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THE PROPERTIES OF CHERT AGGREGATE IN RELATION TO THEIR DELETERIOUS EFFECT IN CONCRETE

INSTITUTE of MINERAL RESEARCH
MICHIGAN COLLEGE OF MINING AND TECHNOLOGY
Houghton, Michigan

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THE PROPERTIES OF CHERT AGGREGATE IN RELATION TO THEIR DELETERIOUS EFFECT IN CONCRETE

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THE PROPERTIES OF CHERT AGGREGATES IN RELATION TO THEIR DELETERIOUS EFFECT IN CONCRETE

by

E. L. Michaels* and M. E. Volin**

ABSTRACT

The results of the first year of a study of some physical and chemical properties of chert in relation to the freeze-thaw durability of this material when used as concrete aggregate are presented in this progress report.

Compositional variations in the cherts are described on the basis of petrographic observations and chemical analysis. The variations in composition for different particle sizes are shown to be significantly related to other physico-chemical properties of chert. The low specific gravity cherts (less than 2.50) are found to be more deleterious under freeze-thaw conditions than the higher gravity cherts; this is without relation to particle size. Fractures and large pore spaces are more prominant in these low specific gravity cherts.

Although simple linear regression may afford solutions to the correlations of freeze-thaw durability with various properties of chert, complex relationships between variables may require higher order relationships in their analysis.

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The project has been carried on in the Institute of Mineral Research at Michigan Technological University, Houghton, Michigan. Many staff members have made helpful suggestions and contributed to the progress of the work. R. F. Langill, graduate student, conducted a mineralogical study of the cherts as a thesis problem in partial fulfillment of the requirements for the Master of Science degree in Geological Engineering at Michigan Technological University. The results of his study are included in full or in summarized form in this report. T. Travis, undergraduate student in mathematics, made the correlation analyses with the IBM 1620 computer. L. O. Bacon, Professor of Geophysics and Research Engineer, supervised work having the objective of developing new methods of measuring the deterioration under freeze-thaw conditions of aggregate particles enclosed in concrete.

INTRODUCTION

Problem

Cherts are generally classified as a deleterious constituent of natural aggregates when used in concrete, and the presence of cherts in the aggregate products constitutes a problem of great concern to both the consumers and producers in many area. This is particularly the case in Michigan where cherts occur in the gravels used for aggregate and many cycles of freezing and thawing may take place during the year.

Extensive laboratory and field studies have shown that many types of cherts cause "popouts" or other forms of deterioration in concrete exposed to the weather. Since the cherts are ubiquitous in occurrence and indefinite in classification, and there is no standard method for differentiating the various kinds of cherts with respect to deleterious character, all cherts are considered undesirable, and specifications, which vary from state to state, limit the amount of cherts allowable in an aggregate product to be used to make concrete for highways and structures. The chert content of an aggregate product, however, is determined by hand picking a sample, which introduces the element of human judgment. Furthermore, the durability of cherts is predicted by freeze-thaw tests on specimens of concrete incorporating the cherts; this test takes considerable time to make and requires elaborate equipment.

A need exists, therefore, for a better understanding of the basic properties that cause cherts to be deleterious in exposed concrete. A reliable test, or series of tests, of performance based on measurable properties is needed for classification of the cherts and for identifying them according to the degree of deleteriousness.

Objectives of Study

The objectives of this study are:

(1) To classify the physical and chemical characteristics of Michigan cherts that will better describe the effects of this material when used as aggregate in concrete;

(2) To determine the relationships that may exist between characteristics or classification variables;

(3) To identify the characteristics which contribute to the deleterious effects of this material;

(4) To determine the effect of chert particle size on concrete durability; and

(5) To devise and study improved aggregate testing methods (quicker and better performance prediction) for determining the deleterious character of cherts in concrete.

Scope

This is a progress report of the research results for the first year, or phase, of the project. This phase has emphasized studies leading to results on objectives (1), (2), and (4), but includes preliminary freeze-thaw tests and other tests performed to date on objective (3). The project is in continuation and is scheduled for completion in fiscal year 1964-65.

Sponsor

The research project is sponsored by the Michigan State Highway Department in cooperation with the United States Department of Commerce, Bureau of Public Roads, as a part of the Highway Planning and Research Program.

EXPERIMENTAL MATERIALS AND PREPARATION

General Description of Cherts

Cherts have been described in many ways. Stanton Walker[1] defined chert as "almost any rock composed of microcrystalline or cryptocrystalline silica." W. B. Scott[2] defined chert as being "exceedingly dense and fine-grained masses, which the microscope shows to be made up of very minute grains of chalcedony mixed with more or less amorphous silica and crystals of quartz. The mode of origin of these masses is not at all well understood but is believed to be by precipitation from sea water." W. A. Tarr[3] described cherts as "those cryptocrystalline varieties of quartz which are opaque, save on thin edges, and are white, pink, green, gray, or blue-gray in color."

The terminology used in this study follows that presented by Carozzi[4], with some modification. He stated, "though cherts appear to be of high polygenetic character, they nevertheless display definite relations to their host rocks, which permit the outline of a broad classification. In each of the larger lithological groups that will be distinguished, it is possible to establish secondary subdivisions according to the stages in the mineralogical evolution of the cherts from the amorphous opaline gel, through cryptocrystalline chalcedony and quartz, to a pseudomicroquartzitic texture."

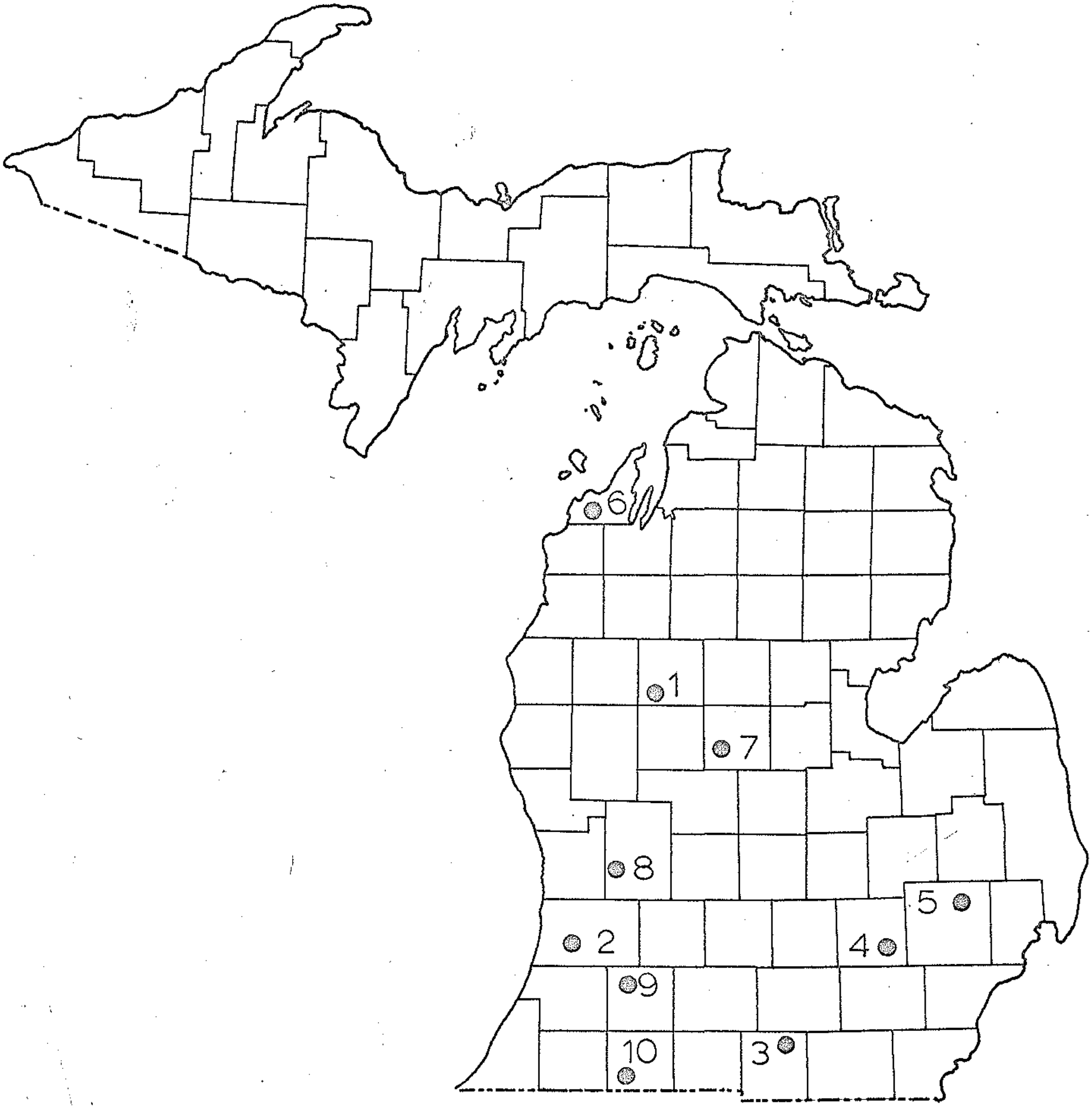
Briefly, cherts are siliceous rocks with a variable silica content; their texture and structure depending upon how, when, and where the silica was deposited, and to what degree of diagenesis it was subjected. The most common impurities are Al_2O_3, Fe_2O_3, $CaCO_3$, $MgCO_3$, Fe_2S, and carbonaceous material. Despite the variability in cherts, it is possible to use a qualitative and semiquantitative classification for descriptive purposes. In this study, a code system is used to simplify analysis of the data.

To clarify the designations of flint and novaculite, both of which are associated with carbonate rocks[4], the former is regarded as a carbonaceous chert, while light-colored novaculite is considered as a pure chert which has been subjected to pressure with subsequent recrystallization. Other than for the color differences due to carbonaceous pigmentation, flint is of cryptocrystalline texture and often contains organic remains, while novaculite possesses a microquartzitic texture.

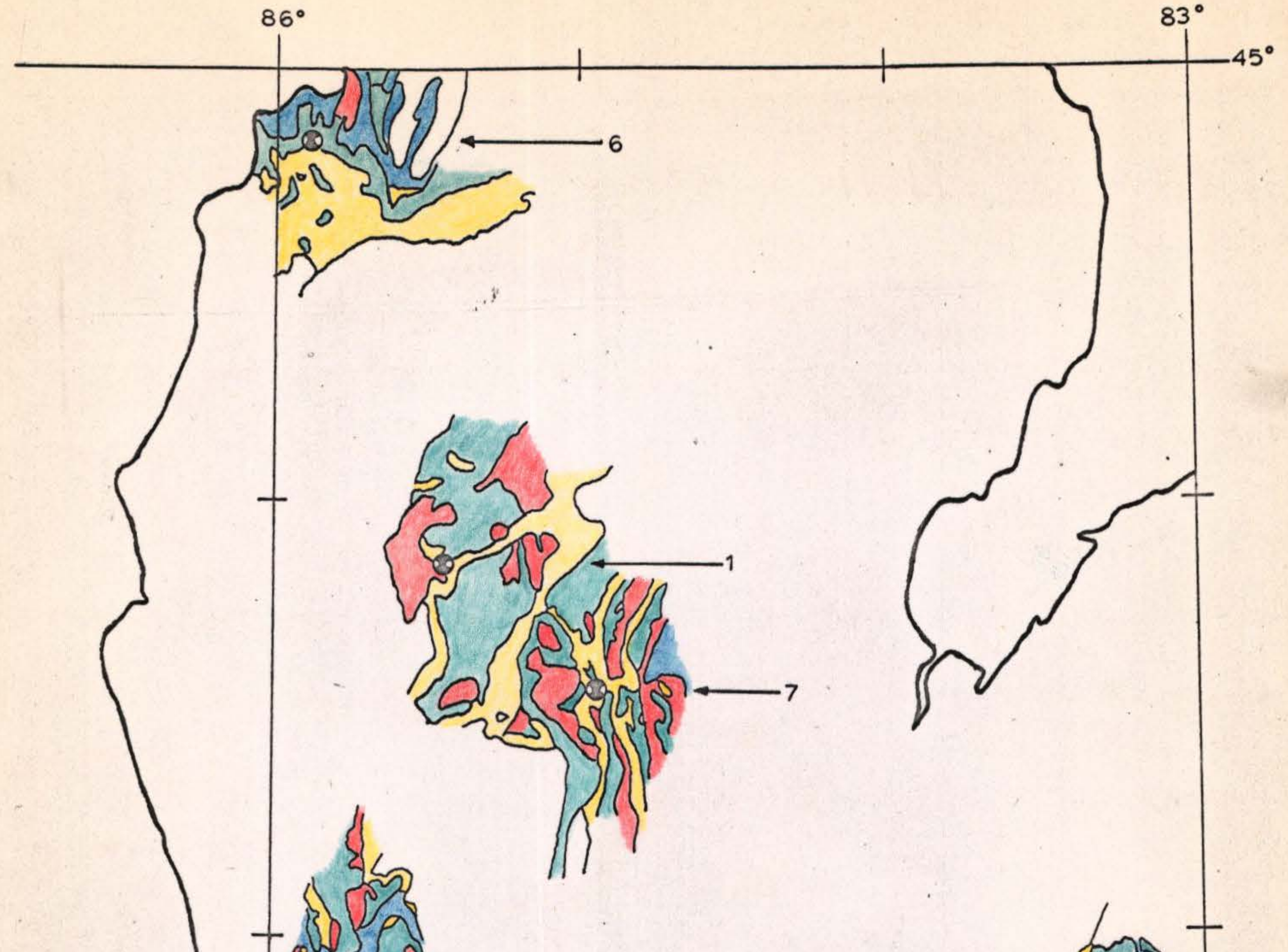
Sample Sources

For the purpose of this study, the Michigan State Highway Department collected and submitted chert samples from ten different aggregate sources in Michigan. The approximate locations of these sources are shown on Maps 1 and 2.

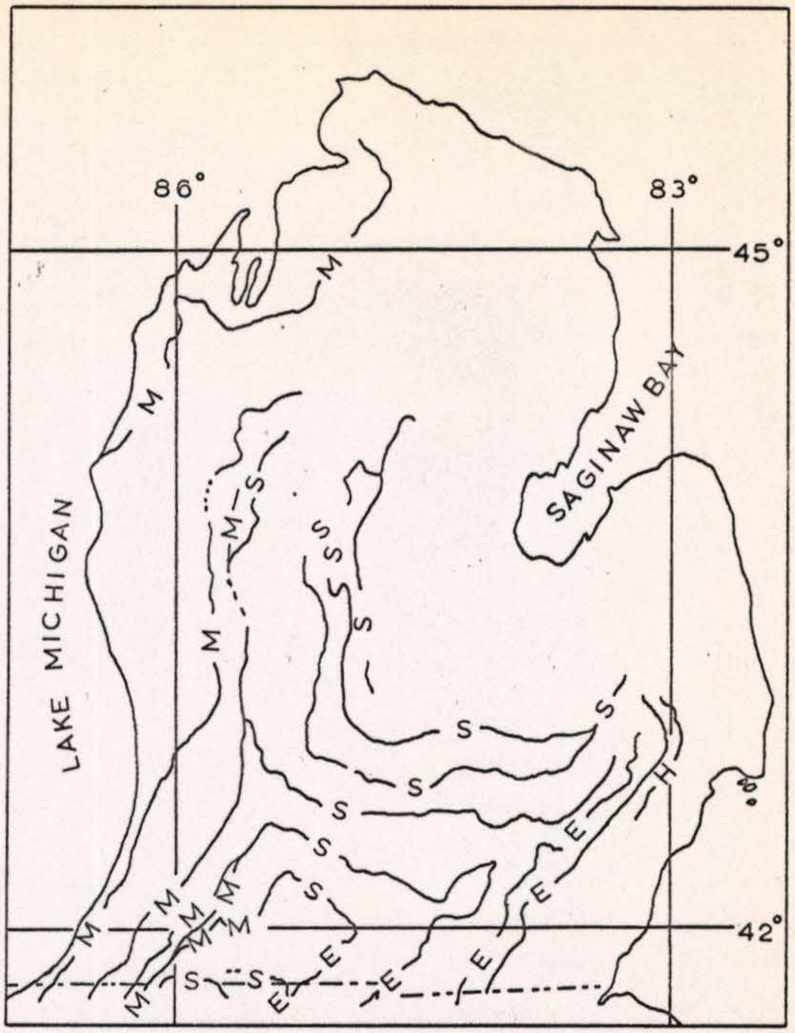
Map 1 shows the locations with respect to counties, and Map 2 shows the approximate positions of the sample sites in relation to the Pleistocene glacial lobes and associated sediments or moraines as designated in Figure 1. Only approximate locations are shown since no attempt is made to determine the relative abundance of deleterious chert either on a pit-to-pit basis or by association with any sedimentary feature. Although samples from all locations were used in various portions of this study, the cherts selected for detailed evaluation came from Locations 1 through 5.



MAP 1 -- MAP OF MICHIGAN LOCATING SOURCES OF CHERTS USED IN THIS STUDY



MAP 2 -- MAP SHOWING SAMPLE LOCATIONS AND ASSOCIATED GLACIAL MORAINES



EXPLANATION

← LOCATION NUMBER

● SAMPLE LOCATIONS

M — LAKE MICHIGAN LOBE

E — ERIE LOBE

S — SAGINAW LOBE

H — HURON LOBE

🟦 LACUSTRINE SEDIMENTS

🟨 OUTWASH SEDIMENTS

🟧 ICE CONTACT STRATIFIED DRIFT

🟩 END MORAINES OF WISCONSIN AGE

🟥 DRIFT, OTHER THAN END MORAINES AND OUTWASH, OF WISCONSIN AGE

FIGURE 1 -- KEY TO MAP 2 AND APPROXIMATE POSITION OF THE MORAINE BUILDING FRONTS IN SOUTHERN MICHIGAN

Information for preparing Map 1 was obtained from "Mineral Production Map, 1961" published in Michigan Mineral Industries 1961 by H. O. Sorensen and E. T. Carlson, Michigan Geological Survey Division. The approximate locations of the ten gravel deposits sampled were plotted from information supplied by the Michigan State Highway Department. Map 2 and accompanying Figure 1 were taken from "Map of the Surface Formations of the Southern Peninsula of Michigan" by Helen M. Martin, Publication 49, 1955, Michigan Geological Survey Division, and from "Glacial Map of the United States East of the Rocky Mountains," published by the Geological Society of America, first edition, 1959.

The cherts were collected from gravel deposits of Pleistocene age. They were probably derived from Paleozoic formations which border the Michigan Basin and Hudson Bay area, and thus have been subjected to considerable movement within the area during the different stages and substages of the Pleistocene.

Except for some of the smaller pebbles, most of the cherts could be classified as being associated with carbonate rocks. Dolomite and limestone are abundant in the cherts and the cherts often grade into these carbonate rocks.

The samples sent to the Institute contained a variety of types or kinds of cherts in three sizes according to the Wentworth-Udden grade scale: pebbles, cobbles, and boulders. In most cases, a sufficient quantity of chert boulders was available so that equidimensional cores could be drilled from them to facilitate the study.

On the basis of exterior appearance, the assumption was made that the cherts of cobble and boulder size would be identical in composition to the pebbles. Portions of individual pebbles were sufficient to supply samples for chemical analysis, thin sections or polished sections, and differential thermal analysis. The large cherts were of sufficient size to furnish samples for alkali-reactivity and freeze-thaw tests, for cutting cores for the physical property measurements, and for the other purposes previously listed.

Specimens of dolomite and of iron-bearing clays from Lower Michigan aggregate deposits were also prepared for comparative purposes in this study so as to have the extremes of durability in the proposed freeze-thaw tests. The procedures for preparation, primary classification, and determinations of the various properties of these control specimens were the same as those used for the chert cores.

Classification of Cherts

The chert samples from each location were prepared and classified as they were needed for the study. All the large (plus 2 inch) and small cherts first were checked for surface coatings. Preparation of the larger cherts involved diamond sawing to facilitate the initial classification according to specific gravity in the sink-float vessels. Felker diamond core drills and saws were then used to prepare 3/4 inch diameter by 3/4 inch long cores from the sawed pieces so that measurements of physical properties could be made by nondestructive methods on equidimensional pieces.

The initial classification consisting of heavy liquid separation using a mixture of carbon tetrachloride and tetrabromoethane was perfomed on all the large chert pieces prior to coring and on the minus 2-inch chert pebbles that were eventually to be used in freeze-thaw experiments. These cherts were separated into the following specific gravity groups: less than 2.40, 2.40-2.50, 2.50-2.60, and greater than 2.60.

MACROSCOPIC AND MICROSCOPIC FEATURES OF CHERTS

Classification of Cored Cherts by Appearance

The cores from the chert boulders were classified into four groups by appearance, as illustrated in Figure 2. The basis of the classification follows:

Group 1 -- Chalky white or light colored

- a. white to light hues of yellow and brown
- b. dull to subvitreous luster
- c. homogeneous color and texture

Group 2 -- Mottled

- a. mottled white with darker hues of yellow, blue-gray, gray, brown, or black
- b. white portions dull or earthy
- c. darker areas usually subvitreous

Group 3 -- Dense and light colored

- a. light hues of blue-gray, gray, brown, or black
- b. indications of nodular character
- c. usually vitreous

Group 4 -- Dense and dark colored

- a. dark hues of reddish-brown, gray, brown, or black
- b. reddish-brown variety usually dull in luster
- c. gray, brown, and black varieties ordinarily vitreous

Obviously, surface features and original shape are lost as a result of core preparation, but other significant features are retained.

Classification of Chert Pebbles by Appearance

Selected chert pebbles were classified into four appearance groups, as illustrated in Figure 3. The basis for this classification follows:

Group 1 -- Chalky white

- a. white or light gray in color, occasionally light tan
- b. very porous
- c. displays surface irregularities and fractures
- d. breaks with irregular fracture
- e. well-rounded to subrounded shape
- f. commonly displays fossil remnants

Group 2 -- Mottled

- a. mottled gray, shades of green, brown, and black
- b. semiporous
- c. breaks with irregular to subconchoidal fracture
- d. subrounded to subangular shape
- e. often displays fossil remnants
- f. fractures generally cemented with calcite

Group 3 -- Dense and light-colored exterior

- a. includes white, light grays, and browns (may have white, chalky exterior)
- b. breaks with subconchoidal to conchoidal fracture

c. subrounded to angular shape

d. sometimes rounded or nodular in appearance, like flint

e. fractures usually healed

Group 4 -- Dense and dark hued

a. hues of blue-gray, brownish-black, reddish-brown, brown, and gray and black

b. subvitreous, vitreous, or waxy

c. displays smooth surfaces

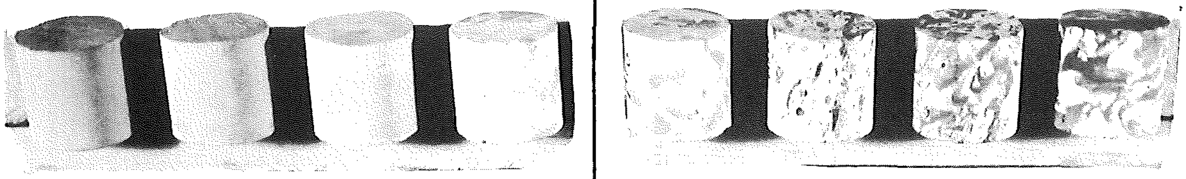
d. usually subconchoidal to conchoidal fractures

e. usually subrounded to subangular shape

f. fractures often healed

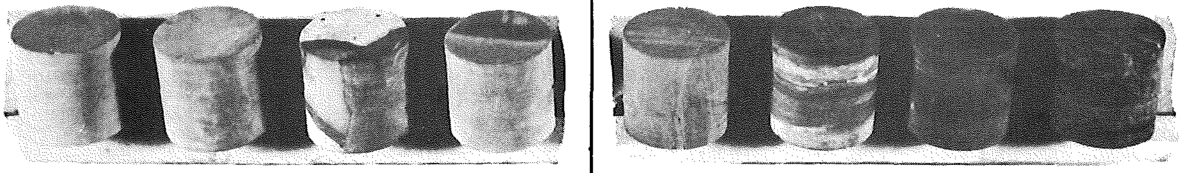
Demarcation between appearance groups is not well defined; however, classification by appearance provides a visual method of selection and reference and useful information for field testing procedures. The angularity description approximates that defined by Pettijohn[5].

One of the significant macroscopic features of the cherts is the wide variation in appearance. It might be anticipated that the microscopic features of texture, structure, and composition would also display inhomogeneity. With respect to composition, Schuster and McLaughlin[6] found that southern Indiana chert gravels contain more limonite ($2Fe_2O_3 \cdot 3H_2O$) than gravels from the northern part of the state. Comparisons of the soluble iron contents of the chert cores from random locations more southerly than Location 1 show a similar trend in Michigan (see Table 1 of Appendix A and Map 2).



1 - WHITE, CHALKY

2 - MOTTLED



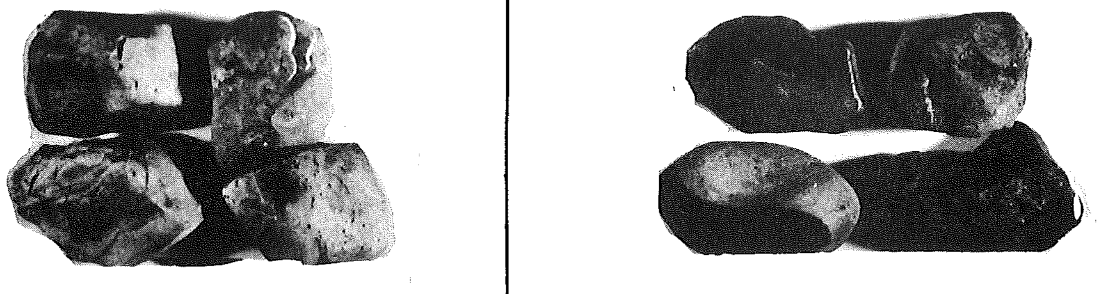
3 - DENSE, LIGHT COLORED

4 - DENSE, DARK COLORED

FIGURE 2 - THE FOUR CHERT APPEARANCE GROUPS

1 - WHITE, CHALKY

2 - MOTTLED



3 - DENSE, LIGHT COLORED

4 - DENSE, DARK COLORED

FIGURE - 3 THE FOUR CHERT APPEARANCE GROUPS

Microscopic Examination and Classification

The polarizing microscope has been frequently used to determine the suitability of aggregate by evaluating certain physical and chemical properties[7, 8, 9, 10]. Investigation of cherts with the petrographic microscope has led to the conclusions that their physical unsoundness is due to porosity and incipient fractures[11], specific ranges of pore sizes encountered in lightweight cherts[6], and irregularities of texture[12].

The microscopic study of cherts in this project originally was to include quantitative measurements of pore size distributions. Preliminary examination of thin sections using a Leitz-Wetzlar microscope revealed that the majority of visible pores were larger than 30 microns in diameter. In some lightweight cherts which should have been porous, according to their specific gravity and chemical composition[6], no porosity was observed. It was concluded that the pores were submicroscopic in these cryptocrystalline and microcrystalline varieties of silica[13]. Since the pore sizes and distributions could not be determined with the microscope, the porosities of the chert cores and pebbles were measured by volumetric displacement[14] prior to cutting thin sections.

The chemical composition of chert can be highly variable[4, 5]. The chert may have varying proportions of opal, quartz, calcite, dolomite, and accessory minerals such as the clays, sericite, limonite, siderite, ankerite, or pyrite. Although cherts normally contain at least 50% silica, the thin-section observations and comparative data from calculated mineral compositions showed that this criterion was not always met due to an abundance of calcite or dolomite in the samples. A large proportion of the samples from all size classes showed a transition from a porous siliceous exterior to an interior with a percentage of carbonate frequently exceeding 50%. Thus, these cherts were predominantly associated with carbonate rocks. Preliminary inspection of the carbonate content in thin sections stained with hematoxylin[15] showed that the distinguishable fossils were usually composed of calcite. Euhedral carbonate occurring in the same sections (unstained by this method) was assumed to be dolomite[16], and this relationship was used throughout the thin section study to identify the mineral constituents. The carbonate-rich rocks were identified as potential cherts, which would have been more fully developed if diagenesis by replacement had continued.

Organic structure is related to texture. To classify the cherts by texture, it is necessary to adopt an arbitrary system related to the mineralogy. The difficulty lies in describing the mixed gradations in silica textures, the fine-grained silica occurring in chalcedonic, opaline, cryptocrystalline, microcrystalline, and granular or granoblastic (equigranular due to diagenesis) forms. The classification by texture was clarified by first placing a chert in a major rock group, and then by listing the primary and secondary textural characteristics of the two major constituents.

Petrographic Classification of Cherts

The four major divisions in the classification of chert as outlined by Carozzi[4] are based on whether the chert occurs in association with siliceous rocks of organic origin, carbonate rocks, clastic rocks, or evaporites. The host rock of the smaller pieces used in this investigation was not available but may readily be inferred from the cored cobbles and boulders to be limestone or dolomite. Classification was accomplished by determining the subgroup (variety of chert) according to the texture, structure, and composition observed in thin sections. No cherts positively associated with clastic rocks or evaporites were identified.

The difference between texture and structure has been defined by Pettijohn[5]:

> "Texture is the size, shape, and arrangement of the component elements of a sedimentary rock. These properties are geometrical. Unlike texture, structure deals with the grain to grain relations; structure takes account of such features as bedding, ripple marking, and the like. Texture is commonly studied in thin section, in the hand specimen, or by analysis of a small sample. Structure, on the other hand, is usually studied in the outcrop, less commonly in the hand specimen or thin section."

A number of mechanical, organic, and chemical structures may be present in cherts. Those of principal interest were defined to the extent practicable by observations of thin sections. Mechanical structures include fractures and pores. Micro and macro fractures in the cherts may be open, or sealed by secondary mineralization. The former were more frequently observed in this study. Secondary mineralization in fracture zones may occur as carbonate or some micro form of silica. Porosity was usually observed only where dissolution of carbonate had taken place or where silicification of fossils was incomplete. Laminations were sometimes observed in the cherts; the transitions between zones which were principally siliceous and zones which contained a greater percentage of carbonate were marked by porous areas. Contraction phenomena in cherts, noted by Taliaferro[17] and supposedly due to volume changes in the conversion of opal to quartz, were not observed. The open fractures observed in some cherts of this study are presumed to have resulted from mechanical action due to transportation and subsequent frost action.

Cherts Associated With Siliceous Rocks. The cherts occurring in association with siliceous rocks were found to be characterized by the remains of siliceous sponges, radiolaria, and diatoms. These cherts best illustrate the variations in the texture of silica which may be observed in thin sections, ranging from isotropic areas which may be opaline to normal quartz. The microforms of silica occurring in chert are described according to optical properties as follows:

a. Granular, granoblastic, or mosaic quartz -- grains are greater than 5 microns in diameter, are equidimensional, and some exhibit undulatory extinction; the texture is assumed to be due to diagenesis;

b. Microcrystalline quartz -- average grain size is 3 to 5 microns, and may exhibit undulatory extinction due to intracrystal strain;

c. Cryptocrystalline silica, somewhat isotropic -- clear to yellowish-brown in plane light, but under crossed nicols, pinpoint birefringence colors of quartz may be observed within isotropic areas; this designation includes quartz below the 3 to 5 micron range of microcrystalline silica, possibly admixed with opal;

d. Chalcedonic quartz -- fibrous appearance in polarized light, colorless to brown in plane light;

e. Opal -- isotropic, colorless, pale gray or brown in plane light; cloudy under crossed nicols.

This classification is applied only to those cherts exhibiting abundant siliceous organisms and cryptocrystalline or microcrystalline silica; however, small amounts of carbonate were noted. If diagenesis has resulted in complete recrystallization of the silica to the granoblastic variety and the original fossils can no longer be distinguished, the chert is classified as a pure chert associated with carbonate rocks. Only 11 of 125 thin sections examined could be identified as spiculitic or radiolarian (i.e., siliceous) cherts; the remaining cherts were those associated with carbonate rocks.

<u>Cherts Associated With Carbonate Rocks.</u> The cherts occurring with carbonate rocks have a large range of petrographic features. Variations in quartz texture may be present in the same manner as described for the cherts associated with siliceous rocks; however, the quartz is usually microcrystalline or granular. A common feature of these cherts is a variable proportion of unreplaced carbonate residue, leading to a nomenclature ranging from highly impure calcareous to pure cherts.

The calcite is present primarily as unreplaced fossil remnants, although it may occur as minute grains, possibly representing relics of limestone inclusions[18]. The rhombic carbonate is usually identified as dolomite; however, euhedral carbonate may occur in chert as siderite, ankerite, or calcite[17]. Other accessory minerals such as clay, pyrite, or limonite may be present in cherts associated with either carbonate or siliceous rocks.

Calcareous cherts are identified by an abundance of unreplaced fossil remnants. The most abundant microforms of quartz are usually microcrystalline or granoblastic, but these microforms may in some cases be subordinate to chalcedony. Anhedral and euhedral carbonate was often noted in the siliceous groundmass.

Macroscopically, the pure cherts appear light to gray in color and may be mottled[19]. Microscopically, the pure cherts are those consisting primarily of chalcedonic, microcrystalline or granoblastic quartz, with calcite occurring only as minute grains disseminated throughout the silica and recognizable only by the interference colors. A few euhedral rhombs of dolomite may constitute an impurity[20]. A number of cherts in this class were noted to be highly porous due to complete or partial dissolution of carbonate rhombs. These euhedral areas were rimmed with an opaque constituent identified as limonite[6, 17].

The flints (carbonaceous cherts associated with carbonate rocks) are assigned to either the calcareous or pure chert groups since the primary difference is only a matter of color. Novaculite is a pure chert with a well-developed microquartzitic texture; rhombohedral cavities may be present[21]. The porous cherts with rhombic cavities, previously described, closely resemble novaculite but display more variety in texture.

The rhomb-bearing cherts are those varieties usually displaying siliceous pseudomorphs after rhombohedral carbonate[17]. The pseudomorphs may be composed of quartz polarizing as a single crystal, mosaic quartz, chalcedony, or iron-bearing minerals. The small and well-formed rhombs are embedded in translucent or opaque siliceous cement. This definition does not precisely fit all the rhomb-bearing cherts categorized in this study. For descriptive purposes, some calcareous cherts not exhibiting fossil remnants and marked by abundant euhedral dolomite, are assigned to this particular subgroup. The silica is usually cryptocrystalline but may range to the coarse granular variety. Dissolution of the carbonate would result in a pure chert.

The spherulitic cherts are characterized by opalescent spheres with limonite nuclei or minute rhombs in the centers. Some varieties which are red, brown, or black with white patches of silica are composed of spherulitic chalcedonic silica[17]. The orbicular chalcedony is associated with acicular grains of granular quartz discolored by red iron impurities.

For petrographic purposes, two major classifications of cherts are set up, based on the original nature of the host rock. The subgroup, or particular chert variety, within each classification is designated primarily on the basis of composition and secondarily on texture. No descriptions are given for subgroups of major classifications not observed in thin section. The cherts associated with siliceous rocks are commonly of the spiculitic variety; only one radiolarian chert was noted. The cherts associated with carbonate rocks are largely of the calcareous and pure variety; some rhomb-bearing cherts were identified, but spherulitic cherts were rarely noted.

The principal advantage of this classification is the manner in which a limestone or dolomite may be designated as a calcareous or rhomb-bearing chert, although the silica content as observed in thin section may be less than 50%. A serious disadvantage of the classification is the failure to take full account of the inhomogeneous nature of chert; gradations of cherts occurring within single specimens preclude positive qualitative or quantitative description.

The microscopic work included preparation and study of 125 thin sections; 27 sections were photographed in plane or polarized light. Ten photomicrographs selected to illustrate important features of the cherts in thin section are shown in Appendix B.

PETROGRAPHIC CODE CLASSIFICATION

In an effort to facilitate the presentation of the data accumulated in the microscopic portion of this study and for purposes of reference, correlation, and computations, a petrographic code was devised for summarizing this data.

The petrogenetic association and the primary and secondary mineral constituents, determined microscopically and described as to texture, furnish the first three digits in the petrographic code classification. The subgroup variety of chert is designated by letters at the end of the code number and can be digitized at a later time if necessary for digital computer computations. The remaining digits designate the structural or potential alkali-reactivity features observed in thin or polished sections. The code descriptive terms and corresponding numbers or letters are listed below.

PETROGRAPHIC CODE KEY

Code Description	Code Number or Letter
I. Petrogenetic Classification	
Chert associated with siliceous rocks	1
Chert associated with carbonate rocks	2
Chert associated with clastic rocks	3
Chert associated with evaporites	4

PETROGRAPHIC CODE KEY (continued)

Code Description	Code Number or Letter
II. Most abundant mineral and texture	
Microcrystalline quartz	1
Granular, granoblastic, or mosaic quartz	2
Chalcedonic silica	3
Opal (hyalite)	4
Cryptocrystalline or isotropic silica	5
Carbonate as fossiliferous remnants	6
Carbonate, anhedral to euhedral, as matrix	7
Accessory minerals, principally ferruginous	8
III. Secondary mineral	
Same list as for most abundant mineral	
IV. Predominant fracture type	
No fractures	1
Fractures filled with carbonate	2
Fractures filled with chalcedony	3
Fractures filled with microcrystalline quartz	4
Fractures filled with granular quartz	5
Open fractures of mechanical origin	6
V. Porosity class (in percent)	
0-5	1
5-10	2
10-15	3
15+	4

PETROGRAPHIC CODE KEY (continued)

Code Description	Code Number or Letter
VI. Fracture index class*	
No fracture visible	0
1-5	1
6-10	2
11-15	3
16-20	4
21-25	5
26-30	6
31-36	7
36+	8
Not determined	9
VII. Alkali-reactivity	
Not determined	0
Reaction indicated	1
Reaction not apparent	2
VIII. Variety of chert	
Spiculitic	S
Red radiolarian	RB
Calcareous	C
Pure	P
Rhomb-bearing	R
Spherulitic	SP

---

* Numbers denote length of fracture per square inch of area in 1/16 inch units.

An example of the petrographic code classification for Core No. 214 follows:

Code 2216412P

2 - chert associated with carbonate rocks
2 - principal mineral, granoblastic quartz
1 - secondary mineral, microcrystalline quartz
6 - open fractures of mechanical origin
4 - porosity greater than 15%
1 - less than 5/16 open fractures per square inch
2 - alkali-reactivity not noted
P - pure chert

Predominant Fracture Type

Open fractures are frequent in the thin sections; however, other fractures may be sealed with secondary carbonate or silica of the chalcedonic or crystalline variety. If minerals are present in the fractures, they usually do not vary throughout the section. The mineralized fractures commonly transect a chert and may form networks. Open fractures in the pure cherts exhibiting rhombs due to dissolution generally increase in number toward the border of the particle. Care was exercised in distinguishing between open fractures of constant width and irregular fractures near the border which might result from improper preparation of the thin section. The purpose of setting up the predominant fracture type in the petrographic code was to delineate the cherts which contained structural imperfections according to composition and texture.

Porosity Estimation

An estimation of porosity is included in the code to supplement the measurements made by pycnometer. The porosities determined from the thin sections were intended for delineation similar to that for the predominant fracture designation, and their values assigned are ordinarily considerably less than those determined by pycnometer or mercury porosimeter measurements because of the abundance of submicroscopic pores. The submicroscopic porosity may be measured volumetrically in large samples but is not usually observable with the microscope at the available magnifications even if the oil immersion technique is used. The porosity of the chert pebbles was determined on the basis of absorbed water after a prolonged soaking period.

Fracture Index

The fracture index in the petrographic code furnishes a quantitative method of classifying the areal distribution of open fractures or open fractures which are filled with a porous material capable of absorbing an organic dye. The procedure for determining the index involved measurements of fracture lengths per unit area of specimen. A number of specimens remaining from the cored cherts was embedded in cement paste slabs. Information about mix proportions, curing period, and other procedures for these slabs is included in the following section on alkali-reactivity. The slabs were cut by diamond saw, exposing surfaces of the embedded particles previously marked for position. The surface area of the exposed particles was measured by planimeter before immersing the sectioned slabs in methylene blue to expose structural features in the chert[16]. The lengths of the fractures as marked by the dye penetration were measured directly by means of an American Optical microscope at 30x, to the nearest sixteenth of an inch, using a scale marked in thirty-seconds of an inch. A neutral solution of water and methylene blue should be maintained in this procedure; if the solution becomes alkaline, dolomitic areas will become stained[22] and possibly interfere with fracture detection.

The principal disadvantage in this quantitative measurement is the apparent lack of correlation between data acquired from the polished section, the thin section, and the core due to variations within individual samples of chert.

Alkali-reactivity

The alkali-reactivity indication designated in the petrographic code was determined on the embedded chert aggregate employed in the fracture index measurements. Eighty-four chert particles from Locations 1 through 5 were placed in four slabs of cement paste made with a 1:2 water-cement ratio by weight. Two of the slabs were made with Type 1 cement (regular portland) and two with Type A (air-entraining portland). The position of each previously numbered particle was marked on the surface of the slab. After curing seven days in the 100% relative humidity room, the slabs were soaked in a 0.1 molal sodium hydroxide solution for 14 days. The solution was allowed to evaporate, and the slabs were moistened with tap water for 21 days to prevent dehydration of the paste. After cutting the slabs with a diamond saw, every chert specimen revealed an unweathered portion of the border which had previously been cut while coring or preparing a thin section. If this unweathered portion of the chert displayed an abnormal transition in color, the chert was designated as possibly reactive in alkaline solution. Alkali content of the cement and solution becomes important if laboratory experiments are to be realistically representative of field conditions.

The basis for petrographic determination of alkali-reactivity indications has been presented by other investigators. Alkali etching tests supplemented with microscopic examinations of aggregate particles have been outlined by Parsons and Insley[23] and also Tremper[24]. Tremper performed mortar-bar expansion tests and freeze-thaw tests in conjunction with numerous chemical testing procedures; all tests indicated that the aggregate was reactive with high alkali-cement; however, only the mortar-bar test and the freeze-thaw test indicated that the aggregate was sound in concrete of low alkali content.

Opaline cherts, chalcedonic cherts, and siliceous limestones are known to be reactive in alkali solutions. Stanton[25] concluded, "Undoubtedly opaline shales and cherts are acted upon by the caustic reaction products of cement with the formation of sodium or potassium silica gel."

Recognition of cement-aggregate reaction in thin section or hand specimen may be accomplished by observation of silica gel formation or the presence of alteration rims on certain rock types[26]. Further studies by Hadley[27] and Bisque and Lemish[28] showed that reaction may also occur in the carbonate rocks, principally in the argillaceous dolomitic limestones. Hadley[27] presented the dedolomitization reaction as:

$$CaMg(CO_3)_2 + 2MOH \longrightarrow M_2CO_3 + Mg(OH)_2 + CaCO_3$$

with M representing potassium, sodium, or lithium. Expansion accompanies the chemical reaction. Bisque and Lemish[28] also noted the presence of reaction rims in their study of Iowa limestones.

Reaction rims, if properly interpreted, can serve as a visual method for the identification of deleterious siliceous or carbonate rocks. The interpretation is based upon distinguishing whether a transition in color on the border of aggregate particles is due to normal weathering or induced chemical reaction. The experimental procedure was designed to furnish an unweathered border for microscopic observation and provide the information for the designation of possible reactivity as presented in the petrographic code.

CHERT PROPERTY MEASUREMENTS -- PROCEDURES AND EQUIPMENT

The tests and procedures used to determine those properties that might influence the durability of cherts when used in concrete are described in this section. Measurements were made on equidimensional chert cores, or a fraction thereof, to determine chemical composition, specific gravity, effective porosity, pore size distribution, permeability, water absorption and absorption rate, water saturation, tensile strength, and elastic constants. Other measurements were made on extra chert cores, on chert pieces assumed to be representative of the chert cores, or on minus 2-inch pebbles; these measurements consisted of alkali-reactivity, differential thermal analysis, and preliminary freeze-thaw tests, which varied both in purpose and technique. The extensive petrographic study of thin sections of many of the chert cores and pebbles has already been described.

Chemical Composition

In a preliminary study of thin sections prepared from some of the chert pebbles, it was noted that the principal minerals present were quartz, calcite, and dolomite. Chemical analysis of the oxides indicated that silica was always the predominant constituent, although the abundance of calcite and dolomite observed in the thin sections suggested that carbonate-forming oxides should predominate in some cases. A more-detailed inspection of the thin sections showed that the exterior portions of some chalky white and mottled cherts were highly siliceous while the interior showed less dissolution of the carbonate minerals. Under the conditions of occurrence of the carbonate, it is noteworthy that proportionately more carbonate would be found in the plane of a thin section than would be contained in the volume selected and ground for chemical analysis. This consideration helps to reconcile the difference between the mineralogical composition calculated from the chemical analysis and the relative abundance of the principal mineral constituents observed and entered in the petrographic code. It was anticipated that discrepancies between the thin section observations and the chemical analyses of the cored cherts would be frequent, although the thin sections were cut as close to the cores as possible. Usually one-half of a pebble was taken for chemical analysis, while the portions of the chert cores taken for analysis were selected at random and more often than not included a part of the weathered exterior.

Because of the large number of chemical analyses desired and the small size of the pieces remaining after the preparation of cores, the number of oxides which could be determined was limited. The oxides SiO_2, CaO, and MgO were used to compute the mineralogical composition[29, 30]. Based on the relative abundance of dolomite and calcite in the thin sections observed, the MgO and sufficient CaO were computed as dolomite. The remaining CaO was computed as calcite. All of the SiO_2 was designated as quartz, although the presence of opal (low-cristobalite) should not be excluded. Soluble iron was determined but not used in the calculations of dolomite, limonite, or other ferruginous minerals since this would seriously complicate the mineralogy without any apparent benefit to the study.

A typical computation showing the method of converting chemical analysis to mineral composition by weight is illustrated below; the data from similar calculations are listed in Table 1.

MINERAL COMPOSITION COMPUTED FROM CHEMICAL ANALYSIS FOR OXIDES

Chemical Analysis, %			Molecular Weight		
SiO_2	=	60.4	Quartz, SiO_2	=	60.06
MgO	=	6.3	Dolomite, $CaMg(CO_3)_2$	=	184.42
CaO	=	12.6	Calcite, $CaCO_3$	=	100.08
Fe (sol.)	=	2.5	Lime, CaO	=	56.08
			Magnesia, MgO	=	40.32
			Ferric Oxide, Fe_2O_3	=	159.70

Quartz = 60.4%

Dolomite $= \frac{184.42}{40.32} \times 6.3 = 28.8\%$

CaO in dolomite $\frac{56.08}{40.32} \times 6.3 = 8.8\%$

Remaining CaO $= 12.6 - 8.8 = 3.8\%$

Calcite $= \frac{100.08}{56.08} \times 3.8 = 6.8\%$

Computed Mineral Composition, % Wt.

Quartz	=	60.4
Dolomite	=	28.8
Calcite	=	6.8
Ferric Oxide	=	3.6
		99.6

The 0.4% by weight deficiency can be accounted for as elements present in small amount but not determined in the chemical analysis.

Specific Gravity

All cherts used in this study were initially separated into four specific gravity groups using a heavy liquid mixture; however, the specific gravity for final classification of each chert core was determined with an air pycnometer of new design[31]. The specific gravity was computed as

$$\text{Specific gravity} = \frac{W + V_{Pd}}{V_B}$$

where W = Oven-dried weight

V_{Pd} = Pore volume x density of H_2O

V_B = Bulk volume

The specific gravity measurements were made on the chert cores after oven drying and cooling them to room temperature before they were placed in the pycnometer sample holder. A standard pycnometer operating procedure was followed with the following exception: after placing the sample in the holder, both were evacuated to 200 microns of mercury. The sample and holder were then flushed several times with helium before making the pycnometer measurement with this gas. With this procedure, results were reproducible within 2%.

Helium was used in the pycnometer determination as good reproducibility in measurements could not be achieved with air. It was concluded that air was adsorbed onto the surfaces of the sample, resulting in an error in apparent volume.

Effective Porosity

The effective porosity, made up of surface connected voids and expressed as the percent of bulk volume of each chert core, was determined by pycnometer using the same procedure as described for the specific gravity measurements. The percent effective porosity was computed as:

$$\text{Percent porosity} = \frac{V_P}{V_B} \times 100$$

where V_A = Apparent volume (pycnometer determination)

V_B = Bulk volume (calculated from micrometer measurements)

V_P = Pore volume = $V_B - V_A$

The porosities included in the petrographic code, made to supplement the pycnometer measurements, were computed from measurements made on chert pebbles as described in the petrographic code classification section of this report.

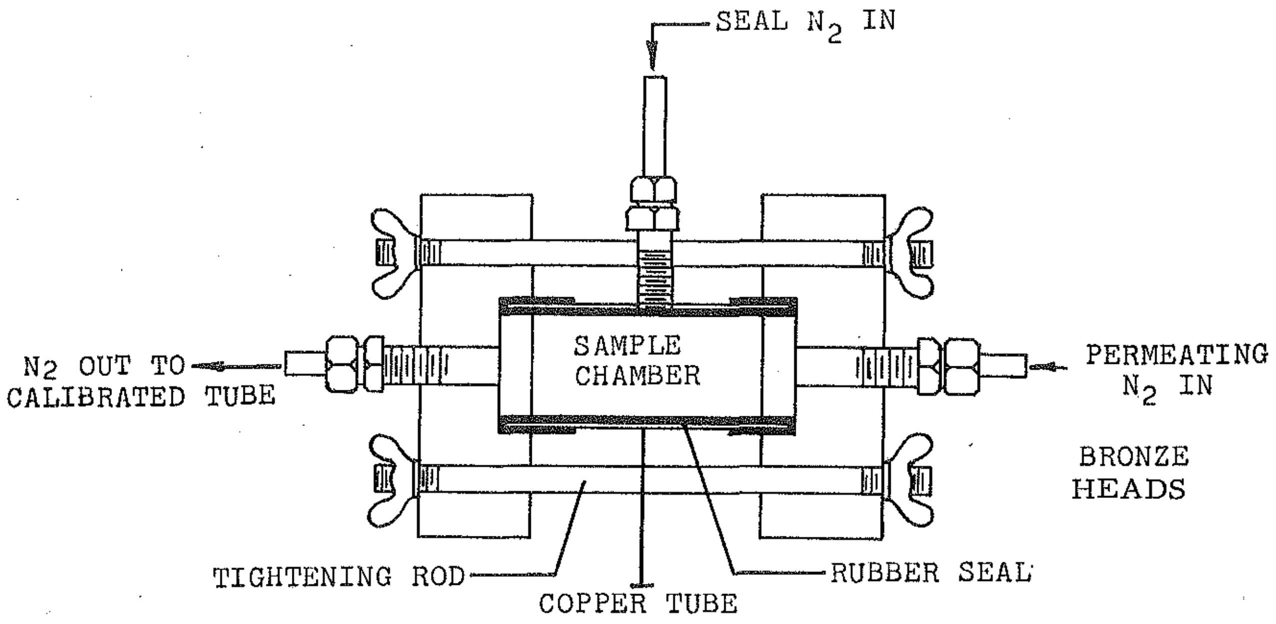
Pore Size Distribution

A 15,000-psi, Aminco-Winslow porosimeter was used to measure pore size distributions. Pore volumes as small as 0.0001 ml can be measured for decreasing pore diameters from 0.1 mm to 0.012 microns. To determine the size-volume distribution of pores smaller than 17 microns, mercury is forced into the sample at pressures varying inversely with the pore sizes. The distribution of pores from 17 to 100 microns in diameter is determined at pressures less than atmospheric by intrusion of the mercury at successive degrees of evacuation. The porosity due to pores greater than 100 microns (outside the operating limits of the porosimeter) is determined by subtracting the displacement volume as measured with the porosimeter from the bulk volume of the sample. The displacement volume is that enclosed by the outside surface of the sample less the known volume of pores of 100 microns or less in diameter. The sample bulk volume may be determined by various methods. The method used here was to measure each core with a micrometer and weigh it in the oven-dried condition. The sample cut from the core for the porosimeter determination was also weighed in the oven-dried condition, and the volume was computed on the basis of the weight ratio.

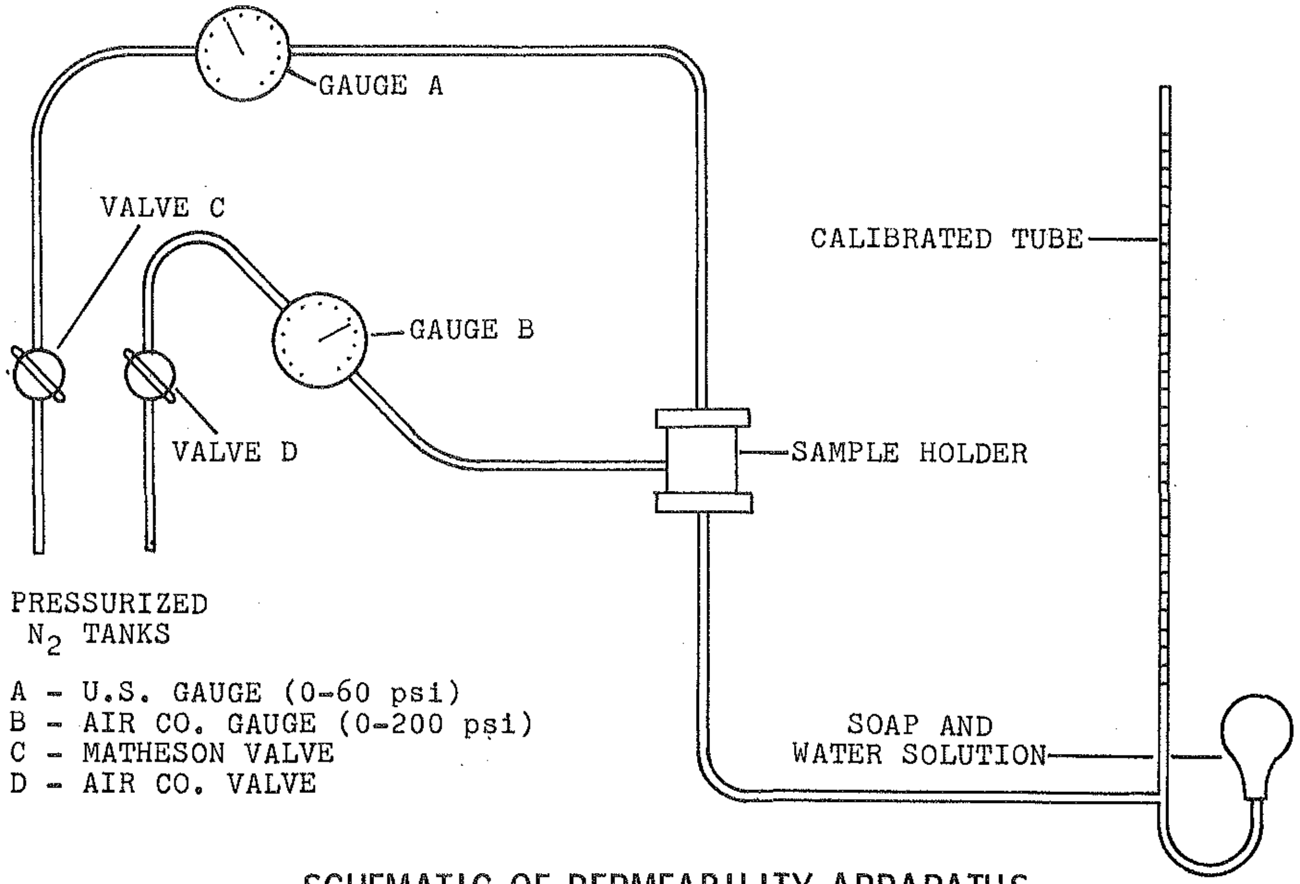
Permeability

The permeability of each chert core was determined using the apparatus illustrated in Figure 4. This permeability apparatus was built by Dr. D. O. Wyble, Professor of Physics, Michigan Technological University, and was modified for this study so that higher pressures could be applied to the cores.

The oven-dried cores that had been cooled to room temperature were placed in the rubber sleeve of the sample holder, and spacers having only point contact with the core were placed on each end, as shown in the illustration, to prohibit restriction of the core end by the sealing rubber sleeve under pressure. The sample holder was then assembled, and the tightening rods pulled down by the wing nuts sufficiently to seal the core from gas leakage. Compressed nitrogen at 160 psi (gauge pressure) was then applied to the sealing chamber. A soap bubble was introduced into the calibrated column at the outlet end of the core and observed for a sufficient interval of time to assure that there was no leakage from the sealing gas. Nitrogen was then applied at one end of the core at 40 psi (gauge pressure), and the system was allowed to stabilize for another five minutes. Another soap bubble was then introduced and the time for the bubble to pass through



PERMEABILITY APPARATUS SAMPLE HOLDER



A – U.S. GAUGE (0–60 psi)
B – AIR CO. GAUGE (0–200 psi)
C – MATHESON VALVE
D – AIR CO. VALVE

SCHEMATIC OF PERMEABILITY APPARATUS

FIGURE 4

the calibrated column was determined with a timer to 0.1 second. The time for a known volume of gas to pass through the core was measured at two-minute intervals until a constant was reached. The permeability measurements were reproducible to within 3%.

The permeability was computed using the equation described by Krutter[32]

$$K = \frac{1,000\ QPnl}{APm\,\Delta P}$$

where K is the permeability in millidarcies, Q is the gas flow through the core in cubic centimeters per second, P is the gas pressure at the discharge end of the core (usually atmospheric pressure), n is the viscosity of the gas in centipoises, Pm is the average absolute gas pressure in the core, A is the cross sectional area of the core in square centimeters, l is the length of the core in centimeters, and Δ P is the pressure difference across the core measured in atmospheres.

All the variables on the right-hand side of the equation, with the exception of n, were determined experimentally. The viscosity, n, was obtained from tables.

Absorption Characteristics

Absorption was determined according to ASTM C127-59* "Method of Test for Specific Gravity and Absorption of Coarse Aggregate." This method gives a value for absorption after 24 hours immersion in water at room temperature. The percent absorption was determined as:

$$\text{Percent Absorption} = \frac{B - A}{A} \times 100$$

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* ASTM Standards, Part 4, 1961, p. 605.

where A is the weight in grams of the oven-dried sample in air and B is the weight in grams of the saturated sample in air after surface drying.

Absorption rates were determined by immersing the individual cores in water and measuring the weight gain with time. The chert cores were oven dried at 100°C. to constant weight and allowed to cool to room temperature before measurements were made. Each core was suspended by a fine wire from a Mettler balance to make the immersed weight determinations. The change in weight with respect to time generally stabilized after 20 days, and measurements were discontinued. A typical example of the data recorded for a chert core is shown in Table 2.

The degree of saturation of the oven-dried chert cores was computed from the porosimeter and the absorption rate determinations as follows:

$$\text{Percent saturation} = \frac{\Delta W}{V_P} \times 100$$

where ΔW is the weight of water absorbed after 20 days of soaking, and V_P is the effective pore volume (surface connected voids).

Elastic Properties

Measurements of longitudinal travel times of ultrasonic pulses were made on each chert core after vacuum saturation using the apparatus shown in the block diagram in Figure 5. Phenyl salicylate was used to cement barium titanate transducers to the ends of the chert core for these measurements. The phenyl salicylate (melting point 42°C.) was melted on a piece of aluminum heated in water to 50°C. The transducers were dipped into the melted phenyl salicylate and then transferred to the ends of the

TABLE NO. 2

TYPICAL RATE OF ABSORPTION DATA RECORD

Sample No. 31: 3/4" x 3/4" chert core
Oven Dry Weight: (before) 13.92 gms. (after) 14.18 gms.
Weight of Water Absorbed in 20-day Soak: 0.26 gms.

Date 1963	Time	Wt. gms.	Cum. Change in wt. gms.	Change in Time			Abs.(1) %	Degree of Sat.(2) %
				Min.	Hour	Day		
11-25	8:35am	8.71	0	0			0	0
	8:36	8.78	.07	1			0.5	22.6
	8:40	8.82	.11	5			0.8	35.5
	8:45	8.83	.12	10			0.9	38.7
	8:55	8.85	.14	20			1.0	45.2
	9:05	8.89	.18	30			1.3	58.1
	9:35	8.92	.21		1		1.5	67.7
	10:35	8.92	.21		2		1.5	67.7
	11:35	8.92	.21		3		1.5	67.7
	12:35pm	8.92	.21		4		1.5	67.7
	1:35	8.92	.21		5		1.5	67.7
	2:35	8.93	.22		6		1.6	71.0
	3:35	8.93	.22		7		1.6	71.0
	4:35	8.93	.22		8		1.6	71.0
11-26	8:35am	8.94	.23			1	1.7	74.2
11-27	8:35	8.94	.23			2	1.7	74.2
11-28	8:35	8.94	.23			3	1.7	74.2
11-29	8:35	8.96	.25			4	1.8	80.6
11-30	8:35	8.96	.25			5	1.8	80.6
12- 1	8:35	8.96	.25			6	1.8	80.6
12- 2	8:35	8.96	.25			7	1.8	80.6
12- 3	9:05	8.96	.25	30		8	1.8	80.6
12- 4	8:35	8.96	.25			9	1.8	80.6
12- 5	8:35	8.96	.25			10	1.8	80.6
12- 6	8:35	8.96	.25			11	1.8	80.6
12- 7	8:35	8.96	.25			12	1.8	80.6
12- 8	8:35	8.96	.25			13	1.8	80.6
12- 9	8:35	8.97	.26			14	1.9	83.9
12-10	9:05	8.97	.26	30		15	1.9	83.9
12-11	8:35	8.97	.26			16	1.9	83.9
12-12	9:00	8.97	.26	25		17	1.9	83.9
12-13	10:30	8.97	.26	55	1	18	1.9	83.9
12-14	8:35	8.97	.26			19	1.9	83.9
12-15	8:35	8.97	.26			20	1.9	83.9

(1) (Weight of Absorbed Water/Weight of Oven-dried Sample) x 100

(2) (Weight of Absorbed Water/Effective Pore Volume of Sample) x 100

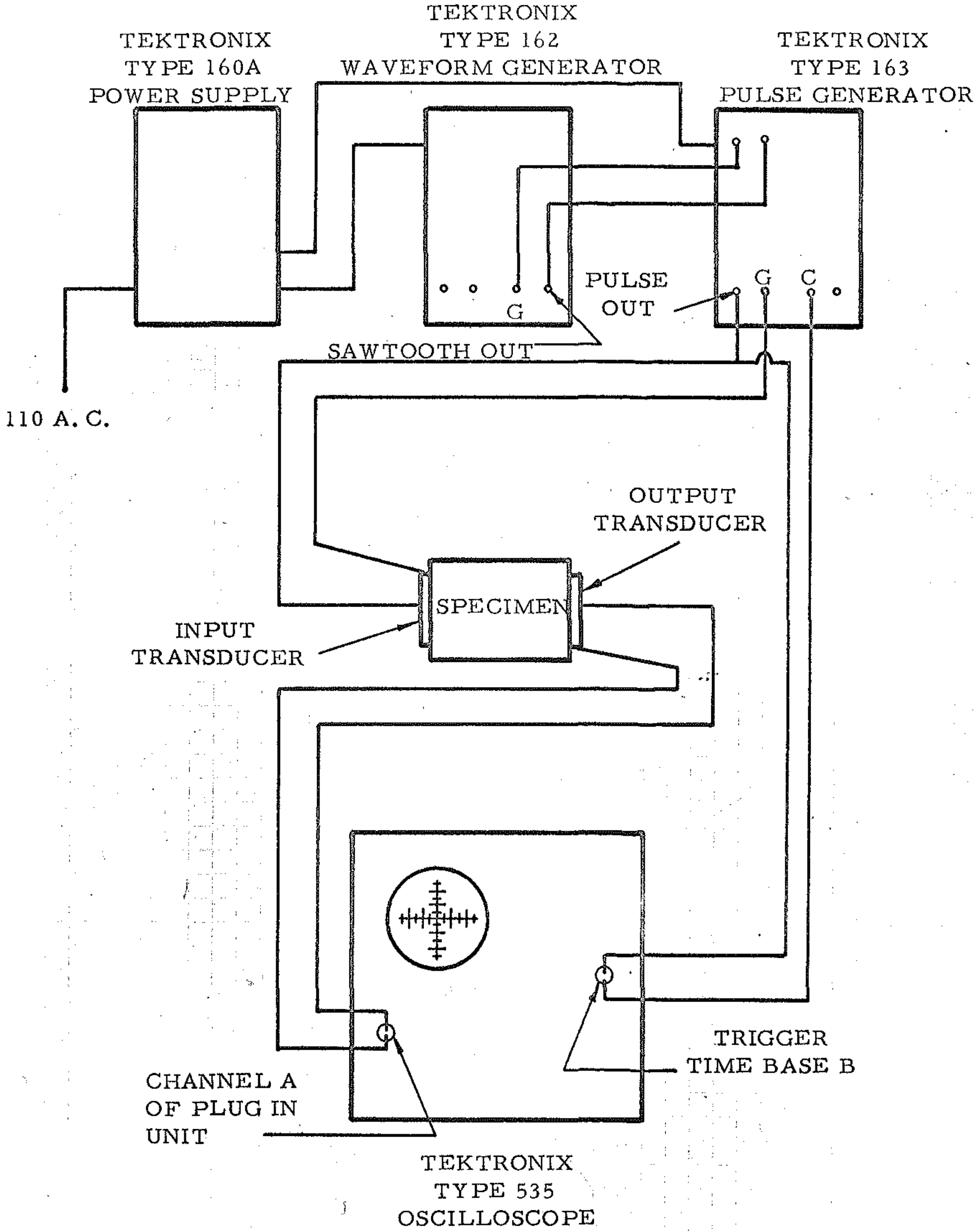


FIGURE 5 -- ULTRASONIC PULSE VELOCITY MEASURING APPARATUS

core. At room temperature, the phenyl salicylate hardened almost instantly and cemented the transducers firmly to the ends of the core. The transducers were easily removed from the core after measurement by dipping it into 50°C. water; excess phenyl salicylate was removed in the same manner.

After the transducers were cemented to the core on which a measurement was to be made, the pulse generator caused a force to be induced through a transducer at one end of the core, which was propagated as a repetitive longitudinal pulse through the chert core at a velocity computed as:

$$V_P = \left(\frac{K + \frac{4}{3}\mu}{\rho}\right)^{1/2}$$

where V_P is the velocity in centimeters per second, K is the bulk modulus in dynes per square centimeter, μ is the ridigity modulus in dynes per square centimeter, and ρ is the density of the core in grams per cubic centimeter. The pulse travel time through the core was measured in microseconds by a Tektronix 535A oscilloscope triggered at the same instant the first transducer was excited.

Tensile Strength. The tensile strength of each chert core was determined by making a diametrical compression measurement on a disc one-eighth inch thick sawed from the end of the core. A Research Product Company testing machine with micromatic pressure control was used to make the measurement. The method for determining the tensile strengths of brittle materials by diametrical compression is described by Berenbaum and Brodie[33, 34].

Alkali-reactivity

Alkali-reactivity tests were made on chert pebbles by a modification of a technique outlined by Woolf and Smith[35]; this method is based upon the expansion of mortar and aggregate confined in a glass container. The method as used here was designed to provide a rapid evaluation of materials as opposed to the measurement of mortar-bar elongation over longer periods. The principal deleterious material was chert in mortar with a water-cement ratio of 1:2 by weight. Although this procedure admittedly is not as definitive as the standard mortar-bar test, it can be concluded that a simple and rapid method of testing mortar or concrete for the alkali-aggregate reaction is furnished by the Mason jar test. A test period of 28 days appears to be sufficient for detection of aggregates which are susceptible to reaction with high alkali cement to such an extent that they would be deleterious in concrete.

The principal modifications applied to the method were the use of coarse chert pebbles, approximately 1/2 to 1 1/2 inches in size, and a variable chert-cement ratio so as to promote a more rapid reaction. Since alkali-reactivity was not anticipated, the purpose of the experiment was corroboration of the commonly accepted statement that Michigan cherts are not normally considered reactive and to suggest, through analysis of the results, the changes which are necessary to quantify the alkali content which will produce expansive reaction.

The aggregate used in this experiment consisted of pebbles of chert from Location 2. The pebbles were classified into the four appearance groups illustrated in Figure 3. The average specific gravities at saturation and the effective porosities computed for these cherts were:

SPECIFIC GRAVITY AND POROSITY OF CHERTS

Group No.	Spec. Grav., Saturated	Eff. Porosity, %
1	2.47	14.6
2	2.54	11.6
3	2.56	5.8
4	2.66	5.3

New Mason jars with self-sealing caps were obtained, and two coats of chlorinated rubbed base paint were applied to the interiors to prevent reaction between alkali and glass. Saturated chert, Type 1 portland cement, and water were mixed to fill several jars at least half full; the amounts of materials for these tests were:

CONDITIONS FOR ALKALI-REACTIVITY TESTS

Water, grams	Cement, grams	Chert, grams	Appearance Group	No. of Jars
450	900	900	1	3
450	900	900	2	3
300	600	800	3	2
275	650	470	4	2

The mixtures were cured with covers removed for 24 hours at 100% relative humidity; then water was added in the amount of approximately 50 milliliters, the covers were replaced, and the jars inverted. After curing 14 days at room temperature, one container was opened. The pH of the fluid in the jar was determined with Phydrion paper and found to be slightly greater than 12. The jars were broken open after 30 days, and the paint scraped from the specimens. A half-inch slab was then sawed from each specimen and examined with a binocular microscope for indications of silica gel.

Differential Thermal Analysis

The cryptocrystalline microforms of silica observed in some of the thin sections could not be identified specifically as opal, chalcedony, or quartz. Since these microforms may be chemically deleterious through reaction with alkali, or physically deleterious due to microporosity, differential thermal analysis determinations were made on 22 samples of chert and related siliceous rocks. The DTA curves were interpreted qualitatively for indications of opal, presence of water, and crystallinity.

A DTA furnace, Model GS-2, manufactured by Robert L. Stone Company, was used. The analyses were made in an air atmosphere and at ambient pressures, employing a constant furnace heating rate of 10°C. per minute. Platinum-rhodium thermocouples were used, with alumina as the inert material. The samples were ground in a mixer mill to minus 200 mesh (less than 74 microns). The DTA analyses were then made through a temperature range from 20° to 600°C., with the exception of one control sample of opal for which the analysis was carried only to 400°C.

Freeze-Thaw Tests

Both the polished and thin sections of chert pebbles revealed many uncemented fractures and solution channels, which would be expected to offer sites for failure under freezing and thawing conditions. To investigate the effect of these fractures under freezing and thawing conditions, chert pebbles in two sizes (minus 1 1/2 plus 3/4 inches and minus 3/4 plus 1/2 inches) were selected from each appearance group. Five pebbles were sawed in half, and one of the halves was polished and observed with the microscope for fractures. In these polished sections, 115 openings were detected. Five additional chert pebbles were then selected from each size and appearance group and subjected to freeze-thaw cycles wholly immersed in water. The cycles consisted of seven hours of freezing, a half hour of thawing with warm water, followed by 16 hours of freezing, and a half hour of thawing until 20 freeze-thaw cycles had been made.

Another group of pebbles was selected from both size classes, but from only three of the appearance groups, to study further the effect of fractures on the durability of the chert pebbles under freeze-thaw cycles. One appearance group was not included since no failure was observed in this group during the previous freeze-thaw tests. The chert pebbles selected were oven dried for 24 hours, then soaked in a methyl blue dye solution for 30 hours so that the dye would absorb into the fractures. These chert pebbles were then subjected to the same freeze-thaw procedure.

Another preliminary investigation was designed to trace the migration of water into the chert pebbles when confined in concrete slabs and subjected to freeze-thaw cycles. The chert pebbles were dried prior to being incorporated into the concrete mix and methylene blue dye was added to the mix water. A similar investigation was made to detect migration of the dye from the cherts to the mortar. In this test, the methylene blue dye was absorbed into the chert pebbles, and they were then dried prior to being mixed into the concrete which was molded into slabs.

A water-cement ratio of 1:2 by weight was used, corresponding to seven gallons of water per sack. A fine aggregate obtained locally and nonair-entraining portland cement were used in preparing the concrete containing the dyed chert pebbles. Slabs were molded in oiled pans and cured for 21 days at 100% relative humidity. After removal of the slabs from the mold, a three-eighths inch section was diamond sawed from each slab for observation of dye movement. The remaining large section of each slab was then dried for 72 hours, and soaked in water for 72 hours prior to the freeze-thaw cycles. After 12 cycles, each slab was sawed in half so that the chert pebbles could be viewed for possible deterioration.

Freeze-thaw tests were made on chert cores enclosed in concrete for familiarization with this procedure and as a basis for setting up any special procedures that might be required. A dozen concrete specimens were prepared using extra chert cores and one core of iron-bearing claystone. These cores were soaked in water until no further change in weight with respect to time was observed, and then embedded in cylindrical molds containing fresh concrete that had been hand mixed using a fine aggregate and an air-entraining portland cement in proportions of 1:3 by weight, with a water-cement ratio of approximately six gallons per sack. After a day in the moist room and 13 days of curing under water at constant temperature, the specimens were subjected to freeze-thaw cycles.

After making these preliminary freeze-thaw tests, concrete specimens were prepared to establish a standard procedure and conditions for the final freeze-thaw tests which will be made on the suite of chert cores after the physical property measurements are completed. These concrete specimens were prepared in the manner described below.

1. Coarse Aggregate.

   Both the chert cores and chert pebbles were soaked in water to constant weight.

2. Fine Aggregate.

   The fine aggregate was always placed in the mix in the condition it came from the storage bin, i.e., with natural moisture and at ambient conditions. All fine aggregate was obtained locally from the Superior Gravel Company, Hancock, Michigan. The specific gravity determined for the fine aggregate was 2.52. The grading of the fine aggregate was:

GRADING OF FINE AGGREGATE

Sieve Size (U.S.)	Percent Passing
4	96.6
8	75.3
16	55.0
30	38.5
50	16.2
100	3.3

3. Cement.

   An air-entraining portland cement was obtained locally.

4. Mixing and Molding.

The preliminary specimens, 2 1/4 inches in diameter by 2 1/2 inches long, were formed in polyethylene molds. The paste was hand mixed; the fine aggregate and cement in proportions of 1:3 by weight were thoroughly blended before adding the mix water using a water-cement ratio of six gallons per sack. Standard chert cores, 3/4 inches in diameter by 3/4 inches long, were embedded in the center of each cylindrical specimen. To determine the effect of chert particle size on concrete durability, either two pebbles, minus 1 1/2 plus 3/4 inches in size, or three pebbles, minus 3/4 plus 3/8 inches in size, were embedded in some specimens. All concrete mixtures were given the same amount of rodding within the molds, and the surfaces were struck off with a trowel.

The specimens were removed from the molds after setting 24 hours in a 100% relative humidity room and then were cured in a constant temperature bath for 13 days.

5. Freeze-Thaw Testing.

After curing, the specimens containing the chert cores were prepared for longitudinal pulse velocity measurements by diamond sawing two surfaces along the length of each specimen to facilitate mounting of the transducers. No cuts for longitudinal pulse velocity measurements were made on those specimens containing the two different sizes of chert pebbles as visual observations were to be made during the freeze-thaw tests to detect deterioration.

All specimens were brought to 10°C. in a water bath, and the initial longitudinal pulse velocities were made on the specimens containing the chert cores. Although the chert core had been centered in each specimen, the measurements were made across the diameter of the cylinder at three intervals so that velocity determinations would be obtained both through the concrete alone and through the chert core and surrounding concrete.

All specimens were then introduced to the freeze-thaw test cycles. During both freezing and thawing, the specimens were supported on a three-quarter inch screen with no contact between them. Each 24-hour cycle consisted of seven hours of freezing in air from 10°C. to -18°C., one hour thawing in water at 10°C., and 15 hours of freezing overnight before the next one hour thawing period. The temperature of the thawing water at no time exceeded 10°C.

RESULTS AND DISCUSSIONS

The petrographic data for chert cores and pebbles are summarized in Table 3 (Appendix A), using the petrographic code. The purposes and uses of this code have been explained previously.

The measurement data for the 104 chert cores are listed in Table 1 (Appendix A); these include specific gravity, effective porosity, percent absorption after 24 hours, percent absorption after 20 days, percent saturation, permeability, longitudinal pulse velocity, tensile strength, and computed mineral composition. The appearance class of each chert core is also listed.

Pore size distributions for the chert cores are shown in histograms in Figures 6a through 6l (Appendix C).

Chemical Composition

Comparison of the mineral compositions of the various cherts indicates higher silica content for the chert pebbles than for the cores, which were cut from cobbles and boulders. As previously noted, variation in oxide composition exists in the carbonate-silica zoning within a piece of chert; the usual pattern is a higher amount of porous, weathered silica in the exterior portion. Assuming that the errors due to sampling and chemical analysis are small, the two chert populations can be compared with respect to silica content on the basis of the estimated means and standard deviations. On the basis of the t test at the 5% confidence level, the null hypothesis that the means are equal must be rejected, leading to the conclusion that the populations making up the two size classes have significantly different silica contents. This conclusion is further confirmed by application of a nonparametric sign test to the classed data. Distribution plots of the chert cores and pebbles, illustrated in Figure 7, display skewness, or departure from a normal distribution for the high content classes.

An explanation of the difference in silica content between pebbles and cores is furnished by the petrographic data from the thin section study. Sixty-five percent of the sections from cobbles and boulders are characterized by some unreplaced fossil remnants while only 29% of the sections from pebbles showed such calcareous chert. Taking the class interval of 75-79% as an average silica content for all chert populations, 62% of the larger size cherts fall below this average, but only 19% of the smaller sizes have less than average silica content. On the basis of the average standard deviation for each chert population, it may be inferred that 38% of the larger size cherts and 6% of the pebble sizes fall into the classification of extremely impure cherts. If chert is defined as having a silica content of at least 50%, 26% of the larger size cherts and 2% of the pebbles must be classed as carbonates.

If the skewness noted in the silica distributions is due to the presence of subpopulations, it can be inferred that the highly siliceous subpopulation of the chert pebbles is made up of the predominant spiculitic, rhomb-bearing, and pure cherts identified petrographically.

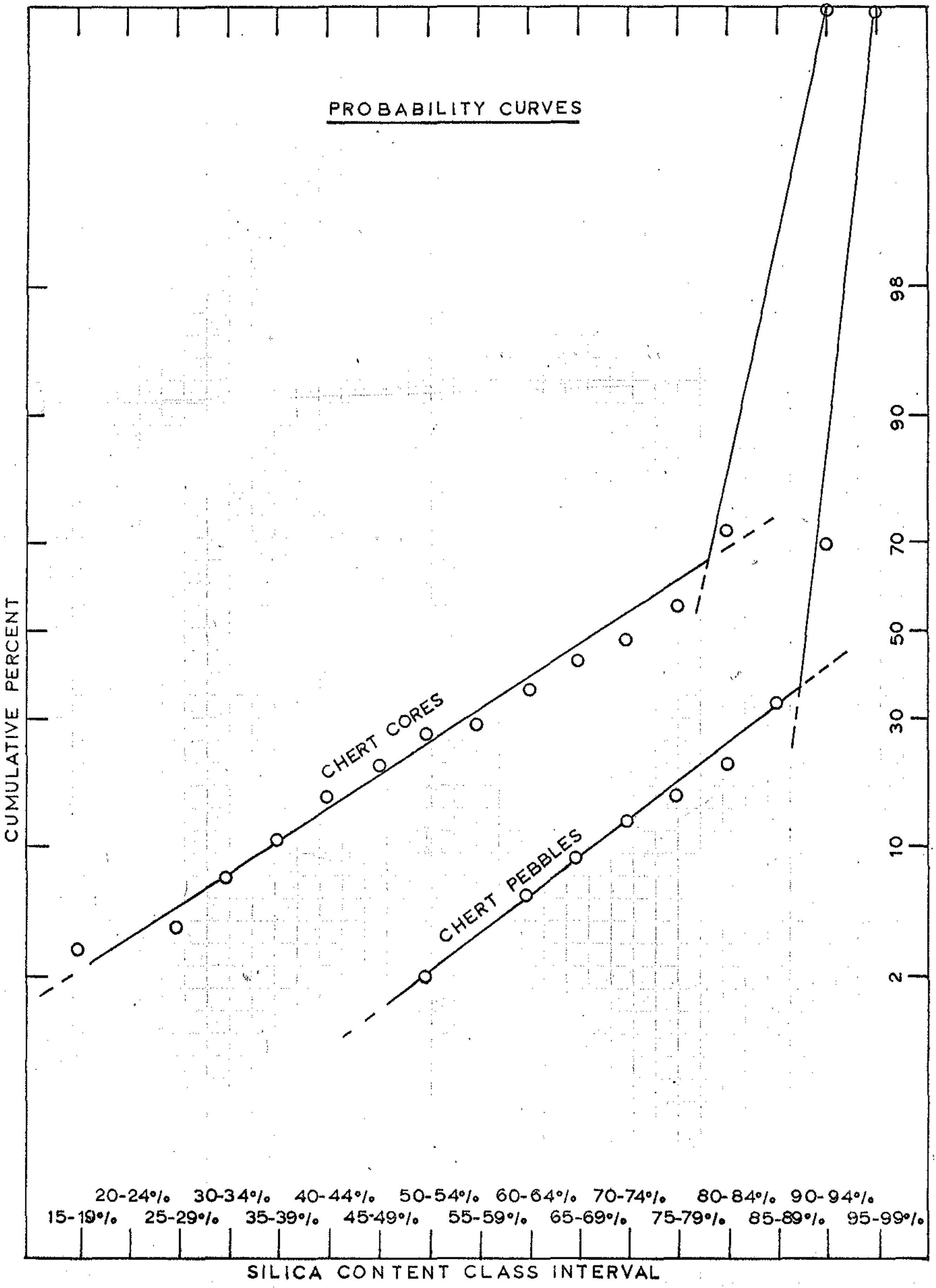

PROBABILITY CURVES
CUMULATIVE PERCENT
98
90
70
50
30
10
2
CHERT CORES
CHERT PEBBLES
20-24%
30-34%
40-44%
50-54%
60-64%
70-74%
80-84%
90-94%
15-19%
25-29%
35-39%
45-49%
55-59%
65-69%
75-79%
85-89%
95-99%
SILICA CONTENT CLASS INTERVAL

FIGURE 7

Triangular plots of the computed mineral compositions of the chert cores as classified by porosity are shown in Figure 8. The calcite component includes the soluble iron and undetermined accessory minerals in order that the results can be shown on a three-coordinate system. The individual compositions are grouped in class intervals by silica content, and the average quartz and dolomite content for each class determines the position of a point. The porosity data does not closely reflect wide variations in porosity of individual cherts; changes in composition can result in minor shifts in the plotted points. The graphic presentation of the mineral composition and porosity data shows mineralogical features and relationships later confirmed by linear regression. These mineralogical features are as follows:

1. Calcite, soluble iron, and undetermined minerals, as designated by this graphic method, are more abundant in the less porous cherts.
2. Porosity increases with decreasing amounts of calcite and residual components; the highest porosities are associated with cherts containing less than 20% calcite as shown by the distribution of the Code 4 porosities.
3. Cherts containing dolomite show high variations in porosity relative to silica content; although the general trend is a decrease of porosity with increasing dolomite, a number of the more porous cherts (Code 3 and 4) range from 35 to 60% silica, 10 to 20% calcite, and 25 to 55% dolomite.

DISTRIBUTION OF AVERAGED CALCULATED MINERAL COMPOSITION AND POROSITY DATA

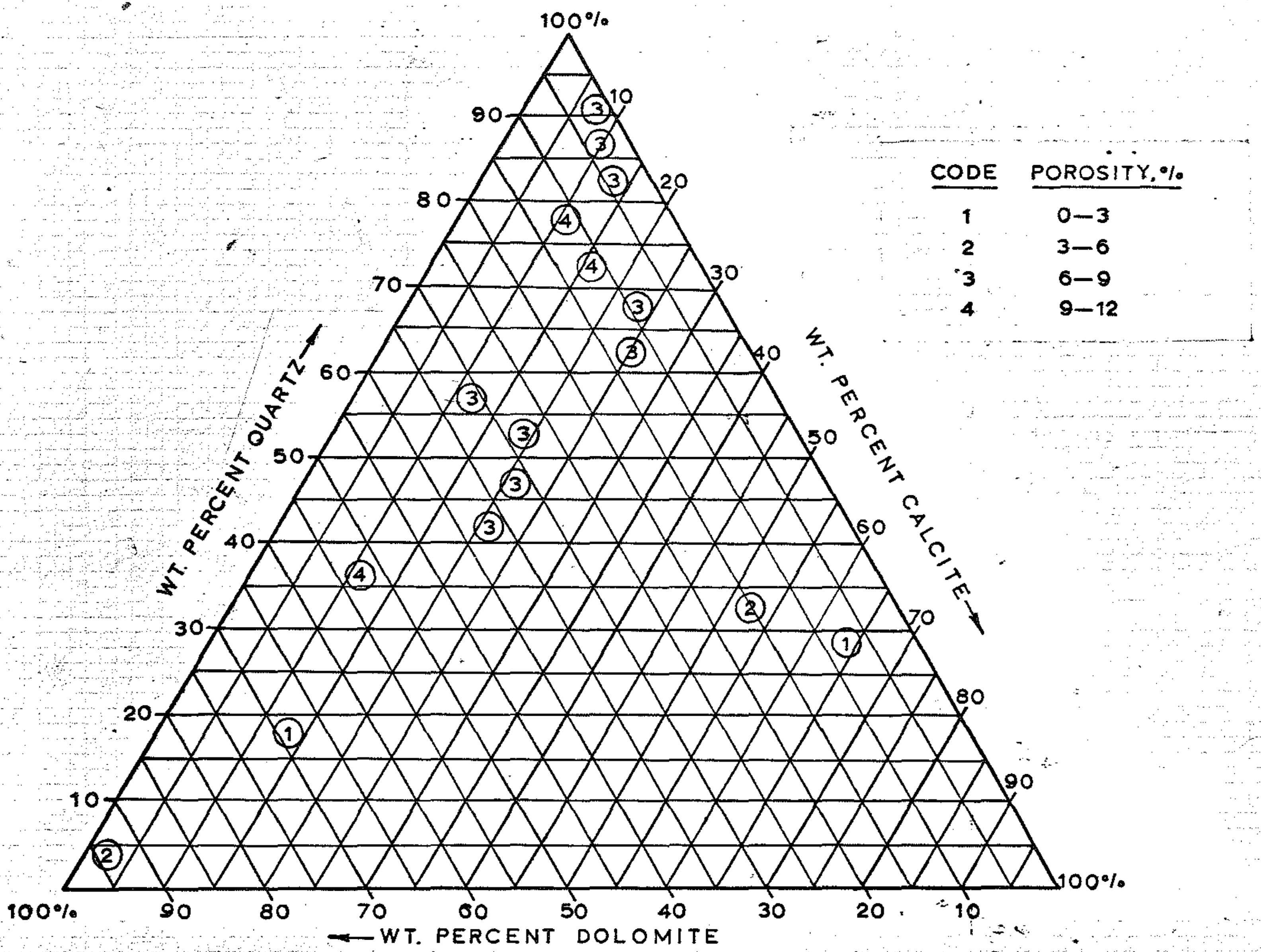


FIGURE- 8

4. The concentration of points along the left portion of the figure further defines the general character of the chert core population; the cherts are actually represented by rocks ranging in composition from dolomite to cherty dolomite to chert. Cherty limestones are indicated in a small group in the right portion of the figure.

The coefficients of correlation for the linear regressions against the paired variables are shown in Figure 9; each listed physical property was individually paired with each other property. This analysis was similar to that reported by Judd and Huber[36]. An IBM 1620 computer was used to make the computations.

The correlation coefficients greater than ± 70 are considered to indicate a significant relationship between properties. It is seen from the correlation coefficients that a strong linear relationship exists between specific gravity and effective porosity and between specific gravity and the 24-hour and 20-day absorptions. Effective porosity also has a strong linear relationship with 24-hour and 20-day absorption.

A strong linear relationship between the silica and dolomite contents of the chert cores is indicated; this is a logical relationship, however, as Table 1 shows that in all but a few cases the primary and secondary constituents of the cherts are silica and dolomite.

The low correlation coefficients between porosity and silica, dolomite, calcite, or soluble iron substantiate that porosity is not strongly dependent upon individual calculated mineral components as illustrated in Figure 8.

		SG	EP	24A	SAT	PER	LPV	TS	SIL	DOL	CAL	20A	SFe	PC	SC	FD	POR	FI
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Specific Gravity	1	100	-77	-75	-4	-22	51	3	-57	45	29	-80	-31	51	-8	6	-15	19
Effective Porosity	2	-77	100	96	-4	32	-62	-16	17	3	-25	98	-4	-27	6	-10	9	-15
24-Hour Absorption	3	-75	96	100	8	24	-60	-14	20	0	-25	97	-8	-27	13	-9	5	-14
Saturation	4	-4	-4	8	100	-16	-11	2	9	-4	-6	5	2	2	8	-10	-1	-4
Permeability	5	-22	32	24	-16	100	-14	-14	-0	17	-15	32	-17	-0	12	7	24	16
Longitudinal Pulse Velocity	6	51	-62	-60	-11	-14	100	8	-14	-1	23	-59	3	8	0	6	-3	0
Tensile Strength	7	3	-16	-14	2	-14	8	100	19	-15	-8	-13	17	-13	5	7	-1	26
SiO_2	8	-57	17	20	9	-0	-14	19	100	-74	-55	22	60	-60	26	29	24	-3
$CaMg(CO_3)_2$	9	45	3	0	-4	17	-1	-15	-74	100	-9	-1	-53	47	-8	-13	-13	9
$CaCO_3$	10	29	-25	-25	-6	-15	23	-8	-55	-9	100	-25	-37	37	-26	-23	-14	-0
20-Day Absorption	11	-80	98	97	5	32	-59	-13	22	-1	-25	100	-5	-29	11	-8	12	-13
Sol. Fe	12	-31	-4	-8	2	-17	3	17	60	-53	-37	-5	100	-46	9	8	3	-19
Primary Constituent	13	51	-27	-27	2	-0	8	-13	-60	47	37	-29	-46	100	-11	5	2	18
Secondary Constituent	14	-8	6	13	8	12	0	5	26	-8	-26	11	9	-11	100	44	54	21
Fracture Designation	15	6	-10	-9	-10	7	6	7	29	-13	-23	-8	8	5	44	100	53	18
Porosity	16	-15	9	5	-1	24	-3	-1	24	-13	-14	12	3	2	54	53	100	20
Fracture Index	17	19	-15	-14	-4	16	0	26	-3	9	-0	13	-19	18	21	18	20	100

FIGURE 9--CORRELATION COEFFICIENTS

Specific Gravity

Since gravity separation (heavy media or jigging) is the principal method now in use in Michigan for beneficiating gravels for use as aggregate in concrete, the character of chert with respect to this property is an important part of this study. The specific gravity of chert is strongly influenced by its mineralogical character; thus, the cherts in this study might be expected to show considerable variation in specific gravity.

The abundance of carbonate in the chert cores is reflected in higher specific gravity. However, considering the inhomogeneous texture and structure of the cored cherts and the fact that some of the carbonate constituents may have high porosity resulting from dissolution, it seems likely that a large percentage of the cores will be found to fail under freeze-thaw conditions, despite their higher specific gravity and carbonate content.

A good correlation between specific gravity and appearance was not found for the cored cherts in the four appearance groups set up in this study. Specific gravity is better correlated with appearance in the chert pebbles, the low specific gravity pebbles occurring more frequently, but not being limited to, the chalky white and mottled appearance groups. For these particular cherts, it is noteworthy that few in appearance group 4 have a specific gravity exceeding 2.60, and that while those in appearance group 3 are mostly in the specific gravity range 2.40-2.50, many are higher or lower. On the whole, it is unlikely that appearance alone will serve as a reliable index of specific gravity in the cherts.

Porosity

Since porosity has been frequently associated with failure of aggregate under freeze-thaw conditions, definition and quantification of the porosity characteristics of cherts are an important part of this study. The features of pore systems usually measured are total void volume, surface connected void volume (effective porosity), rate of absorption, saturation, permeability, and related features of tortuosity, surface area, and capillarity[37]. Porosity and mineral composition both affect specific gravity, and though these properties are independent in a physical sense they may interact in their combined effect on specific gravity.

On the basis of the petrographic results, the low specific gravity chalky white and mottled cherts (appearance groups 1 and 2) generally have the highest total porosity. This observation is similar to that found by Schuster and McLaughlin[6] in lightweight, highly porous Indiana chert which lacked freeze-thaw durability.

In the petrographic study, large pores which were often prominent because of limonite borders were more commonly noted in the cherts associated with carbonate rocks. Small pores (15 microns or less) were less commonly noted in the spiculitic cherts, but since they were not conspicuous some could have been missed in the optical examinations. These small pores possibly were formed in the transition of the silica from the colloidal to the crystalline state. The higher porosity cherts contain more microcrystalline and cryptocrystalline quartz.

The microscopic observations suggest that two families, or populations, of voids occur in the cherts, large voids or pores associated with the carbonate constituents and small pores associated with certain microforms of silica. This is supported by the pore size distribution results, as it is apparent from the histograms (Appendix C, Figures 6a to 6l, inclusive) that many of the cores display two distinct populations with respect to pore size, one made up of pores larger than 100 microns in diameter and the other of pores less than 10 microns. In making this division of pores on the basis of the pore size distribution determinations, it must be remembered that the large size classification includes voids that might be described as surface irregularities as well as large diameter pores. Nevertheless, the postulation of two families of pores has important implications with respect to freeze-thaw durability of the cherts, and the validity of the implications will be tested in the further analysis of the data.

The possibility of a relationship between permeability and freeze-thaw durability of aggregate has been suggested by Verbeck and Landgren[38]. There are many methods of measuring permeability, and most of them are complicated as well as time consuming; moreover, while reproducibility of results can be realized with a given method, agreement of results by different methods on the same material generally is not realized. The gas flow method used to measure permeability in this study is one of the more convenient techniques, but a liquid flow method would better simulate the conditions of the system under study.

The porosity and permeability data for 25 chert cores are shown in Table 4. The impervious character of some of these cherts is designated by BL (below measurable limits).

A relationship between permeability and porosity was expected but not found in the measurements made on the cherts. The qualitative statement can be made that, in general, high permeability accompanies high porosity, but the amount of variation precludes acceptance of a qualitative relationship.

Absorption

The absorption data include rate of absorption and percent saturation. Plots of absorption rates all display a similar pattern, an initial high rate of absorption generally taking place in the first hour abruptly changing to a very slow rate which persists for a relatively long time measured in days. This pattern is in accord with the postulation that there are two populations of porosity, but implies that the larger population is zoned to the exterior of the chert particle, or that the large pores have continuity, that is, this population has high permeability.

Only 25% of the chert cores were fully saturated after 20 days of immersion, and about half of them became critically saturated (92%) in this time. Critical saturation is one of the conditions considered to be necessary for rapid deterioration of aggregate under freeze-thaw conditions.

Longitudinal Wave Velocity

Measurements of the elastic constants of the chert cores were made by ultrasonic methods as part of an associated research program. Repeated

TABLE 4

POROSITY AND PERMEABILITY DATA

SAMPLE	EFFECTIVE POROSITY, %	TRANSIT TIME M/SEC. FT.	PETROGRAPHIC CODE	PERMEABILITY K, (md) K x 10^{+2}
1111	5.4	50.3	2176490 P	3.56
1132	8.2	53.5	2176290 C	8.83
1223	17.6	68.6	2176181 P	157.53
-26	9.3	56.3	2573131 C	.24
-210	9.9	53.8		1.31
212	7.4	55.2	2131212 P	BL.
-213	1.9	49.4	2121102 P	BL.
-214	16.9	57.7	2216412 P	70.65
-216	14.6	55.0	2161302 C	3.08
-219	2.7	49.2	2236142 Sp.	BL.
220	14.6	62.0		.70
32	3.4	48.9	2276412 P	BL.
33	5.7	52.0	2276302 P	60.32
34	8.7	52.2	2261102 C	.24
35	3.6	50.5	2216202 P	BL.
36	2.4	49.8	2276202 P	BL.
37	.9	46.7	2266121 C	BL.
38	1.6	50.2	2716102 C	7.54
310	3.5	49.5	2161190 P	BL.
46	8.1	51.5	2286142 P	.99
411	4.0	49.0		BL.
419	16.2	55.5		1.15
52	2.0	51.3	2276222 P	BL.
56	24.0	69.8	2173362 C	5.84
59	1.6	50.5	2276342 P	10.08

measurements indicated that consistent values of the shear wave velocity could not be obtained. The inconsistencies can be attributed to core geometry, placement of the transducers, and possibly to internal changes occurring within the chert cores between measurements. The longitudinal wave velocity measurement, however, could be repeated within reasonable limits. The longitudinal transit time has been shown by Wyllie et al.[39] to be correlative with porosity. The empirical equation for this relationship is based on the assumption that the composition and water saturation must remain constant for any given longitudinal wave velocity measurement.

A direct plot of longitudinal wave velocity versus porosity was made for 25 water-soaked chert cores. The silica content of the cores ranged from approximately 80 to 100% by weight. The core numbers and other pertinent data are shown in Table 4; for convenience, the reciprocal of the longitudinal wave velocity (transit time) is shown for each core. A plot of effective porosity versus transit time is shown in Figure 10. Theoretical values of transit time for quartz obtained from Wyllie's time-average equation failed to fit the data. The original equation

$$\frac{1}{V_m} = \frac{P}{V_{lucite}} + \frac{1 - P}{V_{aluminum}}$$

was transposed to

$$\frac{1}{V_m} = \frac{P}{V_{water}} + \frac{1 - P}{V_{chert}}$$

for making these computations. A transit time for chert of no porosity was computed to be 47.1 microseconds per foot. Using this value in

LONGITUDINAL TRANSIT TIME VS. POROSITY

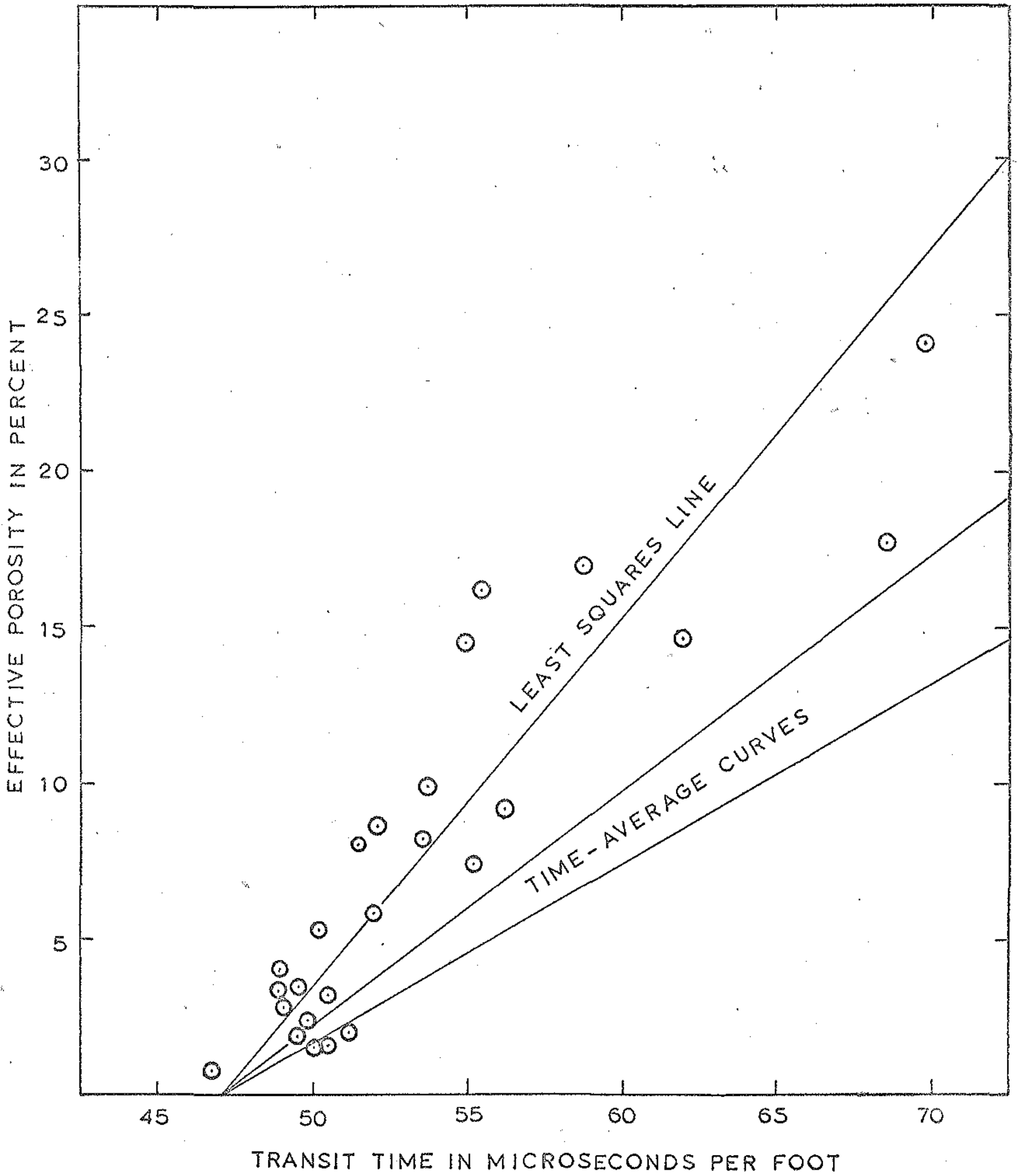


FIGURE 10

the time-average equation resulted in the two lower lines shown in Figure 10 for velocities of 4800 f. p. s. and 5300 f. p. s.

A least squares line provided a better fit to the data, a coefficient of correlation of +0.84 indicating a strong relationship between porosity and longitudinal transit time. These results suggest that porosity may be approximated by longitudinal pulse measurements. If porosity can be quantitatively correlated with freeze-thaw deterioration of the cherts, the longitudinal pulse measurement technique might be investigated for adaptation to field testing of bulk samples.

Tensile Strength

It was expected that the cherts would behave as a brittle material and that their tensile strengths therefore would be related to longitudinal pulse velocity. A good correlation of these measurements is not evident in Figure 9, but further analysis is required before reaching a conclusion.

Alkali-reactivity

Michigan cherts are considered to be relatively nonreactive to cement of moderate alkali content, but some tests of a preliminary nature were made to determine how the cherts under study would perform in this respect and also to test cherts of various specific gravities and appearances. Chert pebbles were chosen for testing to obviate the effects of high carbonate content present in the cored cherts. The Mason jar method used, if modified, could be readily applied in the field.

The only indications of alkali-reactivity were reaction rims noted on some of the chert pebbles which were cut through when the test specimens were sectioned. No particular variety of chert showed a significant difference in abundance of rims or in depth of penetration. Apparently the amount of opal, isotropic silica, and chalcedony in these cherts was insufficient to produce expansion of cement paste and aggregate. Possibly the disseminated character of the silica microforms also inhibited expansive reaction. The inference can be drawn from these preliminary test results and from the observations of Bisque and Lemish[28] that some of the cores from weathered cobbles and boulders might be expected to be more susceptible to formation of reaction rims. While this does not imply that significant expansion would take place, such rim formation could possibly weaken the bond between hardened mortar and the aggregate particles and accelerate freeze-thaw deterioration. The calcite-dolomite ratio in the computed mineral composition should furnish a clue to reactivity.

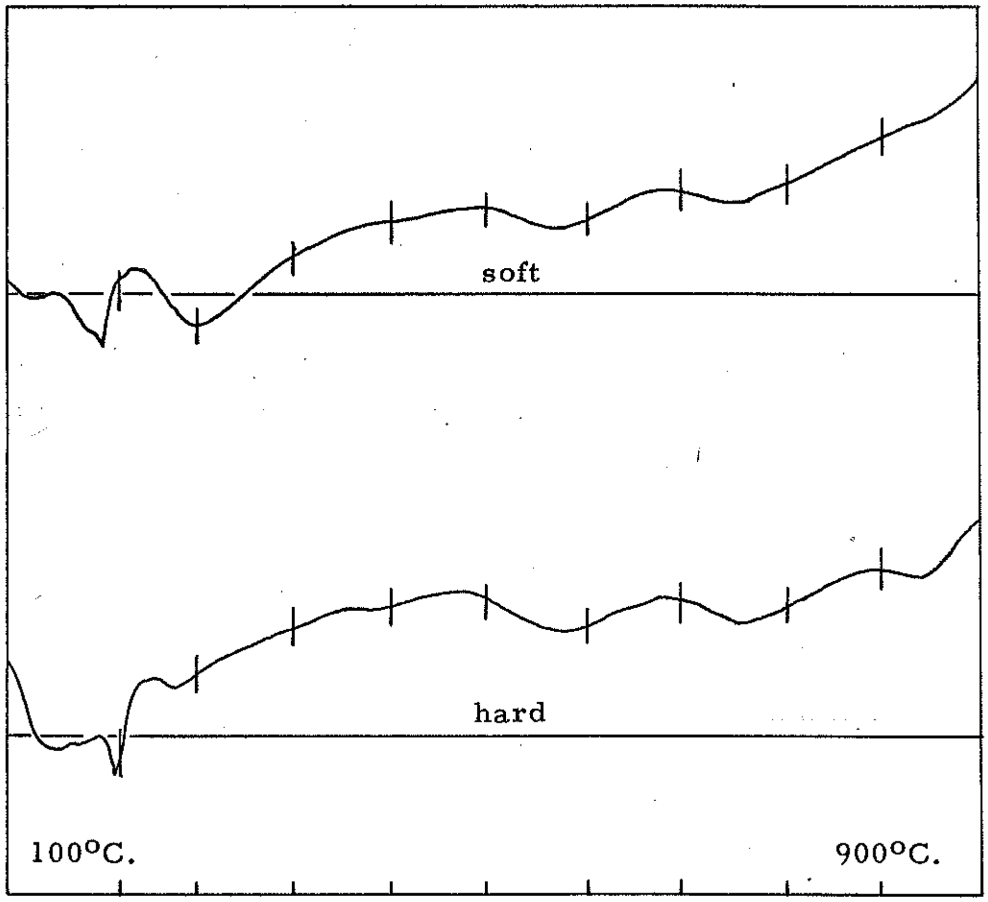
Differential Thermal Analysis

From electron microscope studies of cherts by Folk and Weaver[40] and by Monroe[41], a reasonable certainty exists that the variety of silica described in this study as cryptocrystalline or isotropic has a spongy-porous texture, and that this texture probably extends also into the quartz designated as microcrystalline.

A preliminary DTA analysis was made of selected cherts to determine whether the microforms of silica noted in the petrographic study were essentially opal, chalcedony, or quartz, since some of these microforms are a potential cause of concrete deterioration through their microporosity and chemical nature. The DTA thermograms are shown in Figures 11 and 12a-d, inclusive. The DTA curves are referenced to the composition, appearance group, and other descriptions of the cherts and associated siliceous rocks in Table 5. These thermograms are interpreted qualitatively for indications of opal, presence of water, and crystallinity.

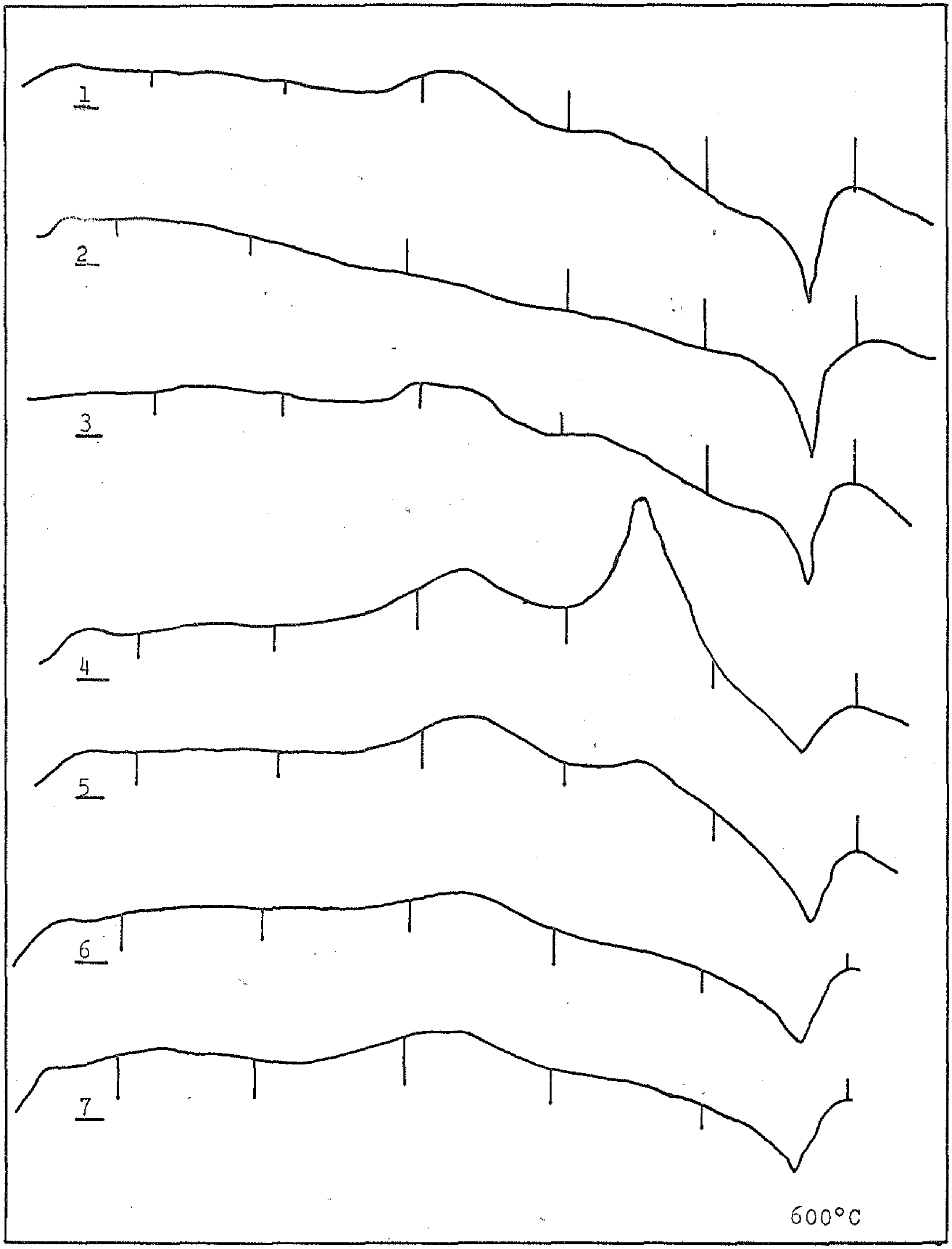
Comparing the curves for opal shown in Figure 11 with those for chert and associated siliceous rocks in Figures 12a-d, weak to strong indications of opal content are evident in a number of thermograms. The peak and strength of inversion are noted in Table 6. It was presumed that the opal inversion (low cristobalite to high cristobalite) would be well defined in DTA curves 7-14 since opal was known to be present in these samples, but erratic behavior even in reruns is evident in the thermograms.

The effect of crystallinity is shown in the strength of the alpha to beta quartz inversion, appearing as an endothermic peak at about 573°C. It was expected that the thermograms for the appearance group 4 cherts (curves 1-3) would show the strongest effect of crystallinity because granular silica was found in the petrographic study to be more abundant in these cherts. It was also inferred that base line fluctuations and minor inversions caused by opal or water content would be less in the group 4 cherts. These features are readily noted by comparing curve 3 with curves 4, 5, and 6 for the samples from the other three appearance groups. The



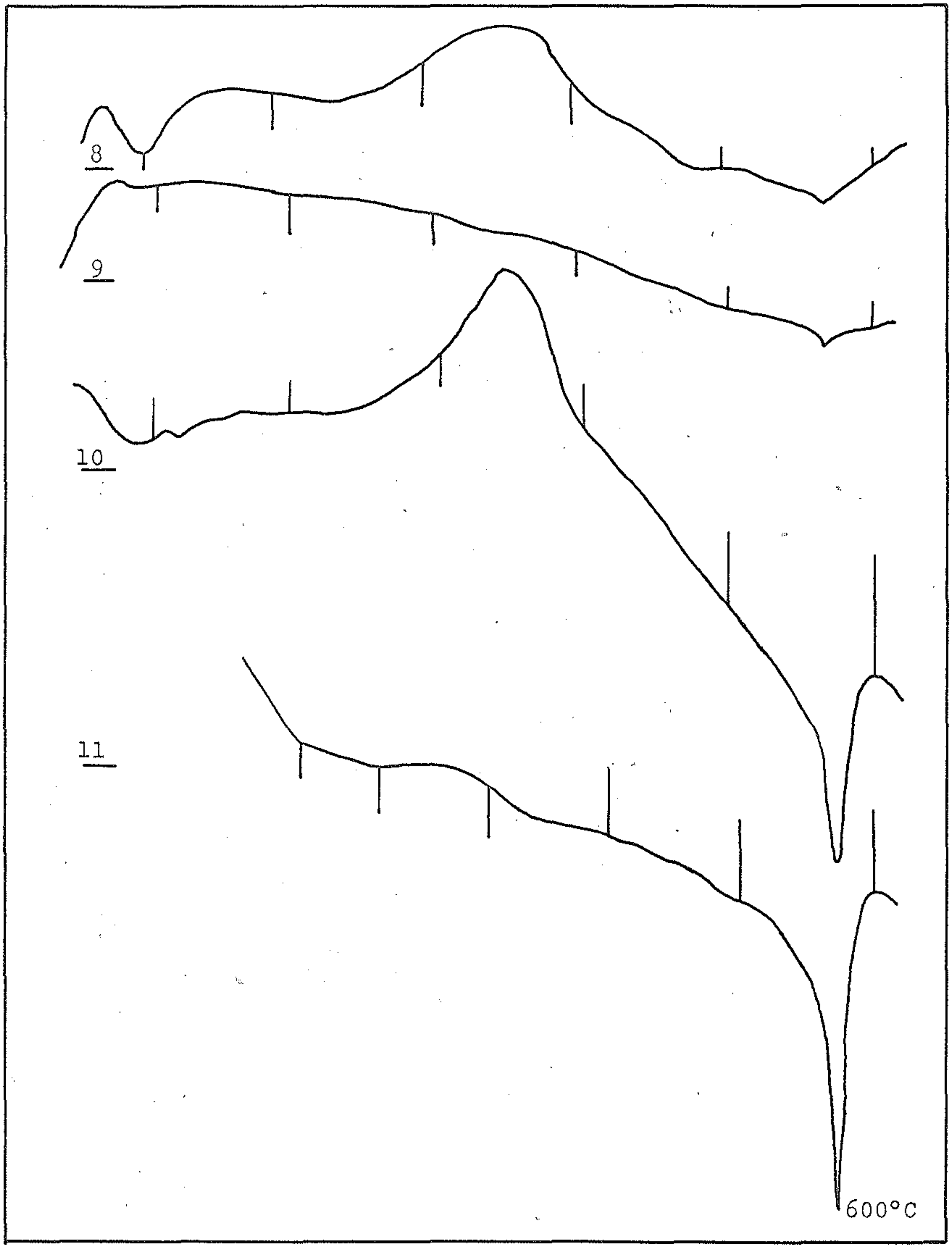
DIFFERENTIAL THERMAL ANALYSIS CURVES OF SOME HARD AND SOFT OPAL (after Franks and Swinford, page 190)(42)

FIGURE 11



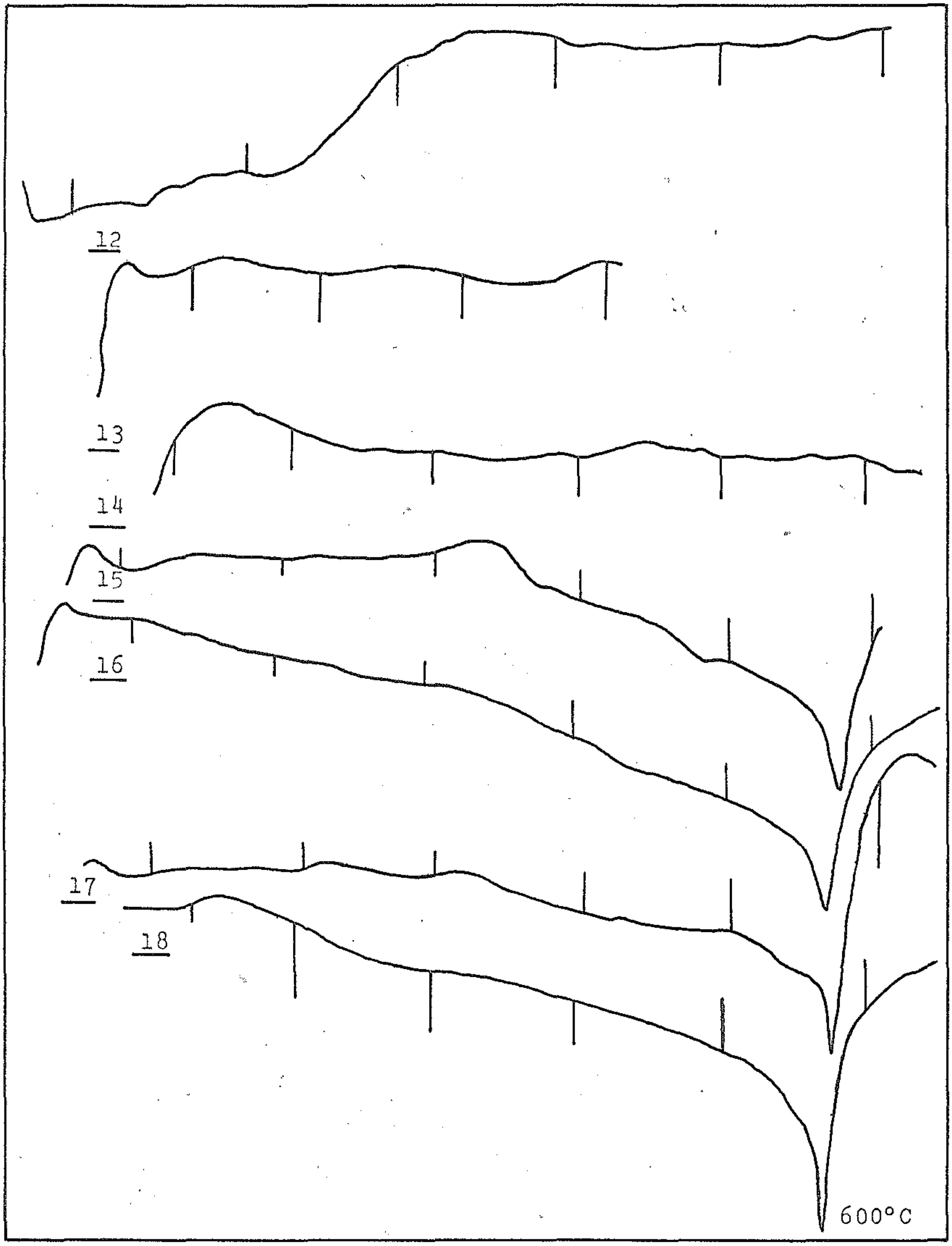
DIFFERENTIAL THERMAL ANALYSIS OF SOME SELECTED CHERTS AND SILICEOUS COMPOUNDS

FIGURE 12a



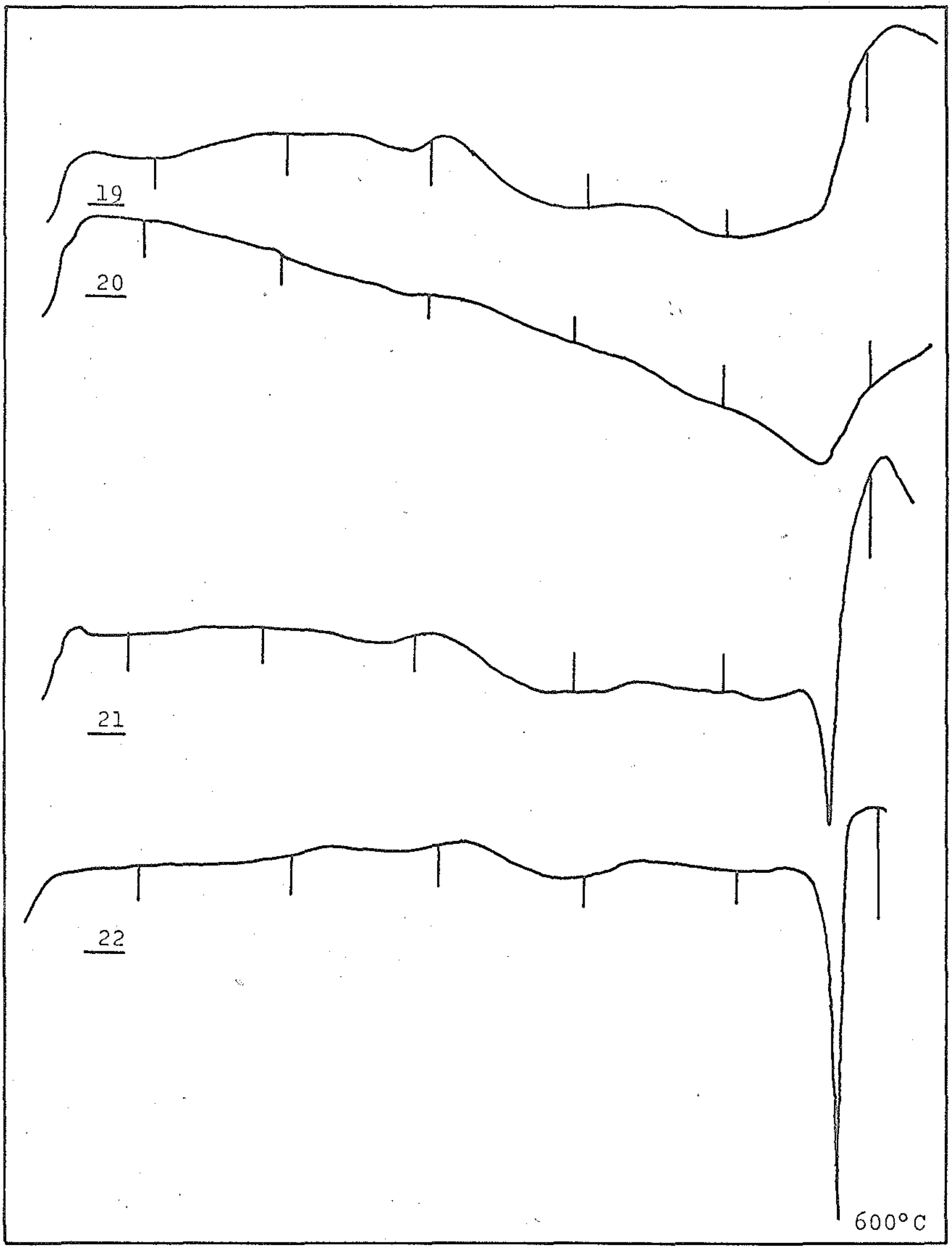
DIFFERENTIAL THERMAL ANALYSIS OF SOME SELECTED CHERTS AND SILICEOUS COMPOUNDS

FIGURE 12b



DIFFERENTIAL THERMAL ANALYSIS OF SOME SELECTED CHERTS AND SILICEOUS COMPOUNDS

FIGURE 12c



DIFFERENTIAL THERMAL ANALYSIS OF SOME SELECTED CHERTS AND SILICEOUS COMPOUNDS

FIGURE 12d

TABLE 5

DIFFERENTIAL THERMAL ANALYSIS SAMPLES

DTA Curve	Calculated Chemical Composition or Petrographic Identification				Remarks
	SiO_2	Dolomite	Calcite	Sol Fe	
1	91.3	2.3	1.2	.7	Group 4 appearance cherts
2	91.3	2.3	1.2	.7	Rerun of above
3	91.3	2.3	1.2	.7	Group 4 appearance cherts
4	90.7	8.3	.6	.4	Group 3 appearance cherts
5	80.6	12.9	5.0	1.0	Group 2 appearance cherts
6	95.1	2.2	1.2	.7	Group 1 appearance cherts
7	9.8% opal and 91.2%				
8	Chalcedonic silica and opal				A reference opal
9	Chalcedonic silica and opal				Rerun of above
10	Quartz, opal, carbonate				A reference opal
11	Quartz, opal, carbonate				Rerun of above
12	Hydrothermal opal				A reference opal
13	Hydrothermal opal				Rerun of above
14	Hydrothermal opal				Rerun of above
15	94.9	.4	.3	.9	Chert core No.1119 material
16	94.9	.4	.3	.9	Rerun of above
17	93.2	.6	.2	1.4	Chert core No.1345 material
18	93.2	.6	.2	1.4	Rerun of above
19	94.4	.5	--	2.1	Chert core No. 1343 material
20	94.4	.5	--	2.1	Rerun of above
21	98.1	--	.6	1.2	Chert core No.1331 material
22	96.8	.3	.6	1.4	Chert core No.1447 material

TABLE 6

OPAL INDICATIONS FROM DTA CURVES

DTA Curve	Temperature, °C	Opal Indication
1	290	weak
3	290	weak
4	230	possible
5	260	possible
6	260	weak
7	230	possible
8	235	strong
10	235	strong
12	220	strong
13	210	weak
14	230	weak
15	280	weak
19	290	possible
21	285	possible

apparent exothermic inversions and base line shifts are probably due in part to differences in water content and rate of water loss[42].

It is possible that opal is present in all the cherts analyzed, but on the basis of the DTA results, it is estimated that opal content does not exceed 10%. In general, crystallinity and water content were more positively detected than opal content. Presence of carbonate up to 18% by weight or low amounts of iron apparently had little effect on the thermograms.

The preliminary results are encouraging for further differential thermal analysis of the cherts. Better definition of the low-to-high crystobalite and the alpha to beta quartz inversion probably could be achieved by careful control of sample composition and grain size, by use of a lower heating rate, and by effluent gas analysis. Additional information might be obtained by the use of temperatures through the tridymite range.

The differential thermal analysis results in conjunction with the petrographic information and pore size distribution determinations, confirm the presence of pores in microforms of silica less than 5 microns in diameter. Microporosity of this type was noted by Sweet[42] in aggregate susceptible to freeze-thaw deterioration. Since this kind of porosity may be present in the high specific gravity as well as in the lightweight cherts, the possibility that deleterious cherts may not be completely eliminated from aggregate by gravity beneficiation methods must be recognized.

Freeze-Thaw Testing

The freeze-thaw testing of concrete specimens containing the chert cores was not completed in this first year of work, and thus the results were not yet available for making the final analysis of chert behavior. However, much preliminary work has been done. Part of it has been devoted to development of procedures for freeze-thaw testing of concrete specimens of smaller size and different geometry than are used in standard procedures, and also to the development of nondestructive measurements of aggregate failure in a specimen containing only one piece of aggregate, an oriented chert core, instead of a number of pieces. Other preliminary work has been done on unconfined cherts to observe directly the effects of freezing and thawing cycles. The observations during unconfined testing are based on the supposition that any chert which becomes critically saturated will fail at places of structural weakness under freezing and thawing conditions. In the cherts, structural weaknesses may exist as fractures or large pores, or they may exist in association with certain microforms of silica.

The preliminary freeze-thaw results of unconfined chert pebbles were about as expected: unsaturated cherts generally did not break, but saturated cherts broke readily along single or multiple planes. The cherts representative of the chalky white and mottled appearance groups suffered more deterioration than did those with dark centers or dark hues. Degradation of the dark cherts generally appeared as spalling of the light-colored exterior zones or secondary coatings. A direct relationship was found between the number of fractures and freeze-thaw deterioration, and failure along fractures was confirmed by staining the cherts before freeze-thaw testing. The results of an experiment with nitrobenzene, a liquid which contracts on freezing, were inconclusive, but additional work should be done with this idea.

The effects of freezing and thawing cycles on confined chert pebbles and cores were observed primarily in the preliminary tests by sectioning the concrete specimens. Degradation was evidenced more by cracking of the concrete specimens than by "popouts"; this was due at least in part to the small size of the specimens. Much fracturing along single and multiple planes in the cherts was noted in the sections, in many cases without cracking of the enclosing cement matrix. Tests on specimens containing the two different size classes of chert pebbles, minus 3/4 plus 1/2 inches and minus 1 1/2 plus 3/4 inches, did not show much difference in failure of the two sizes, but this observation must be checked further in view of the pronounced size effect found in the unconfined tests. The use of dye in the mix water showed that the cherts exert a high degree of absorption during concrete hardening, suggesting that chert particles in aggregate can exert an effect on the amount of moisture available in the paste for hydration. However, there was an indication that the use of methylene blue dye resulted in decreased resistance of the concrete to freezing and thawing cycles.

Freeze-thaw tests were made on 12 cylindrical concrete specimens, one containing an iron-bearing claystone and the other containing chert cores, to determine the rate of deterioration as a function of the number of cycles. The iron-bearing claystone showed extensive fracturing after five cycles, but there was no sign of failure of the cherts. Some fracturing of one chert core occurred after 20 cycles but without visible exterior evidence of failure, and extensive fracturing of another chert core took place after 100 cycles but with no exterior evidence of failure. The rest of the specimens showed no failure in the cherts or exterior evidence of failure after 100 cycles. Other freeze-thaw tests on concrete specimens containing pebbles in two size classes or chert cores in various specific gravity and appearance classes are in progress, and deterioration of the chert aggregate is being measured by the longitudinal pulse velocity method.

The work to date indicates that the low specific gravity cherts in appearance groups 1 and 2 start deteriorating earlier and fracture more extensively under freeze-thaw conditions. The freeze-thaw observations of enclosed cherts in general confirm those of unconfined cherts, indicating that this test can be used on unconfined cherts to compare effects of physical properties as well as to afford direct observation of deterioration.

CONCLUSIONS AND RECOMMENDATIONS

Inasmuch as all measurements of chert properties have not been completed, and in particular the final freeze-thaw tests of the suite of chert cores have not been made, firm conclusions cannot be stated at this time. However, some tentative conclusions can be offered on the basis of the observations made during this first phase of the study.

1. The many irregularities in texture, structure, and composition found in the cherts of this study may be an indication that their durability is influenced by these irregularities when they are used as aggregate in concrete; this does not mean that some chert cannot be used as aggregate and still have satisfactory durability in concrete.
2. The concept of what constitutes chert, as based on the samples available to this study, embraces a wide range of silica content; however, discrete chert particles in the smaller sizes are made up mostly of silica.
3. Alkali reaction resulting in expansion or silica exudation was not noted; however, there was some indication that cherts principally of the calcareous variety developed reaction rims when subjected to immersion in NaOH solution.
4. Large pore spaces and pores less than five microns in diameter are both associated with the low specific gravity

cherts known to be deleterious. The large pores, as observed microscopically, are primarily due to dissolution of anhedral and euhedral carbonates. The small pores, as inferred from differential thermal analysis and microscopy, are thought to be associated with microforms of silica present in some of the chert. Fractures are also abundant in many of the cherts, especially in those of low specific gravity. Fractures were found to be preferred planes of failure under freeze-thaw conditions.

5. A strong relationship was not found between effective porosity and gas permeability; this may be due to inherent differences in rock structure.
6. A relationship was found between porosity and longitudinal wave transit time in individual cores.
7. Freeze-thaw tests on both unconfined and confined specimens indicated that the low specific gravity cherts are most susceptible to damage.
8. Preliminary freeze-thaw tests indicated no apparent relationship between size of unsound aggregate particles and durability.
9. A relationship was found between freeze-thaw durability of cherts and their appearance, but this must be further confirmed.

10. The only general features observed in the high specific gravity cherts which might account for their better freeze-thaw durability were the absence of dissolved carbonates and the presence of silica with a coarser texture, designated as granoblastic.

The work to date suggests a number of favorable areas for research.

1. The association of polymorphic silica and carbonates should be investigated by differential thermal analysis and the electron microscope to confirm and study the presence of pore systems which cannot be observed optically.
2. Large pores and microfractures in cherts may contribute to structural weakness, while the submicroscopic pores influence the absorption rate, saturation, and water retention properties which cause failure under freezing and thawing conditions. It is suggested that these factors be separated by obtaining homogeneous artificial or natural samples of silica microforms and subjecting them to controlled, unconfined freezing and thawing.
3. A field study of concrete undergoing freeze-thaw deterioration is recommended to determine whether pure cherts or cherty carbonates are more deleterious. Organic dyes are suggested for use in preliminary examinations since they permit rapid identification of various carbonates.

4. The relationship of carbonate and silica content to specific gravity and porosity should be examined in more detail. In certain localities, heavy media separation may not be wholly effective in separating good from bad gravels containing cherty carbonates.

5. The technique of measuring longitudinal wave velocity should be studied for field use in determining the average porosity of bulk samples.

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SECOND PHASE WORK

The chert property measurements are in continuation and will be completed early in the second phase of work.

The deleterious character of the chert cores enclosed in concrete will be determined by freeze-thaw tests using a modified procedure being developed specifically for a small concrete cylinder with only one aggregate particle, a chert core, embedded in an oriented position. The determination of deleteriousness is one of the most important measurements in the whole investigation, as it is the dependent variable in correlations to be made with the individual property measurements by linear, and perhaps curvilinear regressions. Analysis of the deleterious character of the various cherts, both with respect to degree and mechanism of deterioration, will be based on the correlation results.

It is expected that the correlation analysis will identify the properties which contribute to the deterioration of concrete in which the cherts are used as aggregate. Having identified these properties, the final work will comprise investigations designed to take advantage of the significant properties in improved beneficiation processes yielding aggregate products of higher quality, in improved field testing methods that will provide more definitive and rapid identification of deleterious cherts, and perhaps in improved laboratory testing methods for determining concrete durability. The results of these investigations could also lead to better quality control of gravel plant products through improvements in operating methods.

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APPENDIX A

Michigan State Highway Department
Project R-121

Institute of Mineral Research
Houghton, Michigan

TABLE NO. 1

(Page 1 of 6)

SUMMARY OF CHERT CORE PROPERTY DATA (LOCATION ONE)

Core No.	Specific Gravity Range^A	Appearance Class^B	Effective Porosity, Percent	24-Hour Absorption, Percent	21-Day Absorption, Percent	Saturation, Percent	Permeability, Millidarcies	Longitudinal Pulse Vel., Ft./sec.x10^{-3}	Tensile Strength, Psi	Chemical and Mineralogical Character SiO_2	$CaMg(CO_3)_2$	$CaCO_3$	Sol.Fe
1111a	3	1	5.4	1.8	1.9	90.0	.0356	19.23	3311	94.1	0.1	2.6	1.9
1132	3	3	8.2	2.8	4.0	91.3	.0883	18.80	3837	81.1	13.0	2.3	1.2
1113	1	1	34.7	12.4	18.0	91.1	3.000	17.19	910	78.7	18.2	0.7	1.2
1124a	1	2	23.0	11.7	11.7	95.2	.0546	13.78	1066	85.6	10.9	1.8	1.2
1124b	1	2	26.5	13.0	13.1	96.6	.0892	20.47	1424	85.6	10.9	1.8	1.2
1211	4	1	5.8	2.9	3.1	100.0	.2665	17.16	ND	41.7	52.6	1.9	1.9
1223	1	2	17.6	6.6	7.6	93.9	1.5753	14.47	2133	86.8	5.4	2.5	3.7
1224	4	2	3.2	0.8	1.0	77.8	BL	20.57	2990	69.2	13.4	15.8	0.8
1215	2	1	13.6	5.5	5.7	97.3	.0123	16.77	ND	62.3	35.8	0.8	1.1
1331a	4	3	1.1	0.3	0.6	100.+	.0034	20.05	ND	28.8	7.2	64.5	0.3
1331b	3	3	6.5	1.5	1.9	76.5	.0032	20.14	1511	28.8	7.2	64.5	0.3
1331d	3	3	5.6	1.6	1.8	80.6	ND	19.29	ND	28.8	7.2	64.5	0.3
1331e	3	3	3.2	1.2	1.4	100.0	BL	19.55	2294	28.8	7.2	64.5	0.3
1322	4	2	6.4	2.2	2.2	91.4	1.2944	17.82	ND	49.8	44.0	2.9	1.7
1323	3	4	5.1	1.3	1.7	82.1	.0006	19.23	4092	62.9	9.2	28.1	1.3
1324	3	2	6.2	1.8	2.0	82.4	.0811	17.85	ND	48.1	0.5	46.6	0.5
1315	4	1	1.8	0.6	0.6	90.0	ND	20.44	2925	34.7	22.3	43.2	0.3
1337a	3	3	7.0	1.8	2.1	71.1	.2125	19.46	1449	33.4	11.8	55.1	0.3
1337c	4	3	2.1	1.3	1.3	100.0	.0016	19.16	1994	33.4	11.8	55.1	0.3
1318a	3	1	10.2	2.8	3.1	75.0	.1936	19.32	1546	43.0	54.3	2.8	0.9
1318b	3	1	7.7	2.5	2.8	92.9	2.6518	18.70	ND	43.0	54.3	2.8	0.9
1318c	4	1	7.2	2.2	2.5	87.2	.0295	18.34	2028	43.0	54.3	2.8	0.9
1330	3	3	2.2	1.2	1.5	100.0	BL	18.31	7066	82.3	13.2	1.6	1.7
1319	4	1	4.9	1.4	1.6	85.2	.0067	17.55	2739	50.4	46.5	2.5	1.1
1413a	4	1	2.3	0.7	0.8	100.0	.0010	22.50	ND	3.7	91.4	5.6	0.2
1413b	4	1	2.9	0.8	1.0	93.8	.0026	21.49	2966	3.7	91.4	5.6	0.2
1414	4	1	9.7	2.5	3.4	88.9	.0721	12.99	1720	1.1	96.2	3.2	0.1
1435	4	3	ND	ND	1.9	ND	ND	20.18	ND	42.8	51.0	4.3	0.6
1426	4	2	2.9	1.2	1.3	100.0	.0008	20.18	3608	36.9	60.2	0.4	1.3
1427	2	2	23.1	6.1	7.3	71.1	.8960	16.57	803	35.6	59.6	3.8	1.2

A - Specific gravity ranges 1, 2, 3, & 4 are: (1) less than 2.40; (2) 2.40-2.50; (3) 2.51-2.60, & (4) greater than 2.60.
B - Appearance classes 1, 2, 3, & 4 are: (1) Chalky White - very porous appearing commonly fossiliferous; (2) Mottled - mottled grey, brown & white, semi-porous appearing, commonly fossiliferous; (3) Dense, Light Colored - includes solid greys, grey-whites, usually have light colored exteriors, conchoidal fractures, may or may not be fossiliferous; (4) Dense, Dark Hues - of blue-grey, brown or black - smooth surfaces, conchoidal fractures, usually non-fossiliferous.
ND- Not Determined
BL- Below Measureable Limits

Michigan State Highway Department
Project R-121

Institute of Mineral Research
Houghton, Michigan

TABLE NO. 1

(Page 2 of 6)

SUMMARY OF CHERT CORE PROPERTY DATA (LOCATION TWO)

Core no.	Specific Gravity Range^A	Appearance Class^B	Effective Porosity, Percent	24-Hour Absorption, Percent	20-Day Absorption, Percent	Saturation, Percent	Permeability, Millidarcies	Longitudinal Pulse Vel., Ft./sec.x10^{-3}	Tensile Strength, Psi	Chemical and Mineralogical Character			
										SiO_2	$CaMg(CO_3)_2$	$CaCO_3$	Sol. Fe
21	2	4	11.8	4.6	4.6	90.9	.0002	17.95	2057	88.6	0.6	0.3	8.9
22	3	3	2.2	0.7	0.9	100.0	BL	20.05	5034	70.0	2.6	15.6	8.9
24	3	2	10.9	3.5	3.7	83.1	1.5183	23.33	1315	46.4	48.5	0.2	4.5
25	3	4	1.2	0.5	0.8	100.0	BL	20.24	4782	60.8	1.4	31.1	4.1
26	3	4	9.3	3.4	3.5	92.2	.0024	17.65	3697	79.1	10.8	00.0	7.6
27	4	4	2.5	0.8	1.1	100.0	BL	20.01	2906	69.3	2.6	16.6	8.5
28	4	4	1.7	0.4	0.4	60.0	.0040	23.88	1847	17.5	68.6	7.6	2.1
29	4	4	1.5	0.6	0.6	100.0	.0002	22.51	3196	87.8	2.3	0.0	6.5
210	2	2	9.9	3.1	3.9	89.1	.0131	19.06	5735	87.7	3.4	0.2	8.4
211	4	4	3.3	0.9	0.9	72.2	.0002	24.24	2022	56.4	37.0	0.6	5.2
212	2	3	7.4	2.9	3.2	100.0	BL	18.54	ND	91.6	0.7	0.0	5.7
213	3	4	1.9	0.5	0.7	100.0	BL	20.80	ND	92.4	1.0	0.1	7.5
214	1	2	16.9	4.3	7.4	88.9	.7065	17.22	ND	92.1	0.5	0.4	6.9
215	3	4	3.5	1.7	1.9	100.0	BL	19.55	5788	79.1	7.2	1.2	9.2
216	2	2	14.6	5.9	6.2	95.0	.0308	18.44	ND	81.5	7.7	5.4	5.7
217	2	2	8.7	2.7	3.5	83.7	.0009	19.06	6810	90.2	1.5	0.7	7.9
218	2	2	5.7	1.6	2.0	87.1	.0002	20.05	4917	89.2	0.4	1.6	8.4
219	3	4	2.7	0.4	0.9	86.7	BL	20.73	3473	91.0	0.4	1.1	7.6
220	1	3	14.6	5.9	6.0	92.5	.0070	15.99	3624	93.4	0.9	1.1	5.2
221	3	4	1.1	0.4	0.7	100.0	BL	24.21	2601	65.8	3.9	23.2	5.9
222	2	2	11.7	3.7	4.7	84.5	.0069	18.80	ND	75.7	6.9	0.0	7.8
223	3	4	8.6	3.0	3.1	88.9	.0040	17.98	ND	74.6	18.1	1.1	4.6

A - Specific gravity ranges 1, 2, 3, & 4 are: (1) less than 2.40; (2) 2.40-2.50; (3) 2.51-2.60, & (4) greater than 2.60.
B - Appearance classes 1, 2, 3, & 4 are: (1) Chalky White - very porous appearing, commonly fossiliferous; (2) Mottled - mottled grey, brown & white, semi-porous appearing, commonly fossiliferous; (3) Dense, Light Colored - includes solid greys, grey-whites, usually have light colored exteriors, conchoidal fractures, may or may not be fossiliferous; (4) Dense, Dark Hues - of blue-grey, brown or black - smooth surfaces, conchoidal fractures, usually non-fossiliferous.
ND- Not Determined
BL- Below Measureable Limits

Michigan State Highway Department
Project R-121

Institute of Mineral Research
Houghton, Michigan

TABLE NO. 1

(Page 3 of 6)

SUMMARY OF CHERT CORE PROPERTY DATA (LOCATION THREE)

Core No.	Specific Gravity Range^A	Appearance Class^B	Effective Porosity, Percent	24-Hour Absorption, Percent	20-Day Absorption, Percent	Saturation, Percent	Permeability, Millidarcies	Longitudinal Pulse Vel., Ft./sec.x10^{-3}	Tensile Strength, Psi	Chemical and Mineralogical Character			
										SiO_2	$CaMg(CO_3)_2$	$CaCO_3$	Sol. Fe
31	4	4	5.7	1.7	1.9	83.9	.0122	22.54	1853	40.4	21.7	38.5	1.0
32	3	4	3.4	1.1	1.4	100.0	BL	20.37	ND	91.9	0.5	0.1	7.1
33	3	4	5.7	1.4	2.2	87.5	.6032	19.62	2210	86.6	1.1	0.7	12.7
34	3	4	8.7	2.9	3.3	91.7	.0024	19.23	ND	82.7	4.2	5.9	5.7
35	3	4	3.6	1.2	1.4	95.0	.0007	20.37	ND	87.4	0.8	0.6	11.8
36	3	4	2.4	0.6	1.1	100.0	BL	20.37	ND	89.3	2.5	0.0	8.7
37	4	4	0.9	0.1	0.2	60.0	BL	21.33	3663	84.1	1.5	8.2	6.7
38	4	4	1.6	0.3	0.5	88.9	.0754	20.28	ND	79.9	1.6	6.8	11.9
39	3	4	2.9	0.6	0.9	81.2	.0011	20.60	4807	62.1	1.2	24.2	9.6
310	3	4	3.5	1.3	1.5	100.0	BL	19.98	6498	87.6	1.9	0.0	11.8
311	4	3	0.9	0.4	0.8	100.0	.0013	21.03	2291	52.1	2.3	35.8	8.9

A - Specific gravity ranges 1, 2, 3, & 4 are: (1) less than 2.40; (2) 2.40-2.50; (3) 2.51-2.60, & (4) greater than 2.60.
B - Appearance classes 1, 2, 3, & 4 are: (1) Chalky white - very porous appearing, commonly fossiliferous; (2) Mottled - mottled grey, brown & white, semi-porous appearing, commonly fossiliferous; (3) Dense, Light Colored - includes solid greys, grey-whites, usually have light colored exteriors, conchoidal fractures, may or may not be fossiliferous; (4) Dense, Dark Hues - of blue-grey, brown or black - smooth surfaces, conchoidal fractures, usually non-fossiliferous.
ND- Not Determined
BL- Below Measureable Limits

TABLE NO. 1

(Page 4 of 6)

SUMMARY OF CHERT CORE PROPERTY DATA (LOCATION FOUR)

Core No.	Specific Gravity Range[A]	Appearance Class[B]	Effective Porosity, Percent	24-Hour Absorption, Percent	20-Day Absorption, Percent	Saturation, Percent	Permeability, Millidarcies	Longitudinal Pulse Vel., Ft./sec.x10^{-3}	Tensile Strength, Psi	Chemical and Mineralogical Character			
										SiO_2	$CaMg(CO_3)_2$	$CaCO_3$	Sol. Fe
41	2	2	10.5	3.0	4.3	82.5	.0076	17.78	1238	82.4	0.5	1.2	13.5
43	2	2	13.3	5.1	5.3	93.3	.0076	17.59	3743	70.6	17.5	8.4	4.4
44	2	4	9.1	2.4	3.3	74.0	.0030	19.16	4316	84.8	0.6	1.0	12.0
45	2	2	11.6	4.1	4.7	90.6	.0044	18.47	4529	83.3	0.6	1.4	10.7
46	2	2	8.1	2.4	3.0	88.9	.0099	19.26	6719	86.4	0.5	1.3	10.0
49	3	4	13.2	4.0	5.0	90.3	.4556	18.41	995	54.9	28.6	6.8	7.5
411	2	3	4.0	0.7	1.2	77.3	BL	20.37	ND	88.1	0.3	1.0	8.8
412	2	3	14.1	5.1	5.5	90.9	.0572	17.26	ND	68.8	7.9	9.7	10.6
413	2	4	13.0	4.7	5.0	90.3	.0076	17.72	ND	56.7	25.8	8.6	7.1
414	3	3	7.5	2.2	2.6	79.1	.0008	19.72	ND	64.9	1.0	18.9	14.8
415	3	3	7.9	2.6	2.9	90.7	.0032	19.39	3339	42.6	19.1	35.3	4.2
416	2	4	2.4	0.2	1.6	100.0	.0079	19.59	6041	84.4	0.2	3.4	12.6
417	3	4	7.0	2.3	2.3	82.1	.0117	20.31	ND	81.6	1.8	7.0	10.5
418	2	2	14.1	5.4	5.7	93.6	.0155	18.08	3798	75.5	16.8	1.8	5.8
419	1	2	16.2	4.8	6.8	76.4	.0115	17.78	3761	86.5	0.3	3.7	10.1
420	2	2	13.8	5.2	5.6	93.3	.0332	19.03	3692	54.5	37.3	4.0	5.0
421	3	3	9.3	3.2	3.5	96.0	.0089	16.63	3735	64.4	20.7	2.8	9.2
422	2	3	14.9	5.9	5.9	91.2	.0142	17.49	2823	83.7	1.8	2.8	10.8
425	3	4	5.9	2.0	2.2	93.8	.0043	20.60	4168	68.5	11.8	10.0	8.7
426	3	4	7.3	1.6	1.7	100.0	.0003	20.51	3196	61.6	6.2	21.4	10.6
427	2	4	9.8	3.5	3.9	96.4	.0925	18.35	2648	74.0	5.3	10.1	9.0
428	2	3	11.4	4.8	5.0	100.0	.0254	17.26	ND	73.5	10.3	4.1	11.0
429	3	4	6.6	1.8	2.3	80.6	.0613	20.73	2351	31.4	10.4	54.4	3.4
430	2	4	7.4	2.3	3.1	90.0	.0015	18.86	2746	84.5	1.9	0.6	12.5
432	3	4	8.9	2.6	3.2	91.8	.1857	16.96	ND	54.3	28.5	7.0	7.9
433	2	4	5.5	2.2	2.4	100.0	.0006	19.52	ND	83.4	0.4	1.3	12.6
434	2	4	12.6	4.8	5.0	94.2	.0048	17.88	2788	67.7	14.8	4.1	11.6
435	2	4	7.7	2.0	2.8	73.8	.0013	19.36	3396	81.9	0.1	1.2	15.8
436	3	4	1.3	0.4	0.8	100.0	BL	20.34	5543	85.8	0.4	2.7	11.1

A - Specific gravity ranges 1, 2, 3, & 4 are: (1) less than 2.40; (2) 2.40-2.50; (3) 2.51-2.60, & (4) greater than 2.60.

B - Appearance classes 1, 2, 3, & 4 are: (1) Chalky White - very porous appearing, commonly fossiliferous; (2) Mottled - mottled grey, brown & white, semi-porous appearing, commonly fossiliferous; (3) Dense, Light Colored - includes solid greys, grey-whites, usually light colored exteriors, conchoidal fractures, may or may not be fossiliferous; (4) Dense, Dark Hues - of blue-grey, brown or black - smooth surfaces, conchoidal fractures, usually non-fossiliferous.

ND- Not Determined

BL- Below Measureable Limits

TABLE NO. 1

(Page 5 of 6)

SUMMARY OF CHERT CORE PROPERTY DATA (LOCATION FIVE)

Core No.	Specific Gravity Range[A]	Appearance Class[B]	Effective Porosity, Percent	24-Hour Absorption, Percent	20-Day Absorption, Percent	Saturation, Percent	Permeability, Millidarcies	Longitudinal Pulse Vel., Ft./sec.x10^{-3}	Tensile Strength, Psi	Chemical and Mineralogical Character			
										SiO_2	$CaMg(CO_3)_2$	$CaCO_3$	Sol Fe
51	4	4	3.9	1.2	1.4	90.5	BL	20.77	1653	45.4	16.5	35.9	1.6
52	3	3	2.0	0.6	0.8	100.0	BL	19.85	ND	92.4	1.3	1.5	3.3
53	4	4	2.0	0.8	0.9	100.0	BL	20.73	3205	76.7	18.3	1.0	3.5
54	4	3	5.0	1.9	1.9	96.3	.0004	19.55	4187	45.5	49.6	2.3	2.7
55	4	4	4.5	1.5	1.7	96.0	.0004	18.80	4982	37.5	37.3	20.4	2.0
56	2	1	24.0	10.9	11.2	93.8	.0584	14.11	3002	84.0	8.0	1.5	3.5
57	4	3	4.7	1.8	1.9	100.0	.0679	19.23	ND	53.5	25.5	12.9	3.4
58	3	2	10.8	3.4	3.7	81.0	.4386	16.93	2256	87.7	4.0	1.0	5.8
59a	3	3	1.6	0.2	0.4	77.8	.1008	20.37	2412	90.2	2.5	0.4	5.8
59b	3	3	1.1	0.1	0.2	66.7	.3000	20.11	4104	90.2	2.5	0.4	5.8

A - Specific gravity ranges 1, 2, 3, & 4 are: (1) less than 2.40; (2) 2.40-2.50; (3) 2.51-2.60, & (4) greater than 2.60.
B - Appearance classes 1, 2, 3, & 4 are: (1) Chalky White - very porous appearing, commonly fossiliferous; (2) Mottled - mottled grey, brown & white, semi-porous appearing, commonly fossiliferous; (3) Dense, Light Colored - includes solid greys, grey-whites, usually have light colored exteriors, conchoidal fractures, may or may not be fossiliferous; (4) Dense, Dark Hues - of blue-grey, brown or black - smooth surfaces, conchoidal fractures, usually non-fossiliferous.
ND- Not Determined
BL- Below Measureable Limits

Michigan State Highway Department
Project R-121

Institute of Mineral Research
Houghton, Michigan

TABLE NO. 1

(Page 6 of 6)

SUMMARY OF CHERT CORE PROPERTY DATA (CONTROL)

Core No.	Specific Gravity Range^A	Appearance Class^B	Effective Porosity, Percent	24-Hour Absorption, Percent	21-Day Absorption, Percent	Saturation, Percent	Permeability, Millidarcies	Longitudinal Pulse Vel., Ft./sec.x10^{-3}	Tensile Strength, Psi	Chemical and Chemico Mineralogical Character SiO_2	$CaMg(CO_3)_2$	$CaCO_3$	Sol.Fe
611	4	NA	0.3	0.1	0.1	100.0	BL	ND	1254	Neg.	98.2	1.7	Neg.
612	4	NA	0.5	0.1	0.2	100.0	BL		ND	Neg.	98.2	1.7	Neg.
613	4	NA	1.1	0.2	0.3	66.7	.0022		ND	Neg.	98.2	1.7	Neg.
614	4	NA	0.9	0.1	0.2	60.0	.0005		ND	Neg.	98.2	1.7	Neg.
621	4	NA	1.3	0.3	0.2	42.9	.0009		ND	Neg.	93.3	4.0	Neg.
622	4	NA	1.2	0.2	0.3	57.1	.0015		2558	Neg.	93.3	4.0	Neg.
623	4	NA	0.7	0.1	0.2	75.0	.0007		ND	Neg.	93.3	4.0	Neg.
631	4	NA	1.8	0.2	0.3	50.0	.0005		ND	Neg.	98.8	0.9	Neg.
632	4	NA	2.6	0.3	0.4	42.9	.0007		ND	Neg.	98.8	0.9	Neg.
633	4	NA	1.8	0.2	0.3	40.0	.0002		ND	Neg.	98.8	0.9	Neg.
71	2	4	14.8	4.0	5.4	85.0	.0886		ND	66.0	ND	ND	3.3
72	2	4	18.7	6.9	8.0	96.1	.0582		ND	60.3	ND	ND	8.2
73	2	4	39.2	ND	15.9	100.0	.0653		ND	20.5	ND	ND	29.3
74	3	4	29.2	11.4	13.2	100.0	.0270		ND	20.9	ND	ND	35.1
75	3	4	30.9	13.7	13.9	100.0	.5445		ND	19.7	ND	ND	31.6

A - Specific gravity ranges 1, 2, 3, & 4 are: (1) less than 2.40; (2) 2.40-2.50; (3) 2.51-2.60, & (4) greater than 2.60.
B - Appearance classes 1, 2, 3, & 4 are: (1) Chalky White - very porous appearing, commonly fossiliferous; (2) Mottled - mottled grey, brown & white, semi-porous appearing, commonly fossiliferous; (3) Dense, Light Colored - includes solid greys, grey-whites, usually have light colored exteriors, conchoidal fractures, may or may not be fossiliferous; (4) Dense Dark Hues - of blue-grey, brown or black - smooth surfaces, conchoidal fractures, usually non-fossiliferous.
ND - Not Determined
BL - Below Measureable Limits

Table 3

Petrographic Data for Chert Pebbles and Cores

Location One - Chert Pebbles

Sample No.	Petrographic Code Classification	Sample No.	Petrographic Code Classification
1311	21762 C	1331	11561 S
1112	21711 R	1332	11361 S
1113	25151 R	1233	22812 P
1114	21661 C	1234	25751 R
1215	26163 C	1235	25762 C
1116	25214 C	1336	22751 P
1117	23561 P	1237	25731 R
1118	11314 S	1238	21611 C
1119	21311 P	1239	22761 P
1119A	12164 S	1239A	22131 P
1221	11561 S	1241	22751 R
1222	11261 S	1342	21261 P
1223	21762 C	1343	12162 S
1224	21712 C	1344	22751 P
1225	22763 P	1345	22361 P
1326	21711 C	1446	12861 S
1327	26513 C	1447	22361 P
1228	13511 S	1448	11211 S
1229	26511 C	1349	21731 P
1229A	15311 S	1349A	11211 S
1229B	21264 P		

Table 3, Continued

Petrographic Data for Chert Pebbles and Cores

Location One - Chert Cores

Sample No.	Petrographic Code Classification	Sample No.	Petrographic Code Classification
1111	2176490 P	1324	2611101 C
1132	2176290 C	1315	2621202 C
1113	2171401 C	1337	2621290 C
1124	2174101 C	1318	2621132 C
1211	2726102 C	1330	2721131 C
1223	2176181 P	1319	2726131 C
1224	2266222 C	1413	2761112 C
1215	2721102 C	1414	2721121 C
1331	2721102 C	1435	2721102 C
1322	2721190 C	1426	2721192 C
1323	2621190 C	1427	2726301 C

Table 3, continued

Petrographic Data for Chert Pebbles and Cores

Location Two - Chert Cores

Sample No.	Petrographic Code Classification	Sample No.	Petrographic Code Classification
21	2321101 C	28	2716102 C
22	2571112 C	29	2176302 C
23	2136142 P	211	2362131 C
24	2162181 C	212	2131212 P
26	2573131 C	213	2121102 P
27	2711131 C	214	2216412 P

Table 3, continued

Location Two - Chert Cores, continued

Sample No.	Petrographic Code Classification	Sample No.	Petrographic Code Classification
215	2131101 P	218	2326212 P
216	2161302 C	219	2236142 SP
217	2216202 P	223	2371101 C

Table 3, continued

Petrographic Data for Chert Pebbles and Cores

Location Three - Chert Cores

Sample No.	Petrographic Code Classification	Sample No.	Petrographic Code Classification
31	2751152 C	37	2266121 C
32	2276412 P	38	2716102 C
33	2276302 P	39	2271122 C
34	2261102 C	310	2161190 P
35	2216202 P	311	2726190 C
36	2276202 P	312	2231190 P

Table 3, continued

Petrographic Data for Chert Pebbles and Cores

Location Four - Chert Cores

Sample No.	Petrographic Code Classification	Sample No.	Petrographic Code Classification
41	2211222 P	422	2271102 C
45	2276312 P	426	2711102 C
46	2286142 P	428	2572101 C
413	2571102 R	430	2171222 C
415	2166202 C	433	2276111 C
416	2271432 P	434	2276302 R
417	2161101 C	435	2276471 P
421	2274131 C	436	2266142 C

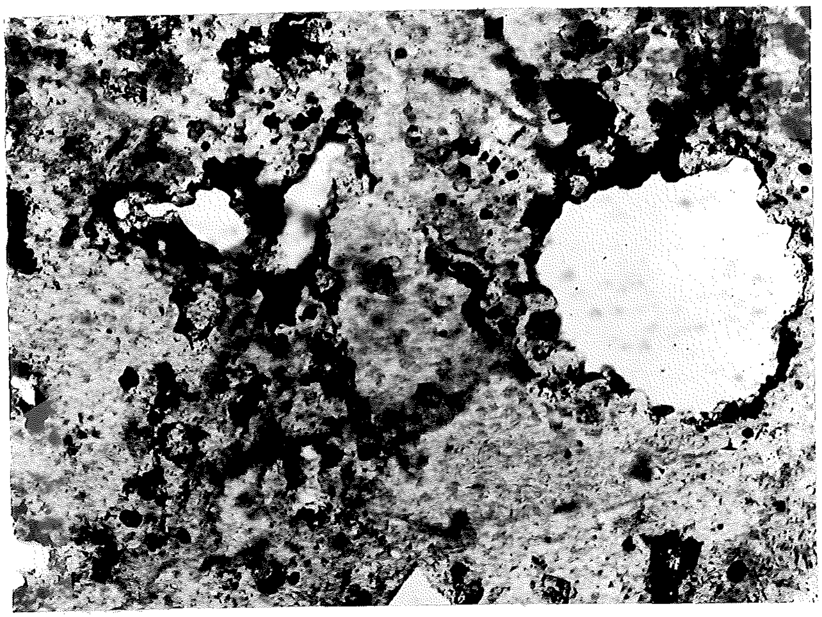
Table 3, continued

Petrographic Data for Chert Pebbles and Cores

Location Five - Chert Cores

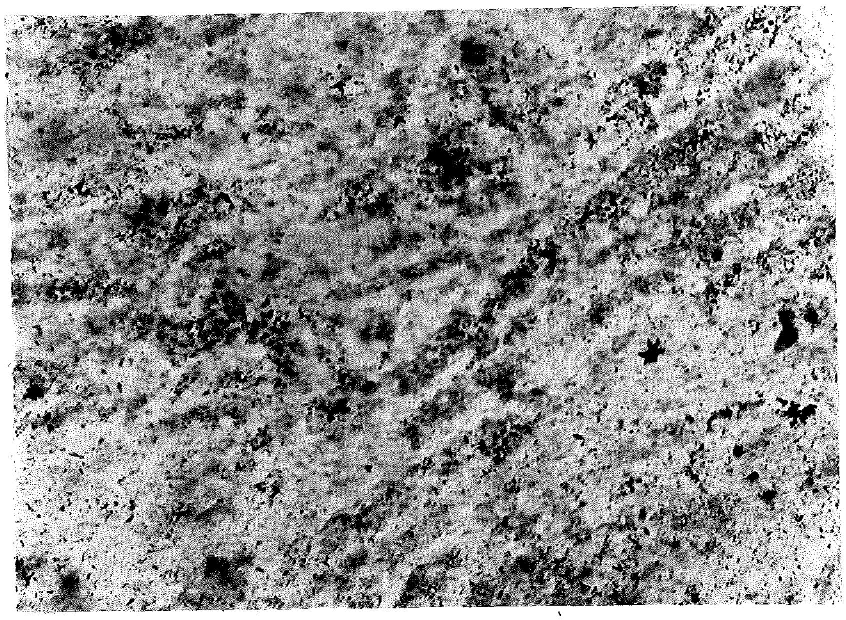
Sample No.	Petrographic Code Classification	Sample No.	Petrographic Code Classification
51	2726112 C	56	2173362 C
52	2276222 P	57	2271201 C
53	2726102 R	58	2175111 C
54	2262152 C	59	2276342 P
55	2721101 R		

APPENDIX B



Sample 1116 Calcareous Chert 25214

Highly porous calcareous chert. The porosity is due to the dissolution of rhombic and anhedral carbonate and fossil interiors. Chalcedony and cryptocrystalline quartz are the most abundant forms of silica. Ordinary light, 145X

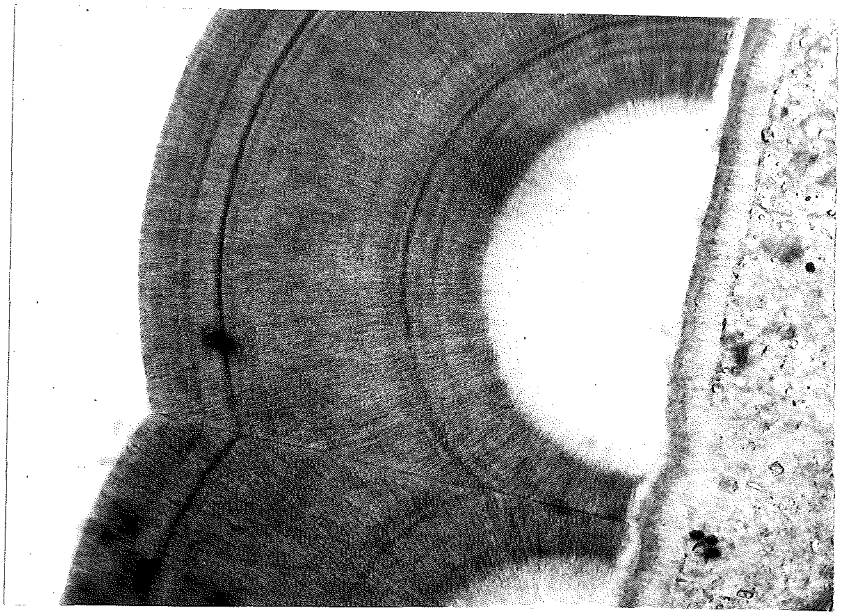


Sample 1331 Spiculitic Chert 11561

Fine particles of clay and ferruginous matter color the central portions of the spicules principally composed of chalcedonic and cryptocrystalline silica. The organic structures are not readily observed with crossed nicols. Ordinary light, 145X

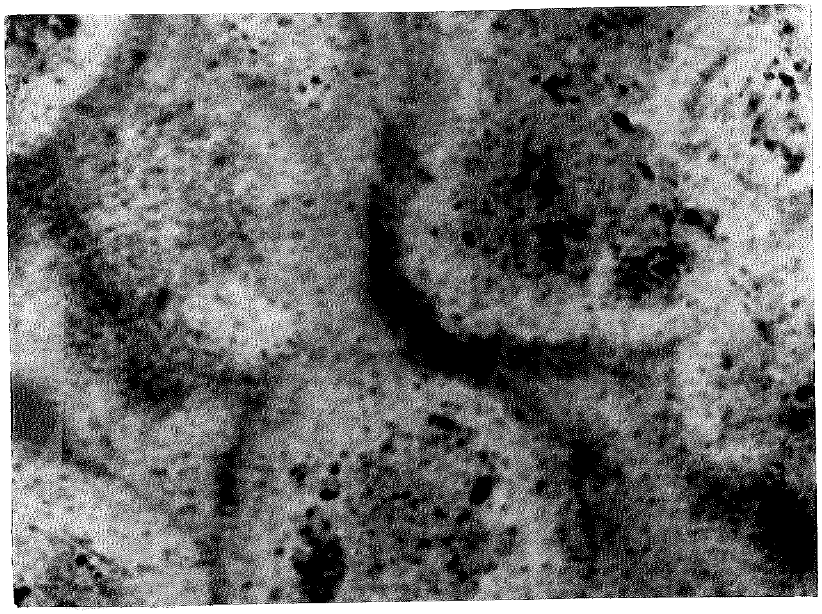
Sample 1229B Pure Chert 21264

Granular mosaic quartz vein in a microcrystalline quartz matrix with a few rhombs of dolomite, spicules, and faint calcareous remnants. Considerable porosity in bands due to carbonate dissolution. Crossed nicols, 145X



Sample 1237 Rhomb-bearing Chert 25731

Chalcedonic silica filled fracture transecting a fine grained, rhomb-bearing chert. The rhombs have not undergone corrosion or replacement, and the silica is primarily cryptocrystalline. Ordinary light, 145X

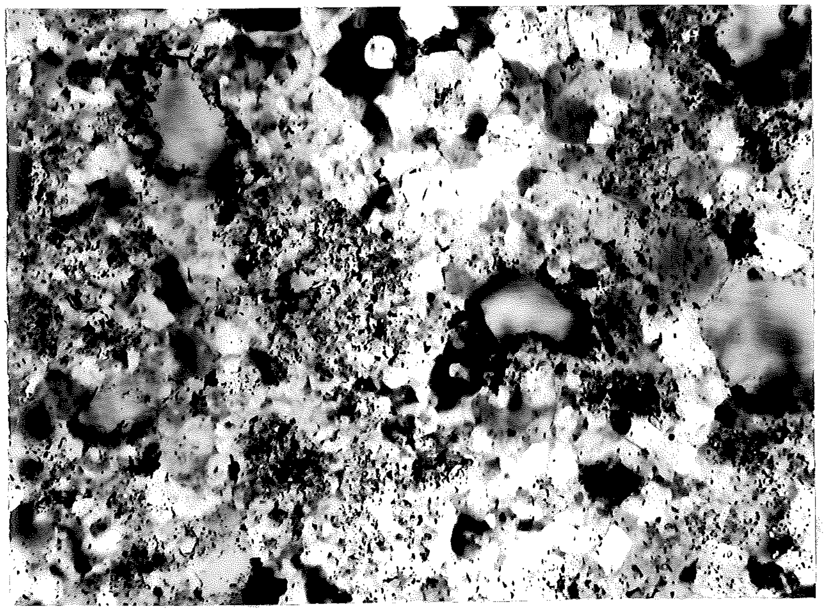


Sample 1345 Pure Chert 22361

Variable fossil assemblage replaced primarily by chalcedony and granular quartz. Spherulitic chalcedony and granular quartz occupy the replaced central portions of the fossils, with chalcedonic silica and microcrystalline quartz forming the matrix. Ordinary light, 145X

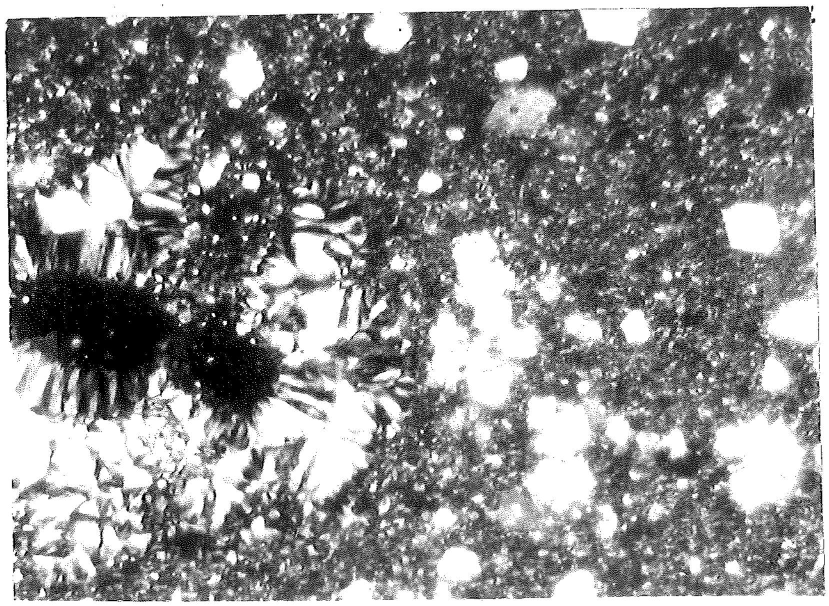
Sample 21 Calcareous Chert 2321101

Partially open fracture transecting a chert composed of granular quartz, chalcedonic silica, and calcareous remnants. The lines of impurities within the fracture generally delimit the boundary between chalcedony and granular quartz exhibiting undulatory extinction. Other areas show carbonate residue within the fractured zone. Crossed nicols, 145X



Sample 32 Pure Chert 2276412

Light-colored areas enclosed by ferruginous borders are pore spaces. Dusty carbonate colors portions of the quartz which is mostly granular. Sparse fossils also show faint carbonate rims. Porosity is probably due to dissolution of testes or rhombs since pore areas increase near the edge of the section. Partially crossed nicols, 145X

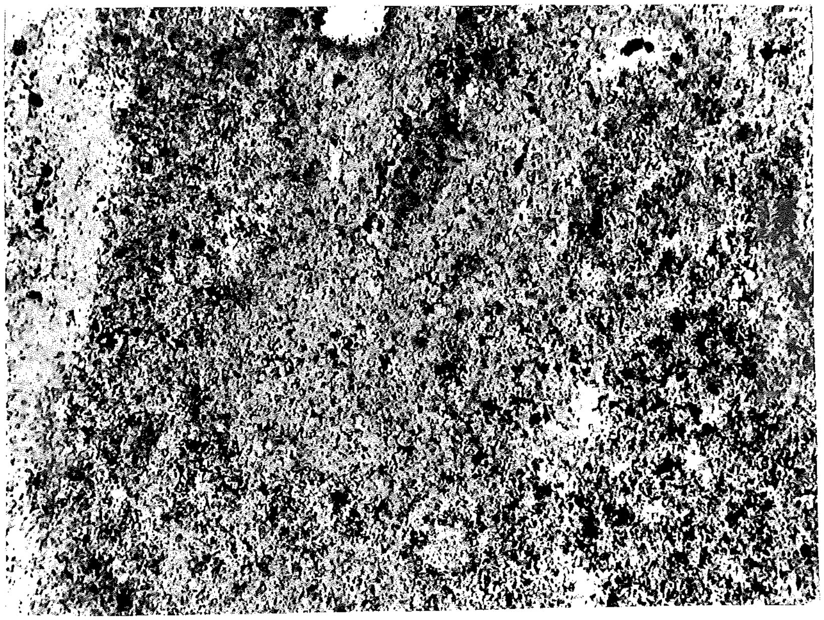


Sample 422 Calcareous Chert 2271102

Dark area surrounded by chalcedonic silica is brown in ordinary polarized light. Most of the rhombs are dolomite but some are quartz pseudomorphs after dolomite. Calcareous fossiliferous portions of this chert are only partially replaced. Silica is predominantly granoblastic. Crossed nicols, 145X

Sample 433 Rhomb-bearing Chert 2276111

Porous chert; carbonate, possible ankerite bands show ferruginous rhombs in various stages of corrosion without replacement. Silica is predominantly granoblastic with coarser mosaics present as fossil replacements. Ordinary light, 145X



Sample 52 Pure Chert 2276222

Sparsely fossiliferous and laminated chert. Fractures and pore spaces parallel the laminations comprised of light-colored granoblastic quartz alternating with darker layers which contain disseminated carbonate and accessory minerals. Ordinary light, 145X

APPENDIX C

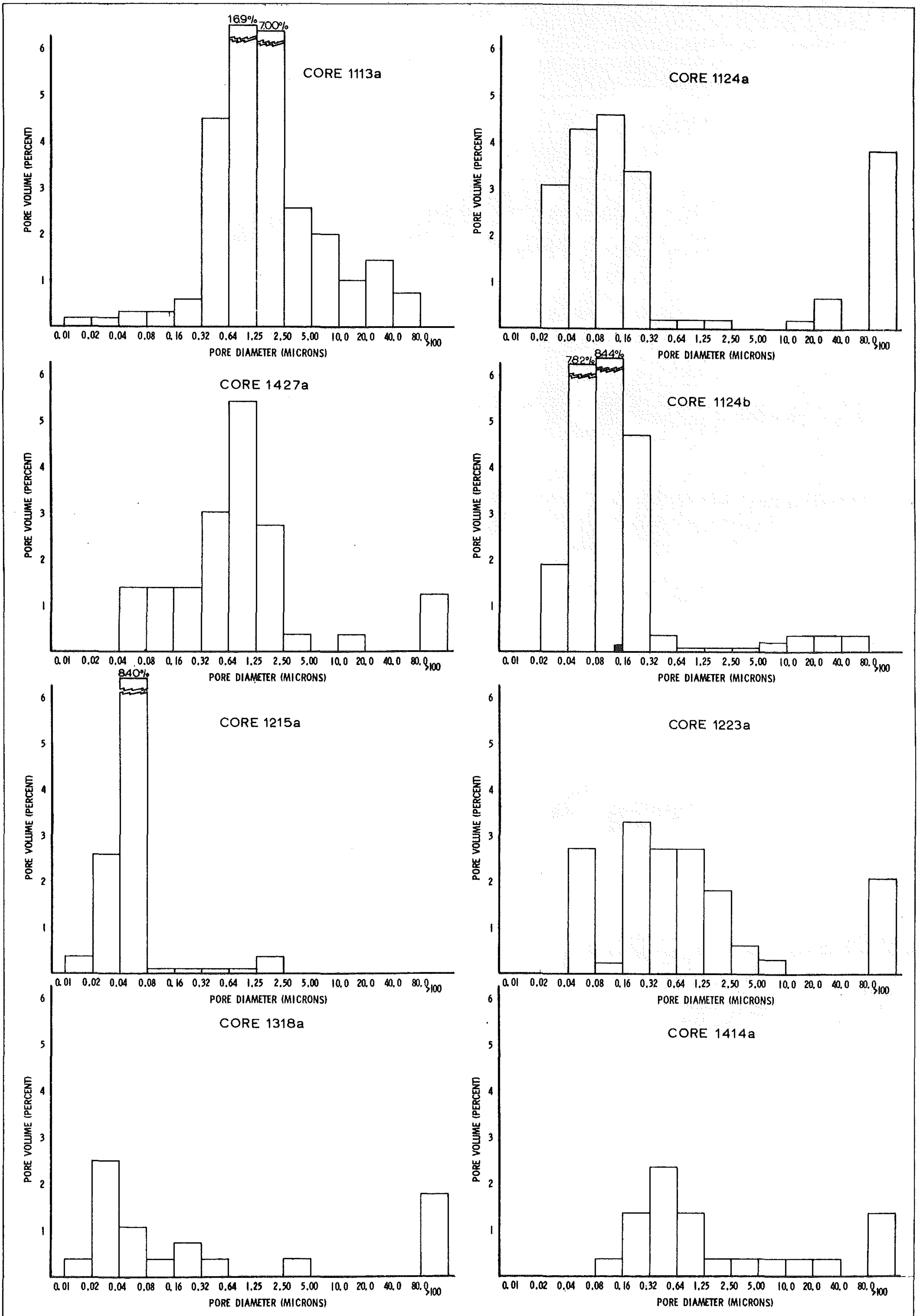


FIGURE 6a--PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES

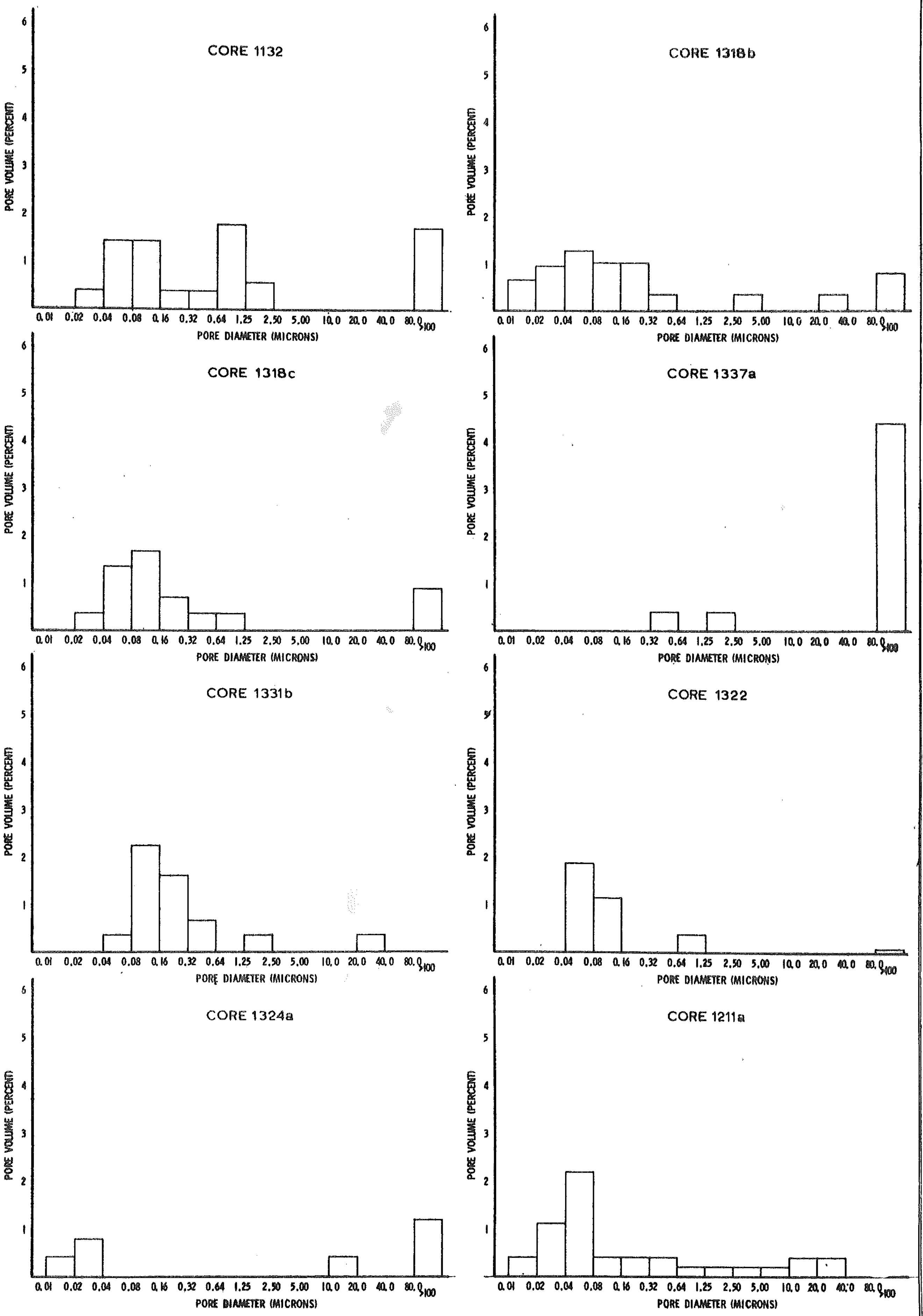


FIGURE 6b--PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES

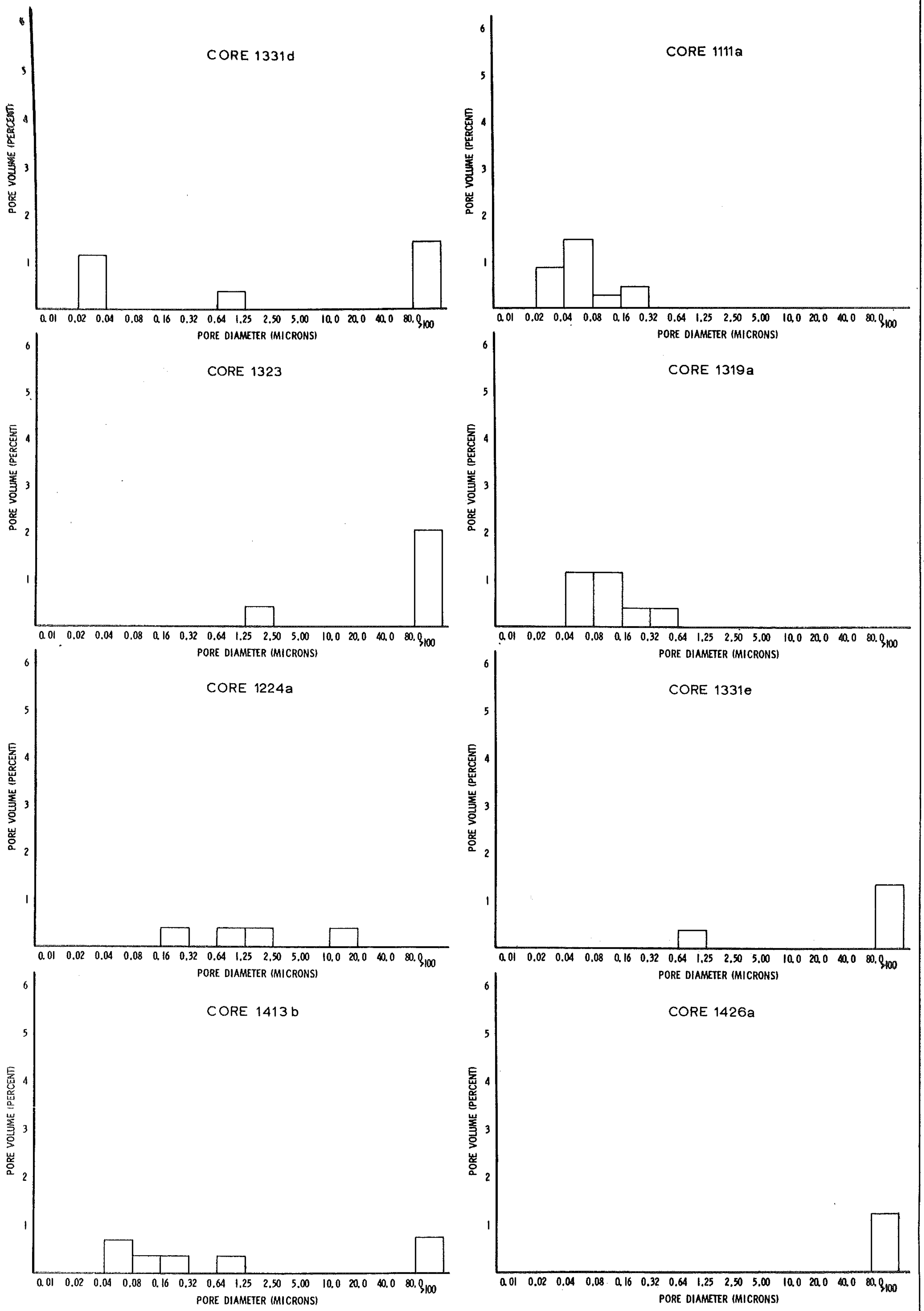


FIGURE 6c--PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES

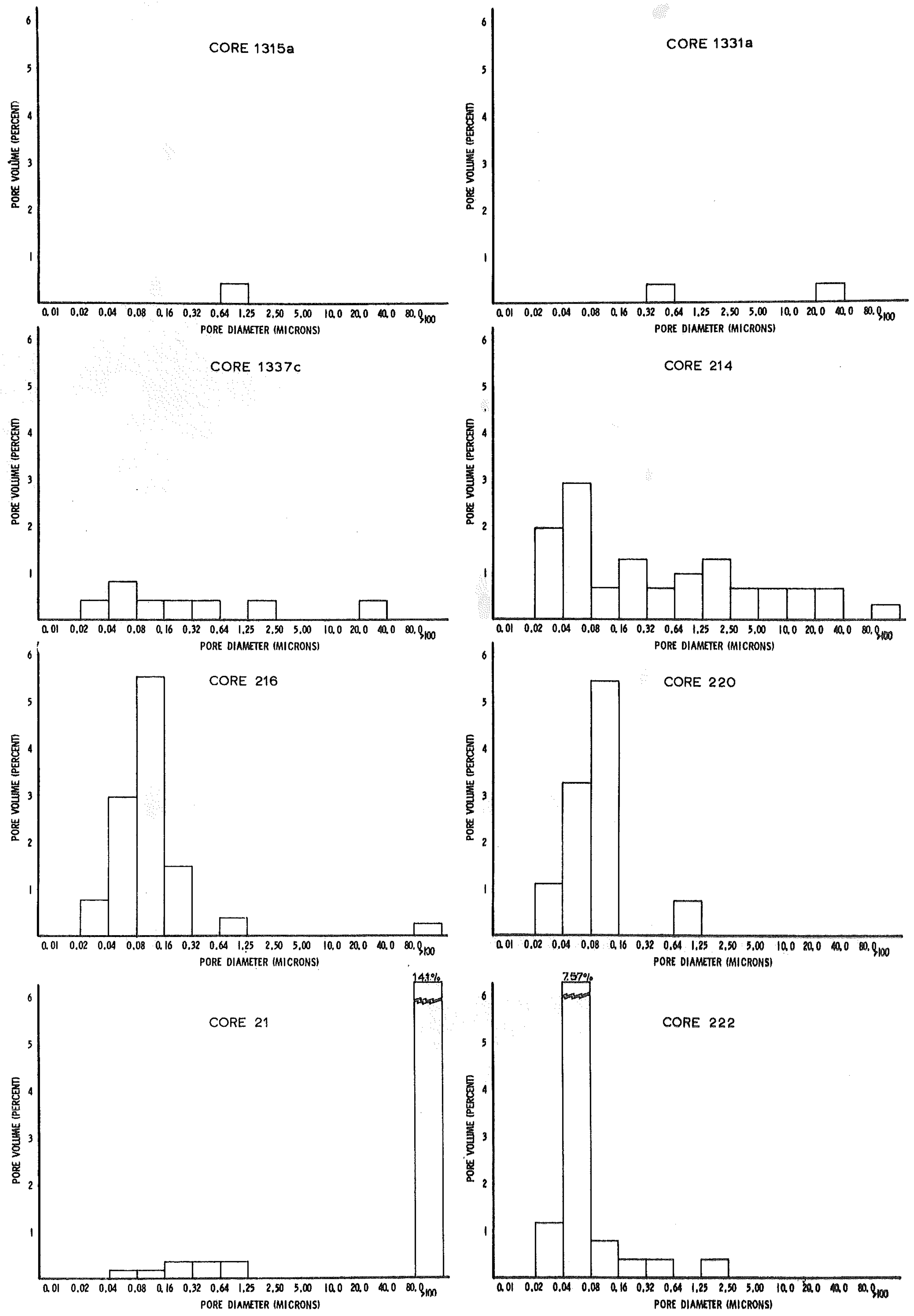


FIGURE 6d-- PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES

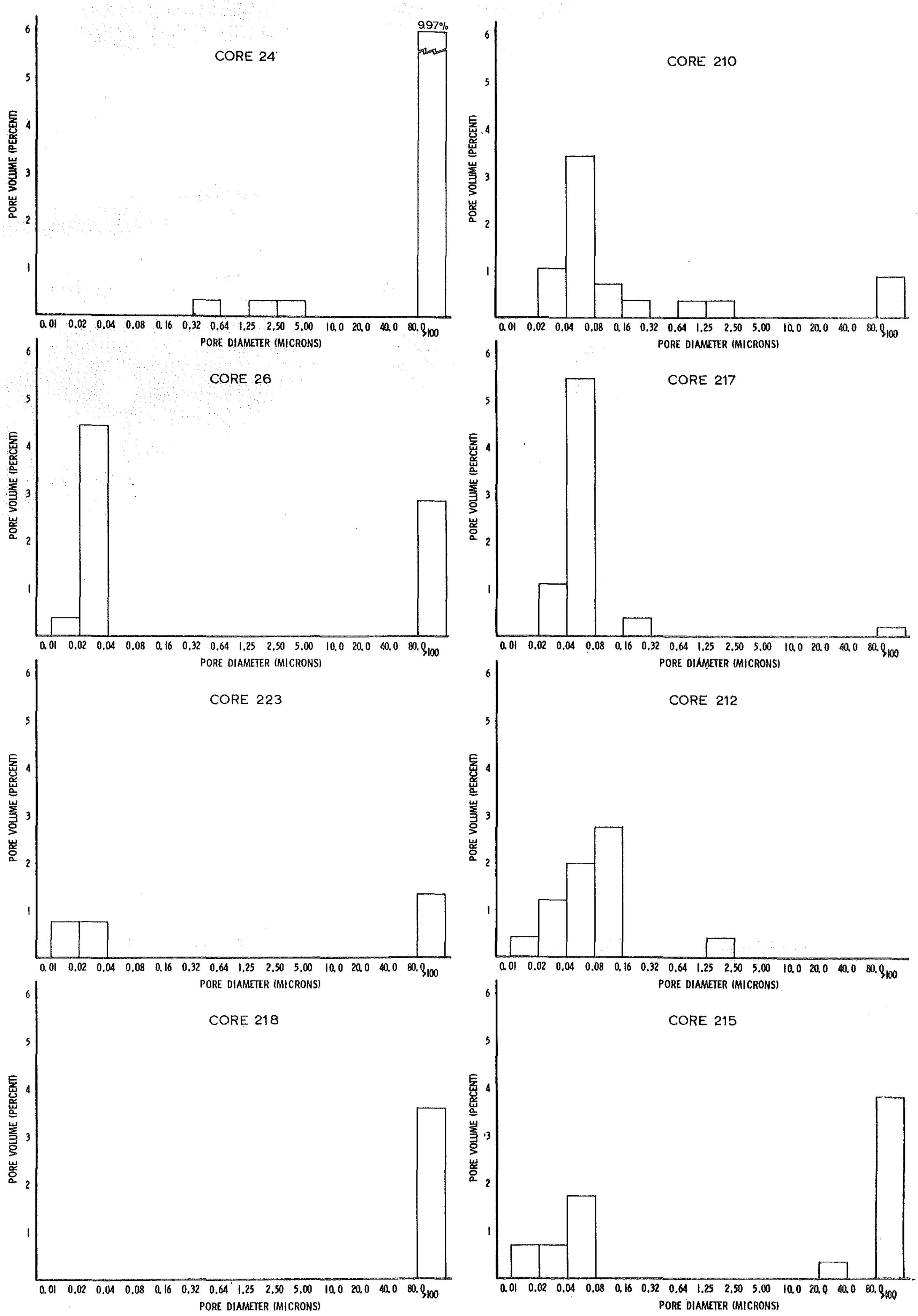


FIGURE 6e-- PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES

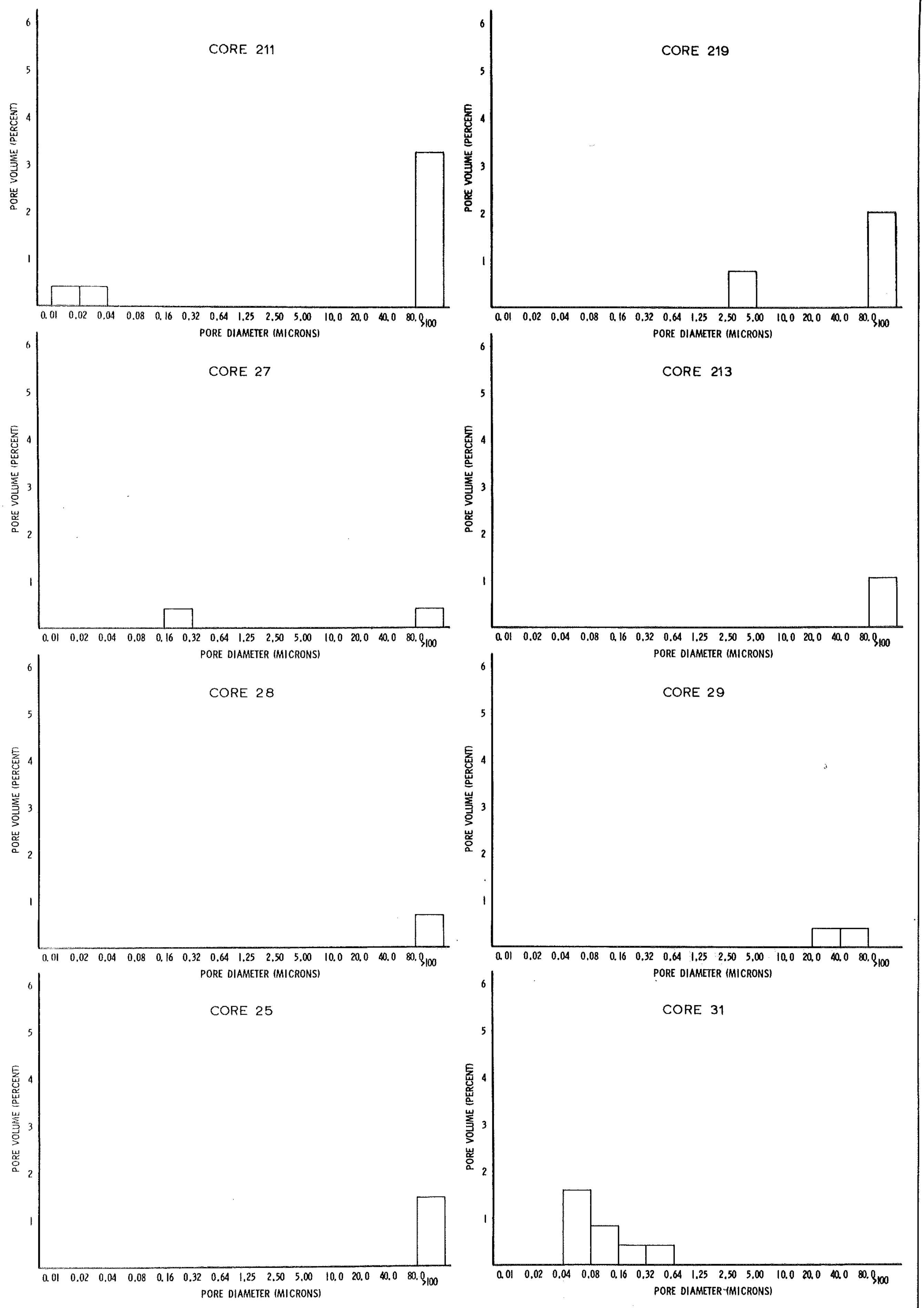


FIGURE 6f--PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES

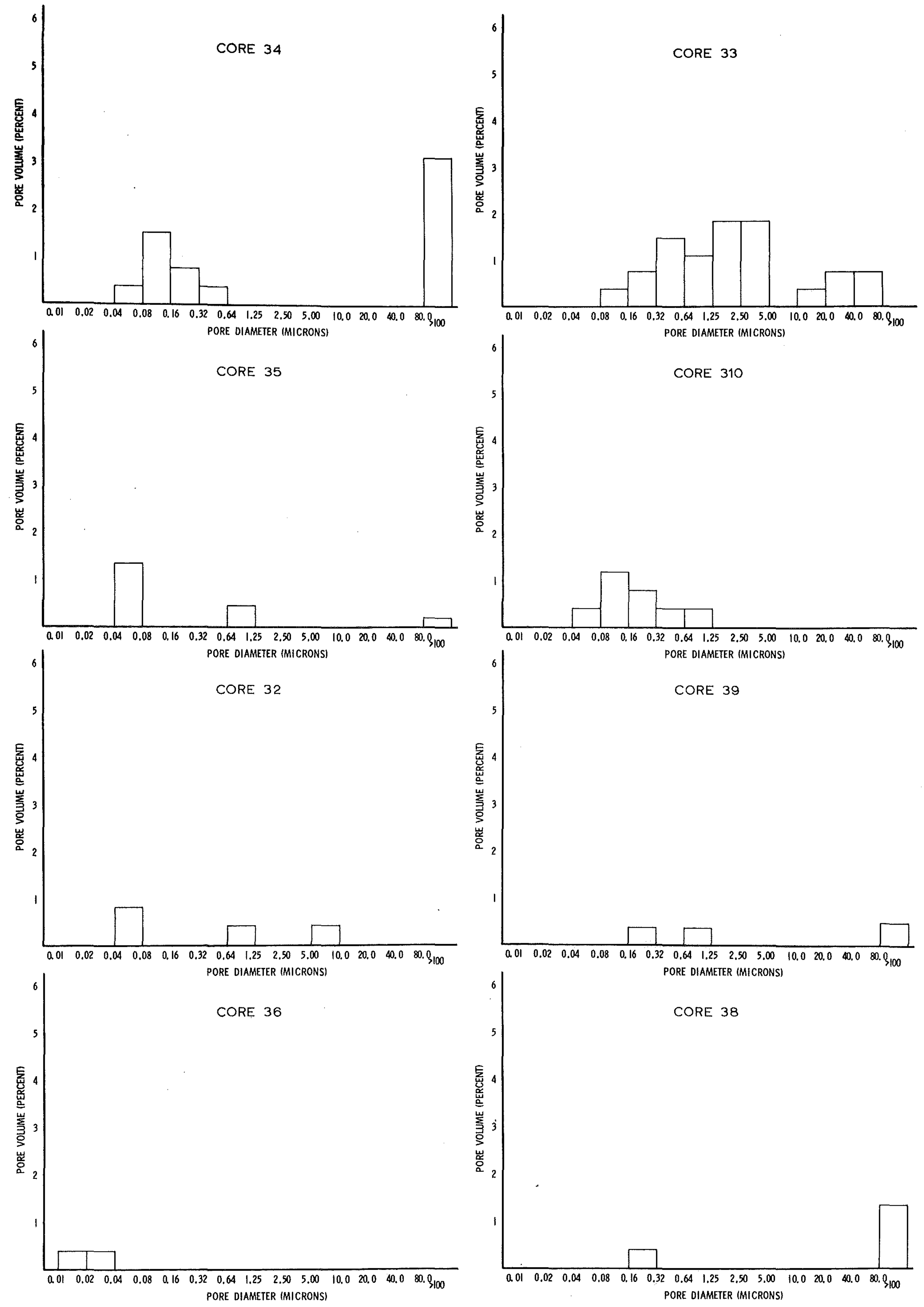


FIGURE 6g-- PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES

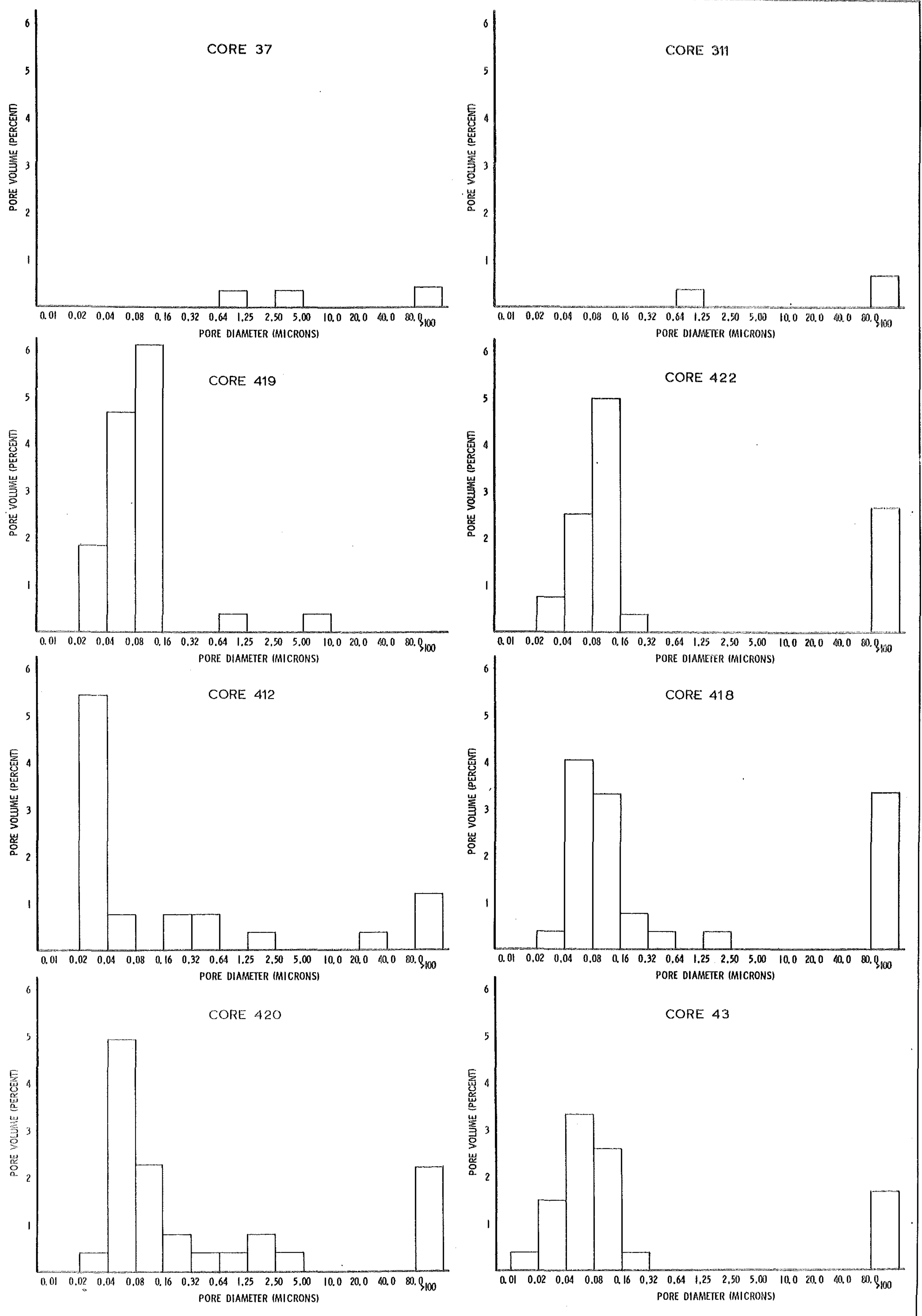


FIGURE 6h-- PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES

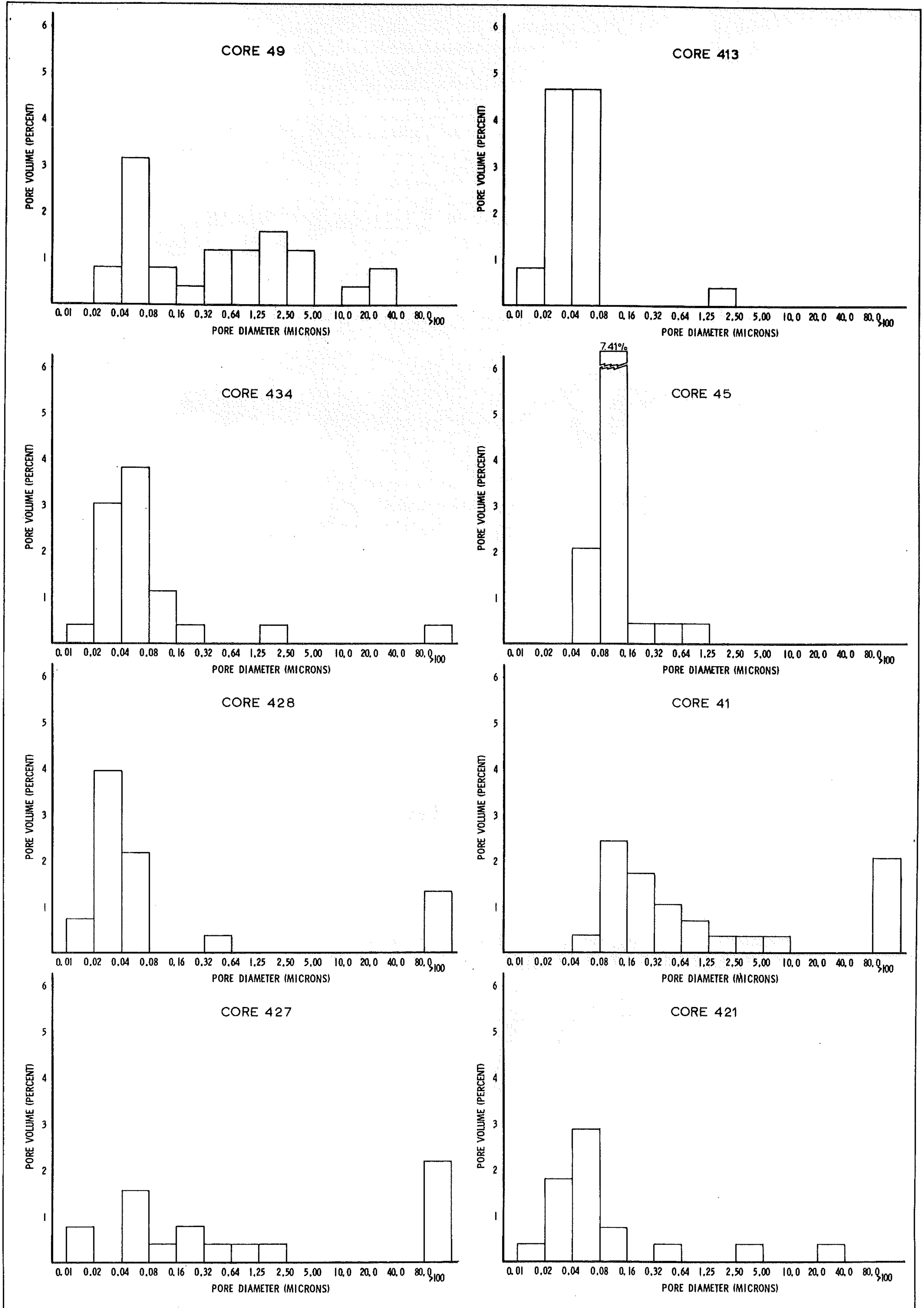


FIGURE 6i--PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES

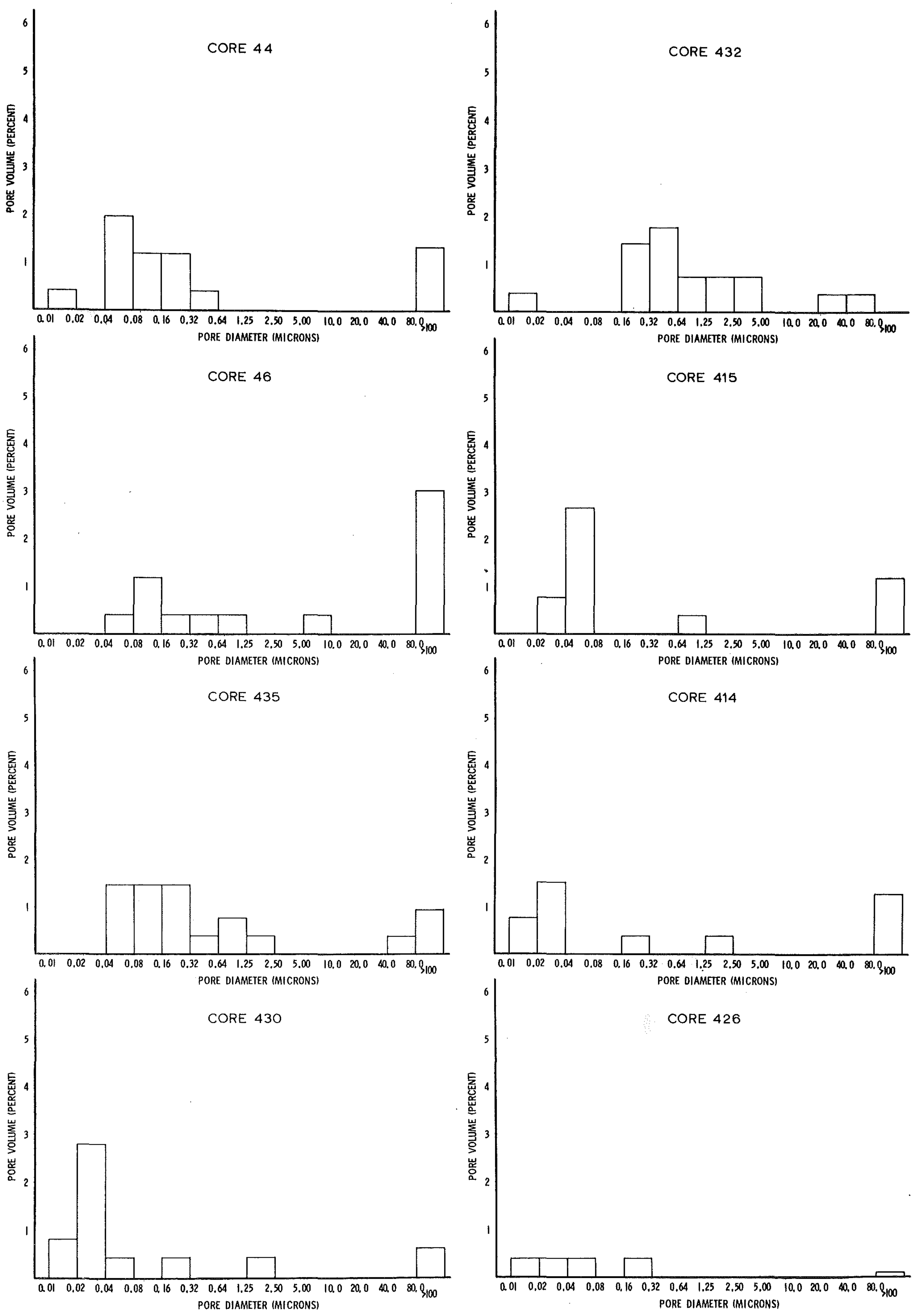


FIGURE 6j -- PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES

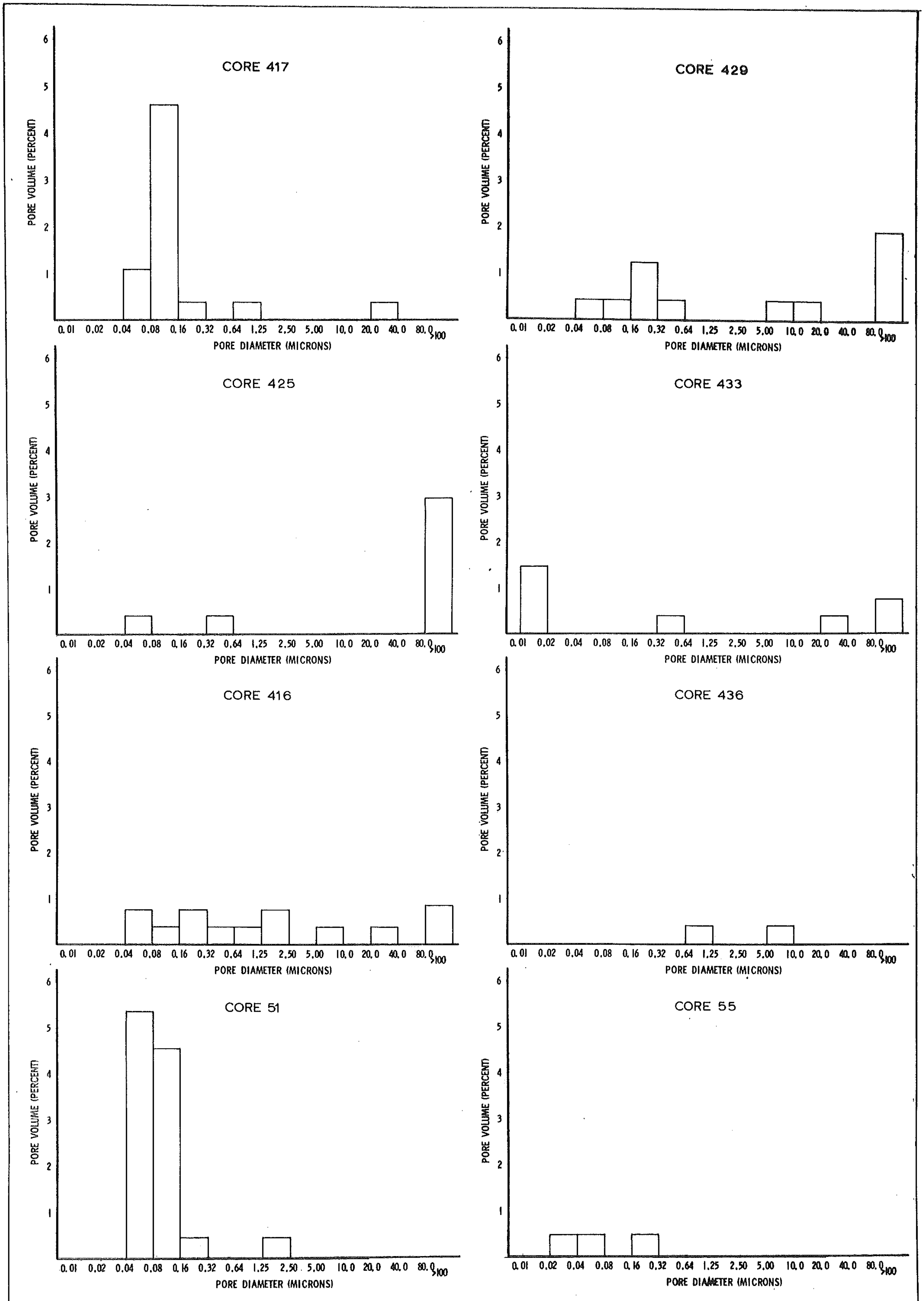


FIGURE 6k--PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES

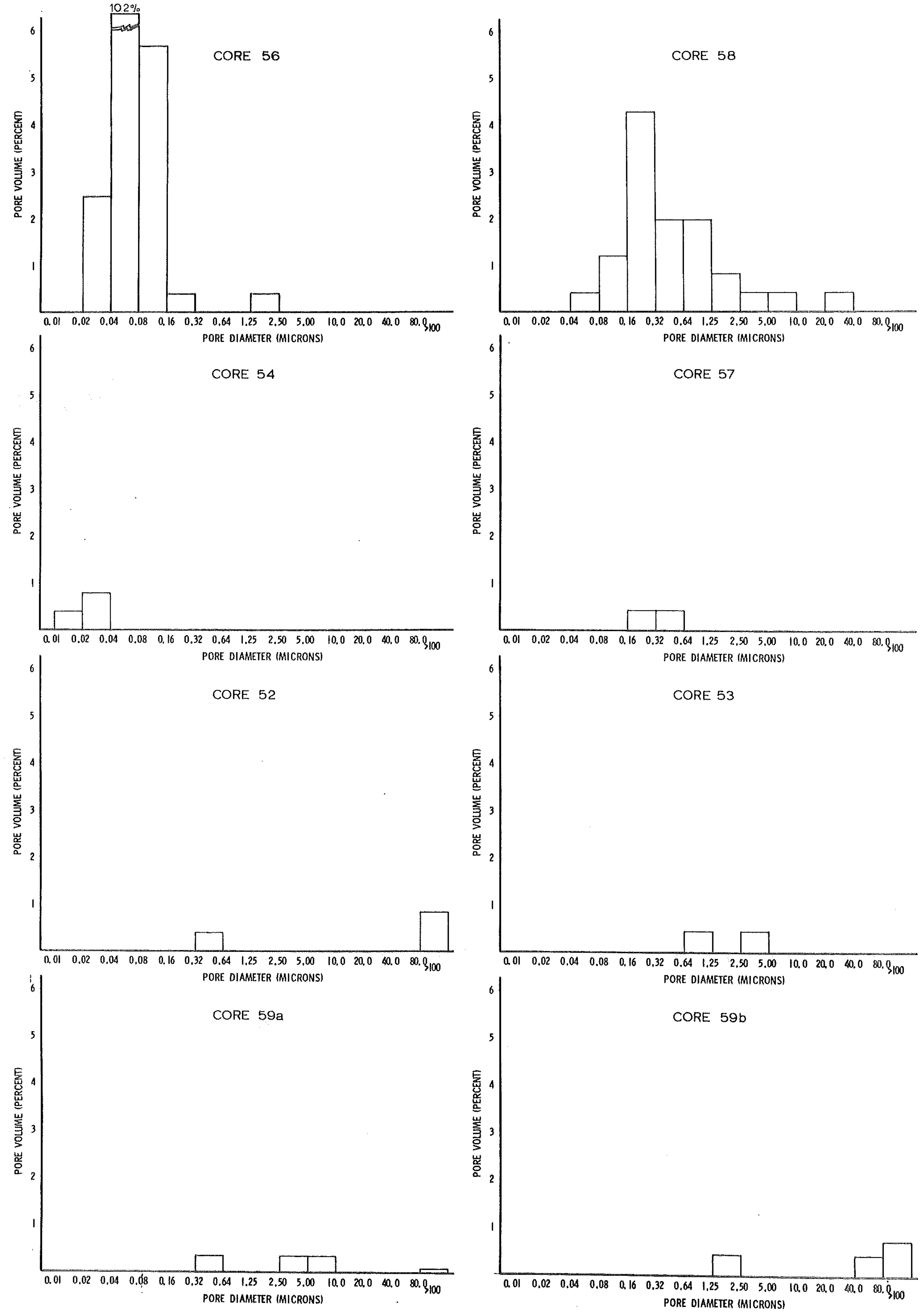


FIGURE 61--PORE SIZE DISTRIBUTIONS of SECTIONS REPRESENTATIVE of CHERT CORES