

Diagenesis of Tuffs in the Barstow Formation, Mud Hills, San Bernardino County, California

GEOLOGICAL SURVEY PROFESSIONAL PAPER 634



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By RICHARD A. SHEPPARD and ARTHUR J. GUDE 3d

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*Physical properties, chemistry, and origin of
silicate minerals formed in silicic tuffs of a
lacustrine deposit*



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CONTENTS

	Page		Page
Abstract.....	1	Altered tuffs.....	17
Introduction.....	1	Field description.....	17
Previous work.....	1	Petrography.....	18
Scope of investigation.....	2	Nonalcalimic zeolitic tuff.....	19
Laboratory methods.....	3	Alcalimic tuff.....	20
Acknowledgments.....	4	Potassium feldspar-rich tuff.....	20
Regional geology.....	4	Clinoptilolite-analcime-potassium feldspar relation- ships in the Skyline tuff.....	21
Stratigraphy and lithology of the Barstow Formation.....	5	Relationship of authigenic silicate mineralogy to thickness of tuffs.....	26
Conglomerate, sandstone, and siltstone.....	6	Genesis of the authigenic silicate minerals.....	26
Mudstone.....	7	Interpretation of a saline, alkaline depositional environment for parts of the Barstow Formation.....	27
Carbonate rocks.....	8	Correlation between salinity of depositional en- vironment and authigenic silicate mineralogy.....	27
Tuff.....	8	Solution of glass to form alkali- and silica-rich zeolites.....	28
Authigenic minerals.....	10	Reaction of alkalic, silicic zeolites to form analcime.....	28
Analcime.....	10	Reaction of zeolites to form potassium feldspar.....	30
Chabazite.....	12	Metasomatism during diagenesis of tuff.....	32
Clay minerals.....	12	References.....	32
Clinoptilolite.....	12	Index.....	35
Erionite.....	14		
Mordenite.....	14		
Opal.....	15		
Phillipsite.....	15		
Potassium feldspar.....	16		
Quartz.....	17		

ILLUSTRATIONS

		Page
FIGURE	1. Index map showing location of the Mud Hills.....	2
	2. Diagrammatic sketch showing X-ray diffractometer patterns of authigenic silicate minerals.....	3
	3. Generalized geologic map of the Mud Hills and vicinity.....	4
	4. Photograph of the Barstow Formation along the axis of the Barstow syncline.....	5
	5. Generalized columnar section of the upper part of the Barstow Formation.....	6
	6. Photographs of typical lacustrine mudstone of the Barstow Formation.....	7
	7. Photograph of casts of mud cracks on bottom of Dated tuff.....	9
	8. Photomicrograph of altered tuff, showing analcime crystals.....	10
	9. Determinative curve for the anhydrous composition of analcime.....	11
	10. Histogram of the silicon content of analcime.....	12
	11. Photomicrograph of zoned clinoptilolite crystal.....	13
	12. Photomicrograph of oscillatory zoning in clinoptilolite.....	13
	13. Photomicrograph of spherulitic phillipsite.....	16
	14. Electron micrograph of potassium feldspar.....	17
	15. Photomicrograph of altered Skyline tuff, showing segregations of quartz in finely crystalline potassium feldspar.....	17
	16. Photograph of hogbacks formed by altered tuffs.....	18
	17. Photograph of clinoptilolite-rich part of Skyline tuff.....	18
18-22.	Photomicrographs:	
	18. Zeolitic tuff, showing pseudomorphs of shards.....	19
	19. Zeolitic tuff, showing pseudomorphs of fibrous clinoptilolite.....	19
	20. Zeolitic tuff, showing pseudomorphs of clinoptilolite and mordenite.....	19
	21. Plagioclase with potassium feldspar overgrowth.....	21
	22. Potassium feldspar pseudomorph after plagioclase.....	21
23.	Geologic sketch map showing the sampled locations of the Skyline tuff.....	22

	Page
FIGURE 24. Photograph of Skyline tuff, showing remnants of clinoptilolitic tuff surrounded by analcimic tuff.....	25
25. Photograph of Skyline tuff, showing remnants of clinoptilolitic tuff surrounded by analcimic tuff and potassium feldspar.....	26
26. Plot showing the correlation between the silicon content of analcime and the precursor zeolite.....	29
27. X-ray diffractometer traces of synthetic potassium feldspar, natural potassium feldspar, and natural clinoptilolite.....	31

TABLES

	Page
TABLE 1. Mineral content of the finer than 2μ fraction of five mudstones.....	8
2. Chemical analysis of mudstone.....	8
3. Chemical analysis, molecular norm, and semiquantitative spectrographic analysis of shards from Hemicyon tuff.....	9
4. Formulas of selected alkalic zeolites.....	10
5. Chemical analyses and composition of unit cell of analcime and chabazite.....	11
6. Chemical analyses and composition of unit cell of clinoptilolite.....	14
7. Chemical analyses and composition of unit cell of mordenite and phillipsite.....	15
8. Mineralogic composition of the Skyline tuff as estimated from X-ray diffractometer patterns of bulk samples.....	24

DIAGENESIS OF TUFFS IN THE BARSTOW FORMATION, MUD HILLS, SAN BERNARDINO COUNTY, CALIFORNIA

By RICHARD A. SHEPPARD and ARTHUR J. GUDE 3D

ABSTRACT

The Barstow Formation of Miocene age consists chiefly of lacustrine and fluvial clastic rocks. Lacustrine rocks are mainly mudstone with interbedded tuff and carbonate rocks. The tuffs make up about 1-2 percent of the stratigraphic section and are the most conspicuous and continuous strata. Most tuff layers are less than 1 foot thick, but some are as much as 7 feet thick. All tuffs were originally silicic, and most were vitric and fine to very fine grained. This report summarizes the physical properties, chemistry, and genesis of those silicate minerals that formed in the tuffs during diagenesis.

Zeolites, monoclinic potassium feldspar, silica minerals, and clay minerals now compose the altered tuffs; parts of some tuffs, however, contain as much as 90 percent relict glass. The zeolites are chiefly analcime and clinoptilolite, but local concentrations of chabazite, erionite, mordenite, and phillipsite have also been found. The zeolites and potassium feldspar occur in nearly monomineralic beds or associated with other authigenic silicate minerals. The zeolites, except analcime, are locally associated with relict glass; analcime commonly is associated with the other zeolites; and potassium feldspar is associated with analcime as well as some of the other zeolites. Nowhere in tuffs of the Barstow Formation is either analcime or potassium feldspar associated with relict glass.

Solution of silicic glass by moderately alkaline and saline pore water provided the materials necessary for the formation of zeolites and, subsequently, the potassium feldspar. The zeolites, except analcime, formed directly from the glass by a solution-precipitation mechanism. The observed paragenesis of zeolite minerals is attributed to variations in the activity of SiO_2 , the activity of H_2O , and the proportion of cations in the pore water during diagenesis. Much, if not all, of the analcime in the tuffs seems to have formed from alkalic, silicic zeolite precursors. Analcime in the Barstow Formation ranges in its Si:Al ratio from about 2.2 to 2.8 and thus falls at the silica-rich end of the analcime series. The silicon content of analcime is believed to be inherited, at least in part, from the precursor zeolite—relatively siliceous analcime formed from a zeolite such as clinoptilolite, whereas relatively aluminous analcime formed from a zeolite such as phillipsite. Potassium feldspar, like analcime, has apparently not formed directly from the silicic glass. The formation of potassium feldspar from analcime and clinoptilolite is documented; however, feldspar may have also formed from the other precursor zeolites.

Tuffs such as the Skyline tuff of informal use show a lateral gradation in authigenic mineralogy of nonanalcimic zeolites to analcime, and then to potassium feldspar. The chief factor responsible for this lateral gradation is probably a variation in

the salinity of the pore water trapped in the tuff during deposition. Highly saline pore water during diagenesis favors the ultimate formation of analcime or potassium feldspar in the silicic tuffs, rather than the formation of zeolites such as clinoptilolite and phillipsite.

INTRODUCTION

The Mud Hills are in west-central San Bernardino County (fig. 1), Calif., mainly in T. 11 N., Rs. 1 and 2 W. The nearest principal town is Barstow, about 10 miles to the south. The Fort Irwin Road, a paved highway between Barstow and Fort Irwin, provides access to the Mud Hills by way of the graveled Fossil Bed Road. The area is shown on the 15-minute topographic maps of the Lane Mountain and Opal Mountain quadrangles by the U.S. Geological Survey.

The Mud Hills are in the western part of the Mojave Desert, which is characterized by isolated mountain ranges surrounded by broad alluvial plains. The Mud Hills range in elevation from about 2800 to 4200 feet. Numerous canyons radiate southward from the north-central part of the Mud Hills and provide access to nearly continuous exposures of the Barstow Formation.

PREVIOUS WORK

The Barstow Formation contains rich vertebrate faunas that have received much attention since the pioneer work of Merriam (1911). Lewis (1964, 1968) reviewed the nomenclature of the Barstow Formation and discussed the faunas. As these topics will not be considered here, the reader is referred to Lewis' reports.

The rocks of the Barstow Formation, unlike the fossils, have received only cursory study except in recent years. Baker (1911, p. 342-347), Pack (1914, p. 145-150), and Knopf (1918, p. 257-259) briefly described the Tertiary deposits of the Mud Hills. These deposits include the Barstow Formation as well as the underlying formations. Durrell (1953) studied the stratigraphy of the Tertiary deposits during an investigation of strontianite deposits at the eastern end of the Mud Hills. Like most earlier workers, Durrell (1953, p. 24)

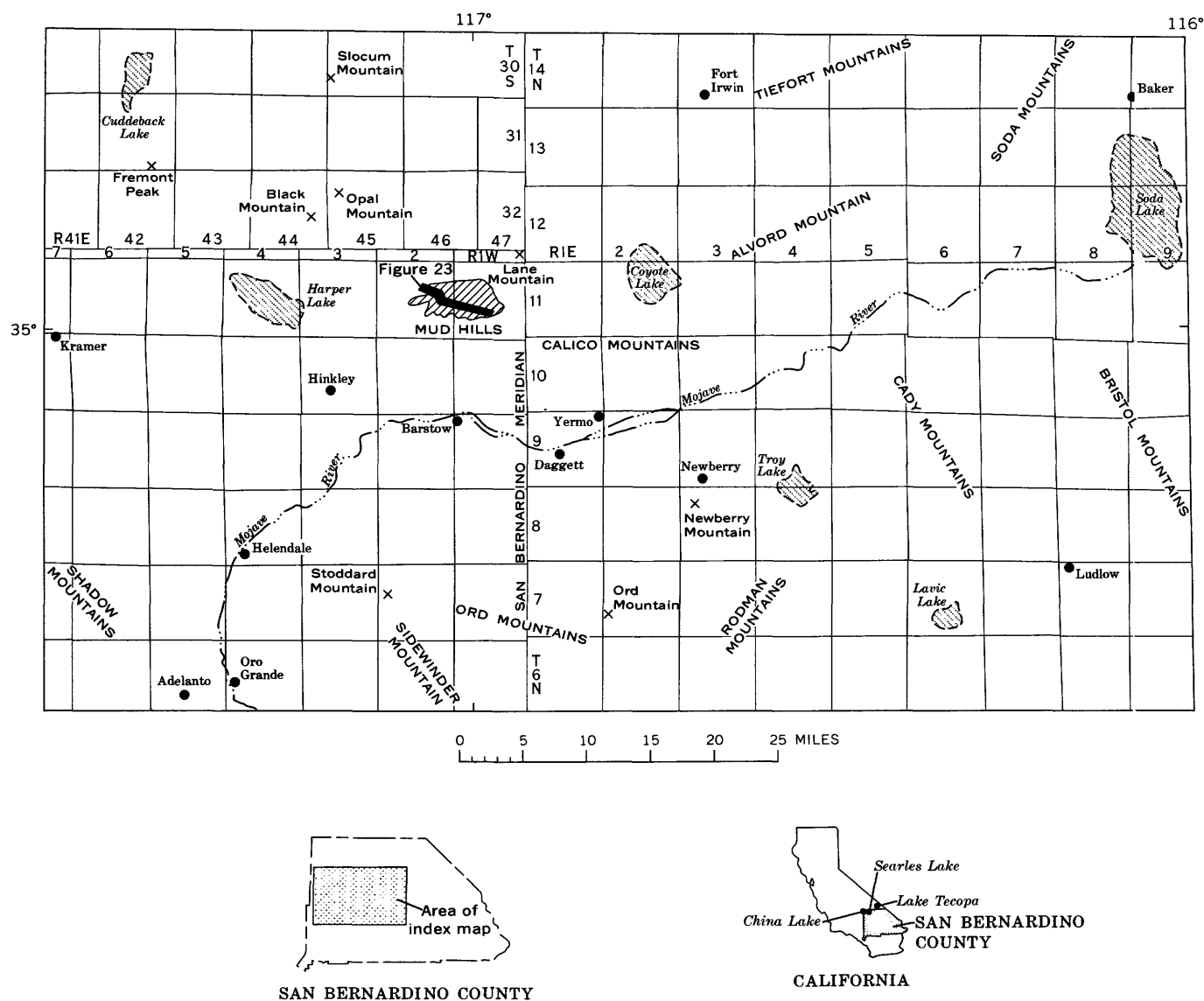


FIGURE 1.—Index map of the Mojave Desert in western San Bernardino County, Calif., showing the location of the Mud Hills. Base from U.S. Geological Survey, State of California, 1 : 500,000, 1953.

assigned the Tertiary strata to the Rosamond Series, a name abandoned by the U.S. Geological Survey (Dibblee, 1958). T. W. Dibblee, Jr. (1967, p. 88-89), mapped in detail the geology of the Mud Hills. Several short reports on the Barstow Formation (Sheppard and Gude, 1965a; Gude and Sheppard, 1966; Sheppard, 1967) have been published as part of the present study. R. P. Steinen (1966) recently mapped the geology of the Mud Hills and studied the stratigraphy of the Barstow Formation.

SCOPE OF INVESTIGATION

This investigation of the Barstow Formation is primarily a study of the genesis and distribution of zeolites

and other associated authigenic silicate minerals in the tuffaceous rocks. Zeolites are common authigenic minerals in tuffaceous rocks of Cenozoic age throughout the desert regions of southeastern California (Sheppard and Gude, 1964). The tuffs of the Barstow Formation in the Mud Hills were chosen for detailed study because reconnaissance in 1963 showed an abundance and variety of authigenic silicate minerals, and because the tuffs are well exposed. The common occurrence of authigenic potassium feldspar in the tuffs also provided the opportunity to study the genetic relationships of the feldspar to vitric material and zeolites. Although authigenic clay minerals are common in the tuffs, their min-

eralogy received only a cursory examination in this study.

Sampling was confined to surface outcrops and weighted heavily in favor of the tuffs, although the other rock types were sampled sufficiently to obtain representative material. Weathered surface outcrops were avoided. No cores were available to this investigation.

LABORATORY METHODS

X-ray diffractometer patterns were made of all bulk samples of tuffs. The samples were first ground to a powder and packed in aluminum sample holders and then exposed to nickel-filtered copper radiation. Relative abundances of authigenic minerals were estimated from the diffractometer patterns by using peak intensities. Estimates are probably less reliable for mixtures

containing glass or opal because these materials yield a rather poor X-ray record. Artificial mixtures of glass and zeolites were prepared and used as standards to obtain more reliable estimates of these constituents.

Optical studies using immersion oil mounts and thin sections supplemented the abundance data obtained by X-ray diffraction and provided information on the age relationships of the authigenic minerals. All measurements of the indices of refraction are considered accurate to ± 0.001 .

Most samples of altered tuff contained more than one authigenic mineral. To identify each mineral in the diffractometer patterns of bulk samples, the patterns were compared with a "sieve" (fig. 2) prepared from pure mineral separates at the same scale as the patterns of the bulk samples. One mineral at a time can be "sieved"

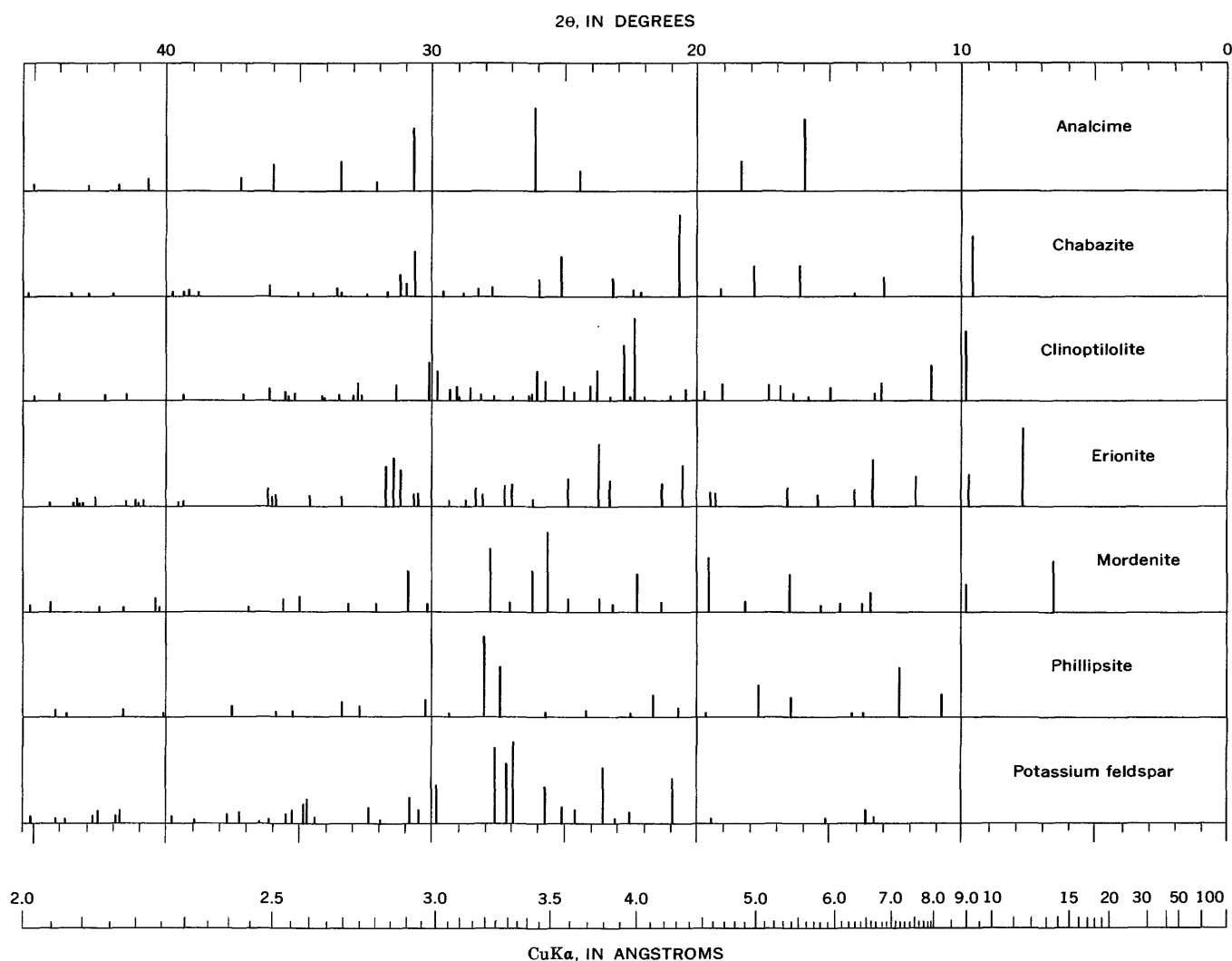


FIGURE 2.—X-ray diffractometer patterns of authigenic silicate minerals. Copper radiation with nickel filter. Relative intensities indicated by height of lines above base line.

from the bulk patterns until all lines are identified. This procedure made the identifications routine and helped the analyst recognize minor or trace amounts of constituents.

Mordenite in samples that are chiefly clinoptilolite is difficult to detect on X-ray diffractometer patterns because these zeolites have many coincident peaks. The technique described by Sudo, Nisiyama, Chin, and Hayashi (1963, p. 10) was found useful for the discrimination. Powdered tuff is treated with 6*N* HCl for 1 hour. This treatment causes decomposition of the clinoptilolite, but the mordenite persists.

The "pure" mineral separates were prepared for chemical analysis from nearly monomineralic tuffs. The zeolites were separated by disaggregation followed by flotation in a heavy liquid mixture of bromoform and acetone, utilizing the equipment and technique described by Schoen and Lee (1964).

ACKNOWLEDGMENTS

Grateful appreciation is expressed to those in the Geological Survey who provided technical assistance during this investigation. Ellen S. Daniels, Harriet Neiman, and Elaine L. Munson performed the chemical analyses. Paul D. Blackmon determined the clay mineralogy of representative mudstones and altered tuffs. Melvin E. Johnson prepared the thin sections.

We are especially grateful to Robert G. Schmidt, who suggested this investigation and who had recognized the occurrence of authigenic zeolites and potassium feldspar in the Barstow Formation as early as 1954. Thomas W. Dibblee, Jr., kindly provided us with his unpublished geologic maps of the Mud Hills and adjacent areas.

REGIONAL GEOLOGY

The generalized geology of the Mud Hills and vicinity is shown in figure 3, which is modified from Dibblee

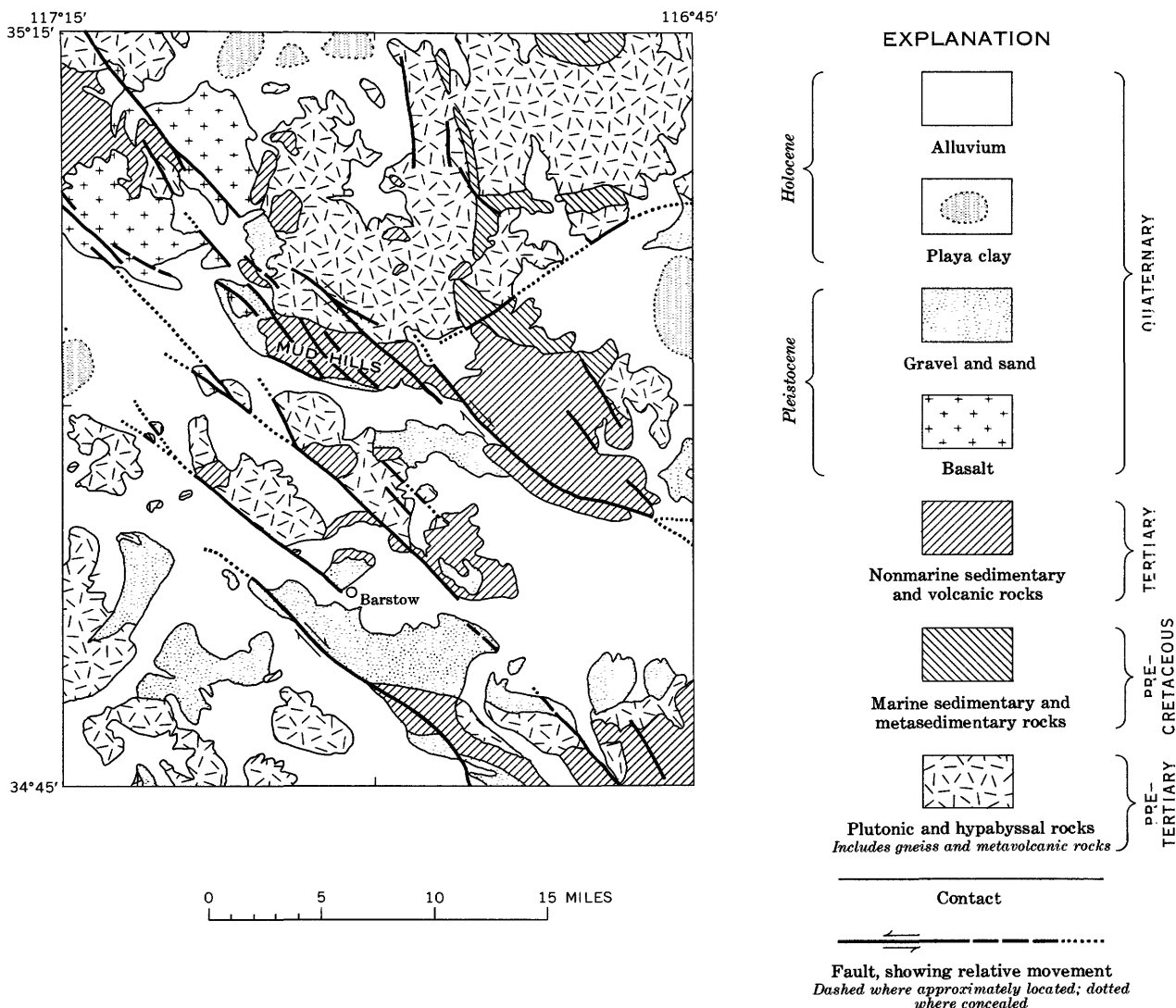


FIGURE 3.—Generalized geologic map of the Mud Hills and vicinity. (Modified from Dibblee, 1963, pl. 11.)

(1963, pl. 11). Other generalized geologic maps of the area have been published by Dibblee (1961, p. B198) and the California Division of Mines and Geology (1963).

The Tertiary deposits of the Mud Hills are about 6,000–7,000 feet thick and include in ascending order the following: Jackhammer Formation, Pickhandle Formation, and Barstow Formation. Both the Jackhammer Formation and the Pickhandle Formation consist of sedimentary and volcanic rocks. The Tertiary deposits are folded into the Barstow syncline, whose axis trends nearly east. The Barstow syncline is nearly symmetrical, and both limbs generally dip 20°–40° (fig. 4). Numerous faults, trending mainly northwest, cut the deposits. Movement along some of these faults has been predominantly right lateral (Dibblee, 1961). The Tertiary deposits are locally unconformably overlain by Quaternary alluvial deposits. Renewed movement on

some faults apparently continued into Holocene time, because the Quaternary deposits are displaced.

The hills north of the Mud Hills are underlain chiefly by granitic rocks and intermediate to basic plutonic rocks of Mesozoic age (McCulloh, 1960). The Calico Mountains, east of the Mud Hills, are underlain chiefly by sedimentary rocks, volcanic rocks, and silicic to intermediate intrusive rocks, all of Tertiary age (McCulloh, 1960, 1965). Paleozoic metasedimentary and metavolcanic rocks flank the Calico Mountains on the north. The hills south of the Mud Hills are underlain mainly by granitic rocks of Mesozoic age and a complex sequence of metamorphic rocks of probable Precambrian age (Miller, 1944; Bowen, 1954; Dibblee, 1960; McCulloh, 1965). In the vicinity of Opal Mountain and Black Mountain, northwest of the Mud Hills, the rocks are chiefly Miocene silicic volcanic rocks and Pleistocene basalt.



FIGURE 4.—View of the Barstow Formation eastward along the axis of the Barstow syncline at Rainbow Basin. The upper part of the Barstow Formation, shown in the photograph, is chiefly lacustrine mudstone and interbedded tuff. Gently dipping Pleistocene alluvial deposits unconformably overlie the Barstow Formation.

STRATIGRAPHY AND LITHOLOGY OF THE BARSTOW FORMATION

The Barstow Formation, of Miocene age (Lewis, 1964, 1968), consists chiefly of fluvialite and lacustrine rocks that are about 3,000–4,000 feet thick. The formation unconformably overlies the Pickhandle Formation (Bowen, 1954) and is unconformably overlain by sand and gravel of Quaternary age. An unknown thickness of the Barstow Formation was eroded prior to deposition of the Quaternary alluvium.

The lacustrine rocks of the formation interfinger with relatively coarse clastic rocks of fluvialite origin. The

lacustrine rocks are chiefly mudstones and interbedded carbonate rocks and tuffs. Fluvialite rocks include conglomerate, sandstone, and siltstone. Some sandstone and siltstone are tuffaceous. Sandstone and conglomerate have locally channeled into mudstone and, more rarely, into tuff. Areas underlain by thick mudstone units are commonly badlands; and differential erosion of the more resistant rocks, such as sandstone, conglomerate, carbonate rock, and altered tuff, has produced hogbacks.

A generalized columnar section for the upper part of the Barstow Formation is shown in figure 5. Detailed measured sections of the formation have been

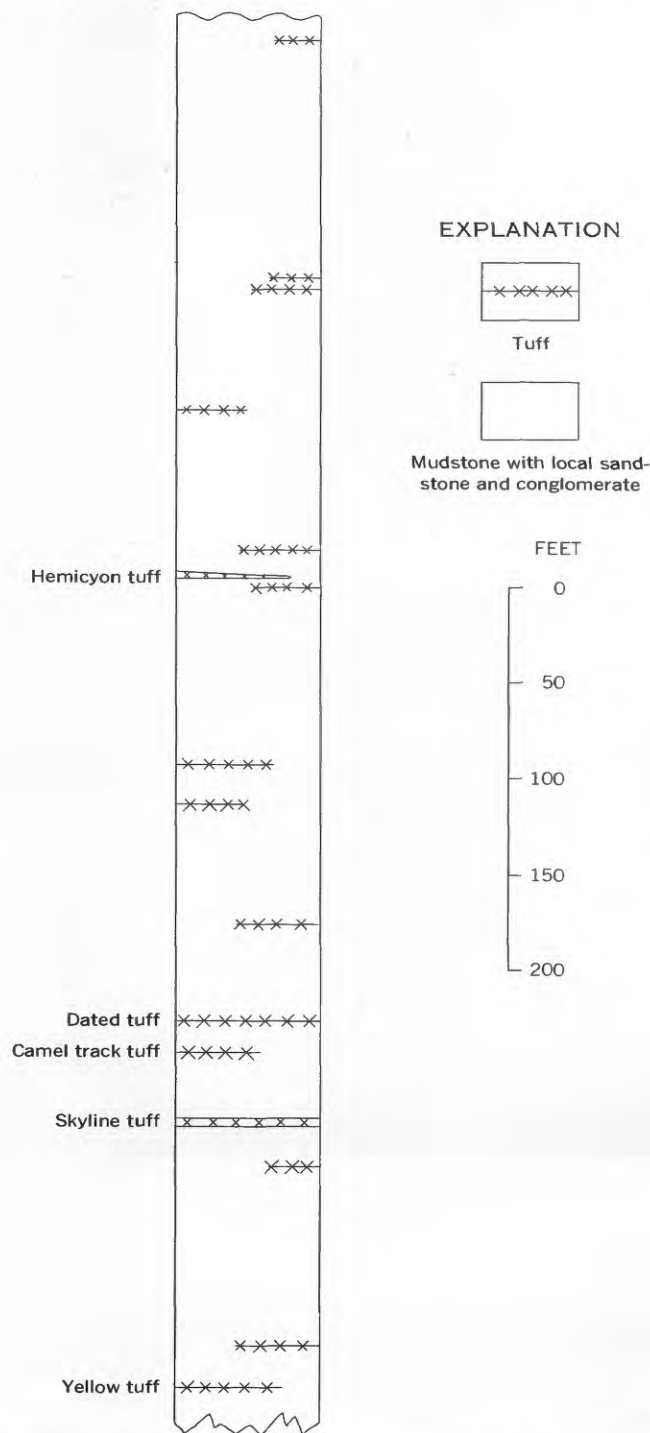


FIGURE 5.—Generalized columnar section of the upper part of the Barstow Formation. Five of the most persistent tuffs are assigned informal field names.

given by Steinen (1966) and Sheppard (1967). Five of the most persistent tuffs in the upper part of the formation are assigned informal field names, in ascending order: Yellow tuff, Skyline tuff, Camel track tuff,

Dated tuff, and Hemicyon tuff. The Skyline and Dated tuffs crop out the length of the Mud Hills, but the other tuffs are less extensive. The Yellow tuff crops out eastward from the western part of Rainbow Basin; the Camel track tuff crops out between Rainbow Basin and Owl Canyon; and the Hemicyon tuff crops out in about the western third of the Mud Hills.

CONGLOMERATE, SANDSTONE, AND SILTSTONE

Conglomerate, sandstone, and siltstone occur throughout the formation and throughout the Mud Hills; however, the thick accumulations are in the southwestern, south-central, and northeastern parts of the area. These coarse fluviatile rocks interfinger with mudstone of lacustrine origin. Highlands both north and south of the Mud Hills probably supplied detritus for these coarse clastic rocks.

The conglomerate is green, brown, or red; medium to thick bedded; and poorly to moderately well indurated. The framework constituents of the conglomerate range in size from pebbles to boulders up to 3 feet in diameter. The pebbles generally are angular to subrounded, whereas the cobbles and boulders generally are subrounded to rounded. The composition of the fragments also is variable, but generally the fragments are medium- to coarse-grained granitic rocks, or granitic rocks with minor volcanic and metamorphic rocks. Fragments of quartz and pegmatitic, granitic rock also are present. Some conglomerates contain only volcanic fragments that include pink and green silicic or intermediate lavas and, rarely, pink lapilli tuff.

The sandstone and siltstone are green, brown, gray, or red and generally poorly to moderately well indurated. Local cementation by brown-weathering calcite makes these rocks very hard and resistant. The sandstone is thin to thick bedded and fine to coarse grained; the siltstone is generally laminated or thin bedded. In addition to calcite, clay minerals and clinoptilolite locally are cements in the sandstone and siltstone. Primary sedimentary structures other than bedding are rare in the sandstone; however, the siltstone is commonly ripple laminated. The sandstone is locally crossbedded and, more rarely, ripple marked. The siltstone generally contains abundant spherical or irregular calcareous concretions.

The framework constituents of the sandstone and siltstone consist of varying amounts of mineral grains and rock fragments. Sorting is generally poor; and the clasts have an estimated roundness of 0.2–0.6, although most are in the lower part of this range. The matrix is chiefly clay minerals and is less than 15 percent of the rock. The detrital minerals are mainly quartz and feldspar and lesser amounts of biotite, hornblende, epi-

dote, clinopyroxene, muscovite, chlorite, zircon, magnetite apatite, and sphene. Generally quartz exceeds feldspar; and plagioclase exceeds alkali feldspar. Much of the plagioclase is sericitized. Biotite is very abundant in some of the sandstone. The rock fragments are chiefly granitic and volcanic rocks and lesser amounts of sedimentary and low-grade metamorphic rocks. Volcanic rock fragments include hyalopilitic and spherulitic lavas and sand-sized pumice or pseudomorphs of clay minerals and clinoptilolite. Following the classification of Pettijohn (1957, p. 291), these sandstones and siltstones are termed arkose or subgraywacke, depending on whether feldspar or rock fragments predominate.

MUDSTONE

Mudstone, or a silty or calcareous variant, is the predominant rock in the lacustrine deposits of the Barstow Formation. The mudstone has an earthy luster and is pastel green, gray, brown, and, rarely, red. Calcareous concretions are common, particularly in the green mudstone. Most mudstone is even bedded and medium to thick bedded. Fresh mudstone breaks with a subconchoidal or conchoidal fracture (fig. 6A), and the fractures are commonly filled or partly filled with gypsum. Where weathered, the mudstone has a characteristic punky "pop corn" surface coating that is several inches thick (fig. 6B). A white efflorescence of thenardite (Na_2SO_4) commonly coats weathered mudstone in the eastern part of Rainbow Basin and much of the mudstone to the east.

In addition to clay minerals, most of the mudstone contains calcite, detrital silt and sand, authigenic silicate minerals, and, locally, angular fragments of charcoal. The silt and sand fractions make up as much as 15 percent of the rock, although they generally are less than 5 percent. Most of these relatively coarse grains are angular to subangular and are chiefly mineral fragments and rarely granitic rock fragments. Quartz, plagioclase, biotite, and hornblende compose most of the silt and sand fractions; and sanidine, zircon, muscovite, and epidote are minor constituents locally. Neither vitric material nor pseudomorphs after vitric material were recognized in the mudstone.

The mineral content of the finer than 2μ fraction of five mudstones is given in table 1. Standard X-ray techniques were used to identify the clay minerals. After disaggregation in water and complete removal of soluble salts, the finer than 2μ fraction was sedimented on tiles and oriented by suction. X-ray data were then obtained from untreated, glycolated, and heated (400°C and 550°C) samples. Montmorillonite and illite occur in all samples, and two samples also contain mixed-layer illite-montmorillonite. Neither chlorite nor kao-



A



B

FIGURE 6.—Typical lacustrine mudstone of the Barstow Formation. A, Small excavation showing contrast of fresh and weathered mudstone. Fresh mudstone breaks with a subconchoidal to conchoidal fracture, but weathered mudstone has a punky "pop corn" coating several inches thick. Bedding dips toward right of photograph. B, Characteristic "pop corn" coating on weathered mudstone.

linite was recognized. The clay mineral suite is presumably detrital, although the possibility that some of the clay minerals are authigenic cannot be rejected.

Analcime and potassium feldspar in the mudstones are probably authigenic, although petrographic evidence is lacking. X-ray diffraction data of bulk samples indicate that the mudstone generally contains 10–20 percent analcime and 10 percent or less potassium feldspar. The analcime is anhedral to subhedral and ranges in size from less than 0.002 mm to about 0.4 mm. Clay minerals adjacent to large analcime crystals are aligned parallel to the surface of the analcime. Possibly the clay minerals were pushed aside during growth of the analcime.

TABLE 1.—*Mineral content of the finer than 2 μ fraction of five mudstones*[Relative abundance expressed in parts of 10; Tr., trace; ---, looked for but not found.
Analyst: Paul D. Blackmon]

Minerals	Samples				
	1	2	3	4	5
Montmorillonite.....	2+	Tr.	4	3	1+
Illite.....	3	6	3+	4+	+
Mixed-layer illite-montmorillonite.....	2	1	---	---	---
Analcime.....	2	2	<1	<1	1+
Potassium feldspar.....	Tr.	Tr.	1	<1	<1
Calcite.....	---	---	Tr.	Tr.	Tr.
Ferroan dolomite.....	Tr.	---	Tr.	---	---
Quartz.....	---	---	---	Tr.	Tr.
Goethite.....	Tr.	---	Tr.	Tr.	Tr.

A chemical analysis of a typical mudstone is given in table 2. The K₂O and Na₂O contents of this mudstone are higher than generally reported for pelitic rocks (Shaw, 1956). However, the abundance of K₂O and Na₂O in this mudstone is similar to that of lacustrine mudstone in the Triassic Lockatong Formation of New Jersey (Van Houten, 1965). Authigenic analcime and potassium feldspar in the Barstow mudstone probably account for the high alkali contents.

Some mudstone contains numerous disseminated cavities, 0.5–3.0 mm long, that are filled or nearly filled with calcite. Inasmuch as many cavities are bounded by planar surfaces, they may be crystal molds. The shape of some cavities resembles the morphology of crystals of gaylussite (CaCO₃·Na₂CO₃·5H₂O). Calcite occurs in the cavities as clusters of anhedral and subhedral crystals. Apparently the calcite precipitated in cavities that formed by solution of a readily soluble saline mineral.

TABLE 2.—*Chemical analysis of mudstone*

[Lab. No. D100507; field No. SM-1-31C. Locality: Rainbow Basin, SE1/4 sec. 24' T. 11 N., R. 2 W., San Bernardino County, Calif. Analyst: Ellen S. Daniels]

SiO ₂	47.95	P ₂ O ₅13
Al ₂ O ₃	14.97	MnO.....	.11
Fe ₂ O ₃	4.78	CO ₂	3.70
FeO.....	.90	SO ₃30
MgO.....	5.08	Cl.....	.03
CaO.....	5.00	F.....	.14
BaO.....	.05		
Na ₂ O.....	2.96	Subtotal.....	99.72
K ₂ O.....	4.54	Less O.....	.07
H ₂ O ⁺	3.97		
H ₂ O ⁻	4.53	Total.....	99.65
TiO ₂58		

CARBONATE ROCKS

Carbonate rocks are locally common in the Barstow Formation and include limestone and dolomite, although the former is much more abundant. The limestone is light gray to light brown, finely to coarsely crystalline, and thin to thick bedded. Much of the limestone weathers dark brown. Some of the limestone

is wavy bedded or vuggy or contains irregular segregations of dark-green to black opal. Most of the limestone contains some clastic grains, locally as much as 40 percent of the rock. Thin interbeds of green calcareous mudstone are common in the thick limestone units. Ostracodes are locally common in thin beds of finely crystalline limestone. Apparently some of the limestone is of algal origin (Knopf, 1918, p. 258–259).

The dolomite is light gray, finely crystalline, and thin bedded. The beds characteristically weather light brown. Clastic material locally makes up as much as 20 percent of the rock.

TUFF

Tuffs in the Barstow Formation of the Mud Hills make up about 1–2 percent of the stratigraphic section and are the most conspicuous and continuous strata. At least 35 tuffs are recognized; most occur in the upper half of the formation, and most were deposited in lakes. The tuffs range in thickness from 0.25 inch to 7.0 feet, but most are less than 1 foot thick. The thicker tuffs generally are more continuous than the thinner ones. Thin tuffs commonly are single beds, but tuffs thicker than 6 inches generally are multiple bedded. Individual beds of multiple-bedded tuffs are 1/16 inch to 3.5 feet thick but generally are less than 6 inches thick.

The original textural and structural features of the tuffs generally are preserved even though no vitric material remains. Most tuffs are even bedded, but beds of some thick multiple-bedded tuffs channel into lower beds as much as several inches. Individual beds of both single-bedded or multiple-bedded tuffs are commonly graded, being coarser at the base. The lower contact of a tuff generally is sharp, but the upper contact commonly is gradational into the overlying rock. Cross-bedding and ripple marks or ripple laminations are present but not common. Some tuffs show contorted laminations that probably formed after deposition by internal flowage. Casts of mud cracks (fig. 7) or vertebrate animal tracks are locally common on the bottoms of some tuffs.

Accretionary lapilli are common in the lower part of basal beds of two thick tuffs, the Skyline tuff and the Hemicyon tuff. The lapilli are spherical or flattened slightly in the plane of the bedding and are 2–5 mm in diameter. Broken lapilli are very rare. Each accretionary lapillus characteristically consists of a structureless core surrounded by one or more concentric layers. The diameter of the core is generally more than half of the total diameter of the lapillus. Lapilli and matrix consist chiefly of vitric shards or pseudomorphed shards, and minor angular crystal fragments. The grain size of shards in the cores of the lapilli and in the matrix is

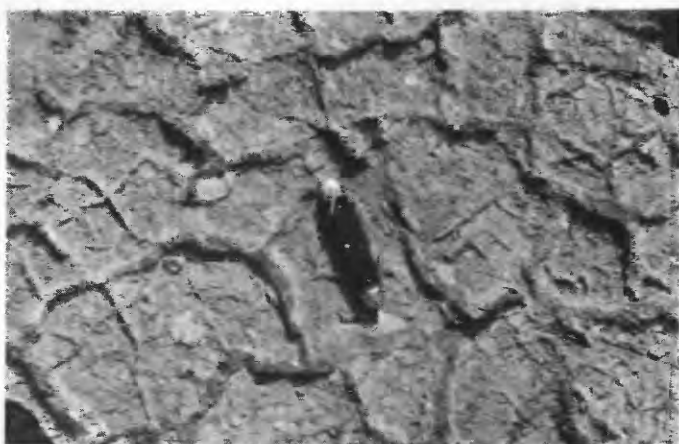


FIGURE 7.—Casts of mud cracks on bottom of Dated tuff at Rainbow Basin.

similar, but the shards of the concentric layers are distinctly smaller. Each concentric layer is graded outward from relatively coarse to fine material. In contrast to the shards of the structureless core, those shards of the concentric layers are oriented with their long dimension tangential to the core or concentric layers. This preferred orientation and fine grain size of shards in the concentric layers enables the lapilli to be recognized in thin section.

Accretionary lapilli apparently form by accretion of moist ash in eruptive clouds and then fall as mud-pellet rains (Moore and Peck, 1962). The lapilli in the Barstow Formation probably fell directly into a lake, because prolonged, or perhaps any, transport by streams would disaggregate them. The source of the ash in the Barstow Formation is unknown, but the occurrence of accretionary lapilli suggests that the vent was nearby. Moore and Peck (1962, p. 191) found that, with rare exceptions, accretionary lapilli occur within a few miles of the vent.

Most of the tuffs are vitric and fine or very fine grained. The vitric material commonly is of two types: platy bubble-wall shards that formed from the walls of relatively large broken bubbles; and pumice shards that contain small elongated bubbles. Most tuffs are composed of both types, but the platy shards are predominant. The index of refraction of unaltered shards ranges from 1.495 to 1.498.

Crystal and rock fragments in the tuffs are generally angular and range from less than 1 percent to about 60 percent of the rock. Most tuffs, however, contain less than 5 percent crystal and rock fragments. The crystals are chiefly plagioclase (An_{21-36}), quartz, sanidine, biotite, and hornblende. Minor amounts of any or all of the following are also present: Zircon, clinopyroxene,

apatite, magnetite, and, rarely, hypersthene. All these crystals are presumably pyrogenic.

Rock fragments are chiefly volcanic and granitic but also include quartzite, chert, and schistose and gneissic metamorphic rocks. The volcanic rock fragments, mainly spherulitic and hyalopilitic lava, could have been torn from the vent area during the eruption of the ash. Although the other rock types could also have been derived from the vent during an eruption, some probably are epiclastic and were carried to the basin by streams or wind.

The upper part of some tuffs, particularly thick tuffs, probably contains reworked ash mixed with epiclastic grains derived from highlands surrounding the basin. This part generally has an abundance of nonvolcanic rock fragments as well as grains of epidote, muscovite, chlorite, microcline, perthite, and altered plagioclase. Commonly, these constituents are subangular to subrounded.

The only available chemical analysis of vitric material from the Barstow Formation is the one prepared for this study (table 3). The shards were separated from the other constituents of a relatively fresh part of

TABLE 3.—Chemical analysis, molecular norm, and semiquantitative spectrographic analysis of shards from Hemicyon tuff

[Lab. No. D100550; field No. M4-32B. Locality: tributary to Fossil Canyon, NE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 15, T. 11 N., R. 2 W., San Bernardino County, Calif. Chemical analysis by Ellen S. Daniels; semiquantitative spectrographic analysis by Harriet Neiman]

Chemical analysis					
SiO ₂	71.26	K ₂ O.....	2.68	Cl.....	0.11
Al ₂ O ₃	12.44	H ₂ O ⁺	6.02	F.....	.05
Fe ₂ O ₃65	H ₂ O ⁻75		
FeO.....	.31	TiO ₂15	Subtotal.....	99.98
MgO.....	.35	P ₂ O ₅02	Less O.....	.05
CaO.....	.65	MnO.....	.06		
Na ₂ O.....	4.47	CO ₂01	Total.....	99.93
Molecular norm					
Q.....	33.14	C.....	1.20	hm.....	0.42
or.....	17.09	en.....	1.08	ap.....	.05
ab.....	43.15	mt.....	.18		
an.....	3.45	il.....	.24	Total.....	100.00
Semiquantitative spectrographic analysis ¹					
B.....	0.002	Ga.....	0.003	V.....	0.001
Ba.....	.07	La.....	.005	Y.....	.002
Be.....	.0003	Nb.....	.001	Yb.....	.0002
Cr.....	.0001	Pb.....	.002	Zr.....	.01
Cu.....	.0007	Sr.....	.01		

¹ Results are reported in percent to the nearest number in the series 1, 0.7, 0.5, 0.2, 0.15, 0.1, and so forth, which represent approximate midpoints of group data on a geometric scale. The original group for semiquantitative results will include the quantitative value about 30 percent of the time. The following elements were looked for but not found: Ag, As, Au, Bi, Cd, Ce, Co, Ge, Hf, Hg, In, Li, Mo, Ni, Pd, Pt, Re, Sb, Sc, Sn, Ta, Te, Th, Tl, U, W, and Zn.

the Hemicyon tuff by disaggregation followed by flotation in a heavy-liquid mixture of bromoform and acetone. The shards were then "scrubbed" in an ultrasonic bath in an attempt to remove adhering authigenic chabazite and montmorillonite. This treatment was only partly successful, so the vitric material that was analyzed included about 3-4 percent impurities, chiefly montmorillonite. The analysis shows that the shards are silicic and hydrated. The $K_2O:Na_2O$ ratio of the glass is lower than expected from the SiO_2 content, but the ratio may have been modified during the secondary hydration (Noble, 1967). This hydrated glass could be classified as rhyodacite if the normative minerals (table 3) are applied to the rock classification of Nockolds (1954, p. 1008). Inasmuch as the original composition of the glass is unknown, the shards are considered rhyolitic in further discussions. On the basis of phenocryst content, the other tuffs in the formation probably also were rhyolitic.

AUTHIGENIC MINERALS

ANALCIME

Analcime, commonly referred to as analcite, is one of the more abundant zeolites in sedimentary rocks. Since its discovery in the Green River Formation (Bradley, 1928) and in lacustrine tuffs near Wikieup, Ariz. (Ross, 1928), analcime has been reported in rocks that are diverse in age, lithology, and sedimentary environment (Hay, 1966). Analcime has an ideal formula of $NaAlSi_2O_6 \cdot H_2O$, but the analcime of sedimentary rocks is generally more siliceous (table 4).

Analcime is a very common zeolite in the tuffs of the Barstow Formation, where it ranges from trace amounts to nearly 100 percent. The analcime is associated with each of the other zeolites, but the association with chabazite is rare. Analcime is also commonly associated with authigenic clay minerals and potassium feldspar and

less commonly associated with authigenic quartz. Unlike the other zeolites, analcime is not associated with relict glass.

Analcime occurs in the tuffs as anhedral to euhedral crystals, although most are subhedral to euhedral (fig. 8). The crystals range from 0.006 to 0.3 mm in size, but most are 0.01-0.05 mm. The analcime is isotropic and could easily be overlooked in thin section except that it is generally pale tan in transmitted light but milky in reflected light due to abundant inclusions of opal. Commonly, the outer part of the analcime crystals is free of inclusions and is colorless and clear.

The index of refraction of analcime from the Barstow Formation ranges from 1.484 to 1.487. Saha (1959, p. 302-303) showed that the index of refraction of synthetic analcimes decreases with increasing silicon content. The above indices are consistent with high silicon contents.

A chemical analysis of an analcime from the Barstow Formation is given in table 5. The analcime was sep-

TABLE 4.—*Formulas of selected alkalic zeolites*

[Formulas are standardized in terms of a sodium end member that has one aluminum atom. Formulas are taken from Hay (1966, p. 7); however, the formulas for chabazite, clinoptilolite, and erionite are modified from the writers' unpublished data]

Name	Dominant cations	Formula
Analcime ----	Na	$NaAlSi_{2.0-2.8}O_{6.0-7.6} \cdot 1.0-1.3H_2O$
Chabazite ----	Na, Ca	$NaAlSi_{1.7-3.8}O_{5.4-9.6} \cdot 2.7-4.1H_2O$
Clinoptilolite --	Na, K, Ca	$NaAlSi_{4.2-5.0}O_{10.4-12.0} \cdot 3.0-4.0H_2O$
Erionite -----	Na, K, Ca	$NaAlSi_{3.0-3.7}O_{8.0-9.4} \cdot 3.0-3.4H_2O$
Mordenite ----	Na, Ca, K	$NaAlSi_{4.5-5.0}O_{11.0-12.0} \cdot 3.2-3.5H_2O$
Phillipsite ----	Na, K	$NaAlSi_{1.3-3.4}O_{4.6-8.8} \cdot 1.7-3.3H_2O$

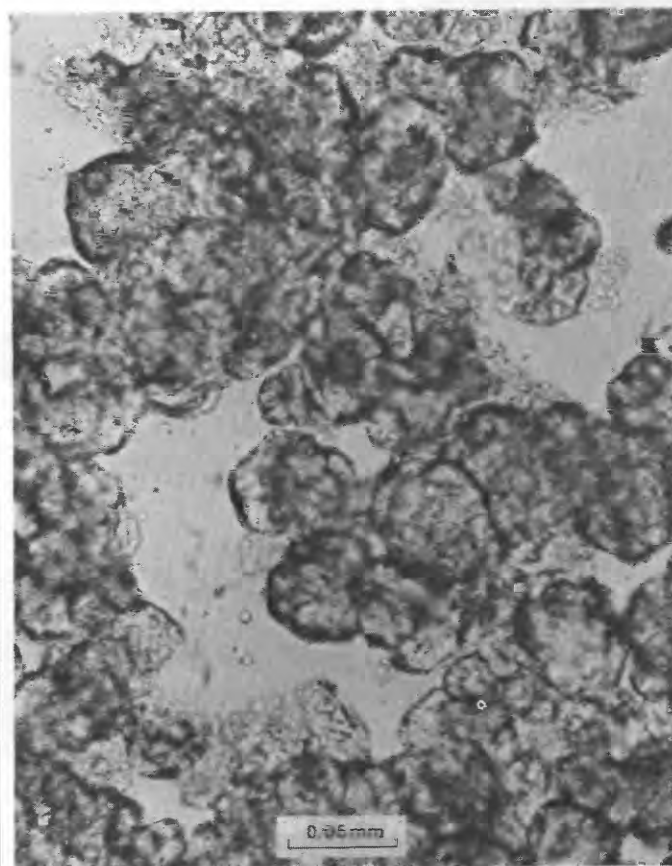


FIGURE 8.—Photomicrograph of altered tuff, showing subhedral and euhedral crystals of analcime. Unpolarized light.

arated from a nearly monomineralic tuff; however, the analcime contained abundant inclusions of opal. Even so, the analysis shows that the analcime contains only minor amounts of cations other than sodium.

TABLE 5.—Chemical analyses and composition of unit cell of analcime and chabazite

[a, in column head, uncorrected analysis; b, analysis corrected for opal impurities]

	Analcime		Chabazite
	a	b	a
Chemical analyses			
[Analyst of analcime: Elaine L. Munson. Analyst of chabazite: Ellen S. Daniels]			
SiO ₂ -----	67.68	60.24	59.68
Al ₂ O ₃ -----	14.10	19.75	13.11
Fe ₂ O ₃ -----	.21	.28	.13
FeO-----	.00	.00	.02
MgO-----	.12	.16	.79
CaO-----	.10	.13	1.13
Na ₂ O-----	8.38	11.15	5.30
K ₂ O-----	.14	.18	.62
H ₂ O ⁺ -----	6.12	8.95	10.25
H ₂ O ⁻ -----	2.24		
TiO ₂ -----	.06	.08	.04
P ₂ O ₅ -----	.01	.01	.02
MnO-----	.00	.00	.00
CO ₂ -----			.01
Cl-----	.04	.05	
F-----	.01	.01	
Subtotal-----	99.21	99.99	99.86
Less O-----	.01	.01	.00
Total-----	99.20	99.98	99.86
Molecular SiO ₂ :Al ₂ O ₃ +Fe ₂ O ₃ -----		5.40	7.68

Composition of unit cell

[Fe²⁺, Ti, P, and Mn were omitted in calculation of the unit cell]

Si-----	35.00	28.53
Al-----	12.84	7.39
Fe ²⁺ -----	.12	.05
Mg-----	.14	.56
Ca-----	.08	.58
Na-----	12.56	4.91
K-----	.13	.38
H ₂ O ⁺ -----	17.34	16.34
H ₂ O ⁻ -----		
O-----	96.00	72.00
Si+Al+Fe ²⁺ -----	47.96	35.97
Si:Al+Fe ²⁺ -----	2.70	3.83

Analcime.—Lab. No. D100242; field No. M3-105A; separated from a thin tuff about 1,330 ft stratigraphically below the Skyline tuff. Locality: south part of Rainbow Basin, SW1/4SE1/4 sec. 24, T. 11 N., R. 2 W., San Bernardino County, Calif.
Chabazite.—Lab. No. D100593; field No. M4-32F; separated from the upper part of the Hemicyon tuff. Locality: tributary to Fossil Canyon, NE1/4SE1/4 sec. 15, T. 11 N., R. 2 W., San Bernardino County, Calif.

An attempt to correct for the opal impurities was made by utilizing the data of Saha (1959; 1961) on synthetic analcimes. Saha showed that the (639) peak of analcime falls at higher angles (degrees 2θ, CuKα₁ radiation) for analcimes of higher silicon content. Displacement of this (639) peak was measured against the (331) peak of a silicon internal standard. The compositions and corresponding displacements of the (639) peak for the synthetic analcimes (Saha, 1961, p. 865) were replotted and are given in figure 9. The displacement of the (639) peak for the analyzed specimen was then measured and the SiO₂ content calculated from figure 9. Excess SiO₂ in the original analysis is assumed to be in the opal inclusions. Subtraction of this excess SiO₂ from the original analysis and recalculation of the analysis to 100 percent resulted in the corrected analysis that is given in table 5. This corrected analysis was recalculated into atoms per unit cell, on the basis of 96 oxygen atoms, and is also given in table 5.

The composition of analcime from 24 other tuffs was determined by measurement of the displacement of the (639) peak (figs. 9 and 10). These analcimes show a compositional range of (NaAl)_{15.2}Si_{132.8}O₉₆·nH₂O to (NaAl)_{12.6}Si_{35.4}O₉₆·nH₂O. Thus, the analcimes from tuffs of the Barstow Formation range in Si:Al ratio from about 2.2 to 2.8. Coombs and Whetten (1967) studied analcimes from many sedimentary environments and determined a range in Si:Al ratio of about 2.0–2.7.

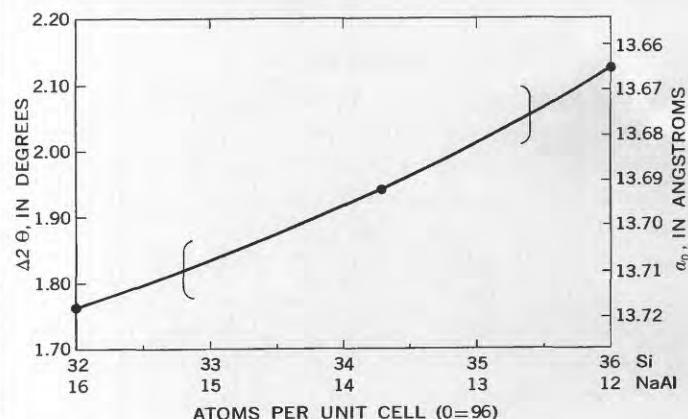


FIGURE 9.—Determinative curve for the anhydrous composition of analcime from X-ray diffractometer data. Dots are replotted from the data of Saha (1961) for synthetic analcimes. Δ2θ is the 2θ of the (639) peak for analcime minus the 2θ of the (331) peak for the silicon internal standard. Radiation is CuKα₁. The brackets show the compositional range of analcime from tuffs of the Barstow Formation.

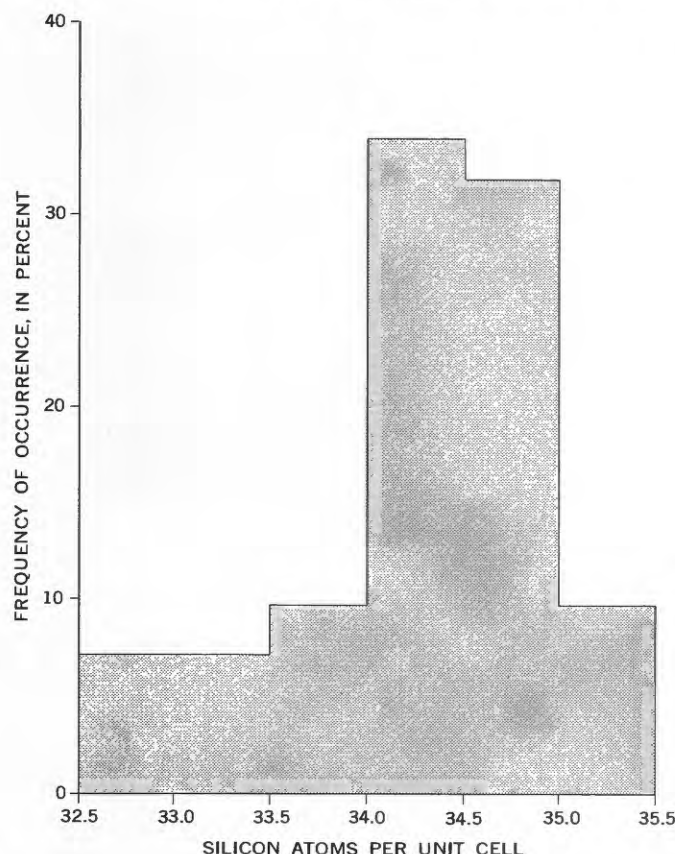


FIGURE 10.—Histogram showing the distribution of the silicon content of analcime in 41 samples from 25 tuffs of the Barstow Formation. Composition of analcime determined from X-ray diffractometer data by measurement of the displacement of the (639) peak of analcime.

CHABAZITE

Chabazite was unknown in sedimentary deposits prior to its discovery by Hay (1964, p. 1377) in tuffs and tuffaceous clays at Olduvai Gorge, Tanzania. Since then, authigenic chabazite has been recognized in tuffs from Arizona (Sand and Regis, 1966), Nevada (Hoover and Shepard, 1965), and Oregon (Gude and Sheppard, 1966, p. 914), as well as in the Barstow Formation. The physical properties and chemistry of these chabazites differ from that of the common chabazite that occurs in cavities of mafic igneous rocks. Chabazite has an ideal formula of $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 12\text{H}_2\text{O}$, but natural chabazites show considerable variation in cation content and Si:Al ratio (table 4).

The chabazite of the Barstow Formation rarely occurs in monomineralic beds. Generally it is associated with clay minerals and the following zeolites: Clinoptilolite, erionite, mordenite, and, rarely, analcime. Authigenic quartz or opal are rarely associated with the chabazite in altered tuffs. Most of the chabazite-bearing

tuffs in the formation also contain relict glass; however, the other authigenic zeolites of the formation are rarely associated with relict glass. The chabazite occurs as aggregates of anhedral crystals that are 0.002–0.05 mm in size.

The mean index of refraction ranges from 1.461 to 1.468, and the birefringence is about 0.002. This compares with a range of 1.470–1.494 given by Deer, Howie, and Zussman (1963, p. 387) for chabazite from nonsedimentary environments.

An analysis of chabazite from the Barstow Formation is given in table 5. The chabazite was separated from a nearly monomineralic part of the Hemicyon tuff. The analysis was recalculated into atoms per unit cell, on the basis of 72 oxygen atoms, and this is also given in table 5. Monovalent cations exceed divalent ones, and the Si:Al + Fe⁺³ ratio (3.83) is much higher than that for ideal chabazite. Gude and Sheppard (1966, p. 914) attributed the relatively low indices of refraction ($\alpha=1.460$, $\gamma=1.462$) and small cell dimensions ($a=13.712 \pm 0.001$ Å, $c=14.882 \pm 0.002$ Å) of this analyzed specimen to its high silicon content.

CLAY MINERALS

Most altered tuffs in the Barstow Formation contain authigenic clay minerals, and some consist predominantly of clay minerals. The clay mineralogy of the finer than 2μ fraction for seven samples was determined by Paul D. Blackmon using the standard X-ray techniques described previously. Montmorillonite occurs in all samples, commonly with trace to minor amounts of mixed-layer illite-montmorillonite. A sample of the Yellow tuff also contains illite as well as montmorillonite and mixed-layer illite-montmorillonite. Montmorillonite is generally the predominant clay mineral reported in altered tuff; however, illite and mixed-layer illite-montmorillonite are known from tuffs subjected to diagenesis (Schultz, 1963).

CLINOPTILOLITE

Clinoptilolite is a member of the heulandite structural group (Hay, 1966, p. 11). Although there is still some disagreement on the distinction between these closely related zeolites, most workers agree that clinoptilolite is the silicon-rich (Hey and Bannister, 1934; Mumpton, 1960) and alkali-rich (Mason and Sand, 1960) member. Indices of refraction (Mason and Sand, 1960, p. 350) and reaction to thermal treatment (Mumpton, 1960, p. 359–361; Shepard and Starkey, 1964) have also been used to distinguish clinoptilolite from heulandite.

Clinoptilolite is a very common zeolite in tuffs of the Barstow Formation, where it ranges in content from trace amounts to nearly 100 percent. The clinoptilolite is associated with each of the other zeolites and with one or more of the following authigenic silicate minerals: Clay minerals, potassium feldspar, opal, and quartz. The clinoptilolite occurs as prismatic or platy crystals that are 0.005–0.25 mm long; however, most clinoptilolite is 0.01–0.02 mm long.

The mean index of refraction ranges from 1.471 to 1.482 and is within the range considered by Mason and Sand (1960, p. 350) to be characteristic of clinoptilolite. Most clinoptilolites from tuffs of the Barstow Formation have a mean index of refraction less than 1.476. The birefringence is low, about 0.003. All clinoptilolites examined have parallel extinction and, except for the rims of some large zoned crystals, are length slow.

Large crystals, 0.04–0.25 mm long, in some tuffs are zoned. The zoned crystals generally consist of a uniform core and a progressively zoned rim (fig. 11). The core is length slow, but the rim is length fast. The index of refraction of the rim is as much as 0.010 higher than

that of the core. Electron microprobe analyses of two large zoned clinoptilolites by R. C. Surdam (written comm., 1967) showed that the rim contains 2.9–3.5 weight percent less SiO_2 than the core. Some large crystals show oscillatory zoning (fig. 12), but no attempt was made to study the differences in the index of refraction across the zones.

Three chemical analyses of clinoptilolite from the Barstow Formation are given in table 6. The analyses were recalculated into atoms per unit cell, on the basis of 72 oxygen atoms, and these are also given in table 6. Monovalent cations exceed divalent ones, and the $\text{Si}:\text{Al}+\text{Fe}^{+3}$ ratio is 4.20–4.37. Sodium exceeds potassium, as is generally true for clinoptilolite; however, potassium-rich clinoptilolites have been reported from other areas (Minato, 1964; Sheppard and others, 1965, p. 247).

The BaO content of clinoptilolite 2 is unusual, and the barium may be present as barite impurities. The analyzed separate contained minor barite that was recognizable in immersion oil grain mounts. An attempt

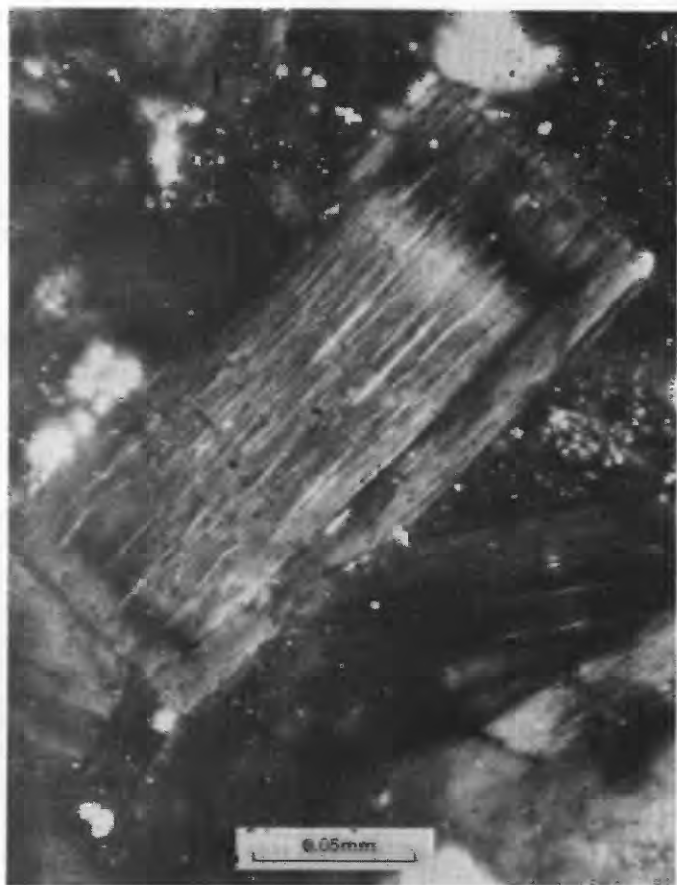


FIGURE 11.—Photomicrograph of large zoned clinoptilolite crystal, showing uniform core and progressively zoned rim. Crossed nicols.

336-374 O-69—3



FIGURE 12.—Photomicrograph of zeolitic tuff, showing oscillatory zoning in relatively large crystals of clinoptilolite. Crossed nicols.

TABLE 6.—*Chemical analyses and composition of unit cell of clinoptilolite*[a, in column head, uncorrected analysis; b, analysis corrected for CO₂ plus equivalent CaO to make calcite or for SO₃ plus equivalent BaO to make barite]

	1		2		3
	a		a	b	a b
Chemical analyses					
[Analyst: Ellen S. Daniels]					
SiO ₂ -----	63. 69	64. 38	64. 70	64. 23	64. 71
Al ₂ O ₃ -----	12. 47	12. 37	12. 43	12. 20	12. 29
Fe ₂ O ₃ -----	. 62	. 44	. 44	. 41	. 41
FeO-----	. 02	. 02	. 02	. 03	. 03
MgO-----	1. 42	. 34	. 34	. 74	. 75
CaO-----	2. 25	1. 25	1. 26	1. 83	1. 64
BaO-----		. 78	. 53		
Na ₂ O-----	2. 46	4. 30	4. 32	3. 17	3. 19
K ₂ O-----	1. 80	2. 27	2. 28	3. 97	4. 00
H ₂ O+-----	8. 93	7. 85	7. 89	6. 60	6. 65
H ₂ O-----	5. 97	5. 64	5. 67	6. 11	6. 16
TiO ₂ -----	. 07	. 07	. 07	. 08	. 08
P ₂ O ₅ -----	. 02	. 01	. 01	. 02	. 02
MnO-----	. 01	. 01	. 01	. 00	. 00
CO ₂ -----				. 16	
SO ₃ -----		. 13			
Cl-----	. 03	. 01	. 01	. 01	. 01
F-----	. 02	. 01	. 01	. 05	. 05
Subtotal-----	99. 78	99. 88	99. 99	99. 61	99. 99
Less O-----	. 02	. 00	. 00	. 02	. 02
Total-----	99. 76	99. 88	99. 99	99. 59	99. 97
Molecular SiO ₂ :Al ₂ O ₃ + Fe ₂ O ₃ -----	8. 40		8. 64		8. 75

Composition of unit cell[Fe⁺², Ti, P, and Mn were omitted in calculation of the unit cell]

Si-----	28. 99	29. 19	29. 09
Al-----	6. 69	6. 61	6. 51
Fe ⁺³ -----	. 21	. 15	. 14
Mg-----	. 96	. 23	. 50
Ca-----	1. 10	. 61	. 79
Ba-----		. 09	
Na-----	2. 17	3. 78	2. 78
K-----	1. 04	1. 31	2. 30
H ₂ O+-----	13. 56	11. 87	9. 97
H ₂ O-----	9. 06	8. 53	9. 24
O-----	72. 00	72. 00	72. 00
Si+Al+Fe ⁺³ -----	35. 89	35. 95	35. 74
Si:Al+Fe ⁺³ -----	4. 20	4. 32	4. 37

1.—Lab. No. D100555; field No. SM-6-5C; separated from the Hemleyon tuff. Locality: tributary to Fossil Canyon, NW1/4NE1/4 sec. 15, T. 11 N., R. 2 W., San Bernardino County, Calif.

2.—Lab. No. D100554; field No. SM-4-4A; separated from the Skyline tuff. Locality: about 1 mile east of mouth of Owl Canyon, NW1/4NE1/4 sec. 29, T. 11 N., R. 1 W., San Bernardino County, Calif.

3.—Lab. No. D100594; field No. SM-4-11-I; separated from a tuff about 525 ft stratigraphically below the Skyline tuff. Locality: about 1 mile east of Owl Canyon, SW1/4SE1/4 sec. 20, T. 11 N., R. 1 W., San Bernardino County, Calif.

was made to correct the chemical analysis for the barite by subtracting the SO₃ content plus an equivalent amount of BaO to make barite. The excess BaO, 0.53 per cent, is presumed to be in the clinoptilolite. If the SO₃ content of the analysis is in error and is low, some, or perhaps all, of the excess BaO may be in additional barite.

ERIONITE

Erionite was considered an extremely rare mineral prior to the work of Deffeyes (1959a, b) and Regnier (1960, p. 1207), who showed it to be a common authigenic zeolite in altered rhyolitic vitric tuffs in north-central Nevada. Since then, erionite has been recognized in altered tuffs from many of our Western States.

Erionite in the altered tuffs of the Barstow Formation is associated with each of the other zeolites but is more commonly associated with clinoptilolite. The erionite is also commonly associated with authigenic clay minerals but rarely associated with authigenic quartz or opal. The erionite content of an altered tuff is generally 20 percent or less. Like most erionite of sedimentary deposits (Hay, 1966, p. 10), erionite of the Barstow Formation is acicular or prismatic. Individual crystals are 0.006–0.04 mm long. Erionite rarely occurs in aggregates of radiating crystals.

Indices of refraction for erionite are $\omega=1.461$ – 1.465 and $\epsilon=1.465$ – 1.469 . These indices are lower than those reported by Deer, Howie, and Zussman (1963, p. 398) and may be due to a relatively high silicon content of the Barstow erionite. Birefringence is 0.004, higher than that of the other associated zeolites. The erionite shows parallel extinction and is length slow.

Inasmuch as erionite occurs in small amounts and invariably is associated with some other zeolite in the altered tuffs, no attempt was made to separate material for chemical analysis. Erionite is alkali-rich (table 4) and generally has a Si:Al+Fe⁺³ ratio range of 3.0–3.5 (Hay, 1966, p. 9).

MORDENITE

Mordenite has been confused with clinoptilolite or heulandite in sedimentary rocks because of their similar indices of refraction and chemistry (Coombs and others, 1959, p. 69; Shumenko, 1962). X-ray diffractometer techniques, fortunately, are adequate for positive identification (fig. 2). In recent years, mordenite has commonly been identified in Cenozoic tuffaceous rocks from several areas of the Western United States (Moiola, 1964; Sheppard and Gude, 1964; Curry, 1965; Hoover and Shepard, 1965; Surdam and Hall, 1968).

Mordenite in the altered tuffs of the Barstow Formation is associated with each of the other zeolites, but it

is more commonly associated with clinoptilolite. Mordenite is also associated with authigenic clay minerals and rarely with authigenic quartz, opal, or potassium feldspar. The mordenite content of an altered tuff generally is 20 percent or less and only rarely is as much as 40 percent. Mordenite crystals are acicular or prismatic and generally 0.01–0.04 mm long. They commonly are larger than the crystals of other associated zeolites.

Indices of refraction for mordenite are fairly constant and are within the lower part of the range (1.472–1.487) given by Deer, Howie, and Zussman (1963, p. 401). The mean index ranges from 1.474 to 1.478 and the birefringence is low, about 0.003. All mordenites examined have parallel extinction and are length fast.

An analysis of mordenite from the Barstow Formation is given in table 7. The mordenite was separated from a nearly monomineralic tuff about 4 feet above the Skyline tuff in the western part of the Mud Hills. The analysis was recalculated into atoms per unit cell, on the basis of 48 oxygen atoms and is given in table 7. Monovalent cations exceed divalent ones and the Si:Al+Fe³⁺ ratio is 4.71. Sodium exceeds potassium as is true for most mordenites regardless of genesis. However, a potassic mordenite was recently found in tuffs of the Miocene Obispo Formation of Surdam and Hall (1968) in southern California.

OPAL

Opal is difficult to recognize in altered tuffs because of its isotropic and nondescript character. Opal is colorless to pale brown in thin section and has an index of refraction near 1.46. Most identifications of opal from the Barstow Formation are based on X-ray diffractometer powder data of bulk samples. The opal has characteristically broad peaks at the following *d* spacings: 4.26 Å, 4.09 Å, and 3.82 Å. Opal is commonly associated with clinoptilolite and clay minerals and rarely associated with chabazite, mordenite, and erionite. Segregations containing as much as 70 percent opal are locally common.

PHILLIPSITE

Phillipsite has long been known to occur in deposits on the sea floor (Murray and Renard, 1891, p. 400–411). Since the discovery by Deffeyes (1959a) of phillipsite in altered rhyolitic tuffs of Nevada, this zeolite has been commonly reported as a rock-forming constituent of tuffs deposited in saline lakes (Hay, 1964).

The phillipsite in tuffs of the Barstow Formation is commonly associated with clinoptilolite and analcime and less commonly associated with erionite and mordenite.

TABLE 7.—Chemical analyses and composition of unit cell of mordenite and phillipsite

[a, in column head, uncorrected analysis; b, analysis corrected for CO₂ plus equivalent CaO to make calcite, and for SO₃ plus BaO to make barite]

	Mordenite	Phillipsite	
	a	a	b
Chemical analyses [Analyst: Ellen S. Daniels]			
SiO ₂	66.31	55.18	56.60
Al ₂ O ₃	11.52	14.97	15.35
Fe ₂ O ₃67	.41	.42
FeO.....	.02	.00	.00
MgO.....	.54	.26	.27
CaO.....	2.58	.20	.07
BaO.....		1.47	
Na ₂ O.....	3.09	6.77	6.95
K ₂ O.....	.96	3.39	3.48
H ₂ O+.....	8.46	9.40	9.64
H ₂ O-.....	5.50	6.73	6.90
TiO ₂12	.25	.26
P ₂ O ₅00	.01	.01
MnO.....	.00	.00	.00
CO ₂10	
SO ₃78	
Cl.....	.09	.04	.04
F.....	.02	.01	.01
Subtotal.....	99.88	99.97	100.00
Less O.....	.03	.01	.01
Total.....	99.85	99.96	99.99
Molecular SiO ₂ :Al ₂ O ₃ + Fe ₂ O ₃	9.42		6.15

Composition of unit cell

[Fe²⁺, Ti, P, and Mn were omitted in calculation of the unit cell]

Si.....	19.78	12.06
Al.....	4.05	3.85
Fe ³⁺15	.07
Mg.....	.24	.09
Ca.....	.82	.02
Na.....	1.79	2.87
K.....	.37	.94
H ₂ O+.....	8.42	6.85
H ₂ O-.....	5.47	4.90
O.....	48.00	32.00
Si+Al+Fe ³⁺	23.98	15.98
Si:Al+Fe ³⁺	4.71	3.08

Mordenite.—Lab. No. D100551; field No. M4-54B; separated from a tuff 4 ft stratigraphically above the Skyline tuff. Locality: about 1 mile north of Fossil Canyon, NW1/4SE1/4 sec. 9, T. 11 N., R. 2 W., San Bernardino County, Calif.

Phillipsite.—Lab. No. D100592; field No. M4-5A; separated from the lower part of the Yellow tuff. Locality: west wall of Owl Canyon, NW1/4SW1/4 sec. 19, T. 11 N., R. 1 W., San Bernardino County, Calif.

nite. The association of phillipsite with chabazite has not been recognized in these tuffs, although this association has been noted in tuffs from other areas (Hay, 1964, p. 1377; Sheppard and Gude, 1968). Phillipsite is also commonly associated with authigenic clay minerals and potassium feldspar and rarely associated with authigenic quartz.

Most of the phillipsite occurs as spherulites in the altered tuffs, although prismatic crystals 0.01–0.02 mm long occur locally. The spherulites range in diameter from 0.04 to 1.0 mm, but most are 0.1–0.3 mm (fig. 13). Clusters of several mutually interfering spherulites are common, and many spherulites are malformed.

Indices of refraction for phillipsite vary considerably, much more than for any other zeolite in the Barstow Formation. The mean index ranges from 1.448 to 1.476, and the birefringence is very low, about 0.002. Most of the phillipsites have a mean index between 1.460 and 1.470. The spherulites generally are zoned; the outer part of the spherulite invariably has a higher index. A difference in index of as much as 0.018 has

been measured between the interior and exterior parts. All phillipsites have parallel or nearly parallel extinction, and except for one specimen, are length slow. The length-fast phillipsite has the highest (1.476) mean index of refraction that was measured.

These indices of refraction for phillipsite from the Barstow Formation are similar to those of phillipsites from saline lakes (Hay, 1964, p. 1374), but are much lower than those of phillipsite from other environments. Deer, Howie, and Zussman (1963, p. 386) reported a range of 1.483–1.514 for presumably nonsedimentary phillipsites.

A chemical analysis of spherulitic phillipsite that was separated from the Yellow tuff is given in table 7. The analysis was corrected for barite and calcite impurities associated with the phillipsite. The corrected analysis was then recalculated into atoms per unit cell, on the basis of 32 oxygen atoms, and is given in table 7. Monovalent cations greatly exceed divalent cations and sodium is greatly in excess of potassium. The $\text{Si}:\text{Al}+\text{Fe}^{+3}$ ratio is 3.08 and is much higher than the range of 1.3–2.2 given by Deer, Howie, and Zussman (1963, p. 393) for phillipsite. The high potassium plus sodium and silicon contents of this phillipsite distinguish it from phillipsites in nonsedimentary deposits. However, the analysis is very similar to analyses of phillipsites from altered rhyolitic tuffs in lacustrine deposits of southern California (Hay, 1964, p. 1375; Sheppard and Gude, 1968), and southeastern Oregon (Regis and Sand, 1966). Phillipsite from the Barstow Formation does differ from other similar phillipsites by its high sodium content.

POTASSIUM FELDSPAR

Potassium feldspar occurs as an authigenic mineral in sedimentary rocks that are diverse in lithology, depositional environment, and age (Hay, 1966). The authigenic feldspar is a pure or nearly pure potassium variety and may occur as authigenic crystals or overgrowths or replacements of plagioclase. The authigenic potassium feldspar in tuffs of the Barstow Formation occurs chiefly as authigenic crystals and only rarely as overgrowths or replacements of plagioclase. The feldspar occurs in monomineralic beds or associated with one or more of the following authigenic minerals: Quartz, clay minerals, analcime, clinoptilolite, morde-nite, and phillipsite. The association of potassium feldspar with analcime and clay minerals is especially common. Nowhere in the Barstow Formation has authigenic feldspar been found associated with relict glass.

Potassium feldspar occurs in the altered tuffs as low-birefringent aggregates of crystals that range in size from less than 0.002 mm to about 0.01 mm. Paul D. Blackmon, using electron microscopy, has shown that



FIGURE 13.—Photomicrograph of spherulitic phillipsite in altered tuff. Matrix consists of clay minerals and minor potassium feldspar. Arrow indicates relict shard outlined by clay mineral. Crossed nicols.

the crystals are subhedral to euhedral and generally less than 0.005 mm in size (fig. 14). The feldspar is identical with authigenic potassium feldspar from sediments of Searles Lake, Calif. (Hay and Moiola, 1963, p. 323), and altered tuffs of Pleistocene Lake Tecopa, Inyo County, Calif. (Sheppard and Gude, 1968). The mean index of refraction is 1.518 which suggests nearly pure potassium feldspar. Other optical data could not be obtained because of the small size of the crystals.

The feldspar is monoclinic inasmuch as X-ray diffractometer patterns of powders show only the (131) peak rather than the pair, (131) and ($\bar{1}\bar{3}\bar{1}$), the criterion suggested by Goldsmith and Laves (1954, p. 3) for distinguishing monoclinic from triclinic potassium feldspar. The following cell constants were refined on a digital computer by least-squares analysis of X-ray diffractometer powder data:

$$a = 8.593 \pm 0.002 \text{ \AA}$$

$$b = 12.967 \pm 0.003 \text{ \AA}$$

$$c = 7.165 \pm 0.001 \text{ \AA}$$

$$\beta = 116^\circ 3.3' \pm 1.0'$$

$$\text{Cell volume} = 717.25 \pm 0.19 \text{ \AA}^3$$

The structural state estimated from the b and c cell edges is that of sanidine, but the cell seems to be distorted (D. B. Stewart, 1965, written commun.).

QUARTZ

Authigenic quartz is a common constituent in the altered tuffs and is associated with all the other authigenic silicate minerals except opal. Quartz is commonly associated with analcime and potassium feldspar, less commonly associated with clay minerals and clinoptilolite, and only rarely associated with the other zeolites.

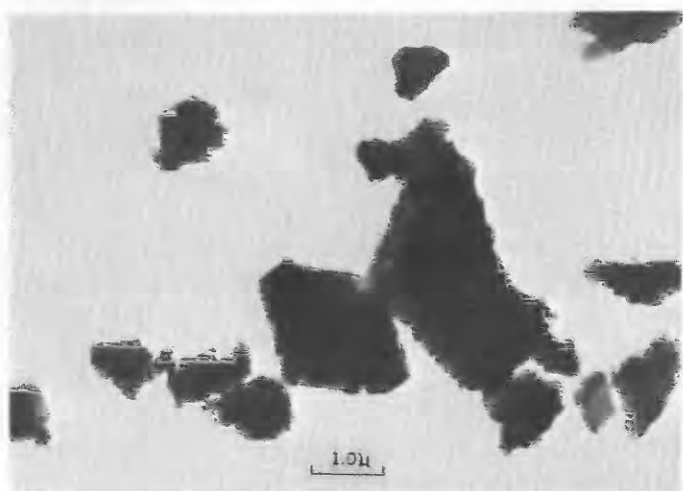


FIGURE 14.—Electron micrograph of potassium feldspar, showing subhedral to euhedral outlines of crystals. Electron micrograph by Paul D. Blackmon.

Some bulk samples contain as much as 80 percent quartz.

The quartz occurs as veinlets and spheroidal or irregular segregations of anhedral crystals 0.005–0.2 mm in size. The spheroidal segregations are 0.25–2.0 mm in diameter (fig. 15). Some quartz is evidently chalcedonic, because it occurs in fibrous aggregates and has indices of refraction below 1.54. The X-ray diffractometer powder pattern of this material is identical with that of quartz.

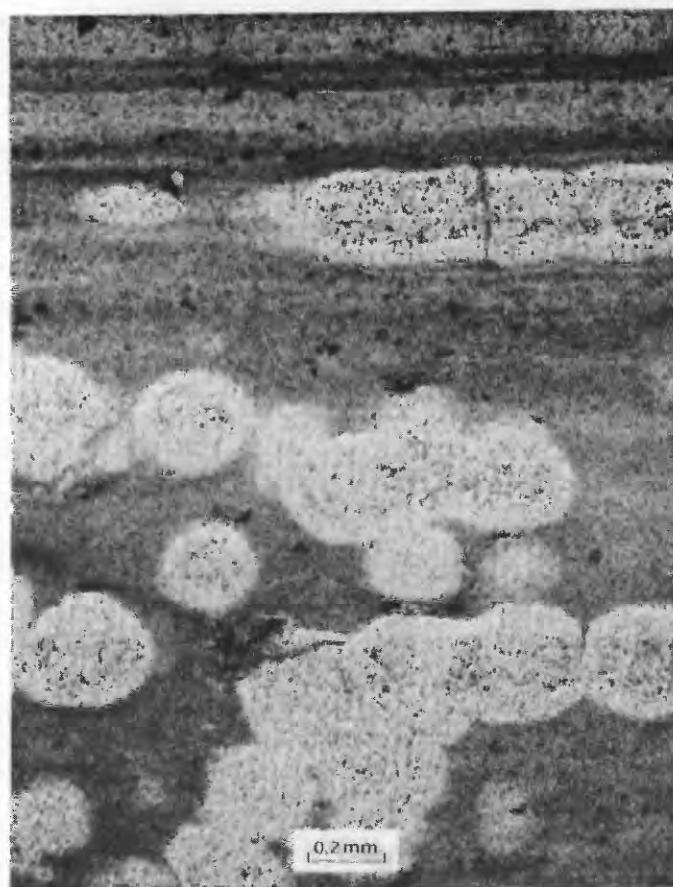


FIGURE 15.—Photomicrograph of sample from upper part of the Skyline tuff. Tuff has been replaced by finely crystalline potassium feldspar (gray) and spheroidal segregations of anhedral quartz (white). Unpolarized light.

ALTERED TUFFS

FIELD DESCRIPTION

All tuffs in the Barstow Formation of the Mud Hills are altered, at least in part. Relict glass is rare, but parts of some tuffs contain as much as 90 percent relict glass. The altered tuffs are generally white to pale gray or pastel shades of yellow, brown, or green with a dull or earthy luster. Relict vitric material, if present, can be recognized by its distinct vitreous luster. Altered tuffs are resistant and form ledges (fig. 16). Original textures



FIGURE 16.—View looking west along the north limb of the Barstow syncline at Rainbow Basin, showing resistant hogbacks formed by altered tuffs. Tuff near the center of the photograph is the Skyline tuff.

and sedimentary structures, such as crossbedding and ripple marks, are generally preserved in the altered tuffs. Preservation of these features is convincing evidence that the present differences in composition and mineralogy of the tuffs are due to postdepositional processes.

Authigenic silicate minerals in the altered tuffs generally cannot be positively identified in the field because of the very small size of the crystals. If the altered tuff is nearly monomineralic, certain gross physical properties of the rock may aid field identification. On this basis, then, the following tuffs generally can be recognized: Tuffs that contain a zeolite other than analcime, tuffs that are analcime rich, and tuffs that are potassium feldspar rich. Certain of the nonanalcimic zeolitic tuffs commonly can be further differentiated.

Those tuffs that are nonanalcimic are relatively hard and generally show good preservation of the original vitroclastic texture. Tuffs rich in clinoptilolite commonly are white to pale gray, very well indurated, and low in porosity, and they generally break with a blocky to conchoidal fracture (fig. 17). Phillipsite-rich tuffs are generally yellow and characteristically are spherulitic. Phillipsite is the only authigenic silicate mineral in the altered tuffs that is spherulitic. Tuffs rich in mordenite generally cannot be distinguished from clinoptilolite-rich ones; however, the former tend to be more porous and break with an irregular or blocky fracture rather than a conchoidal fracture. Tuffs rich in erionite or chabazite cannot be distinguished from one another; however, they commonly can be distinguished from clinoptilolite- or mordenite-rich tuffs by their greater porosity and irregular fracture.

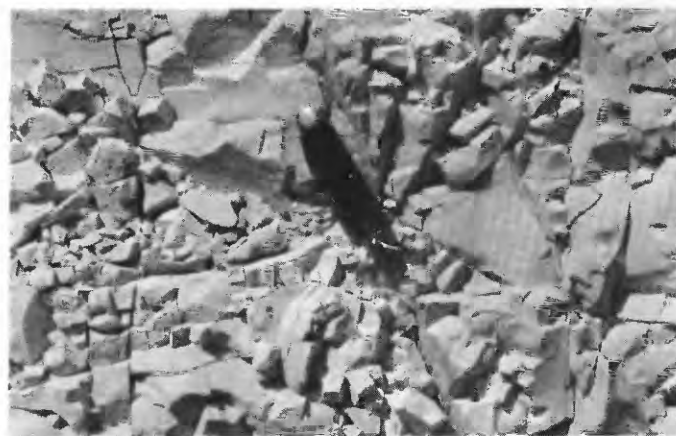


FIGURE 17.—Clinoptilolite-rich part of the Skyline tuff, showing typical blocky and conchoidal fractures.

Tuffs that contain mostly analcime are porous, friable, and generally a pastel shade of green, yellow, or brown. Perhaps the most characteristic features are their sugary texture and poor preservation of the original vitroclastic texture. Individual euhedra of analcime commonly can be seen with a hand lens. Analcimic tuffs break with an irregular fracture or, more rarely, a blocky fracture.

Tuffs replaced mainly by potassium feldspar are porous, very friable, punky, and white to pale green. If only minor authigenic quartz is associated with the feldspar, the tuffs can be disaggregated with the fingers. The feldspar-rich tuffs generally break with an irregular fracture and show poor preservation of the original vitroclastic texture.

PETROGRAPHY

The authigenic mineralogy of the altered tuffs was determined chiefly by study of X-ray diffractometer powder data of bulk samples, supplemented by thin-section and oil-immersion study. Thin sections were especially useful for determining the age relationship of the authigenic minerals; however, they generally were not examined until the mineralogy of the altered tuffs was known by X-ray methods. Optical identification of the zeolites is particularly difficult because of their small crystal size and similar optical properties and habits.

Crystal fragments, unlike vitric material, in the altered tuffs generally are unaltered. However, plagioclase locally is replaced by analcime or potassium feldspar; and plagioclase, biotite, and rarely hornblende are locally replaced by calcite. Hornblende and apatite locally show marginal solution.

NONANALCIMIC ZEOLITIC TUFF

The vitroclastic texture is preserved in most tuffs that are chiefly zeolites other than analcime. Some zeolitic tuffs lack relict texture or have only vague ghosts of shards where the zeolite is coarsely crystalline or where authigenic clay minerals are absent. Typical pseudomorphs of bubble-wall shards consist of a thin marginal film of montmorillonite that is succeeded inward by crystals of one or more zeolites (fig. 18). The pseudomorphs may be either solid or hollow, and commonly both occur in the same specimen. The larger pseudomorphs commonly are the hollow ones. Hollow pseudomorphs characteristically consist of the marginal clay film succeeded inward by a single layer of zeolite (commonly clinoptilolite) crystals that are oriented perpendicular to the shard wall (fig. 19). The solid pseudomorphs are of two types: those in which the single layer of zeolite grew until crystals from opposite walls joined in the central part of the shard, and those which resemble the hollow pseudomorphs except that what was the central cavity is now filled with another zeolite, quartz, or calcite (fig. 19). The zeolite of the central filling is generally more coarsely crystalline than the marginal zeolite and is randomly oriented. Some pseudomorphs still have a small central cavity (fig. 20) even though a second zeolite grew on the marginal layer of zeolite crystals.

Spherulites of phillipsite are characteristic of the Yellow tuff. The spherulites (fig. 13) resemble oolites except that they have a radial internal structure rather than a concentric structure that is so characteristic of

oolites. The spherulites lack nuclei, but some have engulfed scattered pyrogenic crystals during their growth. Most spherulites are malformed. The spherulites commonly enclose ghosts of shards that are outlined by a continuous or discontinuous film of montmo-

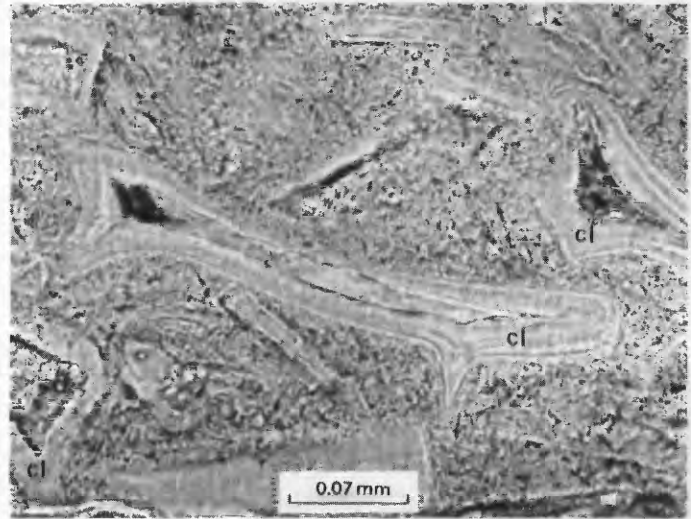


FIGURE 19.—Photomicrograph of zeolitic tuff, showing pseudomorphs of fibrous clinoptilolite (cl) after shards. The bands in the clinoptilolite are due to variations in the index of refraction along the length of the fibers. The large pseudomorph in the center of the photograph has a hollow interior. Other pseudomorphs are filled with calcite (co). A thin outer film of montmorillonite surrounds the pseudomorphs but is not obvious. Matrix is finely crystalline clinoptilolite and montmorillonite. Unpolarized light.

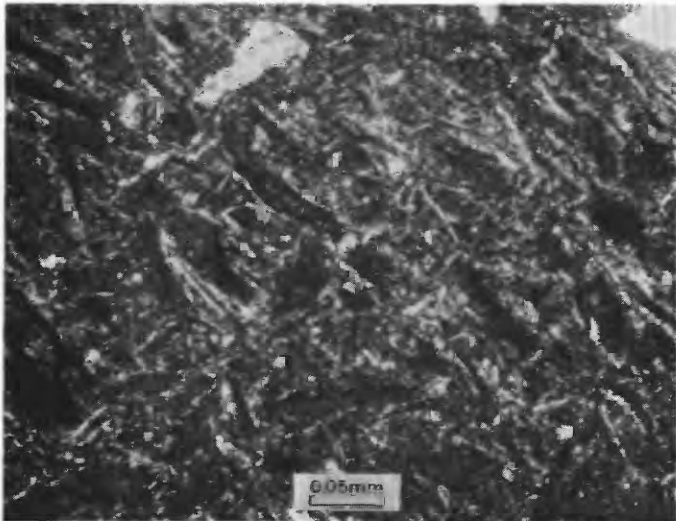


FIGURE 18.—Photomicrograph of zeolitic tuff, showing pseudomorphs of platy bubble-wall shards that consist of an outer film of montmorillonite (light) and a filling of clinoptilolite (dark). Matrix is finely crystalline clinoptilolite and montmorillonite. Crossed nicols.

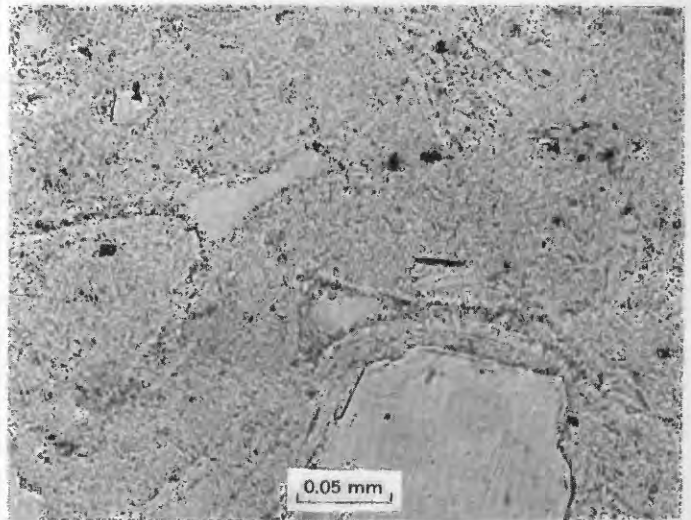


FIGURE 20.—Photomicrograph of zeolitic tuff, showing pseudomorphs of shards that contain a prismatic layer of clinoptilolite and an interior filling of randomly oriented mordenite. Matrix is chiefly clinoptilolite with minor montmorillonite. Large crystal in lower part of photograph is a pyrogenic feldspar. Unpolarized light.

rillonite. Individual fibers of phillipsite pass undistorted through these relict shards. The same alinement of relict shards persists within the spherulites of a bed and attests to the formation of the spherulites during diagenesis rather than by direct precipitation on the lake floor.

The stages of alteration of fresh vitric tuff to zeolitic tuff can be observed by thin-section study of the Hemicyon tuff. The earliest recognizable alteration is the development of a thin film of montmorillonite that envelops the shards. An advanced stage shows only the large vitric particles that are enclosed by a montmorillonite film and set in a matrix of finely crystalline zeolite and montmorillonite. The finer glass particles apparently alter before the coarser ones. Pumice shards commonly are altered to a greater degree than platy bubble-wall shards of comparable size, probably because of their greater porosity and surface exposure. A more advanced altered variant consists of ragged remnants of large glassy shards "floating" in a matrix of zeolite and montmorillonite. The small shards are pseudomorphed by zeolite and montmorillonite. A final stage shows zeolite and montmorillonite pseudomorphs after shards in a finely crystalline matrix of the same minerals. The smaller pseudomorphs generally are solid, but the larger ones commonly are hollow.

Thin-section study indicates that at least some of the zeolite pseudomorphs formed by crystallization of the zeolite(s) in cavities from which the glass had been dissolved. The hollow pseudomorphs, such as those illustrated in figures 19 and 20, are difficult to explain in any other way. Other zeolite replacements probably were formed contemporaneously with solution of the glass, but convincing evidence is lacking.

The paragenesis of the authigenic silicate minerals in the zeolitic tuffs can be ascertained by studying the sequence of filling of the shard cavities and by contrasting the mineralogy of the matrix with the mineralogy of the pseudomorphed shards, particularly the larger shards. Presumably, the mineral in the interior of a pseudomorph formed later than the minerals nearer the periphery of the pseudomorph. Those minerals in the finely crystalline matrix are presumed to have crystallized prior to the minerals that compose the large pseudomorphs. The following sequences of crystallization were determined using the above criteria:

Paragenesis of authigenic silicate minerals

[Earliest mineral listed on left]

Montmorillonite—chabazite—clinoptilolite
 Montmorillonite—chabazite—erionite
 Montmorillonite—phillipsite—clinoptilolite
 Montmorillonite—clinolite—mordenite
 Montmorillonite—clinoptilolite—quartz

These relationships indicate that montmorillonite consistently was the earliest silicate mineral to form in the tuffs. Chabazite and phillipsite are early zeolites; but clinoptilolite, erionite, and mordenite are relatively late zeolites. The age relationship between erionite and clinoptilolite and between erionite and mordenite is unknown. According to X-ray diffractometer study, erionite occurs with each; but the critical textural relations were not recognized in thin sections.

ANALCIMIC TUFF

Analcime in the altered tuffs is characteristically subhedral to euhedral and isotropic. Most analcime is pale tan in transmitted light and milky in reflected light because of abundant minute inclusions of opal. Vitroclastic texture in analcimic tuffs is vague and is spotty if at all recognizable. Most nearly monomineralic analcimic tuffs lack any evidence of a relict vitroclastic texture.

X-ray diffractometer study has shown that analcime is associated with each of the other zeolites, but paragenetic relationships could be observed in thin sections for only analcime and clinoptilolite, and analcime and phillipsite. Several specimens of the Skyline tuff clearly show clinoptilolite pseudomorphs after shards that have been replaced by analcime. In the Yellow tuff and a tuff about 750 feet stratigraphically below the Yellow tuff, analcime has replaced spherulites of phillipsite. Remnants of the spherulites can be seen in some thin sections. Analcime has also replaced pyrogenic plagioclase locally in the Dated tuff.

POTASSIUM FELDSPAR-RICH TUFF

Authigenic potassium feldspar occurs in trace to major amounts and is associated with each of the zeolites except chabazite and erionite. The association of potassium feldspar with analcime in the altered tuffs is especially common. Similar to the analcime occurrences, the potassium feldspar is not associated with relict glass. These occurrences contrast with those of the other zeolites which are locally associated with relict glass.

Potassium feldspar generally occurs as aggregates of minute subhedral to euhedral crystals. Relict vitroclastic texture is vague or nonexistent in tuffs or those parts of tuffs where potassium feldspar is abundant. The vitroclastic texture is recognizable in the form of quartz pseudomorphs after shards, remnants of clinoptilolite pseudomorphs after shards, remnants of a clay mineral film that vaguely outline shards, and, rarely, hollow molds of shards.

Thin-section study of tuffs that contain analcime and potassium feldspar shows that the feldspar has formed from the analcime. All stages of the replacement are recognizable: from marginal replacement, that commonly gives the analcime crystals a ragged appearance,

to complete pseudomorphs of finely crystalline potassium feldspar. Locally, the crystal outlines of the pseudomorphed analcime are noticeable because of clay minerals or irresolvable opaque material. Analcimic tuffs generally have a vague vitroclastic texture, and replacement by potassium feldspar causes further degradation or obliteration of the texture.

Formation of potassium feldspar from zeolite precursors is clearly shown by the feldspar replacements of analcime and the occurrence of remnants of clinoptilolite pseudomorphs after shards in a finely crystalline matrix of potassium feldspar. The absence of associated relict glass and potassium feldspar in tuffs of the Barstow Formation strongly suggests that most, if not all, potassium feldspar formed from zeolite precursors rather than directly from glass. Feldspathic tuffs that have a vague vitroclastic texture probably formed from a tuff rich in a zeolite such as clinoptilolite which generally preserves the texture, whereas feldspathic tuffs that lack vitroclastic texture probably formed from analcimic tuffs.

Authigenic potassium feldspar also occurs as over-

growths on plagioclase or as replacements of plagioclase in some feldspar-rich tuffs. The overgrowths (fig. 21) are thin continuous or discontinuous sheaths that characteristically have an irregular outline but are in sharp contact with the plagioclase host. Replacement of plagioclase by potassium feldspar generally is complete, although rare partial replacements have been observed. These partial replacements consist of potassium feldspar surrounding isolated but optically continuous remnants of plagioclase. The complete replacements are generally hollow pseudomorphs; solid pseudomorphs are rare. The hollow pseudomorphs (fig. 22) retain the general shape of the plagioclase grain; however, the outline is very irregular rather than smooth. The hollow pseudomorphs consist of a boxwork of potassium feldspar that extinguishes uniformly. Potassium feldspar in the pseudomorphs, like that of the overgrowths, is untwinned.

CLINOPTILOLITE-ANALCIME-POTASSIUM FELDSPAR RELATIONSHIPS IN THE SKYLINE TUFF

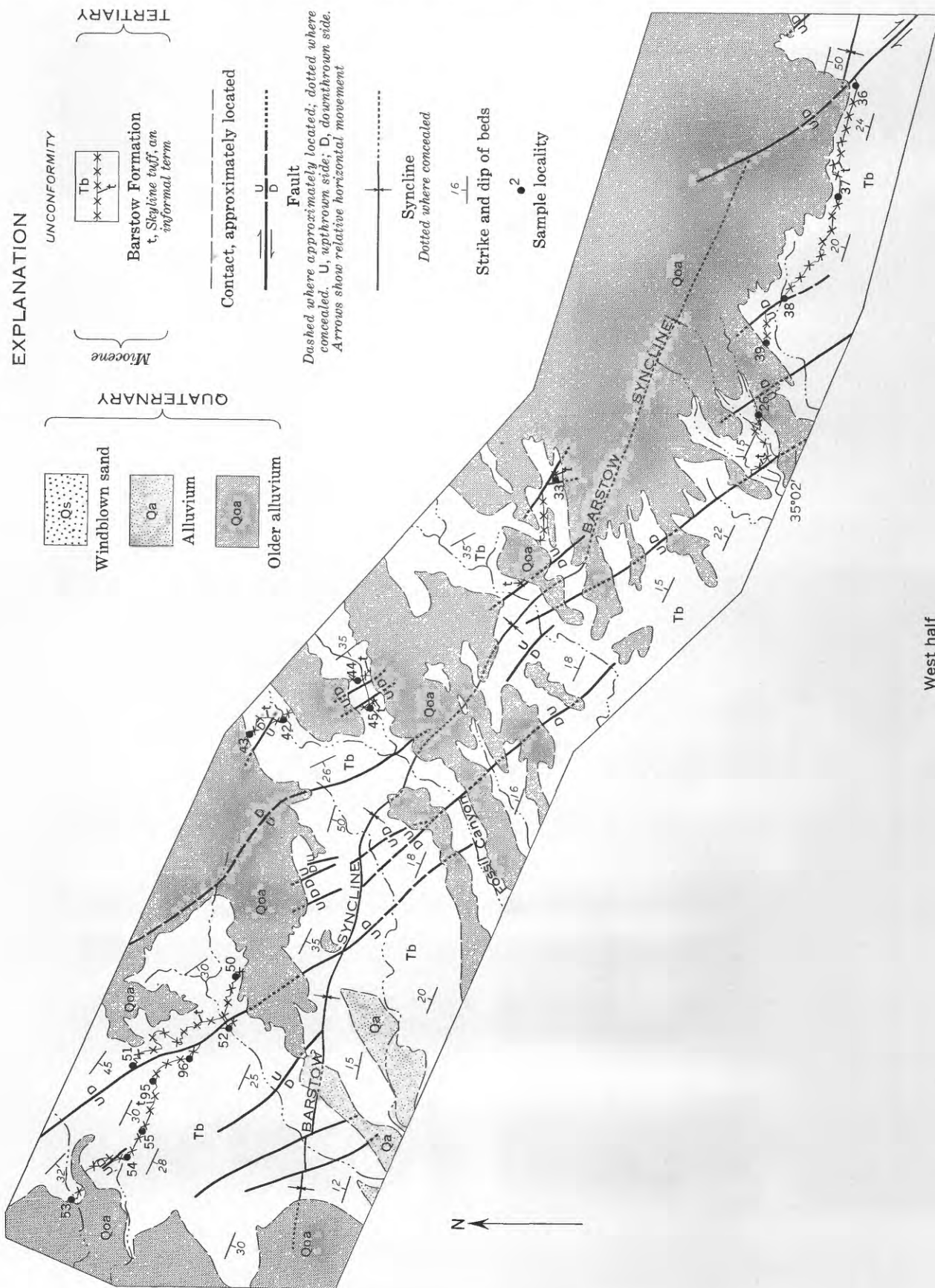
The Skyline tuff is a relatively thick tuff that crops out from one end of the Mud Hills to the other (fig. 23).



FIGURE 21.—Photomicrograph of plagioclase grain (P) with a partial overgrowth of potassium feldspar (K). The overgrowth is untwinned. Matrix is chiefly finely crystalline authigenic potassium feldspar. Crossed nicols.



FIGURE 22.—Photomicrograph of a potassium feldspar pseudomorph after plagioclase, showing typical boxwork structure. Matrix consists of finely crystalline potassium feldspar, clay minerals, and calcite. Crossed nicols.



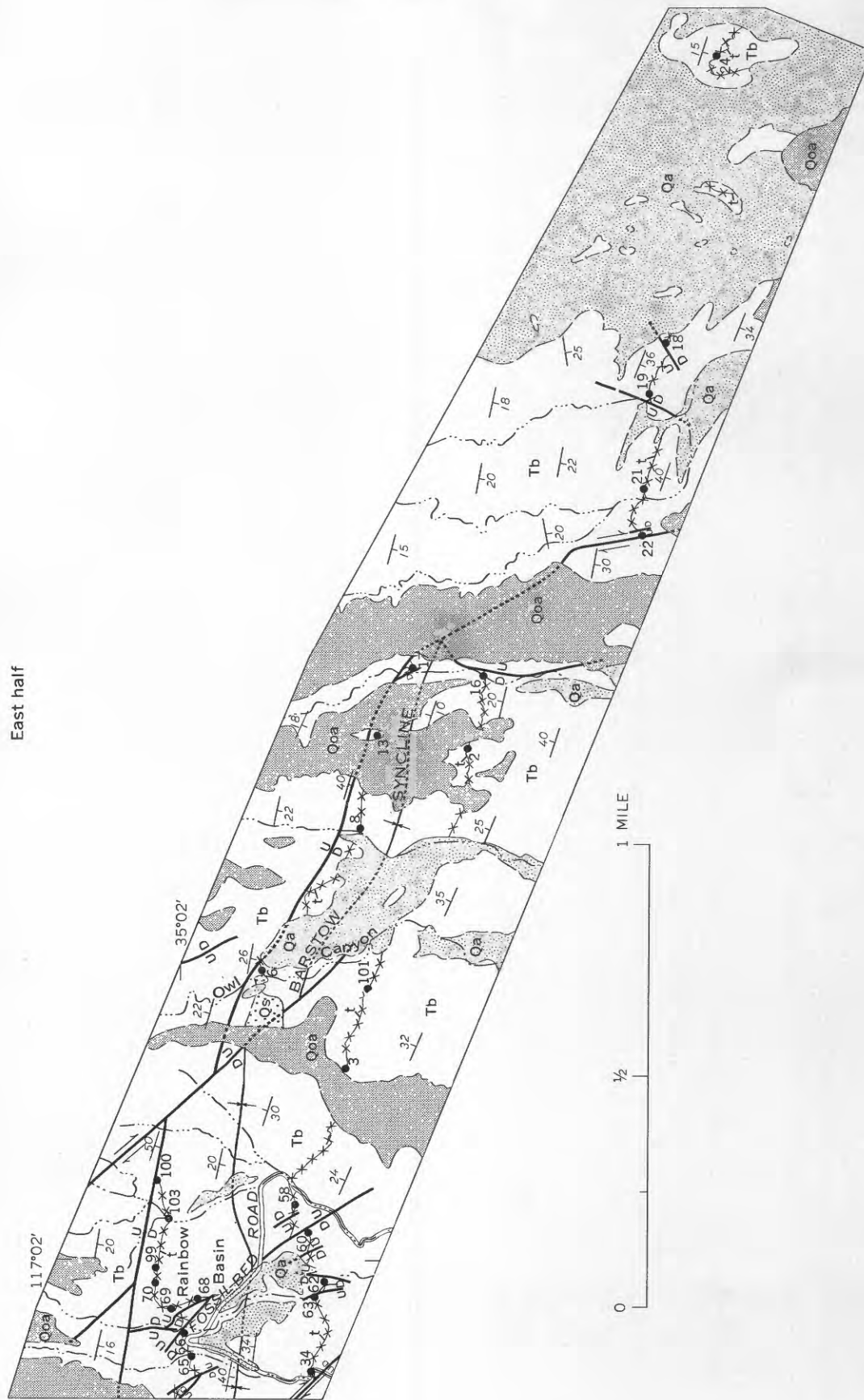


FIGURE 23.—Geologic sketch map of the southern part of the Mud Hills, showing the sampled locations of the Skyline tuff. Mineralogy of samples is given in table 8. Geology mapped by R. A. Sheppard, 1964. Planimetric base from aerial photographs taken December 15, 1962.

In the central part of the Mud Hills, the tuff is chiefly potassium feldspar or potassium feldspar and analcime (Sheppard and Gude, 1965a). The tuff at either end of the Mud Hills is zeolitic and consists chiefly of

clinoptilolite (table 8). Minor erionite or mordenite, and rare phillipsite or chabazite, are locally associated with the clinoptilolite. As much as 30 percent relict glass occurs in parts of the tuff at the westernmost exposure.

TABLE 8.—Mineralogic composition of the Skyline tuff as estimated from X-ray diffractometer patterns of bulk samples

[—, looked for but not found; Tr., trace]

Locality (fig. 23)	Sample	Sample taken	X-ray analysis (parts in 10)											Quartz ³	Calcite	Other ⁴
			Clay, 10 A ¹	Clay, 14 A ²	Chaba- zite	Phillip- site	Erionite	Clinopti- lolite	Morden- ite	Analcime	Potassi- um feld- spar					
2	CT	At top											10			
	CB	22 in. above base		Tr.									10			
	B	8 in. above base		Tr.									10			
	A	At base		5						4			1			
3	D	At top	Tr.										10			
	C	Near middle	Tr.										10			
	A	Near middle, 4 ft west of C	Tr.	1				8			8	Tr.	2			Tr.
	B	At base	Tr.										1			
6	A	8 in. above base	Tr.	Tr.				Tr.					10			
8	A	6 in. above base	1										10			
13	A	6 in. above base	1										9			
16	B	At top		Tr.									10			
	A	6 in. above base		1									9			
17	A	At upper part	1	Tr.									9			
18	B	Near top	Tr.	1												
	A	Near base	Tr.	1												
19	SM-4-4A	At top		Tr.					10							
	4B	Near middle	2	Tr.					7							
	4C	At base							10							
21	A	Near top														
	B	Near middle		1					8				1	9		
22	B	New top	1						7				2	1		
	A	Near middle	Tr.					Tr.	10							
24	B	Near middle	Tr.	1					7							
	A	Near base	Tr.	1					9							
26	C	At top	Tr.	2				Tr.	2							
	B	Near middle		Tr.					1							
	A	At base	Tr.	1					9		3					
33	A	8 in. above base							8							
34	D	At top	Tr.	Tr.					9			2				
	C	72 in. above base	1	1					8		Tr.	1				
	B	40 in. above base	1	1					5		Tr.					
	A	At base	1	Tr.					8		1					
36	C	42 in. above base		Tr.				Tr.	10							
	B	14 in. above base		Tr.					9							
	A	5 in. above base		Tr.					10					1		
37	B	12 in. above base		1					9							
	A	At base							10							
38	C	At upper part		2					6							
	B	At lower part	Tr.						9		2					
39	B	10 in. above base		Tr.					3							
	A	At lower part		Tr.					8							
42	SM-6-2D	At top	Tr.	2					7							
	2C	36 in. above base	1	1			1		7							
	2B	12 in. above base	Tr.	Tr.			Tr.		10							
	2A	At base		1					7		Tr.					
43	A	At lower part	Tr.	3			2		3			2				
44	B	At upper part		2					6							
	A	At base							9							
45	B	18 in. above base		5			1		4							
	A	At base		Tr.					10							
50	B	Near top							9							
	A	At base		1			2		5		1					
51	B	12 in. above base		2					8		2					
	A	At base	Tr.						10							
52	A	14 in. above base		Tr.					10		Tr.					
53	C	Near top		4				1	1							
	B	6 in. above base	Tr.	2		5			3		1					
	A	At base							6							
54	A	Near middle							10							
55	C	At upper part		Tr.					10							
	B	8 in. above base		1					9		Tr.					
	A	At base		Tr.					10							
58	SM-1-8A	At top	Tr.										1	9		
	A	Near middle	Tr.	1							8			1		
	XT	10 in. above base									5		5			
	XB	8 in. above base	Tr.										10			
	SM-1-8C	At base											10			
60	D	Near top	1	Tr.					Tr.			4	Tr.	5		Tr.
	C	Near middle in septum									8			2		
	A	At upper part of clinoptilolite remnant	1						8			1				
	B	At lower part of clinoptilolite remnant	Tr.	1					3			6				Tr.
	E	At base		Tr.							5	Tr.		5		
	X	At base, 2 ft west of E		Tr.								10				
62	A	At lower part	Tr.						Tr.			8	1	1		Tr.
	X	At base		Tr.								3	Tr.	7		
63	A	6 in. above base		Tr.								6		4		
65	SM-3-9F	At top	1									4		5		
	9C	44 in. above base	1									4		5		
	9B	20 in. above base							8		2					
	9A	8 in. above base							4		Tr.					
	9E	At base		Tr.								1		9		

See footnotes at end of table.

TABLE 8.—Mineralogic composition of the Skyline tuff as estimated from X-ray diffractometer patterns of bulk samples—Continued

[—, looked for but not found; Tr., trace]

Locality (fig. 23)	Sample	Sample taken	X-ray analysis (parts in 10)											
			Clay, 10 A ¹	Clay, 14 A ²	Chaba- zite	Phillip- site	Erionite	Clinopti- lolite	Morden- ite	Analcime	Potassi- um feld- spar	Quartz ³	Calcite	Other
66	A	6 in. above base	Tr.	1					Tr.			9		
68	A	Near middle	1	1					Tr.		Tr.	8		
69	B	30 in. above base	2								7		1	Tr.
	A	Near middle in clinoptilolite remnant.	2						6		2			
	X	Near middle, 7 ft north of A	2								3	1	4	
	C	At lower part		Tr.								10		
70	C	Near top	1									9		
	B	Near middle	2						Tr.			8		
	A	6 in. above base		Tr.								10		
95	A	9 in. above base		Tr.					10					
96	B	27 in. above base		1				1	8					
	A	6 in. above base		1					9					
99	B	12 in. above base		Tr.							1	9		
	A	At base	Tr.									10		
100	A	6 in. above base									9	1		
101	B	12 in. above base	Tr.									10		
	A	At base		5							2	3		
103	C	At top	Tr.									10		
	B	18 in. above base	Tr.	Tr.								10		
	A	At base										10		

¹ Authigenic illite and pyrogenic biotite.² Chiefly clay minerals with a basal spacing of 12-14 Å.³ Includes authigenic, pyrogenic, and detrital quartz.⁴ Chiefly plagioclase. Sample A from locality 26 contains a trace of halite; sample A from locality 53 contains 4 parts opal; and sample C from locality 53 contains 3 parts glass.

Parts of the zeolitic Skyline tuff between Fossil Canyon and Rainbow Basin commonly are analcemic. The analcime occurs in irregular discontinuous zones at the top and bottom of the tuff. The content of analcime ranges from trace amounts to about 90 percent. Locally, the Skyline tuff is analcemic throughout its entire thickness. Analcemic tuff can readily be distinguished from the predominantly clinoptilolitic tuff because it is light brown or yellowish green and granular in contrast to the white conchoidal-fracturing clinoptilolitic phase. Vitroclastic texture is obvious in the clinoptilolitic part but vague or absent in the analcemic parts.

Remnants of zeolitic tuff occur locally in the predominantly feldspathic Skyline tuff at Rainbow Basin and the western wall of Owl Canyon. The remnants are in the middle part of the tuff and are generally analcemic. Contacts between the remnants and the potassium feldspar-rich tuff are irregular and gradational. At several localities, notably on the north limb of the Barstow syncline in the northwestern part of Rainbow Basin and on the south limb of the syncline near the top of the west wall of Owl Canyon, the remnants consist of one or more irregular clinoptilolitic cores (figs. 24 and 25) that are enclosed or nearly enclosed by an irregular sheath of analcemic tuff. The contacts are gradational and are not controlled by bedding within the tuff.

The analcemic and clinoptilolitic remnants in the Skyline tuff are interpreted as relicts of a diagenetic alteration that preceded the formation of potassium feldspar. This interpretation is consistent with the paragenetic relationship observed in thin sections of the gradational zones. The sequence of formation was (1) rhyolitic glass to clinoptilolite to analcime to potassium

feldspar, or (2) rhyolitic glass to clinoptilolite to potassium feldspar. Nowhere is there any evidence that analcime or potassium feldspar formed directly from the rhyolitic glass.

Other tuffs of the Barstow Formation show a similar gradation of clinoptilolitic or phillipsitic tuff to analcemic tuff, and zeolitic (chiefly clinoptilolite and analcime) tuff to feldspathic tuff. The complete sequence from nonanalcemic zeolitic tuff, to analcemic



FIGURE 24.—Skyline tuff, showing irregular remnants of clinoptilolitic tuff (white) surrounded by analcemic (gray) tuff. Uppermost part of tuff is not visible in photograph but consists chiefly of authigenic quartz and potassium feldspar. Base of tuff is generally analcemic; but locally the clinoptilolitic remnants extend to the base, or the base is potassium feldspar-rich. The tuff overlies brownish mudstone. Locality: south limb of syncline in southeastern part of Rainbow Basin; SE¼NE¼ sec. 24, T. 11 N., R. 2 W.



FIGURE 25.—Skyline tuff, showing irregular remnants of clinoptilolitic (cl) tuff that are surrounded by analcimic (A) tuff. Remainder of tuff consists chiefly of potassium feldspar (K). Note that potassium feldspar-rich tuff is locally in contact with the clinoptilolitic remnant. Locality: north limb of syncline in northern part of Rainbow Basin; NW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 24, T. 11 N., R. 2 W.

tuff, and then to feldspathic tuff, however, has not been recognized in these other tuffs, probably because of their limited distribution.

RELATIONSHIP OF AUTHIGENIC SILICATE MINERALOGY TO THICKNESS OF TUFFS

In addition to the previously described vertical and lateral variations in authigenic mineralogy of the tuffs, there seems to be a relationship between the authigenic mineralogy and the thickness of the tuffs. Thin tuffs generally consist of analcime and (or) potassium feldspar, whereas thick tuffs consist of zeolites other than analcime. Analcime and (or) potassium feldspar occurs in 98 percent of the tuffs that are 6 inches or less thick. Ninety-four percent of those zeolitic tuffs that lack analcime or potassium feldspar are more than 6 inches thick.

A similar relationship between the authigenic mineralogy and thickness of tuffs was recognized by Hay (1966, p. 43) at Olduvai Gorge, Tanzania. Pleistocene tuffs less than 1 inch thick generally are chiefly potassium feldspar, but thicker tuffs contain phillipsite or phillipsite and potassium feldspar. The tuffs were originally similar in composition and were deposited in a saline lake.

GENESIS OF THE AUTHIGENIC SILICATE MINERALS

Zeolites and feldspars of authigenic origin occur throughout the world in sedimentary rocks that are diverse in lithology, depositional environment, and age. Zeolites and feldspars are especially abundant in

altered rhyolitic vitric tuffs of Cenozoic age. The zeolites, except analcime, formed during diagenesis by reaction of the vitric material with interstitial water (Deffeyes, 1959a), which may have originated as either connate water of a saline lake (Hay, 1964; Sheppard and Gude, 1968) or meteoric water (Hay, 1963). Most analcime and feldspar in the altered tuffs formed during diagenesis by reaction of precursor zeolites with the pore water (Sheppard and Gude, 1965a, p. 4; Hay, 1966, p. 90-98).

Hay (1966) discussed those factors that may control the formation and distribution of zeolites and associated authigenic silicate minerals in sedimentary rocks. The authigenic mineralogy correlates with temperature, pressure, and chemistry of the pore water, and composition, permeability, and age of the host rock. Inasmuch as all the authigenic silicate minerals of the Barstow Formation occur within certain tuffs, differences in the composition, permeability, and age of the host rock cannot explain their distribution. The Barstow Formation was probably subjected to only shallow burial, and there is no evidence of hydrothermal activity; thus, the temperature and pressure must have been relatively low during the formation of the silicate minerals. Comparison of the authigenic mineralogy of these tuffs in the Barstow Formation with the authigenic mineralogy of tuffs in relatively young saline-lake deposits suggests that the mineralogy reflects differences in the chemistry of the pore water during diagenesis.

Experimental work by others indicates that the activity ratio of alkali ions to hydrogen ions and the activity of silica are the major chemical parameters of the water that control whether clay minerals, zeolites, or feldspars will form at conditions that approximate surface temperatures and pressures (Hemley, 1959, 1962; Garrels and Christ, 1965, p. 359-370; Hess, 1966). Zeolites and feldspars are favored over clay minerals by relatively high alkali ion to hydrogen ion activity ratios and by relatively high silica activities. The high alkali ion to hydrogen ion activity ratio necessary for the formation of zeolites in a tuff can be attained in the depositional environment of a saline, alkaline lake (Hay, 1964) or in the postdepositional environment by solution and hydrolysis of rhyolitic vitric material by subsurface water (Hay, 1963, p. 237-242).

There is no direct indication of the chemical environment that existed during the deposition of the tuffs of the Barstow Formation. The chemistry of the water must be inferred from the sedimentary rocks of the basin. Most tuffs were deposited in lakes which probably varied in number, location, and size. The abundance

of mammal tracks in lacustrine mudstones suggests that the lakes were, at least locally, very shallow. Mud cracks further suggest that the lakes occasionally desiccated. Inasmuch as relatively coarse clastic rocks locally inter-tongue with the lacustrine rocks, some lakes or some parts of the lakes were relatively fresh. Other lakes or parts of the lakes probably were alkaline and moderately to highly saline.

INTERPRETATION OF A SALINE, ALKALINE DEPOSITIONAL ENVIRONMENT FOR PARTS OF THE BARSTOW FORMATION

The obvious evidence for a saline lake, bedded saline minerals, has not been found in the Barstow Formation at the Mud Hills, although bedded colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) occurs in contemporaneous lacustrine rocks on the southern flank of the Calico Mountains, about 10 miles southeast of the Mud Hills (Campbell, 1902, p. 12-13; Baker, 1911, p. 349-353; Noble, 1926, p. 59-60; McCulloh, 1965). Disseminated crystal molds that are filled or partly filled with calcite occur in mudstone and tuff of the upper part of the formation at the northeastern part of Rainbow Basin. The molds resemble the morphology of gaylussite ($\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$) and suggest saline conditions during deposition. The interbedded tuffs at this locality consist chiefly of analcime and (or) potassium feldspar. The common efflorescence of thenardite (Na_2SO_4) on the surface of weathered mudstone, particularly at Rainbow Basin and eastward, suggests a depositional environment of moderate salinity. Although the conditions under which dolomite precipitates at nearly room temperature is not known, the beds of dolomite and dolomitic mudstone in the eastern part of the Mud Hills suggest a depositional or diagenetic environment of high pH and moderate salinity (Smith and Haines, 1964, p. P52-P53; Jones, 1965, p. A44). Dolomite occurs at Searles Lake in muds mainly near contacts with salines.

A saline, alkaline depositional environment for parts of the Barstow Formation can be inferred from the occurrence of certain authigenic silicate minerals that have been found by other mineralogists to indicate saline waters. Zeolites such as clinoptilolite and mordenite occur in altered silicic tuffs that were deposited in either fresh or saline waters; however, zeolites such as erionite and phillipsite in altered silicic tuffs are found almost exclusively in saline-lake deposits (Hay, 1964, p. 1384; 1966, p. 67). The common occurrence of analcime and potassium feldspar in the apparently non-tuffaceous mudstones of the Barstow Formation may also indicate a saline-lake environment, because these authigenic minerals are rare in nontuffaceous mudstones deposited in fresh water (Hay, 1966, p. 67).

CORRELATION BETWEEN SALINITY OF DEPOSITIONAL ENVIRONMENT AND AUTHIGENIC SILICATE MINERALOGY

Studies of tuffs deposited in relatively young saline lakes where water analyses are available have shown a strong correlation between salinity and the authigenic silicate mineralogy (Hay, 1964, 1966). Tuffaceous sediments deposited in fresh water still contain unaltered glass, but those deposited in saline water are altered and contain zeolites, potassium feldspar, or searlesite. Hay (1966, p. 68) found that potassium feldspar is a major constituent of tuffs saturated with sodium carbonate brine in Searles Lake, but potassium feldspar is absent and zeolites are common in equivalent deposits that contain mildly saline water at China Lake.

Older lacustrine deposits that contain interbedded saline minerals also show a correlation between the inferred salinity of the depositional environment and the authigenic mineralogy of rhyolitic tuffs. In the Pleistocene deposits of Lake Tecopa, Calif. (Sheppard and Gude, 1968), glass is unaltered in tuff deposited in fresh water; however, the tuffs consist chiefly of phillipsite, clinoptilolite, and erionite where they were deposited in moderately saline water, and potassium feldspar and searlesite where they were deposited in highly saline water. Miocene tuffs at Kramer, Calif., contain potassium feldspar and analcime where they are associated with high concentrations of sodium borate but contain clinoptilolite and phillipsite where they are associated with rocks indicative of lower salinity (Hay, 1966, p. 68). Tuffs in the Eocene Green River Formation of Wyoming are altered to montmorillonite where they were deposited in fresh water; to clinoptilolite and mordenite (Goodwin and Surdam, 1967), in slightly saline water; to analcime, in moderately saline water; and to potassium feldspar and albite, in highly saline water (Hay, 1965; 1966, p. 44-52).

The diverse authigenic mineralogy of the tuffs in the Barstow Formation seems to have resulted from differences in pH and salinity of the lake water trapped in the tuffs during deposition. The lake water probably ranged from fresh water to water with a pH of 9 or higher and a moderate to high salinity. Those tuffs that consist of unaltered glass with minor zeolite and montmorillonite probably were deposited in relatively fresh water; whereas those tuffs that consist of zeolites exclusive of analcime, or of only analcime, or of potassium feldspar were deposited in water of relatively low, moderate, and high salinity, respectively.

The gradational change in the areal distribution of authigenic silicate minerals in the Skyline tuff (fig. 23 and table 8) from chiefly clinoptilolite with minor

relict glass to clinoptilolite plus analcime to analcime plus potassium feldspar to chiefly potassium feldspar was probably due to a chemical zonation of the pore water during diagenesis. This zonation may have been inherited from the chemical zonation that existed in the lake during deposition of the Skyline tuff. Fresh water along shore may have been succeeded basinward by increasingly saline water. Such a mechanism seems the best explanation for a similar distribution of authigenic silicate minerals in tuffs of Pleistocene Lake Tecopa, Calif. (Sheppard and Gude, 1968). At Lake Tecopa, however, the margin of the lake is readily discernible. An alternate explanation for the chemical zonation of the pore water in the Skyline tuff is post-depositional "freshening" by meteoric water. Uniformly alkaline and saline water trapped as pore water in the tuff during deposition may have been freshened along shore by the encroachment of fresh water after deposition (Eugster and Smith, 1965, p. 518).

SOLUTION OF GLASS TO FORM ALKALI- AND SILICA-RICH ZEOLITES

Solution of silicic glass by moderately alkaline and saline pore water provides the materials necessary for the formation of the zeolites. Deffeyes (1959a, p. 607) emphasized that zeolites form during diagenesis—not by devitrification of the shards but by solution of the shards and subsequent precipitation of zeolite from the solution.

Tuffs in the Barstow Formation are generally interbedded with relatively impermeable mudstones and after deposition may have behaved as closed systems consisting of silicic glass and the connate lake water. The early formation of montmorillonite probably was favored by a relatively low $\text{Na}^+ + \text{K}^+ : \text{H}^+$ activity ratio (Hemley, 1962). This activity ratio would have been at its lowest value at the time of deposition. Subsequent solution of glass or the formation of montmorillonite by an initial marginal hydrolysis of the glass would cause an increase in the pH and the concentration of alkali ions (Hay, 1963, p. 240), thereby increasing the $\text{Na}^+ + \text{K}^+ : \text{H}^+$ activity ratio of the pore water and providing an environment more suitable for the formation of zeolites rather than additional montmorillonite.

Inasmuch as the zeolites of the Barstow Formation differ noticeably in chemical composition, the following factors may influence which zeolite will form: Activity of SiO_2 , activity of H_2O , and the proportion of cations in the pore water. Where relationships are clear, the petrographic evidence indicates that phillipsite and chabazite formed before clinoptilolite, and clinoptilo-

lite formed before mordenite. Phillipsite and chabazite contain more H_2O and less SiO_2 than clinoptilolite. Thus, the formation of phillipsite or chabazite should be favored over clinoptilolite by a relatively high activity of H_2O and (or) low activity of SiO_2 . Such conditions may have prevailed in the silicic tuffs during early diagenesis.

Continued solution of the glass coupled with the early formation of phillipsite or chabazite in a tuff probably has the effect of enriching the pore water in SiO_2 and cations. The activity of SiO_2 may thus increase and the activity of H_2O decrease to levels suitable for the formation of clinoptilolite rather than phillipsite or chabazite. Mordenite rather than clinoptilolite probably formed when the activity of SiO_2 reached a maximum.

That the SiO_2 concentration can effect which zeolite will form was demonstrated experimentally by Ciric (1967). At temperatures of 80° – 90°C , Ciric synthesized zeolites with a range of Si:Al ratios in a sealed Pyrex tube into which sodium aluminate had been added at one end and sodium metasilicate added at the other. A relatively siliceous zeolite formed at the silica-rich end, an aluminous zeolite formed at the aluminate end, and a zeolite of intermediate Si:Al ratio formed in the middle of the tube.

REACTION OF ALKALIC, SILICIC ZEOLITES TO FORM ANALCIME

Analcime in some nontuffaceous lacustrine rocks apparently formed during diagenesis by reaction of aluminosilicate minerals with the pore water. For example, solution of plagioclase and quartz in sediments of Searles Lake probably supplied some of the silicon and aluminum for the formation of analcime, searlesite, and potassium feldspar (Hay and Moiola, 1963). Montmorillonite and kaolinite may also have reacted to form analcime in certain nontuffaceous sediments (Hay and Moiola, 1963, p. 330; Pipkin, 1967).

Analcime in other nontuffaceous saline lacustrine deposits probably formed by direct precipitation from the lake water. The analcime in the Triassic Lockatong Formation either precipitated directly or formed at an early stage of diagenesis from a colloidal precursor or aluminosilicate mineral (Van Houten, 1960; 1965, p. 835–836). At Lake Natron, Kenya, analcime in nontuffaceous clays was precipitated from a sodium carbonate brine (Hay, 1966, p. 36–38).

Ever since the discovery of analcime in tuffaceous sedimentary rocks, most workers have assumed that the analcime formed directly from vitric material. The

presence of vitroclastic texture and pyrogenic crystals in some analcimic tuffs seemed sufficient evidence; however, Hay (1966, p. 91) showed that these criteria do not necessarily prove that the glass altered directly to analcime. Hay (1966, p. 90–93) concluded from a comparison of the authigenic mineralogy of tuffs in modern and ancient saline-lake deposits that analcime commonly formed at low temperatures by reaction of alkalic, silicic zeolite precursors. Furthermore, relict fresh glass has not been confirmed in analcimic tuff; thus, there is doubt that analcime ever has formed directly from glass.

Much, if not all, of the analcime in tuffs of the Barstow Formation seems to have formed from alkalic, silicic zeolite precursors. These alkalic zeolites, because of their open structure (Smith, 1963) and large internal surface area, would seem to be particularly susceptible to alteration in the diagenetic environment.

Experimental low-temperature work by other mineralogists, and theoretical considerations, indicate that the formation of analcime is favored over an alkalic, silicic zeolite such as clinoptilolite by a high $\text{Na}^+:\text{H}^+$ ratio (Hess, 1966), relatively low activity of SiO_2 (Coombs and others, 1959; Senderov, 1963; Campbell and Fyfe, 1965), and, perhaps, relatively low activity of H_2O . A comparison of chemical analyses of rhyolitic glass and clinoptilolite (Hay, 1963, p. 230; Sheppard and Gude, 1965b) suggests that sodium is lost from the glass during the formation of clinoptilolite. Perhaps this sodium, plus that originally in the pore water, was sufficient to provide an environment suitable for crystallization of analcime some place else. A relatively high salinity of the pore water would decrease the activity of H_2O and thus favor the formation of the less hydrous analcime over any of the other zeolites in the Barstow Formation, all of which are much more hydrous than analcime. An increase in pH during diagenesis would decrease the activity of SiO_2 (Coombs and others, 1959; Senderov, 1963) and increase the $\text{Na}^+:\text{H}^+$ ratio. Both conditions should favor the formation of analcime over clinoptilolite. Quartz is more common in the analcimic tuffs than in the other zeolitic tuffs of the Barstow Formation. Crystallization of quartz in the tuffs would have lowered the activity of SiO_2 .

These arguments are based on the assumption that chemical factors alone are responsible for the formation of analcime; however, kinetic factors may be equally, or perhaps more, important. Analcime may simply form later than zeolites such as clinoptilolite and phillipsite.

Studies of the composition of analcime in sedimentary rocks have shown a range in Si:Al ratios of about 2.0–2.9 (Coombs and Whetten, 1967; Iijima and Hay, 1968). Coombs and Whetten (1967) studied analcime from

rocks that are diverse in age, lithology, depositional environment, and geographic location and concluded that (1) analcime in the high part of the above compositional range formed by the reaction of silicic glass with saline water, (2) analcime in the intermediate part of the range formed by “burial metamorphic reactions” due to increased temperature and pressure, and (3) analcime in the low part of the range formed either by direct precipitation from alkaline water or by reaction of clay minerals and other materials with alkaline water.

Analcime in tuffs of the Barstow Formation ranges in Si:Al ratio from about 2.2 to 2.8 and, thus, nearly spans the compositional range known for sedimentary rocks. Unlike the analcimes studied by Coombs and Whetten (1967), these analcimes in the Barstow Formation formed in rocks that originally were similar in composition and were deposited in a similar environment. None of the tuffs were deeply buried; furthermore, there is no correlation between analcime composition and stratigraphic position.

Analcime in the tuffs of the Barstow Formation formed from zeolite precursors and not directly from rhyolitic glass. Petrographic study showed that analcime formed from clinoptilolite and phillipsite; however, analcime probably formed from the other authigenic zeolites as well. Inasmuch as the zeolites have a wide range of Si:Al ratios (table 4), it is tempting to suggest that the silicon content of analcime was affected by the silicon content of the precursor. To check the validity of this idea, the composition of analcime associated with phillipsite was compared with the composition of analcime associated with clinoptilolite. Figure 26 shows that analcime associated with phillipsite has 33.1–34.4 silicon atoms per unit cell, whereas analcime associated with clinoptilolite has 34.5–35.1 silicon atoms per unit cell. Inasmuch as phillipsite and clinoptilolite are relatively low- and high-silicon zeolites, respectively, a correlation between the compositions of the precursor and analcime is suggested. Additional determinations, particularly from another formation, are needed for confirmation.

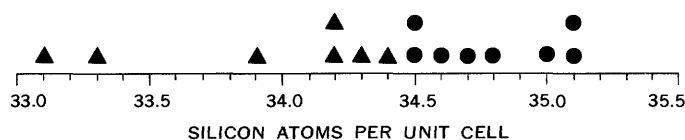


FIGURE 26.—Plot showing the correlation between the silicon content of analcime and the precursor zeolite. Composition of analcime determined from X-ray diffractometer data by measurement of the displacement of the (639) peak of analcime. ▲, composition of analcime associated with phillipsite; ●, composition of analcime associated with clinoptilolite.

REACTION OF ZEOLITES TO FORM POTASSIUM FELDSPAR

The formation of potassium feldspar by the reaction of zeolite precursors in tuffs that were never buried deeply was well documented by the studies of Hay (1966, p. 93-98) and Sheppard and Gude (1968). Analcime is replaced by potassium feldspar and albite in tuffs of the Green River Formation in Wyoming (Hay, 1965, 1966; Iijima and Hay, 1968) where the formation of feldspar can be correlated with high salinities of the depositional environment. Phillipsite is replaced by potassium feldspar and searlesite in rhyolitic tuffs of Pleistocene Lake Tecopa, Calif. (Sheppard and Gude, 1968), where high salinities prevailed. Some zeolitic tuffs of Lake Tecopa contain abundant clinoptilolite and erionite as well as phillipsite; therefore, these zeolites could also have been precursors for the potassium feldspar.

Petrographic study of the feldspathic tuffs in the Barstow Formation has shown that potassium feldspar replaced analcime and clinoptilolite. Other zeolites such as chabazite, erionite, mordenite, and phillipsite may also have been precursors for the feldspar, but the textural evidence was not observed. Relict glass is nowhere associated with the potassium feldspar; thus, the direct formation of feldspar from rhyolitic glass seems unlikely in these tuffs.

Zeolites, because of their open structure (Smith, 1963), apparently are particularly susceptible to alteration in the diagenetic environment. The initially high salinity of the pore water trapped in the tuffs during deposition probably was the major factor that controlled the alteration. A relatively high salinity would lower the activity of H_2O and favor the formation of anhydrous potassium feldspar from the hydrous zeolites, including analcime.

Other factors such as the $K^+ : H^+$ ratio and the activity of SiO_2 also affect the formation of potassium feldspar (Hemley and Jones, 1964; Hess, 1966). Hydrolysis experiments by Garrels and Howard (1959, p. 87) suggested that potassium feldspar will form at 25°C in environments with a $K^+ : H^+$ ratio greater than about $10^{9.5}$. Potassium feldspar may form at near surface conditions where the $K^+ : H^+$ ratio is as low as about 10^{5-6} and the pore water is saturated with amorphous SiO_2 (Orville, 1964).

The zeolitic tuffs of the Barstow Formation that are rich in clinoptilolite commonly contain opal which may have contributed a favorable chemical environment for the formation of potassium feldspar. However, feldspathic tuffs in the formation now contain quartz or chalcedonic quartz but lack opal. If the activity of SiO_2 was controlled by quartz rather than by opal, rela-

tively high concentrations of K^+ would have been necessary for the formation of potassium feldspar. Unfortunately, the relative ages of potassium feldspar and quartz are unknown.

Studies by Iijima and Hay (1968) on the composition of analcime in tuffs of the Green River Formation showed that analcime associated with authigenic potassium feldspar is less siliceous than that not associated with potassium feldspar. Iijima and Hay concluded that siliceous analcime became partly desilicated during the reaction to form feldspar. Analcime in the tuffs of the Barstow Formation show about the same compositional range whether associated with authigenic potassium feldspar or not. Unlike the analcime in the Green River tuffs, the Barstow analcime seems to be crowded with inclusions of opal. Thus, a highly reactive form of SiO_2 was nearby when the analcime reacted to form potassium feldspar. Desilication of analcime was unnecessary.

Although silicate reactions are generally regarded as sluggish at low temperatures, potassium feldspar has been synthesized from aluminosilicate precursors at temperatures no higher than 250°C. Gruner (1936) synthesized potassium feldspar from montmorillonite in a 10 percent solution of $KHCO_3$ heated to 245°C for 42 days. Barrer and Hinds (1950) synthesized potassium feldspar from leucite in a solution saturated with K_2CO_3 and Na_2CO_3 and heated to 195-200°C for 16 hours. The leucite had been prepared from analcime by cation exchange in a solution saturated with KCl at 150°C. Nemecek and Varju (1962, p. 425) reported the synthesis of potassium feldspar from clinoptilolite in a solution containing potassium ions and heated to not more than 250°C for 12 hours.

The authors, unaware of the work by Nemecek and Varju (1962), independently synthesized potassium feldspar from clinoptilolite. Clinoptilolite from the Barstow Formation was ground finer than 100 mesh and then heated over a steam bath in a saturated solution of KOH at about 80°C for 44 hours. After repeated washings followed by drying, the material was X-rayed. The diffractometer pattern (fig. 27) showed that the clinoptilolite was converted to potassium feldspar. This synthetic feldspar is compared in figure 27 with the natural potassium feldspar that occurs in the Barstow Formation, and the similarity is obvious. Although the synthetic feldspar was prepared at a higher temperature than that which probably prevailed during diagenesis and was prepared in a chemical environment that probably did not even closely approximate the diagenetic environment, the simple experiment demonstrates the rapidity of the reaction of clinoptilolite to form potassium feldspar in a favorable environment.

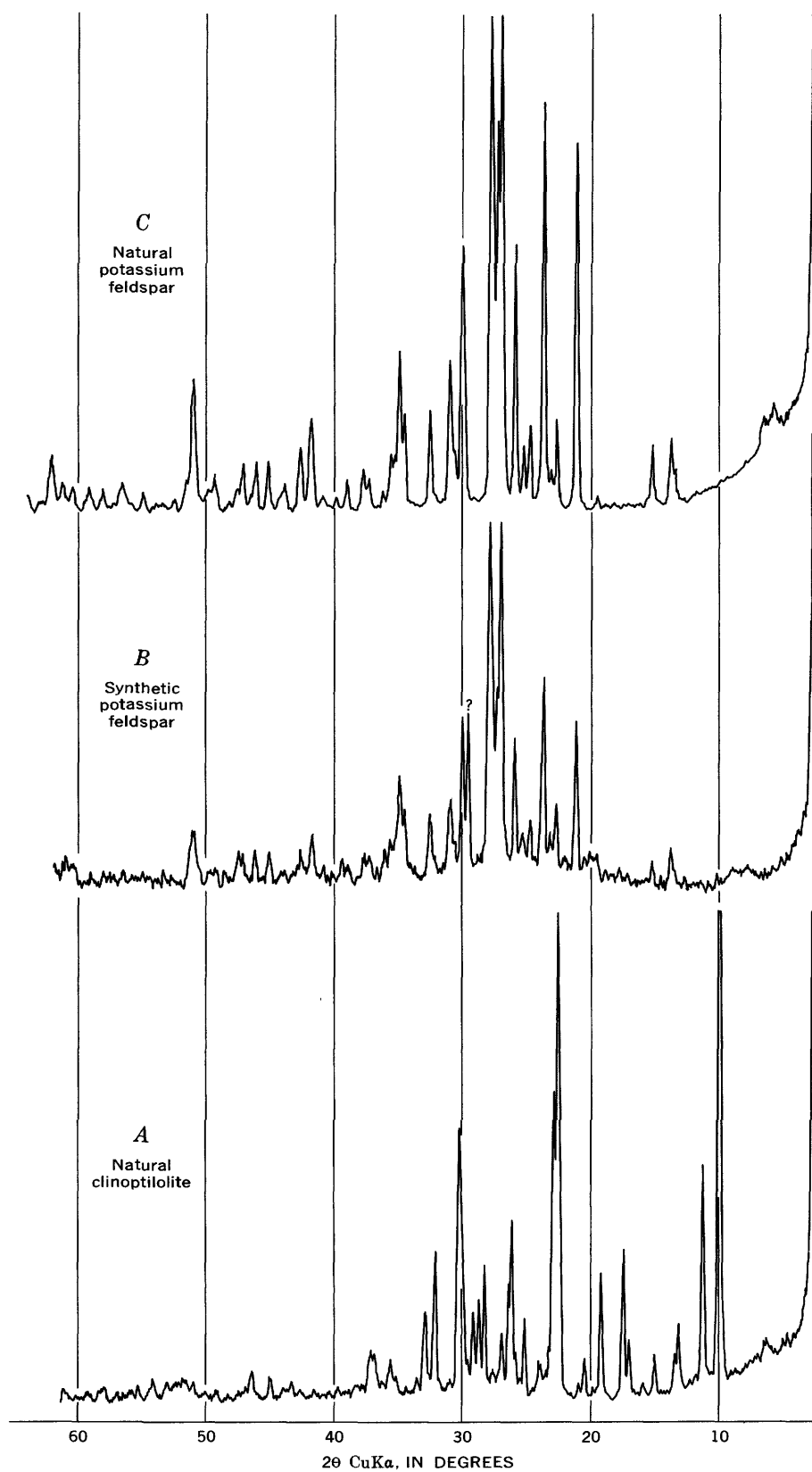


FIGURE 27.—Comparison of X-ray diffractometer traces of synthetic potassium feldspar with those of natural clinoptilolite and natural potassium feldspar from the Barstow Formation. A, Clinoptilolite. B, Synthetic potassium feldspar prepared from clinoptilolite (A) in a saturated solution of KOH at about 80 °C for 44 hours; peak marked by query is unidentified. C, Natural potassium feldspar from the Skyline tuff. Radiation is CuKα.

METASOMATISM DURING DIAGENESIS OF TUFF

The transition of rhyolitic glass to an alkalic silicic zeolite, then to analcime, and finally to potassium feldspar is well documented for the Barstow Formation and other Cenozoic formations (Hay, 1966). Formation of alkalic silicic zeolites from rhyolitic glass results mainly in losses of silicon and potassium, and gains of calcium and H₂O (Hay, 1963, p. 230-231; 1964, p. 1382-1383; Sheppard and Gude, 1965b). The reaction of alkalic silicic zeolites to form analcime involves mainly losses of silicon, calcium, potassium, and H₂O, and a gain of sodium. The final transformation of analcime to potassium feldspar results in losses of sodium and H₂O, and gains of potassium and silicon.

These metasomatic changes apparently are mostly restricted to the tuff bed and take place between the solid phases and the pore fluid. Except for H₂O, a chemical balance is probably maintained for a given tuff if the entire extent of the tuff is considered. Gains and losses of constituents between the tuff and the enclosing strata probably are slight; however, the metasomatic changes within the tuff bed must be considerable. The changes that involve silicon are not too difficult to understand because most altered tuffs, whether zeolitic or feldspathic, contain free silica. The most puzzling aspect of the metasomatic changes is the "plumbing" that permits the drastic removal of potassium to form analcime, and then the subsequent addition of potassium to form potassium feldspar.

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INDEX

[*Italic page numbers indicate major references*]

	Page
Acknowledgments.....	4
Alteration, stages, fresh vitric tuff to zeolitic tuff.....	20
Analclime.....	10
composition.....	11
formation.....	26
formed from reaction of zeolites with water.....	28
in mudstones.....	7
indicator of saline-lake environment.....	27
replacement by potassium feldspar.....	20
Analclite. <i>See</i> Analclime.	
Analyses, chemical, analclime.....	11
chemical, chabazite.....	11
clinoptilolite.....	14
mordenite.....	15
mudstones.....	8
phillipsite.....	15
mineral content, mudstones.....	8
mineralogic, Skyline tuff.....	24
shards, Hemicyon tuff.....	9
unit cell composition, analclime.....	11
chabazite.....	11
clinoptilolite.....	14
mordenite.....	15
phillipsite.....	15
Animal tracks.....	8
Barite.....	13
Barstow Formation, chemical environment.....	26
depositional environment.....	27
fossils.....	1, 8
stratigraphy and lithology.....	5
topographic features.....	5
Barstow syncline.....	5
Blackmon, Paul D., analyst.....	8
Calcite, in cavities in mudstone.....	8
Camel track tuff, outcrop extent.....	6
Carbonate rocks.....	8
Chabazite.....	12
composition.....	11
Chemical parameters controlling formation of silicates.....	26
Clay minerals.....	12
in mudstones.....	7
Clinoptilolite.....	12
analyses.....	14
zoning.....	13
Colemanite.....	27
Conglomerate.....	6
Crystals in tuffs.....	9
Daniels, Ellen S., analyst.....	8, 9, 11, 14
Dated tuff, outcrop extent.....	6
Dolomite.....	8, 27
Erionite.....	14
Feldspar, formation.....	26
Formulas of selected alkalic zeolites.....	10

	Page
Fossils in Barstow Formation.....	1, 8
Gaylussite.....	8, 27
Geology, regional.....	4
Glass, solution to form zeolites.....	28
Gypsum.....	7
Hay, R. L., zeolite formulas.....	10
Hemicyon tuff, accretionary lapilli.....	8
analyses of chabazite.....	11
analyses of clinoptilolite.....	14
analyses of shards.....	9
outcrop extent.....	6
states of alteration.....	20
Laboratory methods.....	3
Lapilli, accretionary, in tuffs.....	8
Limestone.....	8
Lithology, Barstow Formation.....	5
Location of area.....	1
Mammal tracks.....	27
Metasomatism during diagenesis.....	32
Mineral associations, analclime.....	10
chabazite.....	12
clinoptilolite.....	13
erionite.....	14
mordenite.....	14
opal.....	15
phillipsite.....	15
potassium feldspar.....	16, 20
quartz.....	17
relationship to depositional environment.....	27
Montmorillonite.....	20
Mordenite.....	14
detection method.....	4
Mud cracks.....	8, 27
Mudstone.....	7
Munson, Elaine L., analyst.....	11
Neiman, Harriet, analyst.....	9
Opal.....	15, 30
in analclime.....	11
Ostracodes.....	8
Paragenesis, authigenic silicate minerals.....	20
zeolites.....	28
Petrography, altered tuffs.....	18
pH, relation to mineral formation.....	27, 28
Phillipsite.....	15
spherulites.....	16
in Yellow tuff.....	19
Plagioclase feldspar, replacement by potassium feldspar.....	21
Potassium feldspar.....	16
factors affecting formation.....	30
formation from zeolitic precursors.....	21
formed by reaction of zeolites with water.....	30
in mudstones.....	7
indicator of saline-lake environment.....	27
synthesized.....	30

	Page
Previous studies.....	1
Quartz.....	17, 30
References.....	32
Regional geology.....	4
Rock fragments in tuffs.....	9
Salinity, correlation with silicate minerals.....	27
Sampling.....	3
Sandstone.....	6
Scope of study.....	2
Searlesite.....	27
Shards.....	9
Silicate minerals, authigenic, paragenesis.....	20
genesis.....	26
Siltstone.....	6
Skyline tuff, accretionary lapilli.....	8
analyses of clinoptilolite.....	14
effect of chemical zonation of pore water during diagenesis.....	27
mineralogic composition.....	24
outcrop extent.....	6
sequence of formation.....	25
variations in authigenic mineralogy.....	21
Spherulites, phillipsite.....	16
Stratigraphy, Barstow Formation.....	5
Strontianite.....	1
Thenardite.....	7, 27
altered, field description.....	17
analclime.....	20
composition.....	8
distinguishing characteristics of types.....	18
metasomatism during diagenesis.....	32
nonanalclime zeolitic.....	19
original texture and structure.....	8
petrography.....	18
potassium feldspar-rich.....	20
relationship between authigenic mineralogy and thickness.....	26
salinity-silicate mineralogy correlation.....	27
Vitric material in tuffs.....	9
Water, pore, relation to analclime formation.....	29
pore, relation to potassium feldspar formation.....	30
Yellow tuff, analyses of phillipsite.....	15
clay minerals.....	12
outcrop extent.....	6
phillipsite spherulites.....	19
Zeolites, alkalic, formulas.....	10
factors controlling type formed.....	28
formation.....	26
formed from solution of glass.....	28
paragenesis.....	28
reaction with water to form analclime.....	28
reaction with water to form potassium feldspar.....	30
Zoning, in clinoptilolites.....	13