

A Zeolitic Tuff in a Lacustrine
Facies of the Gila Conglomerate Near
Buckhorn, Grant County, New Mexico

U.S. GEOLOGICAL SURVEY BULLETIN 1763



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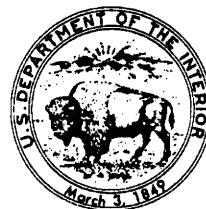
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Figures 4 and 7 are transposed. The sections displayed on page 5 belong on page 8. The sections displayed on page 8 belong on page 5. The figure numbers and captions are not transposed.

A Zeolitic Tuff in a Lacustrine Facies of the Gila Conglomerate Near Buckhorn, Grant County, New Mexico

By ARTHUR J. GUDE, 3rd, and RICHARD A. SHEPPARD

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CONTENTS

Abstract	1
Introduction	1
Geologic setting	1
Geology and description of sampled localities of the study area	1
Prior geologic studies and zeolite mining	7
The present study	7
Lithology	7
Mineralogy	7
Glass	9
Clay minerals	9
Silica minerals	9
Zeolite minerals	14
Clinoptilolite	14
Chabazite	15
Erionite	15
Phillipsite	16
Mordenite	16
Analcime	17
Paragenesis	17
Diagenesis	18
Summary	21
References cited	21

FIGURES

1. Location map showing Buckhorn, Grant County, and other New Mexico localities 2
2. Map showing geology near Buckhorn, Grant County, New Mexico 3
3. Map showing sample localities in the lacustrine rocks 4
4. Measured section compiled at localities BNM-2, BNM-28, and BNM-29, showing mineralogy and lithology of sampled units 5
5. Photograph of the marker tuff at locality BNM-18 6
6. Photograph of the cliff at the measured section at localities BNM-29, BNM-28, and BNM-2 on the skyline 6
7. Short measured sections through the marker tuff at localities BNM-3, BNM-17, and BNM-26, showing mineralogy and lithology of the sampled units 8
8. Scanning electron micrograph showing partially dissolved, pitted glass shard surface with clay mineral flakes attached to (growing on) the shard, at locality BNM-23 9
9. Scanning electron micrograph showing smectite clay coating the surface of glass shards. Notice the pitted surface of the partially dissolved shard from locality BNM-36 9
10. Scanning electron micrograph of chabazite clusters in platelets, showing erionite, from locality BNM-15 16
11. Scanning electron micrograph of erionite needle bundles with clinoptilolite from locality BNM-18 16
12. Scanning electron micrograph of mordenite filaments coating clay and clinoptilolite from locality BNM-24 16
13. Scanning electron micrograph of a large analcime crystal with chabazite and erionite from locality BNM-15 17

FIGURES

- 14. Schematic diagram of paragenesis **18**
- 15. Diagenetic zones: *A*, chabazite zone; *B*, zeolite zone; *C*, analcime zone **19**
- 16. Diagrams of mineral associations: *A*, chabazite zone; *B*, zeolite zone; *C*, analcime zone **20**

TABLES

- 1. Mineralogy and lithology of sampled localities **10**
- 2. Clinoptilolite standard chemical rock analyses **15**
- 3. Chabazite chemical analysis **16**
- 4. Analcime chemical analysis **17**

A Zeolitic Tuff in a Lacustrine Facies of the Gila Conglomerate near Buckhorn, Grant County, New Mexico

By Arthur J. Gude, 3rd, and Richard A. Sheppard

Abstract

Zeolite minerals are abundant and varied in a conspicuous air-fall tuff in a lacustrine facies of Pliocene (?) age in the upper part of the Gila Conglomerate near Buckhorn, New Mexico. Mudstones and siltstones that underlie and overlie the zeolitic tuff contain trace to minor amounts of authigenic zeolites. The white to yellow tuff is a stratigraphic marker 0.45 to 2.75 m thick and was sampled at outcrops over an area of about 11 km². Locally the tuff consists almost entirely of zeolites in sufficient quantity to be mined for commercial use.

A lateral diagenetic mineral zonation basinward is shown by chabazite at the margin where unaltered vitric glass is also present, then clinoptilolite, and then clinoptilolite and analcime. Erionite occurs locally with clinoptilolite and analcime. Analcime is most abundant in the basal part of the tuff, and it is the only zeolite that shows a replacement relationship with the other zeolites. Authigenic silica and silicate minerals associated with the zeolites formed during diagenesis in a silicic vitric ash that had been deposited in a closed-basin saline alkaline lake. In addition to zeolites, the tuff commonly contains authigenic smectite, quartz, opal, potassium feldspar, calcite, fluorite, and gypsum. The minerals and their relative abundance were determined by X-ray diffractometer studies. Scanning electron microscopy examination shows a paragenetic sequence, from early to late, of chabazite, clinoptilolite, erionite, and then analcime. Mordenite, where present, may have formed during a later time of authigenesis.

INTRODUCTION

Zeolites, associated with authigenic silica and silicate minerals, occur near Buckhorn, Grant County, New Mexico (fig. 1) in altered siliceous tuffs in a lacustrine facies of the upper part of the Gila Conglomerate of Pliocene(?) age in this area.

Buckhorn, a hamlet in northwestern Grant County, New Mexico, is on U.S. Highway 180 about 50 km northwest of Silver City. Cliff and Gila are small towns on the Gila River 12 and 15 km southeast of Buckhorn,

respectively. Glenwood is 42 km north on Highway 180. Duck Creek and its tributaries form the stream system that flows southeast through Buckhorn Valley to join the Gila River near Cliff. The present-day valley along Duck Creek is in a topographic and structural feature named the Mangas Trench by Trauger (1965, p. 186). It is flanked by northwest-trending parallel basin-and-range mountains and normal fault systems.

GEOLOGIC SETTING

On the western margin of the valley, about 1.5 km southwest of Duck Creek, the northwestern-trending flanks of Black Mountain consist of andesitic lava flows (T. L. Finnell, personal commun., 1982). The andesitic flows of Miocene and (or) Oligocene age may correlate with the Bear Wallow Mountain Formation of Elston (1976). Miocene and (or) Oligocene silicic volcanic rocks (Ratté, and Gaskill, 1975) at the southern end of the Mogollon Mountains form the eastern edge of Buckhorn Valley, about 15 km east of Duck Creek. Gravels, sands, fanglomerate units, and interfingering lavas and tuffs in the Gila Conglomerate, along with the youngest alluvium, cover the floor of the valley. A pre-Pleistocene fresh-to-slightly brackish or saline lake, which may have covered more than 100 km², "extended from at least several miles southeast of Cliff northwestward to the Cactus flat area 10 miles [16 km] northwest of Buckhorn" (Ratté, and Finnell, 1978, p. 53, and Ratté, 1978, p. 84).

GEOLOGY AND DESCRIPTION OF SAMPLED LOCALITIES OF THE STUDY AREA

Evidence gathered during our field studies shows that a small 25–30 km² closed basin existed in which a saline, alkaline soda-lake environment developed. This

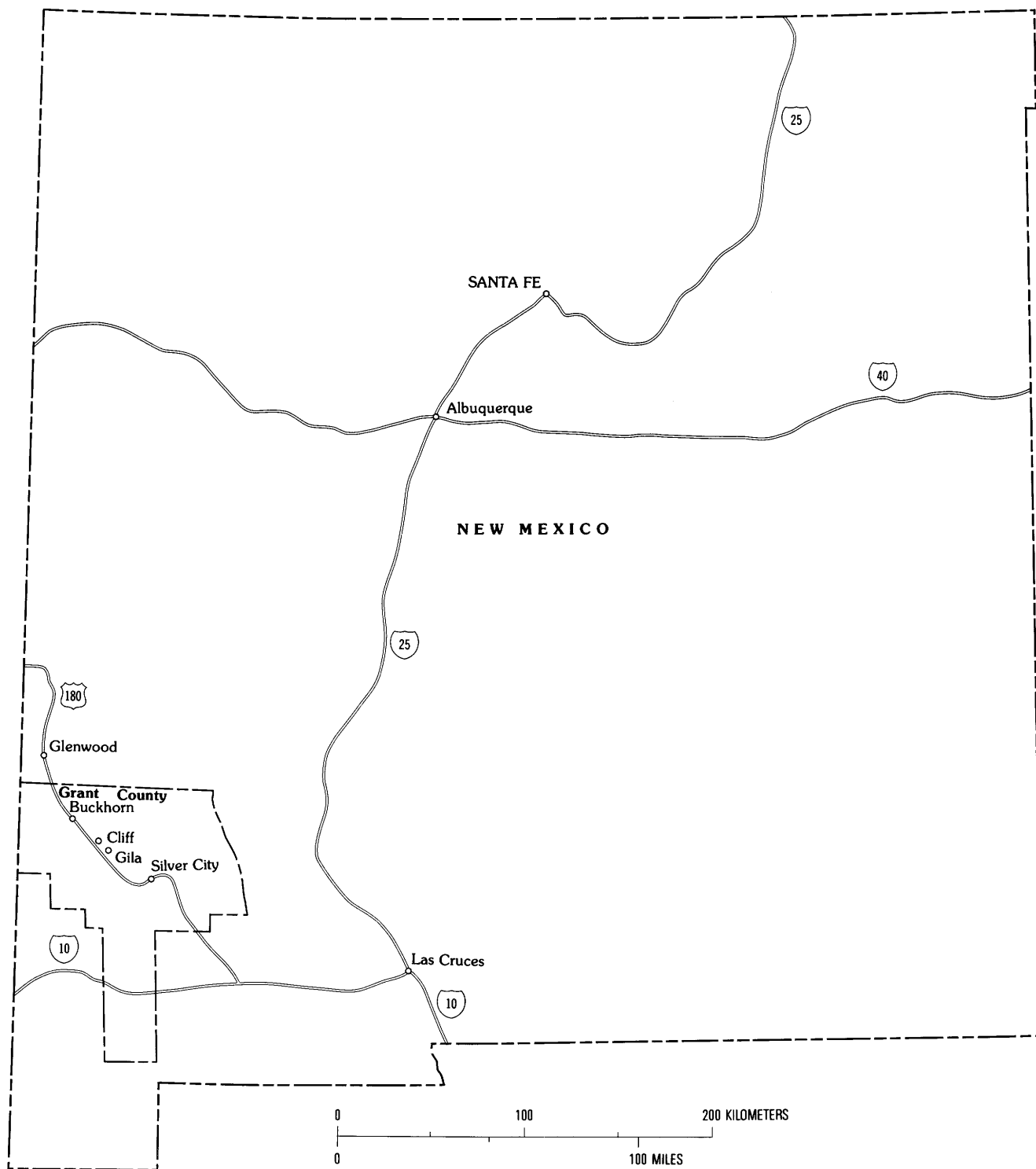


Figure 1. Location map showing Buckhorn, Grant County, and other New Mexico localities.

lake, in early Pliocene(?) time, was the site for lacustrine sediment deposits to develop in the upper Gila Conglomerate. In this closed-system hydrologic setting, zeolite deposits formed during the diagenesis of silicic volcanic vitroclastic sediments. The 11 km² approximate extent of the exposed lacustrine units that were sampled and

studied are shown in the geologic map (fig. 2). Most are south of Highway 180, with a detached site about 1 km east of Buckhorn.

A resistant, conspicuous, 0.45- to 2.75-m thick tuff, in the lower part of the lacustrine sequence, is a marker bed and the subject of this study. It is present at 15 of

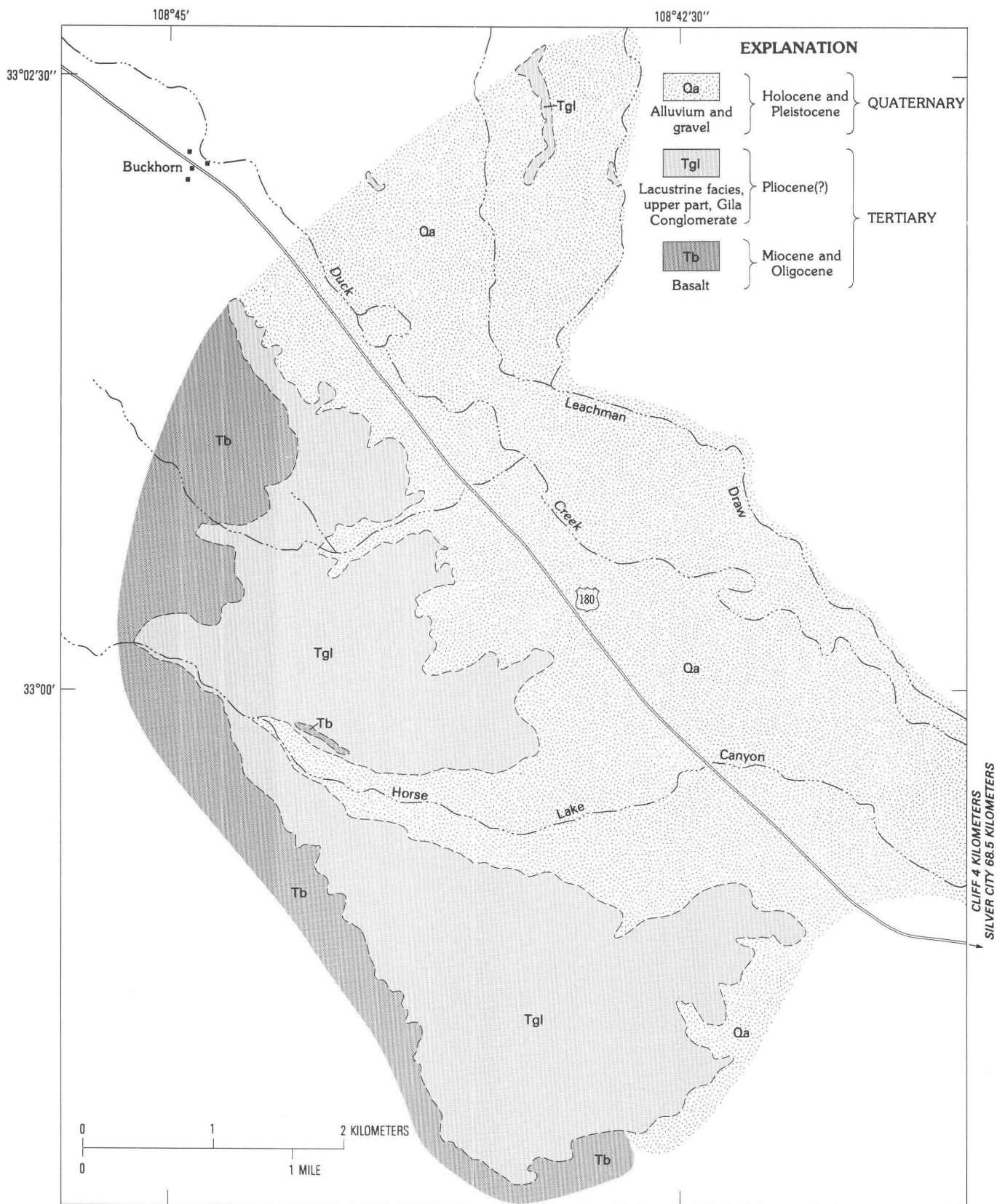


Figure 2. Map showing geology near Buckhorn, Grant County, New Mexico.

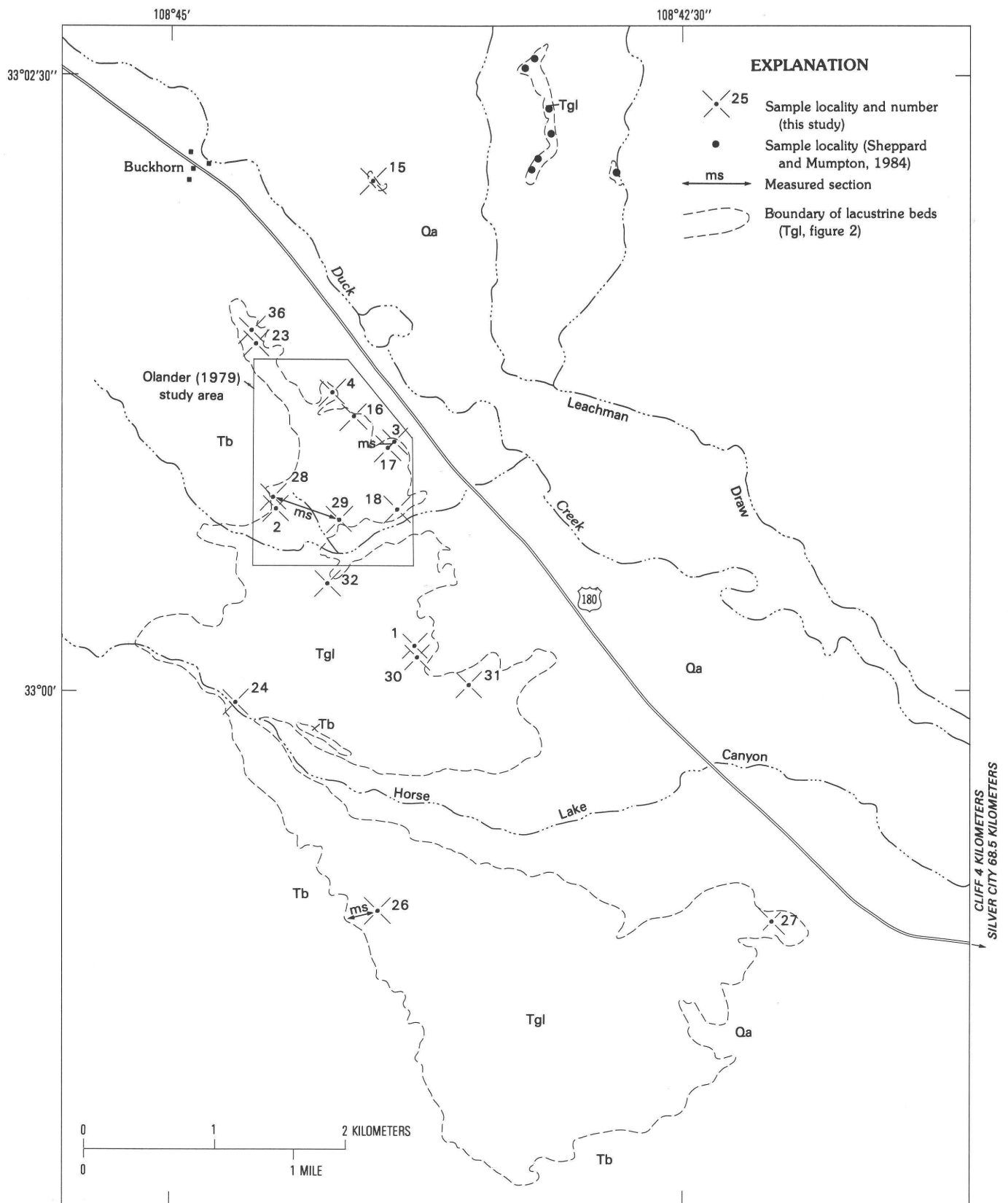


Figure 3. Map showing sample localities in the lacustrine rocks.

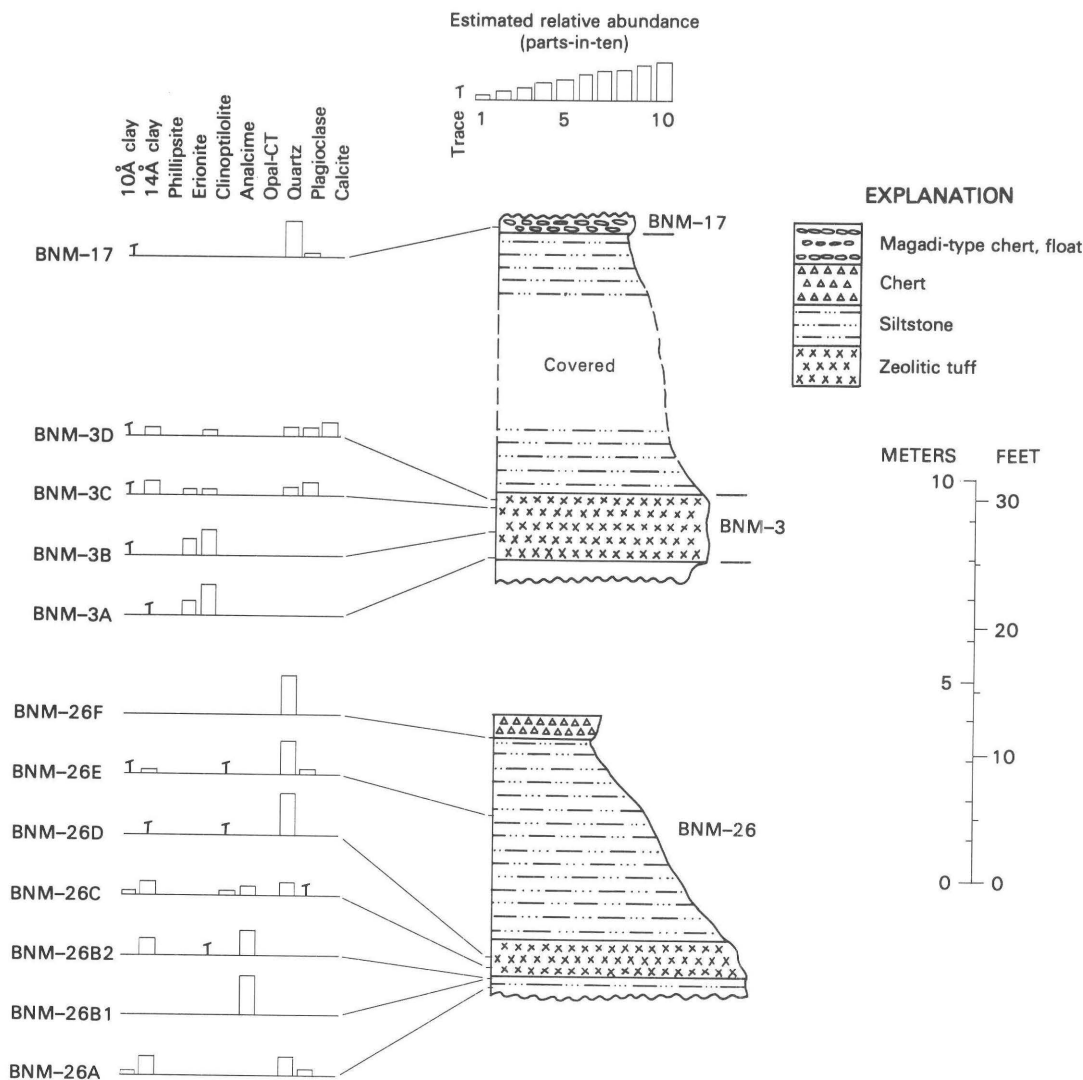


Figure 4. Measured section compiled at localities BNM-2, BNM-28, and BNM-29, showing mineralogy and lithology of sampled units.

the 18 numbered sites on the sample localities map (fig. 3). A stratigraphic section (fig. 4) was measured and sampled from just below the marker tuff at locality BNM-29 up through the lacustrine beds at locality BNM-28 to the topmost exposed lake sediments at locality BNM-2. Figures 5 and 6, respectively, show the outcrop of the full thickness of the marker tuff and the well-exposed cliff where the complete section was measured from the mudstone underlying the marker tuff up to the topmost unit on the skyline (see also fig. 4).

Three other sites were examined outside of the study area, in the same basin, but not in the same lacustrine facies of the Gila Conglomerate. The latest periods of erosion and deposition of Quaternary valley fill have removed or concealed intervening outcrops, thus making correlation between the study area and the other sites dubious without drilling data or other physical exploration.

One of the other localities, about 6 km northwest of Buckhorn and just west of Highway 180, is in diatomaceous beds that are probably younger than the lacustrine units of the study area. According to Ratté and Finnell (1978, p. 53), the diatom assemblage showed "hot spring waters were being fed into a very shallow water environment, probably at least saline. The geologic age * * * may date from about the early-middle Pliocene boundary"

A second locality outside the study area is an isolated hill about 3.5 km northwest of Buckhorn and 1 km east of Highway 180 (beyond the limits of fig. 3). This locality contains prominent, but thin, erosion-resistant Magadi-type chert beds (Surdam and others, 1972; Sheppard and Gude, 1974; Sheppard and Gude, 1972) in a lacustrine, tuffaceous mudstone sequence, which have preserved this small butte-like outcrop. None of this lake-bed sequence can be correlated with certainty with any of the other sites in the valley.



Figure 5. Photograph of the marker tuff at locality BNM-18.

Seven sampled localities (small circles) in figure 3, about 2.7 km east of Buckhorn and 0.5 km east of Leachman Draw, were examined, sampled, and studied by Sheppard and Mumpton (1984) to try and link this area with the lacustrine units in the study area; however, no correlatable beds were found. Some vague resemblance may be seen between these beds and the beds in the upper part of the measured section in our study locale. The tuff at the detached site BNM-15, 1.25 km east of Buckhorn, has dips of a few degrees to the north and east, and its lithology and mineralogy matches that of the marker tuff in the main study area. This allows projection of the marker tuff 40–50 m below the lake beds that are exposed east of Leachman Draw, thus indicating a probable younger age for the sites sampled by Sheppard and Mumpton (1984).

Field observations, supported by mineralogic and petrologic laboratory studies of the samples, indicate that a shallow saline, alkaline lake formed during early Pliocene(?) time in a closed basin that encompassed much of the area of present-day Duck Creek valley. Diagenetic processes at valley floor temperatures and pressures formed zeolites and other authigenic minerals

by reaction of a soda-lake type water with the silicic glass of ash-fall tuffs interstratified in the lacustrine facies in the upper part of the Gila Conglomerate.

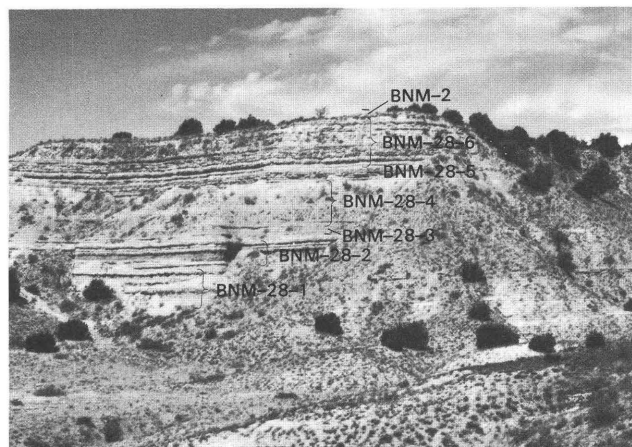


Figure 6. Photograph of the cliff at the measured section at localities BNM-29, BNM-28, and BNM-2 on the skyline.

PRIOR GEOLOGIC STUDIES AND ZEOLITE MINING

Discovery of zeolites in the altered tuffs at Buckhorn by Eyde (1982), and further documented by Mumpton (1984), was made during a Union Carbide (Linde Division) zeolite exploration program in 1960 and 1961. The authors first visited the Buckhorn area in 1974 during a reconnaissance of sites where Magadi-type chert (Surdam and others, 1972; Sheppard and Gude, 1974; Sheppard and Gude, 1982) had been reported. Since then, R. A. Laudon, of Double Eagle Petroleum and Mining Corp. in Casper, Wyo., established a quarry on a leased site and mined clinoptilolite from the marker tuff at locality BNM-16, about 2.3 km south of Buckhorn. Several shipments of a few tons each have reportedly been made for use in various industrial and agricultural applications.

Olander (1979) made a study of the mineralogy, petrology, and sedimentologic setting of clinoptilolite and its polyphase members of the heulandite-clinoptilolite series. The different phases were determined based on variations in X-ray diffraction patterns induced by heating the samples, silica-alumina ratios, and exchangeable cation compositions. This study was restricted to samples taken from the marker tuff in a 1-km² area (fig. 3) in secs. 4, 9, and 10, T. 15 S., R. 13 W.

Field work in and around Duck Creek in the vicinity of Buckhorn Valley has been part of extensive and continuing mapping and resource-study programs of the U. S. Geological Survey. Ratté (1978, p. 84) and Ratté and Finnell (1978, p. 53) noted the clinoptilolite in our marker tuff and also noted the presence of "anomalous lithium and fluorine" based on the report of Tourtelot and Meier (1976). Sheppard and Mumpton (1981) reported on fluorite present as pellets or ooids in the area 2.7 km east of Buckhorn (fig. 3).

Trauger (1972, p. 10, 12, 22, 24) discussed the broad-scale geographic, physiographic, and geologic environment of the Duck Creek valley. Leopoldt (1981) provided an up-to-date review of work on the Gila Conglomerate in New Mexico and Arizona. He selected an area in the vicinity of Cliff and Gila for a detailed investigation of the various aspects of the depositional environments in the Gila Conglomerate. His study area overlapped ours by only about 0.5 km² at the extreme southeast end of our area. He examined the marker tuff at locality BNM-27 and noted its occurrence to the north, up the valley of Duck Creek.

THE PRESENT STUDY

Outcrops containing the marker tuff as well as thinner tuffaceous units higher in the mudstone-siltstone

lacustrine sequence were sampled in detail at the field-numbered localities in figure 3. A nearly continuous stratigraphic section (fig. 4), comprising about 47 m of lacustrine units including the marker tuff, was measured at locations BNM-2, BNM-28, and BNM-29. The top of the lacustrine beds are marked by thin, discontinuous Magadi-type chert units that lap directly onto older volcanic rocks (loc. BNM-2, fig. 3) at the lake's edge.

In addition to the marker tuff, a 1-m-thick tuff bed is present (fig. 4) about 22 m above the marker tuff. At localities where an outcrop is formed by a resistant chert layer near the top of the lake sediments, several thin tuffs are found intercalated with the tuffaceous siltstone and mudstone that comprise most of the lacustrine section.

LITHOLOGY

The lithology of the lacustrine rocks in the study area is simple. Mudstone and siltstone are the most abundant and thickest lithologic units in the exposed stratigraphic section (fig. 4). Thin tuffs 10–20 cm thick are commonly present along with two or three tuffs as much as 2.5–3 m thick at a few localities. Thin, discontinuous, irregular calcareous layers are present in the units above the marker tuff. At least one conspicuous calcareous layer about 0.5–1 m thick, about 5–7 m below the marker tuff, consists of large, 1–2-m-long, grotesquely contorted calcareous concretions. This unit can be found in some deeply eroded gullies such as that incised in the stream bottom between localities BNM-29 and BNM-32. Several thin chert layers form conspicuous litter-covered slopes as at localities BNM-3 and BNM-17 and at locality BNM-26 (figs. 4 and 7), where nodules and plates of Magadi-type chert have weathered out. The chert layers noted at the top of the measured sections (figs. 4 and 7) are especially well exposed. Sandstone and conglomerate are present as intercalated beds with the marker tuff at the north end of the study area near localities BNM-23 and BNM-36.

MINERALOGY

Fourteen minerals plus silicic glass have been found and identified by a combination of X-ray powder diffraction, optical microscopy, and scanning electron microscope studies (table 1). At least 10 of these are authigenic minerals formed during the diagenesis of the tuffaceous, lacustrine sediments. Calcite and gypsum may also have formed as authigenic minerals; however, the evidence is ambiguous. At most localities, some detrital minerals, denoted by the presence of plagioclase with quartz, and some of the "10 Å" clay minerals, are found in the samples and are discernible in the X-ray records.

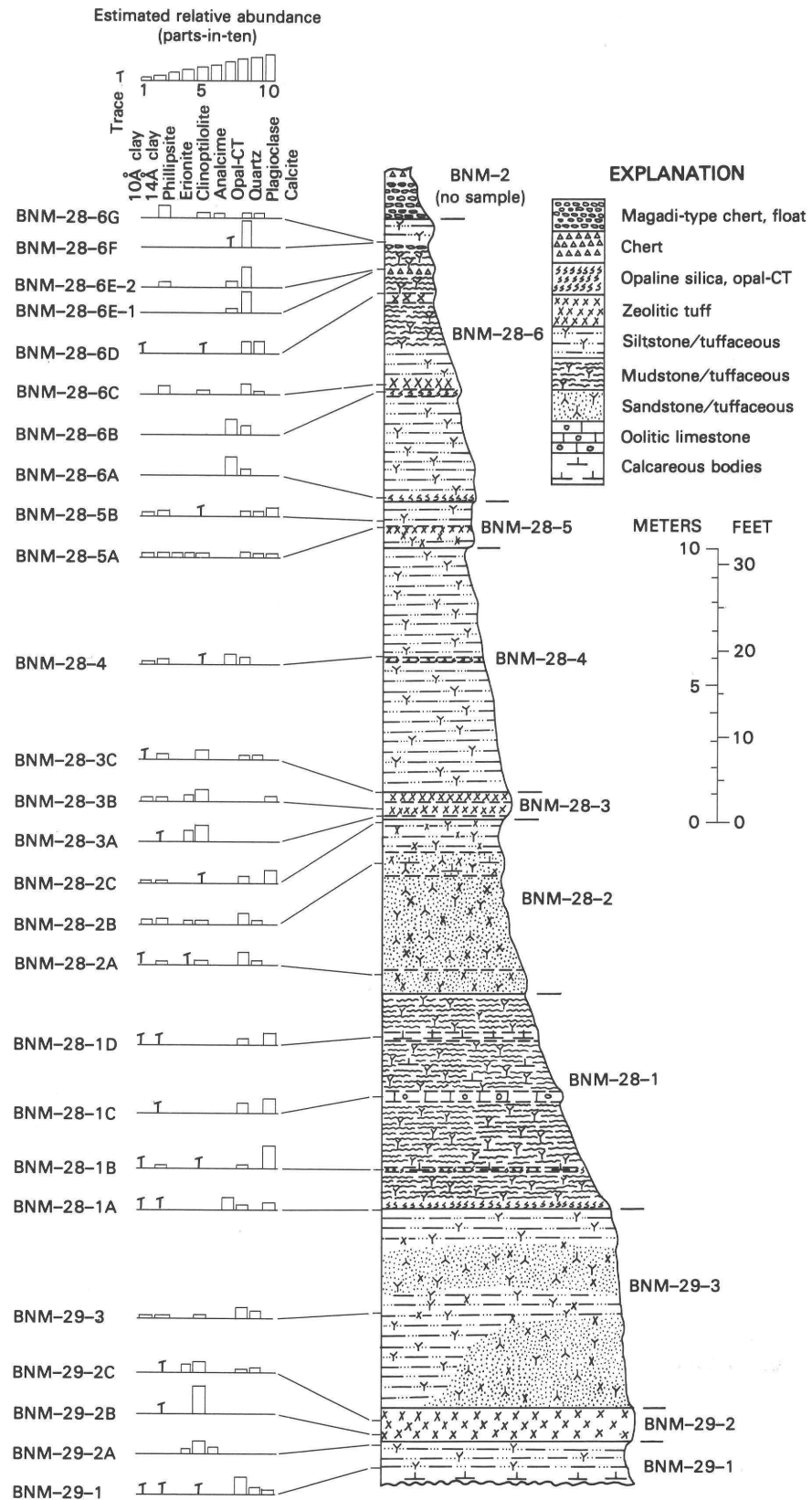


Figure 7. Short measured sections through the marker tuff at localities BNM-3, BNM-17, and BNM-26, showing mineralogy and lithology of the sampled units.

Table 1 presents the mineral phases in approximate paragenetic sequence, along with the silicic glass found at three localities, listed in a north-to-south order of the localities.

Glass

Unaltered or partially dissolved silicic glass is present as bubble-wall shards in the marker tuff at three localities. Two localities, BNM-36 and BNM-23, about 1 km south of Buckhorn, have glass present with chabazite in the marker tuff where the tuff interfingers with sand or gravel beds at or near the margin of the lake beds. The surface of a pitted, partially dissolved glass shard from site BNM-23 (fig. 8) shows flakes of a clay mineral that has formed during the glass alteration. Glass is present at locality BNM-24, which is also at a lake margin site where the tuff laps directly onto the older volcanic rocks.

None of the glass-bearing samples is sufficiently pure to use for separating a clean concentrate of glass shards for a chemical analysis. The index of refraction, n , was measured on a platy bubble-wall shard from BNM-24 as 1.497–1.499. A measurement of n slightly less than 1.500 was obtained from a shard from BNM-36. These optical data are consistent with indices of refraction from silicic volcanic glass. Although most fragments are bubble-wall shards, a few pumice shards have been noted. Crystals of a sodic plagioclase, quartz, biotite, and hornblende form a minor part of a glass-containing specimen. All the shards show well-developed surficial alteration, and shard interiors are “milky” and contain very finely crystalline, low-birefringent material.

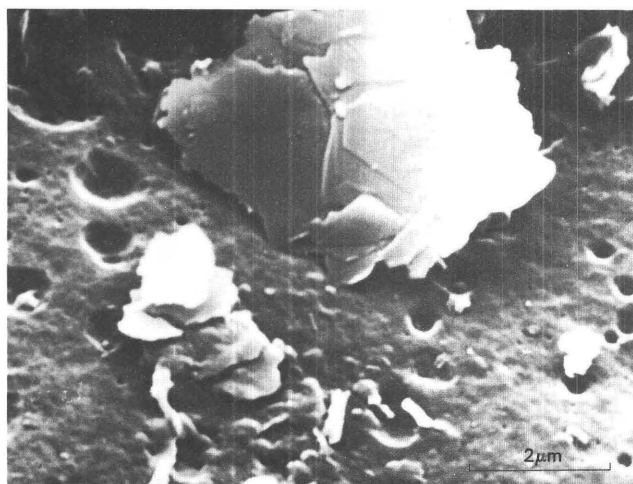


Figure 8. Scanning electron micrograph showing partially dissolved, pitted glass shard surface with clay mineral flakes attached to (growing on) the shard at locality BNM-23.

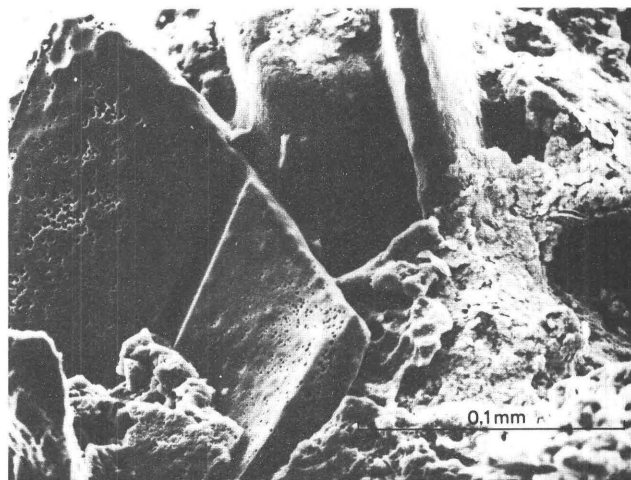


Figure 9. Scanning electron micrograph showing smectite clay coating the surface of glass shards. Notice the pitted surface of the partially dissolved shard. Locality BNM-36.

Clay Minerals

Two clay-mineral phases were identified from routine, X-ray powder patterns of unoriented samples by the first “strong line” presence as “10Å” or “14Å” clays. The 10Å clay is probably a mixed-layer illite, or, if from a detritus-rich sample, it may also contain biotite from the older volcanic rocks. Smectite indicated by the 14Å peak is ubiquitous in samples from nearly all localities. One of the first formed minerals noted in our earlier studies (Sheppard and Gude, 1968, 1969, 1973) is a smectite clay. Thus, it is not surprising to see a readily discernible clay coating lining shards and indicating alteration of the glass surface to a smectite as an early phase in our paragenetic observations. Scanning electron micrographs (SEM), as in figure 9, clearly show the clay lining (or coating) as a common feature.

The mudstone sequences invariably show that the 14Å clay is dominant in relative abundance over the 10Å clay component. This accounts for the commonly noted popcorn texture developed by the swelling property of smectites on weathered mudstone slopes. A freshly exposed mudstone surface generally appears greenish-gray and massive, and breaks with a conchoidal fracture. A tool mark from a hammer, shovel, or knife is typically greasy, slick, and glistening. For this study, no detailed clay-mineral work was done other than identifying the clay as having a 10Å or 14Å basal X-ray diffraction peak of an illitic (or micaceous) or smectitic clay mineral, respectively.

Silica Minerals

“Silica” is conspicuous and abundant in the lacustrine rocks where chalcedonic chert or an opaline

Table 1.—Mineralogy and lithology of sampled localities determined by X-ray diffractometry

[illegible]

BNM-28	36.60 + total	Upper part of measured stratigraphic section (fig.2) which includes BM-29 below and BNM-2 above. The units of BNM-28 are in a well-exposed cliff face which continues the section exposed in BNM-29																			
-28-6	10.40	Siliceous cliff-capping unit, alternating silica layers of diagenetic chert, greenish-gray mudstones, and thin tuffs																			
-6G	9.40	Mudstone, bed in which Magadi-type chert occurs	-	-	5	-	-	-	2	-	1	-	-	1	1	-	-	-	-	-	-
-6F	9.40	Magadi-type chert, thin, reddish-brown, discontinuous lenses (See BNM-2)	-	-	-	-	-	-	-	-	-	-	-	T	10	-	-	-	-	-	-
-6E2	8.40	Chert, reddish brown core material	-	-	1	-	-	-	-	-	-	-	-	2	7	-	-	-	-	-	-
-6E1	8.40	Chert, white reticulated rind	-	-	-	-	-	-	-	-	-	-	-	2	8	-	-	-	-	-	-
-6D	7.50	Tuff, gray	-	T	-	-	-	-	T	-	-	-	-	-	5	5	-	-	-	-	-
-6C	4.00	Mudstone, tuffaceous	-	-	4	-	-	-	1	-	-	-	-	-	4	1	-	-	-	-	-
-6B	3.95	Silicified wood fragments	-	-	-	-	-	-	-	-	-	-	-	6	4	-	-	-	-	-	-
-6A	0.10	Silica, just above base of unit	-	-	-	-	-	-	-	-	-	-	-	7	3	-	-	-	-	-	-
-28-5	1.75	Mudstone and siltstone, greenish, with a thin intercalated tuff																			
-5B	0.85	Tuff, yellow, thin, 10 cm thick, calcareous	-	1	2	-	-	-	T	-	-	-	-	2	2	3	-	-	-	-	-
-5A	0.65	Mudstone, greenish, tuffaceous	-	1	2	1	-	1	1	-	-	-	-	2	1	1	-	-	-	-	-
-28-4	9.05	Siltstone and mudstone, reddish brown, poorly exposed, several thin resistant beds in lower part																			
	5.00	Siltstone, reddish	-	1	2	-	-	-	T	-	-	-	4	3	-	-	-	-	-	-	-
-28-3	1.00	Tuff, yellow, massive in lower part, platy in upper part. Top 35 cm, much detrital material. Basal beds contorted.																			
-3C	0.90	Tuff, dirty, 35 cm thick.	-	T	2	-	-	-	4	-	-	-	-	2	2	-	-	-	-	-	-
-3B	0.30	Tuff, platy, calcareous	-	1	1	-	-	2	4	-	-	-	-	-	-	2	-	-	-	-	-
-3A	0.00	Tuff, base	-	-	T	-	-	4	6	-	-	-	-	-	-	-	-	-	-	-	-
-28-2	6.45	Sandstone and mudstone, brownish-green, tuffaceous, resistant brown tuff at base in sandstone																			
-2C	6.35	Sandstone and mudstone, tuffaceous, calcareous	-	1	1	-	-	-	T	-	-	-	-	3	-	5	-	-	-	-	-
-2B	4.35	Soil (?) zone, red, with calcareous root casts which were not sampled	-	1	2	-	-	1	1	-	-	-	-	4	1	-	-	-	-	-	-
-2A	0.70	Sandstone, brown, 90 cm thick, tuffaceous	-	T	1	-	-	-	T	2	-	-	-	-	5	2	-	-	-	-	-
-28-1	>7.95	Mudstone, light gray-brown, siliceous layers, white, irregular. A prominent oolite bed is in middle of unit																			
-1D	6.25	Calcareous layer, 30 cm thick, in light gray mudstone, white spheroids	-	T	T	-	-	-	-	-	-	-	-	3	1	6	-	-	-	-	-
-1C	4.00	Oolite bed, light gray, 40 cm thick, calcareous	-	-	T	-	-	-	-	-	-	-	-	4	-	6	-	-	-	-	-
-1B	1.40	Siliceous, calcareous layer, 12 cm thick, distinctive brown bed	-	T	1	-	-	-	T	-	-	-	-	1	-	8	-	-	-	-	-
-1A	0.00	Silica layer at base of cliff, calcareous	-	T	T	-	-	-	-	-	-	-	-	5	2	-	3	-	-	-	-
BNM-29	10.15 + total	Lower part of measured stratigraphic section (fig.2) which fits just below BNM-28-1 A. The marker bed tuff and overlying mudstone and siltstone units were sampled and measured in this section																			
-29-3	7.40	Sandstone and siltstone, gray-brown, calcareous																			
-3	3.50	Sandstone, siltstone, brownish, tuffaceous, mostly detrital	-	1	1	-	-	-	1	-	-	-	-	4	3	-	-	-	-	-	-
-29-2	1.25	Tuff, yellow, blocky, or platy fracture, detritus in upper part. This is the marker bed tuff																			
-2C	0.90	Tuff, dirty yellow-gray	-	-	T	-	-	3	4	-	-	-	-	1	2	-	-	-	-	-	-
-2B	0.35	Tuff, yellow	-	-	T	-	-	-	10	-	-	-	-	-	-	-	-	-	-	-	-
-2A	0.00	Tuff, dark yellow, at base	-	-	-	-	-	2	5	-	3	-	-	-	-	-	-	-	-	-	-
-29-1	>1.50	Siltstone, gray, calcareous, collected 1.5 m below base of marker bed. Covered extent of bed unknown																			
-1	-1.50	Siltstone	-	T	T	-	-	-	T	-	-	-	-	6	3	1	-	-	-	-	-

Table 1.—Mineralogy and lithology of sampled localities determined by X-ray diffractometry—Continued

Field numbers of sampled localities (see fig. 3) M = marker bed sample	Thickness of collected unit (meters)	Meters above or below (—) base of collected unit	Description of lithology	Minerals determined by powder X-ray diffraction. Estimated relative abundance reported as parts-in-10, T = trace amount																
				Glass	10Å clay	14Å clay	Phillipsite	Chabazite	Erionite	Clinoptilolite	Mordenite	Analcime	Fluorite	Opal C-T	Quartz	Plagioclase	Calcite	Gypsum		
BNM-32	1.70	Tuff, conspicuous yellow, overlies gray siltstone, uppermost part is grayish, dirty, calcareous																		
M -32D	1.40	Tuff, gray, calcareous			-	-	1	-	-	-	4	-	-	-	-	1	4	-		
M -32C	0.70	Tuff, yellow			-	-	1	-	-	-	9	-	-	-	-	-	-	-		
M -32B	0.00	Tuff, dark yellow, thin layer at base			-	-	3	-	-	1	6	-	-	-	-	-	-	-		
-32A	-0.25	Siltstone, gray, below base of tuff			-	T	1	-	-	-	T	-	-	-	-	3	4	2	-	
BNM-1	2.45	Tuff, yellowish, several thin intercalated siliceous bands. Tuff caps small butte as resistant layer																		
M -1D	1.68	Tuff, silicified			-	T	T	-	-	-	-	-	T	T	-	8	1	1	-	
M -1C	0.61	Tuff, yellow			-	-	2	-	-	-	2	-	3	2	-	-	-	1	-	
M -1B	0.00	Tuff, at base			-	-	1	-	-	3	-	-	6	-	-	-	T	-	T	
-1A	-0.10	Mudstone, gray, below base			-	-	1	-	-	-	-	-	-	-	-	9	T	-	-	
BNM-30	2.70	Tuff, same butte as BNM-1, on south side																		
M -30F	2.30	Tuff, gray, silicified, forms top of butte			-	T	-	-	-	-	-	-	-	-	-	10	-	-	-	
M -30E	1.70	Tuff, some thin silica layers			-	T	1	-	-	-	-	-	1	-	-	7	1	-	-	
M -30D	1.20	Mudstone, tuffaceous, interbedded silica layers			-	T	1	-	-	-	-	-	1	-	-	7	1	-	-	
M -30C	0.65	Tuff			-	-	T	-	-	-	-	-	1	-	-	9	T	-	-	
M -30B	0.00	Tuff, at base			-	T	1	-	-	2	1	-	5	-	-	1	-	-	-	
-30A	-0.40	Mudstone, gray, below base			-	1	2	-	-	-	-	-	T	-	-	6	1	-	-	
BNM-31	2.05	Tuff, yellow, conspicuous, capped by silica as at BNM-1 and BNM-30																		
M -31C	0.30	Tuff, low in unit, 40 cm thick			-	T	3	-	-	T	7	-	T	T	-	-	-	-	-	
M -31B	0.00	Tuff, at base			-	-	-	-	-	1	8	-	1	-	-	-	-	-	-	
-31A	-0.10	Mudstone, gray, with pinkish spheroidal bodies			-	1	2	-	-	-	T	1	-	T	-	5	T	1	-	

BNM-24		Tuff, light gray, locally laminated, contains unaltered glass shards. Another tuff, 50 cm thick and 4.1 m higher at this locality, is similar in appearance to the marker tuff. Still higher, at the top of the lacustrine section, are greenish silicified beds that are similar to those at BNM-3. Quaternary lava boulders overlie the lacustrine beds, and the lake beds lap onto older volcanic rocks to the NW and SE of BNM-24									
M	-24C	4.10	Upper tuff, 50 cm thick	4	-	6	-	-	-	-	-
	-24B	0.30	Lower bed in marker tuff, 1.0 m thick	5	-	5	-	-	-	-	-
	-24A	-0.40	Tuffaceous mudstone below base of marker tuff	T	-	4	-	-	1	-	-
BNM-26		A thick section of exposed white to light gray lacustrine rocks, many siliceous layers. A conspicuous outcrop of the yellow marker bed tuff is in the lowest part of the section at this locality									
M	-26F	6.00	Silica layer, white	-	-	-	-	-	-	10	-
	-26E	4.00	Mudstone, greenish	-	T	1	-	-	-	T	-
	-26D	0.55	Tuff, light gray, siliceous, top of marker tuff	-	-	T	-	-	-	T	-
M	-26C	0.25	Tuff, light yellow	-	1	3	-	-	-	1	2
M	-26B-2	0.00	Tuff base, 5 cm thick	-	-	4	-	-	-	T	6
M	-26B-1	0.00	Underside of tuff base, layer 2-3 mm thick	-	-	-	-	-	-	10	-
	-26A	-0.20	Mudstone	-	1	4	-	-	-	-	4
BNM-27		Tuff, marker bed, in sequence of brown siltstones and mudstones									
M	-27E	2.00	Resistant siliceous bed, greenish, 1.45 m thick	-	-	-	-	-	-	9	1
	-27D	0.55	Tuff	-	-	T	-	-	T	2	6
	-27C	0.25	Tuff, calcareous	-	T	1	-	-	T	4	1
M	-27B-2	0.00	Tuff, base of marker bed	-	-	-	-	-	-	8	-
M	-27B-1	0.00	Underside of tuff base	-	T	1	-	-	-	T	-
	-27A	-0.75	Siltstone, brown, below base of marker bed	-	1	2	-	-	-	1	-

silica forms resistant ledges, and the silica may persist as a capping layer on small buttes or hillocks. Two silica minerals, opal-CT and quartz, are common in the Buckhorn area. Opal may be more abundant than is shown in table 1; it is generally nearly amorphous and thus may be overlooked in X-ray records when it is present in minor or trace amounts. On the other hand, quartz is easily detected, even when present in trace amounts, because of its excellent crystallinity.

Quartz noted in table 1 may be detrital or authigenic, or a mixture of both varieties. Where it is present with plagioclase and a 10Å clay, the quartz is commonly detrital. Where the descriptive notations in table 1 indicate that the sample is chert, or a siliceous bed, and very fine grained, the quartz is authigenic chalcedony.

The chert at several localities is readily distinguishable as "Magadi-type" chert (Sheppard and Gude, 1973, 1974, 1982; Surdam and others, 1972; Hay, 1968). It has the typical reticulated surface of Magadi-type chert with a fine-textured "snake skin" pattern developed on the chert surface. This chert is found at Buckhorn as irregular nodules and plates from a few millimeters thick up to masses 1 cm thick and several centimeters across. The nodule cores are massive, fine grained, opaque and usually gray, green, or brown. In a few places the cores are more translucent and red or pink. A thin, 1–3 mm rind, which often displays the surface reticulation, is always present, unless worn off during surface weathering and abrasion in a water course. At a few localities, the surfaces show more than one stage of shrinkage and cracking during development of the reticulated pattern. Chert fragments are especially common in the float litter on the weathered slopes above the marker tuff localities. At locality BNM-2, and at the topmost unit of measured section BNM-28, Magadi-type chert is found in place. It is exposed in thin, discontinuous layers or lenses, which lap onto the older volcanic rocks at the lake margin.

The chert core and rind are almost entirely composed of silica, except for trace amounts of detritus incorporated during the beginning stages of diagenesis (Hay, 1968; Jones, 1965, 1966, Jones and others, 1977) of the material. Quartz is the only identifiable silica mineral in the core. However, there is a consistent pattern of 3 to 6 X-ray diffraction peaks that are not part of any previously described silica mineral. These peaks are sharp and appear as small diffraction maxima, from 2.4 to 4.5Å. Spectrographic analyses of core material from several localities show only silicon and a few ppm of other elements, which total less than 0.1 percent of the sample. Thus, a trace of a crystalline silica phase that has not been identified is present in Magadi-type chert.

Rind material, carefully selected to be free of core material, may contain silhydrite ($\text{SiO}_2 \cdot 3\text{H}_2\text{O}$) (Gude and Sheppard, 1972), mixed with quartz and some of the surrounding rock. Silhydrite has been shown to be an

intermediate mineral formed during diagenesis of magadiite as it converts to chert. The silhydrite has been noted in this area only from chert specimens collected at the localities 2.7 km east of Buckhorn, away from our study area.

Opal-CT, as defined by Jones and Segnit (1971), is a third silica phase shown to be present at several sites listed in table 1. Silica is released during the alteration of the glass shards in the silicic vitric tuffs during diagenesis. Opaline beds or lenses are often found at lithologic boundaries where a tuff overlies a mudstone unit. Silicified wood fragments, as at BNM-28-6B, are also composed of opal-CT.

Zeolite Minerals

Six zeolite minerals are present in the tuffaceous lacustrine beds at Buckhorn. Clinoptilolite, chabazite, erionite, phillipsite, mordenite, and analcime are found in amounts that vary from a single minor occurrence of phillipsite at BNM-28, to nearly monomineralic beds of clinoptilolite in the marker tuff.

Clinoptilolite

Clinoptilolite is found at every sampled locality in the study area except BNM-15, BNM-23, and BNM-36, where chabazite is present. At BNM-16 the tuff is a nearly monomineralic clinoptilolite bed. The deposit at this site has been leased and quarried, and several tons have been shipped to various agricultural and industrial users.

The variability in relative abundance of clinoptilolite, and in differing mineral associations laterally and vertically within the marker tuff, is readily apparent from table 1. Such variability is a common characteristic of authigenic zeolites formed in lacustrine deposits of this type, and may indicate responses to subtle changes in the low-temperature, low pressure diagenetic conditions in shallow, closed-lake, saline alkaline environments. The chemical analyses of five clinoptilolite-rich samples from three localities, shown in table 2, further document the variability of properties often encountered in any zeolite species that seems to have a uniform lithology and constant appearance in a field setting.

Olander (1979) made detailed collections of clinoptilolite-bearing rocks from five marker tuff sites in a 1 km² area near our localities BNM-4, BNM-29, and BNM-32. He studied mineralogical phase changes in clinoptilolite induced by controlled heat treatment (Boles, 1972; Alietti, 1972) that are shown by changes in X-ray powder diffraction patterns. Chemical analyses and the cation exchange capacity (CEC) were made on the same sample suites. He concluded that "variations in solution and parent ash composition, * * * chemistry, pH, and

Table 2. Clinoptilolite standard chemical rock analyses

[Samples WGP-4 and 27083 collected at locality BNM-16. See figure 3 and table 1 for locations of BNM-16A, BNM-29-2B, BNM-32C. USGS analysts: J. S. Wahlberg, J. Taggart, J. Baker]

	WGP-4	27083	BNM-16A	BNM-29-2B	BNM-32C
Rock Analysis (weight percent by X-ray spectroscopy)					
SiO ₂	63.6	63.4	63.0	63.3	61.5
Al ₂ O ₃	12.6	12.2	12.0	12.5	12.0
Fe ₂ O ₃	1.94	1.33	1.70	1.38	1.43
MgO	1.49	1.7	1.75	1.39	2.24
CaO	3.01	3.37	3.07	2.59	3.80
Na ₂ O	2.46	1.4	1.57	2.13	0.41
K ₂ O	2.25	1.12	1.53	1.42	1.71
TiO ₂	0.28	0.13	0.24	0.11	0.18
P ₂ O ₅	0.05	0.10	0.05	0.05	0.05
MnO	0.02	0.02	0.02	0.02	0.02
L.O.I. 900 °C	11.1	15.06	14.11	15.4	15.5
Σ	98.75	99.83	99.03	100.29	98.84
Atoms per unit cell					
Si	28.37	28.79	28.71	28.78	28.55
Al	6.62	6.53	6.44	6.70	6.57
Fe ³⁺	0.33	0.45	0.58	0.47	0.50
Mg	0.95	1.15	1.18	0.94	1.55
Ca	1.44	1.64	1.50	1.26	1.89
Na	2.50	1.23	1.39	1.90	0.37
K	1.28	0.65	0.89	0.82	1.01
Ti	0.09	0.04	0.08	0.04	0.06
P	0.02	0.04	0.02	0.02	0.02
Mn	0.01	0.04	0.01	0.01	0.01
H ₂ O	16.52	22.81	21.43	23.16	23.99
O	72.00	72.00	72.00	72.00	72.00
Si/Al + Fe ³⁺	4.08	4.12	4.09	4.01	4.04
Al + Fe ³⁺					
2(Mg + Ca) + Na + K	0.81	0.94	0.92	0.99	0.86
Si + Al + Fe ³⁺	35.32	35.77	35.73	35.95	35.61

Si/Al ratios of the solution” could be related to different localized depositional environments. Additionally, he indicated that CEC variations showed “subsequent cation exchange reactions” that modified the original clinoptilolite composition.

Olander’s work and data are detailed and consistent at each of his sites. However, the small 1 km² area where he collected the marker tuff samples that exhibited the chemical-physical differences that he noted is probably too small to account for the basin-wide changes that he postulated. Also, we have seen no evidence here, nor in other places that there has been any in-situ cation exchange of the zeolite minerals.

Chabazite

Three localities, BNM-15, BNM-23, and BNM-36, are chabazite sites. At BNM-23 and BNM-36 chabazite is present as the only zeolite with remnant silicic glass in a setting that is at a lake margin. Similar laustrine settings

have been described from Barstow, Calif. (Gude and Sheppard, 1966; Sheppard and Gude, 1969); Wikieup, Ariz. (Sheppard and Gude, 1973); and Durkee, Oreg. (Gude and Sheppard, 1978) and other like places. Chabazite at BNM-15 (fig. 10) is found with erionite and analcime, but no glass. This site is a detached erosion remnant 1.3 km from other outcrops of the marker tuff. Table 3 is a chemical analysis showing the rock analysis and unit cell composition of BNM-23A. Comparison of the ratios of Si:Al + Fe³⁺ and Na + K:Na + K + Mg + Ca with data from other areas (Gude and Sheppard, 1978) shows that this Buckhorn chabazite is very similar to the chabazite from Wikieup, Ariz., and Durkee, Oreg.

Erionite

No monomineralic samples of erionite were found during this study, and thus no chemical analyses were attempted. The erionite always occurs as fine-grained, needle-like particles, mostly <1 μm across the needles and

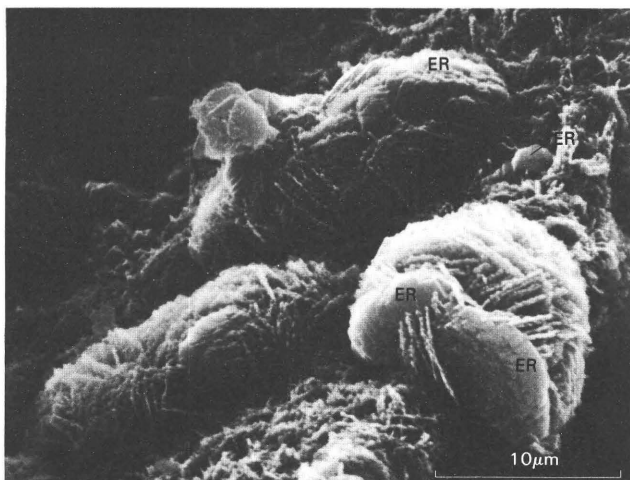


Figure 10. Scanning electron micrograph of chabazite clusters in platelets, showing erionite from locality BNM-15.

8–10 μm long. The erionite needles are in intimate association with other zeolites, as seen at BNM-18 (fig. 11), and thus are not amenable to electron microprobe study.

Table 3. Chabazite chemical analysis

[See figure 3 and table 1 for location of BNM-23A. USGS analyst, L.A. Bradley]

BNM-23A	
Rock Analysis (weight percent by X-ray spectroscopy)	
SiO ₂	58.9
Al ₂ O ₃	13.3
Fe ₂ O ₃	2.30
MgO	1.44
CaO	4.19
Na ₂ O	1.75
K ₂ O	1.42
TiO ₂	0.32
P ₂ O ₅	0.05
MnO	0.02
L.O.I. 900°C	15.2
Σ	98.89
Atoms per unit cell	
Si	27.58
Al	7.34
Fe ³⁺	0.81
Mg	1.01
Ca	2.10
Na	1.59
K	0.85
Ti	0.11
P	0.02
Mn	0.01
H ₂ O	23.64
O	72.00
Si/Al + Fe ³⁺	3.38
Al + Fe ³⁺ / 2(Mg + Ca) + Na + K	0.94
Si + Al + Fe ³⁺	35.73

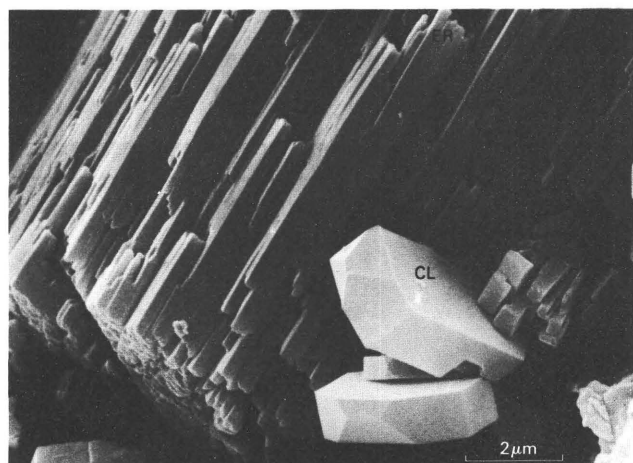


Figure 11. Scanning electron micrograph of erionite needle bundles with clinoptilolite from locality BNM-18.

Phillipsite

Phillipsite was detected by X-ray diffractometer in a single specimen as a minor constituent in a tuff several meters above the marker tuff in BNM-28-5A. Careful searches of scanning electron micrographs of this sample have not been fruitful in finding the phillipsite crystals, thus no other work was done.

Mordenite

Mordenite occurrences noted in table 1 as determined by X-ray diffractometer are limited to two localities, BNM-26 and BNM-31. No monomineralic or high-mordenite content specimen has been found. Examination of an SEM (fig. 12) from BNM-24A shows a typical filamentous web of mordenite present in a

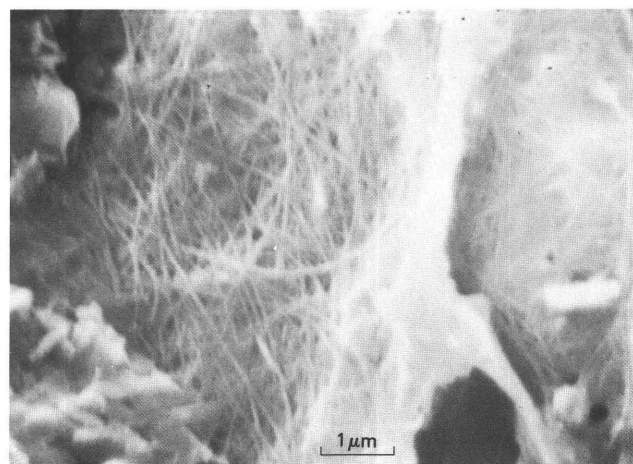


Figure 12. Scanning electron micrograph of mordenite filaments coating clay and clinoptilolite from locality BNM-24.

sample where mordenite had not been detected by X-ray diffraction. It clearly is a very finely crystalline, minute part of that sample, and thus not detected by routine X-ray analysis. The position of mordenite in its paragenetic relation is seen in the SEM (fig. 12) where mordenite filaments coat clay and clinoptilolite. However, it may possibly be deposited as a discrete secondary event, long after the diagenesis that resulted in the formation of the other zeolites had ended.

Analcime

Analcime is present at five of eight sampled sites where erionite and clinoptilolite are also present, and one site where chabazite and erionite are in the same specimen with analcime (fig. 13). These mineral associations fit the zeolite zonation model developed during earlier studies at Rainbow Basin, California, in the Miocene Barstow Formation (Sheppard and Gude, 1969); at Wikieup, Ariz., in the Pliocene Big Sandy Formation (Sheppard and Gude, 1972, 1973); and at a Pliocene lacustrine basin near Durkee, Baker County, Oreg. (Gude and Sheppard, 1978). Authigenic analcime at these and similar closed-basin, saline, alkaline lacustrine localities is an alteration product of a precursor zeolite such as chabazite, phillipsite, erionite, or clinoptilolite. The formation of analcime directly from a glass has not been observed here, nor in any other Cenozoic lacustrine locality.

Table 4 is a whole rock silicate analysis of an analcime sample from BNM-26B where the analcime is the only mineral phase identified by X-ray powder diffractometry. The value for $\text{Si}:\text{Al} + \text{Fe}^{3+} = 2.38$ derived from the calculated atoms per unit cell is less siliceous than we have found in most of our studies of lacustrine zeolite deposits. This ratio is consistent with data obtained where phillipsite may have been the precursor zeolite

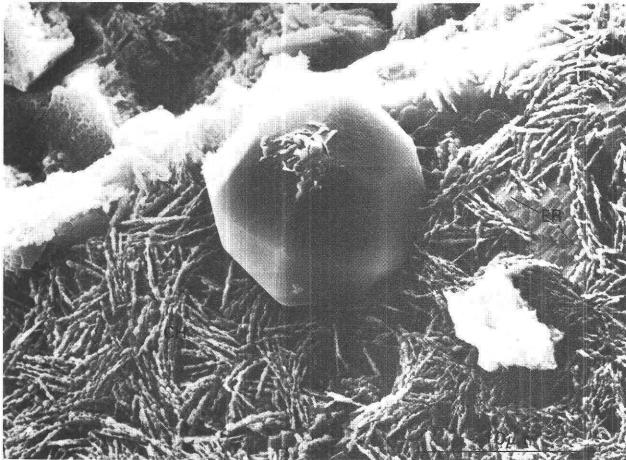


Figure 13. Scanning electron micrograph of a large analcime crystal with chabazite and erionite from locality BNM-15.

Table 4. Analcime chemical analysis
[See figure 3 and table 1 for location of BNM-26. USGS analyst, L.A. Bradley]

BNM-26B	
Rock Analysis (weight percent by X-ray spectroscopy)	
SiO ₂	57.5
Al ₂ O ₃	20.1
Fe ₂ O ₃	0.62
MgO	0.31
CaO	0.40
Na ₂ O	10.9
K ₂ O	0.18
TiO ₂	0.04
P ₂ O ₅	0.05
MnO	0.02
L.O.I. 900°C	8.92
Σ	99.04
Atoms per unit cell	
Si	33.87
Al	13.95
Fe ³⁺	0.28
Mg	0.27
Ca	0.25
Na	12.45
K	0.14
Ti	0.02
P	0.03
Mn	0.01
H ₂ O	17.52
O	96.00
Si/Al + Fe ³⁺	2.38
Al + Fe ³⁺ / 2(Mg + Ca) + Na + K	1.04
Si + Al + Fe ³⁺	48.10

(Gude and Sheppard, 1967). Phillipsite has left no discernible artifact of its existence, however, so it can only be inferred as a possible precursor.

PARAGENESIS

The order of paragenesis of the zeolites in the marker tuff is simply given as glass, then smectite, then zeolites other than analcime, then analcime altered from the precursor zeolites. Figure 14 is a schematic diagram of this process. This sequence is commonly observed in the sedimentological record in most of the lake deposits studied elsewhere (Sheppard and Gude, 1968, 1969, 1973; Surdam and Sheppard, 1978). A detailed listing of paragenetic mineral sequences found at Buckhorn is:

Paragenesis of authigenic silicate minerals
[Earliest mineral listed on left]

Glass-smectite-then:
Chabazite
Chabazite-erionite
Chabazite-erionite-analcime

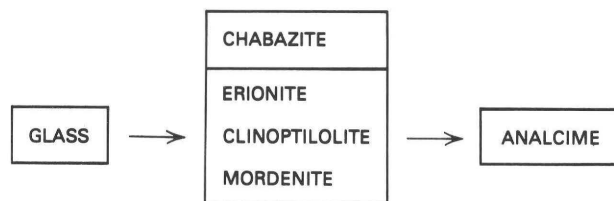


Figure 14. Schematic diagram of paragenesis.

Erionite-analcime
Clinoptilolite
Clinoptilolite-erionite
Clinoptilolite-mordenite
Clinoptilolite-analcime
Mordenite
Unknown precursor (phillipsite?)-analcime

This tabulation is based on petrographic (thin section) microscopy, scanning electron microscopy, and X-ray diffraction studies.

It is notable that here at Buckhorn, erionite and clinoptilolite apparently formed in a reversed paragenetic sequence. The usual order noted elsewhere (Sheppard and Gude, 1968, 1969, and 1973) is erionite preceding clinoptilolite, but at locality BNM-1C we have seen in thin section that erionite formed later than clinoptilolite.

Analcime replacing erionite and clinoptilolite at BNM-18 and BNM-31C is clearly seen in thin section. This is a common sequence elsewhere, especially at Rainbow Basin, Calif. (Sheppard and Gude, 1969) and at Wikieup, Ariz. (Sheppard and Gude, 1973).

The juxtaposition of chabazite, erionite, and analcime in samples from one locality, BNM-15, is unusual. This site is isolated from the well-exposed outcrops west of Duck Creek by extensive erosion and subsequent valley-fill sedimentation. A small bluff less than 20 m long is a very limited exposure of the marker tuff. We are confident that this locality is a "marker tuff" site, based on mineralogy, lithology, and geographic-topographic projection across the valley floor.

DIAGENESIS

A succinct definition of diagenesis by Hay (1966, p. 106) is: "[One may] classify as diagenetic all mineral assemblages produced in sedimentary rocks under conditions in which zeolites are formed." This statement clearly fits the formation of zeolites in the marker tuff in the lacustrine deposits at Buckhorn. Our field and laboratory observations show that diagenesis took place in the tuff at near-surface temperatures and pressures, where conditions were similar to those existing now in playas and deserts in the southwestern United States. Evidence that the lake was shallow, and thus the temperatures and pressures were low, are ripple marks,

cross bedding, and probable animal burrows. The pattern of authigenic zeolite formation fits the model developed by Sheppard and Gude (1968, p. 19) at Lake Tecopa, which stated: "Three diagenetic facies are recognized in the tuffs of the Lake Tecopa deposits. Tuffs nearest the lake margins are characterized by fresh glass and are herein termed the 'fresh-glass facies.' Tuffs in the central part of the lake basin are characterized by potassium feldspar and (or) searlesite and are termed the 'potassium feldspar facies.' Those tuffs intermediate in position between the fresh-glass facies and the potassium feldspar facies and characterized by zeolite are termed the 'zeolite facies.'"

The water in the Cenozoic lake in the Buckhorn Valley, perched in a closed basin in the Gila Conglomerate, probably had a chemistry of the soda-lake type described by Hay (1966), Eugster (1970), Surdam and Eugster (1976), Jones and others (1977), and Surdam and Sheppard (1978), for modern lakes at Magadi in Kenya and Natron in Tanzania and older similar lakes such as Tecopa in California. Highly alkaline (pH > 9.5) and saline lake waters develop in these basins by seasonal evaporation of intermittent input of stream waters that contain dissolved salts derived from the rocks in the watersheds. Fresh water inflow from ground water and surface sources dilutes nearshore and inlet parts of the lakes and may establish brackish-to-fresh water chemistry along the shorelines.

Olander (1979) speculated that a clean, silicic, air-fall ash derived from the Datil-Mogollon volcanic field north of Buckhorn was the source of the marker tuff. The direct air-fall of ash into the saline alkaline lake accumulated a thickness of 0.5–1 m on the muddy bottom. An additional 1–2 m washed in from the air-fall material deposited on the nearby land surfaces. Continuing development of the lake during successive cycles added the units above the marker tuff. Most of these sediments continued to receive tuffaceous material, which underwent the same zeolitic alteration as did the marker tuff.

Three diagenetic zones have been recognized in the marker tuff. Figure 15 shows the three zones in separate diagrams. No locality was found where the tuff consisted completely of unaltered vitric material, thus there is no glass-only zone at Buckhorn. Chabazite is the diagnostic mineral phase for the zone (fig. 15A) where the water chemistry was probably less saline and alkaline, and, being near the existing shoreline or an inlet, may have been diluted by fresh water. Mineral associations for glass, smectite, and the five zeolites are shown for each sampled locality in each zone on figure 16. Glass, smectite, and chabazite are present at each of the two localities, BNM-23 and BNM-36, in the chabazite zone (fig. 16A).

The zeolite zone is delineated by a boundary where glass-smectite-chabazite phases are present with erionite, clinoptilolite, and (or) mordenite, but not with analcime.



Figure 15. Diagenetic zones: A, chabazite zone; B, zeolite zone; C, analcime zone.

	GL	14Å	CH	ER	CL	MO	AN
GL		36 23	36 23				
14Å	36 23		36 23				
CH	36 23	36 23					
ER							
CL							
MO							
AN							

A. Chabazite zone

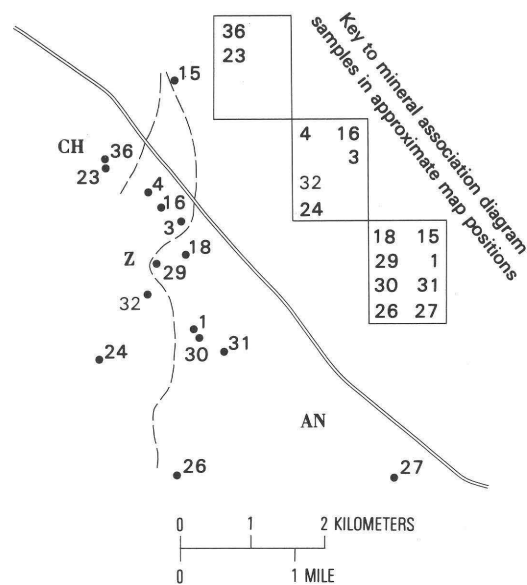
	GL	14Å	CH	ER	CL	MO	AN
GL		24		24			
14Å	24			16 3 32 24	4 16 3 32		
CH							
ER		16 3 32 24			16 3 32		
CL		4 16 3 32		16 3 32			
MO							
AN							

B. Zeolite zone

	GL	14Å	CH	ER	CL	MO	AN
GL							
14Å			15	29 30	1 29 30 27	1 31 26	15 1 30 27
CH		15		15			15
ER		15 29 30 27	15		18 29 30 27		18 29 30 27
CL		29 30 26	1 31 27		18 29 30 27	31	18 29 30 26
MO		31 26			31		26
AN		15 30 26	15	18 29 30 27	18 29 30 26		

C. Analcime zone

EXPLANATION



- GL Glass
- 14Å 14Å clay (smectite)
- CH Chabazite
- ER Erionite
- CL Clinoptilolite
- MO Mordenite
- AN Analcime
- CH Chabazite zone
- Z Zeolite zone (other than analcime)
- AN Analcime zone
- 15● Sampled locality and sample number (see fig. 3)
- — Approximate zone boundary

Figure 16. Diagrams of mineral associations: A, chabazite zone; B, zeolite zone; C, analcime zone.

Locality BNM-15, the detached site east of Buckhorn, is the only place where each of the three zones nearly overlap. This may be a locality where a near-shore embayment developed the highly alkaline and saline conditions needed to alter glass to chabazite and the other zeolite minerals, and then some of the early-formed zeolites to analcime. In figure 16B the associations of the minerals are shown as in figure 15B. The boundary along the east edge of the zeolite zone marks the change toward the middle of the original lake where the chemistry became most alkaline.

In figures 15C and 16C the innermost zone is designated where analcime is found. Three earlier studies (Sheppard and Gude, 1968, 1969, and 1973) found clear evidence for a distinct diagenetic zonation such as that at Buckhorn. The presence of authigenic potassium feldspar with, or instead of, analcime as seen in the above-noted studies is indicated at Buckhorn in samples higher in the measured section (fig. 4 and table 1). If more of the marker tuff were exposed in the basin center, potassium feldspar might have been detected.

SUMMARY

Silicic vitric tuffs in the Cenozoic Gila Conglomerate, deposited in a closed basin lacustrine setting, have been altered to zeolite and associated authigenic silicate minerals. Low-temperature, low-pressure physical conditions, and a saline, alkaline lake chemistry provided the environment for diagenesis of a marker tuff found near the base of the exposed lacustrine sediment section. Three diagenetic zones, arrayed in a partial concentric pattern, are defined by a mineralogical sequence of authigenic zeolites similar to those of other zeolite deposits found in lacustrine rocks in many basins in the southwestern U.S. basin-and-range settings.

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