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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

MINERALOGY AND GEOCHEMISTRY OF VOLCANIC ASH AND BENTONITE IN THE OGALLALA FORMATION (TERTIARY) OF WESTERN OKLAHOMA

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

DAVID MAXWELL PATRICK

Norman, Oklahoma

1972

MINERALOGY AND GEOCHEMISTRY OF VOLCANIC ASH AND

BENTONITE IN THE OGALLALA FORMATION

(TERTIARY) OF WESTERN OKLAHOMA

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MINERALOGY AND GEOCHEMISTRY OF VOLCANIC ASH AND BENTONITE IN THE OGALLALA FORMATION (TERTIARY) OF WESTERN OKLAHOMA

By: David Maxwell Patrick

ABSTRACT

The Ogallala Formation of Pliocene age in western Oklahoma is a sandstone containing some conglomerate layers and lenses. At least 3 volcanic ash deposits and 1 bentonite deposit are present in the lower part of the formation. These lenticular deposits are up to 18 feet in thickness and have a known areal extent ranging from 300-600 acres.

The volcanic ash deposits are composed of silt-sized glass shards. Each deposit grades downward to bentonitic clay at the base. This textural change is accompanied by a downward increase in degree of shard alteration, which is also evident in the bentonite deposit.

Chemical analyses reveal that both the volcanic ash and bentonite deposits exhibit a downward decrease in SiO_2,

Na_2O, and K_2O and an increase in CaO, Fe_2O_3, and MgO. The alteration product of the rhyolitic glass is a Ca-montmorillonite. No other crystalline alteration products are present in either the ash or bentonite, although zeolites are locally present in the subjacent sediments.

The SEM reveals that individual glass shards exhibit from 1 to 3 alteration zones. Chemical analyses of these zones show a loss of SiO_2, Na_2O, and K_2O, and a gain of CaO, MgO, and Fe_2O_3 toward the outer surface of the alteration zone. The montmorillonite is forming on the shard surface and exhibits some optical continuity.

Ground water moves downward and laterally through the porous sandstone and ash deposits. This ground water is believed to be responsible for alteration of the glass shards to montmorillonite and for changes in the bulk chemistry of the ash deposits.

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MINERALOGY AND GEOCHEMISTRY OF VOLCANIC ASH AND BENTONITE IN THE OGALLALA FORMATION (TERTIARY) OF WESTERN OKLAHOMA

INTRODUCTION

Purpose

The purpose of this investigation was to identify, characterize, and evaluate the geochemical and mineralogical processes which affect the alteration of volcanic glass to montmorillonite. The results of these processes were studied by examination of the petrographical, mineralogical, and geochemical variation in the volcanic ash from top to bottom of the stratigraphic section and by comparing the chemistry of the fresh volcanic ash to its surface alteration rinds.

The study attempted to answer the following questions:

1. Given the assumption that the alteration occurred in an aqueous environment and probably by groundwater, what was the direction of water movement?

2. What is the relationship between the observed

textural changes in the stratigraphic section and the geochemistry?

3. Does there appear to be any similarity between individual grain alteration as determined geochemically by non-dispersive chemical analysis and the vertical alteration mentioned in Question Number 2 above?

4. Do there appear to be any intermediate mineral species which have been derived from the volcanic ash and which, in turn, alter to montmorillonite?

5. What is the relationship between the alteration product and the alteration surfaces on the volcanic ash?

6. Is there any difference in the nature of the montmorillonite in the relatively fresh volcanic ash versus the highly altered volcanic ash?

The answers to the above questions will be considered in relation to the analyses of the two following questions:

7. What is the general environment of deposition of the volcanic ash and what was the source of the ash?

8. What is the economic potential of these deposits?

Geographic Areas of Investigation

The Plio-Pleistocene volcanic ash and bentonite deposits in Oklahoma may be divided into three types based

upon petrologic and geologic dissimilarities (Table 1). The fresh type consists of fine to medium, silt-sized glass shards, exhibiting minor surface alteration and is geologically associated with Pleistocene stream terraces. The partially altered variety consists of medium to coarse, silt-sized glass shards with moderately-altered surfaces, and the entire deposit grades into bentonitic clay at the base. These deposits are associated with Tertiary sediments and collapse structures. The collapse structures are suggested by anomalous dips and the chaotic attitude of the underlying Permian strata. The highly altered type, represented by one deposit near Camargo, Oklahoma, consists of highly altered glass shards and excellent development of bentonitic clay throughout. This deposit is associated with fluvial sands of presumed Tertiary age.

The fresh type of deposit occurs at numerous localities in Oklahoma along major drainage systems. Partially altered and highly altered varieties seem to be limited to the Tertiary outcrops in northwestern Oklahoma (Fig. 1).

I have elected to study only the partially altered and highly altered types of deposits for the following reasons: the downward gradation of volcanic ash into bentonitic clay should provide information on the nature of glass alteration;

TABLE 1

PLIO-PLEISTOCENE VOLCANIC ASH AND BENTONITE IN OKLAHOMA

Type	Petrology	Geology
Fresh	Fine to medium silt, little to no surface alteration, minor clay development	Associated with Pleistocene stream terraces.
Partially Altered	Medium to coarse silt, altered surfaces, good development of clay at base.	Associated with Tertiary sediments and collapse structures.
Highly Altered	Original grain size unknown, highly altered surfaces, excellent clay development throughout deposit.	Associated with fluvial sands of presumed Tertiary age.

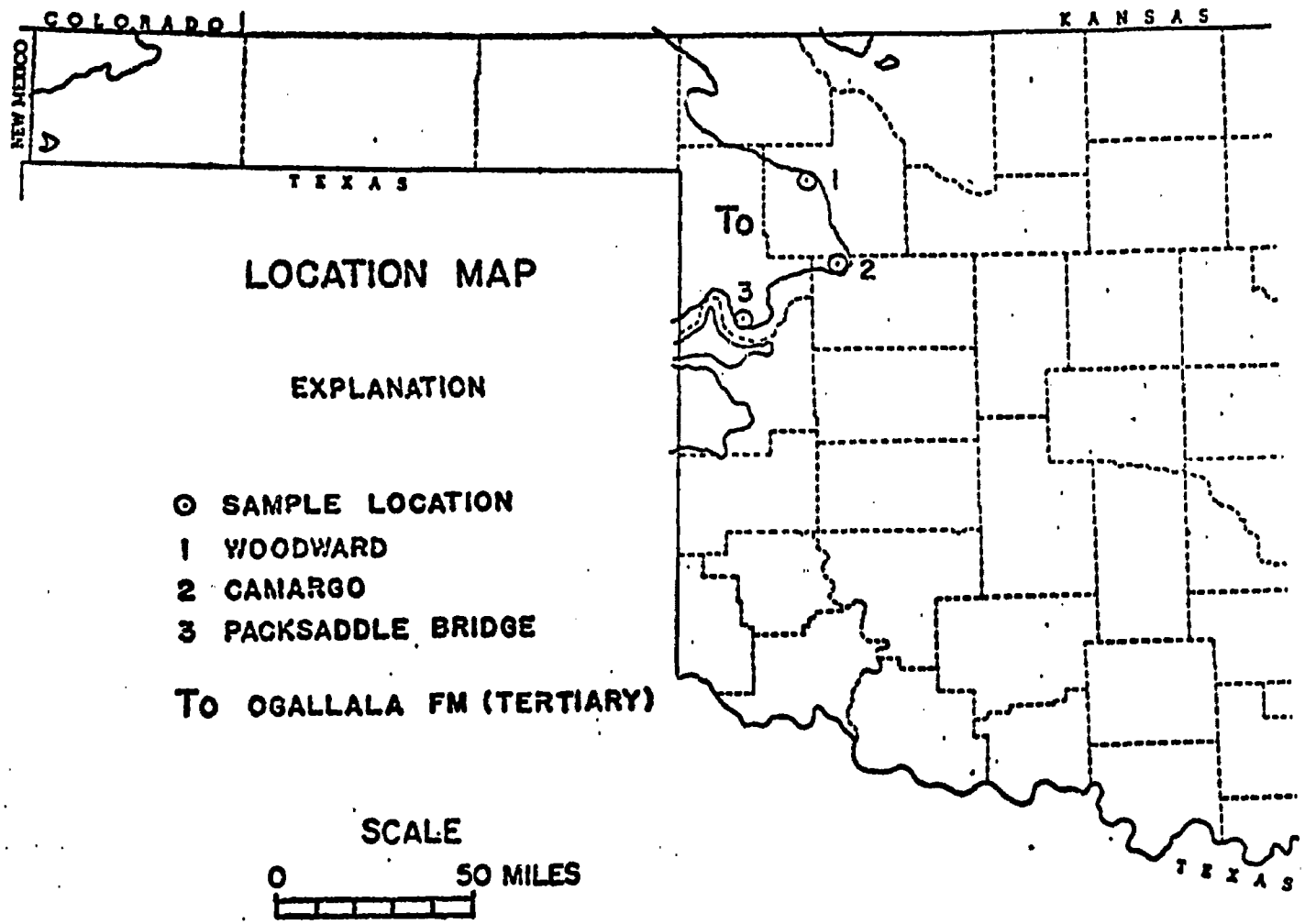

COLORADO
KANSAS
NEW MEX
TEXAS
TEXAS
To
1
2
3
LOCATION MAP
EXPLANATION
⊙ SAMPLE LOCATION
1 WOODWARD
2 CAMARGO
3 PACKSADDLE BRIDGE
To OGALLALA FM (TERTIARY)
SCALE
0
50 MILES

Figure 1

and if these two types are the same age they may represent the same ash fall, in which case comparisons may be made regarding the nature and degree of alteration in differing environments.

There are three known localities in northwestern Oklahoma where partially altered volcanic ash is exposed in quantity (Fig. 1). One is located 5 miles northwest of Woodward in Woodward County; the second is in southern Ellis County near the Packsaddle Bridge on U. S. Highway 283; and the third is 3 miles southwest of the dam of Lake Lloyd Vincent in western Ellis County. The Lake Lloyd Vincent deposit was not studied in detail.

The highly altered deposit occurs approximately midway between Vici and Camargo in Dewey County. The three studied localities will be referred to as Woodward, Packsaddle Bridge, and Camargo localities respectively. Locations and described stratigraphic sections are given in Appendix I.

Geologic Setting

Much of northwestern Oklahoma is covered with a veneer of alluvial sands and gravels of Tertiary age. These sediments are generally uncemented, cross-bedded, yellow to light brown in color, and are locally as much as 400 feet thick.

The presence of vertebrate faunal assemblages (Kitts, 1965) has substantiated a Pliocene age for these deposits and they are considered correlative with the Ogallala Formation of Kansas and Nebraska. In Oklahoma, the Ogallala is also given formation rank and is locally subdivided into the upper, Kimball member and lower, Laverne member. At most locations, however, the Ogallala cannot be subdivided.

The sediments of the Ogallala Formation were deposited by eastward-flowing streams originating in the Rocky Mountains of Colorado and New Mexico. These streams flowed eastward over a surface of low relief (Frye and Leonard, 1957) and at a moderately high gradient as evidenced by the coarse grain size of the sediments deposited. Locally, ponding occurred upon the floodplains and terraces, and accumulated deposits of fine-grained silts and clays. The present day traveler who crosses the High Plains will note the numerous natural depressions, some of which are filled with water and dot the landscape.

The rocks underlying the Ogallala Formation in the area under consideration are Permian in age and consist primarily of terrigenous strata with some evaporite units. The exposed rock units are the Rush Springs and Cloud Chief

Formations. These formations are underlain in the subsurface by the El Reno Group.

Several previous investigators (Lovett, 1960; Smith, 1964; Richardson, 1970) have noted the presence of the surface depressions and have attributed them to the solution of the evaporite units and the corresponding subsidence of the overlying strata. It is possible that depressions such as these were present during the Tertiary and were the sites of volcanic ash accumulation.

Previous Investigations

Only two investigations of any consequence have been made on volcanic ash in Oklahoma. One of the earlier investigations was that of Buttrum (1914). Included in this study were grain-size analyses, chemical analyses, and the general geology of four ash deposits including the one at Woodward. Chemical analyses and firing tests were conducted by Burwell and Ham (1949) on samples of volcanic ash and bentonite collected throughout the state. In this work Ham studied the general geology and petrology which included samples from Woodward and Camargo. Additional references are made to volcanic ash and bentonite deposits in general geologic

reports of which some will be discussed in other sections of this study.

Woodward Locality

The Woodward volcanic ash locality is approximately 5 miles northwest of Woodward, Woodward County, Oklahoma, in Secs. 13 and 24, T. 23 N., R. 22 W., on the northwest side of Sand Creek, a tributary of the North Canadian River. Outcrops are sparse, and surface mining operations have obliterated lateral relationships.

The volcanic ash bed ranges in thickness from 6 to 8 feet and within this range grades, more or less imperceptively, downward into bentonitic clay at the base. The ash is light gray and the bentonitic clay is pinkish white. The unit gradationally underlies 2 or 3 feet of gray, carbonate-cemented coarse sand and gravel, and is directly underlain by approximately 2 feet of brown, silty clay. The silty clay is underlain by not more than 30 feet of uncemented, cross-bedded silts, sands, and gravels which rest upon the Permian Rush Springs Sandstone. Although the strata of the Rush Springs are essentially horizontal near the ash deposit, exposures of red, silty shale and sandstone located in a road cut 5 miles northwest of Woodward on U. S. Route 183 exhibited

a strike of N 30° W and a dip to the north of 20°. The regional dip of Permian strata in this area does not exceed 1° and it is normally to the south or southeast. The anomalous attitude of the Permian rocks suggests the possibility of collapse in the vicinity of the ash deposit.

Packsaddle Bridge Locality

The Packsaddle Bridge locality is situated in southern Ellis County, approximately 22 miles south of Arnett, in Secs. 11 and 12, T. 16 N., R. 24 W. Exposures of volcanic ash and bentonite occur along the valley walls on the north side of the Canadian River. This location is approximately 2 miles northeast of the Packsaddle Bridge on U. S. 283.

Kitts (1965) mapped and described the areal geology of Ellis County including the Packsaddle Bridge locality. In the southern portion of the county, along the Canadian River, Kitts recognized 3 Pleistocene river terraces and approximately 100 feet of the Ogallala Formation overlying Permian bedrock of undifferentiated Cloud Chief and Quartermaster Formations. The lithology, color, and general nature of the upper 50 feet of Ogallala here is similar to that found further to the north of the Canadian River and, in general, throughout the area of Tertiary exposure. The lower 50 feet

here is strikingly different; this interval consists of thin, alternating layers of red shale, red siltstone, and red sandstone.

The recognition and differentiation of Pleistocene, Tertiary, and Permian stratigraphic units in western Oklahoma is sometimes difficult but, lacking fossils, is normally accomplished on the basis of color, grain-size, and unit geometry. The Pleistocene and Tertiary units are, perhaps, the most difficult to differentiate since both are alluvial deposits. The Pleistocene, however, is generally limited in extent to terraces along modern river systems, whereas the Tertiary deposits extend across divides, are more continuous, and exhibit a coarser grain-size as well as a darker tan to brown color. Red color, grain-size, which is normally less than medium sand, and presence of gypsum are the principal criteria to the recognition of the Permian rocks.

Prior to about 1960, the lower 50 feet of Ogallala was considered to be Permian in age and was mapped as such. This decision was based upon the red color and fine grain size of the sediments. The discovery of horse and camel bones in these lower sediments required a reevaluation of their age. Kitts (1965) suggested a Pliocene age, based upon similarities with the vertebrate fauna in adjacent Roger Mills County

(Kitts and Black, 1959), and he has given these red, Pliocene sediments the informal name, "Packsaddle Beds."

The volcanic ash bed ranges in thickness from 10 to 20 feet and within this thickness grades downward into bentonitic clay at the base. The nature of the volcanic ash and bentonitic clay here is similar to that at the Woodward locality. The volcanic ash is overlain by 1 to 20 feet of coarse sands and gravels which are locally cemented. The underlying material consists of about 25 feet of alternating silty clays, sands and silts. Directly beneath the bentonitic clay are 2 to 3 feet of brown, silty clay which is locally cemented within the top one-inch. These alternating clastics lie, in turn, upon the red sediments containing the Pliocene vertebrate fauna which were previously discussed. Figure 2 illustrates the generalized stratigraphic section at this locality.

The outcrop of volcanic ash extends for approximately 2 miles along the river and forms numerous spurs which are separated by small, intermittent, southward-flowing tributaries to the Canadian River. The ash unit is also exposed for as much as 200 yards up the tributaries. The well-exposed outcrops indicate that the nature of the volcanic ash and bentonitic clay is generally quite uniform along the

GENERALIZED STRATIGRAPHIC SECTION
PACKSADDLE BRIDGE LOCALITY

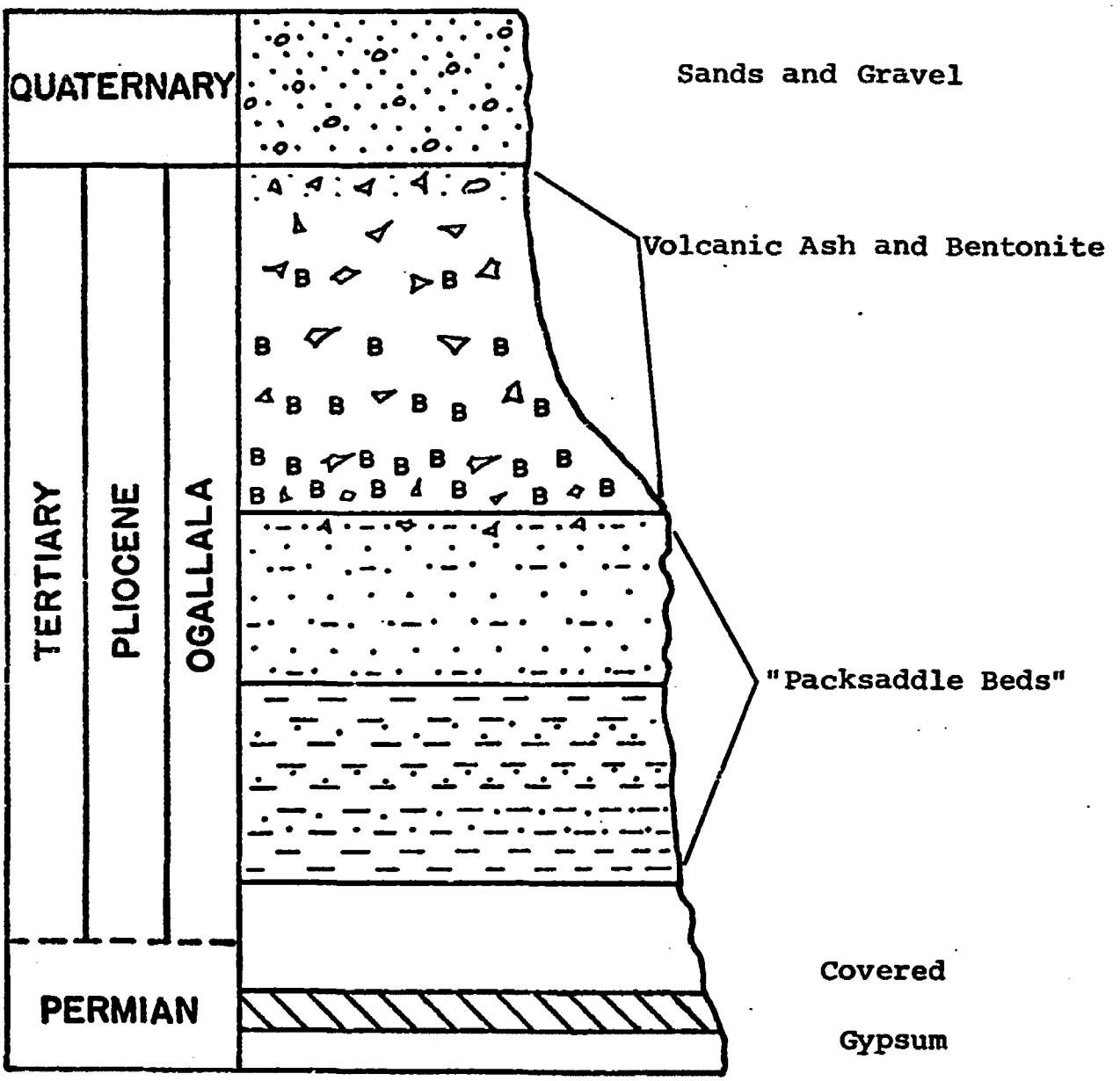


Figure 2

exposure. Lateral contacts or gradation of the volcanic ash unit with the confining sediments could not be found.

Alidade-plane table and altimeter surveys were conducted at this locality for the purpose of determining the geometry of the unit. The results of these surveys are: 1) The unit is thickest near the center of the exposure, 2) The base is nearly 30 feet lower in elevation at the center of the exposure than at the sides, and 3) Three faults with vertical displacements of up to 30 feet are present. Figure 3 illustrates a reconstructed cross-section across the deposit.

The faults emphasize the graben-like nature of the deposit and indicate that subsidence has occurred subsequent to the deposition of the ash.

Approximately 200 yards south of the exposures of volcanic ash are outcrops of gypsum. The gypsum here is approximately horizontal in attitude. In addition to the faults the only other suggestion of collapse in the immediate vicinity is the presence of isolated blocks of volcanic ash, 1 to 2 feet in diameter, in a depression several hundred yards from the nearest outcrop. Approximately 10 miles south of Packsaddle Bridge the Permian strata exhibit high angle dips and chaotic structure.

PARTIALLY RESTORED CROSS-SECTION
OF VOLCANIC ASH AND BENTONITE UNIT
AT PACKSADDLE BRIDGE LOCALITY

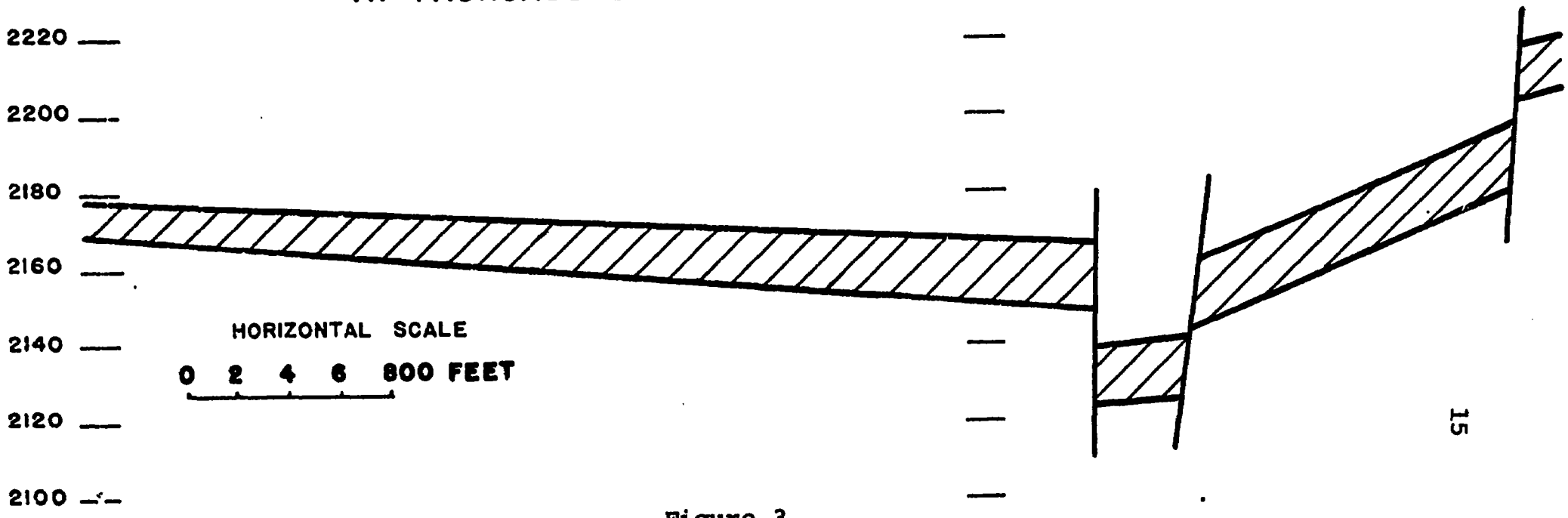


Figure 3

I conclude that the basin of ash accumulation was subject to subsidence after ash deposition and that it is most likely that the origin of the basin is also due to subsidence caused by solution of the underlying Permian evaporites. Furthermore, it appears that the subsidence produced minimal disturbance at the center of the subsiding area and maximum disturbance at the margins.

Camargo Locality

The Camargo bentonite locality is located approximately 3½ miles south of Vici and approximately 6 miles north of Camargo in Dewey County. Fair to good exposures of bentonite occur in a gully system on the west side of State Route 34 in the SW¼, Sec. 18, T. 19 N., R. 19 W. East of State Route 34 the bentonite also occurs in Sec. 17 where it has been mined for several years. The exposures here are poor due to filling of the pits with overburden.

The bentonite is 5 to 6 feet thick, white, and pink to gray, and generally uniform in nature from top to bottom. When wet it is highly plastic and soapy to the touch. In a dry state the material is hard and brittle. In Sec. 17, the bentonite is overlain by 20 to 30 feet of yellow to brown, cross-bedded, medium to fine sand. The sediments that are

underlying the bentonite are poorly exposed but appear to be similar to those overlying it. In Sec. 18, the bentonite is overlain by approximately 2 feet of coarse sand, locally cemented, and underlain by a sequence of medium sand containing a silty clay layer 1-foot thick lying approximately 1 foot below the base of the bentonite. The grain size and cross bedding of the enclosing sediments suggests that the original volcanic ash was deposited on an alluvial plain with localized ponding.

Although the Permian strata to the north are horizontal, there is considerable evidence for collapse, as indicated by chaotic attitudes in the Permian rocks a few miles to the south of the Camargo locality.

Sample Collecting Procedures

At each of the three studied localities one vertical section of volcanic ash and bentonite was sampled. Samples were collected at 1-foot intervals and each interval was represented by 4 to 6 inches of sample. These vertical samples were supplemented by spot samples taken elsewhere along the outcrop. The sediments over and underlying the volcanic ash and bentonite were also collected in a similar fashion at those places where the vertical sections were collected. All

samples collected moist or wet on the outcrop were placed in doublelined plastic sandwich bags and sealed to prevent dehydration.

PETROLOGY

General Statement

Volcanic ash refers to a clastic sediment consisting of sand- and silt-size igneous debris which has been formed in and ejected from a volcanic vent. The ejected material may be deposited nearby or may be carried many miles by winds aloft before deposition. Volcanic ash may consist of a combination of glass particles (shards), igneous-rock fragments, crystal grains (phenocrysts), and terrigenous grains.

The term bentonite was first proposed by Knight (1898) for the argillaceous units within the Ft. Benton group of Cretaceous age in Wyoming. These argillaceous units consist predominantly of the clay material montmorillonite accompanied by minor amounts of terrigenous grains. The montmorillonite was derived from the alteration of volcanic glass as suggested by "ghosts" or outlines of glass shards in the clay (Slaughter and Earley, 1965). The use of the term bentonite is generally restricted to any argillaceous rock derived from the alteration of volcanic glass. Ross and Hendricks (1945,

p. 65) report an earlier definition of Ross and Shannon (1926) which states that,

> Bentonite is a rock composed essentially of a crystalline clay-like mineral formed by the devitrification and the accompanying chemical alteration of a glassy, igneous material, usually a tuff or volcanic ash.

The above authors further recognize the presence of crystal grains which were originally phenocrysts in the volcanic glass and that the "clay-like" mineral is commonly montmorillonite or beidellite.

The grain size, petrographic character, and mineralogy of the volcanic ash and bentonite units, as well as the nature of the enclosing sediments will be discussed in the following sections.

Grain-Size Analysis

The grain-size distribution was determined for the vertically collected samples from the Packsaddle Bridge and Camargo localities. The procedure involved wet sieving utilizing both conventional wet sieves and "Micro Mesh" sieves. The conventional sieves had 149, 62.5, and 44 micron openings. The "Micro Mesh" sieves had 30, 20, 10, and 5 micron openings.

Because the relatively fresh volcanic ash contained some clay, it was important that disaggregation be complete

as possible. Approximately 3 or 4 grams of material was gently disaggregated by hand, placed in a 250 ml beaker with distilled water and then stirred. The suspension was then agitated ultrasonically utilizing a sonde and Branson Sonifier power supply. The suspension was agitated for a duration of 3 or 4 minutes. The suspension was then washed into the top of the nest of conventional wet sieves. The conventional sieves were individually washed with distilled water until it appeared that nothing more could be passed. The particles finer than 44 microns were then sieved utilizing the "Micro Mesh" sieves.

Techniques for using "Micro Mesh" sieves were presented by Nuckolls and Fuller (1966). The procedures used here are those of the above authors with some modifications necessitated by existing equipment. The "Micro Mesh" sieves were not nested. Starting with the 30 micron sieve, each was placed over a plastic bucket. The suspension to be sieved was poured on the sieve and sufficient distilled water was added to insure complete passage of all particles finer than the sieve in question. The greatest difficulty was encountered with the 10 and 5 micron sieves, as approximately 1000 ml of wash water was required for complete passage. The plastic bucket with the sieves inside was, in each case, placed upon

a mechanical vibrator to enhance passing the particles through the sieve openings.

The particles retained on both conventional and "Micro Mesh" sieves were washed into a small beaker which was then heated overnight in a drying over at 130 degrees centigrade. After drying, the small beakers were weighed, then washed and weighed again; the difference in weight being the weight of particles retained for a particular sieve size. The particles passing the 5 micron sieve were treated in a similar fashion. After determining the weight percent retained for each split, histograms were prepared for each sample.

To test the effectiveness of the sieving operation, portions of several splits were examined petrographically. This examination revealed that the material retained on each of the sieves was uniform in size. The size of the openings of the "Micro Mesh" sieves are stated to be accurate to plus or minus 2 microns. The petrographic examination further indicated that the glass shards still had a coating of clay on their surfaces. This means that the percentage of total sample passing the 5 micron sieve should have been slightly higher. Further ultrasonic disaggregation might help remove this clay-coating but it was felt that this might also break-down the glass shards. Regardless, the clay coating did not

appear to cause appreciable aggregation of the sand- and silt-size particles.

Histograms were prepared for each sample from the Packsaddle Bridge and Camargo localities. Figure 4 illustrates the grain-size distribution at Packsaddle Bridge. Here it is evident that there is an increase in percent of particles finer than 5 microns with depth; also, it appears that there is an irregularity in the distribution of particles in the silt and sand range. The grain-size distribution at Camargo is illustrated by histograms in Figure 5. Here the percentage of particles passing the 5 micron sieve decreases with depth. The distribution of silt and sand also appears irregular.

In order to determine changes in the distribution of particles coarser than 5 microns, the percent finer than 5 microns was subtracted from the total for each sample and the cumulative weight percent retained for each split was calculated and plotted on probability paper. Folk's Graphic Mean was calculated from this plot (Folk, 1968). Table 2 illustrates the weight percent finer than 5 microns and the mean grain size of the sand and silt fractions versus depth at the Packsaddle Bridge locality. It is apparent from this table (2, a) that there is a downward increase in the less-than

GRAIN-SIZE DISTRIBUTION
PACKSADDLE BRIDGE LOCALITY

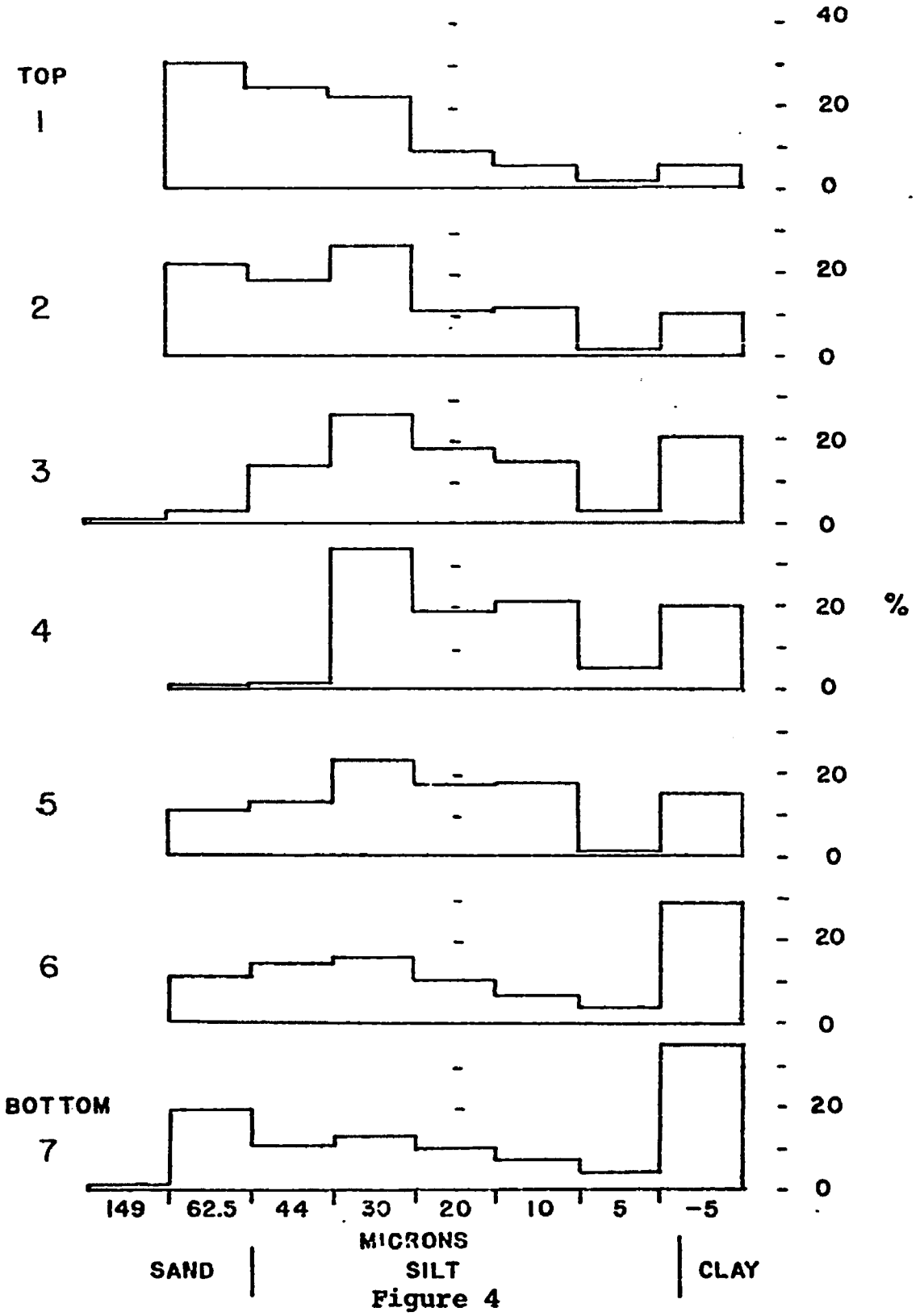


Figure 4

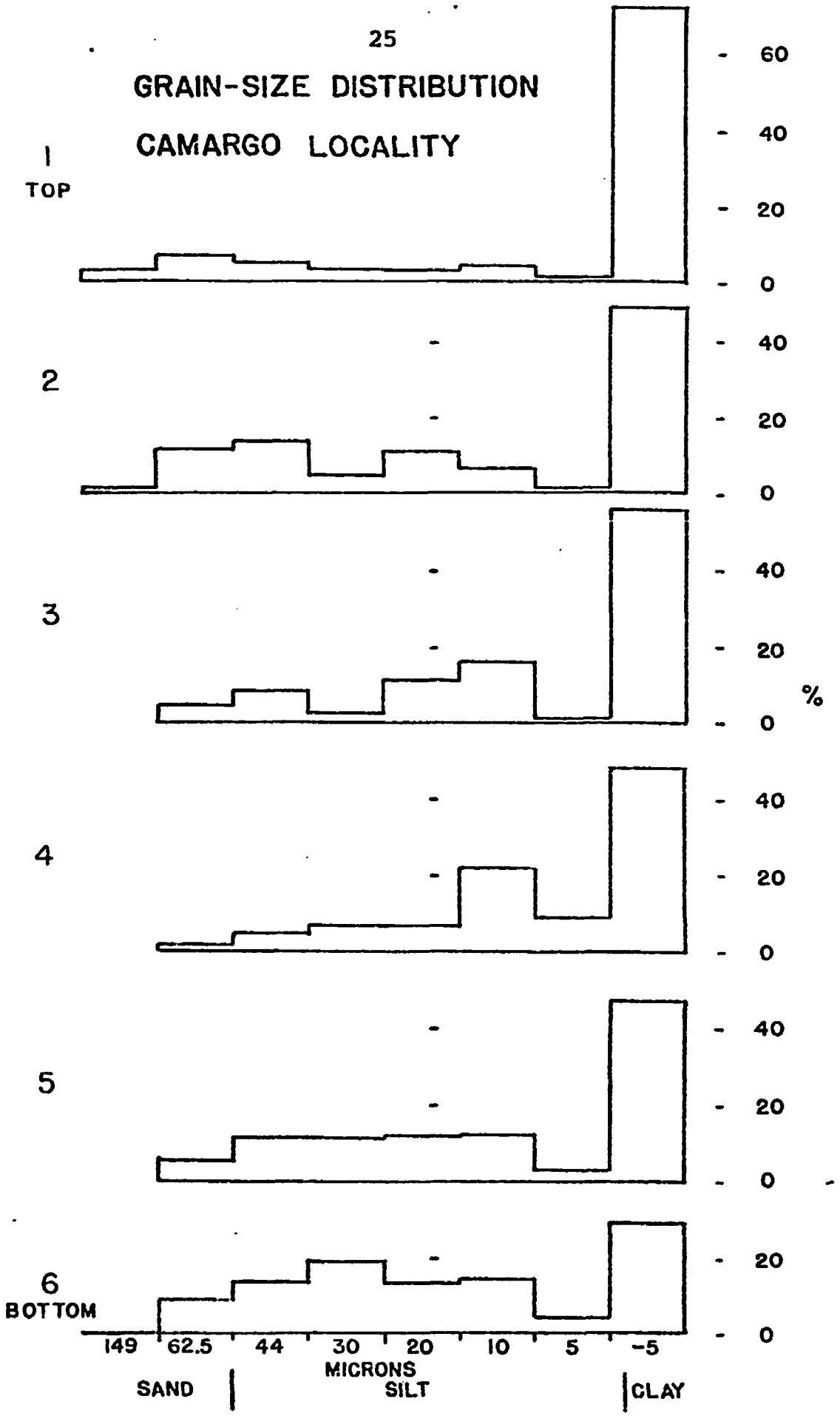

GRAIN-SIZE DISTRIBUTION
CAMARGO LOCALITY
1
TOP
2
3
4
5
6
BOTTOM
60
40
20
0
%
149
62.5
44
30
20
10
5
-5
MICRONS
SAND
SILT
CLAY

Figure 5

5 micron fraction. Part (b) of the same table illustrates that the mean grain size of the sand and silt fraction is higher at the base and top of the deposit than it is in the middle.

TABLE 2

COMPARISON OF COARSE AND FINE SIZE FRACTIONS WITH DEPTH; PACKSADDLE BRIDGE LOCALITY

Sample	(a)	(b)
1	7	40
2	10	34
3	20	26
4	19	21
5	15	27
6	29	25
7	35	34

(a) Percent passing 5 micron sieve.

(b) Mean grain size of sand and silt fraction in microns.

The same type of data were prepared for the Camargo locality. These are shown in Table 3. Part (a) of this table shows a decrease in the percent of particles finer than 5 microns with depth, the reverse of the Packsaddle Bridge

locality. The mean grain size of sand and silt versus depth is shown in part (b). Here the variation with depth is shown to be similar to the one from Packsaddle Bridge.

TABLE 3

COMPARISON OF COARSE AND FINE SIZE FRACTIONS WITH DEPTH; CAMARGO LOCALITY

Sample	(a)	(b)
1	72	46
2	49	40
3	56	27
4	48	19
5	47	29
6	30	30

(a) Percent passing 5 micron sieve.

(b) Mean grain size of sand and silt fraction in microns.

Discussion of Grain-Size Analyses

In discussing the geology of the studied localities, it has been stated that the Packsaddle Bridge volcanic ash and bentonite unit is more bentonitic towards the base. Also, that the Camargo bentonite was, more or less, uniform

throughout. The bentonitic nature of the base of the unit at Packsaddle Bridge is considered to reflect a more advanced state of alteration at the base. Although all the particles passing the 5 micron sieve are not all clay size, the percentage passing this sieve is a good indication of the state of alteration of that particular sample. That is to say, the higher the percent passing the 5 micron sieve, the further the state of alteration of the sample. One basis for this statement is the higher proportion of montmorillonite found in the minus 5 micron split (which will be discussed later). It is suggested here that the minus 5 micron fraction consists primarily of silicate wreckage as well as montmorillonite. The apparent downward increase in alteration, indicated on the outcrop by a more argillaceous nature, at Packsaddle Bridge is reflected in the grain-size distribution.

The grain-size distribution of the Camargo samples indicates that the unit is not as uniform as it appeared in the field. Furthermore, similarities between the mean grain size of sand and silt fractions at Camargo and Packsaddle Bridge localities can be seen. These similarities suggest that both localities represent accumulations of ash of nearly the same age and source.

Petrography

General Statement

The following sections deal with the characteristics of the volcanic ash, bentonite, and underlying sediments as revealed by the petrographic microscope. This examination was conducted utilizing oil mounts, Lakeside 70 mounts, and thin sections. The organization of this section will begin with a discussion of the nature of the underlying sediments followed by that of the volcanic ash and bentonite.

Underlying Sediments

Samples of the sediments underlying the volcanic ash and bentonite unit were collected at each studied locality for the purpose of determining their general nature and the presence or absence of either glass shards or phenocrysts. Phenocrysts were reported by Slaughter and Earley (1965) at the base of the graded bedding in the Mowry bentonites.

The samples were disaggregated by hand and dry sieved. The sieves ranged in size from 0.50 Ø to 4.75 Ø (phi) at a 0.25 Ø interval. The sieving provided a means of examining a particular size range without interference from fine silt and clay. Histograms were prepared for each sample sieved

but no statistical parameters were determined. Oil grain-mounts of the finer sand fractions were prepared and examined by the petrographic microscope. This examination revealed that glass shards were present in those fractions finer than 3.5 Ø. Biotite, a possible phenocryst mineral, also seemed to be more common in those fractions finer than 3.5 Ø.

The 3.75 Ø fraction was selected for detailed study as this was the effective limit of mineral identification with the petrographic microscope. Lakeside 70 grain-mounts were prepared of the 3.75 Ø fraction of selected sediments from each locality. One hundred grains were identified in each mount. Special attention was directed towards the identification of euhedral volcanic quartz, sanidine, and biotite as these minerals commonly are present in sediments derived from a volcanic source. No euhedral quartz was detected in any sample; however, sanidine and biotite appeared to be more common directly underlying the volcanic ash and bentonite units. Table 4 illustrates the variation in percent biotite and sanidine with depth below the volcanic ash and bentonite unit at Packsaddle Bridge.

Although one hundred grains may be insignificant statistically for a thorough mineralogical examination, it is apparent that the "cemented" zone directly beneath the

bentonite contains appreciably more biotite than the sediments underlying it. The results of grain counts at Woodward and Camargo were less conclusive; however, as much as 8 percent biotite was detected from the sandy silt underlying the bentonite at Woodward.

TABLE 4

WEIGHT PERCENT BIOTITE AND SANIDINE VERSUS DEPTH, PACKSADDLE BRIDGE LOCALITY

	Sample	Percent Biotite	Percent Sanidine
Volcanic ash and bentonite			
Bentonite			
Cemented sandy silt	6	17	1
Sandy silt	5	3	0
Silty sand	4	1	1
	3	1	0
Sandy silt	2	4	1
	1	0	0

The glass shards found in the sediments directly under the volcanic ash and bentonite unit were somewhat different in

appearance from those found above in the ash unit in that they were much smaller, more irregular in shape, and commonly seemed to be lying near or upon an unknown prismatic mineral exhibiting a refractive index of approximately 1.492 to 1.501 and blue-gray interference colors. It has some of the features of a zeolite; more will be given on the nature of this unknown mineral in the sections dealing with the mineralogy and scanning electron microscopy.

The petrographic study revealed the presence of several genera of foraminifera in the underlying sediments at Woodward and Packsaddle Bridge. These fossils were encountered in samples 1 through 3 at Packsaddle Bridge (see Table 4). R. W. Harris (Professor of Geology, University of Oklahoma) examined the specimens which included varieties of Gumbelina and Globigerina and concluded that they had been reworked and probably were an Upper Cretaceous assemblage (personal communication, 1970). Numerous outliers of the Lower Cretaceous Kiowa Formation occur within 75 miles of the studied localities. Upper Cretaceous rocks are presently restricted to the extreme western end of the Oklahoma Panhandle. The fossils must have been weathered out of the original rock and transported by wind and/or water during the Tertiary to their present location.

Volcanic Ash and Bentonite

All samples of volcanic ash and bentonite collected at the vertical sections from the studied localities were examintd with oils. The refractive index of the glass shards from these localities was found to be approximately 1.501. Lakeside 70 mounts were prepared for each sieve split for selected samples from Camargo and Packsaddle Bridge. The samples selected for mounting include the top and bottom of the unit at Packsaddle Bridge and the middle of the unit at Camargo. The petrographic examination was intended to determine the nature of the glass shards and the accessory mineralogy.

The glass shards exhibited an angular, platy form with numerous bubble holes and bubble junctions. In plane polarized light the shards are light gray. With crossed polarizers the surfaces of the glass shards are generally dark with small areas exhibiting birefringence. The birefringent areas represent points of alteration of the glass. These areas occur at grain edges (sides) and appear throughout the flat surfaces of the grain. Although samples from the base of the unit at Packsaddle Bridge and most samples from Camargo exhibit extreme alteration on grain surfaces, all samples studied exhibit some alteration.

The petrographic examination failed to reveal any phenocrysts and almost no land-derived accessory minerals. Some grains of quartz and highly-altered feldspar were recognized, but the units studied consist mainly of volcanic glass plus the alteration product, montmorillonite.

Photomicrographs of typical glass shards from the top and bottom of the unit at Packsaddle Bridge are shown in Plates 1 and 2 respectively. The shards from Camargo are similar to those from the base of the unit at Packsaddle Pridge.

Thin-Section Petrography

Thin sections cut perpendicular to stratification were prepared for selected samples of volcanic ash and bentonite. The seven thin sections examined include samples taken at the top, middle, and base at Woodward and Camargo; and from the top of the unit at Packsaddle Bridge. The thin sections of the bentonite and the highly-altered volcanic ash were not useful owing to the large proportion of clay present and to the disruption of the texture which occurred during the preparation of the sections.

Plate 3 shows a sequence of photomicrographs of relatively fresh volcanic ash from the top of the unit at

PLATE 1

PHOTOMICROGRAPHS OF RELATIVELY FRESH VOLCANIC ASH, PACKSADDLE BRIDGE LOCALITY (X 30)

a. Plain polarized light. The platy nature of the glass shards is apparent as well as curved outlines representing bubble holes. The dark, thin band across the grain in the lower right-hand corner is a bubble junction. The dark color of some grains is interpreted as a surface coating of clay.

b. Crossed polarizers. The birefringent areas represent alteration zones and consist of two types. One type consists of small, separate pinpoints of alteration and the second type is represented by narrow bands which ordinarily follow grain edges but also extend across the grains. If, as it is assumed that the birefringent alteration areas consist of montmorillonite, the clay must possess some degree of optical continuity. This is substantiated by the parallel extinction exhibited by these bands of alteration.





PLATE 2

PHOTOMICROGRAPHS OF HIGHLY ALTERED VOLCANIC ASH
PACKSADDLE BRIDGE LOCALITY (X 30)

a. Plain polarized light. The rounded glass shard in the center of the field is representative of this material. Most grains are coated with clay to the extent that surface features of the glass are obscured.

b. Crossed polarizers. The highly birefringent nature is apparent. Here the "pinpoints" of alteration extend over the entire surface.





PLATE 3

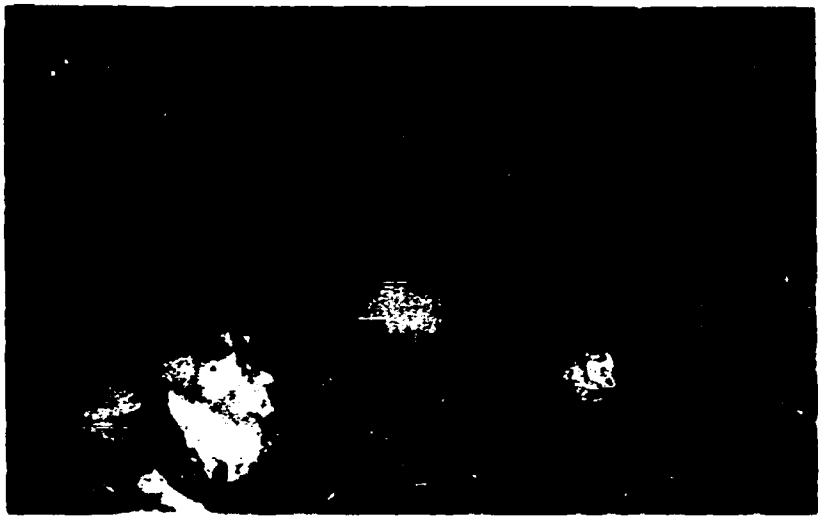
THIN-SECTION PHOTOMICROGRAPHS OF RELATIVELY FRESH VOLCANIC ASH, PACKSADDLE BRIDGE LOCALITY (X 30)

a. Plain polarized light. The glass shards are thin, light blue-gray in color and lie parallel to the stratification.

b. Same view as (a.) under crossed polarizers. Here the grain in the center of the field is in extinction and one can see the birefringent alteration zone bordering the grain. Those grains oriented in the 45 degree position exhibit more birefringence at their edges than those grains not so oriented.

c. Same field rotated 45 degrees. In this position the grain in the center of the field exhibits the strongest birefringence and it is apparent that the material comprising the alteration zone possesses parallel extinction. This birefringent material is believed to be montmorillonite.







Packsaddle Bridge. These photomicrographs reveal the optical continuity between the alteration product (montmorillonite) and the shard surface.

X-Ray Mineralogy

General Statement

In this section the x-ray diffraction characteristics of the volcanic ash and bentonite will be described. The purpose of this portion of the investigation was to more fully characterize the montmorillonitic alteration product and to insure that the accessory mineralogy was correctly determined.

The term montmorillonite, as used here, describes a three-layer, expandable clay mineral member belonging to the smectite group (Grim, 1968). The substitution of magnesium and iron for aluminum in the octahedral layer results in a net charge deficiency on the structure. This deficiency is balanced by the presence of interlayer cations occupying positions between adjacent silicate layers. The expandable nature of montmorillonite stems from the weak bonds existing between adjacent layers and the ability of water and polar organic molecules to enter between the layers. The interlayer

cations, which are ordinarily hydrated, normally consist of sodium, calcium or magnesium.

The identification of a clay mineral as belonging to the smectite group is based upon a (001) d-spacing of 12 to 15 A and an expansion of the (001) to approximately 17 or 18 A in the presence of solvating liquids such as ethylene glycol. Ordinarily higher orders of the (001) are weak. The identification of the particular members of the smectite group is usually based upon chemical analysis.

Two x-ray diffraction techniques were utilized in this study; these included an examination of randomly-oriented powders and of sedimented slides with preferred orientation of clay particles. The powders were employed for the analyses of bulk samples and provided data on the total mineralogy. The sedimented slides were used primarily for the examination of the clay fractions.

The powders were prepared by grinding the specimens and allowing particles finer than 80 mesh to fall upon a vaseline-coated glass slide. The preparation of sedimented slides involved an aqueous, ultrasonic dissagregation of the sample and the formation of a suspension. Particles finer than 4 microns equivalent spherical diameter were obtained from the

suspension by Stokes' Law settling which was followed by sedimentation of the minus-4-micron fraction on glass slides.

X-ray analyses were performed on North American Philips and Siemens diffraction equipment utilizing nickel-filtered, Cu K (alpha) radiation. Scanning rates of 1 degree 2 theta per minute were used throughout the study.

The discussion of the x-ray mineralogy will be described in three parts: the clay fraction of the volcanic ash and bentonite, sieve splits, and underlying sediments.

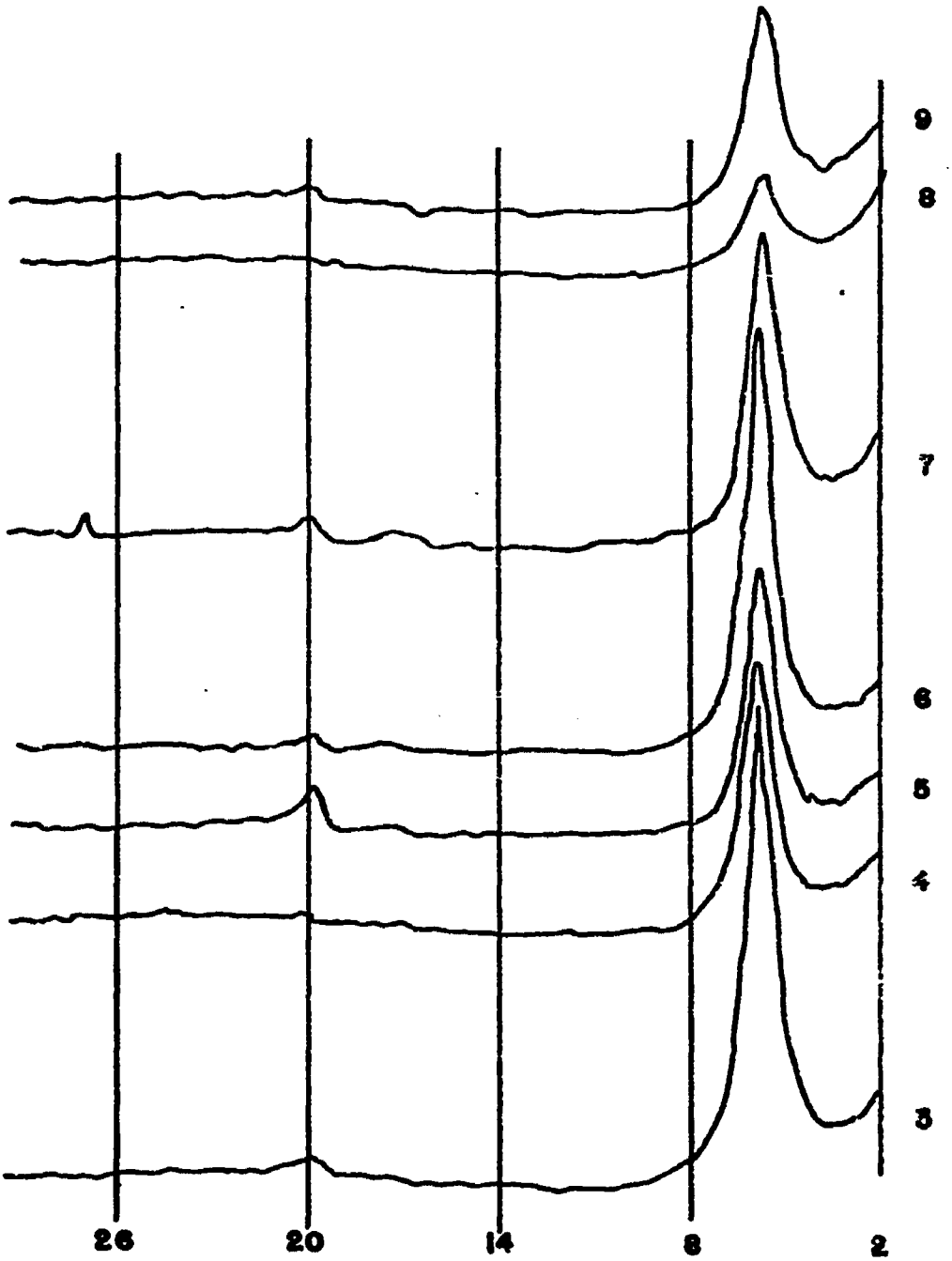
Clay Fraction of Volcanic Ash and Bentonite

X-ray diffractograms of the minus-4-micron fraction of all samples studied revealed the presence of montmorillonite. No other mineral species was detected in quantity. The nature of the montmorillonite reflections, however, were not the same for all samples. The basal (001) d-spacings were more-or-less the same at approximately 15 A. Higher orders of the (001) were absent in all samples. The degree of crystallinity indicated by the intensity and sharpness of the (001) reflection appears to be a function of the sample location.

X-ray diffractograms of the clay fraction from the vertically-collected samples at Packsaddle Bridge are shown in Figure 6. The sharpness of the (001) reflection increases

Figure 6. X-ray Diffractograms of Sedimented Clay Fractions, Packsaddle Bridge Locality

Samples 3 and 9 represent the bottom and top of the section respectively. Except for the weak quartz peak from sample 7, the diffractograms illustrate the essentially monomineralic nature of the clay fraction. It can be seen that the magnitude of the d-spacing is approximately the same throughout and that the sharpness of the (001) reflection increases toward the base of the section. Scale factors are identical for all diffractograms.


9
8
7
6
5
4
3
26
20
14
8
2
DEGREES 2θ

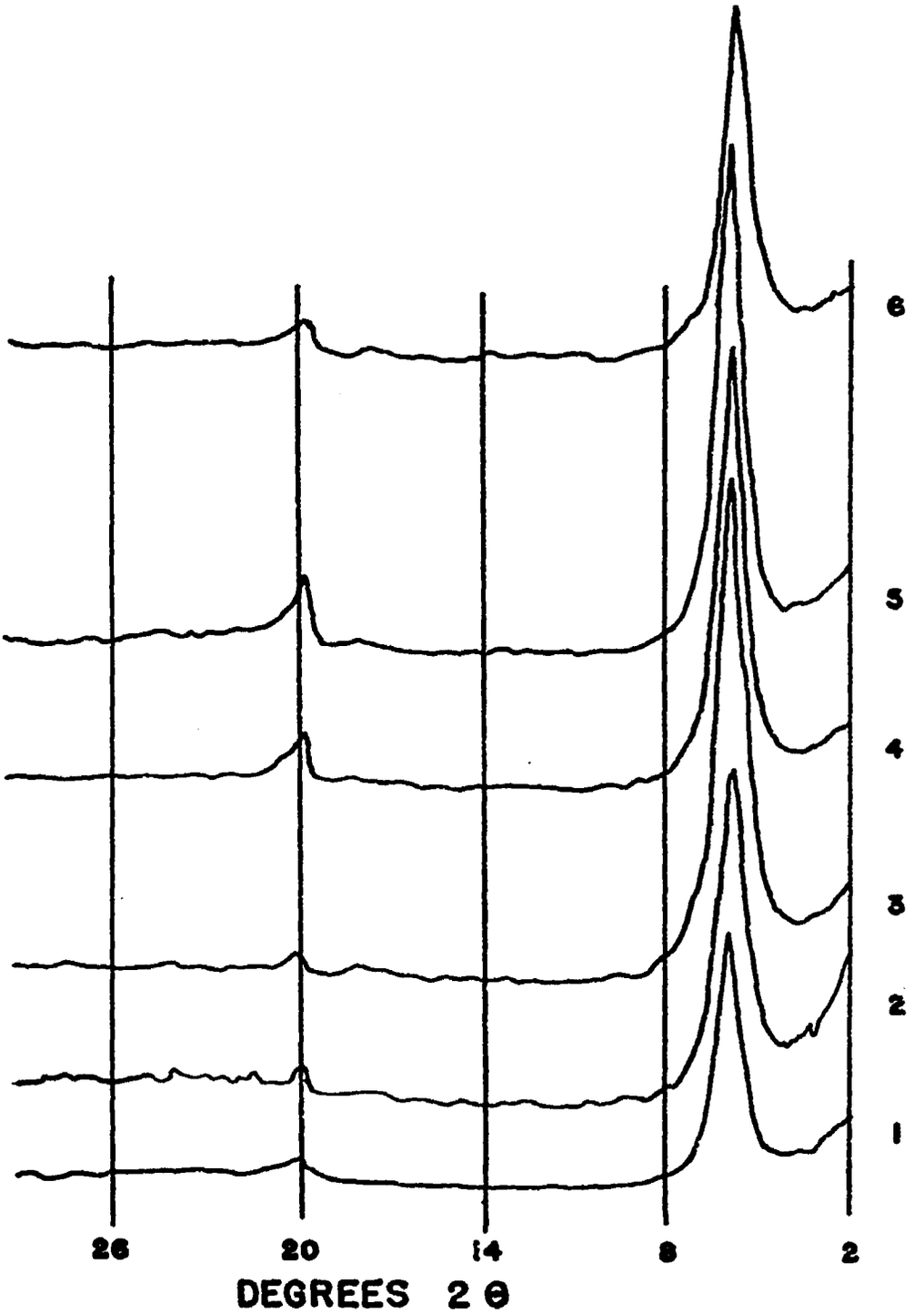
toward the base of the section and the magnitude of the d-spacing is approximately the same throughout. Edge reflections indicated by the weak 4.45 A lines are present suggesting poor orientation of the clay on the slides. This may be due to failure to achieve complete dispersion during sample preparation. Except for the weak quartz peak from sample 7, the diffractograms illustrate the essentially monomineralic nature of the clay fraction.

Several factors affect the shape and size of an x-ray diffraction peak. These include amount of a particular mineral species present in a sample, the structure-factor for the particular d-spacing, and the overall degree of crystallinity of the mineral in question. As the samples from Packsaddle Bridge are all essentially monomineralic and the d-spacing in question is also the same, it is suggested here that there is an increase in the crystallinity of the montmorillonite toward the base of the unit.

The x-ray diffractograms of the clay fraction from the vertically-collected samples from Camargo are shown in Figure 7. These diffractograms reflect the highly altered nature of this deposit by the presence of well-developed montmorillonite throughout the section.

Figure 7. X-ray Diffractograms of Sedimented Clay Fractions, Camargo Locality.

Samples 1 and 6 represent the bottom and top of the section respectively. All samples exhibit montmorillonite with a (001) d-spacing of approximately 15 A and all appear to be monomineralic. There does not appear to be any appreciable difference in degree of crystallinity among these samples. Scale factors here are not identical but have been adjusted to maximize peak heights without appreciably increasing background reflections.


6
5
4
3
2
1
26
20
14
8
2
DEGREES 2 θ

The sedimented clay fractions from all studied localities were placed in an ethylene glycol atmosphere for a period of at least four hours and then reexamined by x-ray diffraction. The resulting diffractograms revealed an expansion of the (001) d-spacing to about 17 A in all samples.

Selected samples of volcanic ash and bentonite were investigated by differential thermal analysis (DTA). The results indicated that in all cases the predominant interlayer cation present on the clay was calcium. This was determined on the basis of the shape of the low temperature (dewatering) endotherm.

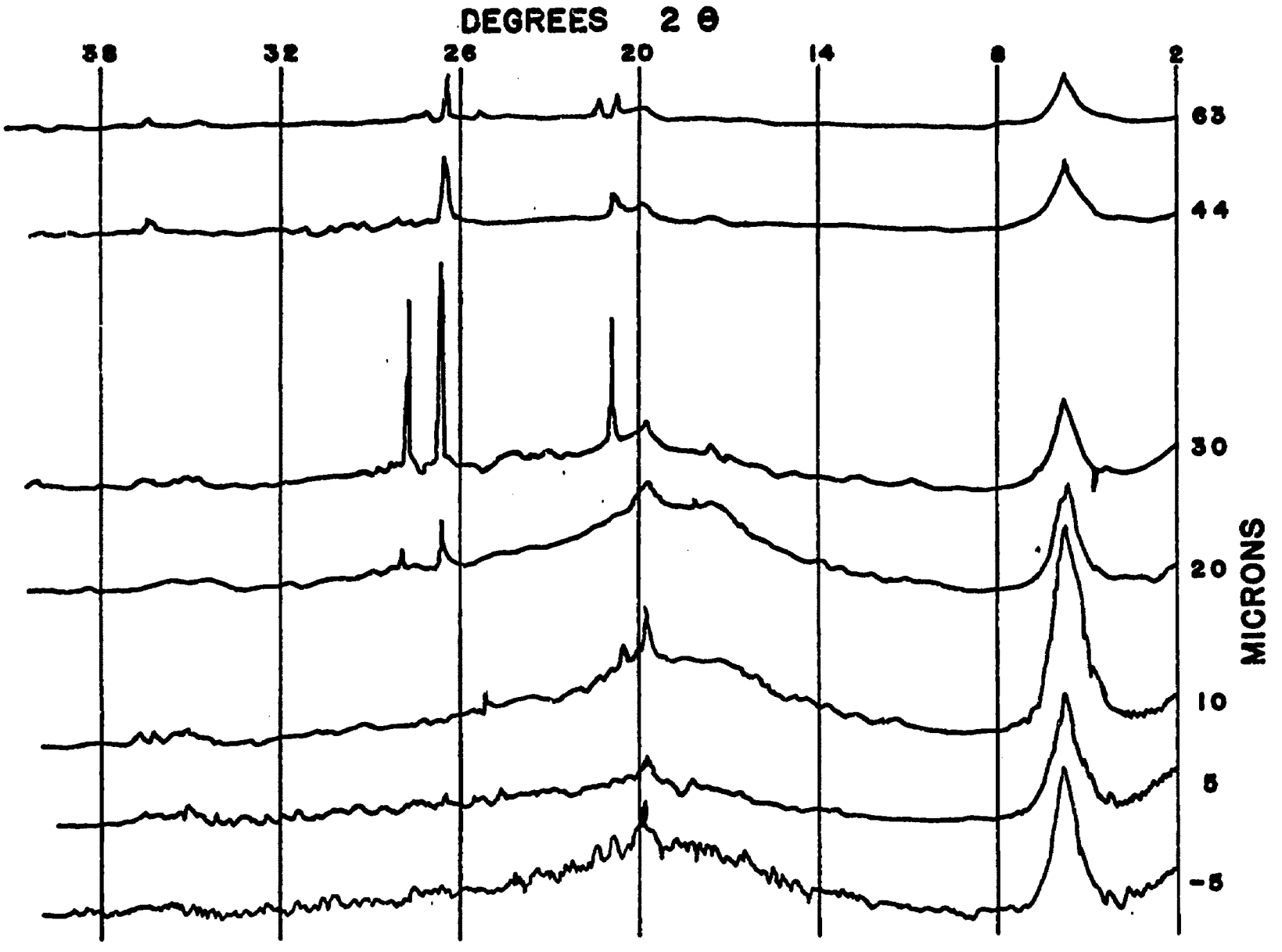
Sieve Splits

X-ray diffraction patterns were obtained for randomly-oriented powders of each sieve split from selected samples from Camargo and Packsaddle Bridge. These samples represent the top and bottom of the section of volcanic ash and bentonite at Packsaddle Bridge and the middle of the bentonite unit at Camargo.

Figure 8 illustrates the diffractograms of sieve splits from the top of the section at Packsaddle Bridge. Note the presence of montmorillonite in all fractions and the broad peak at approximately 18 degrees 2 theta indicating some

Figure 8. X-ray Diffractograms of Randomly-oriented Powders of Sieve Splits from Top of Section (Sample 9), Packsaddle Bridge Locality

The 15 A (001) peak of montmorillonite is present in all splits indicating that the glass shards are coated with clay. Some quartz is present in the 63, 44, 30, and 20 micron size fractions. The 30 micron fraction also shows a peak corresponding to a d-spacing of 3.22 A indicating the presence of feldspar. These size fractions finer than 44 microns exhibit a broad peak centered approximately at 18 degrees 2 theta. This peak indicates some degree of structural order within the glass shards.


DEGREES 2 θ
38
32
26
20
14
8
2
63
44
30
20
10
5
-5
MICRONS

degree of order in the glass. Although the (060) reflections are not shown in the figure, the d-spacing due to the (060) was found to be 1.50 A corresponding to a dioctahedral montmorillonite.

Figure 9 illustrates the diffractograms of sieve fractions of the highly-altered bentonitic material near the base of the section at Packsaddle Bridge. The patterns are similar to those described in Figure 8 except that the basal reflections of montmorillonite are stronger.

Figure 10 illustrates the diffractograms of the size fractions from the middle of the bentonite unit at Camargo. The nature of the patterns are quite similar to those previously discussed.

Underlying Sediments

Sedimented, preferred orientation x-ray diffractograms of selected samples of underlying sediments are illustrated in Figure 11. These samples include one from Packsaddle Bridge and two from Camargo. In general the clay mineralogy of the underlying sediment is similar for all three localities.

Zeolites, represented by the sharp peak at 10 degrees 2 theta (ASTM, 1964), were not found in all samples of subjacent sediments and there did not appear to be any readily

Figure 9. X-ray Diffractograms of Randomly-Oriented Powders of Sieve Splits from Bottom of Section (Sample 3), Packsaddle Bridge Locality

All size fractions are shown to contain montmorillonite as indicated by the strong 15 A (001) and weaker 4.5 A edge reflections. Quartz is absent from all fractions but some feldspar (probably plagioclase) is present in the 44-micron split. The broad peak at 18 degrees 2θ is present in all size fractions but not as pronounced as in Sample 9 (Figure 8).

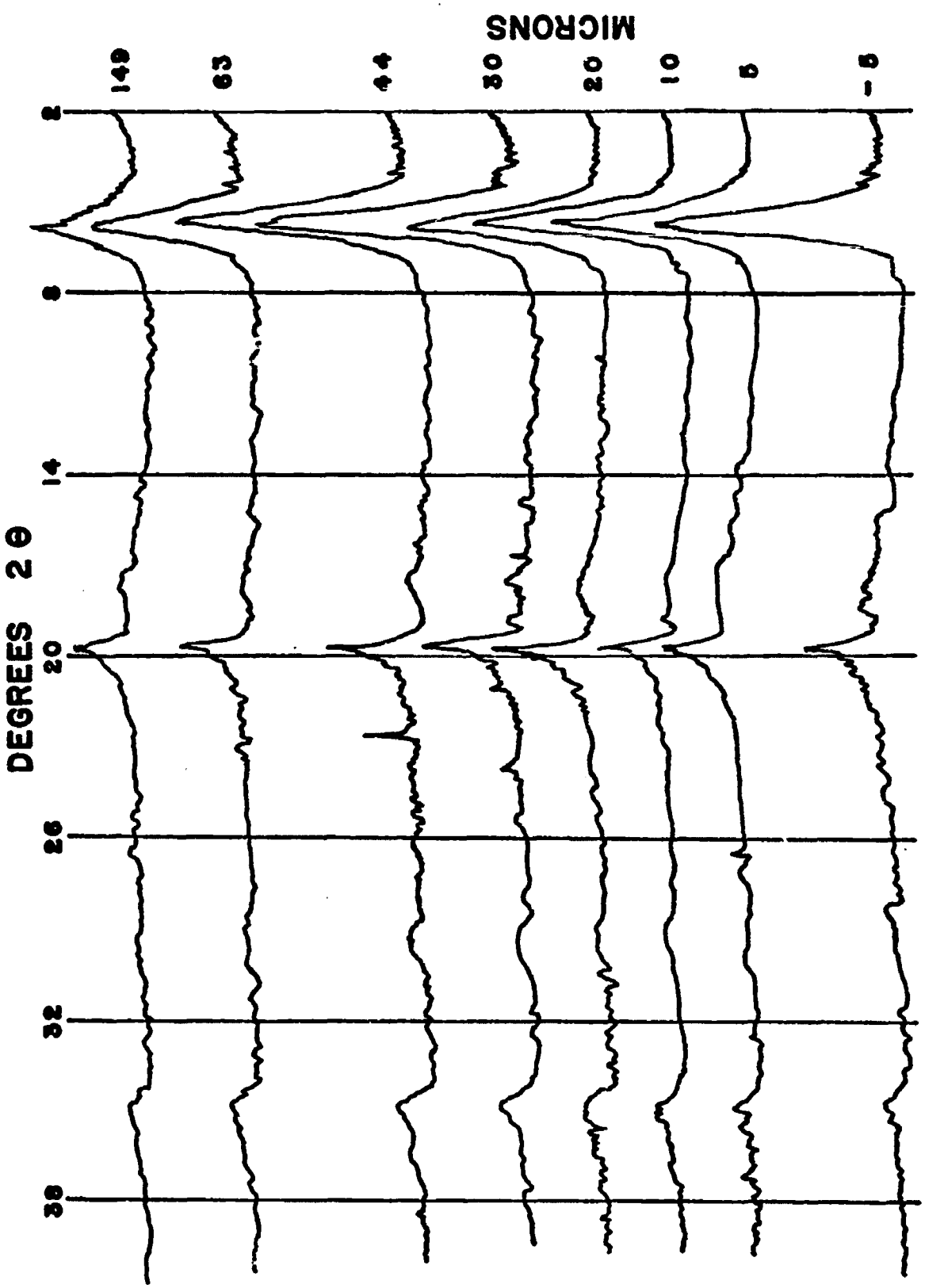

MICRONS
149
63
44
30
20
10
5
-5
DEGREES 2θ
2
8
14
20
26
32
38

Figure 10. X-ray Diffractograms of Randomly-oriented Powders of Sieve Splits from Middle of Section (Sample 4), Camargo Locality

Strong (001) montmorillonite reflections occur for each size fraction. Quartz is present in all but the minus-5-micron fraction and feldspar occurs in the 20 micron fraction. The broad peak at 18 degrees 2θ is present in all fractions but quite pronounced in the 44 micron fraction.

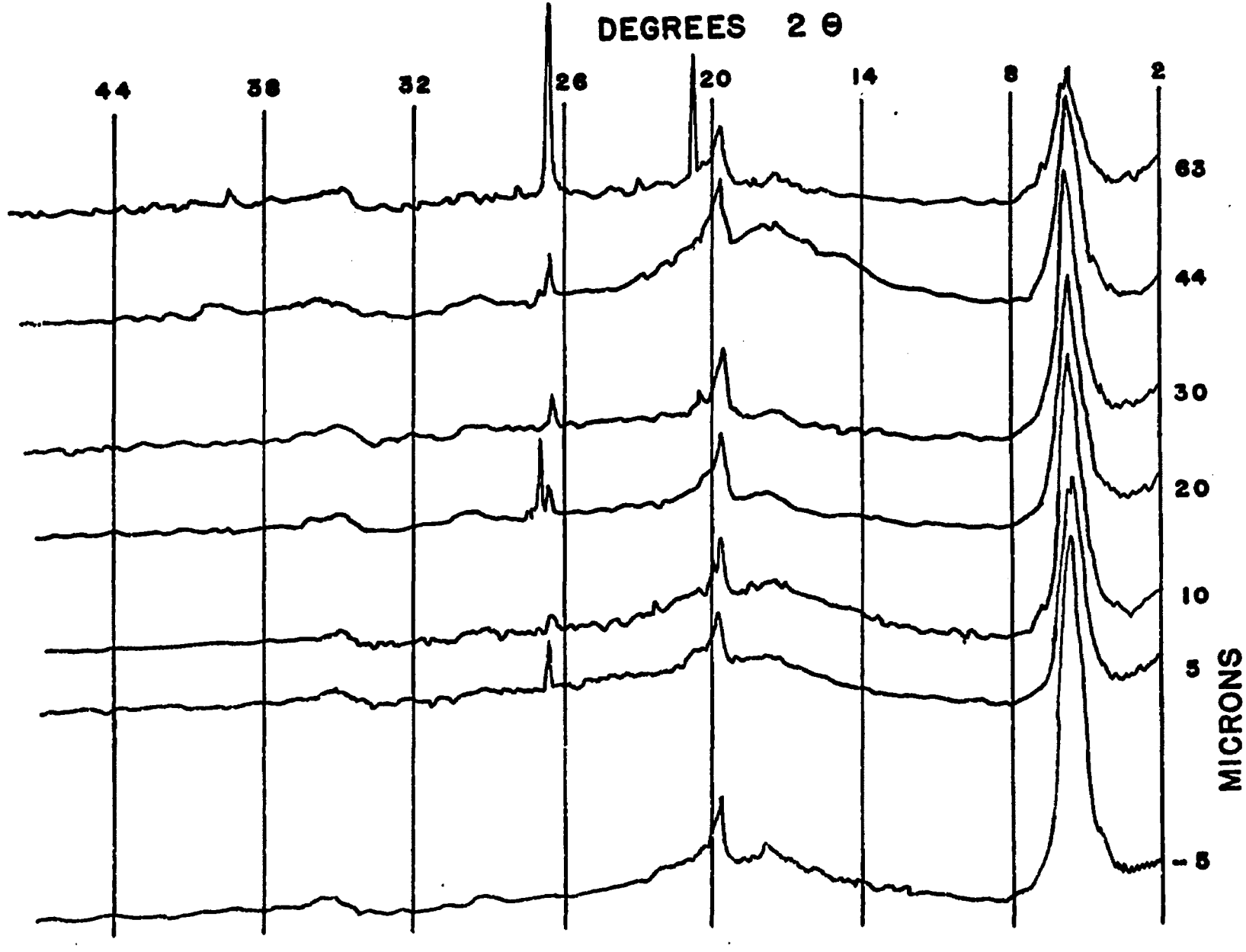
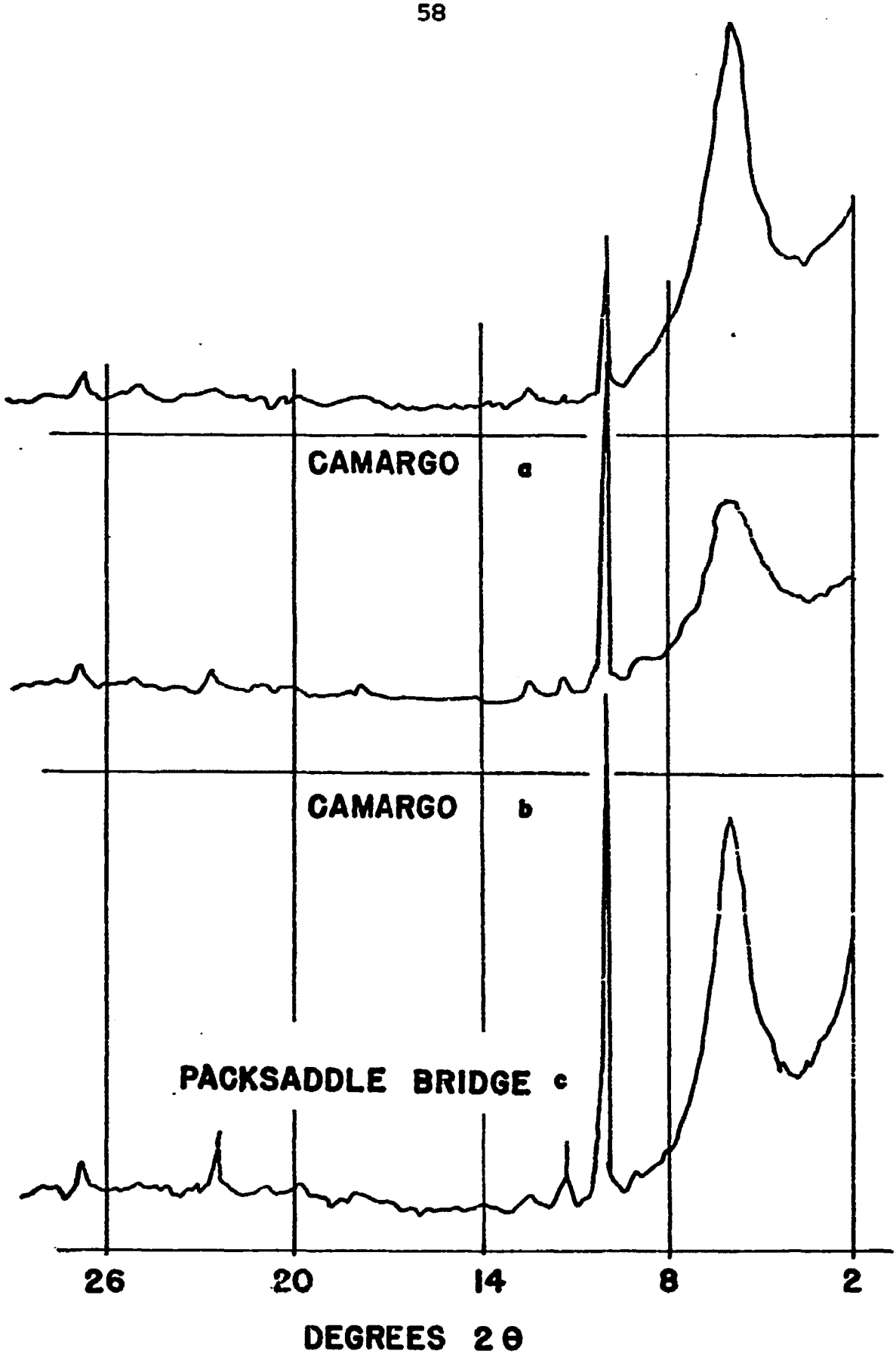

DEGREES 2 θ
44
38
32
26
20
14
8
2
63
44
30
20
10
5
-5
MICRONS

Figure 11. X-ray Diffractograms of Sedimented, Preferred Orientation Slides of the Minus-2-Micron Fraction of the Underlying Sediments at Packsaddle Bridge and Camargo Localities

All diffractograms illustrate strong 15 A montmorillonite peaks. Illite, indicated by the 10 A peak, and possibly kaolinite, indicated by the weak 7 A peak, are present in small amounts. Diffractograms of solvated samples revealed a definite separation of the illite and montmorillonite peaks and therefore preclude the possibility of mixed-layering. The sharp peak at 10 degrees 2θ represents the 8.9 A, (020) reflection of the zeolite, heulandite.


CAMARGO a
CAMARGO b
PACKSADDLE BRIDGE c
26
20
14
8
2
DEGREES 2θ

apparent reason for their presence or absence. The diffractogram shown in Figure 11 was from a silty clay separated from the bentonite by one foot of medium sand which was free of zeolites. This was the only case, however, in which zeolites were encountered more than a few inches from the base of the volcanic ash or bentonite unit.

Discussion

The mineralogic data previously presented have provided some insight into the general nature of the volcanic ash and its alteration. The following discussion will attempt to connect the data together and to relate them to the mechanism of chemical alteration.

The grain size of a sedimentary deposit is a function of the following four variables: 1) particle size of the original source material, 2) energy of the transporting medium, 3) energy at the site of deposition, and 4) the effects of diagenesis after burial. With respect to the volcanic ash and bentonite deposits no information is available on the first two variables. More is known, however, about the environment at the site of deposition where textural and other geologic data support the concept of low energy sedimentation in a lacustrine environment. It also has been shown

that grain diminution has occurred through alteration of the glass shards to montmorillonite. This is substantiated by the more rounded nature of the glass shards in those samples with a high clay content and the relationship of the coating to the grain.

The grain-size distribution recalculated to remove the minus-5-micron fraction (Tables 2 and 3) revealed a non-uniformity in the distribution from top to bottom of the section. This variation may be due to several factors including changes in the nature of the ash over a period of time, variation in kinetic energy at the site of deposition, and stratigraphic variations in the mode and degree of alteration. This last factor describes a situation in which, assuming similar grain-size distribution throughout the section, there is increased chemical alteration at some point in the section thereby reducing the average shard size at this point. If the grain size throughout the section was not similar one would expect that the smaller shards would be more highly altered due to the increased surface area per unit volume.

Another factor affecting the interpretation of the recalculated size distribution is one of primary versus secondary ash falls. Here the term ash "fall" includes either one or, more likely, a sequence of eruptions which has or have

contributed volcanic debris to the area in question. A primary fall is one in which the total accumulation of ash is due to direct fall-out. A secondary fall includes fall-out plus ash which had previously fallen on the land and has subsequently been washed into the basin of accumulation. No doubt included as a secondary fall would be deposits of ash which had fallen in the lake or pond but had been reworked and carried to deeper portions. The grain size of the secondary deposit would be the result of the prevailing climatic and sedimentologic conditions in the lake. The apparently small size of these ancient lakes indicates that it is unlikely that any large stream emptied into them and that most sediments were locally derived and carried into the lake by sheetwash and small, intermittent streams.

R. E. Wilcox (personal communication, 1971) considers most volcanic ash deposits on the Great Plains to be secondary falls. Studies of the ash falls associated with the eruption of Paricutin volcano in Mexico (Segerstrom, 1950) reveal that ash thickness decreases rapidly away from the volcanic vent. Here the ash thickness at a distance of 6000 meters from the vent is less than 0.25 meters. It appears reasonable to conclude that the studied volcanic ash and bentonite deposits do not represent primary ash falls and, furthermore, that any

interpretation of variations in the recalculated grain-size distribution would be tenuous. The percent finer than 5 microns must, however, be an indication of the degree of alteration of the ash.

The petrography of volcanic ash deposits of Kansas has been extensively studied by Swineford and Frye (1946). These authors were able to differentiate Pliocene and Pleistocene ash deposits by the nature of the respective glass shards. It was found that the Pleistocene shards contained appreciably more vescicles. A comparison of the shards from Woodward and Packsaddle Bridge with those Pliocene shards illustrated by Swineford and Frye revealed a set of common characteristics. Although the glass shards from Camargo are highly altered, they bear a strong resemblence to the glass from the other localities. The important aspect of the petrography presented here has been the distinct optical definition of the alteration product on the faces and edges of the glass shards. The locally strong optical continuity of this material has already been discussed. The petrographic evidence indicates that the montmorillonitic alteration product has formed on the grains with a preferred orientation as opposed to coating them.

The reference to the birefringent product as montmorillonite on the basis of optical studies is somewhat

misleading, because the identification of clays is difficult by optical microscopic methods. However, the x-ray evidence points clearly to the presence of montmorillonite (or, at least, a variety of smectite). It is further concluded that the clay detected by x-ray diffraction and seen through the microscope was formed by alteration of the glass and does not include appreciable detrital clay. If there were detrital contributions to the clay fraction there should be indications of illite and the 7 A mineral in the diffractograms of the minus-4-micron fractions of the ash because these two clay minerals occur in the underlying sediments. More will be presented on the nature of the montmorillonite in the section on the geochemistry.

The increase in percent of particles finer than 5 microns and the apparent increase in the crystallinity of the montmorillonite towards the base of the section at Packsaddle Bridge support field indications that there is generally a downward increase in alteration. At Camargo the minus-5-micron fraction reveals the opposite situation with increased alteration towards the top with little information provided by clay crystallinity. The direction of increased alteration must be a reflection of a chemical gradient imposed upon the system by the nature of previous or existing chemical

conditions. The sections dealing with the geochemistry will attempt to determine the chemical gradient and the nature of these chemical conditions.

Other than reporting their presence, little can be offered regarding the occurrence of the accessory grains of quartz and feldspar. Their occurrence in the silt fractions effectively precludes the optical determination of their precise nature and thus it is largely unknown whether they are detrital grains or phenocrysts.

The origin of the volcanic material in the deposits studied here has not been determined. Swineford (1949) originally suggested the Valles Caldera of New Mexico as a source of the Pearlette ash (Pleistocene?) of Kansas. However, the later discovery of Pearlette-like ash deposits further west in Colorado, Utah and Nevada convinced her that the New Mexico area was not the source on the basis of wind patterns (Swineford, 1963).

Wilcox and others (1970) compared the mineralogy and trace-element geochemistry of Pearlette-like ash beds with the ash beds of Valles Caldera, Yellowstone Park region, and the Bishop area of eastern California (all areas of rhyolitic activity). The Pearlette-like ash was found to be comparable to volcanic ejecta at the Yellowstone Park region. Izett and

others (1971) found radiometric evidence for two ages of Pearlette-like ash; one date of 0.6 m.y. and the other of 1.2 m.y. Both ages, derived from K-Ar measurements on sanidine phenocrysts, correlated with ash-flow sheets in the Yellowstone Park area.

Considering these radiometric ages referred to above, it seems reasonable to suppose that the Plio-Pleistocene volcanic ash of Oklahoma also has been derived from the Yellowstone Park or similar areas.

GEOCHEMISTRY

Introduction

The information presented herein will include data from cation-exchange capacity tests and the results of bulk as well as clay-fraction chemical analyses. The data derived from nondispersive fluorescence analyses will be reported in the section on scanning electron microscopy. Chemical data are presented in Appendix II.

The petrologic variations with depth which occur in the volcanic ash and bentonite deposits have been discussed earlier. In this section the chemical variations will be treated with the objective that these will be the key to unravelling the questions of degree and mode of alteration.

Cation-Exchange Capacity

The cation-exchange capacity of a substance is a measurement of its ability to sorb cations and to retain them in an exchangeable state. Among minerals, the clays and particularly montmorillonites and zeolites exhibit a large cation-exchange capacity. With respect to clay minerals, the exchange

occurs at edges and on interlayer surfaces between structural units. In a system consisting of glass shards and montmorillonite the cation-exchange capacity is a relative measure of the amount of clay present and thus the degree of alteration imposed on the system. It is assumed that fresh, unaltered glass would contribute little to the exchange capacity. The shard surfaces undergoing hydrolysis may, however, possess a high reactivity and may thus contribute substantially to the cation-exchange capacity.

The laboratory techniques followed are those described by Kerns (1967a). The technique involves the measurement of 1 to 2 grams of sample and dispersal in approximately 500 ml of distilled water. When the sample is completely dispersed an acid resin is added to the solution. The acid resin provides H^+ ions to the solution which displace cations at exchangeable sites on the sample. An excess of resin should be added to insure complete exchange and the mixture of sample and resin should be thoroughly mixed or stirred. The amount of resin to be added depends upon the exchange capacity as provided by the manufacturer. After stirring the sample is separated from the resin by washing with distilled water. The separation is accomplished with a 325 mesh sieve which permits passage of the dispersed sample but retains the

coarser resin. The solution is then titrated against a standardized base, normally NaOH. Knowing the volume of base required to raise the pH of the solution to 7.0, the weight of sample, and the normality of the base, the cation-exchange capacity may be calculated. Ordinarily a reference clay of known cation-exchange capacity is tested with the unknown samples in order to verify the results.

The results of cation-exchange capacity tests on the vertically-collected, bulk samples of volcanic ash and bentonite from Packsaddle Bridge and Camargo are reported in Table 5. The reference clay was API Number 26 which had a reported CEC of 118.

The low CEC of the reference standard indicates that the solutions were not thoroughly mixed. The samples from Packsaddle Bridge exhibit a generally-downward increase indicating greater alteration and more clay at the base. The Camargo samples are somewhat different in that the center exhibits a higher CEC than either the top or the bottom although the base is higher than the top.

Bulk Chemical Analyses by X-Ray Fluorescence (XRF)

Bulk chemical analyses of the vertically-collected samples from the three studied localities were determined

TABLE 5

CATION-EXCHANGE CAPACITIES OF BULK SAMPLES FROM PACKSADDLE BRIDGE AND CAMARGO LOCALITIES

Packsaddle Bridge		Camargo	
Sample No.	CEC*	Sample No.	CEC*
9	55	6	30
8	52	5	65
7	36	4	55
6	46	3	69
5	45	2	40
4	82	1	54
3	110		

*Milliequivalents of Base per 100 grams of sample.

Note: Measured CEC for API No. 26 = 94; reported CEC = 118.

utilizing a Siemens XRF equipment. The procedures followed were those of Kerns (1967b). In general, sample preparation involved grinding the samples to about minus 200 mesh in a Pitchford Uniform Particle Size grinder; the ground sample is then thoroughly mixed with a polyvinyl alcohol (PVA) binder. The PVA content constituted 40 percent by weight of the mixture. The mixture of sample and PVA is then pressed into briquets using a hydraulic press.

Table 6 illustrates the average chemical composition of the three studied localities. The table was prepared by

TABLE 6

AVERAGE CHEMICAL ANALYSES (FIRED BASIS) OF FULL THICKNESS OF VOLCANIC ASH AND BENTONITE AT THE THREE STUDIED LOCALITIES

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2
Packsaddle Bridge	66.11	15.81	3.91	8.76	3.81	0.56	0.64	0.41
Woodward	70.51	15.66	3.75	4.52	2.32	1.08	1.58	0.40
Camargo	66.29	17.21	4.18	8.10	3.00	0.25	0.31	0.47

averaging the analyses of each sample in the vertical sequence from each locality. The values were adjusted in order for the sum of individual oxide percents to equal 100.

An examination of Table 6 reveals that there is no great difference in chemistry between Packsaddle Bridge and Camargo. The Woodward deposit, however, exhibits less MgO and higher alkalies and SiO_2.

Table 7 gives the chemical composition of the ash and bentonite at the top of the vertically-sampled sections. It will be recalled that the volcanic ash at Woodward and Packsaddle Bridge is relatively fresh and unaltered at the top of

TABLE 7

CHEMICAL ANALYSES (FIRED BASIS) OF SAMPLES OF VOLCANIC ASH AND BENTONITE COLLECTED AT THE TOP OF THE UNIT

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2
Packsaddle Bridge	72.57	14.10	3.25	3.60	1.75	1.78	2.30	0.37
Woodward	75.10	14.17	3.08	1.56	1.37	1.71	2.83	0.28
Camargo	70.65	14.92	3.63	6.39	2.25	0.80	0.97	0.29

the section. In order to provide a better basis for comparison the individual oxide values were adjusted with a constant factor. The unaveraged data are in Appendix II.

The fresh ash (line 1 and 2) is shown in Table 7 to have a composition in the rhyolite-granite range (Turner and

Verhoogen, 1960). The material at Packsaddle Bridge and Woodward is chemically similar except for the greater amount of MgO and less SiO_2 at Packsaddle Bridge. The Camargo bentonite locality exhibits a chemical composition lower in alkalis and SiO_2 and higher in MgO and CaO than the other two deposits.

A comparison of Tables 6 and 7 indicates that there are two differences between the unaltered ash and the average composition of the units. In general, the unaltered ash exhibits: 1) higher content of SiO_2, Na_2O, and K_2O; and 2) less Fe_2O_3, CaO, and MgO.

In order to recognize chemical variations with depth at the studied localities, a technique outlined by Krauskopf (1967) was followed. This technique involves a comparison between the material at the top of the section and each succeeding sample collected beneath it. There are two assumptions involved here; one that the unaltered ash at the top is chemically representative of the whole section before alteration took place, and that there has been negligible addition or removal of aluminum. A sample calculation is included in Appendix III.

Table 8 demonstrates the results of this technique applied to the vertically-collected samples at Woodward and

TABLE 8

PERCENT VARIATION OF CHEMISTRY WITH DEPTH, PACKSADDLE BRIDGE AND WOODWARD LOCALITIES

Sample No.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2
				Packsaddle Bridge				
Top								
8	-4	0	+1	+63	+71	-47	-44	+8
7	-19	0	+7	+130	+114	-100	-89	+11
6	-22	0	+14	+160	+117	-100	-93	0
5	-20	0	+2	+134	+114	-84	-94	+3
4	-26	0	+11	+123	+117	-82	-97	-11
3	-28	0	+18	+187	+114	-78	-95	+5
Bottom								
				Woodward				
Top								
7	-6	0	+4	+48	+22	-18	-17	+32
6	-3	0	+6	+15	+8	-4	-11	+29
5	-14	0	+9	+146	+50	-46	-46	+29
4	-12	0	+36	+111	+34	-23	-35	+29
3	-23	0	+22	+253	+91	-57	-80	+47
2	-26	0	+14	+349	+97	-100	-94	+47
1	-28	0	+20	+300	+105	-74	-94	+39
Bottom								

Packsaddle Bridge. Each sample has been compared to the uppermost sample at the respective locality and the percent increase or decrease of each analyzed oxide is listed opposite the sample number.

There is a definite downward variation in the chemistry at both localities, SiO_2, Na_2O, and K_2O are shown to decrease whereas Fe_2O_3, MgO, and CaO increase. TiO_2 content seems to be irregular. The chemical data presented in Table 8 support field observations, grain-size analyses, and the mineralogy with respect to the question of increased alteration with depth in the section. The loss of SiO_2 and the alkalis, and the gain of CaO, MgO and Fe_2O_3 are therefore, indicators of the degree of alteration of the volcanic ash.

The Camargo bentonite deposit is more difficult to summarize. Tables 6 and 7 show that there is no great difference in the chemistry between Camargo and the other deposits. The main dissimilarities seem to be the increased MgO and decreased alkali content at Camargo.

Table 9 illustrates the variation of the chemistry with depth at Camargo by the same technique represented in Table 8. Each sample has been compared to the unaltered ash from the top of the section at Packsaddle Bridge. It is reasonable to assume that the fresh ash at Camargo had a chemical

composition similar to the composition of the ash at Packsaddle Bridge.

TABLE 9

PERCENT VARIATION OF CHEMISTRY WITH DEPTH AT CAMARGO LOCALITY*

Sample No.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2
Top								
6	- 8	0	+ 2	+68	+22	- 57	-60	-27
5	-26	0	+ 2	+95	+43	-100	-50	+ 3
4	-26	0	+ 2	+90	+44	-100	-92	+ 5
3	-27	0	+ 4	+94	+42	- 80	-94	+30
2	-30	0	+12	+86	+41	-100	-94	+11
1	-31	0	+ 7	+73	+49	- 87	-97	+ 8
Bottom								

*Sample No. 9 from the top of the section at Packsaddle Bridge is the reference unaltered material.

Table 9 demonstrates that the alteration at Camargo is similar to the other localities, that is a decrease of SiO_2, and the alkalis, and retention of Fe_2O_3, and CaO with depth. The increase in MgO, however, seems to be greater near the center of the section.

Chemical Analyses of Clay (minus-2-micron) Fraction

Chemical analyses of the minus-2-micron fraction of samples 1, 3, and 5; and 3, 5, and 7 from Camargo and Packsaddle Bridge respectively were performed by XRF. This size fraction was obtained by Stokes' Law settling procedures. The structural formulas for the analyzed samples were determined by the method of Ross and Hendricks (1945).

Table 10 illustrates the results of these calculations. The structural formulas are for single cells; the parentheses on the left of each formula represent tetrahedral sites and those on the right octahedral positions. The formulas support the contention that the smectite species is montmorillonite.

The clay from Packsaddle Bridge exhibits a regular increase in the amount of aluminum substituting for silicon in the tetrahedral positions with depth. The change in octahedral sites involves an increase in aluminum and iron at the expense of magnesium towards the base.

The Camargo clay also exhibits a downward increase in tetrahedral aluminum with depth. The octahedral positions are filled by more aluminum at the expense of magnesium with iron remaining more or less unchanged.

TABLE 10

STRUCTURAL FORMULAS FOR MONTMORILLONITE CLAYS FROM CAMARGO AND PACKSADDLE BRIDGE LOCALITIES

Camargo	Packsaddle Bridge
Top	
$(Si_{3.95}Al_{.05})(Al_{1.17}Mg_{.82}Fe_{.18})O_{10}(OH)_2$	$(Si_{4.06})(Al_{1.13}Mg_{.79}Fe_{.14})O_{10}(OH)_2$
$(Si_{3.93}Al_{.07})(Al_{1.23}Mg_{.80}Fe_{.16})O_{10}(OH)_2$	$(Si_{3.95}Al_{.05})(Al_{1.28}Mg_{.78}Fe_{.15})O_{10}(OH)_2$
$(Si_{3.93}Al_{.07})(Al_{1.29}Mg_{.69}Fe_{.17})O_{10}(OH)_2$	$(Si_{3.92}Al_{.08})(Al_{1.20}Mg_{.77}Fe_{.17})O_{10}(OH)_2$
Bottom	

The foregoing data suggest that the nature of the clay is a measure of the degree of alteration of a sample of volcanic ash or bentonite.

Table 11 illustrates the percent change in the analyzed oxides of the clay (minus-2-micron) fraction from Packsaddle Bridge and Camargo compared to the relatively unaltered volcanic ash at the top of the section at Packsaddle Bridge. The table shows that the alkalis have been removed and that the lower clays contain less silica, MgO, and CaO. Fe_2O_3 exhibits a decrease towards the base at Camargo but is about the same throughout at Packsaddle Bridge.

Discussion

The chemical data presented here support the field and petrographic evidence that the volcanic ash and bentonite units exhibit increased alteration toward the base. This is particularly shown by the progressive removal of SiO_2 and the alkalis toward the base. The leaching of these elements must have been due to ground water moving through the strata. The data also reveal an absolute gain in CaO, MgO, and Fe_2O_3 toward the base. It is possible that some calcium, magnesium and iron were introduced into the ash unit by the ground water. It is also possible that these elements were removed from the

TABLE 11

PERCENT VARIATION WITH DEPTH; CLAY FRACTION FROM PACKSADDLE BRIDGE AND CAMARGO LOCALITIES*
(Minus-2-Micron Fraction)

Sample No.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2
				Packsaddle Bridge				
Top								
7	-17	0	-12	+114	+94	-95	-97	+5
5	-29	0	-17	+ 89	+92	-92	-97	-8
3	-30	0	-10	+ 85	+78	-97	-98	+5
Bottom								
				Camargo				
Top								
5	-26	0	+ 1	+106	+69	-97	-94	-3
3	-31	0	-15	+ 88	+66	-97	-98	-8
1	-34	0	-14	+ 57	+53	-99	-98	-5
Bottom								

*Samples are compared to Sample 9 (top) at Packsaddle Bridge Locality.

upper portions of the unit during the hydrolysis of the glass and carried downward where they were "fixed" by clay minerals and/or the extremely altered reaction surfaces on the glass.

There may be a cause and effect relationship between the alkalis and SiO_2 removal. The water flowing through the unit will begin to hydrolyze the upper part of the ash bed. The alkalis freed in the process will be removed downward in solution. The increase in the alkali concentration would also increase the pH of the water system thus increasing the solubility of silica and thereby facilitating its removal. It is also possible that the alteration occurred at the groundwater table and was enhanced by its fluctuation but it is hard to relate this process to the geochemical variations observed within the ash unit.

Although the chemical analyses of the clay fraction revealed changes in composition with depth, the significance of the change (if real) is open to interpretation. The differences in composition were not large and could be attributed to analytical error. Assuming a reasonable degree of accuracy in the analyses it is not known to what extent amorphous material is present in the clay fraction. If considerable amorphous material accompanied the montmorillonite in the clay

fraction, the changes in composition could be attributed to the amorphous component.

Assuming a clay fraction essentially free of amorphous components and minimal analytical errors, the vertical changes in composition may be interpreted two ways: 1) the montmorillonite undergoes alteration as the alteration of the deposit continues, and 2) the composition of the subsequently formed crystals of montmorillonite exhibit a progressive change in chemical composition.

SCANNING ELECTRON MICROSCOPY

Introduction

Selected samples of volcanic ash, bentonite, and montmorillonite were examined under a Japan Electron Optics (JSM-II) scanning electron microscope (SEM). The purpose of this portion of the investigation was to determine the nature of the clay and shard surfaces and to relate this to the petrography. Qualitative and semi-quantitative chemical analyses were performed on selected samples of volcanic ash with a Princeton Gamma-Tech nondispersive chemical analyser (NDCA) unit operated in conjunction with the SEM. The purpose of the NDCA study was to determine the chemical characteristics of the fresh glass and compare it to that of the alteration zones on the surfaces of the shards. Techniques and procedures used in the SEM and NDCA studies are outlined in Appendix IV.

Shard Textures

SEM photographs revealed that the surfaces of the glass shards consisted of two different types of textures. One was

smooth and flat whereas the other was rough and appeared to consist of a network or boxwork of curved plates. The smooth surfaces were considered to be unaltered areas. The rough surfaces evidently are areas of alteration and appear similar to SEM photographs of montmorillonite described by Borst and Keller (1969). These authors suggest that the "boxwork fabric" may "represent a highly developed edge-to-face crystallization effect" or "the fabric represents the alteration of glass shards in place."

Plates 4 through 9 illustrate the typical features of the shards from Packsaddle Bridge and Camargo. Descriptions are included on facing pages. In general the more highly altered shards exhibit more pronounced development of the boxwork structure.

Clay Fraction

Plate 10 illustrates SEM photographs of the minus-4-fraction from the top of the section at Packsaddle Bridge. Both samples represent the same material and both exhibit boxwork texture. The sample illustrated in Plate 10b was kept in the SEM considerably longer than the sample illustrated in Plate 10a. It can be seen that Plate 10b exhibits more highly developed boxwork than Plate 10a. This suggests that the

PLATE 4

SEM PHOTOGRAPHS OF GLASS SHARDS FROM THE TOP OF THE SECTION (SAMPLE 9), PACKSADDLE BRIDGE LOCALITY

Both photographs illustrate the boxwork structures as well as the relatively smooth areas. The white areas, appearing over exposed, indicate insufficient coating and are common on altered portions of grains. (a. x1200; b. x1000.)





PLATE 5

SEM STEREOPHOTOGRAPH OF GLASS SHARD (x6000)
FROM THE TOP OF THE SECTION
AT PACKSADDLE BRIDGE

The boxwork structure is imposed upon the otherwise smooth surface of the glass. The curved edge represents a bubble hole. The two crystallites in the upper portion of the pair appear to be calcite.

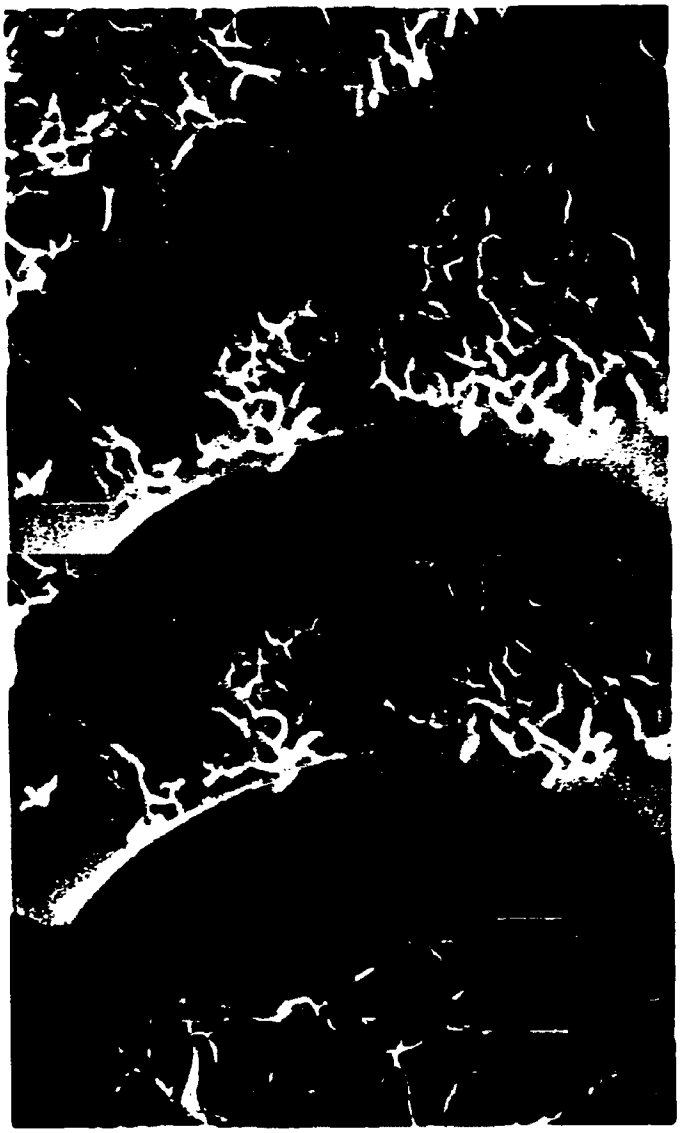
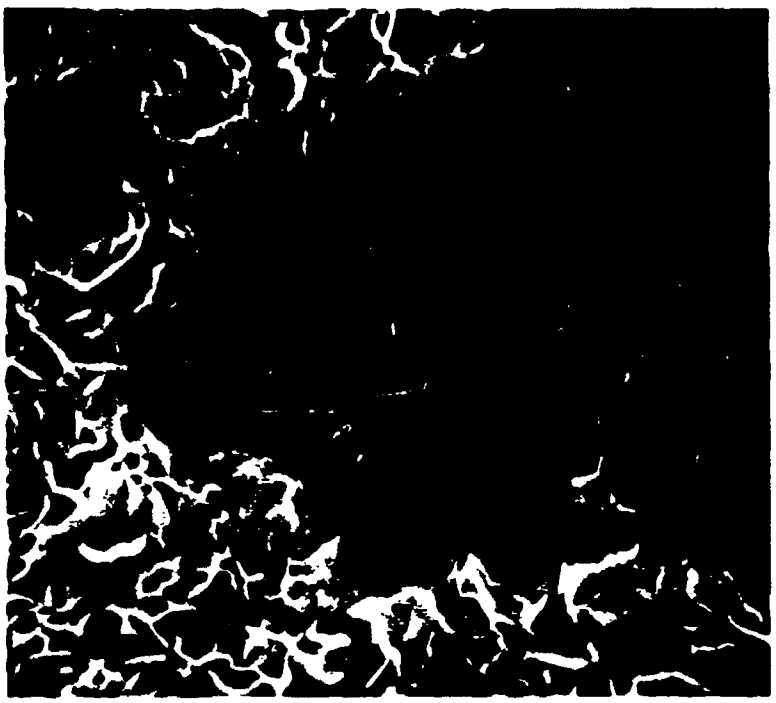


PLATE 6

SEM PHOTOGRAPHS OF GLASS SHARDS AND BOXWORK STRUCTURE FROM THE TOP OF THE SECTION, PACKSADDLE BRIDGE LOCALITY

Both photographs illustrate the boxwork and smooth areas at higher magnification. In (a) the boxwork can be seen to stand out above the smooth area. This was substantiated by the examination of stereo pairs. In (b) the smooth surface exhibits some curling. (a. x7000; b. x5000.)



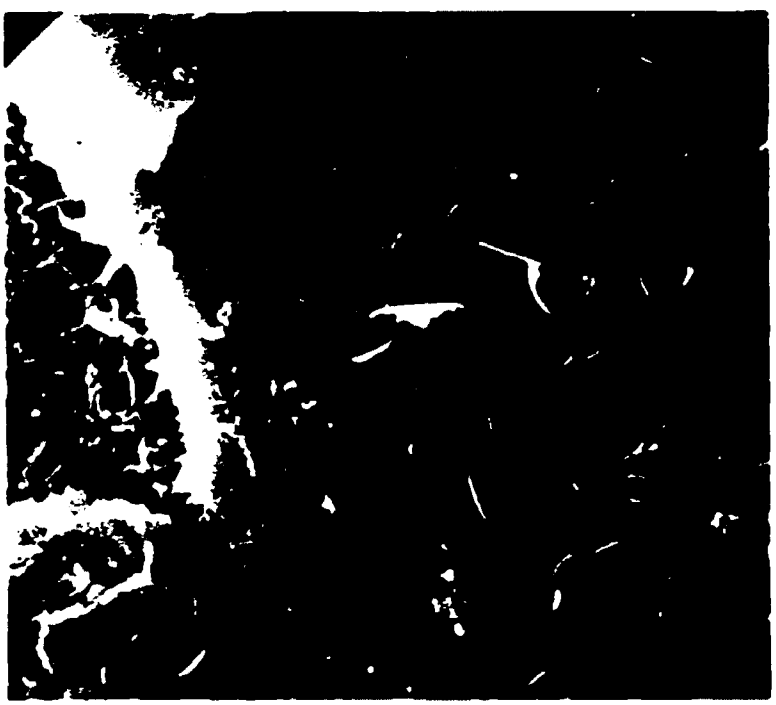


PLATE 7

SEM PHOTOGRAPHS OF GLASS SHARDS FROM THE MIDDLE OF THE SECTION AT PACKSADDLE BRIDGE

Both photographs illustrate the textural characteristics of the boxwork structure. In (a) the boxwork appears to be lower than the smoother area to the lower right corner of the field. (a. x6000; b. x10,000.)



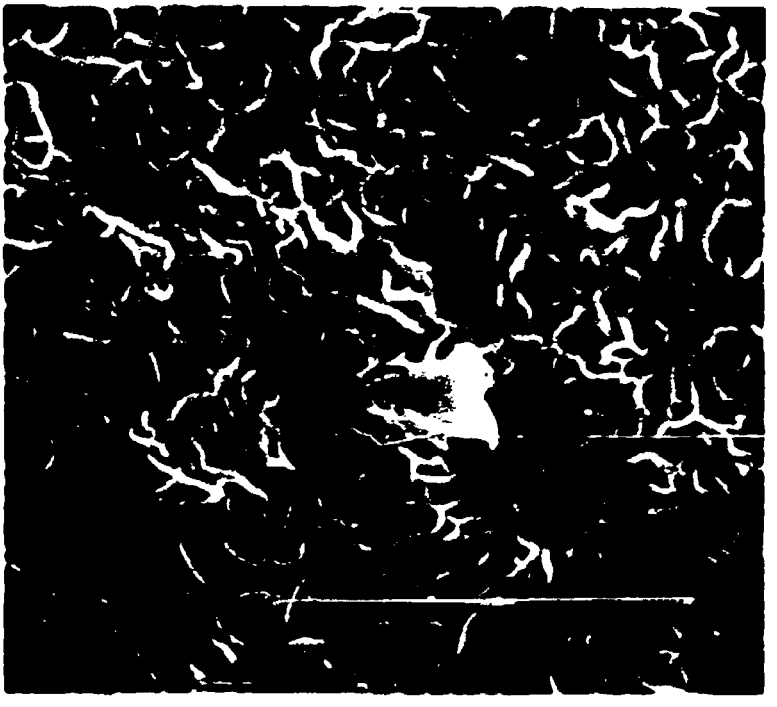


PLATE 8

SEM PHOTOGRAPHS OF HIGHLY ALTERED GLASS SHARDS
FROM THE BASE OF THE SECTION,
PACKSADDLE BRIDGE LOCALITY

a. x300. An illustration of the more rounded nature of these highly altered grains.

b. x3000. Two calcite rhombs in a montmorillonite matrix.



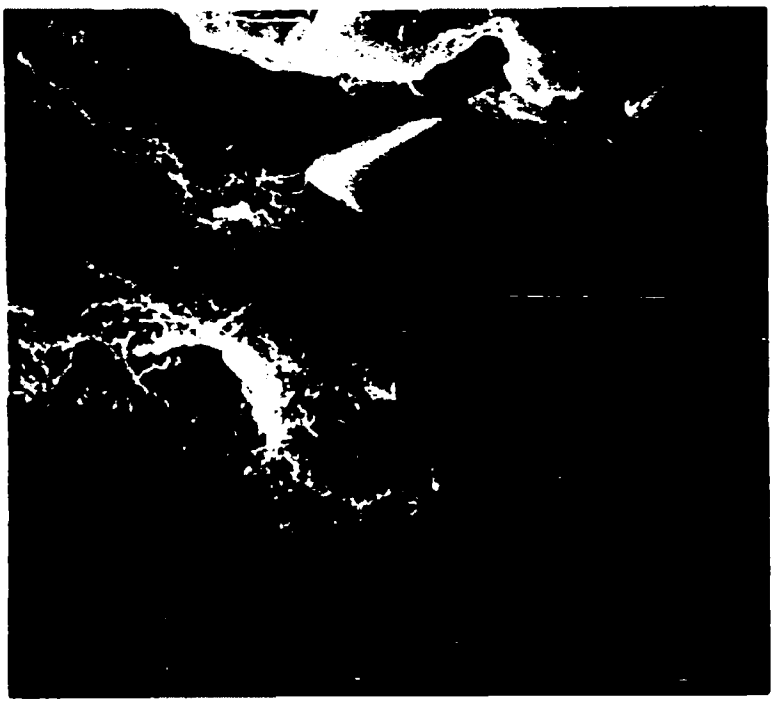


PLATE 9

SEM PHOTOGRAPHS OF BENTONITE FROM THE MIDDLE OF THE SECTION AT CAMARGO LOCALITY

a. x3000. Diatom (center) and a good illustration of boxwork structure (lower right).

b. x5500. Grain coated with clay revealing minor development of boxwork structures.





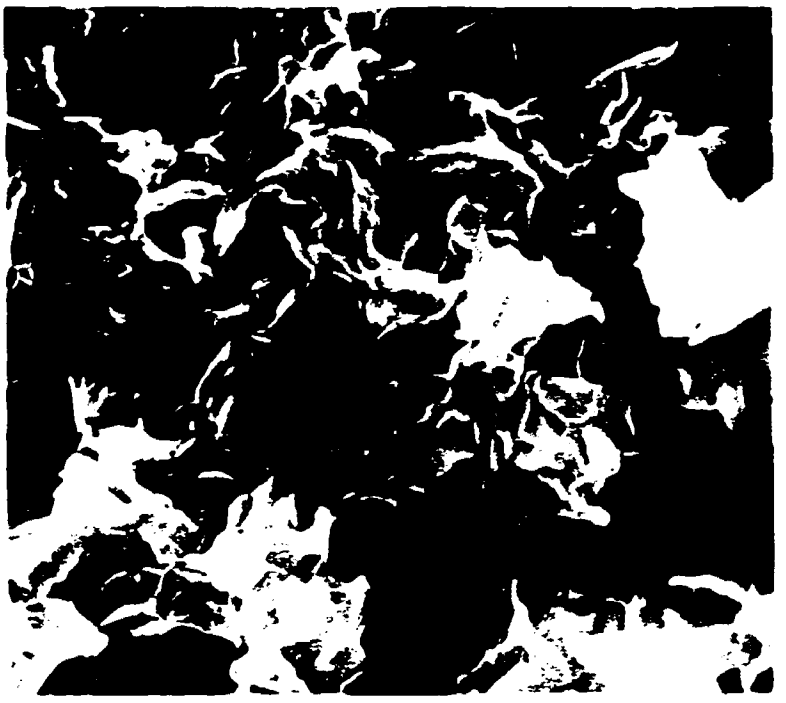
PLATE 10

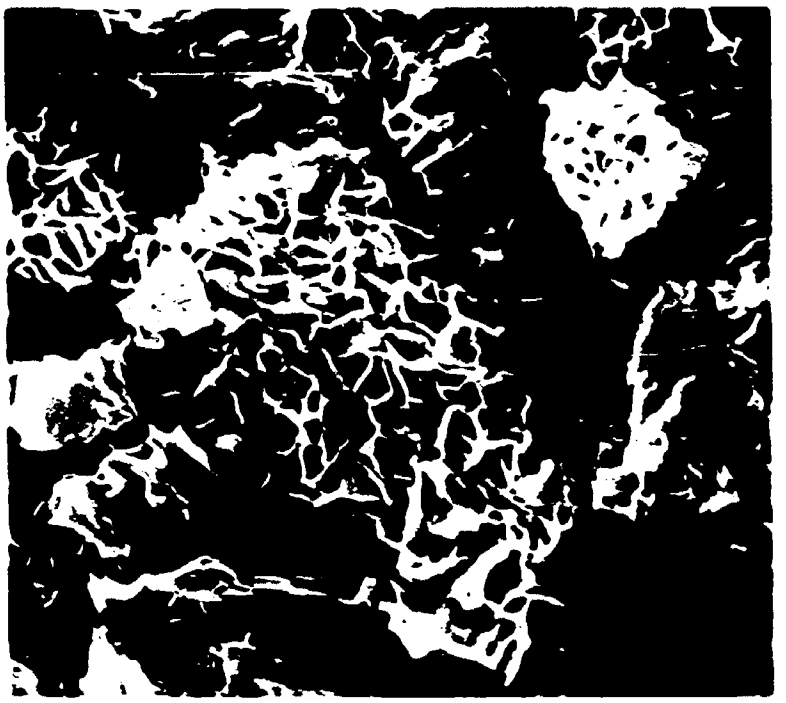
SEM PHOTOGRAPHS OF THE MINUS-4-MICRON FRACTION FROM THE TOP OF THE SECTION AT THE PACKSADDLE BRIDGE LOCALITY

The samples represented by the two photographs were prepared at different times and suggest that the boxwork structure is a result of sample preparation and is not related to clay genesis.

a. x7600. The surface texture shown here is predominantly smooth with minor curling.

b. x6000. Here the clay exhibits a higher degree of curling, approaching a boxwork structure. This sample remained in the SEM considerably longer than 10a.





development of boxwork is, in part, a function of SEM procedures and not necessarily related to clay genesis.

The preparation of the samples (Appendix IV) involves exposures to a vacuum during coating and while within the SEM. The dehydration of the clay during exposure to these extremely low pressures probably explains the boxwork structures. Other possible causes include factors related to the nature of the montmorillonite such as type of interlayer cation, amount of tetrahedral and octahedral substitution, and broken bonds at edges. The chemical changes in the clay fraction as a function of depth in the section has previously been described but there has been no evidence that any particular type of clay exhibits any better developed boxwork structures.

The SEM photographs of glass shards exhibiting incipient curling on relatively smooth surfaces support the contention that the montmorillonite is forming on the surface of the glass and suggest that there may be crystalline continuity of the montmorillonite on the surface being altered. This agrees with the high degree of optical continuity illustrated by the thin sections and grain mounts. The manner in which the clay appears to curling up from the shard surface

does not fit the concept of highly developed edge-to-face crystallization suggested by Borst and Keller (1969).

Underlying Sediments

Samples of the silty clay underlying the bentonite at Packsaddle Bridge were examined by the SEM for the purpose of viewing the zeolites which were identified by XRD. Plate 11 illustrates two crystallites encountered in the 10 micron Micro Mesh sieve split. The matrix is montmorillonite.

Nondispersive Chemical Analyses of Alteration Zones

Introduction

The purpose of the NDCA study was to determine the chemical characteristics of the alteration products on the surfaces of the glass shards. The SEM photographs previously described were all of glass shards whose platy direction was parallel to the face of the photograph. These views provided good illustrations of the general nature of the boxwork structure but did not give any information on the relationship between the boxwork and the shard itself.

A whole-rock sample of volcanic ash from the top of the section at Packsaddle Bridge was glued to the SEM sample

PLATE 11

TWO SEM PHOTOGRAPHS (x4000) OF PRESUMED ZEOLITES
10 MICRON SPLIT, PACKSADDLE BRIDGE

The upper photograph illustrates the elongate form of heulandite. The lower one, which is more equidimensional, may be analcite.





holder such that the stratification was perpendicular to the surface of the holder (and parallel to the viewing axis). This provided a means of viewing the glass shard "in section" permitting a side view of the alteration zones. Furthermore, this view would permit the application of the NDCA to the shard as well as its zones of alteration without one interfering with the other.

The SEM examination of these shard cross sections revealed that the presumed unaltered portion of the shard was dark and smooth and normally contacted the rough textured, lighter alteration zone at a fairly well defined border. The alteration zones were variable from grain to grain but most exhibited a rough stratification paralleling the shard surface. On some shards the alteration zone consisted of three distinct layers. The boxwork structure was not evident on all grains but, when present, it appeared to be restricted to the outer layer of alteration further supporting the idea that this structure is due to the curling of clay platelets on shard surfaces.

Application

The NDCA study consisted of analyzing 50 points along traverses in each definable alteration zone and 50 points

along a line in the center of each grain under consideration. The ratio of the counts for each element to the counts for aluminum was calculated for each point analyzed. The average ratio to aluminum as well as the standard deviation was calculated for each element in the 50-point traverse. With this information, t-tests were run to determine the degree of significance of differences between zones.

Six different grains were examined in this manner. The results obtained from the examination of these grains were not statistically compared but it was felt that there was a fairly consistent pattern among them. Data will be presented here for four of the grains analyzed.

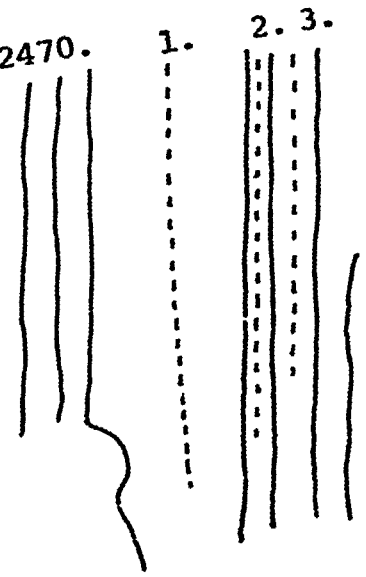
Plate 12a. illustrates a SEM photograph of NDCA No. 2. Several alteration zones are present. The lines or traces along with points were counted are shown on the facing page.

Table 12 lists data derived from the NDCA study of the grain shown in Plate 12a. The table shows the mean ratios of Si, Fe, Mg, Ca, Na and K to Al along the three traces as well as the calculated "t" values for each ratio between adjacent traces or lines. Table 13 lists the tabulated "t" values for the 90, 95, and 97.5 confidence levels.

PLATE 12

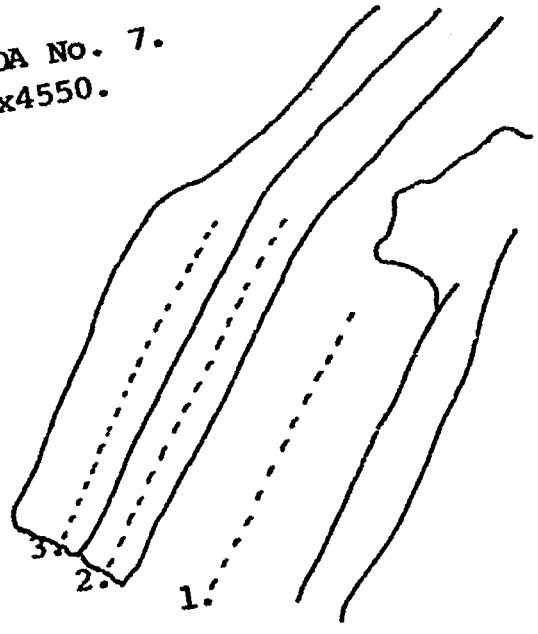
SEM PHOTOGRAPHS OF GLASS SHARDS IN CROSS SECTION

a. NDCA No. 2. x2470.



1 micron

b. NCDA No. 7. x4550.



1 micron

The drawings shown above indicate the zones along which points were analyzed. The numerals define these zones and the data for each grain are listed in Tables 12 and 14 respectively.



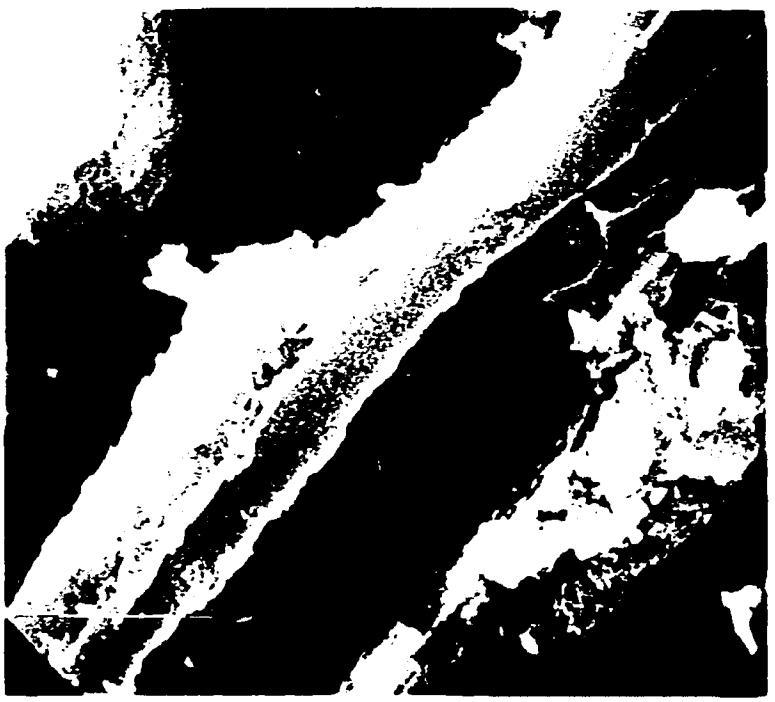


TABLE 12

NDCA DATA DERIVED FROM GRAIN ILLUSTRATED IN PLATE 12a. NDCA No. 2

		Ratios to Aluminum					
		Si	Fe	Mg	Ca	Na	K
Line 1.	$\bar{x}$	3.81	0.318	0.251	0.271	0.128	0.464
	$t_c^* =$	2.08	2.67	7.6	11.7	6.93	0.82
Line 2.	$\bar{x}$	3.74	0.352	0.235	0.351	0.109	0.444
	$t_c^* =$	6.9	1.43	6.15	1.7	2.27	5.1
Line 3.	$\bar{x}$	3.40	0.333	0.268	0.336	0.121	0.364

*The calculated "t" values shown above were derived from comparisons between Lines 1 and 2, and between Lines 2 and 3.

TABLE 13

TABULATED "t" VALUES FOR 98 DEGREES OF FREEDOM (50 + 50 - 2) AT THE 90, 95, AND 97.5 PERCENT CONFIDENCE LEVELS
(After Mood and Graybill, 1963, p. 433)

Level of Confidence	$t_{.10}$	$t_{.05}$	$t_{.025}$	
	1.282	1.645	1.960	Tabulated "t"

An examination of Table 12 reveals a distinct decrease in the Si/Al ratio across the altered area. The same may be said for the K/Al ratio. The changes for the other elements are much more subtle. The Na/Al ratio decreases slightly between lines 1 and 3 but line 3 exhibits an increase over line 2. The ratios of Fe, Mg, and Ca to Al increase from line 1 to line 3 but show no particularly distinct trend between lines 1 and 3, and between lines 2 and 3.

A comparison of the computed "t" values of Table 12 and those tabulated as shown in Table 13 reveals that there is less than a 10 percent probability that these data could be drawn from the same population. This does not apply to the K/Al ratios between lines 1 and 2. Aside from this, most values of "t" correspond to a 5 percent probability indicating that the changes apparent here are real.

Plate 12b illustrates another grain (NDCA No. 7) treated in a similar fashion. The altered zones shown in the photograph in Plate 12b exhibit a somewhat more smooth texture than those shown in Plate 12a. The data derived from the NDCA study of NDCA No. 7 are listed in Table 14. The data shown in Table 14 indicates that the chemistry of this grain is somewhat different than the previous grain. This is particularly true of the Si/Al and K/Al ratios in line 1 (fresh

zone) which are higher than those for NDCA No. 2. Another difference between NDCA No. 7 and NDCA No. 2 is the decrease in Fe/Al and Ca/Al ratios between lines 1 and 3. The Mg/Al ratio increases from line 1 to 2 and Na/Al remains more or less the same. The calculated "t" values given in Table 14 between the analyzed lines reveal that the differences indicated are significant.

TABLE 14

NDCA DATA DERIVED FROM GRAIN ILLUSTRATED IN PLATE 12b. NDCA NO. 7.

		Ratios to Aluminum					
		Si	Fe	Mg	Ca	Na	K
Line 1.	$\bar{x}$	4.989	0.436	0.206	0.386	0.105	0.751
	t_c^* =	8.1	5.48	7.3	7.0	0.55	9.45
Line 2.	$\bar{x}$	4.481	0.500	0.247	0.321	0.106	0.550
	t_c^* =	6.67	6.82	5.03	0.954	0.987	10.45
Line 3.	$\bar{x}$	4.095	0.304	0.274	0.315	0.109	0.417

*The calculated "t" values shown above were derived from comparisons between Lines 1 and 2, and between Lines 2 and 3. Compare with tabulated "t" values shown in Table 13, page 106.

Plate 13a (NDCA No. 3) illustrates a SEM photograph of a glass shard exhibiting one alteration zone. The NDCA data are given in Table 15. The data here are similar to that derived from the previous grains. The altered zone exhibits a strong decrease in Si/Al and K/Al ratios. Fe/Al exhibits

TABLE 15

NDCA DATA DERIVED FROM GRAIN ILLUSTRATED IN PLATE 13a. NDCA NO. 3

		Ratios to Aluminum					
		Si	Fe	Mg	Ca	Na	K
Line 1.	$\bar{x}$	4.08	0.313	0.264	0.289	0.119	0.483
	t_c^* =	14.3	4.36	8.69	2.86	2.83	10.8
Line 2.	$\tilde{x}$	3.29	0.273	0.329	0.302	0.127	0.326

*The calculated "t" values shown above were derived from comparisons between Lines 1 and 2. Compare with tabulated "t" values shown in Table 13, page 106.

a small decrease; and Mg/Al, Ca/Al, and Na/Al exhibit a small increase. The calculated "t" values give a good indication of the significance of the observed changes.

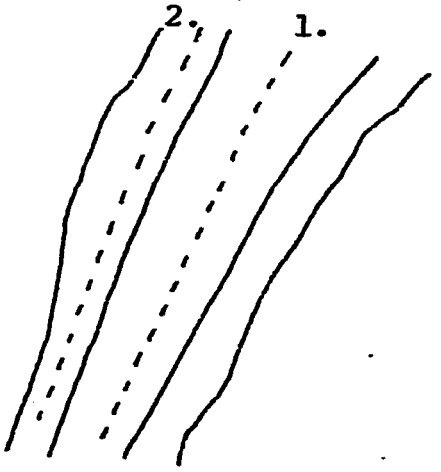
The glass shard illustrated in Plate 13b (NDCA No. 6) exhibits only one definable alteration zone. Traces of

PLATE 13

SEM PHOTOGRAPHS OF GLASS SHARDS IN CROSS SECTION

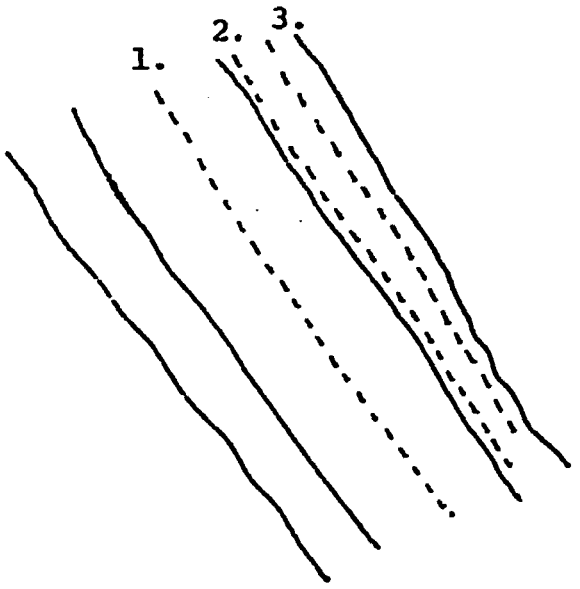
The drawings shown below indicate the zones along points where analyzed. The numerals define these zones and the data for each grain are listed in Tables 15 and 16 respectively.

a. NDCA No. 3. x3902.



1 micron

b. NCDA No. 6. x3900.



1 micron





counts were run along this zone as well as along the border (in the zone of alteration) adjacent to the fresh portion. The NDCA data are given in Table 16.

TABLE 16

NDCA DATA DERIVED FROM GRAIN ILLUSTRATED IN PLATE 13b. NDCA NO. 6

		Ratios to Aluminum					
		Si	Fe	Mg	Ca	Na	K
Line 1.	$\bar{x}$	3.82	0.428	0.234	0.368	0.105	0.442
	t_c*	6.7	4.8	2.3	0.18	1.31	5.8
Line 2.	$\bar{x}$	3.64	0.582	0.222	0.365	0.110	0.565
	t_c*	10.7	10.2	12.2	1.53	6.4	2.2
Line 3.	$\bar{x}$	2.64	0.456	0.328	0.390	0.138	0.617

*The calculated "t" values shown above were derived from comparisons between Lines 1 and 2 and between Lines 2 and 3. Compare with tabulated "t" values shown in Table 13, page 106.

The calculated "t" values shown in Table 16 reveal that there is, with one exception, less than a 10 percent probability that the observed differences could be obtained from a single population. Most of the changes between the

three lines, as revealed by the calculated "t" values, could be obtained from the same population with a probability of less than 2.5 percent. The conclusion is, therefore, that the three lines or zones represent different populations.

The Si/Al ratio decreases sharply from the fresh center of the shard to the alteration rind. The other ratios, including K/Al, increase from the center outward. It will be recalled that the K/Al ratio for the other grains decreased toward the alteration zone.

Discussion

There are two general hypotheses for the formation of clay minerals from the alteration (weathering) of parent materials. One holds that clay minerals may be precipitated from ionic solutions derived from silicate alteration (Correns, 1940). The other considers that clay minerals form directly on grains undergoing alteration and that the clays may be preceded by a colloidal gel formation (Frederickson and Cox, 1954). Both concepts may, in part, be applicable to crystalline silicates and also to glass.

The thin section photomicrographs have revealed the intimate relationship between the shard surface and the development of montmorillonite clay. The high cation-exchange

capacity of samples apparently low in clay manifests the high reactivity of these shard surfaces. Furthermore the SEM photographs of shard cross sections reveal the texture of the alteration zones, and the NDCA study has shown the chemical differences between fresh glass and its altered periphery.

The NDCA study was semi-quantitative in that it only provides information regarding chemical differences between areas. It might be helpful to compare the ratios to aluminum from the chemical analyses (XRF) of the ash from the top of the unit at Packsaddle Bridge to those ratios determined by NDCA and to the montmorillonite analyses (XRF).

Table 17 lists the ratios to aluminum of the bulk sample as well as the minus-2-micron fraction from the top of the section at Packsaddle Bridge (1 and 4). These may be compared to the NDCA ratios determined from NDCA No. 3 (2 and 3).

Other than the Si/Al and perhaps the Na/Al ratios there does not appear to be any similarity between 1 and 2. Appendix IV lists some NDCA data on analyzed glasses of known molar composition. Here there is a direct and almost equal relationship between the ratios determined by counts on the NDCA and the molar ratio of Si to Al. It is, therefore,

suggested that the Si/Al ratios determined by NDCA are very close to actual molar ratios.

TABLE 17

COMPARATIVE MOLAR RATIOS TO ALUMINUM

Sample No.	Si	Fe	Mg	Ca	Na	K
1.	4.37	0.148	0.325	0.112	0.202	0.177
2.	4.08	0.313	0.264	0.289	0.119	0.483
3.	3.29	0.273	0.329	0.302	0.127	0.326
4.	3.59	0.124	0.700	-	-	-

1. Packsaddle Bridge, bulk analyses (XRF). Sample No. 9.
2. NDCA No. 3, line 1.
3. NDCA No. 3, line 2.
4. Packsaddle Bridge, minus-2-micron fraction analyses (XRF). Sample No. 9.

If the above is correct, some of the alteration zones analyzed have Si/Al ratios very close to that of montmorillonite. The other ratios are, however, not known quantitatively. The structural condition or organization of the alteration zones is also unknown.

The NDCA study of many grains has revealed differences in the mean ratios to aluminum in fresh areas between different grains. The range of differences was not determined quantitatively but observation suggests that Si, Fe, and K to Al ratios are the most variable. However, the variation in Al content is also unknown. The original composition of the grain may control the chemical nature of the alteration zones and thus explain the differences encountered during the NDCA study of alteration zones.

The overall chemical variation within the ash bed was described in the section on geochemistry. The NDCA analyses have provided information on the chemical variation within individual shards. Because the alteration of a single shard is the first step toward the alteration of an ash bed it will be appropriate to compare the results of these two variations.

Both situations are characterized by a decrease in Si, Na, and K. Also, both exhibit a general increase in Fe, Ca, and Mg. With the exception of Si and perhaps K the changes across grains for the other elements is more subtle (probably due to the semi-quantitive NDCA approach). The amount of Na appears to exhibit the least change. The difference in the amount of Na between fresh and altered zones of grains is much less than that observed within the stratigraphic

section where most of the Na is removed near the top of the section.

The presence of the Na in the alteration zones in roughly the same proportion as in the fresh ash suggests that this element may be retained in interlayer positions on the montmorillonite.

ECONOMIC POTENTIAL

General Statement

Although the purpose of this study was not to examine in detail the economic potential of Plio-Pleistocene volcanic ash and bentonite deposits in Oklahoma, it was believed that a study of their geology, mineralogy, and geochemistry might lead to a better understanding of their properties and mode of formation which could contribute to the economic development of these deposits.

The deposit at Camargo has been worked continuously for a number of years. The bentonite is shipped to Mississippi and processed. The utilization of this material has not been disclosed but it seems likely that it is processed as a bleaching clay. It is significant that this raw material can be transported such a distance economically.

The deposit at Woodward has also been worked in the past but little is known about the operation or the use of the material. The deposits at Packsaddle Bridge and Lake Lloyd Vincent apparently have never been mined.

The economic usefulness of any naturally occurring deposit is dependent upon all of the following interrelated variables: 1) Property. There must be some characteristic of the material which lends itself to practical utilization. 2) Quality or tenor. The material must be of sufficient purity to permit its development without expensive treatment. 3) Volume. In order to realize gain on land, machinery, and other types of overhead investments involved in developing an operation, there must be sufficient tonnage available. The volume is a function of the thickness and areal extent of the deposit. A thin deposit covering a wide area might not be feasibly worked due to the cost of land procurement. Associated with this is the problem of depth of burial. There is commonly a specific limit to the amount of overburden which may be removed to economically recover a particular material. 4) General economic considerations. In this category are included the costs of labor, transportation, and related costs which will affect the development of a particular deposit.

Evaluation of Materials

The following discussion will be concerned with the application of the first three variables to the volcanic ash and bentonite deposits as revealed by this investigation.

1. Property. The deposits under study consist of two types. One, represented by the Camargo locality, is a bentonite consisting of Ca-montmorillonite clay and highly-altered glass shards. The second type, represented by the deposits at Woodward, Packsaddle Bridge, and Lake Lloyd Vincent localities, consist of relatively fresh volcanic ash grading downward to Ca-montmorillonite clay and highly-altered glass shards. The economic usefulness of these two types of deposits is dependent upon the relative amounts of bentonite and volcanic glass present.

The high percentage of Ca-montmorillonite and the reactive nature of the glass in the deposit at Camargo are indicators that this material is suitable as a bleaching clay or "fullers earth." This clay is normally acid activated (Grim, 1962, p. 322) which enhances the naturally active surfaces and permits its utilization for the decolorization of oils. The presence of Mg in the octahedral layer seems to contribute significantly to the effectiveness of the montmorillonite.

The volcanic ash deposits (Woodward, Packsaddle Bridge, and Lake Lloyd Vincent) appear to possess qualities applicable for additives to abrasives and, as revealed by the chemical

analyses of this study and the testing of Burwell (1949), the material is suitable, after appropriate treatment, as a "popped" or cellular product for use as an insulating material.

It is suggested here that the volcanic ash may be suitable as an additive to lime for the chemical stabilization of road bases. In this type of stabilization process the lime reacts with soil (clay minerals) and removes Si and Al ions which combine with the Ca to form cementitious products; this is called a pozzolanic reaction and leads to higher strength in the soils (Lambe, 1962; Grim, 1962). The importance of the volcanic ash is to provide Si and Al.

2. Quality. The quality or tenor of the materials comprising the deposits studied appear quite good. There seems to be a minor amount of non-volcanic material in the sections studied. The quartz sand pockets encountered in some places may be deleterious for some types of applications. With respect to uniformity, the Camargo locality is the best; it is unknown to what degree the range of alteration exhibited by the deposits at Woodward, Packsaddle Bridge, and Lake Lloyd Vincent would influence the previously mentioned applications. This could be quite significant.

The information derived from this study has revealed the properties of the deposits but more chemical and

mineralogical analyses are needed in order to determine lateral variation within the deposits. Preliminary mineralogical data do not support significant lateral variations but more chemical data would be helpful.

3. Volume. The tonnage available at the studied localities is unknown. Field work has revealed thicknesses of 6 to 20 feet and between zero and 20 feet of overburden. This would indicate that a maximum of 3 feet of overburden would have to be removed to recover 1 foot of volcanic ash or bentonite. The economic feasibility of this ratio would depend, in part, on the application or use of the material.

The Camargo deposit may provide some insight on the volumes to be expected from other deposits. The extent of mining operations and outcrops indicate that the deposit covers approximately 400 acres. Assuming an average thickness of 5 feet, a wet density of 100 pounds per cubic foot, and uniform distribution of the bentonite the recovery would be approximately 11,000 tons per acre.

Exploration Program

The development of an initial exploration program should be guided by two basic principles, these are: 1) the exploration tool should be such that it provides maximum

general information and covers a large area, 2) the geological situation of the undiscovered deposits will be similar to the known deposits.

It appears that all of the studied localities are associated with collapse structures. This fact should be the key to future explorations. Aerial photographs would provide a quick and inexpensive method to search for these structures. This should be accompanied by an investigation of the subsurface extent and thickness of the Permian evaporites utilizing existing logs. Prospects discovered by these methods would be investigated later by more detailed exploration tools.

Seismic refraction and electrical resistivity methods could be used during this "second phase" of the exploration program. Both methods would provide data on the geometry of the collapse structure. The low density and resulting low velocity of the volcanic ash might limit the effectiveness of seismic refraction because, in shallow work, low velocity layers are sometimes "hidden" when surrounded by denser materials. The bentonitic clay at the base of the volcanic ash unit would be detected by electrical resistivity because this material is unique in the Tertiary sequence and because it has a high moisture content.

The last step in the exploration program would consist of a drilling program to define the limits of the deposit and to collect samples.

SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

Conclusions

1. The increased degree of alteration of the volcanic ash toward the base accompanied by the downward decrease of silica and the alkalis, and the retention of iron, calcium, and magnesium suggest that the ground water was flowing, generally, downward through the section.

2. The chemical variation within the vertical section is a resulting balance between the destruction of volcanic glass and the formation of montmorillonite. Presumably the high percentage of magnesium increases the probability of forming montmorillonite. As the clay forms, magnesium, aluminum, iron, and silicon are taken up (retained) in the clay structure. Excess silica is removed as well as potassium. Initially, both sodium and calcium, and possibly magnesium occupy interlayer positions. Eventually, it is believed, most of the sodium is replaced by calcium.

3. The individual grain alteration is similar to the alteration of the unit as a whole.

4. There does not appear to be any intermediate mineral which precedes the formation of montmorillonite. The alteration rinds on shard edges may exhibit more order than the fresh glass, and the Si/Al ratios of some rinds are close to that of montmorillonite; however, the precise nature of the alteration rinds is not known.

5. SEM and petrographic evidence suggest that the montmorillonite forms directly on the surfaces of the glass and possesses a high degree of optical continuity on these surfaces.

6. With increased alteration, the montmorillonite apparently exhibits an increase in tetrahedral aluminum at the expense of silicon.

7. Field and petrologic evidence indicate that the volcanic ash accumulated under conditions of low kinetic energy in small lakes occupying depressions formed by evaporite solution in the subsurface.

8. The economic development of these deposits will depend upon the knowledge obtained from an accurate mapping and exploration program. The materials are believed suitable

for bleaching clays (bentonite), or for abrasives, cellular products, or soil stabilization additives (volcanic ash).

Recommendations for Future Research

The following list includes those areas in which future research might provide additional data on the geology, genesis, and economics of the western Oklahoma volcanic ash and bentonite deposits.

1. The Pleistocene volcanic ash (Fresh type of Table 1) should be collected and studied such that comparisons could be made regarding mode of alteration and geologic setting. It would have been helpful if one of these deposits had been included in the present study.

2. Chemical analyses from additional vertically sampled sections would determine the effect of possible lateral ground-water movement and also help define the chemical consistency of the deposits.

3. A detailed study should be made to determine the chemical variation within the glass shards. This may be considerable and may control the nature of the alteration product on the individual shard. It would be preferable to conduct such a test on Pleistocene material as this would be essentially free of alteration products on the shard surfaces.

4. The NDCA study was conducted on a sample of relatively fresh volcanic ash. A similar study of more highly altered ash lower in the section would determine the degree of difference (if any) between the chemical alteration mechanism at the top and bottom of the section.

5. An attempt should be made to determine to what extent amorphous material is present in the clay fraction and, if present, its chemical composition.

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A P P E N D I C E S

APPENDIX I

DESCRIBED STRATIGRAPHIC SECTIONS

The stratigraphic sections described herein represent those sections at which samples were collected for detailed study. These sections are considered to be representative of the respective deposits and were described in the field.

Camargo Locality

This section is located approximately two hundred yards north of the section-line road at the bentonite pit located in the S½, Sec. 17, T. 19 N., R. 19 W. This pit has been backfilled.

	Feet
Plio-Pleistocene:	
Sands; medium to fine size, some gravel and silt layers; yellow to brown in color, sorting poor, cross-bedded and uncemented. Contact with underlying bentonite either covered or lower part of sands stripped during mining.	20-30
Pliocene (?):	
Bentonite; color varies from white, to pink or gray; highly plastic and greasy when moist and brittle when dry; fairly uniform in texture from top to bottom but exhibits	

some banding or color segregation locally; the bands are somewhat wavy; thin layer of medium quartz sand present in middle of unit; contact with underlying material is distinct and lower 1/8 inch of bentonite is bright green in color. 5 - 6

Sand; medium to fine, with appreciable silt and clay, dark brown color; no apparent structures; lower contact covered. 0.5

The section described below, also from Camargo, was not studied in detail but is included because the material underlying the bentonite was better exposed. Only the underlying material will be described. The section is located in a gully system on the west side of State Route 34 in the SW¼ Sec. 18, T. 19 N., R. 19 W.; approximately seventy-five yards north of east-west section-line road.

Pliocene (?): Feet

Sand; brown, medium to fine size, moderately well sorted, uncemented, few fine particles, no sedimentary structures visible; upper and lower contacts distinct. 1.0

Silt or silty clay; dark brown, compact, no sedimentary structures visible; upper and lower contacts distinct. 1.0

Sand; brown, medium to fine, moderately well sorted, no sedimentary structures visible, few fine particles, lower contact covered. 1.0

Zeolites were later found in the silt or silty clay from the above section as well as from the sand directly underlying the bentonite at the mined area.

Packsaddle Bridge Locality

The section below was described at an erosional outlier of volcanic ash in the N½, SW¼, SW¼, SW¼ of Sec. 2, T. 16 N., R. 24 W, Ellis County, Oklahoma. The site is on a rise located approximately eight hundred feet due east of U.S. Route 283. Most of the deposit extends along the river to the east in Secs. 11 and 12.

Plio-Pleistocene:	Feet
Sands and gravels, brown, poorly sorted, appreciable number of fine particles, pebbles very rounded.	2 -20
Pliocene(?):	
Volcanic ash and bentonite; white to gray cliffs of volcanic ash grading downward to bentonite at base; sandy at upper contact and some small sand lenses locally; ash is blocky and appears to be medium to coarse silt-size; bentonite is gray to pinkish in color, highly plastic when moist, and has a distinct lower contact.	10
Silty clay; brown, hard cemented, with distinct upper and lower contacts.	0.1

Silty clay; brown, uncemented; similar to above except for apparent lack of cement; lower contact covered. 1.0

Underlying these materials are the "Packsaddle Beds" of Kitts (1965).

Woodward Locality

The Woodward section was described in the N½ Sec. 13, T. 23 N., R. 22 W., in Woodward County, Oklahoma. It lies approximately thirty yards south of the east-west section-line road which runs two miles north of the Woodward airport.

	Feet
Plio-Pleistocene:	
Sand and gravel; brown to gray, poorly sorted, locally cemented, appreciable amount of fine material; lower contact irregular and somewhat gradational.	2-3
Pliocene(?):	
Volcanic ash and bentonite; white to gray volcanic ash grading downward to white to pink bentonite at base; ash is blocky, hard, and composed of medium to coarse silt-size particles; bentonite is highly plastic when wet and exhibits a sharp lower contact with the underlying material.	6-8
Silty clay; brown, compact, no apparent sedimentary structures visible, lower contact is covered but other exposures suggest that no greater than thirty feet of interbedded sands, silts, and gravels separate this unit from the underlying Rush Springs sandstone (Permian).	2.0

Lake Lloyd Vincent Locality

Exposures of volcanic ash and bentonite are present in western Ellis County approximately three miles southwest of Lake Lloyd Vincent. The volcanic ash crops out in west-facing bluffs in the W½ of Sec. 23, T. 18 N., R. 26 W. The occurrence of the volcanic ash and bentonite is generally similar to the deposits at Woodward and Packsaddle Bridge and, in hand-specimen, the material is indistinguishable from that at the other deposits. The description below is of an outcrop on the south side of State Route 46 on the southern boundary of Sec. 23, approximately fifty yards east of the southwest corner of this section.

Pliocene(?):	Feet
Volcanic ash and bentonite, gray to white volcanic ash, massive and blocky with some apparent cross-bedding, jointed, lower contact with bentonite gradational but appreciable clay is encountered about 4.5 feet from the top; the bentonite is white to gray; locally pink, highly plastic and has a thin green zone at the contact with the underlying clay.	6.2
Clay, some silt, gray, massive, lower contact covered.	2.0

Although bedrock was not present in the immediate area of these exposures, examination of outcrops of red

Permian shales near the Lake Lloyd Vincent dam revealed an anomalous 10 or 12 degree dip to the southeast. This high dip may be an indicator of local collapse, however, no other evidence was observed.

APPENDIX II

CHEMICAL ANALYSES BY XRF

Preliminary work revealed that samples which had been prepared with the recommended 10 percent PVA (Kerns, 1967b) exhibited a tendency to split and crumble after being pressed into the briquet. The lack of cohesion in the briquets was believed to be due to adsorption of water by the clay in the sample. Therefore, the samples were fired at 1000 degrees Centigrade for at least 12 hours in order to drive off existing water and to so modify the structure as to eliminate the potential for adsorption. The previously discussed procedure was followed after firing. The resulting briquets exhibited a lesser tendency for some samples to crumble but others were still far from ideal.

Trial and error procedures indicated that the percent PVA in the sample also controlled the stability of the briquets. For all samples, 40 percent PVA provided sufficient stability. In order to determine what effect variations in the PVA content had on fluorescence emission, briquets were

prepared from samples of relatively fresh volcanic ash from Packsaddle Bridge; the PVA contents tested included 25, 32, 40, and 50 percent. The resulting chemical analyses of these test briquets revealed that the amount of PVA did not affect, in any predictable fashion, the fluorescence emission. All remaining samples were prepared with 40 percent PVA.

Chemical analyses are shown on Tables 18 and 19. Analyses for iron are based upon total iron converted to Fe_2O_3; the emission was counted by scintillation counter. All other elements were analyzed in a vacuum by gas-flow counter.

TABLE 18

BULK CHEMICAL ANALYSES

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	Cl	P_2O_5	Total
					Packsaddle Bridge							
9	72.57	14.10	3.25	3.6	1.75	1.78	2.3	0.37	tr	0.01	0.08	99.81
8	73.69	15.70	3.55	6.5	3.32	1.05	1.4	0.44	tr	0.011	0.13	105.79
7	67.81	16.2	4.00	9.55	4.20	n.d.	0.3	0.47	tr	0.014	0.20	102.74
6	67.17	16.8	4.30	10.15	4.53	n.d.	0.2	0.45	tr	0.013	0.22	103.83
5	64.91	16.6	3.90	9.90	4.40	0.34	0.15	0.45	tr	0.015	0.21	100.88
4	64.05	16.8	4.30	9.6	4.53	0.38	0.10	0.39	0.04	0.015	0.21	100.42
3	58.47	15.8	4.30	11.60	4.20	0.43	0.10	0.39	1.00	0.034	0.20	96.52

tr = trace, net counts less than lowest standard;

n.d. = not detected, background greater than peak.

TABLE 18--(Continued)

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	Cl	P_2O_5	Total
						Woodward Locality						
8	76.84	14.5	3.15	1.60	1.4	1.75	2.90	0.29	tr	0.013	0.07	102.51
7	72.11	14.4	3.25	2.35	1.7	1.43	2.40	0.37	0.01	0.017	0.10	98.14
6	73.06	14.3	3.30	1.80	1.5	1.66	2.55	0.36	tr	0.014	0.08	98.62
5	68.76	15.2	3.60	4.10	2.2	1.00	1.65	0.39	tr	0.013	0.13	97.04
4	70.27	15.1	3.40	3.50	1.95	1.39	1.95	0.38	tr	0.013	0.12	98.07
3	65.71	16.2	4.30	6.30	3.0	0.83	0.65	0.47	tr	0.013	0.19	97.66
2	65.21	16.8	4.15	8.30	3.2	n.d.	0.20	0.48	tr	0.17	0.21	98.72
1	62.60	16.5	4.30	7.35	3.25	0.52	0.20	0.45	0.04	0.14	0.21	95.56

tr = trace, net counts less than lowest standard;

n.d. = not detected, background greater than peak.

TABLE 19

BULK CHEMICAL ANALYSES

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	Cl	P_2O_5	Total
						Camargo Locality						
6	69.10	14.6	3.55	6.25	2.2	0.78	0.95	0.28	0.09	0.011	0.13	97.94
5	67.26	17.7	4.15	8.8	3.14	n.d.	0.20	0.48	tr	0.015	0.20	101.95
4	68.02	17.8	4.20	8.6	3.17	n.d.	0.24	0.49	tr	0.014	0.20	102.73
3	67.38	17.9	4.30	8.85	3.15	0.45	0.20	0.61	0.04	0.021	0.21	103.11
2	66.91	18.6	4.80	8.8	3.25	n.d.	0.20	0.54	tr	0.014	0.21	103.32
1	63.89	18.1	4.45	8.0	3.35	0.31	0.10	0.51	0.22	0.014	0.21	99.15

tr = trace, net counts less than lowest standard;

n.d. = not detected, background greater than peak.

TABLE 19--(Continued)

CHEMICAL ANALYSES OF MINUS-2-MICRON FRACTIONS

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	Cl	P_2O_5	Total
						Camargo Locality						
5	59.16	15.56	3.60	8.19	3.25	0.06	0.14	0.40	n.a.	n.a.	n.a.	90.39
3	61.71	17.31	3.39	8.32	3.56	0.06	0.06	0.42	n.a.	n.a.	n.a.	94.86
1	63.00	18.49	3.65	7.38	3.50	0.02	0.06	0.46	n.a.	n.a.	n.a.	96.58
						Packsaddle Bridge Locality						
7	60.04	14.18	2.87	7.73	3.34	0.09	0.07	0.39	n.a.	n.a.	n.a.	88.68
5	58.56	16.14	3.06	7.75	3.83	0.17	0.09	0.39	n.a.	n.a.	n.a.	90.00
3	57.28	15.97	3.31	7.52	3.53	0.06	0.05	0.44	n.a.	n.a.	n.a.	88.21

n.a. = not analyzed.

APPENDIX III

THE DETERMINATION OF PERCENT CHEMICAL VARIATION

An example of the technique (Krauskopf, 1967) used to determine the percent chemical variation or change in a sample at a given depth in the section is shown below in Table 20. In this example, sample no. 7 will be compared to sample no. 9; both are from Packsaddle Bridge. The analytical error in the chemical analyses of both samples has been distributed such that the sum of the weight percents of the oxides equals approximately one hundred. Calculations such as those shown on the following table were performed on both bulk and size fraction samples.

TABLE 20

AN EXAMPLE OF THE DETERMINATION OF PERCENT CHEMICAL VARIATION

	A	B	C	D	E
SiO_2	72.57	66.10	59.10	-13.47	- 19
Al_2O_3	14.10	15.78	14.10	0	0
Fe_2O_3	3.25	3.89	3.48	+ 0.23	+ 7
MgO	3.60	9.31	8.31	+ 4.71	+130
CaO	1.75	4.19	3.75	+ 2.00	+114
Na_2O	1.78	n.d.	0	- 1.78	-100
K_2O	2.30	0.29	0.26	- 2.04	- 89
TiO_2	0.37	0.46	0.41	+ 0.04	+ 11
	99.72	100.02			

Column A: The adjusted chemical analysis of fresh ash which is assumed to be representative of the section.

Column B: The adjusted chemical analysis of a sample which is to be compared to the one in Column A.

Column C: Column A is considered to represent 100 grams of ash containing 14.10 grams of alumina. Because

alumina is relatively immobile, the 14.10 grams must still be present in the sample of Columm B. The weight percent in Column B is different because other elements have been partially removed or added. Column B is adjusted by multiplying each weight percent by 14.10/15.78. These products are listed in Column C.

Column D: Each value here is the difference between Column A and Column C and represents the gain or loss in grams for a particular oxide in the more altered sample.

Column E: This is the weight percent change for each oxide calculated by dividing values in Column D by the respective value in Column A and multiplying by 100.

APPENDIX IV

SEM AND NDCA PROCEDURES

All samples investigated by means of the SEM were mounted on copper sample holders and coated with a mixture of gold-palladium. Clay fractions were sedimented upon the copper holders and selected size-fractions from micro mesh sieving were sprinkled on the holders manually. Whole rock samples were glued to the sample holder such that the stratification of the sample was perpendicular to the horizontal surface of the holder.

The operation of the NDCA briefly involves energizing the elements in the sample by the accelerating voltage (25kv) of the SEM beam which causes the elements to emit their characteristic radiation and associated energies. These energies are sorted out by the unit for each element and the number of counts for each element is displayed on a Teletype printout. The counting time in all cases is two minutes. The elements studied were: Si, Al, Fe, Mg, Ca, Na, and K. The counts are presented as a ratio of counts for a particular element to that of aluminum.

In order to test the reliability and effectiveness of the NDCA unit in studying volcanic glass, several test procedures utilizing commercial glasses were performed. One of these involved analyzing 50 points in ordinary plate glass. Table 21 illustrates the mean of the ratios of the counts of the various elements to aluminum, the standard deviation and the coefficient of variation (mean divided by standard deviation).

TABLE 21

MEAN, STANDARD DEVIATION AND COEFFICIENT OF VARIATION OF RATIOS TO ALUMINUM FOR PLATE GLASS

	Si	Fe	Mg	Ca	Na	K
x	7.203	0.7685	0.352	3.00	0.225	0.5423
s	0.628	0.075	0.416	0.284	0.034	0.055
cv	8.7%	9.8%	11.8%	9.5%	15.1%	10.1%

The coefficients of variation are either an indication of the homogeneity of the glass or the ability of the NDCA unit to detect and distinguish homogeneity if present.

Because ordinary plate glasses may not be too homogenous, samples of pure, commercial glasses of known chemical

composition were analyzed with the NDCA unit. A glass having a molar composition of MgO, Al_2O_3, SiO_2 of 1: 1: 4 gave the count ratios for 35 points shown in Table 22.

TABLE 22

MEAN, STANDARD DEVIATION AND COEFFICIENT OF VARIATION OF ANALYZED GLASS

	Si	Mg
$\bar{x}$	2.077	0.271
s	0.0647	0.0155
cv	3.11%	5.73%

Table 23 illustrates the results of the same type of operations conducted on glass with a molar composition of

TABLE 23

MEAN, STANDARD DEVIATION AND COEFFICIENT OF VARIATION OF ANALYZED GLASS

	Si	Mg
$\bar{x}$	1.705	0.290
s	0.044	0.011
cv	2.6%	3.9%

MgO, Al_2O_3, and SiO_2 of 1: 1:3. Thirty-five points were analyzed.

Tables 22 and 23 indicate that the NDCA unit is capable of detecting elements in homogenous glass with a reasonably high accuracy. This capability is, no doubt, partially dependent upon the amount or concentration of an element in a sample.

The detection capability is also dependent upon the number of points which are analyzed. The decision to count 50 or 35 points per sample was somewhat arbitrary but previous work suggested that this range might be satisfactory (i.e., give a low coefficient of variation). The main purpose of the NDCA study was to detect chemical differences between the unaltered centers and the altered edges of glass shards. This involved counting a number of points in the center and comparing these data to that derived from the edges. Sokal and Rohlf (1969, p. 266-269) outline a procedure for determining the minimum number of individuals (in this case points) which must be examined when two populations are to be compared. The procedure is based upon the prior determination of the approximate coefficient of variation among the combined populations. Also one must select the confidence level, the smallest true difference desired between populations, and

the desired probability that a difference will be found to be significant. The following selections were made:

1. Confidence level: 1%.
2. True difference between populations: variable (see Table 24).
3. Probability that a difference will be found: 80%.

TABLE 24

NUMBER OF POINTS TO BE COUNTED IN EACH REGION FOR STATISTICAL SIGNIFICANCE

Element	Number of Points Required	Desired True Difference in Means (%)
Si	5	30
Fe	54	50
Mg	72	10
Ca	410	10
Na	14	10
K	29	10

The test was applied to the counts for each element expressed as a ratio to aluminum. The number of points in each population (center and edge) to be counted are listed in

Table 24. The column labeled "Desired True Difference in Means" contains values obtained from previous work.

As 510 or even 72 points would require excessive time it was decided to try 50 points per region. In most cases this was sufficient to discern differences between regions with a high degree of confidence.