\text{DEPTH(cm)} = \text{TIME(min)} \times 1500 \times A \times D^2\text{(mm)}$$

Where:

> A is a constant which depends on the viscosity of water, which is a function of temperature, the force of gravitation, and the density of the particles; and
>
> D^2 is the square of the particle diameter in mm (which for clay-sized particles is 2 microns, or 0.002 mm).

For example, using an A value of 3.57 for clays or quartz in 20° C water, a 47 minute interval from resuspension to withdrawal gave a withdrawal depth of 1 cm.

The clay particle suspensions were then used for preparing slides for X-ray analysis. Initially, three slides were prepared for each sample. The first was a slide of untreated clay and the remaining two were slides of clay treated with potassium acetate (K-acetate) or magnesium acetate (Mg-acetate) solution. Treating the clay suspension with K- and Mg-acetate facilitated the identification and distinction of various clay mineral assemblages present in a given sample, e.g., kaolinite from chlorite through the K-acetate treatment and smectite from all other clay minerals (particularly illite) through the Mg-acetate treatment.

Slide Preparation-Untreated Samples Two methods were used for preparing each slide; the first involved centrifuging the suspension to produce a clay/water "concentrate", while the second involved merely pipetting the suspension directly onto the glass slide. The former was used in the early stages of X-ray analysis, while the latter was used when an alternative X-ray machine became available.

The first method (centrifuge) was used because the dimensions of the glass slides (50 mm x 50 mm) made it difficult to produce a sufficiently thick and uniform clay coating with the more dilute suspension of the direct pipette method. Ten to twenty ml of clay suspension were transferred to a 50 ml centrifuge tube, diluted with distilled water to 50 ml to balance the machine, and centrifuged at 3000 rpm for one-half hour. Batches of eight samples (capacity of centrifuge) were prepared in this manner. Following centrifuging, excess water was decanted from each tube, with just enough retained to produce a thin clay/water slurry. A 1 ml pipette was then used to transfer the slurry to a pre-labeled (sample number) glass slide, where it was allowed to air-dry.

The second method (direct pipette) was used when another X-ray diffractometer became available. The diffractometer's smaller (15 mm x 25 mm) glass slides allowed the clay suspension to be placed on the slides in such a way that a sufficient coating of clay remained after drying. This was attributable to the liquid's surface tension, whereby a slide could be completely covered with a relatively large volume of clay suspension (analogous to water beading up on a waxed surface of a car).

Slide Preparation - Treated (K- and Mg-acetate) Samples Treating samples with K- and Mg-acetate solution required that the centrifuge method be used exclusively in their preparation. Following withdrawal of two-20 ml aliquots of clay suspension from a sample beaker, each aliquot was added to centrifuge tubes marked "K" and "Mg". Then, 30 ml portions of a 1.67 Normal K- and Mg-acetate solution were added to the appropriate tube, filling the tube (capacity of 50 ml). The tubes were capped, placed in a boiling water bath for one (1) hour and allowed to cool for handling.

> NOTE: The usual procedure for treating clay samples with K- and Mg-acetate calls for first centrifuging the clay suspension, producing a clay concentrate, and pouring off the excess water <u>before</u> adding a <u>1.00</u> Normal K- or Mg solution. To save time, a decision was made to circumvent the preliminary centrifuging step by adding a higher concentration (1.67 N) K- and Mg solution to each 20 ml clay aliquot. Therefore, when 30 ml of the K- and Mg solution were added, the resulting 50 ml solution had a normality of 1.00.

Following cooling, the tubes were shaken vigorously for one minute and transferred to the centrifuge, and centrifuged for 1/2 hour at 3000 rpm. The supernatant was poured off, taking care to retain the clay in each tube. Distilled water was added to each tube and the tubes were shaken for another minute, simultaneously resuspending and rinsing the clay particles. The tubes were returned to the centrifuge for another 1/2 hour session at 3000 rpm. Again, the supernatant was poured off, and again distilled water was added. Shaking was repeated, as was a final 1/2 hour, 3000 rpm centrifuging. Finally, following decantation of the supernatant, a treated clay slurry remained, which was then transferred to a slides labeled as either "K - Sample number" or "Mg - Sample number" and air-dried.

APPENDIX D

GEOCHEMICAL TECHNIQUES

Major element (SiO_2, Al_2O_3, TiO_2, TFe_2O_3, FeO, CaO, MgO, MnO, Na_2O, K_2O, P_2O_5, CO_2, H_2O, and S) geochemical analysis was conducted on 65% of the samples collected. All samples, except Clay-001, -002, and -003, were crushed, pulverized and analyzed at the NRRI Coleraine Research Laboratory in Coleraine, Minnesota. The three Clay series samples were analyzed by Chemex, Ltd. of Vancouver, B.C. The samples were split before the final pulverizing phase, and the respective splits were then ground with steel rings and ceramic rings (the latter was analyzed for FeO). All of the Coleraine analyses were performed by Mr. John Engesser of the Coleraine Research Laboratory. The major element analysis were analyzed by inductively coupled argon plasma (ICP). FeO, CO_2, and H_2O were analyzed by wet chemical methods. Sulfur was analyzed in a Leco furnace. Total Organic Carbon (T.O.C.) analyses were done by Technical Service Laboratories (TSL), Mississauga, Ontario.

Certified reference samples (Appendix D-1) were analyzed to determine analytical accuracy. In general, major element analyses were ±5 percent, with greater errors at the low end of the detection range for CaO, Na_2O, and K_2O. Duplicate (Appendix D-2) and triplicate analyses (Appendix D-3) were analyzed to determine the analytical precision of the analyses. Duplicate analyses vary "on average" $\pm10\%$. Elements with the greatest variations are MnO, Na_2O, K_2O, P_2O_5, CO_2, and Total Organic Carbon (T.O.C.). Two samples, 87-020 and 87-233, were also sent to Chemex, Ltd. of Vancouver, B.C. as laboratory checks. The difference in duplicate analyses of these samples between NRRI's laboratory and Chemex is quite large. Other samples from a different project analyzed at the same time also had similar problems with correspondence with duplicates analyzed at TSL. The samples analyzed at Chemex for major elements had repeated problems with summing to 98-

102%. These problems were never sufficiently corrected, and these duplicate analyses illustrate the differences in the two laboratories.

Additional major element chemistry on glacial clays was obtained from Haas, *et al* (1987; Appendix D-5). However, when the element analyses were converted to oxides and totaled, some totals did not fall in the 98-102 wt.% range. These analyses for these samples were, therefore, not used in the various geochemical plots.

Appendix D-1

Analyses of Certified Reference Standards

SO1

	Assay Value	Certified Value	Percent Difference
Fe	5.96	6.00	-0.8%
SiO2	54.78	55.05	-0.5%
Al2O3	17.44	17.73	-1.6%
MgO	3.85	3.83	0.5%
CaO	2.57	2.52	2.2%
MnO	0.11	0.11	-0.3%
TiO2	0.79	0.88	-10.2%
Na2O	2.66	2.66	-0.1%
K2O	3.08	3.23	-4.7%
P2O5	0.30	0.14	116.4%

679-1

	Assay Value	Certified Value	Percent Difference
Fe	24.12	24.20	-0.3%
SiO2	7.53	7.34	2.6%
Al2O3	3.93	3.76	4.4%
MgO	1.13	1.16	-2.4%
CaO	25.40	25.28	0.5%
MnO	0.36	0.38	-6.1%
TiO2	0.17	0.18	-6.3%
S	0.07		
Na2O	0.16	0.07	121.4%
K2O	0.27	0.19	41.3%
P2O5	1.22	1.28	-4.3%

BR76

	Assay Value	Certified Value	Percent Difference
Fe	1.64	1.66	-1.2%
SiO2	54.99	54.68	0.6%
Al2O3	38.43	37.67	2.0%
MgO	0.58	0.58	-0.7%
CaO	0.35	0.27	31.1%
TiO2	2.16	2.21	-2.3%

BF-SLAG

	Assayed Value	Certified Value	Percent Difference
Fe	0.29	0.32	-8.2%
SiO2	37.00	36.58	1.1%
Al2O3	18.61	18.76	-0.8%
MgO	10.91	10.97	-0.6%
CaO	30.10		
MnO	1.04	1.10	-5.4%
TiO2	0.42	0.39	6.6%
S	1.67		

Appendix D-2

Analyses of Duplicate Samples

Residual Limonitic Kaolinitic Clay
N.W.S.P.C. Mine
Redwood County
87-020

wt. %	average	percent diff.
SiO2	62.60	3.8%
Al2O3	20.73	-1.9%
TiO2	0.56	-3.7%
TFe2O3	5.49	-6.2%
Fe2O3	1.83	3.6%
FeO	3.30	-10.8%
CaO	0.21	-72.5%
MgO	0.20	-44.0%
MnO	0.08	-35.7%
Na2O	0.06	-79.2%
K2O	0.49	-85.0%
P2O5	0.05	-65.7%
LOI	8.80	-4.2%
CO2	0.66	44.4%
H2O+	6.94	107.1%
S	0.02	328.6%
TOTAL	99.28	-0.1%

* Analyzed by Chemex and NRRI.

Brown Cretaceous Shale
Ochs' Springfield Mine
Brown County
87-169

wt. %	average	percent diff.
SiO2	59.18	-2.4%
Al2O3	14.82	2.7%
Fe+2	0.47	13.6%
FeO	0.60	13.6%

Residual Kaolinitic Clay
Fillmore County
87-196

wt. %	average	percent diff.
SiO2	63.17	-2.8%
Al2O3	14.69	-0.3%
TiO2	0.88	-9.9%
TFe	5.26	-6.3%
Fe+2	0.11	0.0%
TFe2O3	7.52	-6.3%
Fe2O3	7.36	-6.4%
FeO	0.14	0.0%
MgO	0.85	-0.4%
MnO	0.05	7.7%
LOI	8.00	5.1%

Residual Kaolinitic Clay
Fillmore County
87-198

wt. %	average	percent diff.
SiO2	49.86	-5.6%
Al2O3	20.74	-1.1%
TiO2	0.58	-3.9%
TFe	6.19	-8.5%
Fe+2	0.09	83.3%
TFe2O3	8.85	-8.5%
Fe2O3	8.73	-9.4%
FeO	0.11	83.3%
CaO	1.81	-3.5%
MgO	1.49	-2.6%
MnO	0.05	10.2%
LOI	14.12	3.9%

Residual Kaolinitic Clay
Winona County
87-199

wt. %	average	percent diff.
SiO2	55.14	-0.2%
Al2O3	18.76	-2.8%
TiO2	0.55	-5.9%
TFe	6.85	-4.2%
Fe+2	0.11	0.0%
TFe2O3	9.79	-4.2%
Fe2O3	9.63	-4.2%
FeO	0.14	0.0%
MgO	1.20	-1.0%
MnO	0.03	22.4%

Residual Kaolinitic Clay
Osmundson Quarry
Mower County
87-229

wt. %	average	percent diff.
SiO2	70.90	-5.5%
Al2O3	9.78	3.1%
TiO2	0.44	26.1%
TFe	2.19	0.4%
Fe+2	0.28	0.0%
TFe2O3	3.14	0.4%
Fe2O3	2.74	0.4%
FeO	0.36	0.0%
CaO	3.12	5.9%
MgO	0.92	-8.3%
MnO	0.068	-12.3%

Glacial Loess
Barr Clay Mine
Goodhue County
87-233

wt. %	average	percent diff.
SiO2	67.61	1.0%
Al2O3	7.13	-16.0%
TiO2	0.40	-16.4%
TFe2O3	3.21	-44.2%
Fe2O3	2.70	-41.8%
FeO	0.46	-55.8%
CaO	9.08	24.5%
MgO	0.69	1.5%
MnO	0.05	17.5%
Na2O	1.09	-4.5%
K2O	2.22	-12.7%
P2O5	0.13	-21.4%
LOI	8.76	17.6%
CO2	7.37	-17.8%
H2O+	1.61	26.8%
S	0.04	288.9%
TOTAL	100.36	0.6%

Pisolitic Kaolinite Clay

Morrison County
88-041

wt. %	average	percent diff.
SiO2	20.08	2.5%
Al2O3	41.36	1.6%
TiO2	1.09	-1.5%
TFe	11.22	4.2%
Fe+2	1.45	-6.0%
TFe2O3	16.04	4.2%
Fe2O3	13.97	5.8%
FeO	1.86	-6.0%
CaO	0.47	-14.5%
MgO	0.23	0.4%
MnO	0.06	3.3%
Na2O	0.20	200.0%
K2O	0.12	107.5%
P2O5	0.12	26.9%
LOI	20.50	-1.5%
CO2	0.35	-54.2%
H2O+	19.59	-0.9%
TOTAL	100.28	1.7%

* Analyzed by Chemex and NRRI.

Secondary Kaolinitic Clay
Enterprise Mine
St. Louis County
88-089

wt. %	average	percent diff.
SiO2	45.95	0.9%
Al2O3	22.12	1.4%
TiO2	0.88	1.2%
TFe	13.31	-2.3%
Fe+2	0.13	16.7%
TFe2O3	19.04	-2.3%
Fe2O3	18.85	-2.5%
FeO	0.17	16.7%
CaO	0.21	0.0%
MgO	0.30	0.0%
MnO	0.05	0.0%
Na2O	0.17	0.0%
K2O	1.04	-3.0%
P2O5	0.18	-22.7%
LOI	10.26	1.7%
CO2	0.48	2200.0%
H2O+	9.49	1.8%
S	0.32	-13.7%
TOTAL	100.18	0.4%

Glacial Till

Crow Wing County
88-097

wt. %	average	percent diff.
SiO2	75.68	1.1%
Al2O3	10.71	2.7%
TiO2	0.70	2.1%
TFe	2.74	5.4%
Fe+2	0.36	-2.8%
TFe2O3	3.92	5.4%
Fe2O3	3.41	6.6%
FeO	0.46	-2.8%
CaO	1.44	1.7%
MgO	0.86	3.7%
MnO	0.04	0.0%
Na2O	1.74	8.4%
K2O	2.07	11.4%
P2O5	0.09	-15.1%
LOI	3.35	-1.8%
CO2	0.41	210.0%
H2O+	2.85	-6.8%
T.O.C.	1.65	-5.9%
TOTAL	100.59	1.6%

Cretaceous Shale

Brown County
88-101

wt. %	average	percent diff.
SiO2	64.08	0.3%
Al2O3	11.37	-0.6%
TiO2	0.56	-1.0%
TFe	2.57	-0.1%
Fe+2	0.29	23.1%
TFe2O3	3.68	-0.1%
Fe2O3	3.26	-2.7%
FeO	0.37	23.1%
CaO	5.88	-3.0%
MgO	1.72	3.7%
MnO	0.02	-8.7%
Na2O	0.23	50.0%
K2O	3.43	18.2%
P2O5	0.35	32.0%
LOI	9.39	1.2%
CO2	3.35	2.1%
H2O+	4.99	5.1%
S	0.01	-79.2%
T.O.C.	3.3	-19.4%
TOTAL	100.69	0.9%

Residual Kaolinitic Clay

Northern Con-Agg Mine
Brown County
88-103

wt. %	average	percent diff.
SiO2	79.52	2.6%
Al2O3	11.85	2.0%
TiO2	0.46	1.3%
TFe	1.59	-0.5%
Fe+2	0.87	23.1%
TFe2O3	2.27	-0.5%
Fe2O3	1.03	-23.1%
FeO	1.12	23.1%
CaO	0.29	38.5%
MgO	0.14	0.1%
MnO	0.04	-2.7%
Na2O	0.14	80.0%
K2O	0.47	24.8%
P2O5	0.05	3.9%
LOI	4.96	-6.3%
CO2	0.47	-10.2%
H2O+	4.35	-0.2%
TOTAL	100.21	2.3%

Glacial Lake Clay
Fertile Brickyard
Polk County
88-135

wt. %	average	percent diff.
SiO2	53.03	0.8%
Al2O3	8.90	2.5%
TiO2	0.37	0.0%
TFe	1.95	4.5%
Fe+2	0.27	-7.1%
TFe2O3	2.79	4.5%
Fe2O3	2.40	6.5%
FeO	0.35	-7.1%
CaO	11.27	-1.8%
MgO	5.13	2.6%
MnO	0.05	-10.4%
Na2O	1.33	3.8%
K2O	1.79	8.2%
P2O5	0.15	29.5%
LOI	15.37	1.2%
CO2	10.08	-19.4%
H2O+	2.44	-5.6%
T.O.C.	2.0	-18.2%
TOTAL	100.16	1.1%

Appendix D-3

Analyses of Triplicate Samples

Residual Chloritic Clay
N.W.S.P.C. Mine
Redwood County
87-009

wt. %	average	std. dev.	variance
SiO2	58.18	0.43	0.18
Al2O3	21.12	0.26	0.07
TiO2	0.54	0.002	0.000003
TFe	4.96	0.10	0.01
Fe+2	3.89	0.04	0.002
TFe2O3	7.09	0.14	0.02
Fe2O3	1.54	0.09	0.01
FeO	5.00	0.06	0.003
CaO	0.27	0.01	0.0002
MgO	0.33	0.01	0.0001
MnO	0.348	0.008	0.0001
Na2O	0.02	0.00	0.00
K2O	0.60	0.04	0.001
P2O5	0.030	0.0005	0.0000002
LOI	10.49	0.02	0.001
H2O+	8.70	0.02	0.0004
S	0.02	0.0022	0.000005
TOTAL	99.03	0.72	0.52

Pisolitic Kaolinitic Clay
Redwood County
87-029

wt. %	average	std. dev.	variance
SiO2	46.73	0.52	0.27
Al2O3	37.62	0.51	0.26
TiO2	1.28	0.04	0.002
TFe	0.73	0.01	0.00021
Fe+2	0.06	0.00	0.00
TFe2O3	1.04	0.02	0.0004
Fe2O3	0.96	0.02	0.0004
FeO	0.08	0.00	0.00
CaO	0.13	0.03	0.001
MgO	0.08	0.00	0.00
MnO	0.006	0.0017	0.000003
Na2O	0.11	0.00	0.00
K2O	0.02	0.005	0.00002
P2O5	0.020	0.000	0.000
LOI	14.53	0.29	0.08
S	0.017	0.001	0.000001
TOTAL	101.58	0.43	0.18

Brown Cretaceous Shale
Ochs' Springfield Mine
Brown County
87-105

wt. %	average	std. dev.	variance
SiO2	59.56	0.29	0.08
Al2O3	15.05	0.04	0.002
TiO2	0.88	0.04	0.002
TFe	4.32	0.06	0.003
Fe+2	0.80	0.02	0.001
TFe2O3	6.18	0.08	0.01
Fe2O3	5.03	0.11	0.01
FeO	1.03	0.03	0.0009
CaO	0.46	0.01	0.0001
MgO	1.01	0.03	0.001
MnO	0.048	0.009	0.00008
Na2O	0.27	0.0047	0.00002
K2O	2.18	0.15	0.02
P2O5	0.047	0.0024	0.000006
LOI	12.16	0.04	0.002
H2O+	8.18	0.07	0.004
TOTAL	97.85	0.33	0.11

Gray Cretaceous Shale
Ochs' Springfield Mine
Brown County
87-164

wt. %	average	std. dev.	variance
SiO2	75.73	0.42	0.18
Al2O3	8.53	0.19	0.04
TiO2	0.95	0.02	0.001
TFe	2.65	0.07	0.005
Fe+2	1.59	0.07	0.005
TFe2O3	3.79	0.10	0.01
Fe2O3	1.51	0.17	0.03
FeO	2.05	0.09	0.01
CaO	0.29	0.03	0.001
MgO	0.65	0.01	0.00003
MnO	0.087	0.003	0.00001
Na2O	0.43	0.04	0.001
K2O	1.93	0.13	0.02
P2O5	0.052	0.002	0.000005
LOI	4.99	0.04	0.001
H2O+	3.11	0.17	0.03
TOTAL	97.42	0.84	0.70

Glacial Till
Lyon County
87-172

wt. %	average	std. dev.	variance
SiO2	57.89	0.70	0.48
Al2O3	10.77	0.21	0.04
TiO2	0.56	0.05	0.002
TFe	2.12	0.07	0.005
Fe+2	0.38	0.0047	0.00002
TFe2O3	3.03	0.10	0.01
Fe2O3	3.03	0.10	0.01
FeO	0.48	0.01	0.00004
CaO	8.54	0.30	0.09
MgO	2.90	0.04	0.002
MnO	0.100	0.00	0.00
Na2O	1.01	0.03	0.001
K2O	1.94	0.08	0.01
P2O5	0.160	0.00	0.00
LOI	12.98	0.09	0.01
TOTAL	99.88	1.07	1.14

Recent Fluvial Clay
Jackson County
87-210

wt. %	average	std. dev.	variance
SiO2	59.13	0.46	0.21
Al2O3	7.59	0.20	0.04
TiO2	0.28	0.02	0.0004
TFe	1.49	0.03	0.0008
Fe+2	0.54	0.03	0.0007
TFe2O3	2.13	0.04	0.0016
Fe2O3	1.37	0.08	0.01
FeO	0.69	0.03	0.001
CaO	9.98	0.17	0.03
MgO	4.10	0.02	0.0005
MnO	0.090	0.002	0.00001
Na2O	1.24	0.05	0.003
K2O	1.81	0.04	0.002
P2O5	0.111	0.001	0.000001
LOI	13.68	0.13	0.02
H2O+	1.53	0.29	0.08
TOTAL	100.15	0.66	0.43

Ordovician Glenwood Shale
Goodhue County
87-232

wt. %	average	std. dev.	variance
SiO2	59.01	0.19	0.04
Al2O3	14.95	0.10	0.01
TiO2	0.55	0.03	0.001
TFe	3.23	0.06	0.004
Fe+2	0.21	0.05	0.003
TFe2O3	4.62	0.09	0.01
Fe2O3	4.33	0.14	0.02
FeO	0.27	0.07	0.004
CaO	0.32	0.02	0.0003
MgO	1.36	0.02	0.0004
MnO	0.007	0.002	0.000004
Na2O	0.09	0.002	0.000005
K2O	8.60	0.40	0.16
P2O5	0.089	0.001	0.000001
LOI	8.56	0.30	0.09
TOTAL	98.16	0.55	0.30

Ordovician Decorah Shale
Twin City Brickyard
Dakota County
87-276

wt. %	average	std. dev.	variance
SiO2	55.94	0.65	0.43
Al2O3	12.15	0.05	0.002
TiO2	0.49	0.04	0.001
TFe	2.65	0.03	0.001
Fe+2	0.71	0.00	0.00
TFe2O3	3.79	0.04	0.002
Fe2O3	3.46	0.48	0.23
FeO	0.91	0.00	0.00
CaO	6.72	0.23	0.05
MgO	2.43	0.03	0.001
MnO	0.053	0.005	0.00002
Na2O	0.11	0.005	0.00002
K2O	7.34	0.10	0.01
P2O5	0.203	0.005	0.00002
LOI	9.64	0.15	0.02
S	0.22	0.32	0.10
TOTAL	98.87	0.81	0.66

Residual Chloritic Clay
N.W.S.P.C. Mine
Redwood County
87-282

wt. %	average	std. dev.	variance
SiO2	63.19	0.35	0.12
Al2O3	21.30	0.11	0.01
TiO2	0.52	0.03	0.001
TFe	3.29	0.03	0.001
Fe+2	1.85	0.03	0.001
TFe2O3	4.71	0.04	0.001
Fe2O3	2.07	0.06	0.004
FeO	2.38	0.03	0.001
CaO	0.09	0.00	0.00
MgO	0.18	0.01	0.00004
MnO	0.040	0.002	0.000004
Na2O	0.02	0.00	0.00
K2O	0.41	0.01	0.0002
P2O5	0.020	0.000	0.000
LOI	8.76	0.10	0.01
S	0.014	0.0005	0.0000002
TOTAL	99.24	0.47	0.22

Residual Chloritic Clay
N.W.S.P.C. Mine
Redwood County
87-285

wt. %	average	std. dev.	variance
SiO2	50.19	0.86	0.75
Al2O3	16.36	0.15	0.02
TiO2	0.76	0.02	0.001
TFe	12.39	0.21	0.04
Fe+2	6.42	0.02	0.001
TFe2O3	17.71	0.29	0.09
Fe2O3	8.53	0.30	0.09
FeO	8.26	0.03	0.001
CaO	0.60	0.01	0.0001
MgO	2.27	0.08	0.01
MnO	0.166	0.006	0.00004
Na2O	0.06	0.005	0.00002
K2O	2.39	0.09	0.01
P2O5	0.227	0.005	0.00002
LOI	9.44	0.02	0.0003
H2O+	7.05	0.29	0.08
S	0.03	0.002	0.000003
TOTAL	100.16	1.03	1.06

Appendix D-4

Clay Geochemical Data

The geochemical data for each sample analyzed are in a Lotus 1-2-3 file named CLAYCHEM.WK1 on Disk 1. The data available for each sample are listed under the following column headings:

Column A: Data sort number.
Column B: Sample number - 87 and 88 stand for year in which the sample was collected.
Column C: U. S. Bureau Mines (USBM) sample number for samples obtained from the USBM.
Column D: Sample type.
Column E: Rock type - this is an abbreviated designation for sorting the different sample types.
Column F: Geologic age.
Column G: Glacial ice lobe/moraine association name.
Column H: Glacial lake name.
Column I: Deposit name - designates mine name or outcrop.
Column J: County name.
Column K: Station number - an alphanumeric designator for identifying which trench and channel sample was collected.
Column L: Unit name - an alphanumeric designator to identify a stratigraphic subunit, e.g., B4 at the Ochs' Springfield mine or 1 lowest most sample in a trench.
Column M: Thickness in feet of the channel sample.
Column N: Bibliographic reference for geochemical data from the literature.
Column O: SiO_2 - wt. %.
Column P: Al_2O_3 - wt. %.
Column Q: TiO_2 - wt. %.
Column R: Total Fe^0 - wt. %.
Column S: Fe^{+2} - wt %.
Column T: Total Fe_2O_3 - calculated from Total Fe°.
Column U: Fe_2O_3 - calculated.
Column V: FeO - wt. %.
Column W: CaO - wt. %.
Column X: MgO - wt. %.
Column Y: MnO - wt. %.
Column Z: Na_2O - wt. %.
Column AA: K_2O - wt. %.
Column AB: P_2O_5 - wt. %.
Column AC: LOI - wt. %.
Column AD: CO_2 - wt. %.
Column AE: H_2O^+ - wt. %.
Column AF: H_2O^- - wt. %.
Column AG: S - wt. %.
Column AH: BaO - wt. %.
Column AI: T.O.C. - total organic carbon - wt. %.

Column AJ: Major element analysis total - wt. %.
Column AK: $Na_2O + K_2O$.
Column AL: FeO/Fe_2O_3.
Column AM: Al_2O_3 - molecular proportion.
Column AN: CaO - molecular proportion.
Column AO: Na_2O - molecular proportion.
Column AP: SiO_2 - molecular proportion.
Column AQ: K_2O - molecular proportion.
Column AR: MgO - molecular proportion.
Column AS: Fe_2O_3 - molecular proportion.
Column AT: blank.
Column AU: CIW index of Harnois (1988).
Column AV: V index of Roaldset (1972).
Column AW: MWPI index of Vogel (1975).
Column AX: WI index of Parker (1970).
Column AY: CIA index of Nesbitt and Young (1982).

Appendix D-5

U.S. Bureau of Mines' Clay Geochemical Data

The geochemical data for each sample analyzed reported by the U.S. Bureau of Mines in Haas, *et al* (1987) are in a Lotus 1-2-3 file named USBMCHEM.WK1 on Disk 1. The data available for each sample are listed under the following column headings:

Column A: Data sort number.
Column B: Sample area/number.
Column C: Auger drill hole number and sample number - alphanumeric code.
Column D: Auger sample depth - from footage in feet.
Column E: Auger sample depth - to footage in feet.
Column F: Sample interval thickness in feet.
Column G: Glacial lake/ glacial till moraine association name.
Column H: Rock type, e.g., till, lake clay, etc.
Column I: Rock type alpha code.
Column J: Rock unit code, e.g., D = Glacial Lake Duluth.
Column K: County.
Column L: Quarter section.
Column M: Section number.
Column N: Township number.
Column O: Range number.
Column P: Si - wt. %.
Column Q: Al - wt. %.
Column R: Ca - wt. %.
Column S: Mg - wt. %.
Column T: Fe - wt. %.
Column U: Ti - wt. %.
Column V: K - wt. %.
Column W: Na - wt. %.
Column X: C - wt. %.
Column Y: P - wt. %.
Column Z: S - wt. %.
Column AA: LOI - wt. %
Column AB: SiO_2 - wt. %.
Column AC: Al_2O_3 - wt. %.
Column AD: TiO_2 - wt. %.
Column AE: Total Fe_2O_3 - calculated from Total Fe^0.
Column AF: CaO - wt. %.
Column AG: MgO - wt. %.
Column AF: Na_2O - wt. %.
Column AI: K_2O - wt. %.
Column AJ: P_2O_5 - wt. %.
Column AK: LOI - wt. %.
Column AL: S - wt. %.
Column AM: T.C. - total carbon - wt. %.
Column AN: Major element analysis total - wt. %.
Column AO: $Na_2O + K_2O$.

APPENDIX E

PARTICLE SIZE DATA

The particle size data for each sample analyzed are in a Lotus 1-2-3 file named PARTSIZE.WK1 on Disk 1. The data available for each sample are listed under the following column headings:

Column A: Data sort number.
Column B: Sample number - 87 and 88 stand for year in which the sample was collected.
Column C: U. S. Bureau Mines (USBM) sample number for samples obtained from the USBM.
Column D: Sample type.
Column E: Rock type - this is an abbreviated designation for sorting the different sample types.
Column F: Geologic age.
Column G: Glacial ice lobe/moraine association name.
Column H: Glacial lake name.
Column I: Deposit name - designates mine name or outcrop.
Column J: County name.
Column K: Station number - an alphanumeric designator for identifying which trench and channel sample was collected.
Column L: Unit name - an alphanumeric designator to identify a stratigraphic subunit, e.g., B4 at the Ochs' Springfield mine or 1-lowest sample in a trench.
Column M: Thickness in feet of the channel sample.
Column N: Sample weight.
Column O: Sand weight.
Column P: >2000 microns.
Column Q: 1000 microns.
Column R: 500 microns.
Column S: 250 microns.
Column T: 125 microns.
Column U: 62.5 microns.
Column V: 44 microns.
Column W: 31 microns.
Column X: 22.1 microns.
Column Y: 15.6 microns.
Column Z: 7.8 microns.
Column AA: 3.9 microns.
Column AB: <2.0 microns.

APPENDIX E-1

PARTICLE SIZE DIAGRAMS

The particle size data are provided in Appendix E (floppy diskette). The data have been summarized on triangular diagrams with clay, silt, and sand at the apexes. Summary diagrams for each clay type follow. Where samples were collected as a part of the continuous channel sample, an arrow connects each successively higher sample in the channel sample or trench to illustrate the vertical changes in particle size. Since the channel samples may represent up to ten feet of material in some places, the particle size value will represent a composite for that interval. However, general differences between different types of clay, e.g., secondary versus residual clays, are distinguished on these diagrams.

Eighteen separate analyses were conducted on an internal standard (88-002). Figure 33 shows the percent of the sample that is coarser than the given phi for the entire phi range. The minimum error is <10 %. The standard error is 7.6 %.

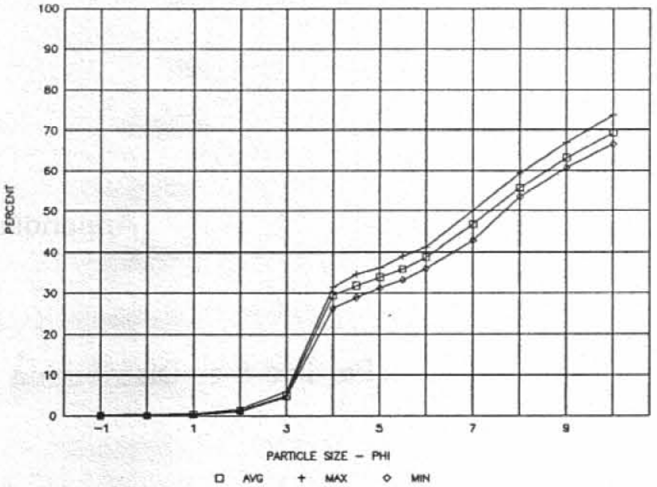


Figure 33. Particle size error on the internal standard 88-002.

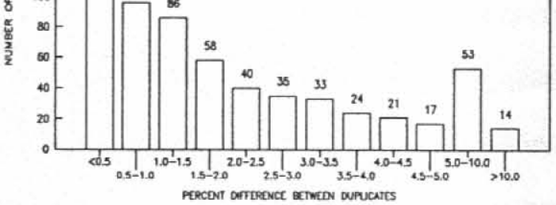


Figure 34. Distribution of the percent difference in particle size between duplicate samples.

Figure 34 illustrates the distribution of the percent difference in the particle size between duplicate samples. A total of 53 duplicate samples (data on diskette) had 742 total determinations or fourteen different size determinations per sample.

Appendix E-1A

Particle Size Distribution of Precambrian Clays

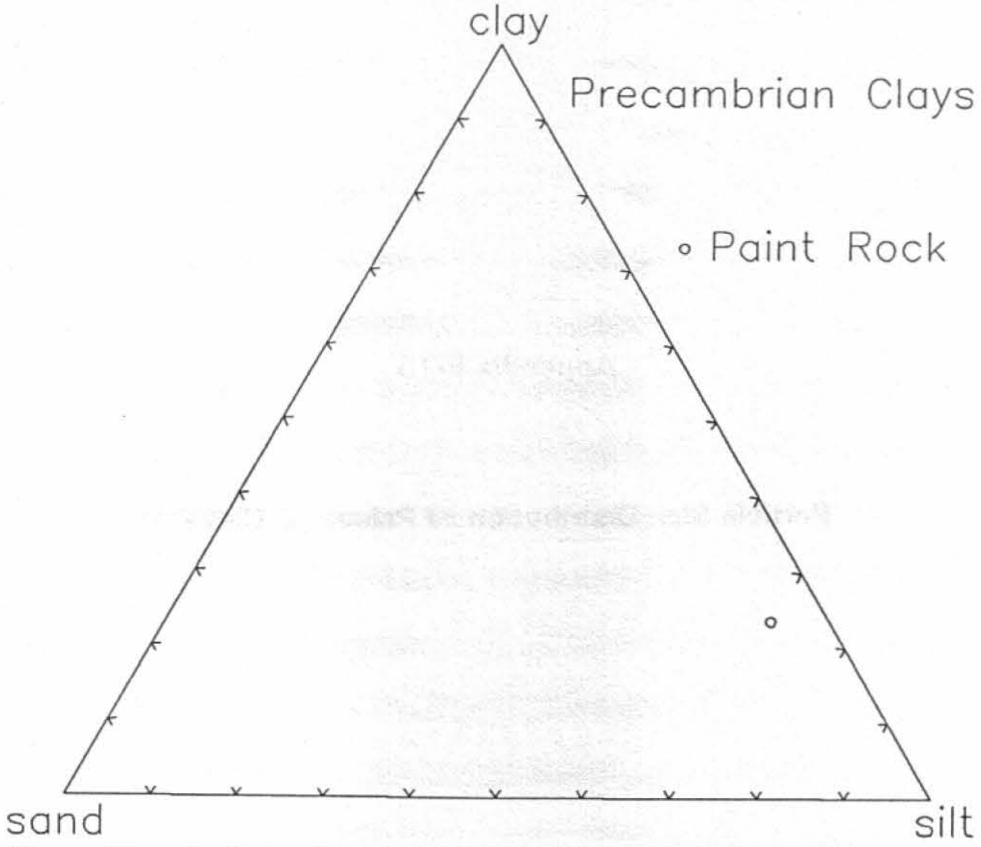


Figure 35. Particle size distribution of Precambrian clays.

Appendix E-1B

Particle Size Distribution of Paleozoic Clays

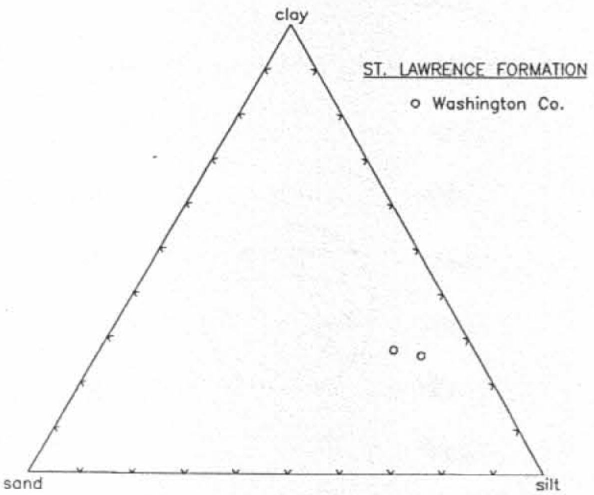


Figure 36. Particle size distribution of St. Lawrence Fm. clays.

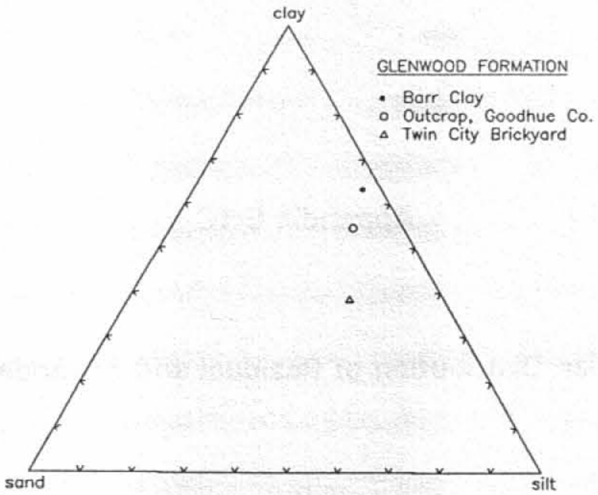


Figure 37. Particle size distribution of Glenwood Fm. clays.

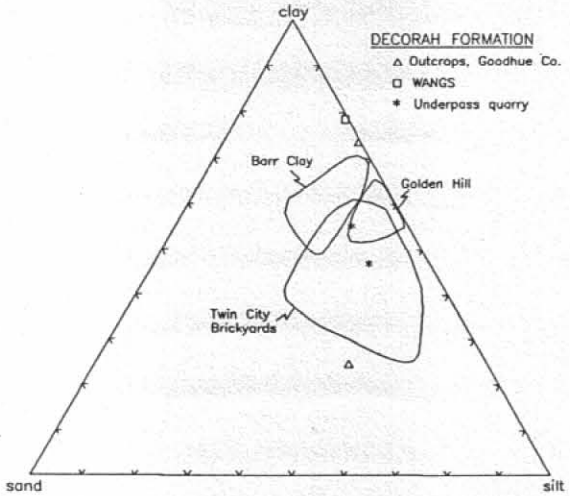


Figure 38. Particle size distribution of Decorah Shale clays.

Appendix E-1C

Particle Size Distribution of Residual and Secondary Clays

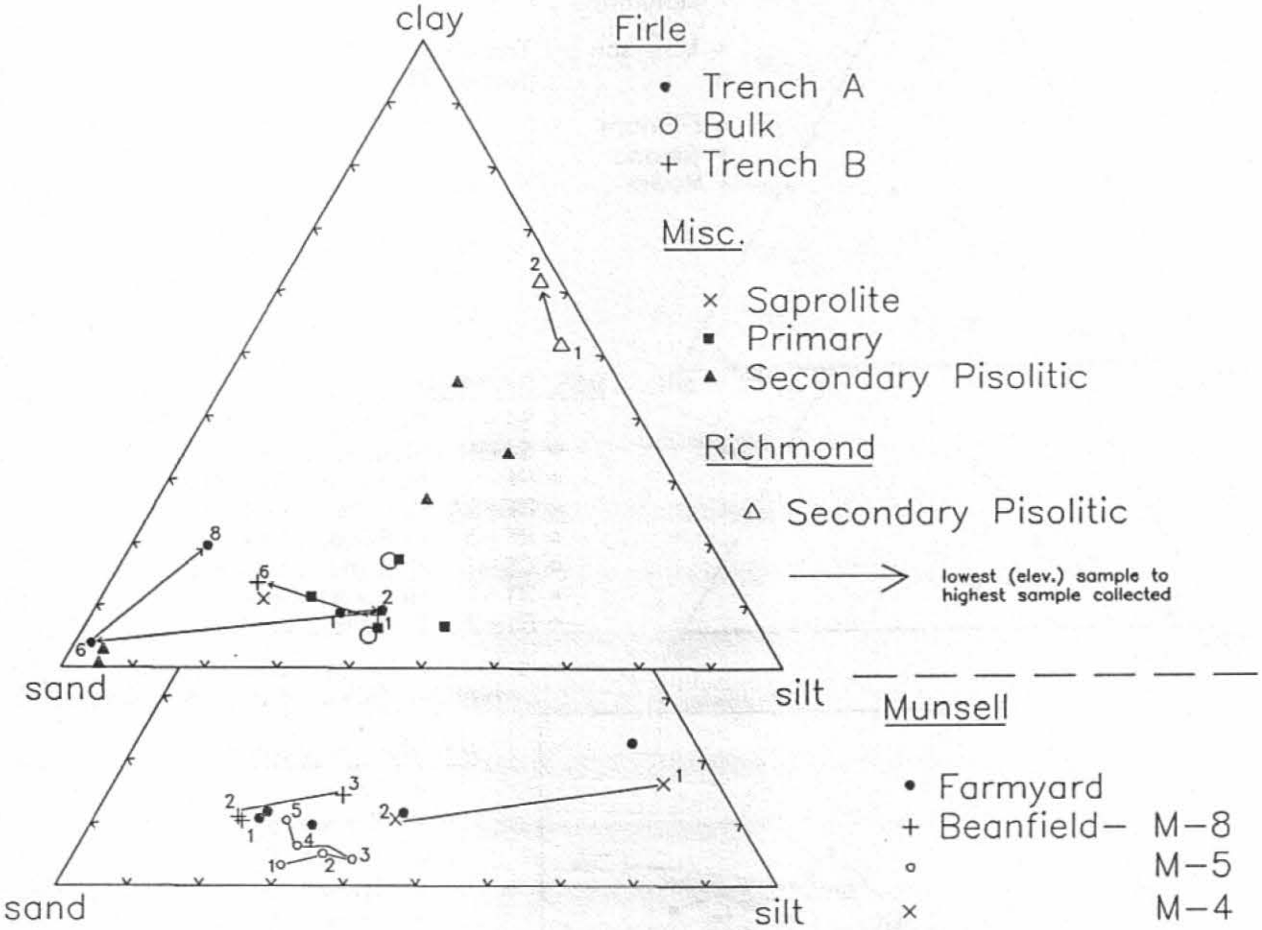


Figure 39. Particle size distribution of residual and secondary clays in the Minnesota River Valley.

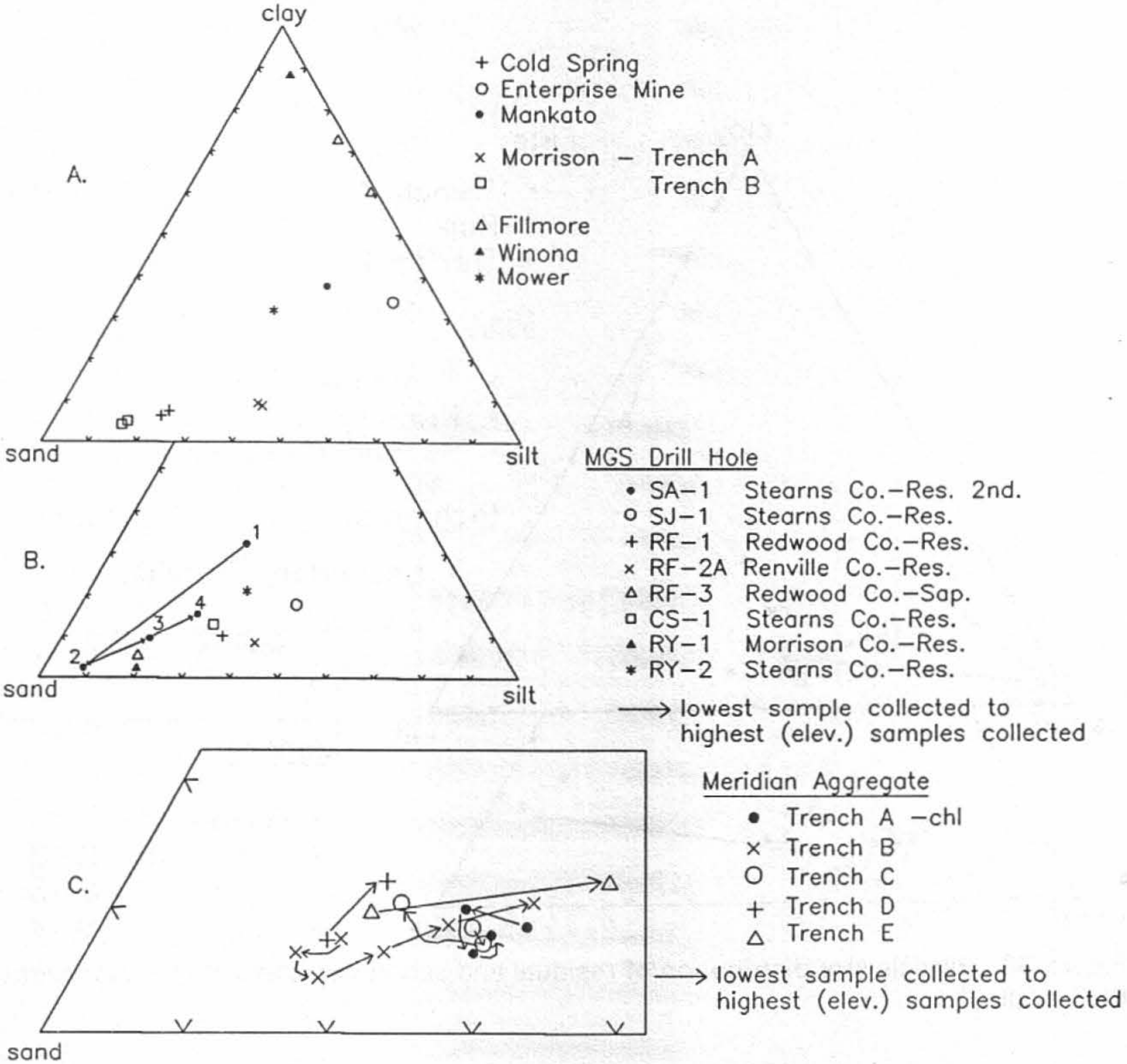


Figure 40. Particle size distribution of residual and secondary clays in MGS drill holes, southeastern Minnesota and in the St. Cloud area.

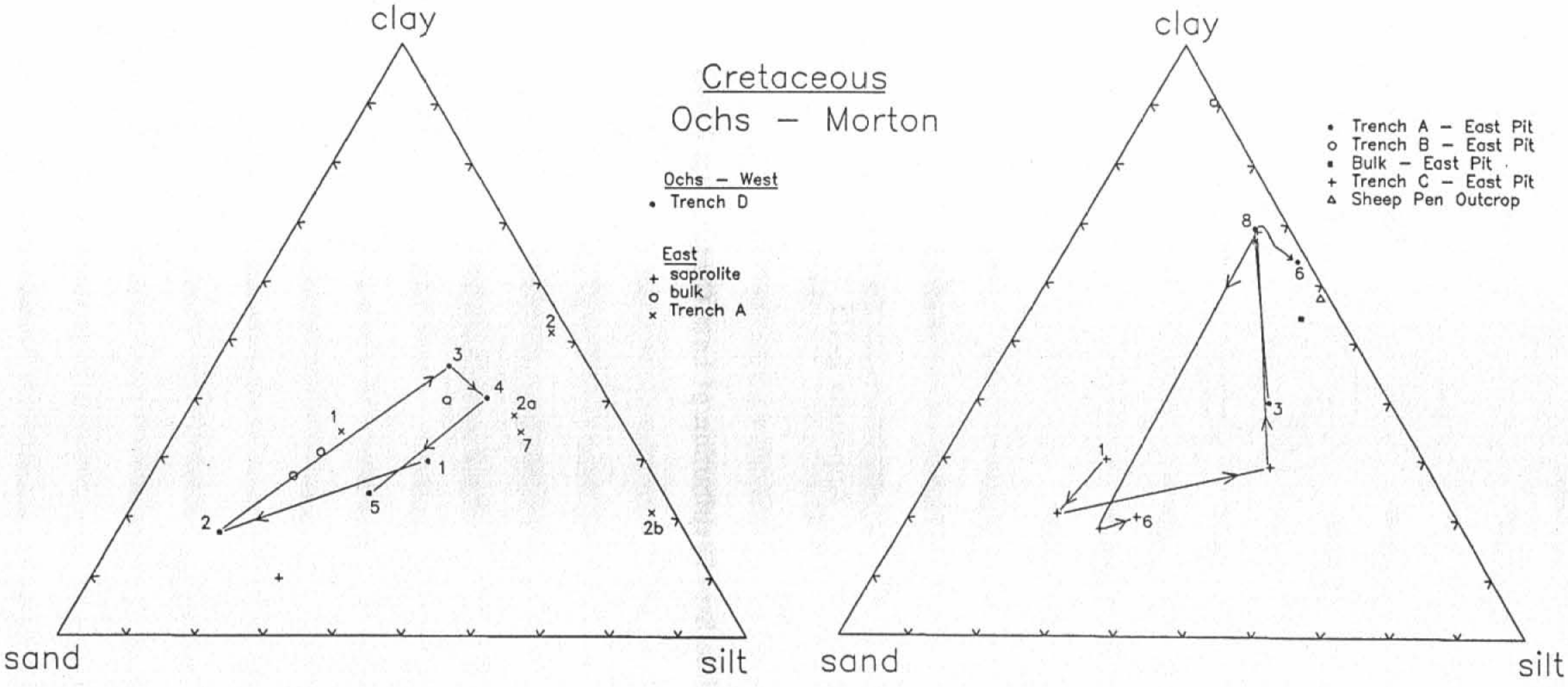


Figure 41. Particle size distribution of residual and secondary clays in the Ochs' Morton mine.

Appendix E-1D

Particle Size Distribution of Late Cretaceous Clays

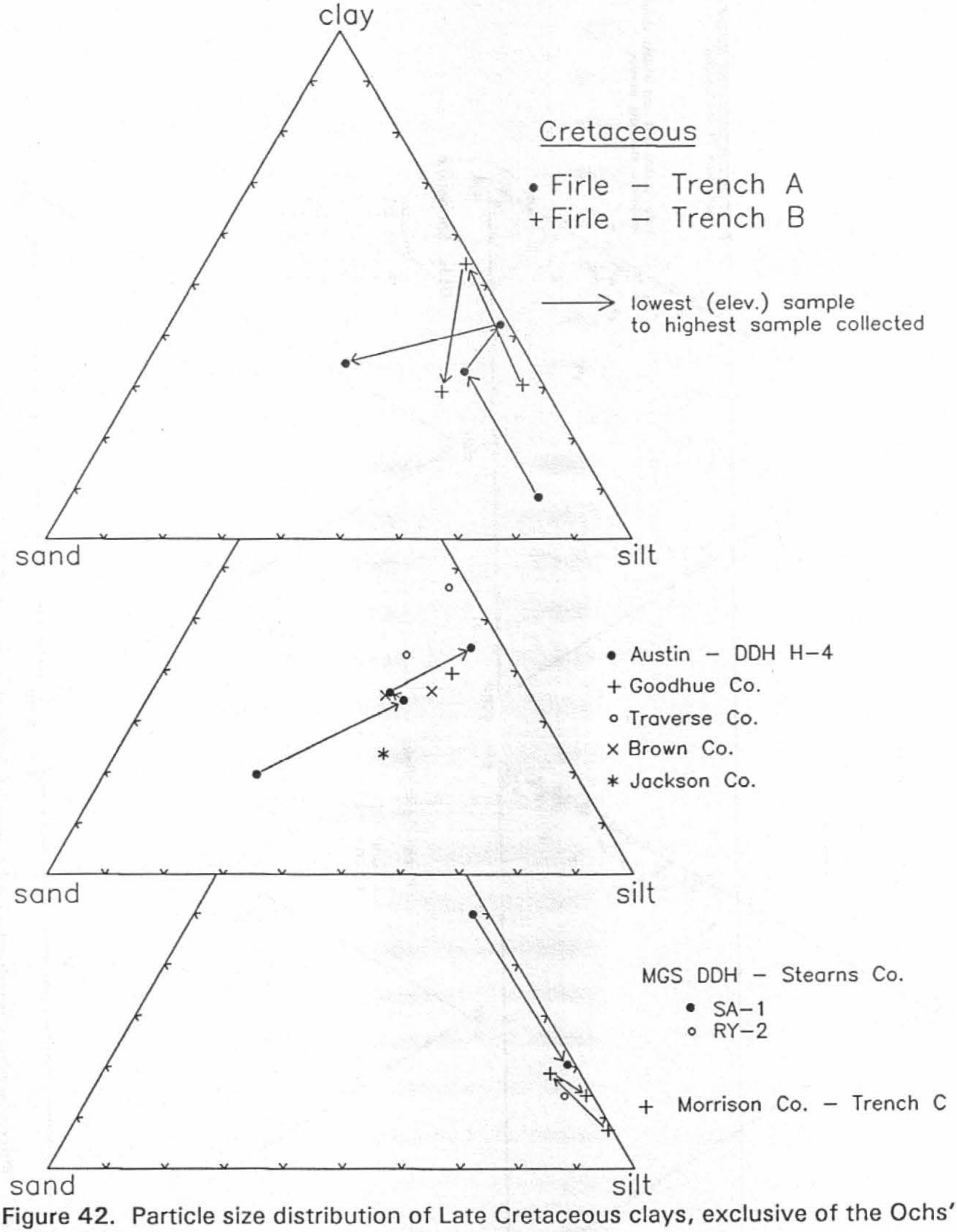


Figure 42. Particle size distribution of Late Cretaceous clays, exclusive of the Ochs' Springfield mine.

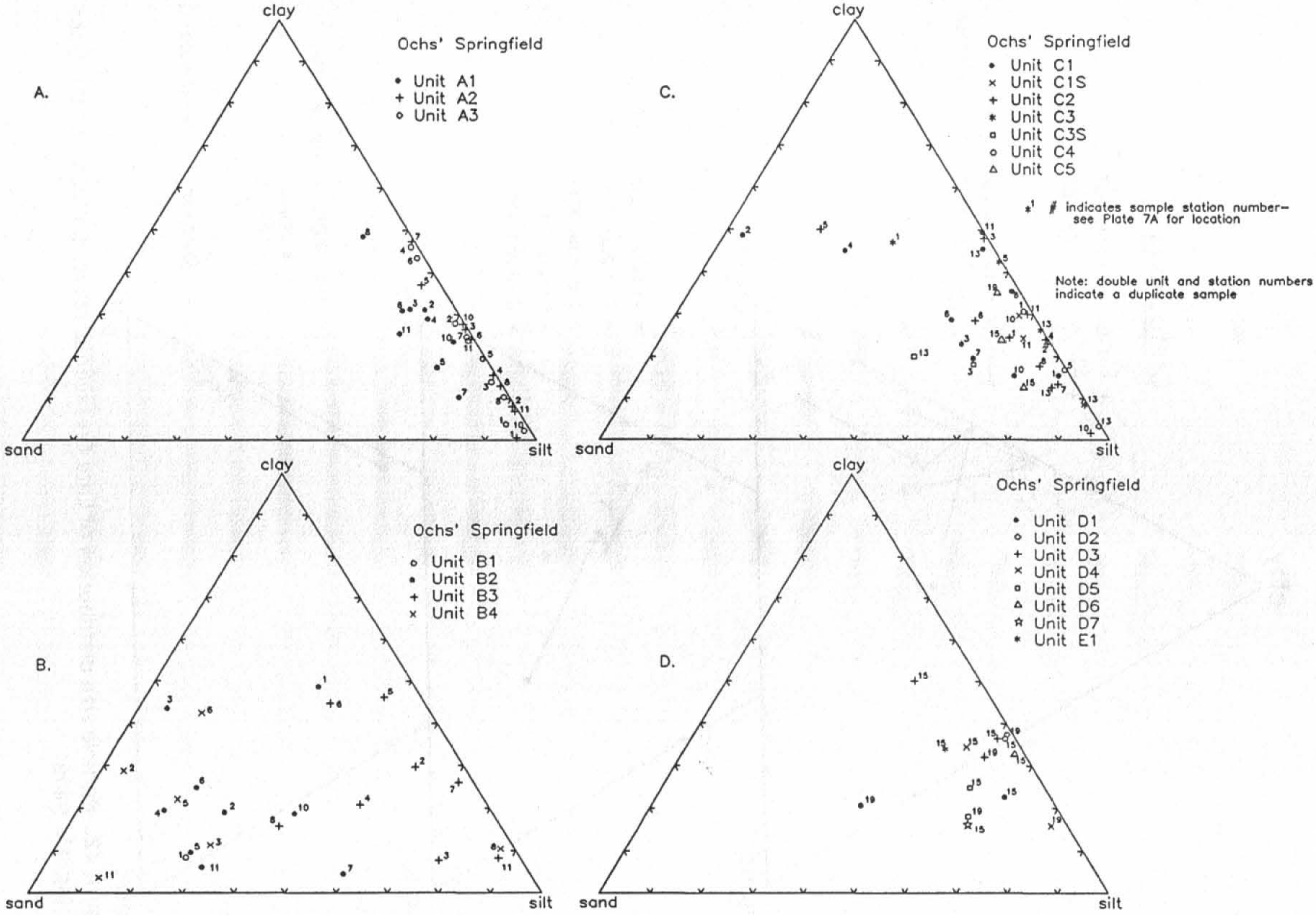


Figure 43. Particle size distribution of clays in units A through E in the Ochs' Springfield mine.

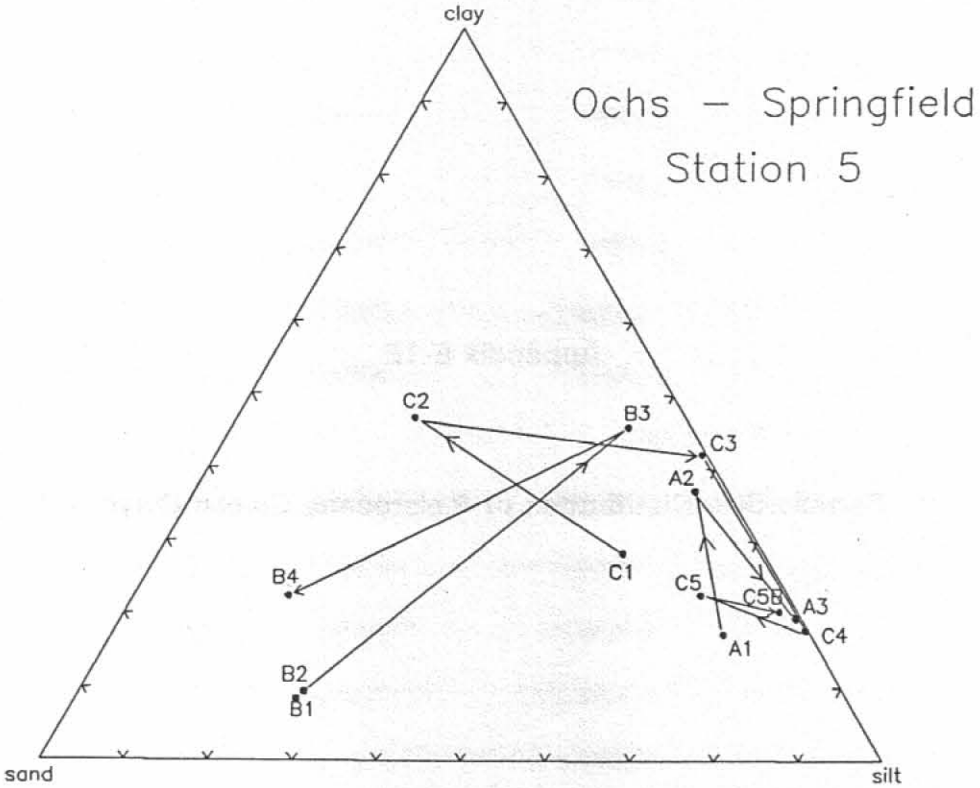


Figure 44. Particle size distribution of clays at station 5 in the Ochs' Springfield mine.

Appendix E-1E

Particle Size Distribution of Pleistocene Glacial Clays

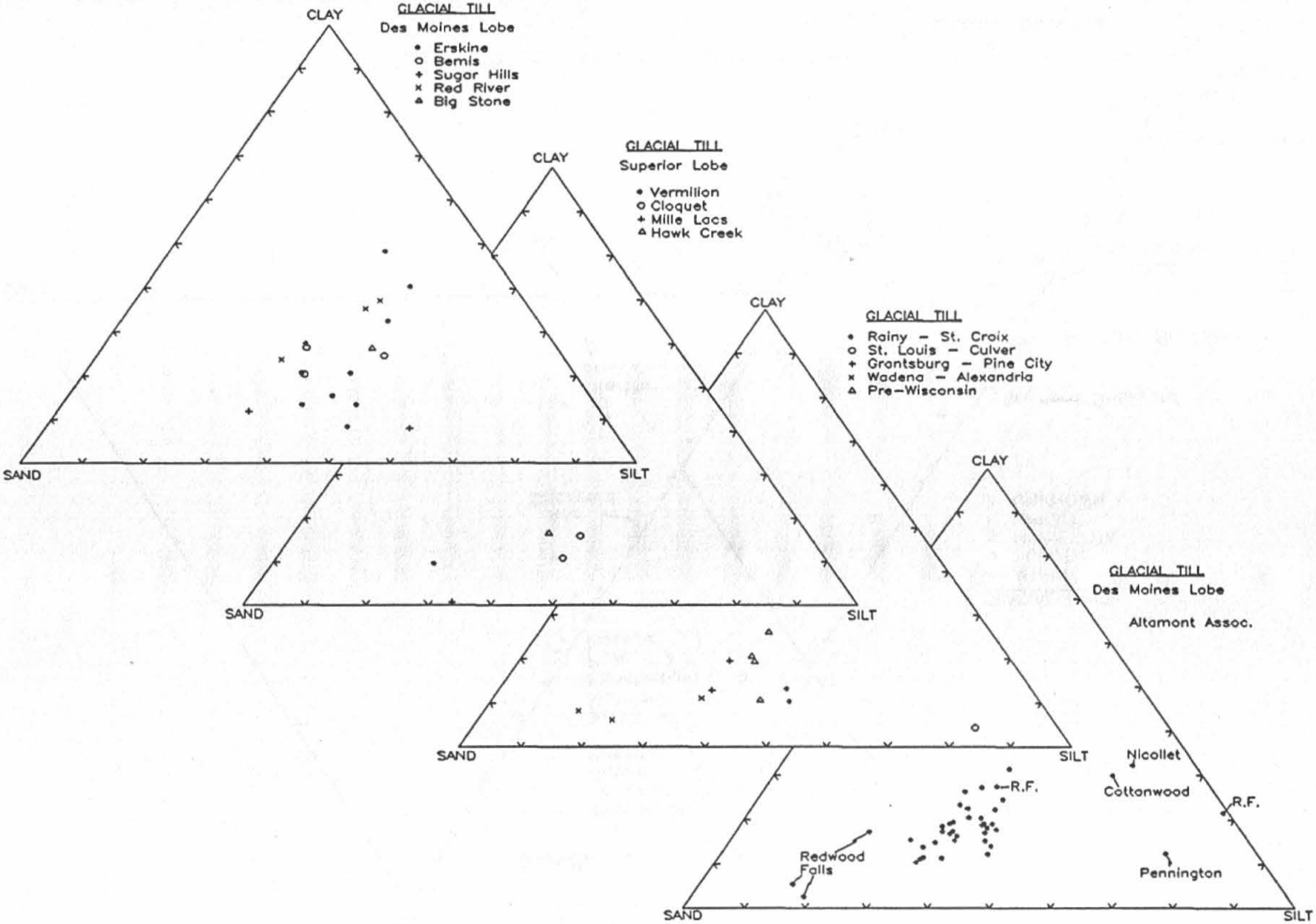


Figure 45. Particle size distribution of glacial till clays.

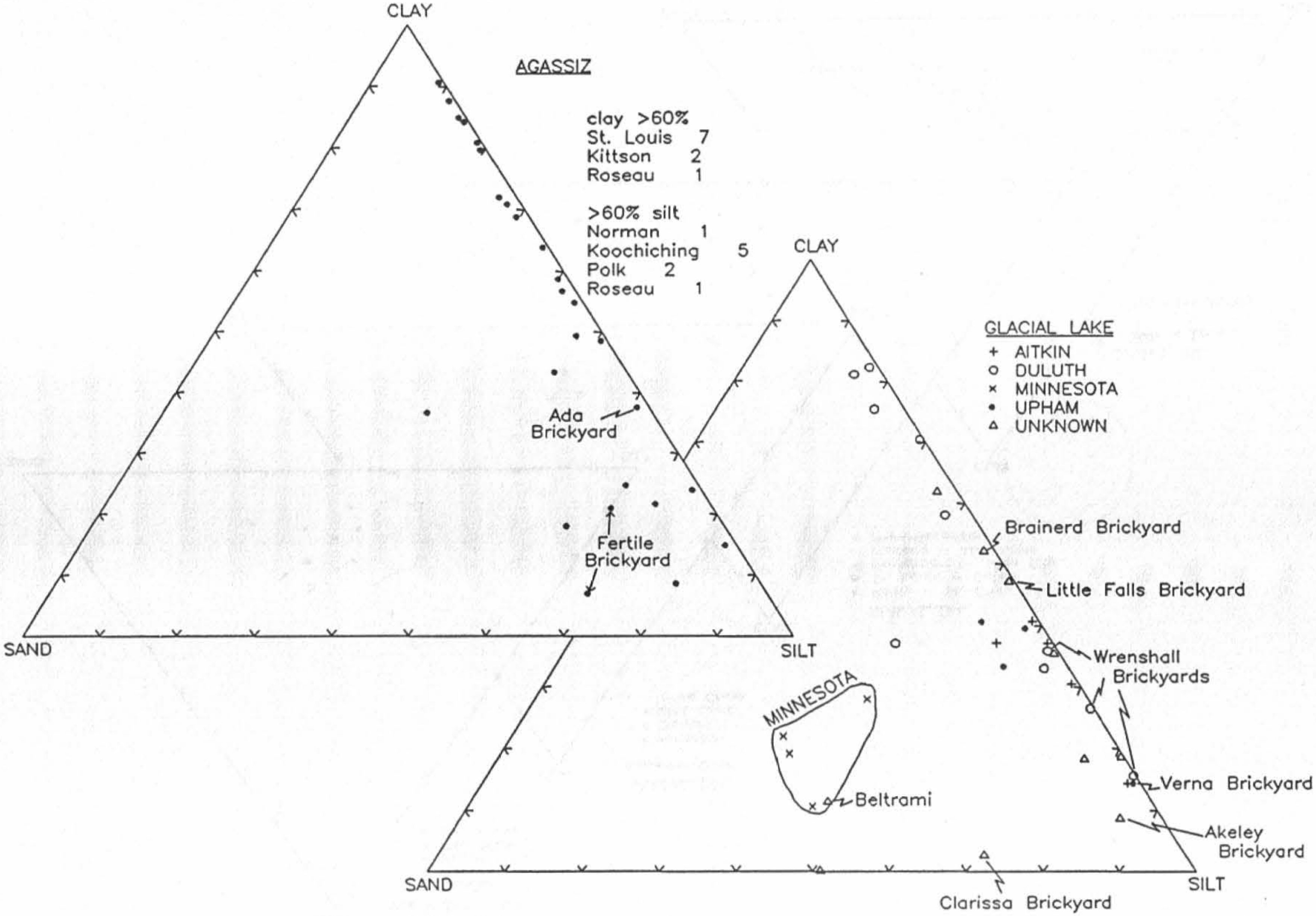


Figure 46. Particle size distribution of glacial lake clays.

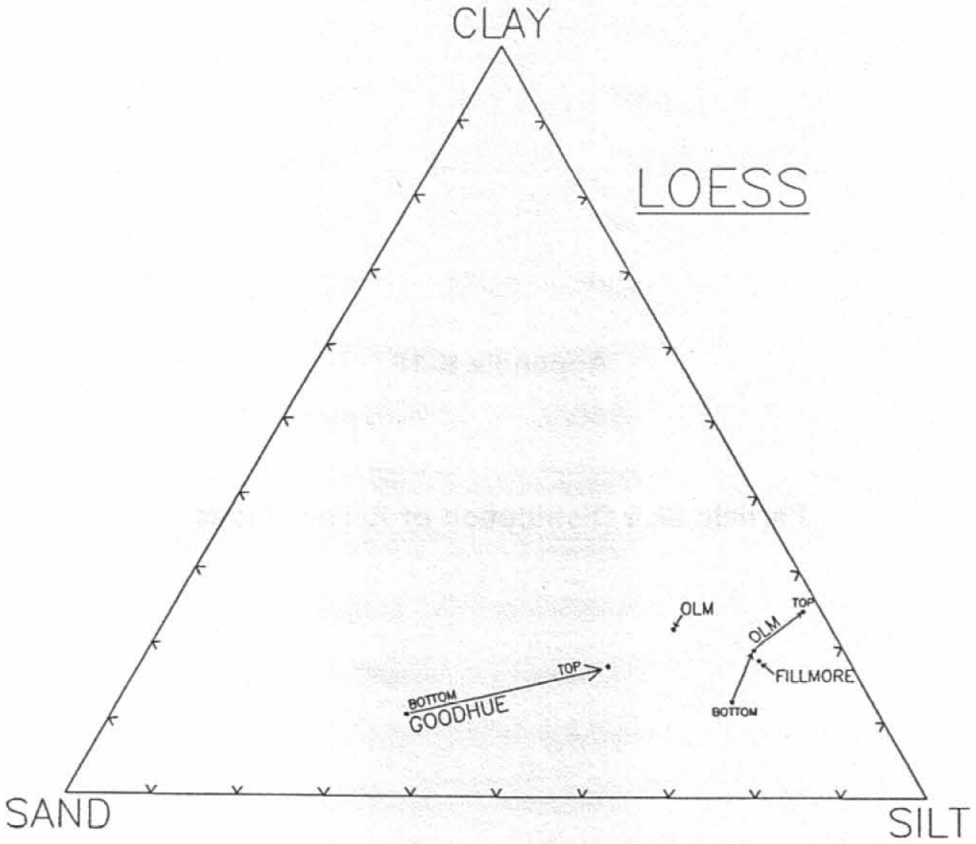


Figure 47. Particle size distribution of glacial loess.

Appendix E-1F

Particle Size Distribution of Recent Clays

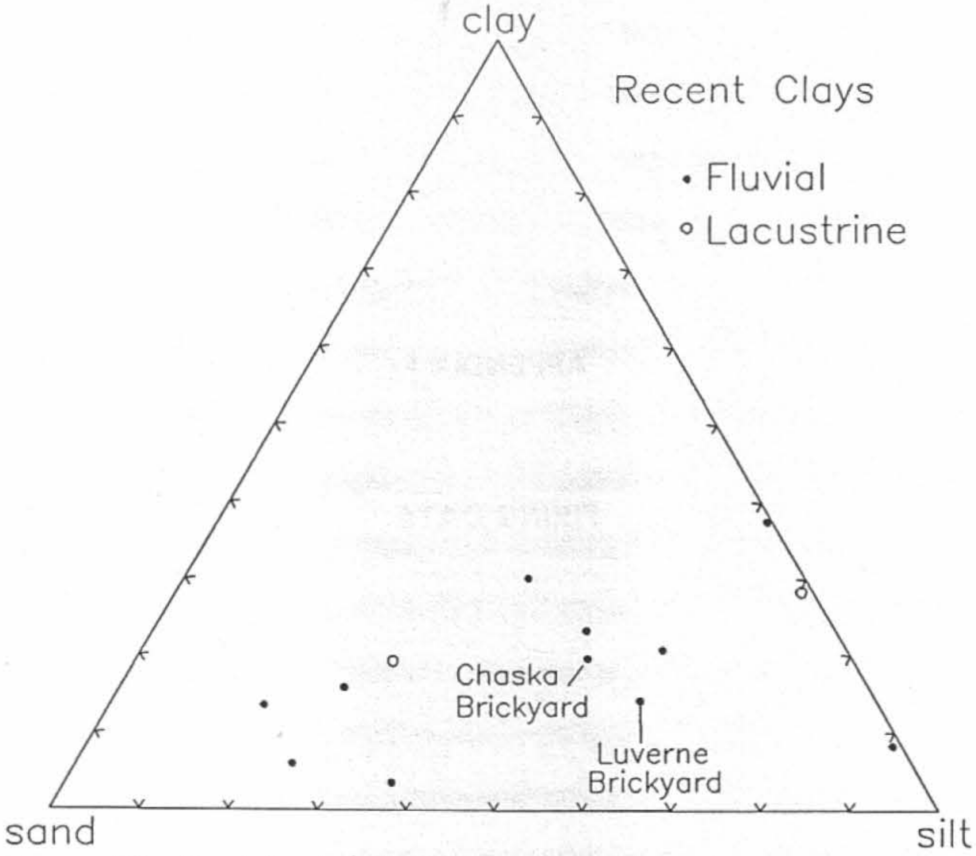


Figure 48. Particle size distribution of Recent clays.

APPENDIX F

FIRING DATA

Three 1.2 Mb, 5.25" floppy disks contain all firing test data (Appendix F; Disks 2, 3, and 4). The three disks are organized as follows:

1) PLEISTOCENE FIRING DATA:
   - GLACLAKE subdirectory (for glacial lake clay samples)
   - GLACTILL subdirectory (for glacial till samples)
   - LOESS subdirectory (for loess samples)
   - RECENT subdirectory (for recent lake and fluvial samples)

2) RESIDUAL, SECONDARY and PRECAMBRIAN DATA:
   - PRIMARY subdirectory (for primary/residual samples)
   - SECONDAR subdirectory (for secondary kaolinitic samples)
   - PRECAMB subdirectory (for Precambrian samples)

3) CRETACEOUS and PALEOZOIC DATA:
   - CRETAC subdirectory (for all Cretaceous samples)
   - PALEO subdirectory (contains the following subdirectories:)
     - DECORAH subdirectory (for Decorah samples)
     - GLENWOOD subdirectory (for Glenwood samples)
     - STLAWRNC subdirectory (for St. Lawrence samples)

The firing data for each sample are stored in individual Lotus 123 worksheets. Most worksheets are approximately 14,000 bytes in size, although there are a few that are larger.

The data are organized as follows, with reference made to worksheet cell, row and column:

Basic Sample Data

E3 = Year of sample collection
F3 = Sample number
K3 = Dry Munsell color code
L3 = Dry Munsell color name
K4 = Percent water added (H_2O of plasticity)

Specific Firing Data

Columns B through U and rows 11 through 30 (range B11..U30) contain all data generated by the firing tests. The following data is contained in each column, starting at row 11:

COLUMN B: Sampling year
COLUMN C: Sample number
COLUMN D: Brick number
COLUMN E: Orton cone
COLUMN F: ** no data **
COLUMN G: Dry unfired weight of brick (grams)
COLUMN H: Dry linear measurement of brick (mm)
COLUMN I: Percent dry linear shrinkage (plastic to dried)
COLUMN J: Fired weight of brick (grams)
COLUMN K: Fired linear measurement of brick (mm)
COLUMN L: Percent fired linear shrinkage (dried to fired)
COLUMN M: Percent total linear shrinkage (plastic to fired)
COLUMN N: Fired Munsell color (code)
COLUMN O: Fired Munsell color (name)
COLUMN P: 24 hour soak weight (grams)
COLUMN Q: Percent 24 hour soak absorption
COLUMN R: 5 hour boil weight (grams)
COLUMN S: Percent 5 hour boil absorption
COLUMN T: Saturation coefficient
COLUMN U: Comments

NOTE: Portions of each worksheet contain macros and other information that are not directly related to the individual sample data; they are present only for operational purposes.

Five batches (13 firings per batch) of standard bricks were fired along with other bricks. The standard brick was made out of a commercial Kentucky-Tennessee Clay Company ball clay (KT-9; #1 SGP). The maximum and minimum percent shrinkage and absorption (24 hr.) for the internal brick standard is illustrated in Figure 49.

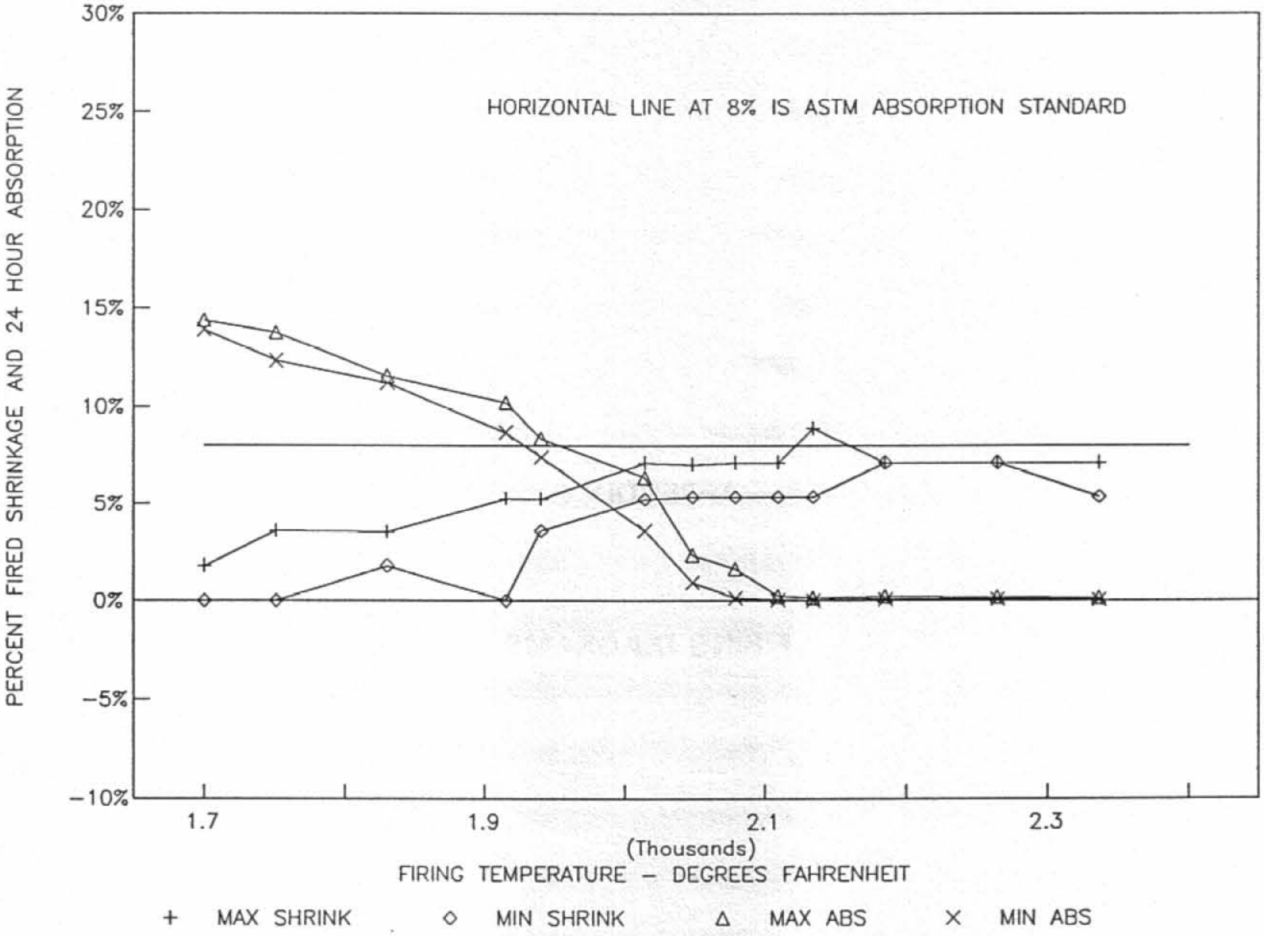


Figure 49. Maximum and minimum percent shrinkage (fired) and absorption (24 hr.) for the internal standard brick.

APPENDIX G

FIRING DIAGRAMS

Firing data for the various types of clays are on Disks 2, 3, and 4, which constitute part of Appendix F. The shrinkage, absorption, and temperature data on these disks were converted to illustrate the changes of shrinkage and absorption of the clays with an increase in temperature. Shrinkage-absorption diagrams for each of the fired samples are provided by clay type in Appendices G-1 to G-6. The fired shrinkage on each diagram is represented by "open boxes". The total shrinkage at each temperature is shown by "pluses". The absorption at each temperature is illustrated using "open triangles".

Appendix G-1

Precambrian Clays

PRECAMBRIAN CLAYS

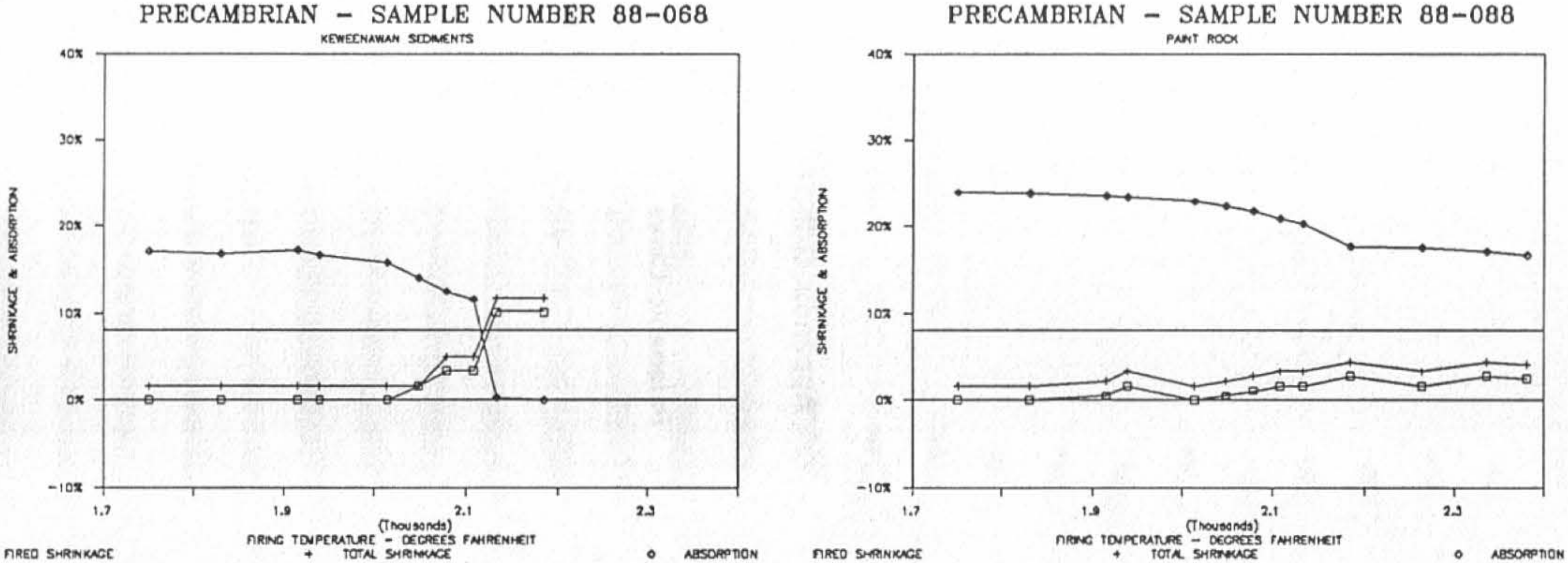
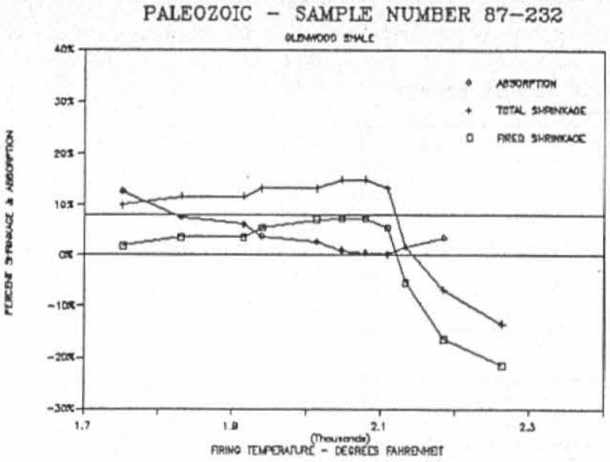
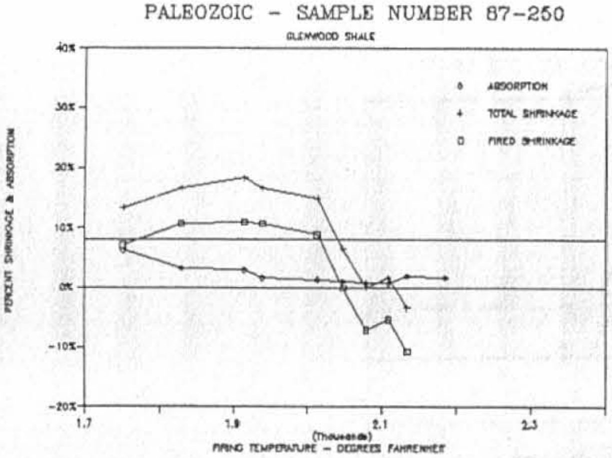


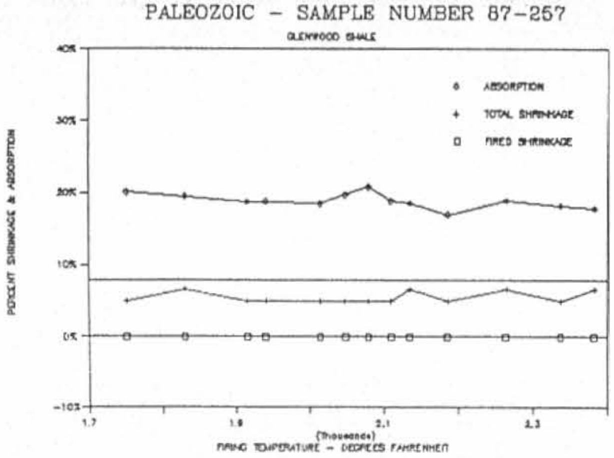
Figure 50. Firing diagrams of Precambrian clays.

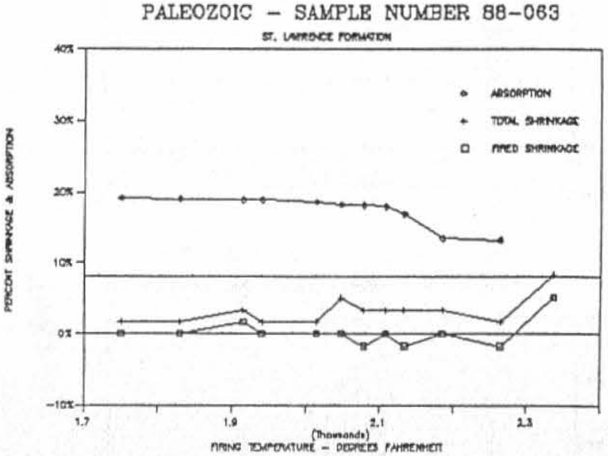
Appendix G-2

Paleozoic Clays









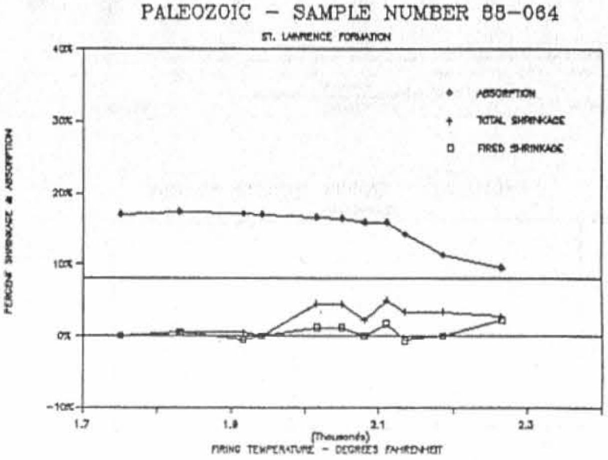
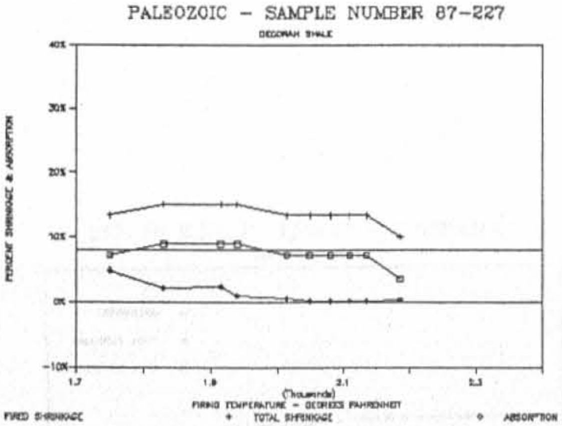
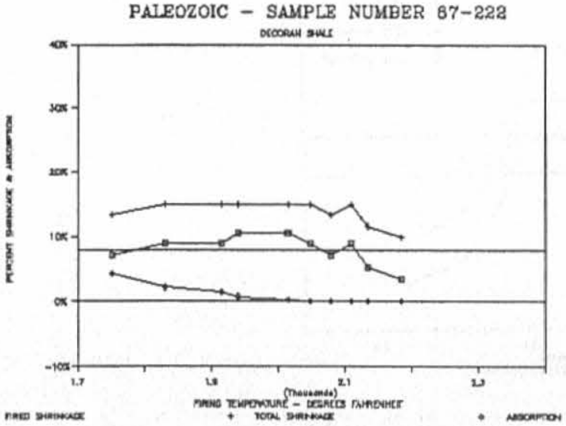
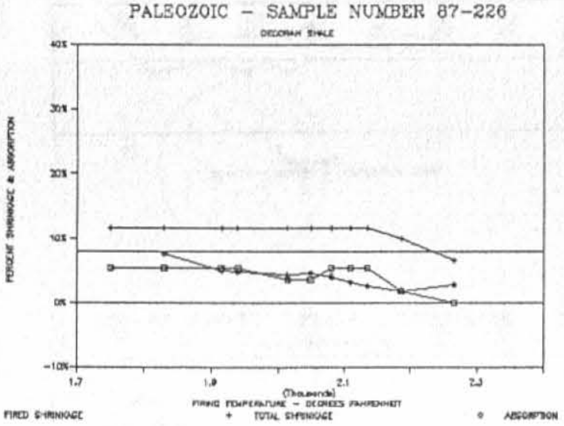


Figure 51. Firing diagrams of St. Lawrence and Glenwood Fms. clays.







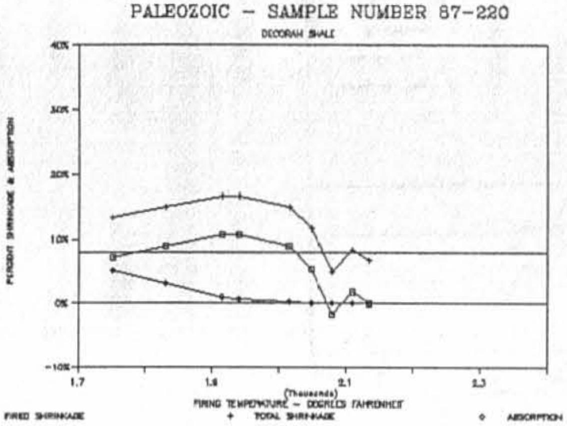
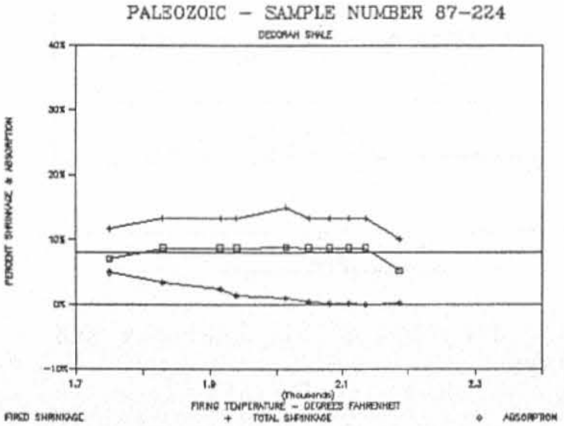
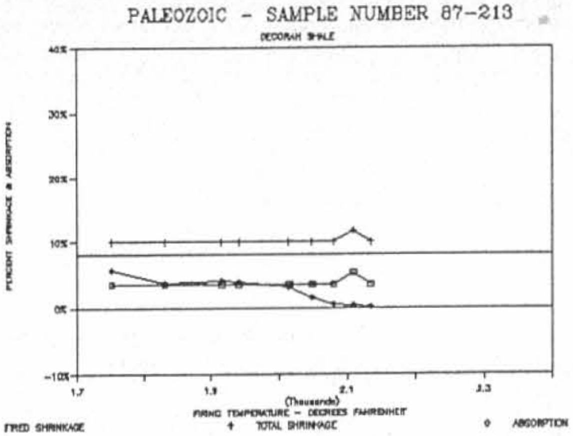
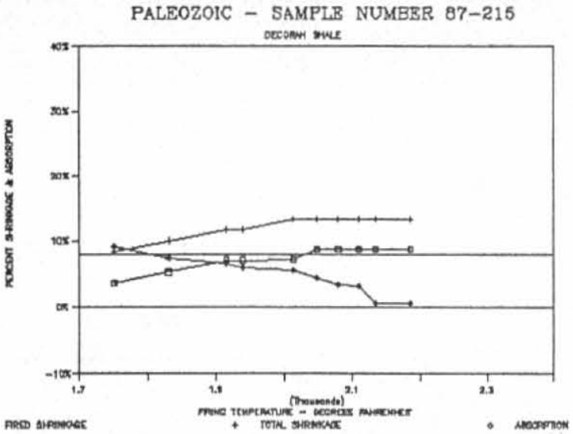


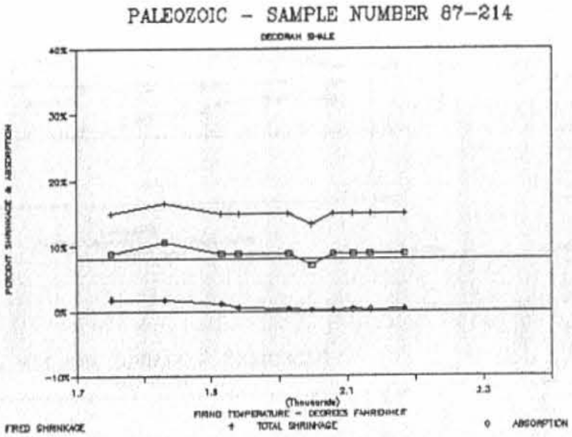
Figure 52. Firing diagrams of Decorah Shale clays from the Golden Hill outcrop.



BARR CLAY


PALEOZOIC - SAMPLE NUMBER 87-213


PALEOZOIC - SAMPLE NUMBER 87-215


PALEOZOIC - SAMPLE NUMBER 87-214

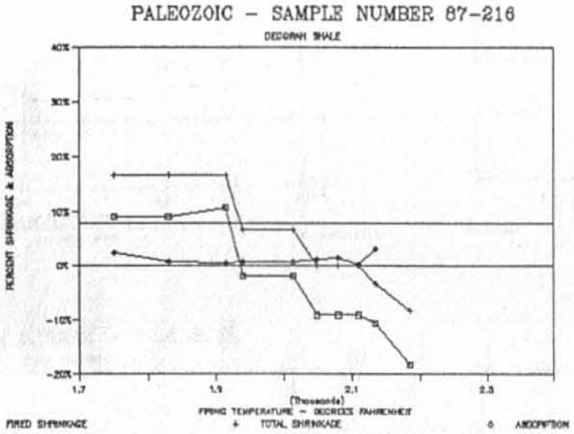
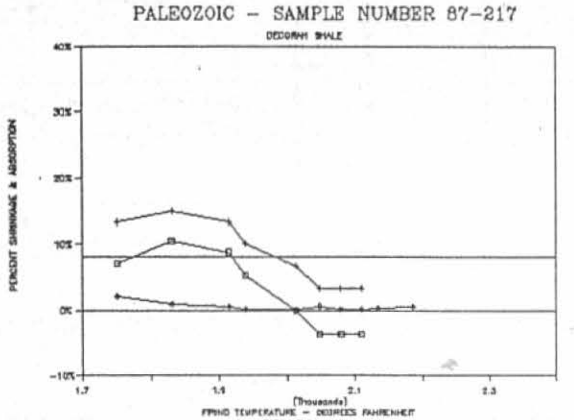

PALEOZOIC - SAMPLE NUMBER 87-216

Figure 53. Firing diagrams of Decorah Shale clays from the Barr Clay mine.


PALEOZOIC - SAMPLE NUMBER 87-217

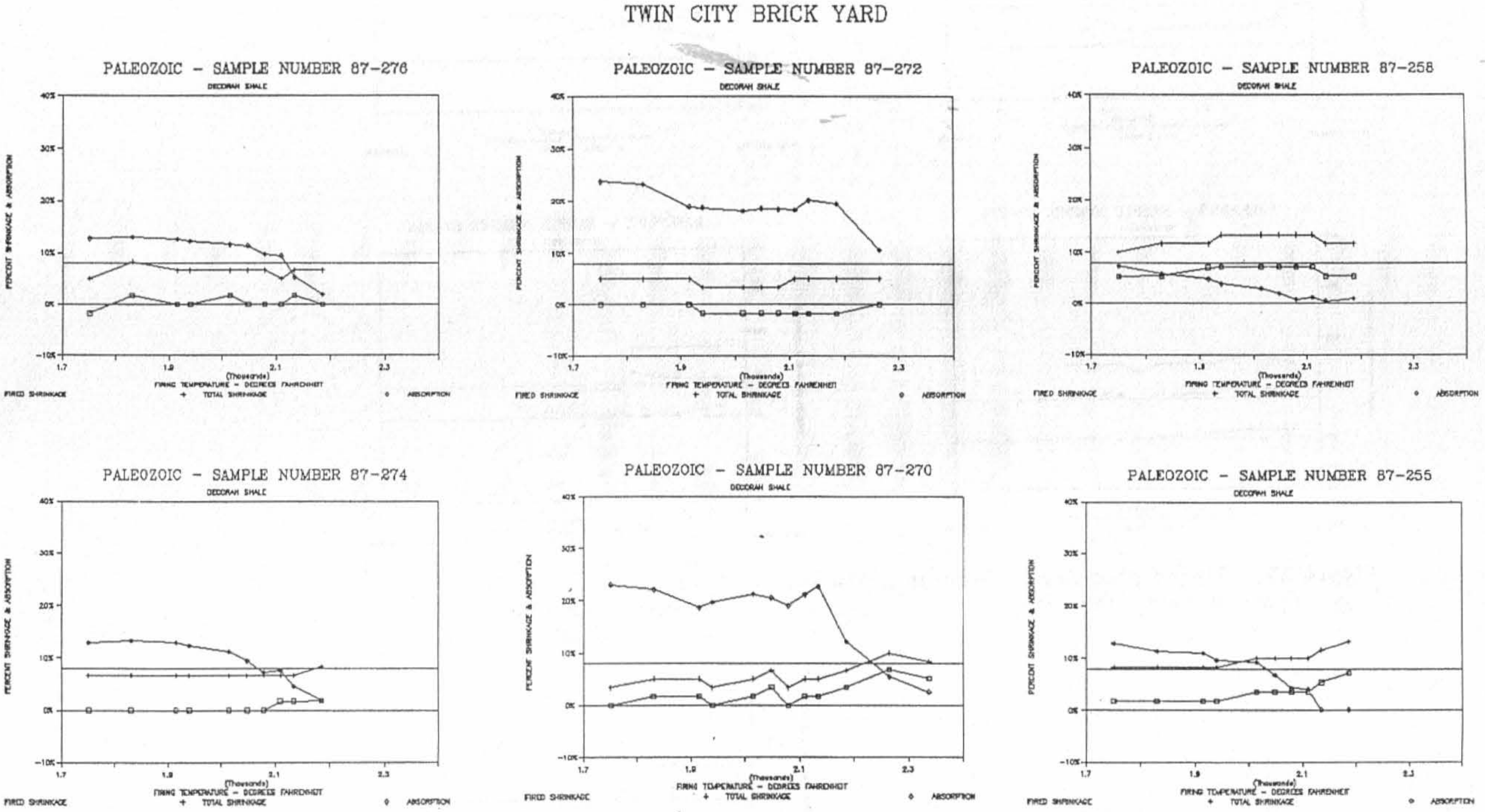


Figure 54. Firing diagrams of Decorah Shale clays from the Twin City brickyard.

Appendix G-3

Residual and Secondary Kaolinitic Clays

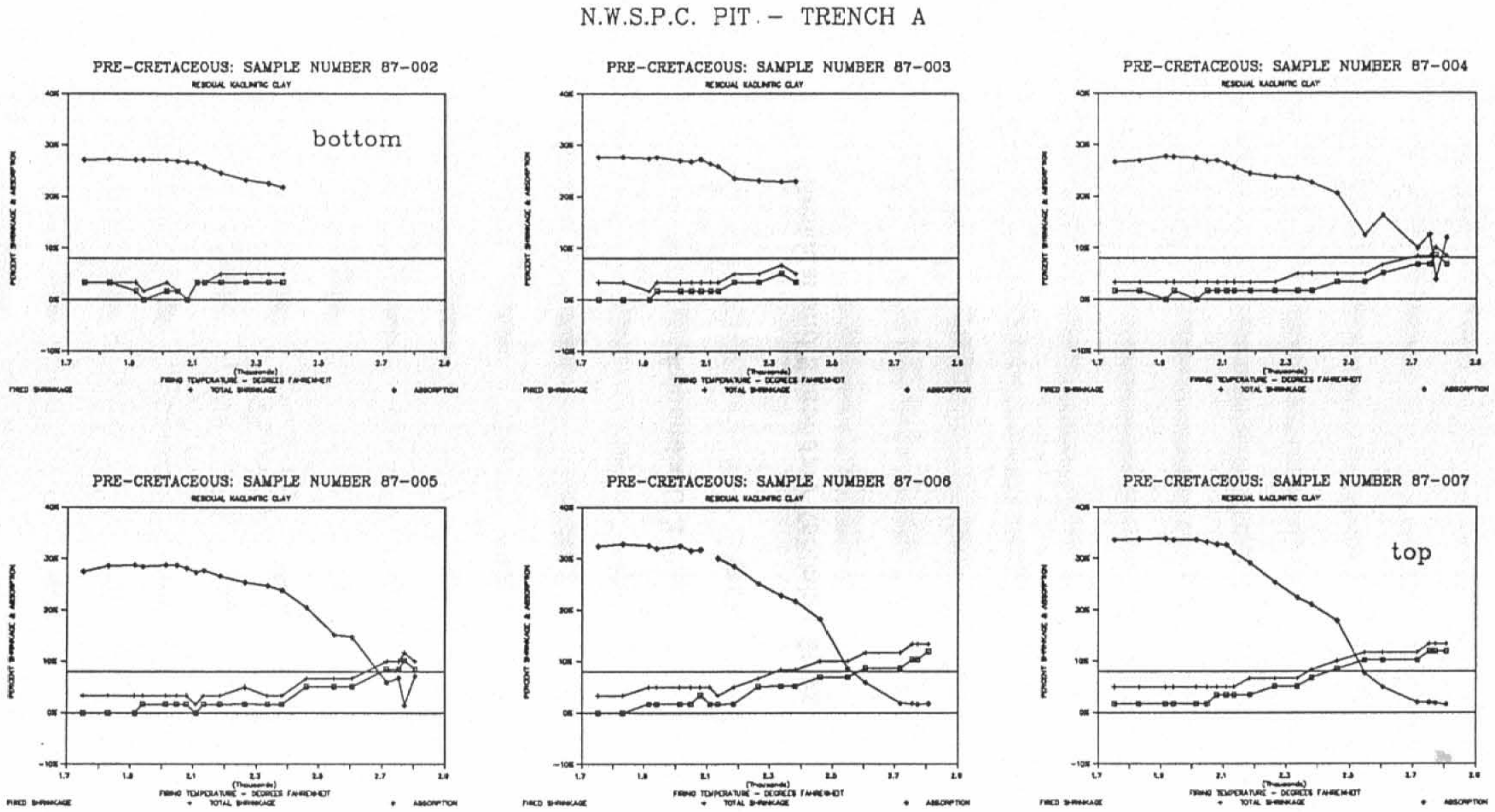


Figure 55. Firing diagrams of clays in Trench A of the NWSPC pit.

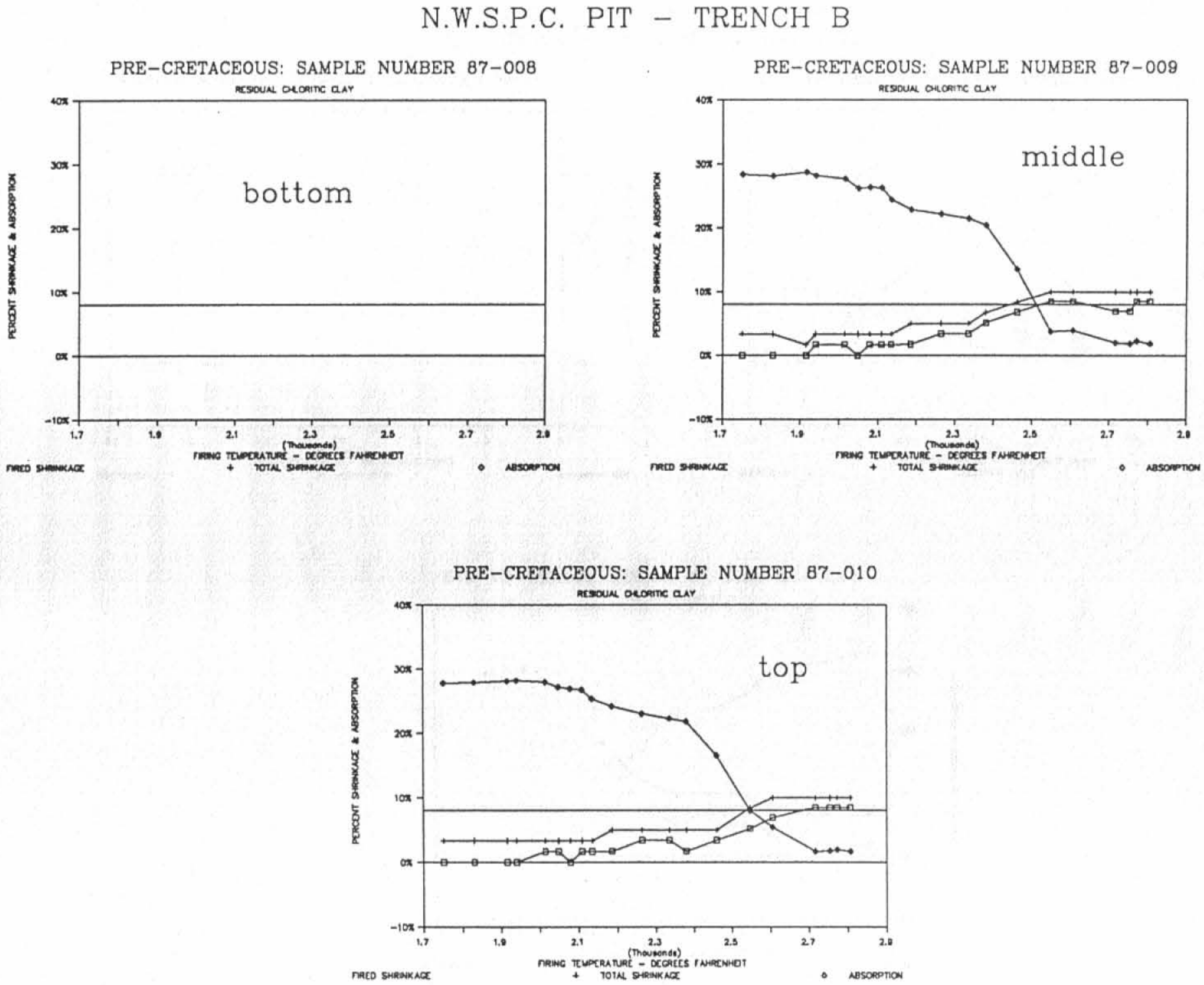


Figure 56. Firing diagrams of clays in Trench B of the NWSPC pit.

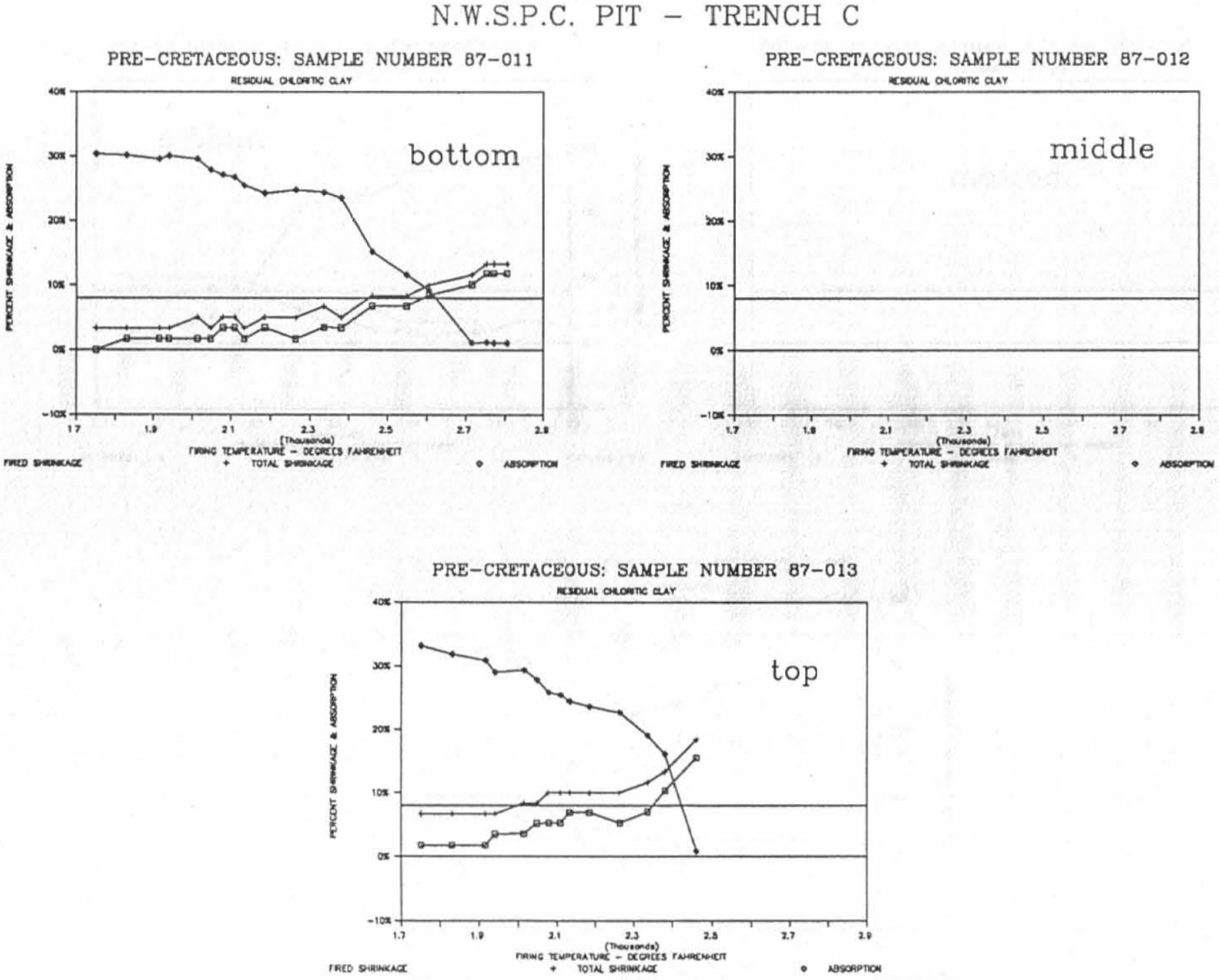
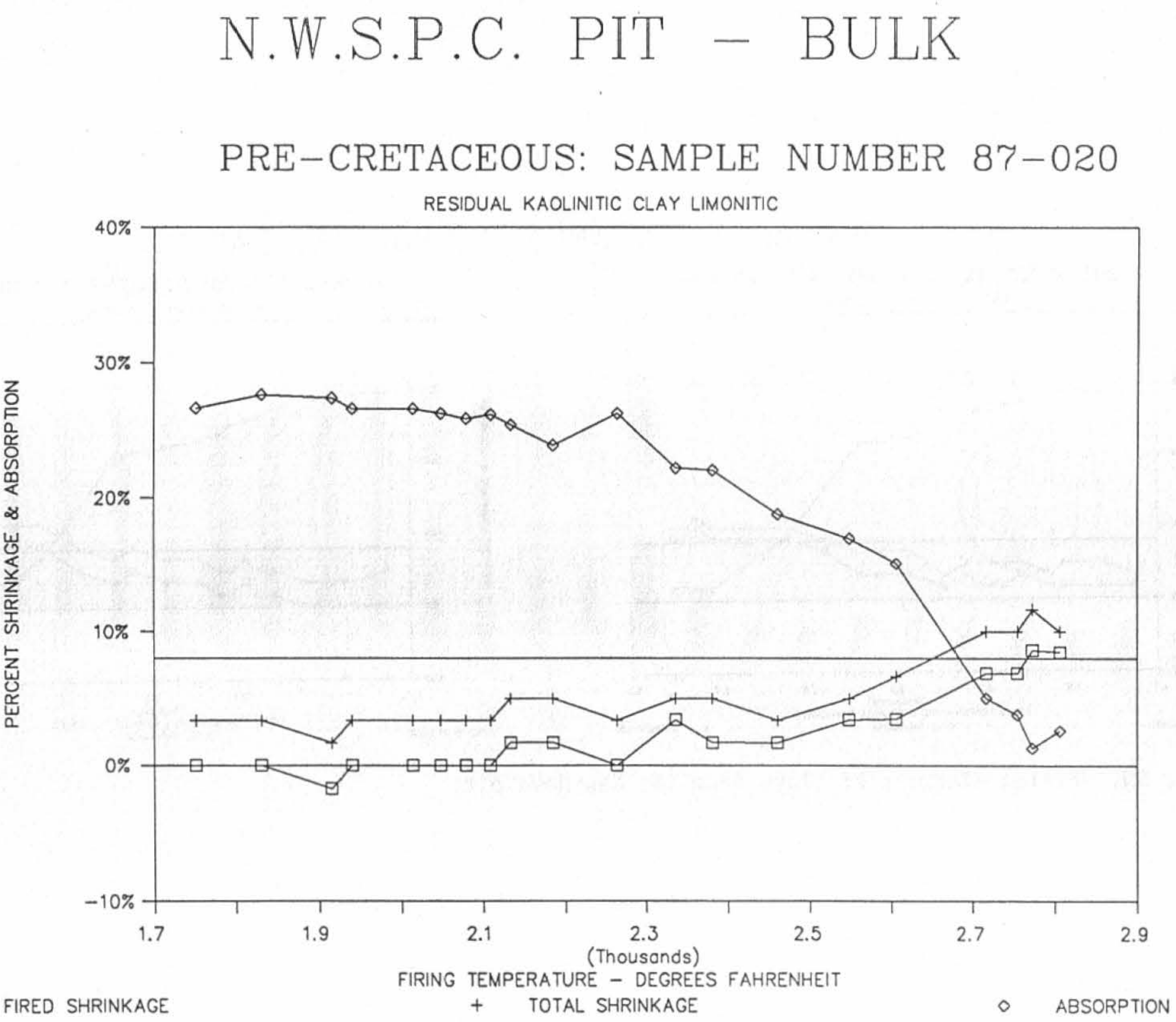


Figure 57. Firing diagrams of clays in Trench C of the NWSPC pit.

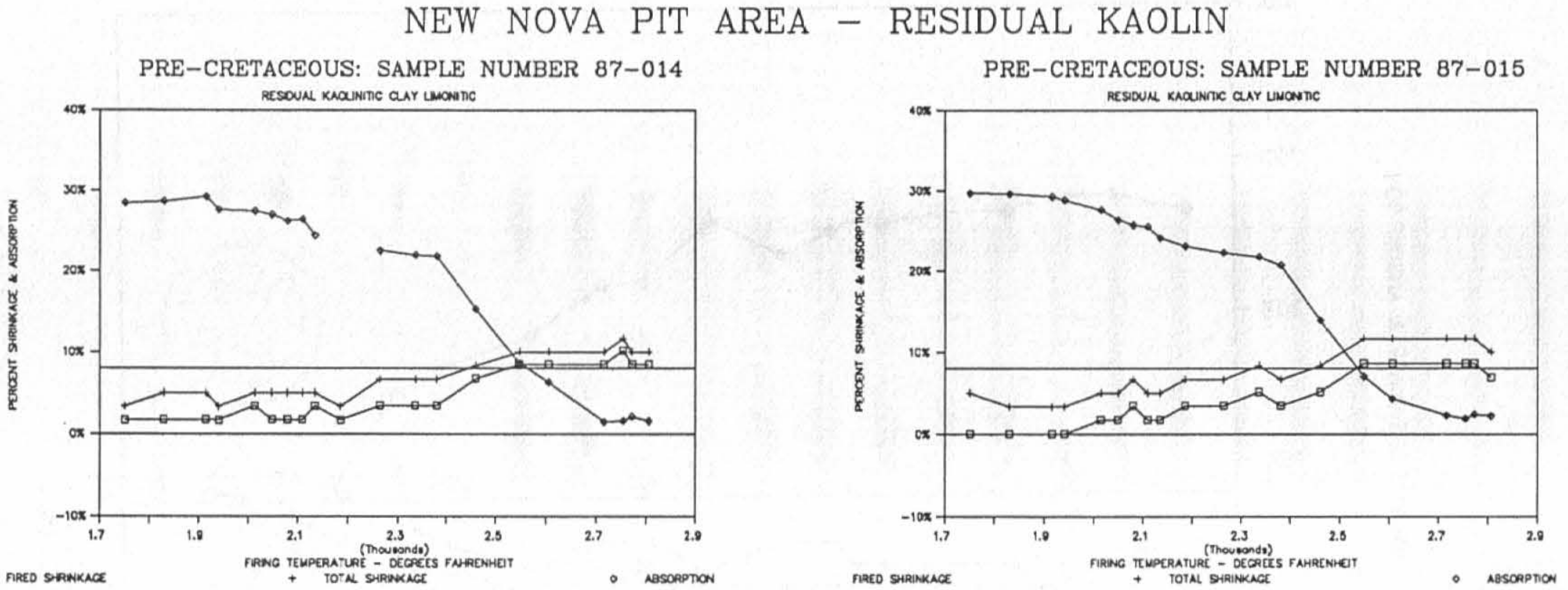


N.W.S.P.C. PIT - BULK

PRE-CRETACEOUS: SAMPLE NUMBER 87-020

RESIDUAL KAOLINITIC CLAY LIMONITIC

Figure 58. Firing diagram of a bulk clay sample from a stockpile in the NWSPC mine.



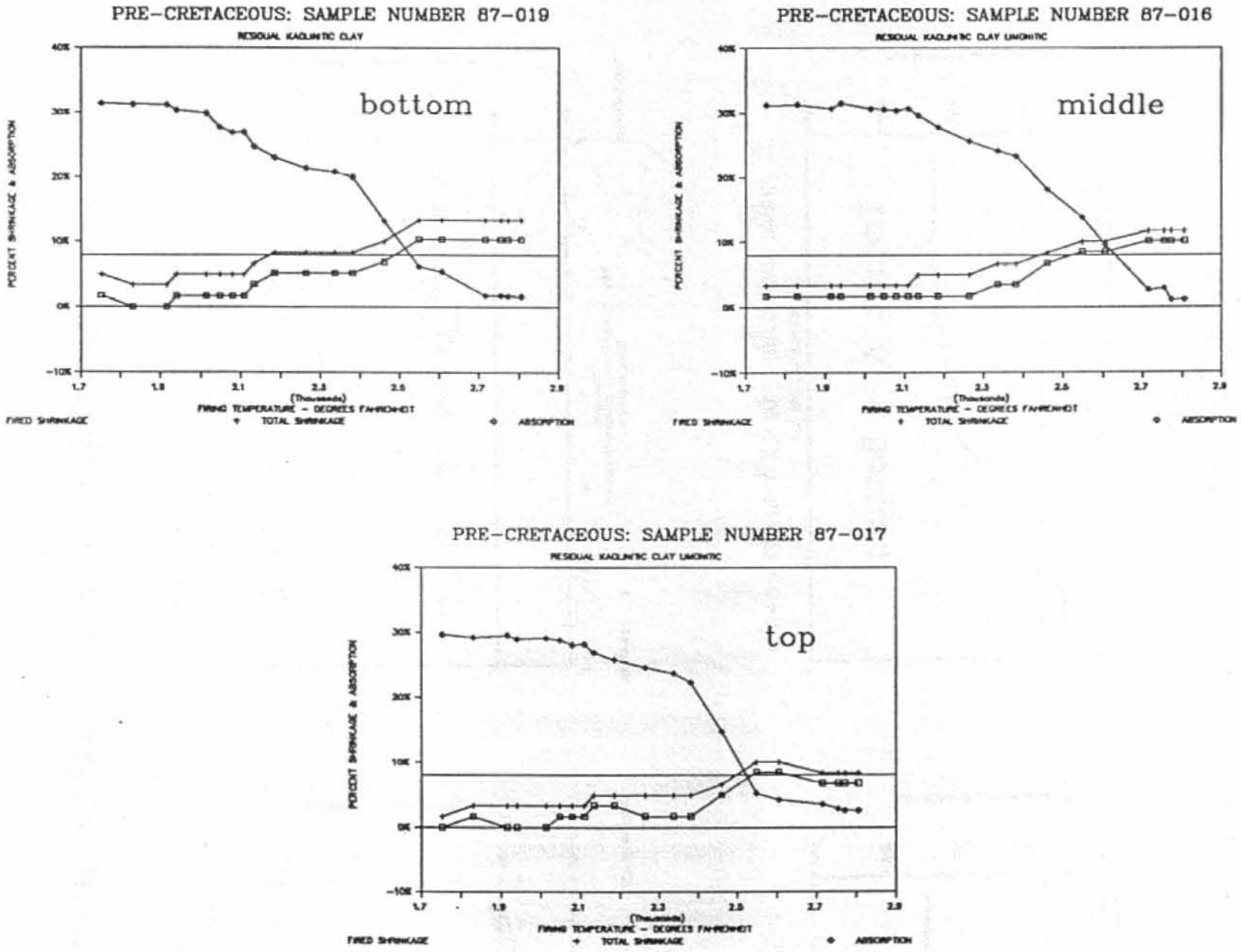
NEW NOVA PIT AREA – RESIDUAL KAOLIN

PRE-CRETACEOUS: SAMPLE NUMBER 87-014

PRE-CRETACEOUS: SAMPLE NUMBER 87-015

Figure 59. Firing diagrams of clays from the New Nova pit.

OLD NOVA PIT – TRENCH D



OLD NOVA PIT – TRENCH E

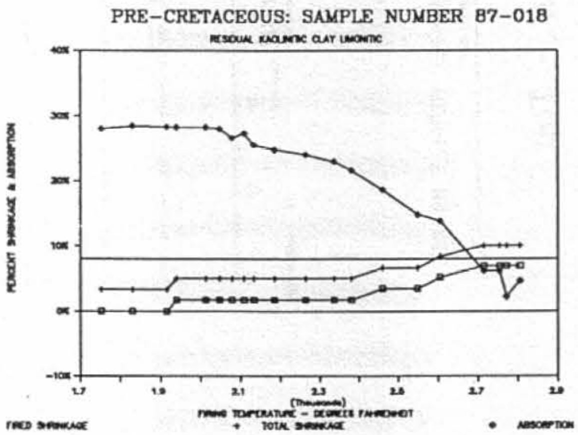
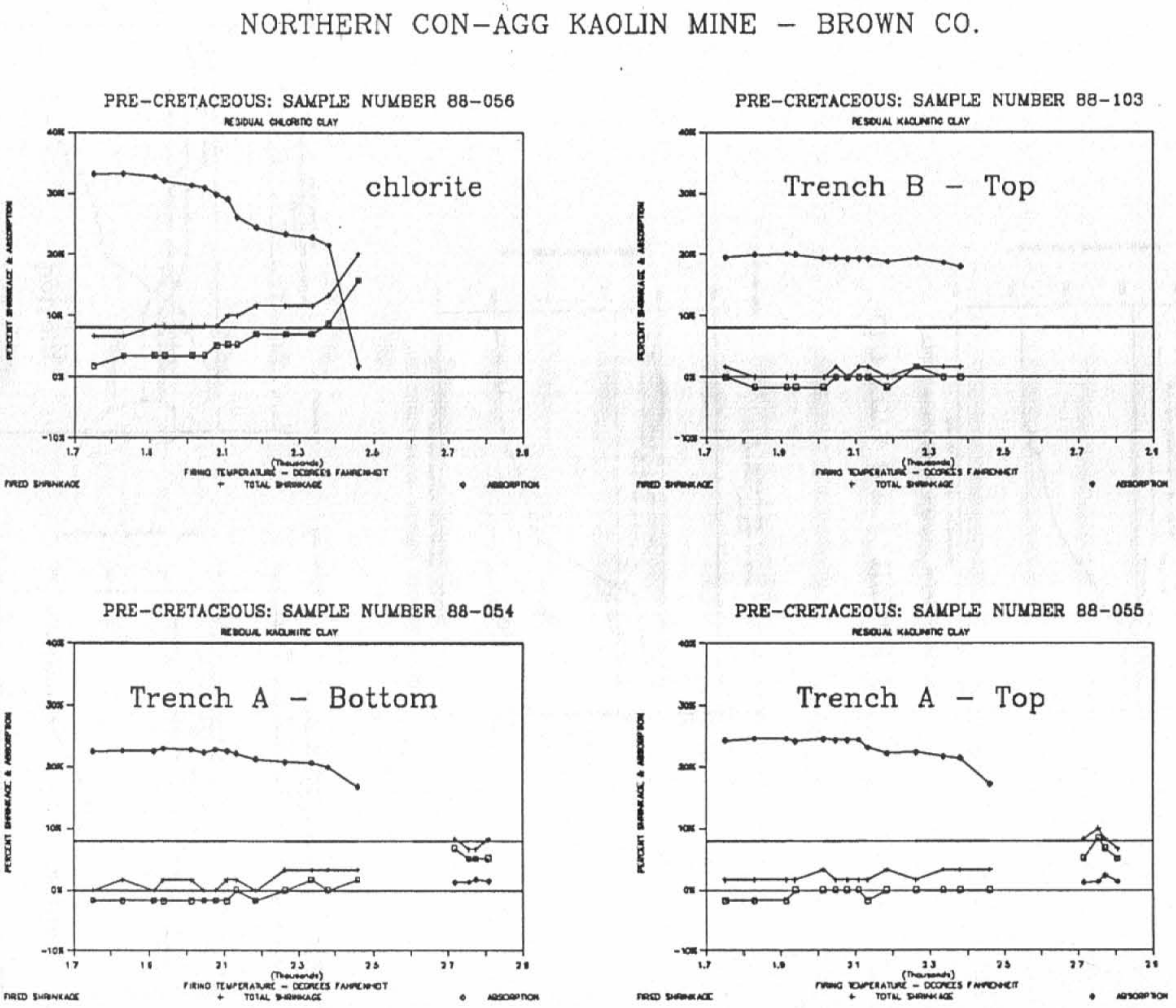


Figure 60. Firing diagrams of clays from Trench D in the New Nova pit.



NORTHERN CON-AGG KAOLIN MINE - BROWN CO.

PRE-CRETACEOUS: SAMPLE NUMBER 88-056

PRE-CRETACEOUS: SAMPLE NUMBER 88-103

PRE-CRETACEOUS: SAMPLE NUMBER 88-054

PRE-CRETACEOUS: SAMPLE NUMBER 88-055

Figure 61. Fining diagrams of clays from the Northern Con-Agg kaolin mine.

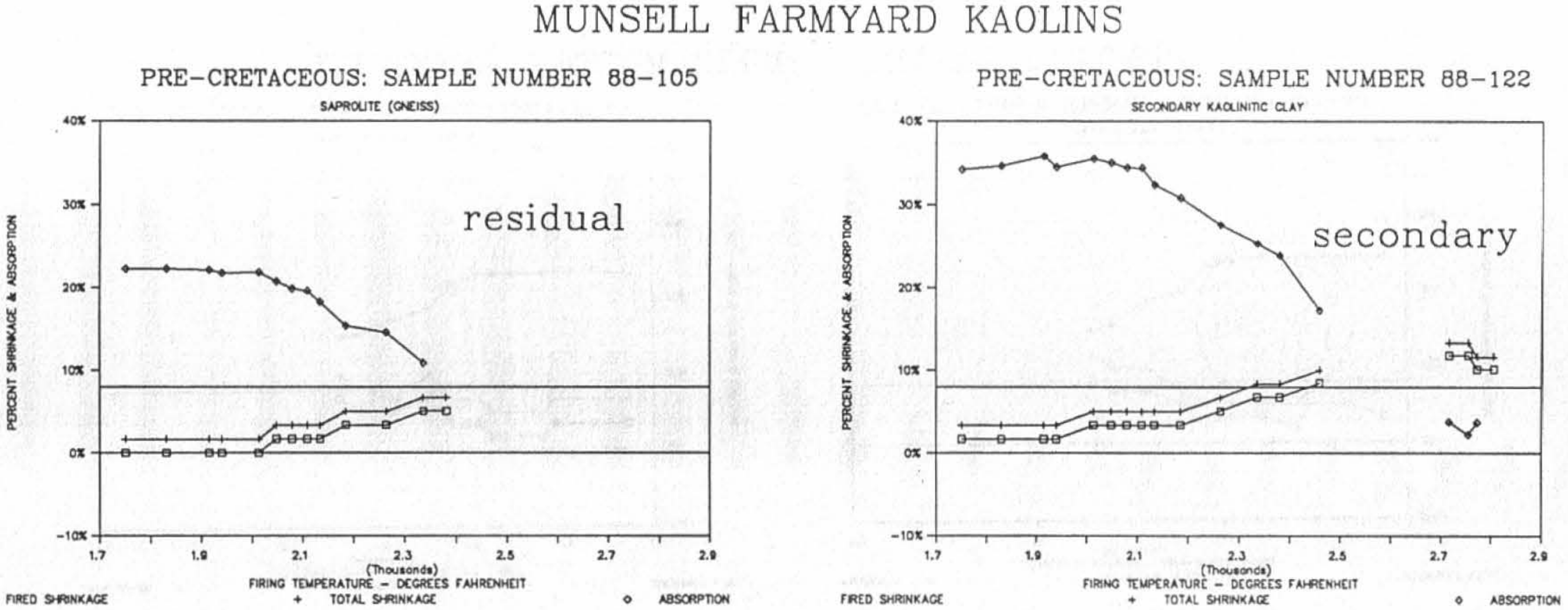


Figure 62. Firing diagrams of clays from the Munsell farmyard.

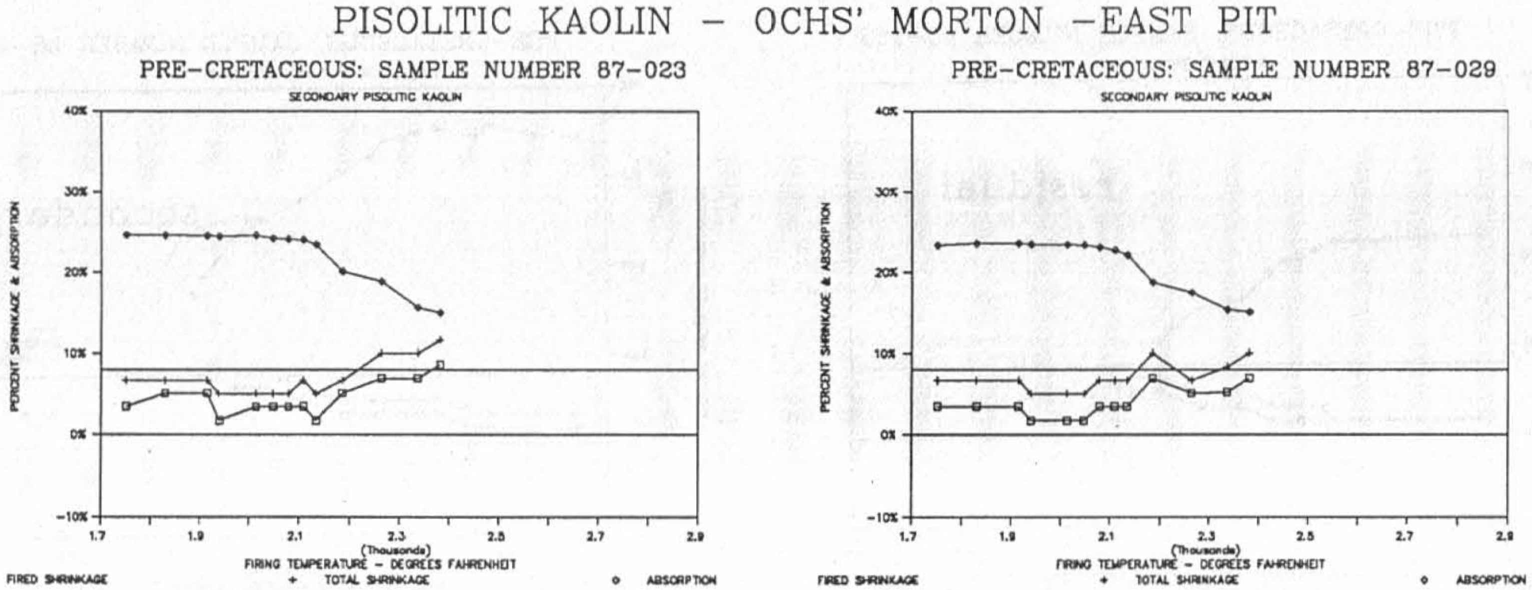


Figure 63. Firing diagram of pisolitic kaolins from the Ochs' Morton - East pit.

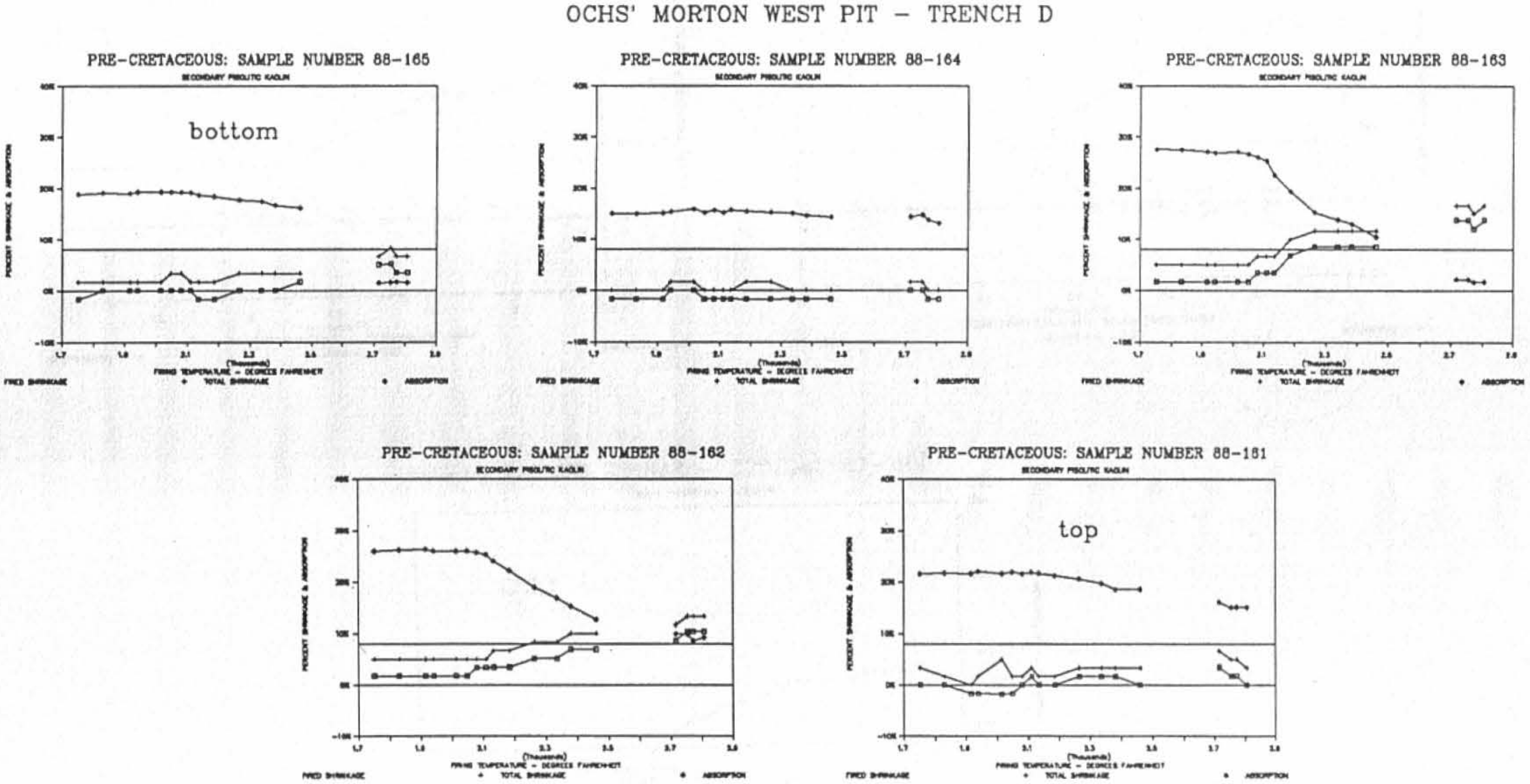


Figure 64. Firing diagram of clays from Trench D in the Ochs' Morton - West pit.

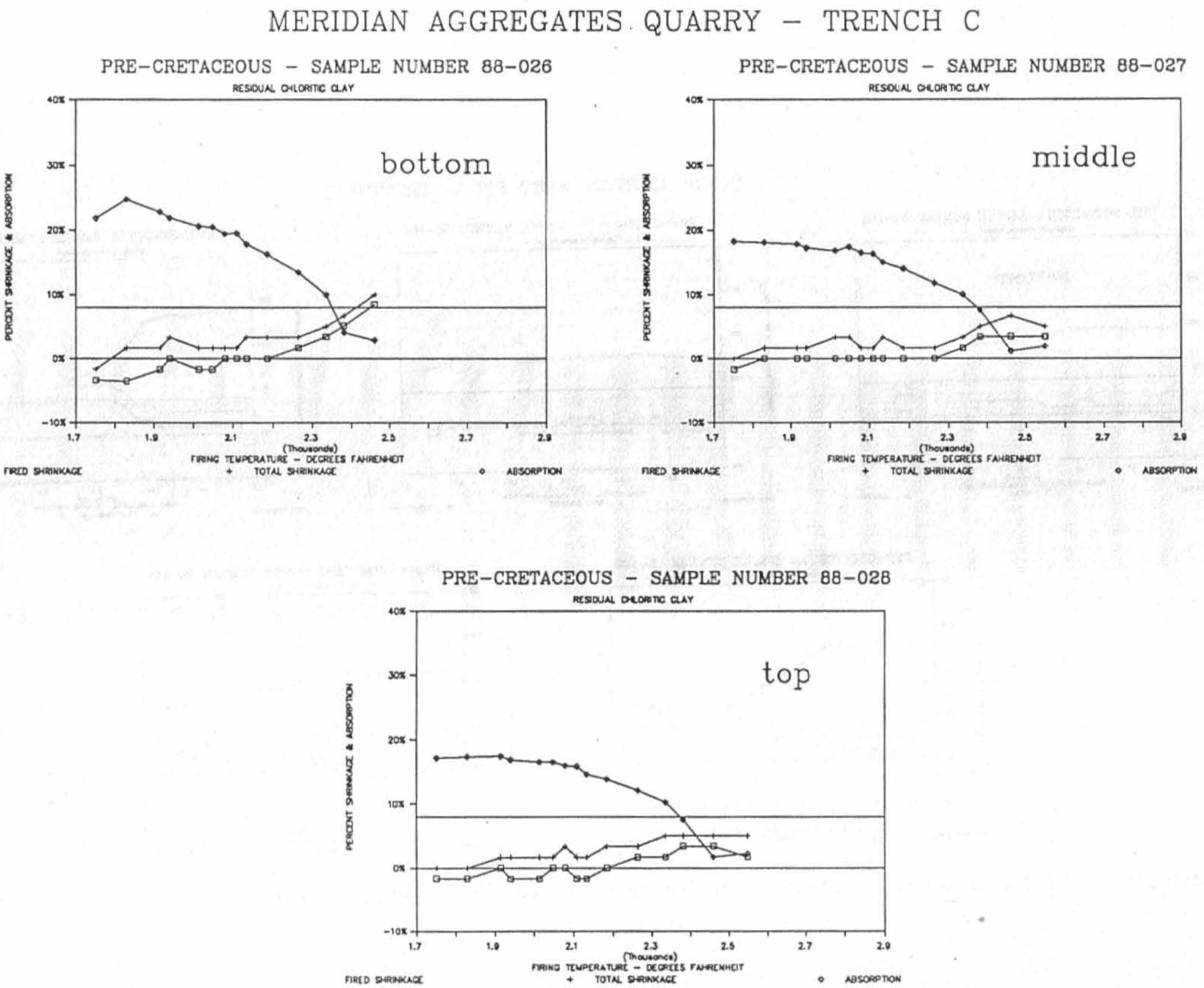
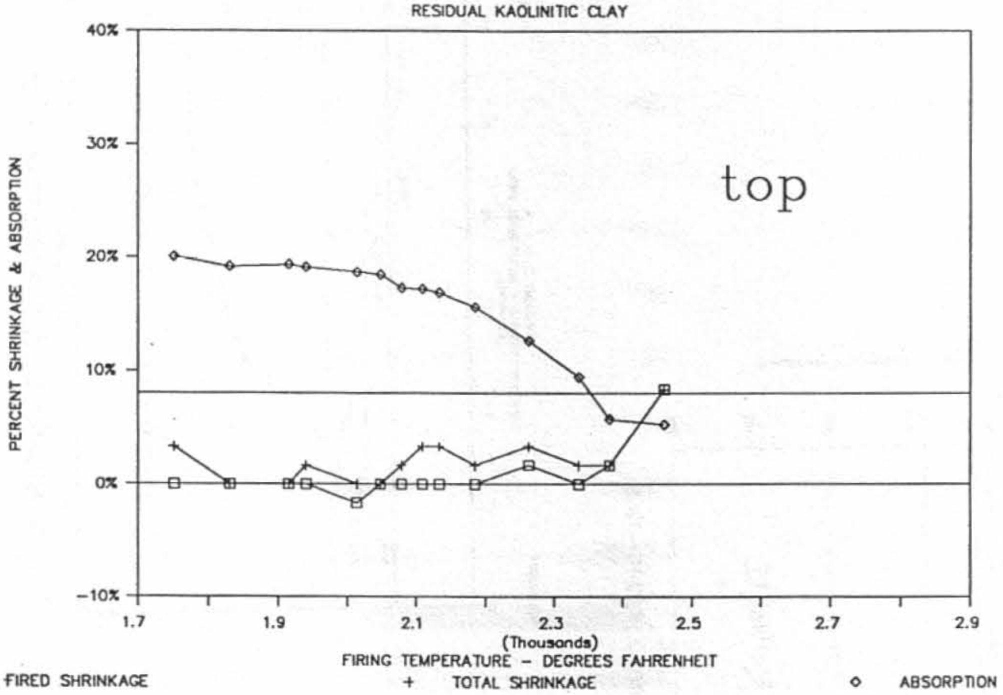


Figure 65. Firing diagram of clays from Trench C in the Meridian Aggregates quarry.

COLD SPRING QUARRY - TRENCH A

PRE-CRETACEOUS: SAMPLE NUMBER 88-037



PRE-CRETACEOUS: SAMPLE NUMBER 88-036

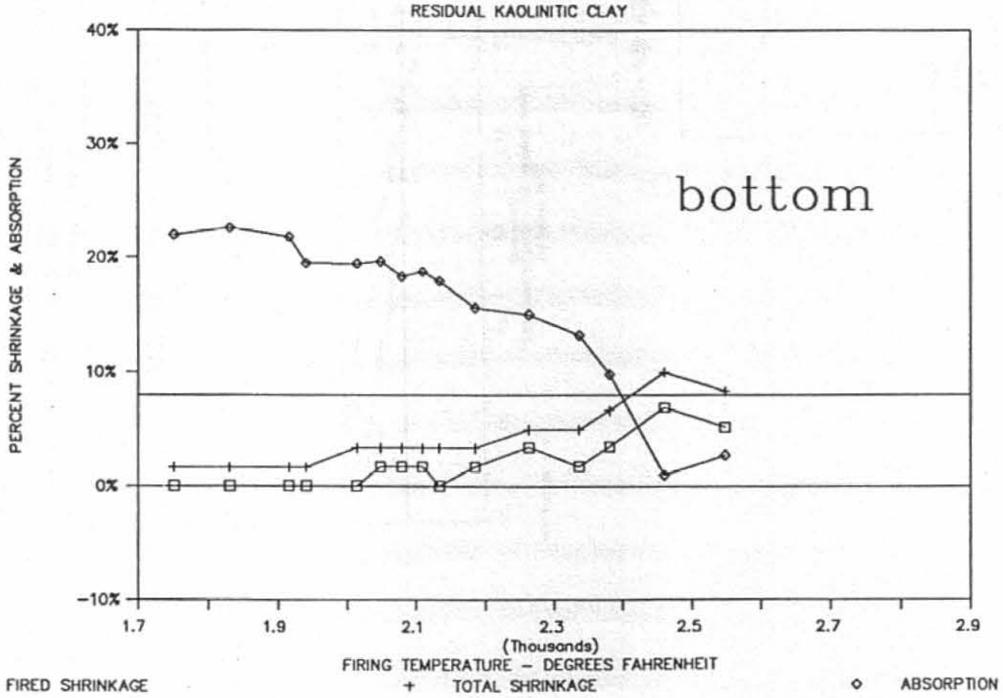
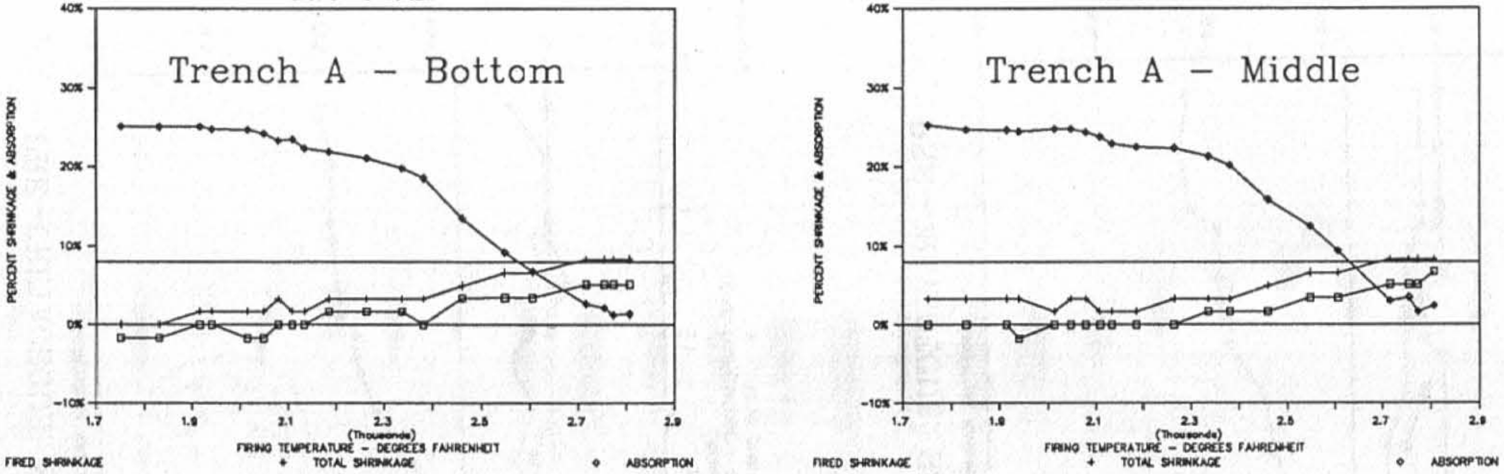


Figure 66. Firing diagram of clays in the Cold Spring quarry.

MORRISON CO. – RESIDUAL KAOLIN

PRE-CRETACEOUS: SAMPLE NUMBER 88-040

PRE-CRETACEOUS: SAMPLE NUMBER 88-039



PRE-CRETACEOUS: SAMPLE NUMBER 88-038

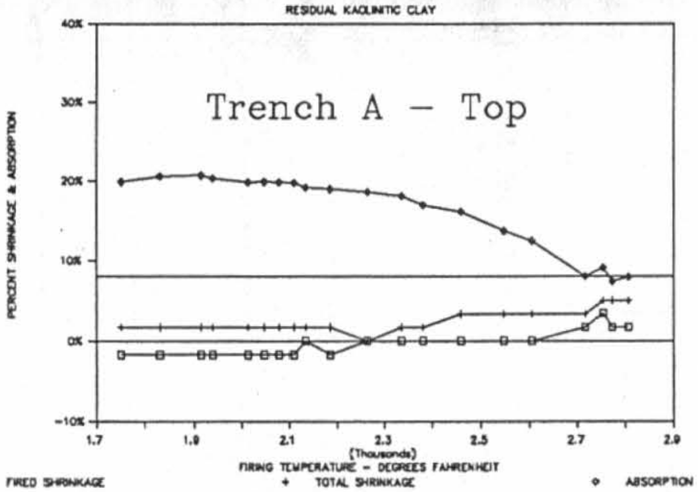


Figure 67. Firing diagrams of clays from Morrison County.

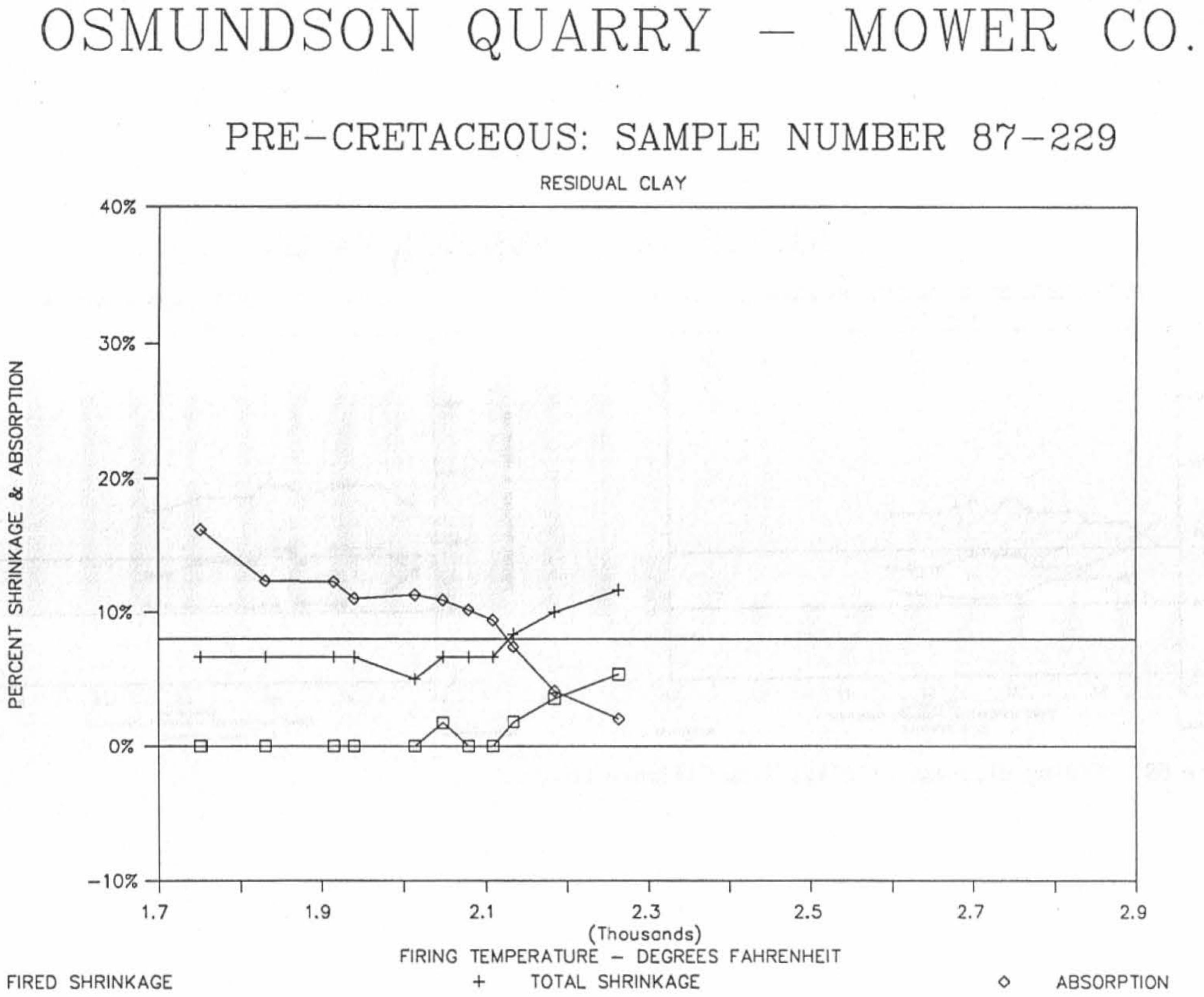
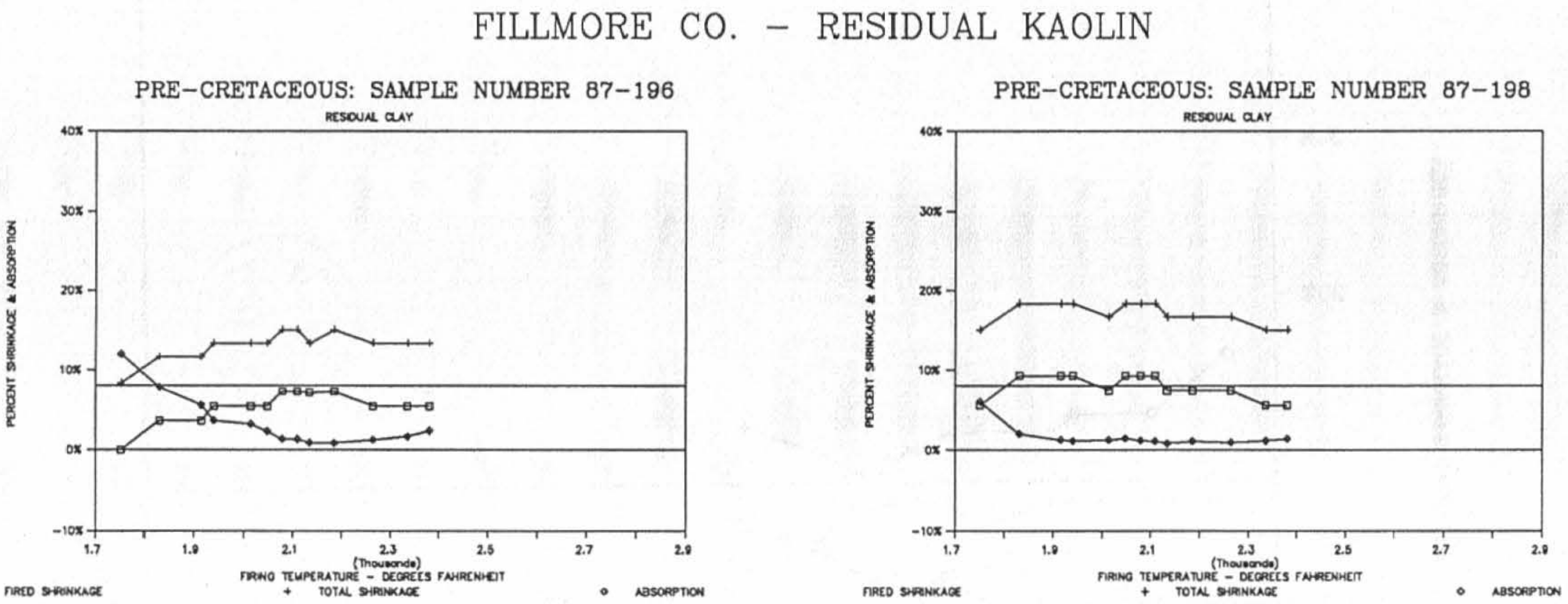


Figure 68. Firing diagram of clay from the Osmundson quarry, Mower County.



FILLMORE CO. - RESIDUAL KAOLIN

PRE-CRETACEOUS: SAMPLE NUMBER 87-196

PRE-CRETACEOUS: SAMPLE NUMBER 87-198

Figure 69. Firing diagrams of clays from Fillmore County.

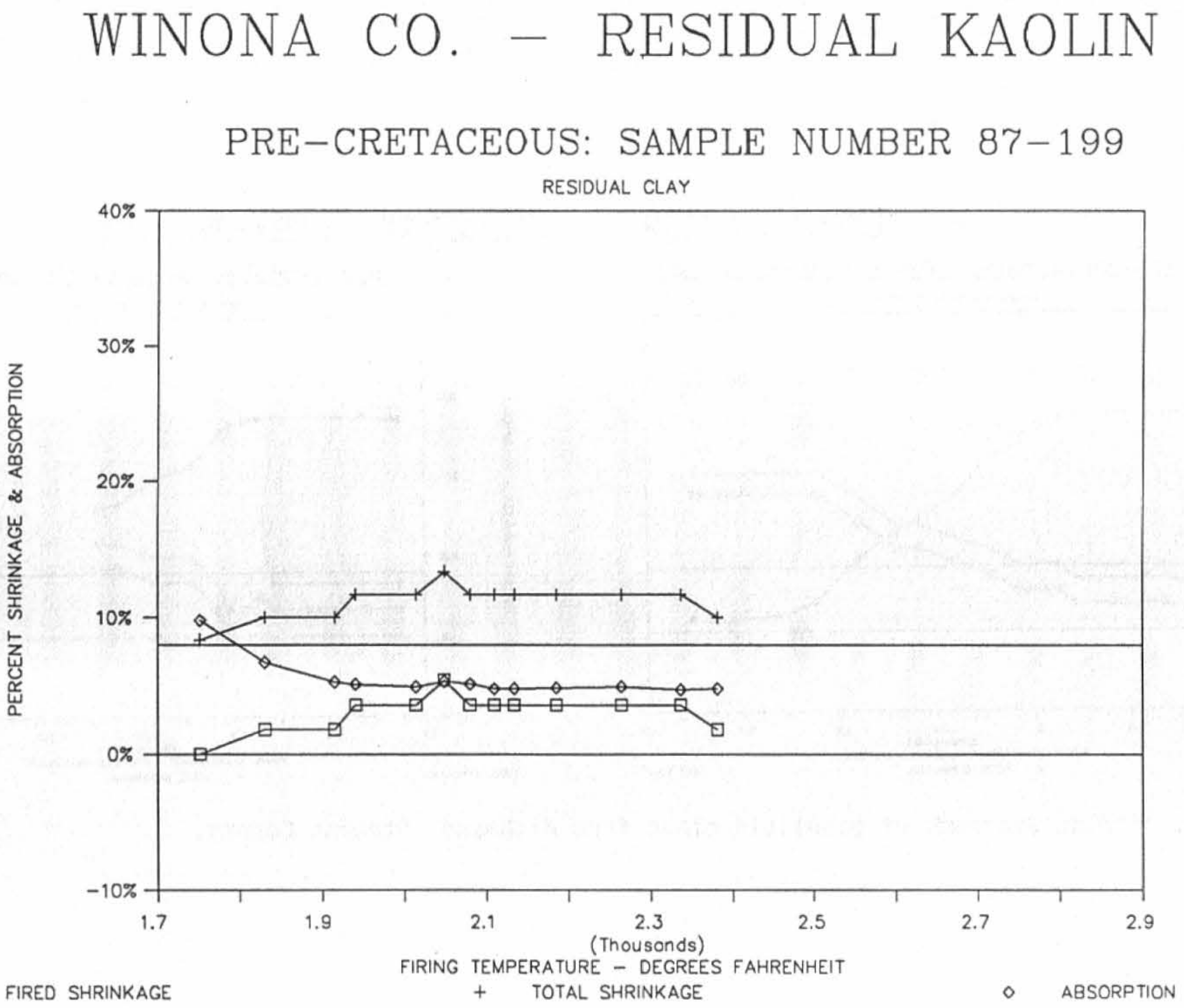
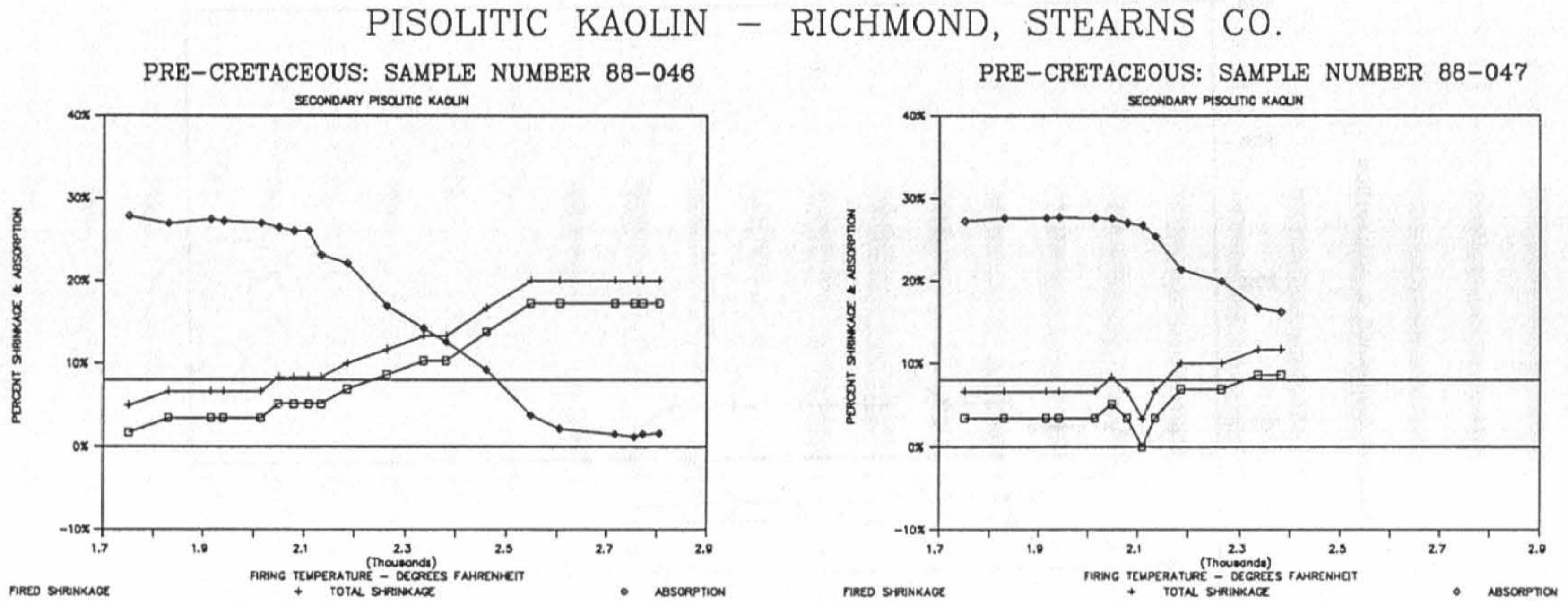


Figure 70. Firing diagrams of clays from Winona County.


PISOLITIC KAOLIN – RICHMOND, STEARNS CO.

PRE-CRETACEOUS: SAMPLE NUMBER 88-046

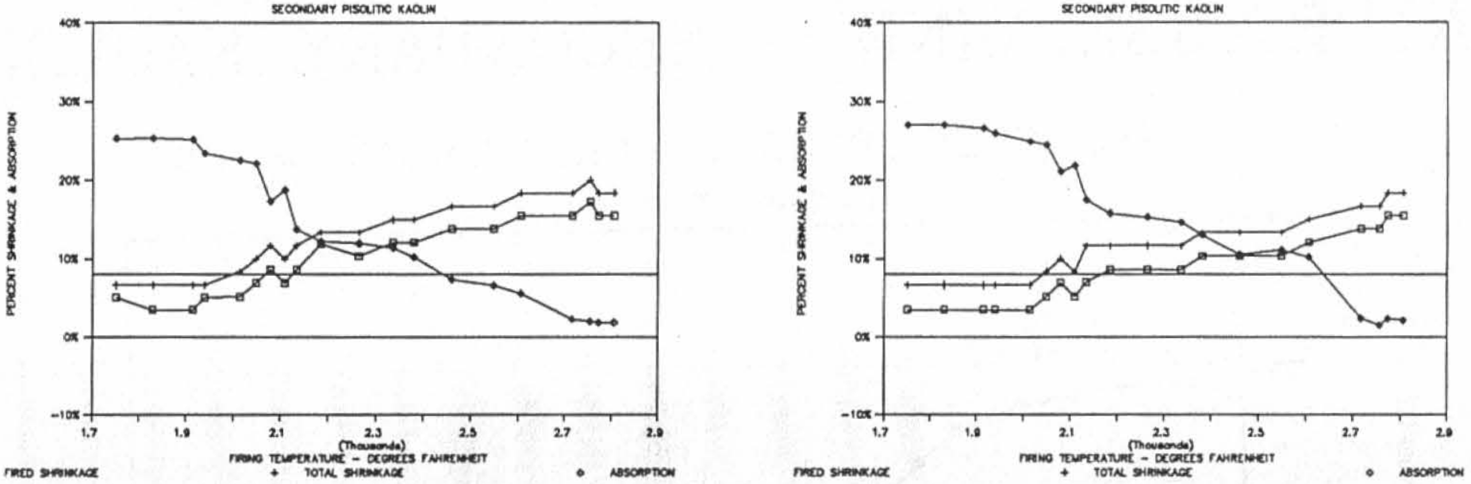
PRE-CRETACEOUS: SAMPLE NUMBER 88-047

Figure 71. Firing diagrams of pisolitic clays from Richmond, Stearns County.

PISOLITIC KAOLIN OUTCROPS - RENVILLE CO.

PRE-CRETACEOUS: SAMPLE NUMBER 88-125

PRE-CRETACEOUS: SAMPLE NUMBER 88-126



PRE-CRETACEOUS: SAMPLE NUMBER 88-127

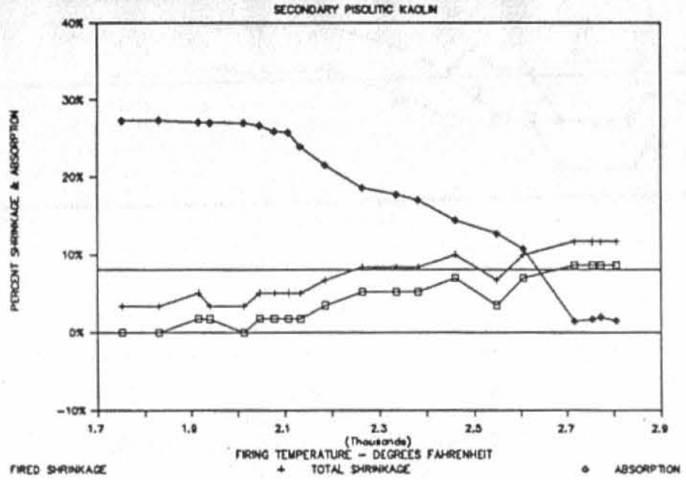


Figure 72. Firing diagrams of pisolitic clays from Renville County.

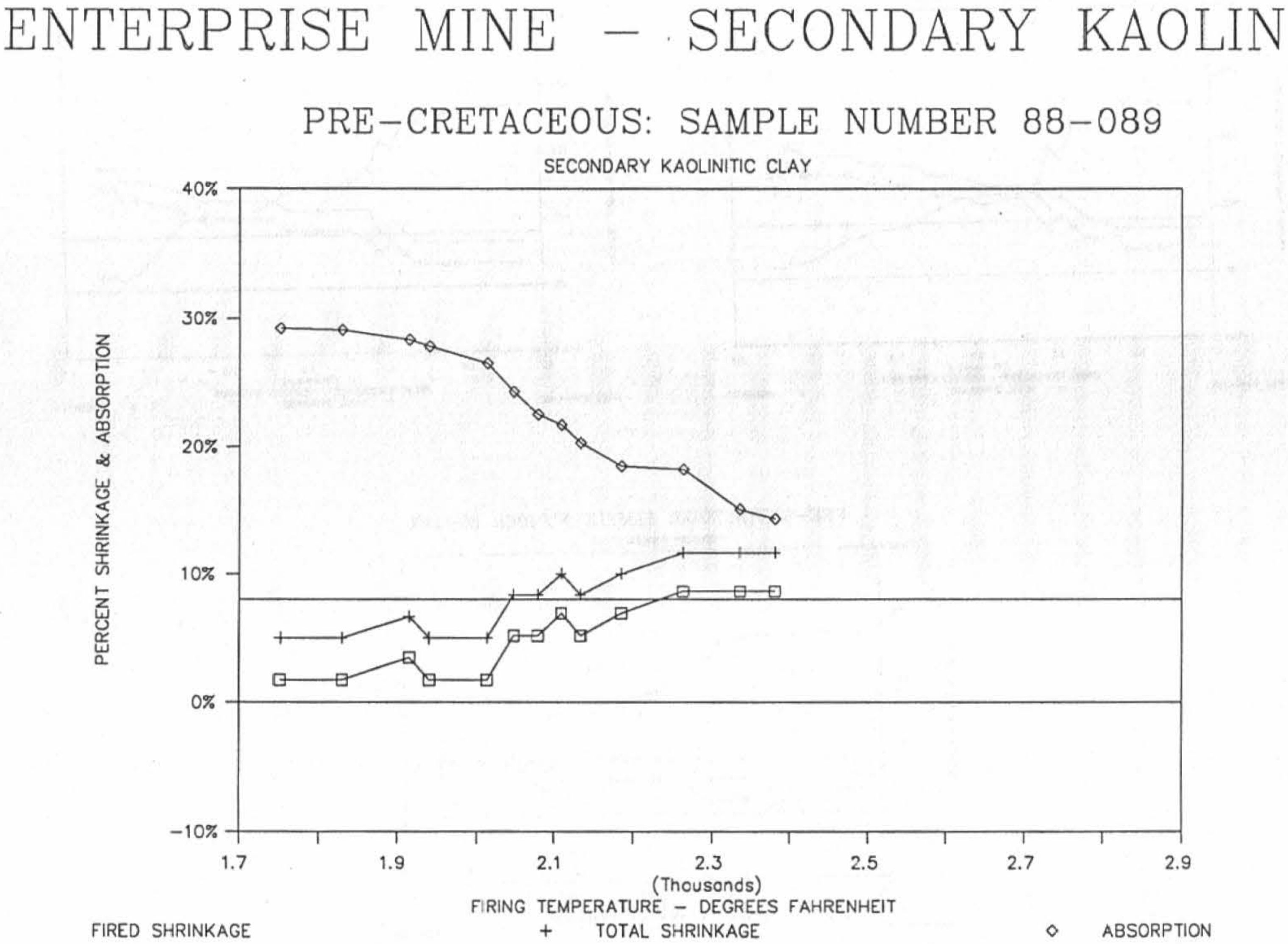


Figure 73. Firing diagrams of secondary clay from the Enterprise mine.

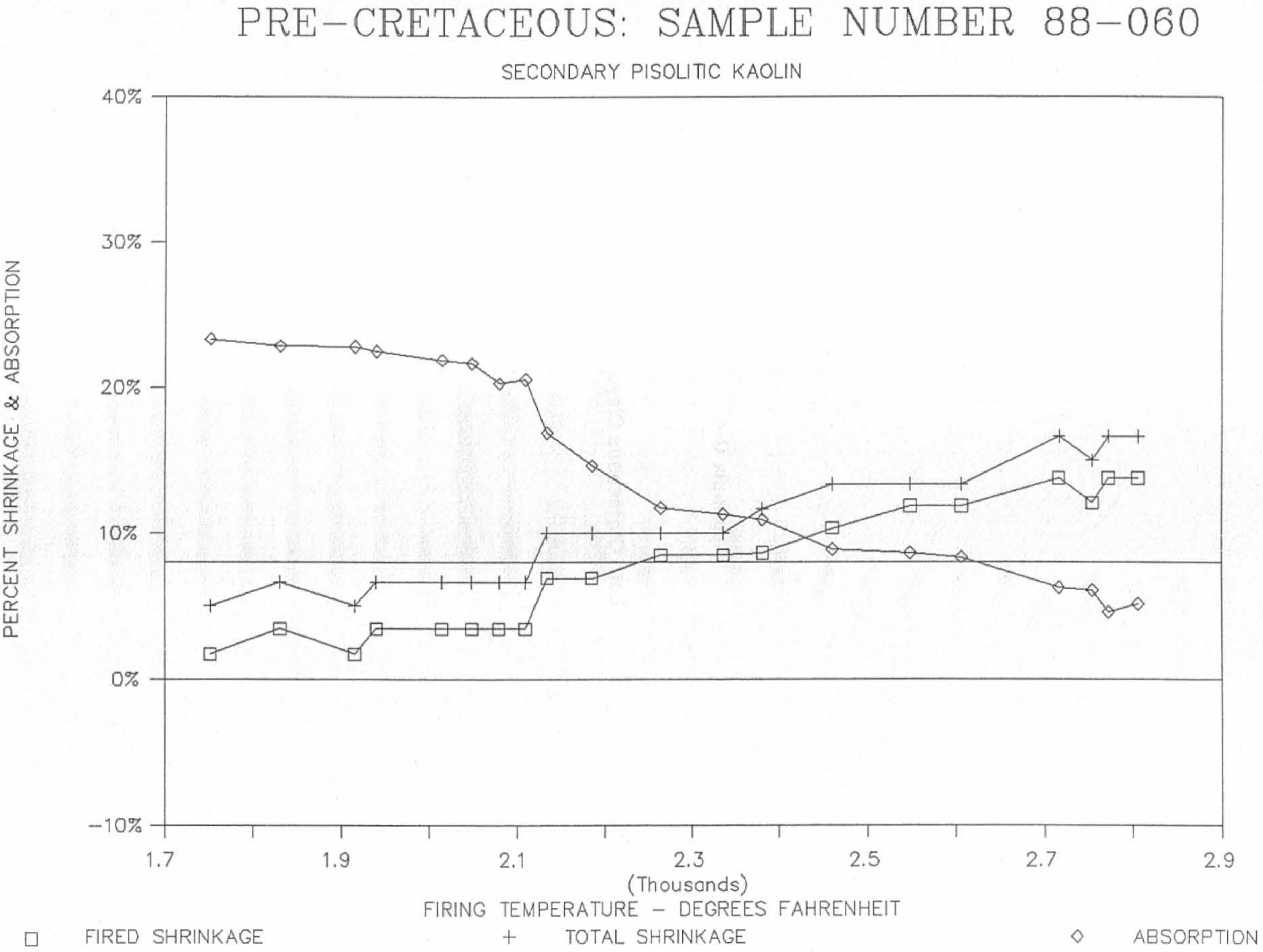
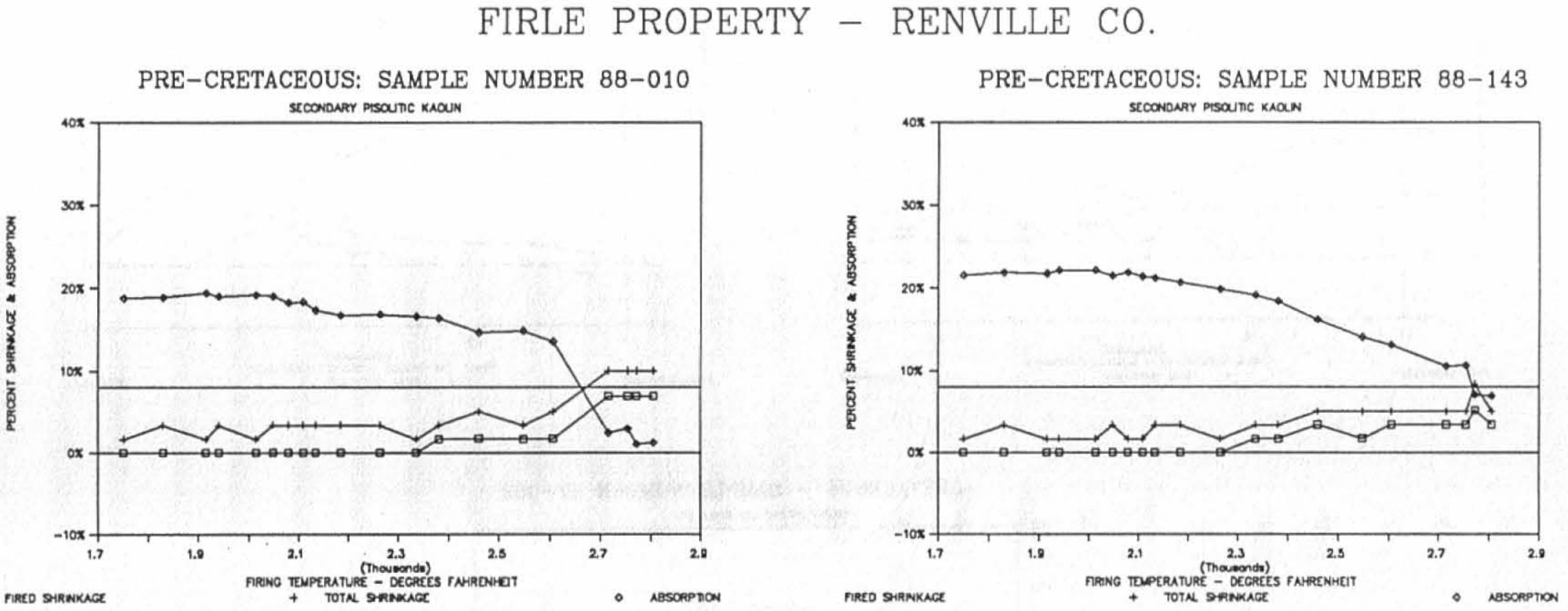


Figure 74. Firing diagram of pisolitic clay from Mankato, Blue Earth County.

Appendix G-4

Late Cretaceous Clays


FIRLE PROPERTY – RENVILLE CO.

PRE-CRETACEOUS: SAMPLE NUMBER 88-010

SECONDARY PISOLITIC KAOLIN

PRE-CRETACEOUS: SAMPLE NUMBER 88-143

SECONDARY PISOLITIC KAOLIN

Figure 75. Firing diagrams of pisolitic clays from the Firle property, Renville County.

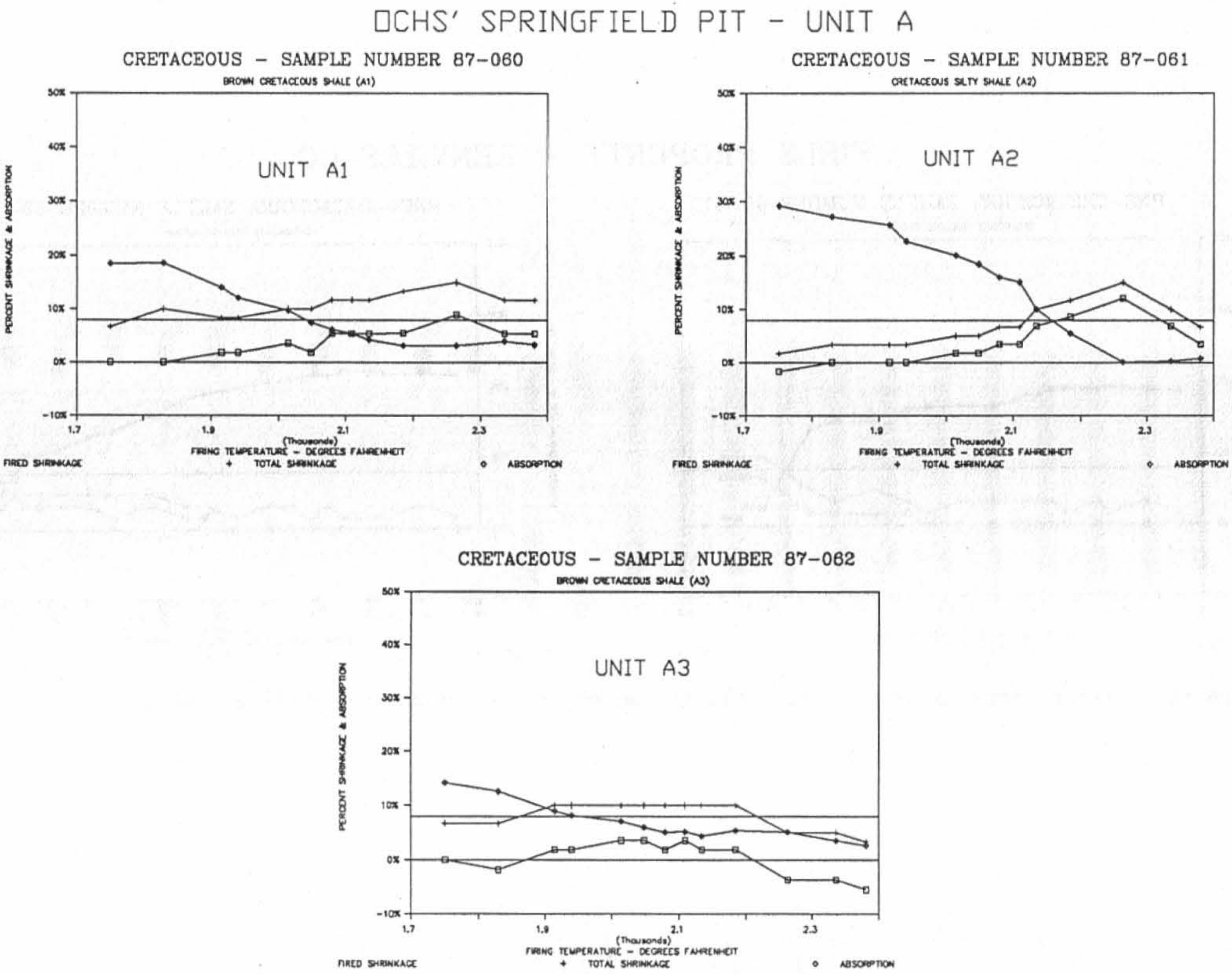


Figure 76. Firing diagrams of clays from Unit A at the Ochs' Springfield mine.

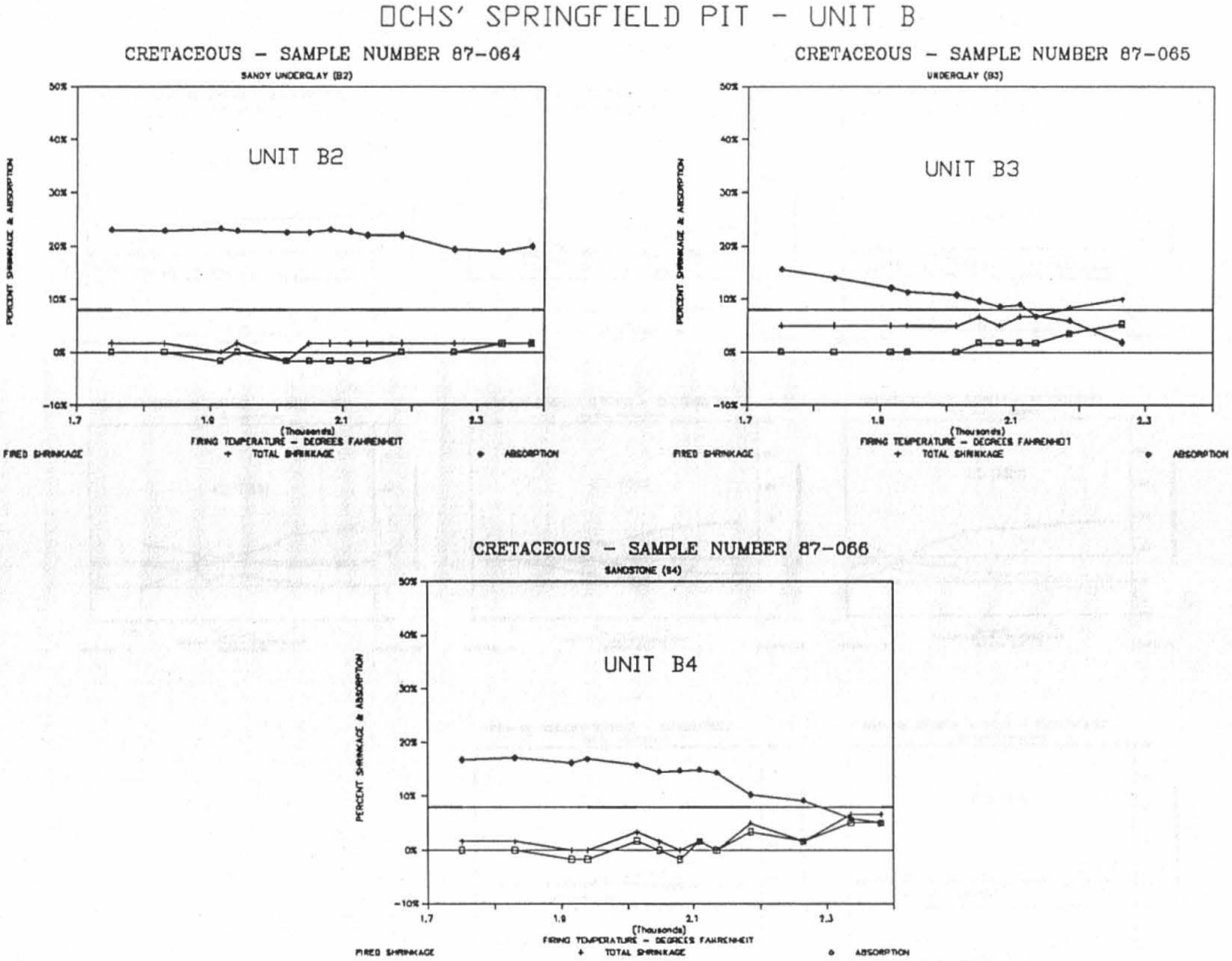


Figure 77. Firing diagrams of clays from Unit B at the Ochs' Springfield mine.

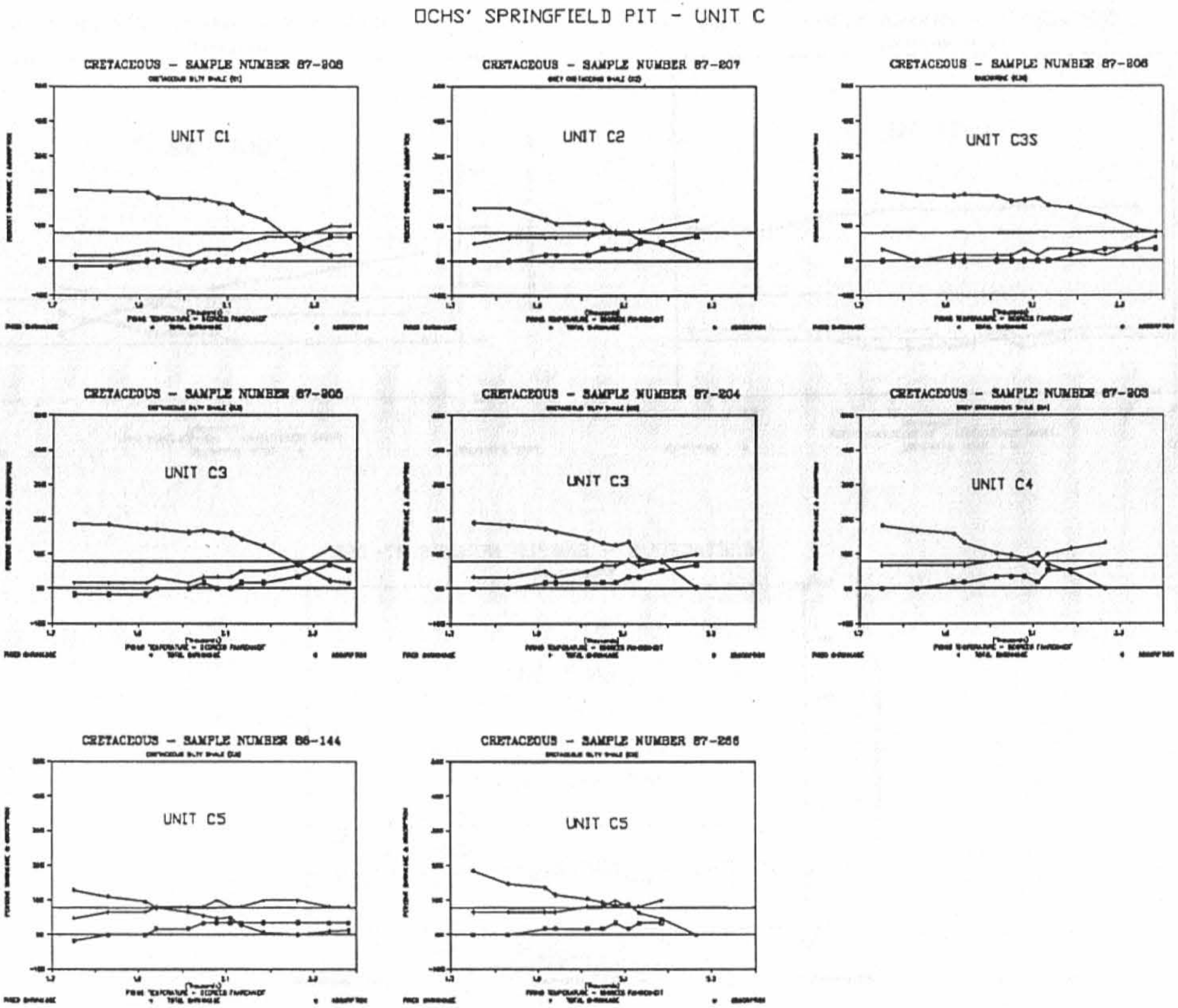


Figure 78. Firing diagrams of clays from Unit C at the Ochs' Springfield mine.

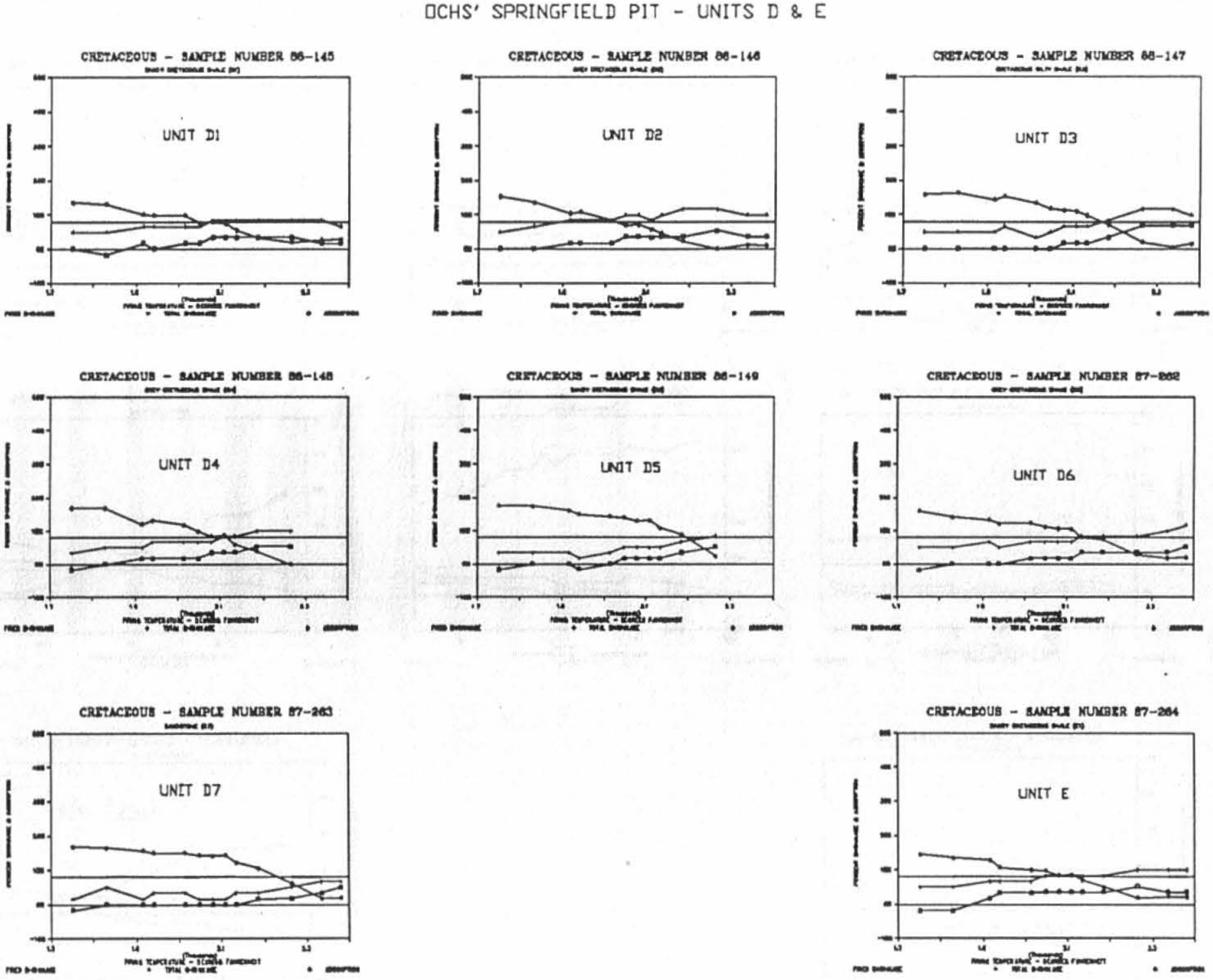


Figure 79. Firing diagrams of clays from Units D and E at the Ochs' Springfield mine.

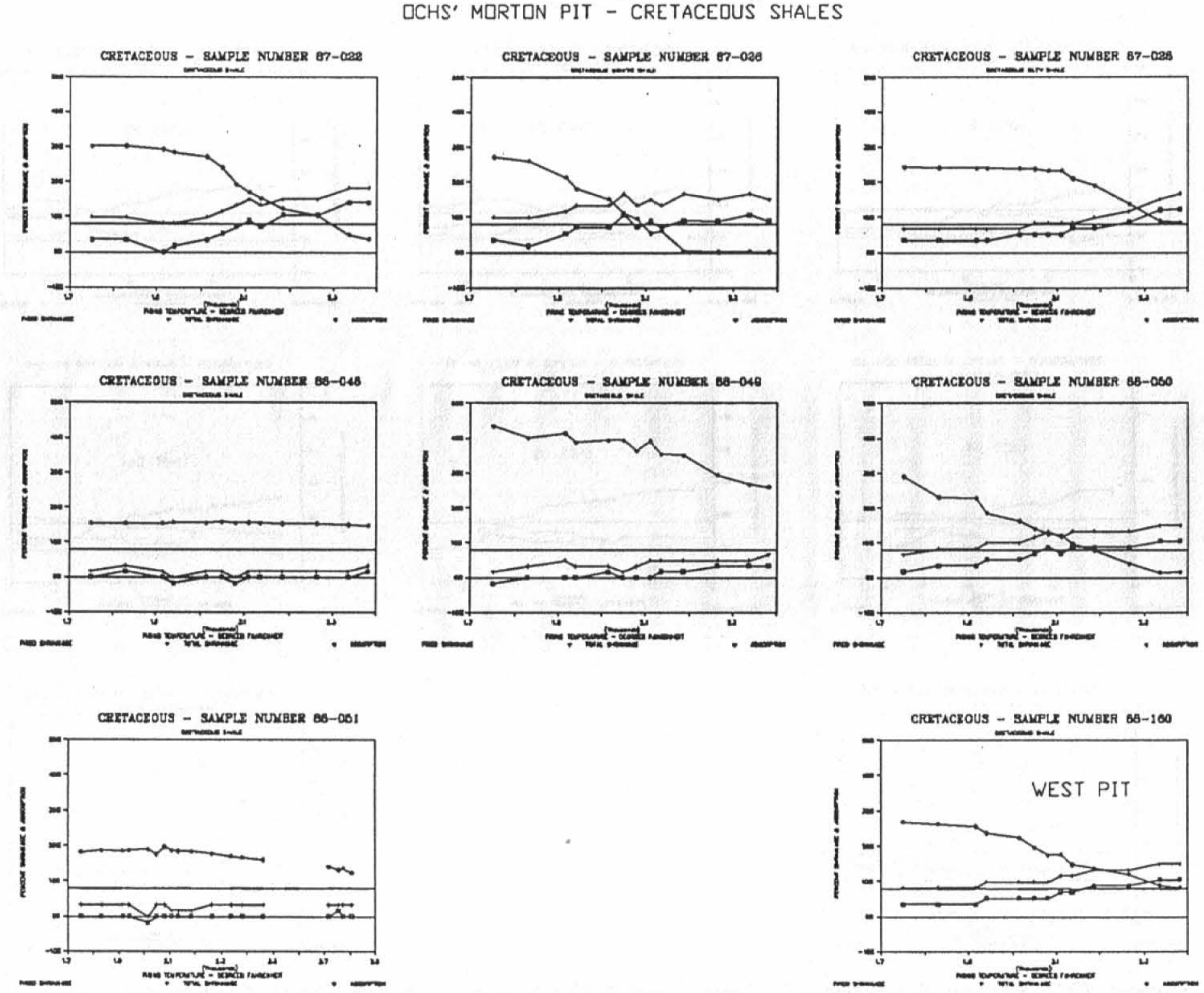


Figure 80. Firing diagrams of Late Cretaceous clays from the Ochs' Morton mine.

MORRISON COUNTY - CRETACEOUS SHALE

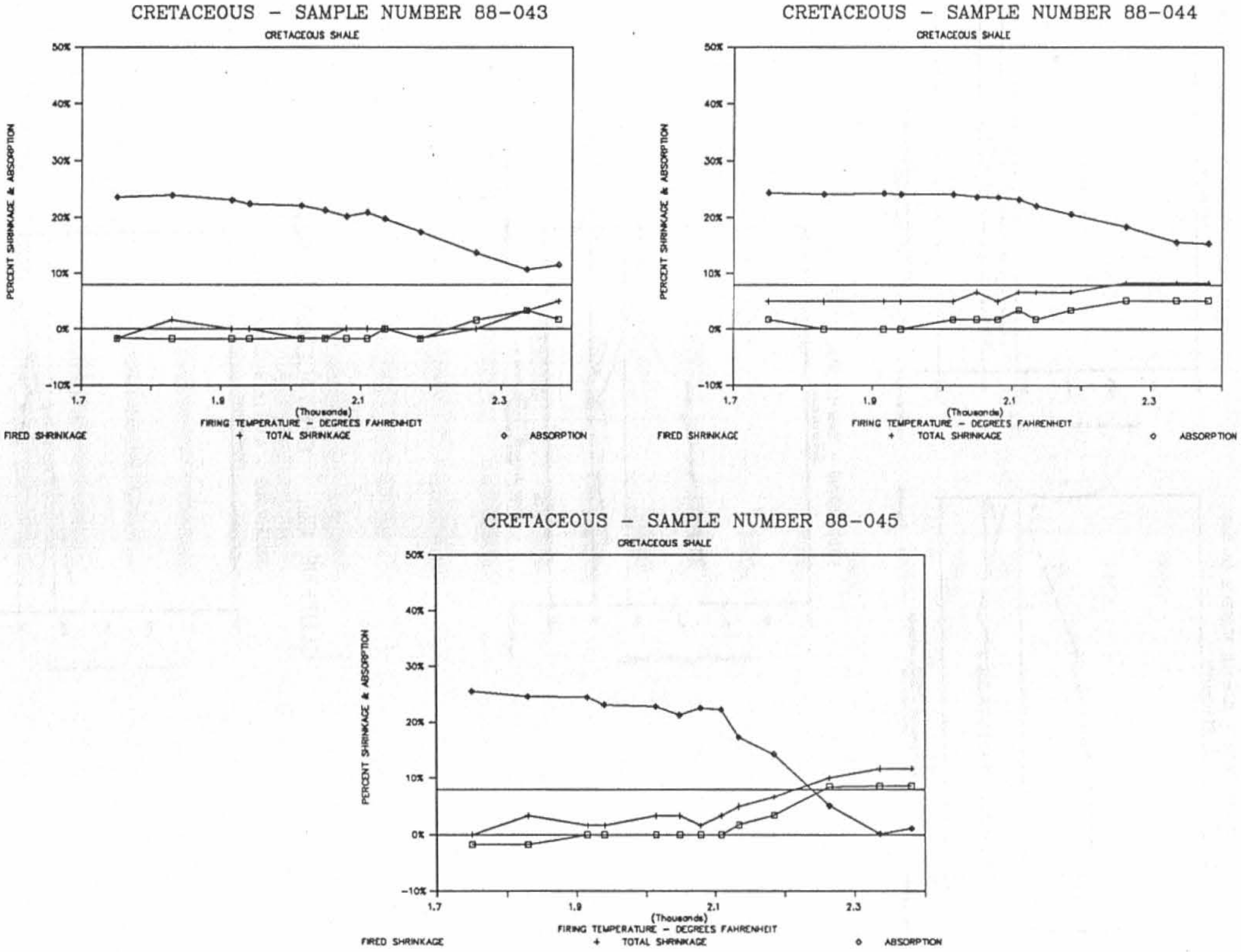
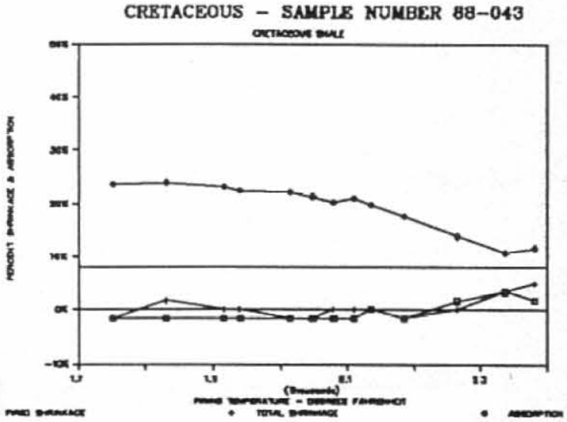
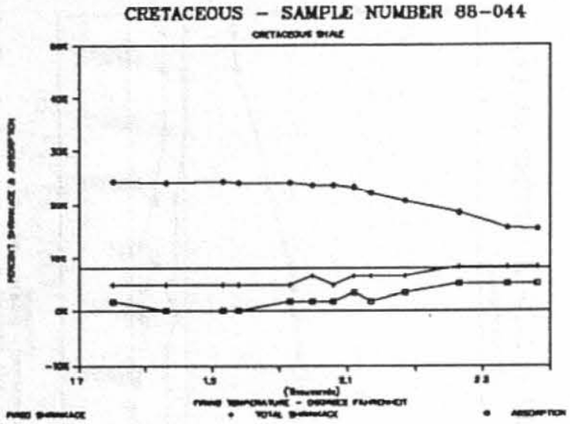
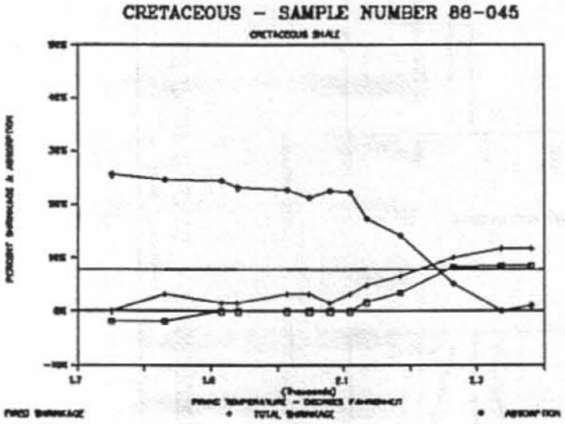


Figure 81. Firing diagrams of Late Cretaceous clays from Morrison County.

MORRISON COUNTY - CRETACEOUS SHALE







GOODHUE CO. - CRETACEOUS SHALE

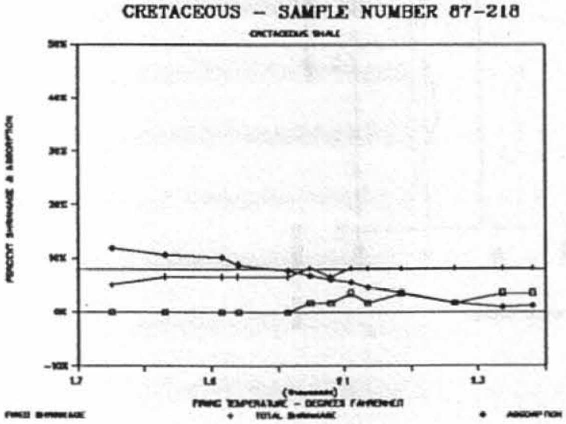


Figure 82. Firing diagrams of Late Cretaceous clays from Morrison and Goodhue Counties.

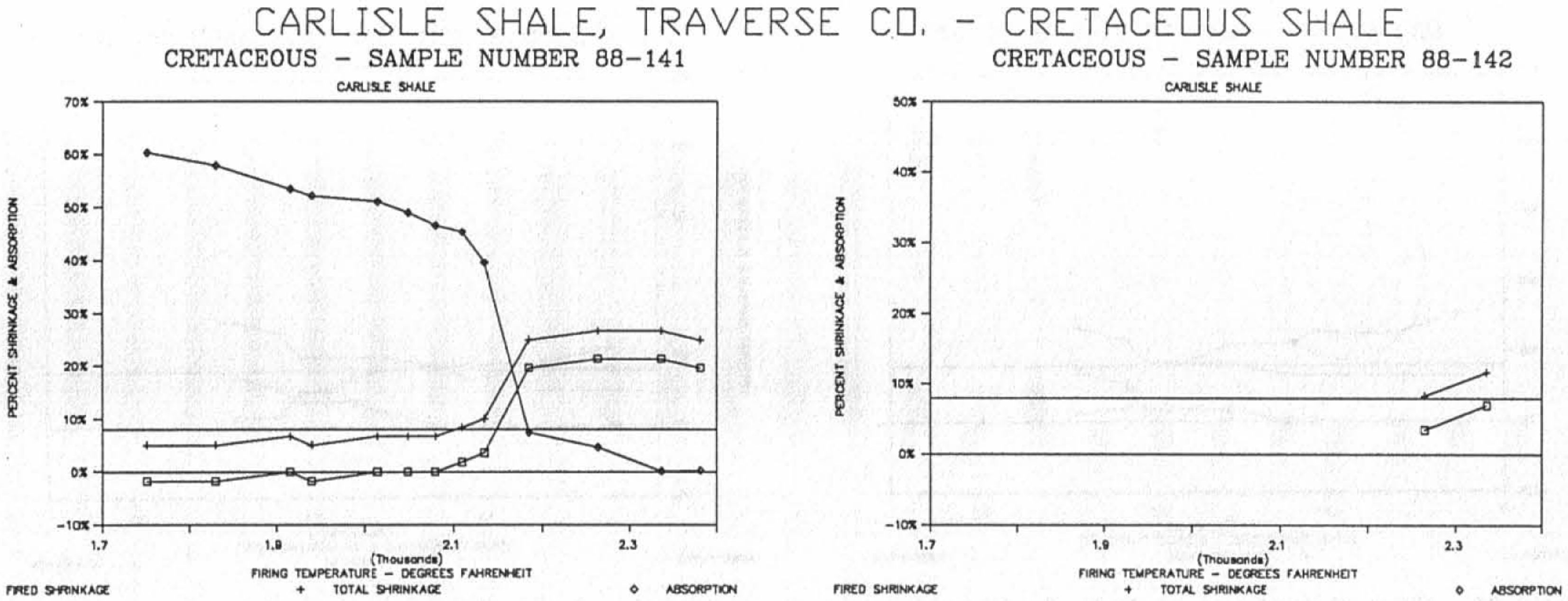


Figure 83. Firing diagrams of Late Cretaceous Carlisle shale from Traverse County.

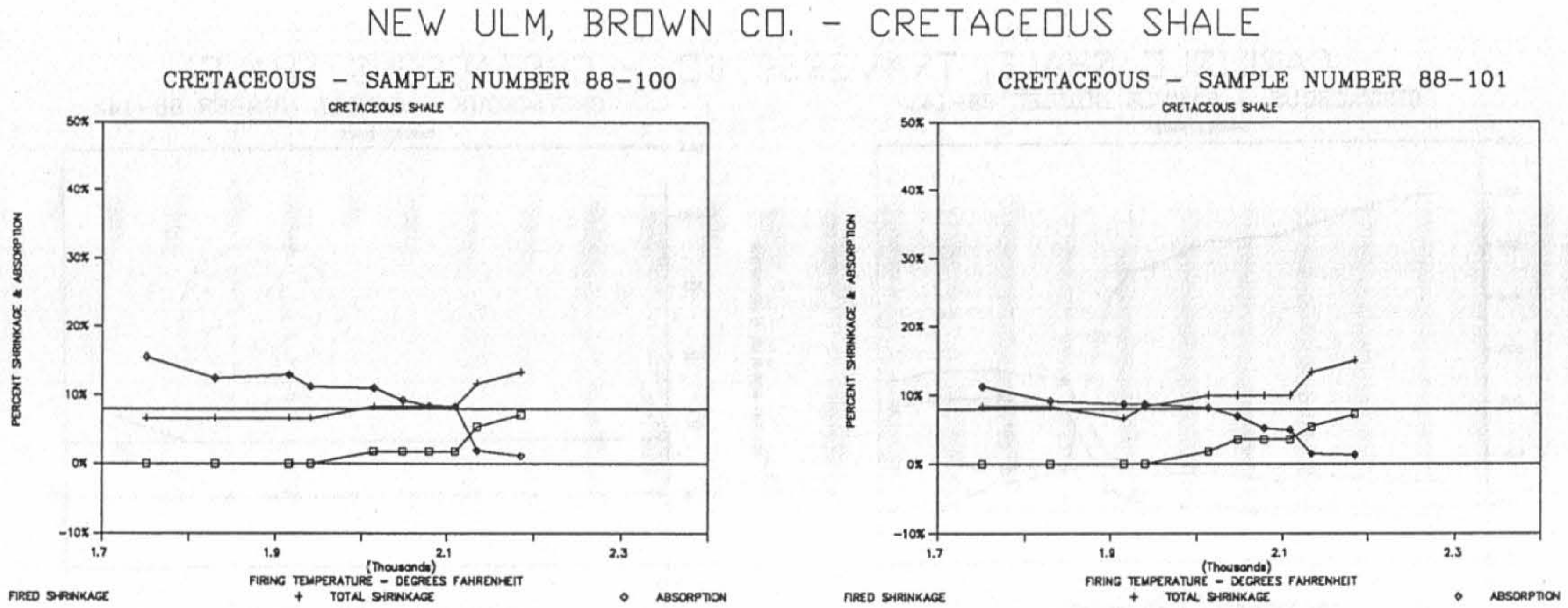


Figure 84. Firing diagrams of Late Cretaceous clays from New Ulm, Brown County.

AUSTIN AREA — CRETACEOUS SHALES

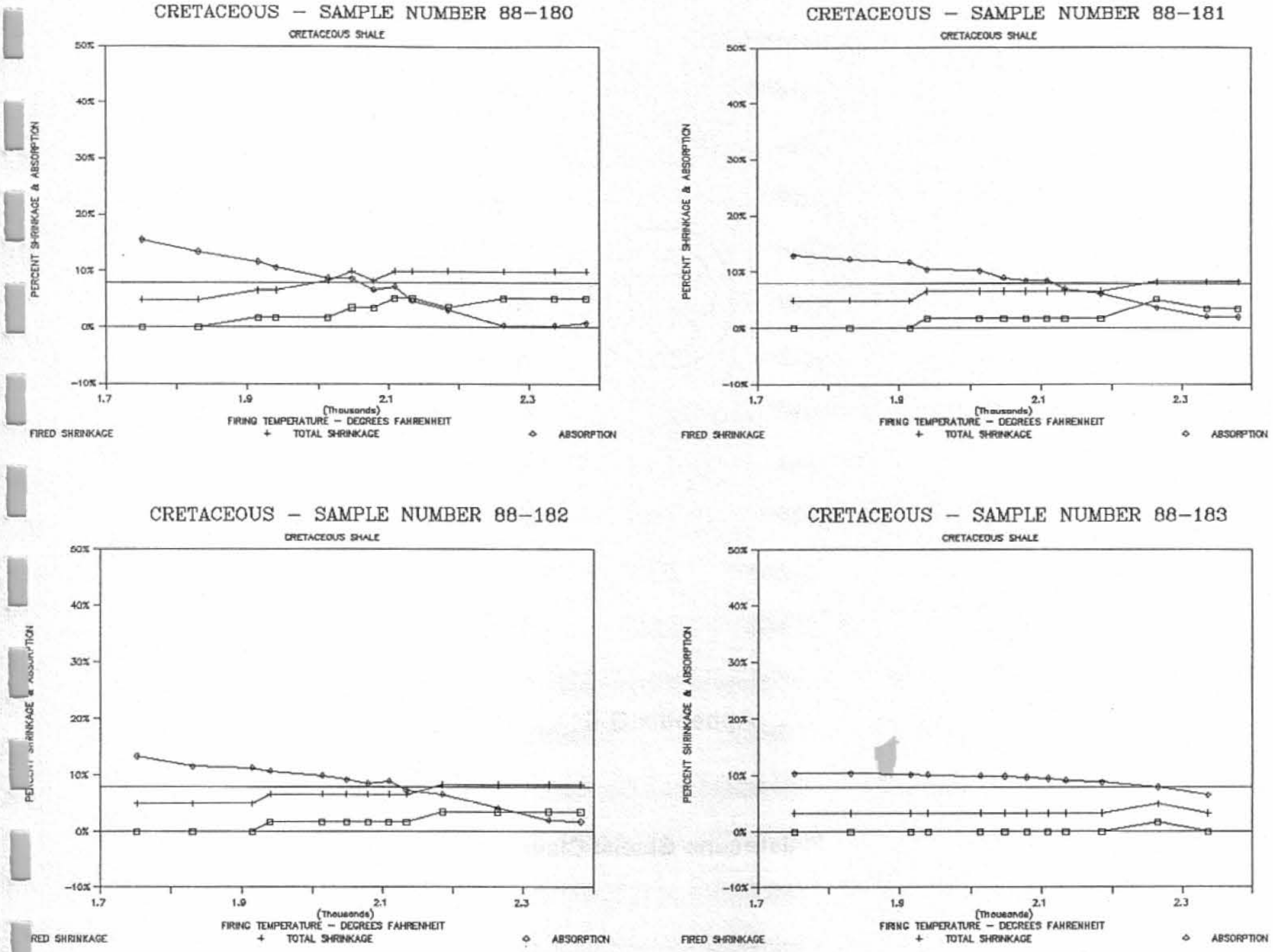


Figure 85. Firing diagrams of Late Cretaceous clays from the Austin area.

Appendix G-5

Pleistocene Glacial Clays

DES MOINES LOBE – ALTAMONT ASSOCIATION

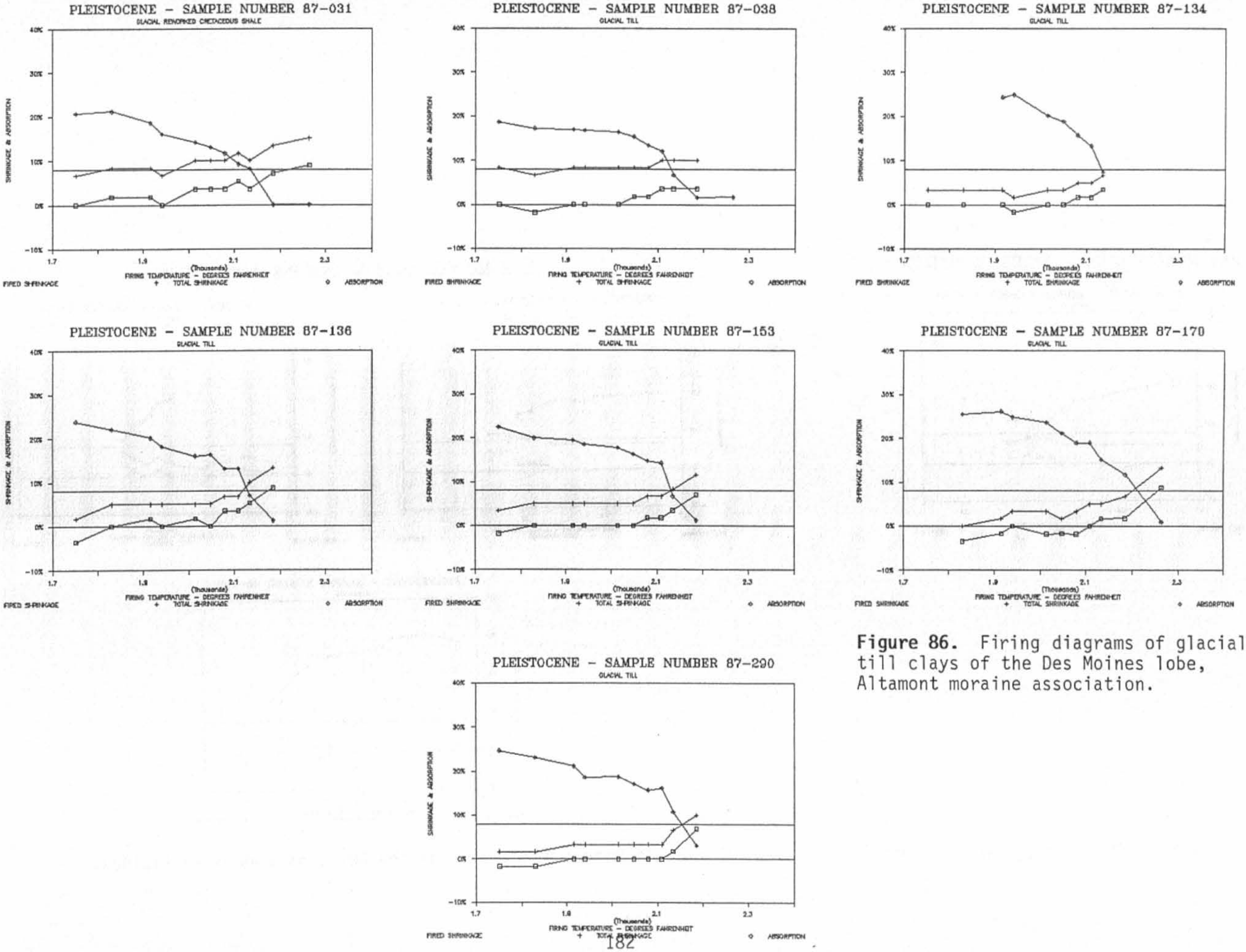
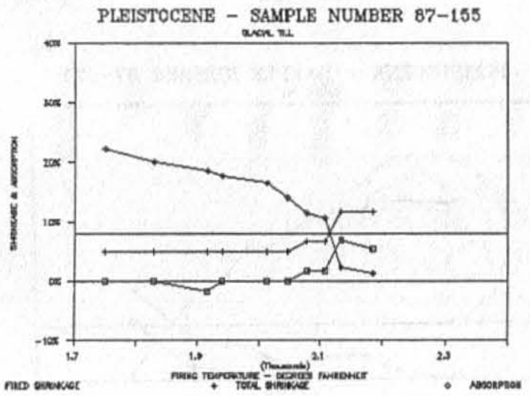


Figure 86. Firing diagrams of glacial till clays of the Des Moines lobe, Altamont moraine association.

DES MOINES LOBE – BEMIS ASSOCIATION



DES MOINES LOBE – ERSKINE ASSOCIATION

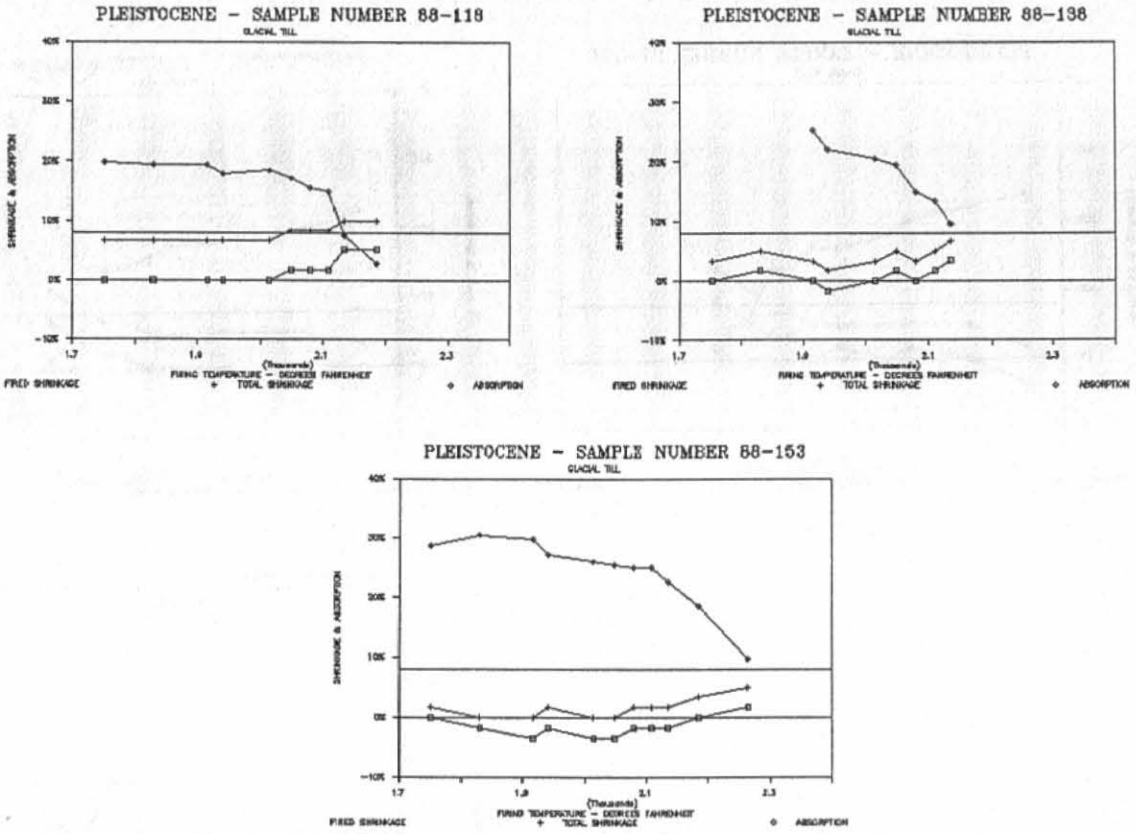


Figure 87. Firing diagrams of glacial till clays of the Des Moines lobe, Erskine and Bemis moraine associations.

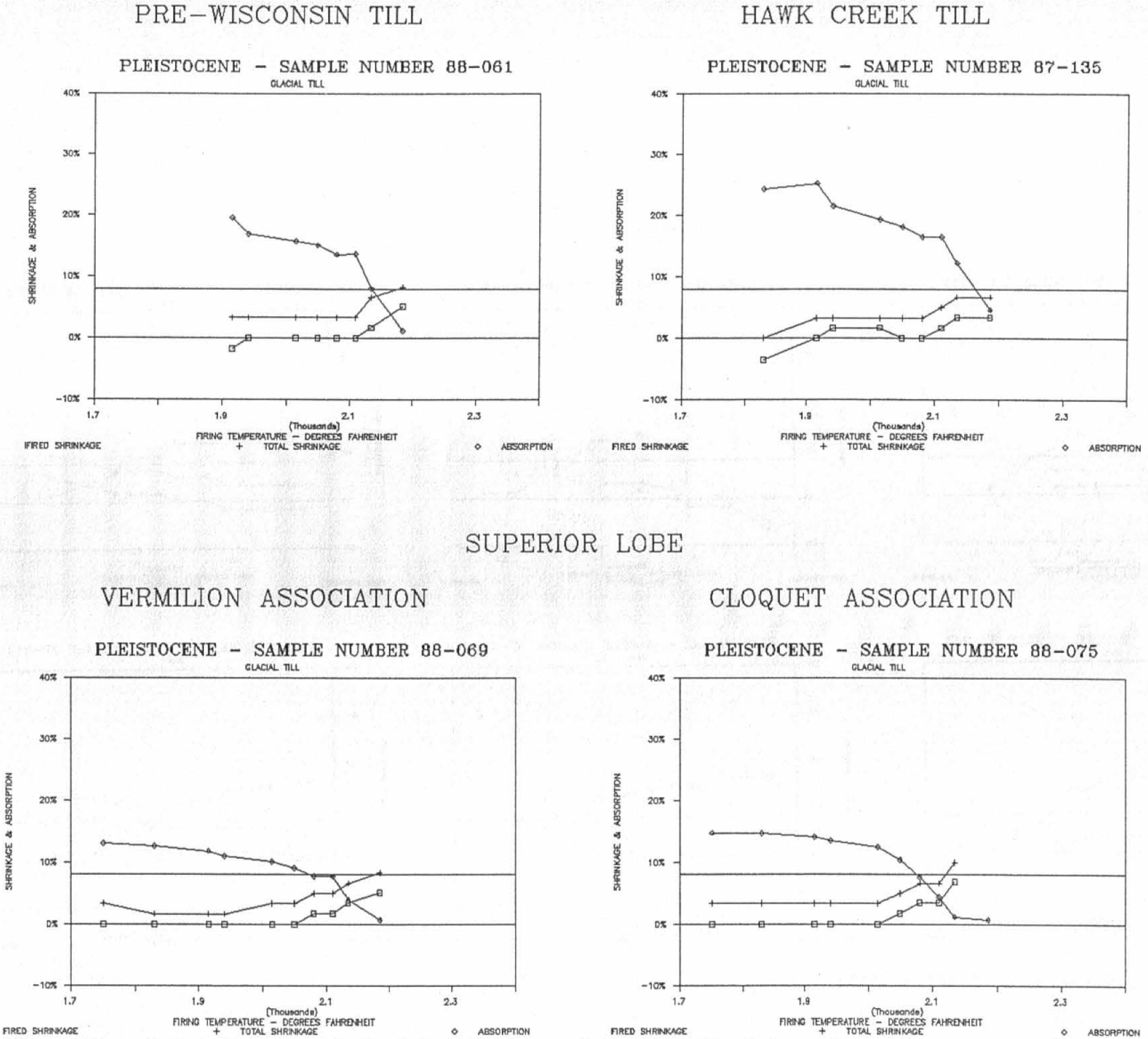
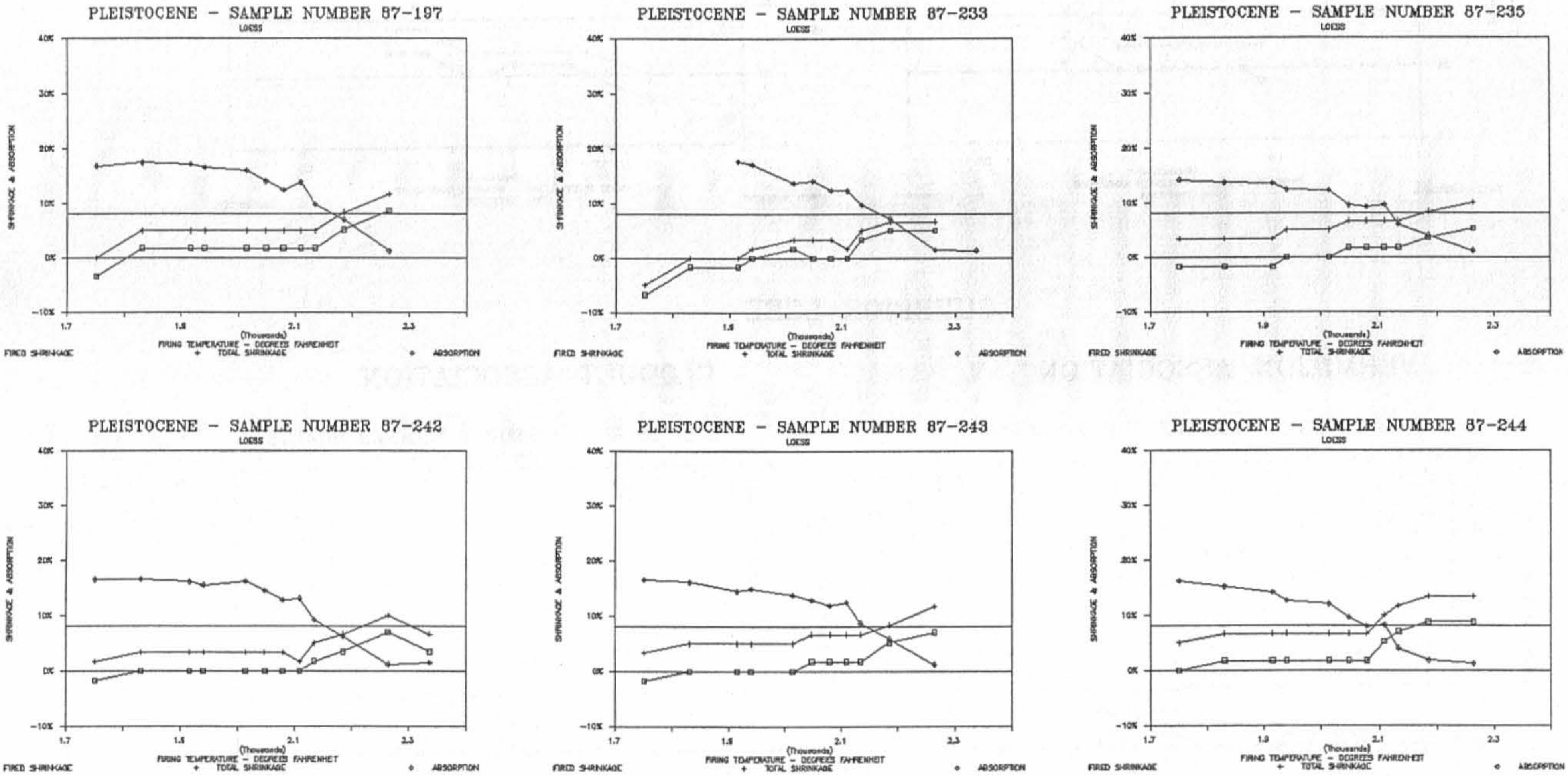


Figure 88. Firing diagrams of glacial till clays of the Superior lobe and pre-Wisconsin moraine associations.

GLACIAL LOESS


PLEISTOCENE - SAMPLE NUMBER 87-197

PLEISTOCENE - SAMPLE NUMBER 87-233

PLEISTOCENE - SAMPLE NUMBER 87-235

PLEISTOCENE - SAMPLE NUMBER 87-242

PLEISTOCENE - SAMPLE NUMBER 87-243

PLEISTOCENE - SAMPLE NUMBER 87-244

Figure 89. Firing diagrams of glacial loess.

GLACIAL LAKE UPHAM

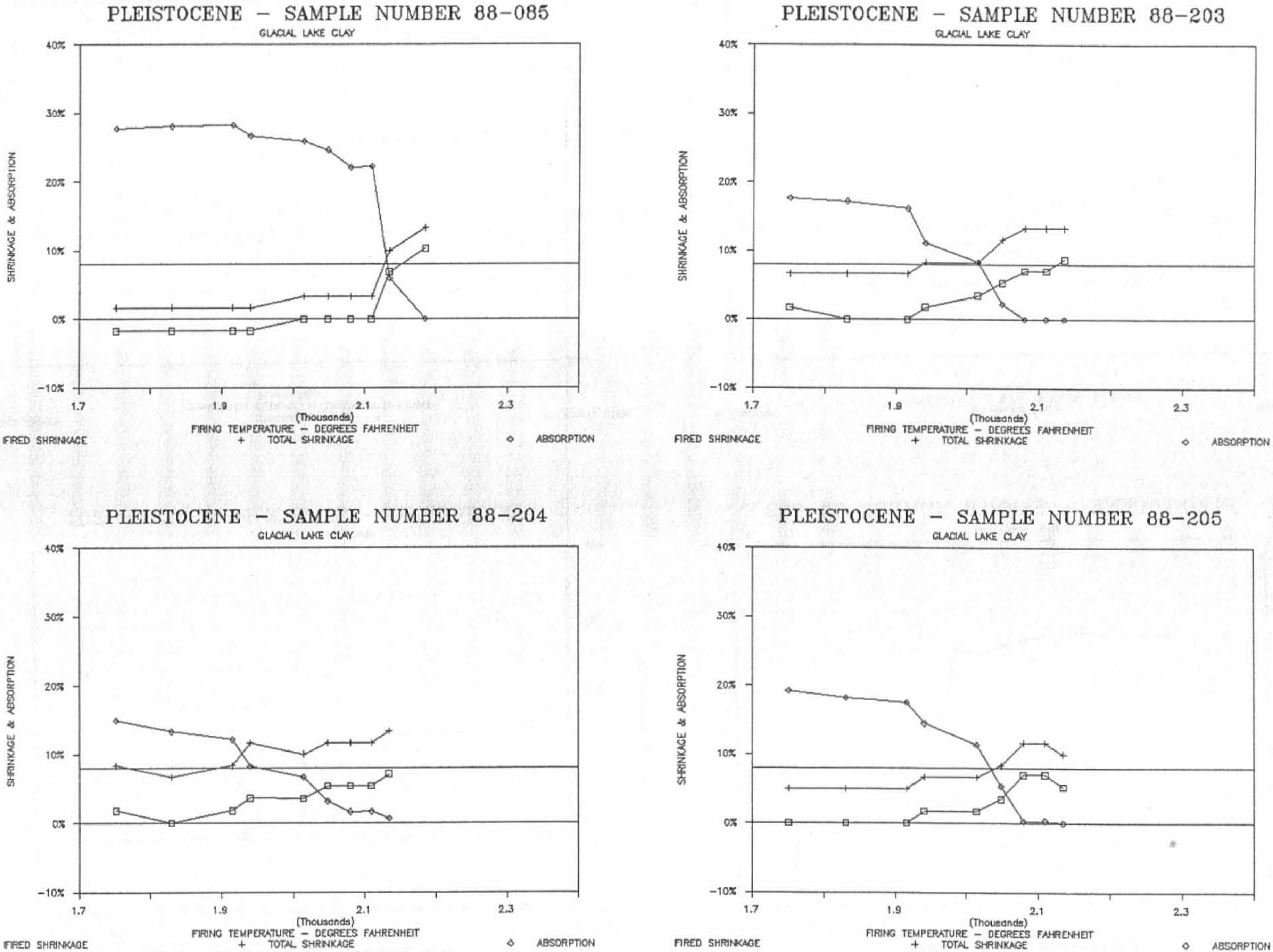


Figure 90. Firing diagrams of Glacial Lake Upham clays.

GLACIAL LAKE AITKIN

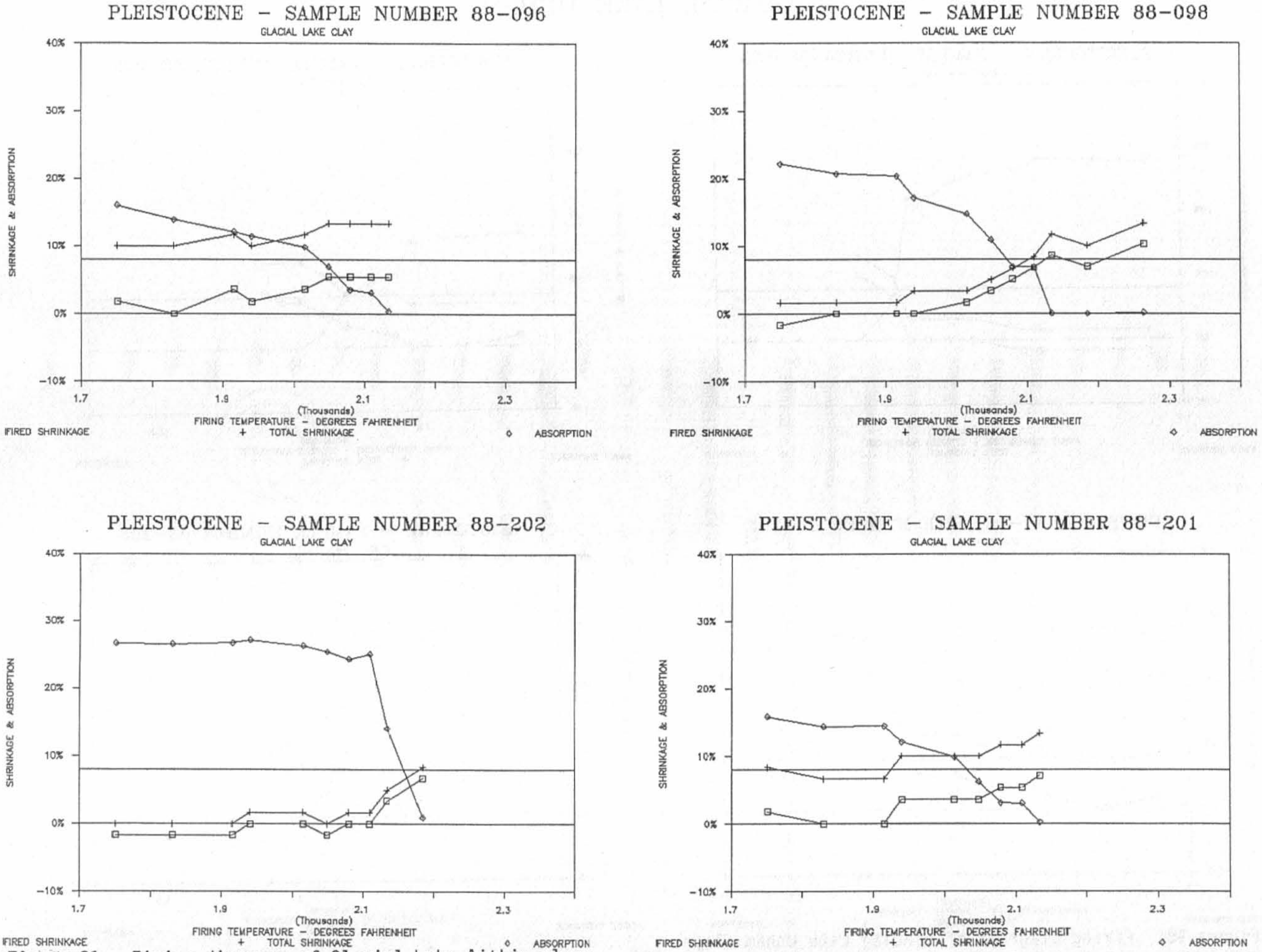


Figure 91. Firing diagrams of Glacial Lake Aitkin clays.

GLACIAL LAKE MINNESOTA

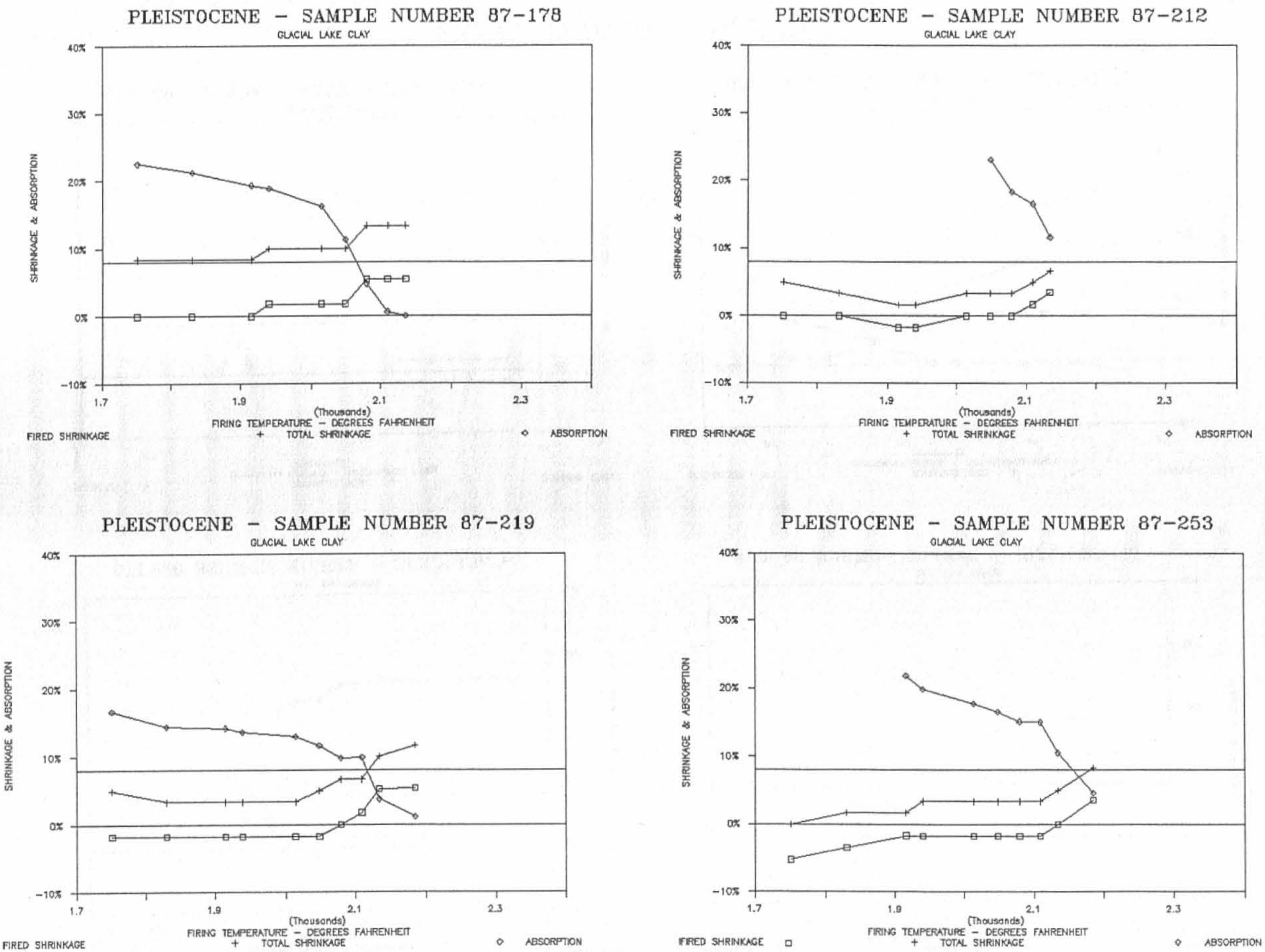


Figure 92. Firing diagrams of Glacial Lake Minnesota clays.

UNKNOWN GLACIAL LAKES

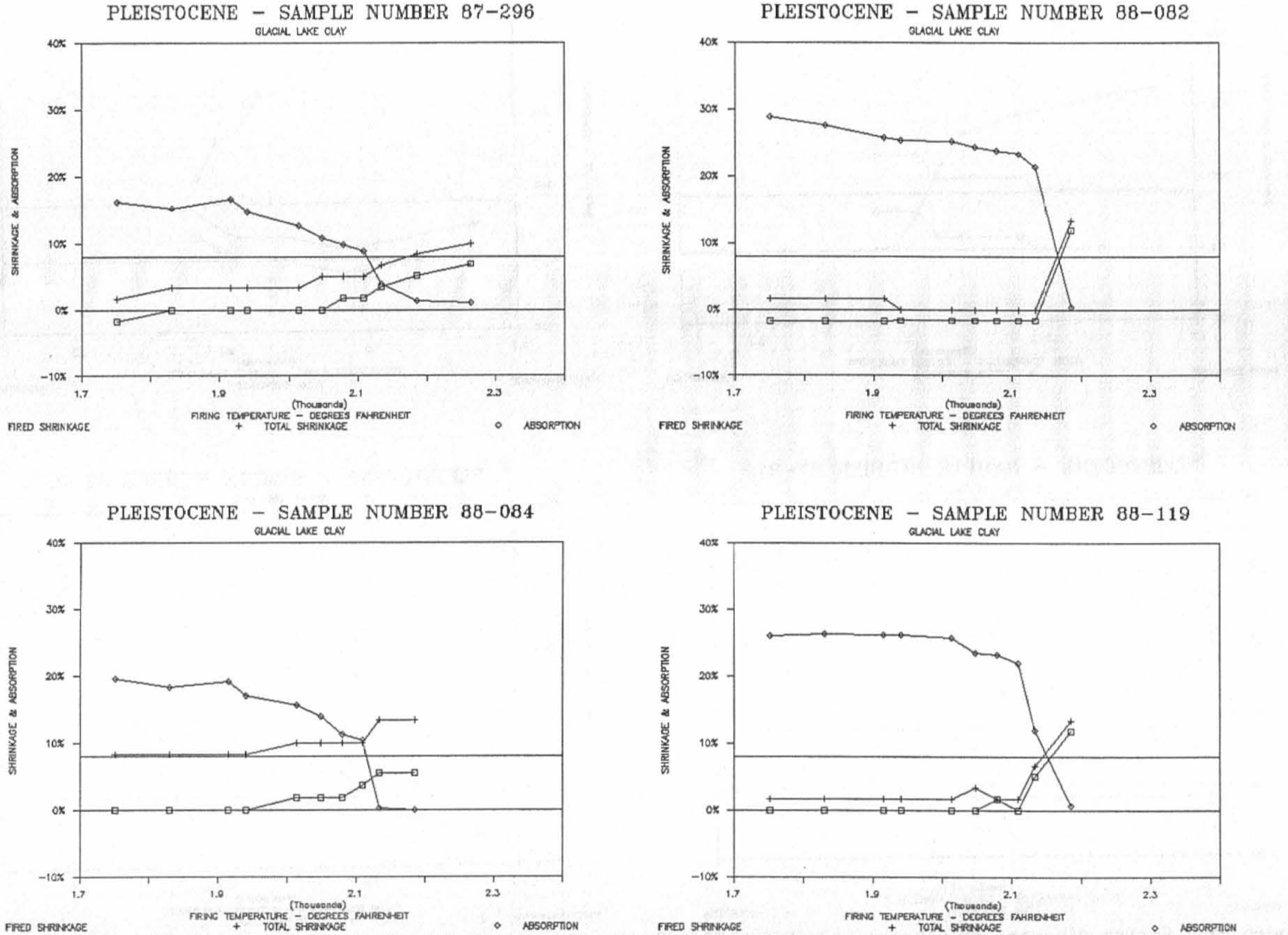
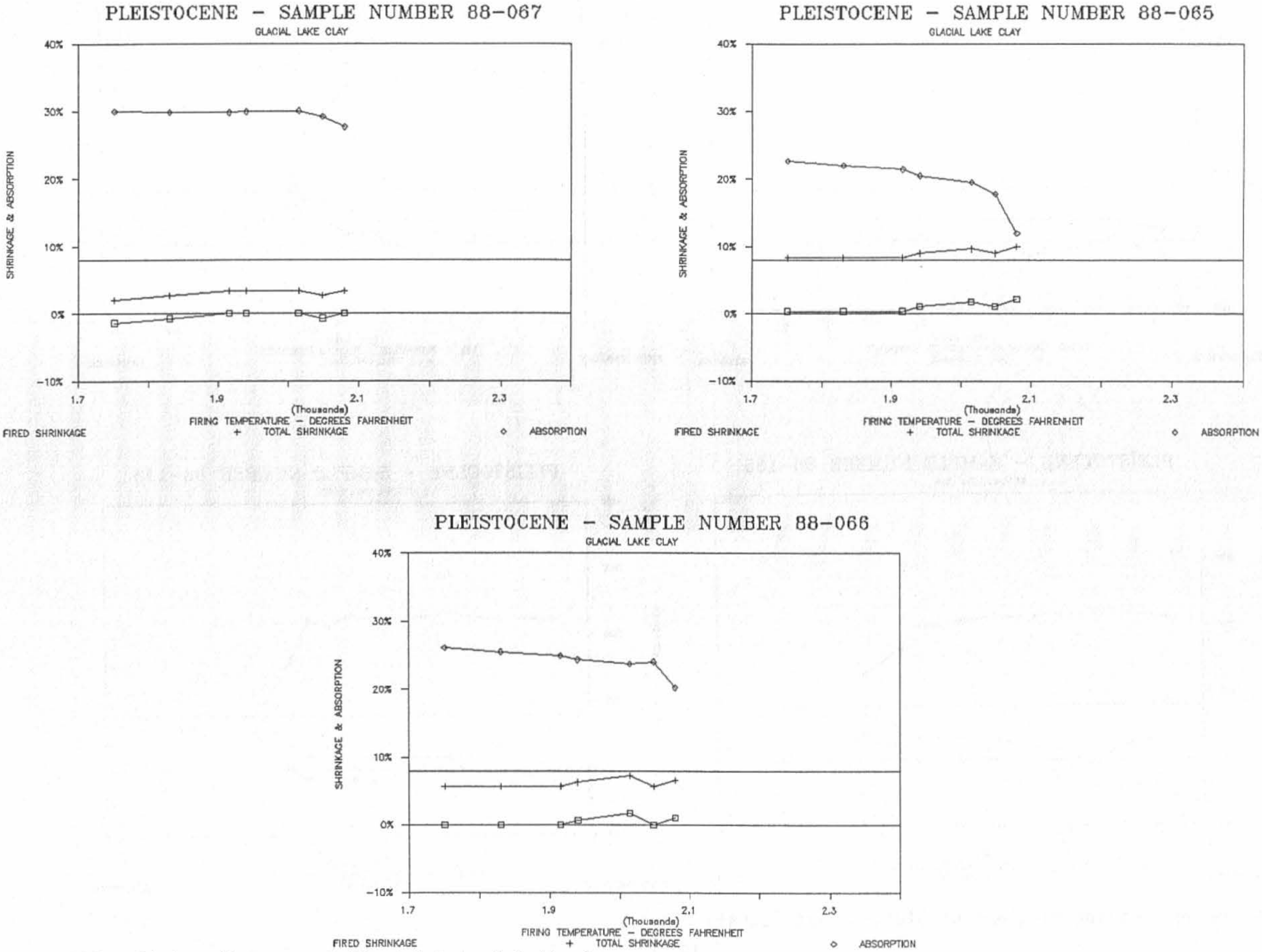


Figure 93. Firing diagrams of glacial lake clays of unknown affinity.

GLACIAL LAKE DULUTH


PLEISTOCENE - SAMPLE NUMBER 88-067

GLACIAL LAKE CLAY

PLEISTOCENE - SAMPLE NUMBER 88-065

GLACIAL LAKE CLAY

PLEISTOCENE - SAMPLE NUMBER 88-066

GLACIAL LAKE CLAY

Figure 94. Firing diagrams of Glacial Lake Duluth clays.

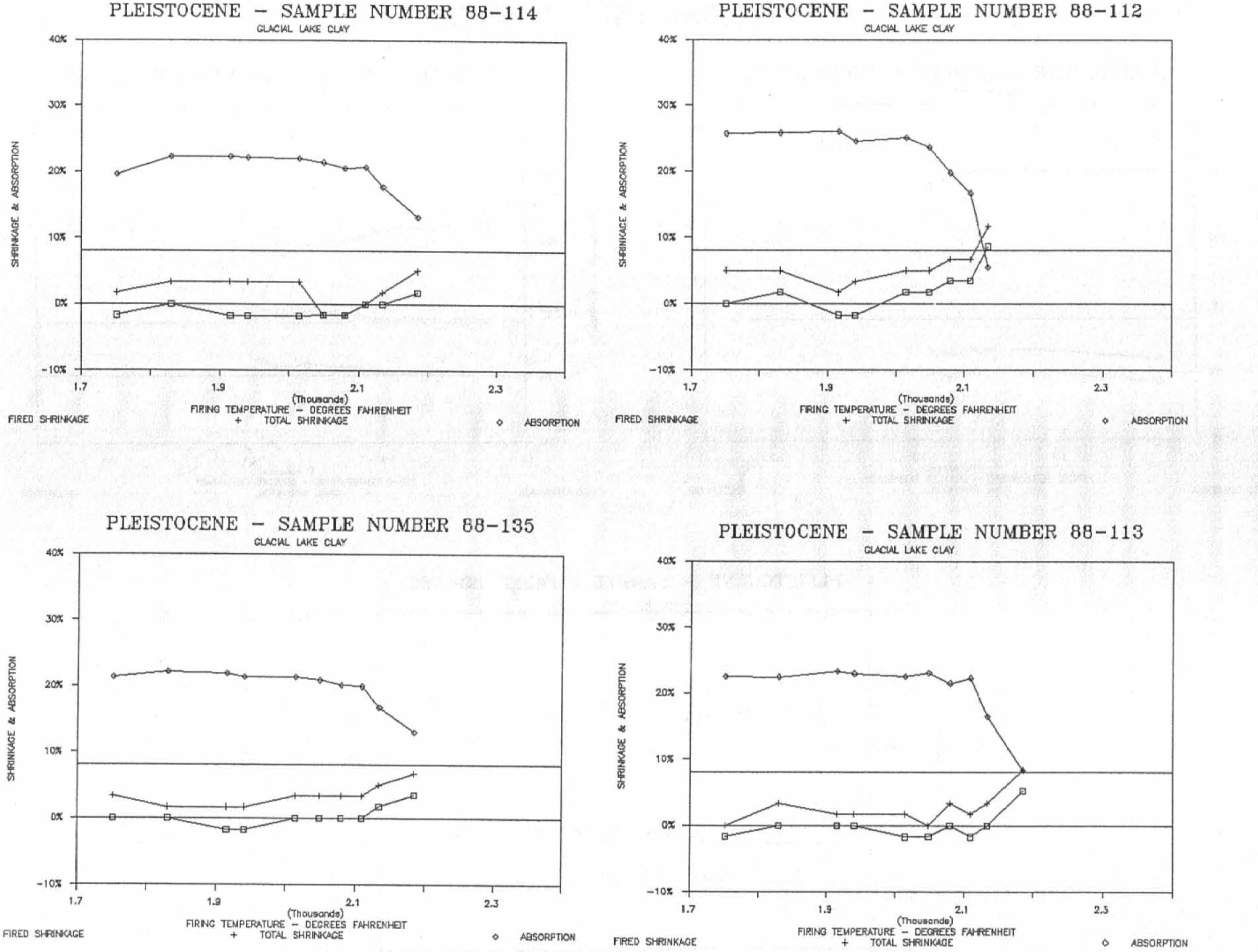


Figure 95. Firing diagrams of Glacial Lake Agassiz clays.

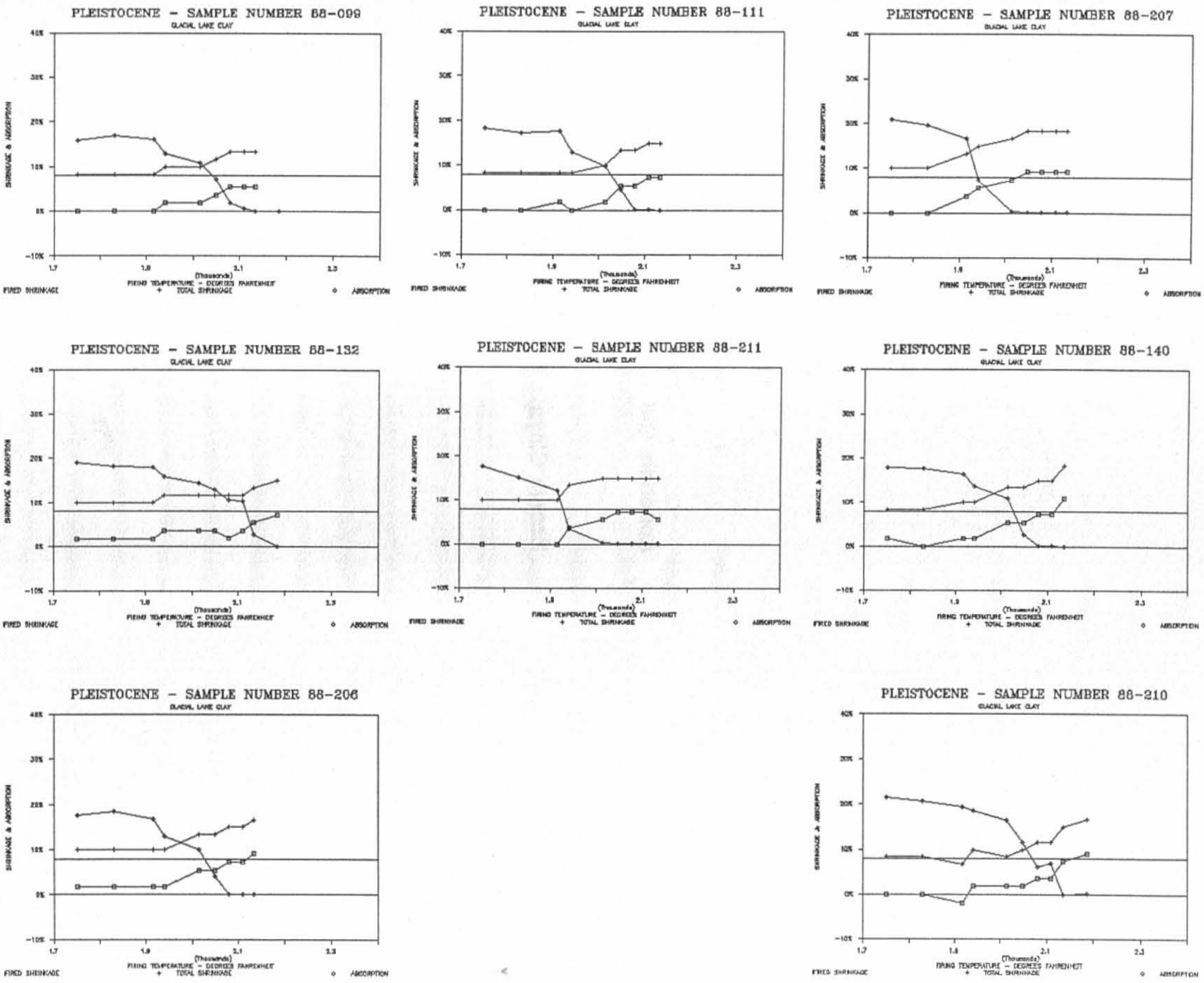
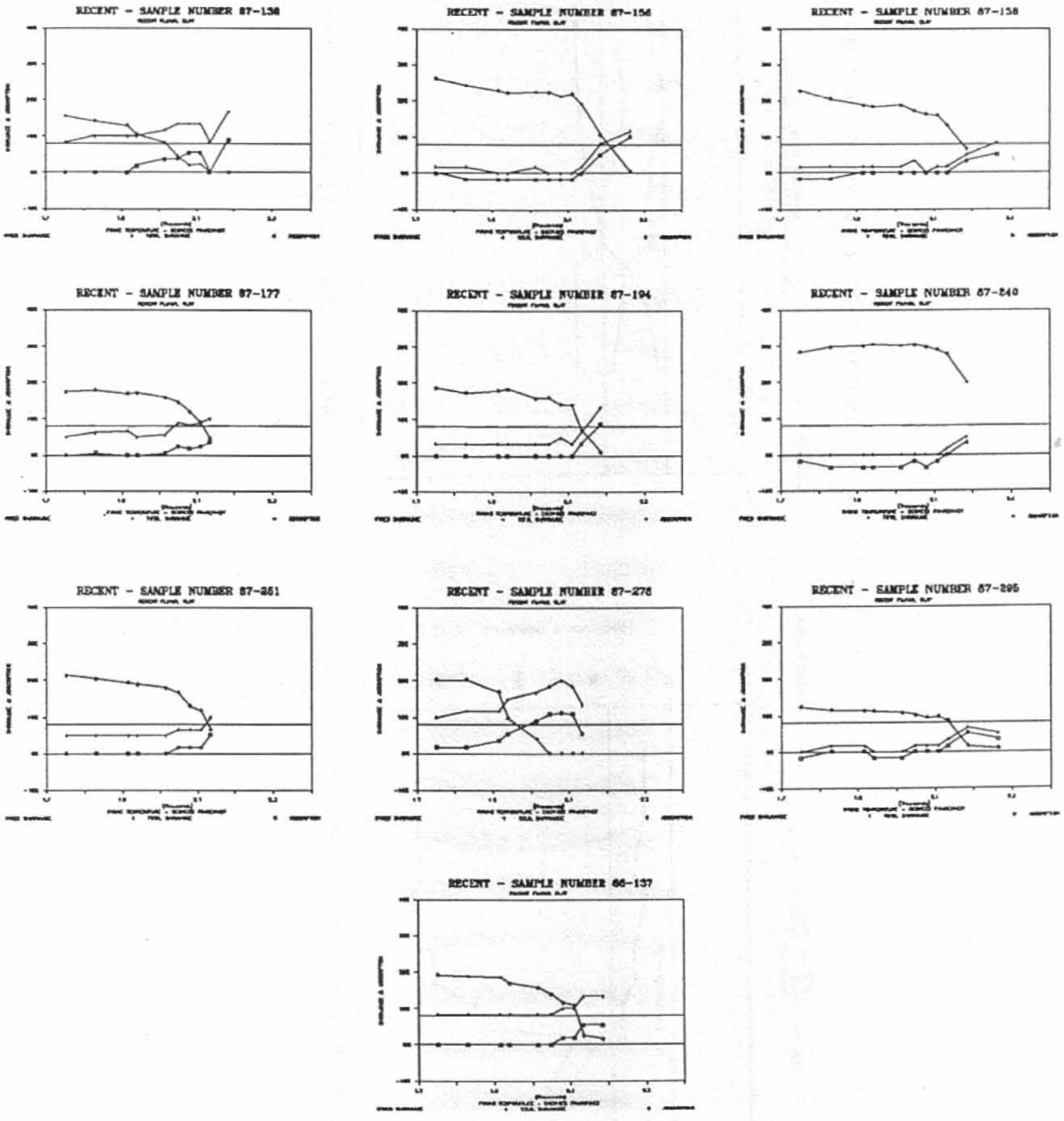


Figure 96. Firing diagrams of Glacial Lake Agassiz clays.

Appendix G-6

Recent Clays

RECENT FLUVIAL CLAYS



RECENT - SAMPLE NUMBER 87-138

RECENT - SAMPLE NUMBER 87-156

RECENT - SAMPLE NUMBER 87-158

RECENT - SAMPLE NUMBER 87-177

RECENT - SAMPLE NUMBER 87-194

RECENT - SAMPLE NUMBER 87-240

RECENT - SAMPLE NUMBER 87-261

RECENT - SAMPLE NUMBER 87-276

RECENT - SAMPLE NUMBER 87-295

RECENT - SAMPLE NUMBER 86-137

Figure 97. Firing diagrams of Recent fluvial clays.

RECENT LAKE CLAYS

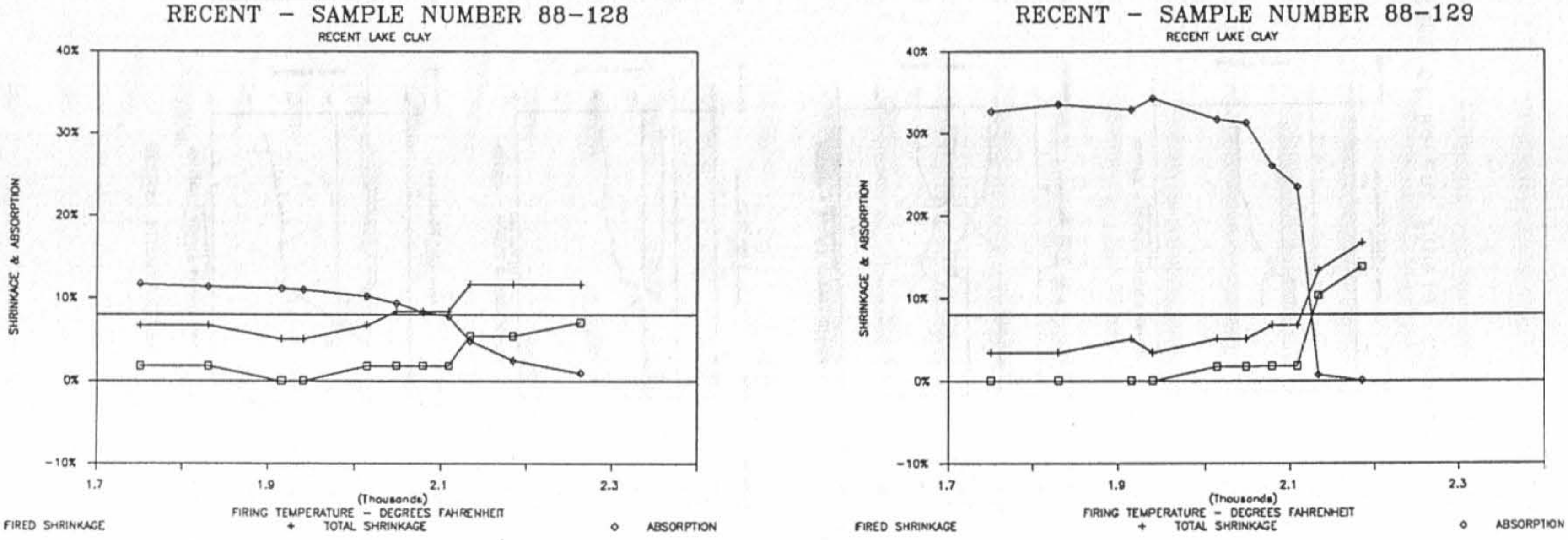


Figure 98. Firing diagrams of Recent lacustrine clays.

APPENDIX H

X-RAY MINERALOGY DATA

The clay X-ray mineralogy data for each sample analyzed are in a Lotus 1-2-3 file named CLAYXRAY.WK1 on Disk 1. The data available for each sample are listed under the following column headings. Columns N to AC indicate the amount of a mineral present in the 2 micron size fraction that was X-rayed:

M = major for major mineral present in the sample.
m = minor amount of mineral in a sample.
T = trace amount present.
blank = mineral not present.

Column A: Data sort number.
Column B: Sample number - 87 and 88 stand for year in which the sample was collected.
Column C: U. S. Bureau Mines (USBM) sample number for samples obtained from the USBM.
Column D: Sample type.
Column E: Rock type - this is an abbreviated designation for sorting the different sample types.
Column F: Geologic age.
Column G: Glacial ice lobe/moraine association name.
Column H: Glacial lake name.
Column I: Deposit name - designates mine name or outcrop.
Column J: Station number - an alphanumeric designator for identifying which trench and channel sample was collected.
Column K: Unit name - an alphanumeric designator to identify a stratigraphic subunit, e.g., B4 at the Ochs' Springfield mine or 1-lowest sample in a trench.
Column L: Thickness in feet of the channel sample.
Column M: Bulk X-ray - indicates bulk X-ray data available in Haas, *et al* (1987).
Column N: Smectite.
Column O: Mixed-layer clay.
Column P: Chlorite.
Column Q: Illite.
Column R: Kaolinite.
Column S: Gibbsite.
Column T: Halloysite.
Column U: Quartz.
Column V: Feldspar.
Column W: Hematite.
Column X: Goethite.
Column Y: Calcite.
Column Z: Dolomite.
Column AA: Ankerite.
Column AB: Gypsum.
Column AC: Other.

APPENDIX I

CATION EXCHANGE CAPACITY DATA

The cation exchange capacity data for each sample analyzed are in a Lotus 1-2-3 file named CATIONX.WK1 on Disk 1. The data available for each sample are listed under the following column headings:

Column A: Data sort number.
Column B: Sample number - 87 and 88 stand for year in which the sample was collected.
Column C: U. S. Bureau Mines (USBM) sample number for samples obtained from the USBM.
Column D: Sample type.
Column E: Rock type - this is an abbreviated designation for sorting the different sample types.
Column F: Geologic age.
Column G: Glacial ice lobe name.
Column H: Glacial lake name.
Column I: Deposit name - designates mine name or outcrop.
Column J: County name.
Column K: Station number - an alphanumeric designator for identifying which trench and channel sample was collected.
Column L: Unit name - an alphanumeric designator to identify a stratigraphic subunit, e.g., B4 at the Ochs' Springfield mine or 1-lowest sample in a trench.
Column M: Thickness in feet of the channel sample.
Column N: Methylene Blue result in milliequivalents.

APPENDIX J

MUNSELL COLOR DATA

The Munsell color data for each sample analyzed are in a Lotus 1-2-3 file named COLORALL.WK1 on Disk 1. The data available for each sample are listed under the following column headings:

Column A: Data sort number.
Column B: Sample number - 87 and 88 stand for year in which the sample was collected.
Column C: U. S. Bureau Mines (USBM) sample number for samples obtained from the USBM.
Column D: Sample type.
Column E: Rock type - this is an abbreviated designation for sorting the different sample types.
Column F: Geologic age.
Column G: Glacial ice lobe name.
Column H: Glacial lake name.
Column I: Deposit name - designates mine name or outcrop.
Column J: County name.
Column K: Station number - an alphanumeric designator for identifying which trench and channel sample was collected.
Column L: Unit name - an alphanumeric designator to identify a stratigraphic subunit, e.g., B4 at the Ochs' Springfield mine or 1-lowest sample in a trench.
Column M: Thickness in feet of the channel sample.
Column N: Color sorting code.
Column O: Munsell color code.
Column P: Munsell color.