Distribution and Properties of Clinoptilolite-Bearing Tuffs in the Upper Jurassic Morrison Formation on the Ute Mountain Ute Reservation, Southwestern Colorado and Northwestern New Mexico

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By PAULA L. HANSLEY *and* RICHARD A. SHEPPARD

GEOLOGIC STUDIES OF THE UTE MOUNTAIN UTE INDIAN RESERVATION

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By Paula L. Hansley *and* Richard A. Sheppard

ABSTRACT

The distribution, purity, chemistry, and ammonium (NH_4^+)-exchange capacity of clinoptilolite on the Ute Mountain Ute Reservation were evaluated to determine the economic potential of this area for this commercially important zeolite. Altered volcanic ash beds in the Brushy Basin Member of the Morrison Formation (Upper Jurassic), which crop out at many locations on the Reservation, contain significant amounts of clinoptilolite. Clinoptilolite-bearing units are easily recognized by their distinctive salmon-orange color. The Brushy Basin Member is believed to be the oldest sedimentary unit in the United States to host clinoptilolite. Clinoptilolite constitutes as much as 55 percent of some tuffs, but most beds contain far less. The NH_4^+-exchange capacity, 0.33–0.51 milliequivalents per gram (meq/g), of the clinoptilolite-bearing tuffs is relatively low. Where the clinoptilolite occurs, the Morrison Formation is covered by a thick overburden of post-Jurassic rocks. Removal of the overburden to mine the zeolitic beds, separation of clinoptilolite from these impure units, and extraction of ferric oxide from the clinoptilolite would be prohibitively expensive. As a result, this clinoptilolite could not compete in the marketplace with zeolitic beds of higher purity and greater accessibility. Commercial development of the clinoptilolite-bearing tuffs on the Ute Mountain Ute Reservation, therefore, is not economically feasible at the present time. No other formations containing zeolitic beds are known to occur on the Reservation.

INTRODUCTION

The purpose of this study was to investigate the occurrence and economic potential of zeolites on the Ute Mountain Ute Reservation in southwestern Colorado and northwestern New Mexico (fig. 1). Zeolites are an important group of minerals that are used in a wide variety of industrial and agricultural applications including sewage-effluent treatment, fertilizers, dietary supplements for livestock, and radioactive waste treatment (Mumpton, 1981b). These applications take advantage of the unique crystal structures and chemical and physical properties that enable zeolites to exhibit reversible dehydration, cation exchange, adsorption, and acid and thermal stability. Zeolites are crystalline hydrated aluminosilicates with open structures characterized by an infinitely extended framework of SiO_4 and AlO_4 tetrahedra enclosing interconnected cavities occupied by relatively large water molecules and various exchangeable alkali and alkaline-earth cations. When placed in a strong ionic solution, zeolites release loosely bound cations and incorporate cations from the solution with a high degree of efficiency. Each zeolite species has cavities and entry channels of unique diameters that afford zeolites, as a group, the capability of accepting or excluding many different sizes of cations and molecules. Because of this adsorption of molecules based on size, zeolites are termed "molecular sieves." Despite the fact that many synthetic species of zeolite are now produced, natural zeolites remain an important commodity because of their low cost and unique properties.

Although zeolites occur in many different rock types and geologic settings, economic concentrations are commonly found in Cenozoic saline, alkaline lake deposits where zeolites formed as alteration products of volcanic ash in a hydrologically closed basin environment (Hay, 1966; Mumpton, 1981a). The zeolites commonly compose more than 90 percent of the altered ash beds. Sedimentary zeolite beds in closed-basin deposits are commonly thick, flat lying, extensive, and exposed at the surface, making them economically attractive targets for mining operations. The thickness

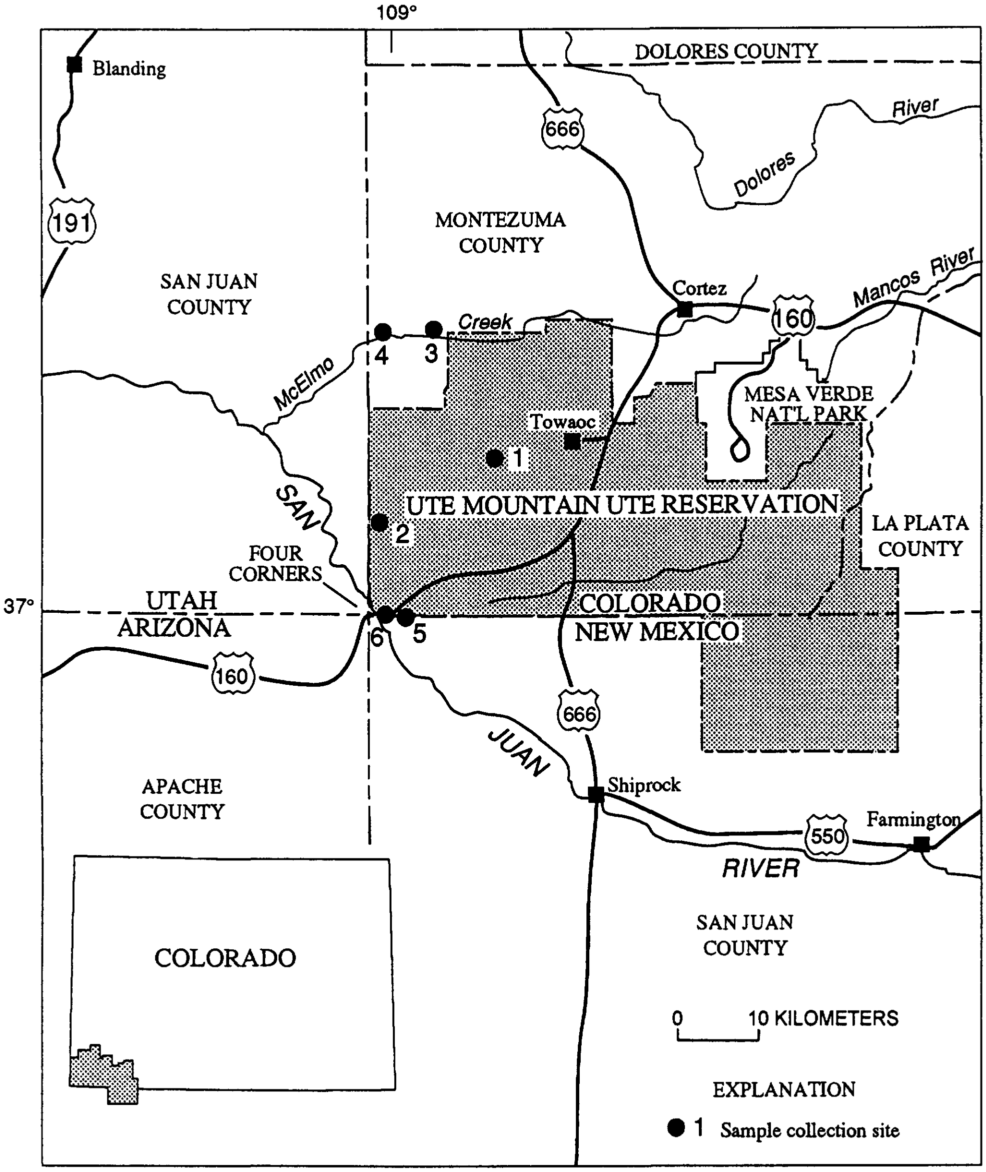

Figure 1. Location of the Ute Mountain Ute Reservation in southwestern Colorado and northwestern New Mexico, showing sample-collection sites for this study. From Irwin (1966, fig. 1).

of the beds ranges from less than a centimeter to several meters, with many beds thicker than 0.5 m. Clinoptilolite is a common zeolite in these lake deposits (Sheppard and Gude, 1982). Examples of ancient saline, alkaline lake deposits are from Pleistocene Lake Tecopa (Sheppard and Gude, 1968) and the Miocene Barstow Formation in southern California (Sheppard and Gude, 1969), the upper Miocene and lower Pliocene Big Sandy Formation in western Arizona (Sheppard and Gude, 1973), and the Eocene Green River Formation in Wyoming (Surdam and Parker, 1972).

In the closed-basin lacustrine environment, volcanic ash reacted with interstitial waters and altered to various authigenic clay minerals, zeolites, feldspars, and silica minerals during early diagenesis. The types of authigenic minerals that formed depended on the chemistry of the pore waters, including the salinity, the pH, and the proportion of ions (Hay, 1966). Lake waters commonly increased in salinity and alkalinity basinward, and corresponding trends in sediment pore waters resulted in the formation of laterally concentric diagenetic alteration patterns, which overlap in most areas. Nearest the lake margins, where waters were freshest because of stream recharge, ash remains unaltered in the most recent deposits; farther basinward, ash altered largely to smectite; still farther out, to clinoptilolite and other zeolites; and finally, in the most saline and alkaline waters near the basin center, to analcime and potassium feldspar. Analcime and potassium feldspar did not form directly from volcanic ash but crystallized slightly later from precursor zeolites (Surdam, 1981).

Clinoptilolite, one of the most commercially important natural zeolites, is found locally in the San Juan basin occurring in the Brushy Basin Member, the uppermost member of the Upper Jurassic Morrison Formation (Santos, 1975; Bell, 1983, 1986). This is probably the oldest known host rock for clinoptilolite in sedimentary deposits of the United States (Sheppard, 1971). Brushy Basin sediments were deposited in a large saline, alkaline lake system that extended over present-day northwestern New Mexico, northeastern Arizona, southeastern Utah, and southwestern Colorado (Bell, 1983, 1986; Turner-Peterson, 1985). Voluminous amounts of volcanic ash fell into the lake and associated streams during deposition of the Morrison, as evidenced by the presence of altered ash beds more than a meter thick. During earliest diagenesis, tuffaceous Brushy Basin sediments were altered to (listed from basin margin to center) smectite, clinoptilolite, analcime, potassium feldspar, and albite, which occur in wide, interfingering alteration bands roughly parallel to former lake margins (Turner-Peterson, 1985; Turner and Fishman, 1991).

Much of the commercial value of clinoptilolite hinges on its ability to accommodate large cations such as ammonium, heavy metals, cesium, and strontium (Flanigen and Mumpton, 1981). This enables it to remove ammonium ions (NH_4^+) from sewage effluent (Ames, 1967; Mercer, 1969), and radioactive cesium (Cs^{137}) and strontium (Sr^{90}) from wastewaters of nuclear power plants (Ames, 1959; Brown, 1962). Natural zeolites such as clinoptilolite are preferred for water purification because they are far less expensive and more stable in the presence of nuclear-particle bombardment than synthetic organic ion-exchange resins (Mumpton, 1981b). Clinoptilolite is also used in paper fillings, fertilizers, and pet litter; as building-stone aggregate; and in processes such as dehydration of liquids and gases and separation of gases (Gottardi and Galli, 1985).

GEOLOGIC SETTING

The Morrison Formation crops out at many locations on the Ute Mountain Ute Reservation and in surrounding areas, including exposures on the southern and northern sides of McElmo Canyon, on the southern flanks of Sleeping Ute Mountain, on cliffs in the San Juan River valley, and in Coyote Gulch near the Colorado-Utah border (Irwin, 1966). Most exposures are partial sections of the upper part of the formation. In this region, the Morrison Formation is 150–200 m thick and is composed of five members (in ascending order): the Tidwell (Fred Peterson, written commun., 1986), Salt Wash, Recapture, Westwater Canyon, and Brushy Basin (Ekren and Houser, 1959; 1965). The Morrison is underlain conformably by the Jurassic Junction Creek Sandstone or equivalent rocks and is overlain by the Lower Cretaceous Burro Canyon Formation. The Brushy Basin-Burro Canyon contact is generally indistinct, lying in a gray-green to gray-red zone of hackly, nonbentonitic mudstone and siltstone.

The Tidwell Member consists of interbedded mudstone, siltstone, and sandstone deposited on a floodplain. The next three members of the Morrison Formation are composed of lenticular, light-gray sandstone interbedded with red and green siltstone and claystone that were deposited by an aggrading system of braided streams (Craig and Dickey, 1956) flowing from source areas located to the west and southwest of the Colorado Plateau. The Brushy Basin Member consists of 50–90 m (Irwin, 1966) of variegated, dark-reddish to purplish-brown and light-greenish-gray bentonitic and zeolitic claystones and mudstones in the Ute Mountains area. Locally, it contains interbeds of silicified siltstone and sandstone and discontinuous beds of limestone and altered tuff. Weathered surfaces of fine-grained Brushy Basin sediments have a characteristic "popcorn" appearance as a result of wetting (and subsequent swelling) and drying of the bentonitic clays. The Brushy Basin Member intertongues with the upper part of the underlying Westwater Canyon Member. The fine-grained, flat-bedded character of the sedimentary units and the regional-facies patterns indicate that the Brushy Basin Member was deposited near the center of a large saline, alkaline lake system that existed in the vicinity of the present-day Ute Mountain Ute Reservation (Turner-Peterson, 1985).

METHODS OF STUDY

Tuffaceous, fine-grained samples suspected of containing clinoptilolite were collected from six localities in and adjacent to the Ute Mountain Ute Reservation (fig. 1). Because of their distinct salmon-orange to red-orange color, clinoptilolite-bearing beds in the Brushy Basin Member are easy to recognize (Bell, 1983). Petrographic thin sections of selected samples were impregnated with blue-dyed epoxy and stained with Alizarin-red S for calcite detection. These sections were examined closely to obtain textural, compositional, and paragenetic data. X-ray diffractograms of packed-powder mounts of all samples were made with a Picker diffractometer to estimate mineralogical composition. The major-element-oxide chemistry of bulk samples containing significant amounts of clinoptilolite was determined by x-ray fluorescence; this technique gave only an approximation of the composition of the clinoptilolite. A better indication of the composition was provided by analyses of clinoptilolite in gold-coated, polished petrographic thin sections with a Tracor Northern Semiquantitative Analysis System (SSQ), an energy-dispersive x-ray system attached to a Cambridge 250 Mark 2 scanning electron microscope (SEM). The analyses were corrected for atomic number, absorption, and fluorescence. Standards in the SSQ program are pure elements that were not analyzed at the same time under the same conditions as the unknowns; therefore, the results are considered to be semiquantitative because of unknown matrix effects and differences in operating conditions between the analyses of standards and analyses of unknowns.

The NH_4^+-exchange capacities of the three samples containing the highest amounts of clinoptilolite as determined from x-ray diffractograms were measured following the method of Busenberg and Clemency (1973). One hundred milligrams of each sample was saturated overnight with NH_4^+ using a 1 N ammonium-acetate solution (pH 7) and then leached with 1 N ammonium chloride. Each sample was washed with methanol and water to remove excess ammonium salts, air dried, and placed in a beaker to which deionized distilled water was added. An ammonia electrode was inserted into the beaker, and drops of 10 M sodium hydroxide were added slowly to displace the NH_4^+ ions and convert them to ammonia. After equilibrium was reached, the ammonia potential of each sample was recorded. The NH_4^+-exchange capacity was then determined by comparison with standard solutions of ammonium chloride.

SAMPLE DESCRIPTIONS

GENERAL DESCRIPTIONS

General descriptions of hand specimens, and results of x-ray diffractometer analyses of all samples collected from the Brushy Basin Member are presented in tables 1 and 2, respectively. Petrographic examination of selected samples revealed well-preserved vitroclastic textures and variable amounts of altered glass shards, lava, and other lithic fragments, along with detrital or pyrogenic grains of quartz and feldspars, in a fine-grained matrix. Accretionary lapilli and originally vitric shards are well preserved in the tuffs. Detrital, rounded quartz grains are present throughout the fine-grained matrix, and authigenic microcrystalline quartz and chalcedony are locally abundant. Feldspars include sodic plagioclase and potassium feldspars—sanidine, orthoclase, and (rarely) microcline. X-ray diffractograms of UT–85–5b and UT–85–5c revealed significant amounts of potassic sanidine, which may be present in small amounts in other samples as well. Some of the sodic plagioclase may be albite that formed during burial diagenesis of the tuffaceous material. However, recent studies suggest that the authigenic albite may have formed during early diagenesis of volcanic ash (Fishman and others, in press). Authigenic albite has been found in Brushy Basin sediments at other locations on the Colorado Plateau (Fishman and others, in press; Hansley, 1984). Clay minerals are chiefly smectitic (expandable smectite/illite), but small, variable amounts of illite, kaolinite, and chlorite(?) are also present. Vermiculite is the dominant clay mineral in samples UT–85–3c and UT–85–3e. All samples contain some calcite as a replacement of the smectitic matrix and clinoptilolite. Gypsum was detected in UT–85–2a and was also noted during SEM examination of UT–85–4a and UT–85–5a. Analcime was identified in only one sample, UT–85–5d.

PETROGRAPHIC DESCRIPTIONS OF SELECTED SAMPLES

Sample UT–85–3d, a well-indurated tuff, was collected on Cannon Ball Mesa, located on the north side of McElmo Canyon just north of the Reservation. It contains altered shards embedded in a smectitic matrix. Most shards have altered to smectite, although irregular red areas and some shard pseudomorphs have been replaced by chalcedony and (or) calcite. Locally, both smectite and chalcedony have been replaced by calcite. Sparse, angular quartz and feldspar occur throughout the microcrystalline, quartz-rich, smectitic matrix. Clinoptilolite was not detected in this sample.

Sample UT–85–4a was collected on the eastern edge of the clinoptilolite-bearing facies of the Brushy Basin Member in McElmo Canyon. The sample has a well-preserved vitroclastic texture, and clinoptilolite forms pseudomorphs of the originally vitric shards (fig. 2) and of the rare pumice fragments. The largest (about 170 µm long) clinoptilolite crystals occur in vugs and are commonly rimmed by chalcedony. Calcite locally has replaced chalcedony and clinoptilolite. Some shards are replaced by smectite and rimmed by chalcedony. Sparse, angular quartz, plagioclase, and rock fragments are scattered throughout the smectitic matrix.

Samples UT–85–5, UT–85–5c, UT–85–5g, and UT–85–5h were collected from the Brushy Basin Member in the San Juan River valley on the extreme southwestern part of the Reservation. Sample UT–85–5 is a mixture of red and green sandy tuff. The reddish portion contains abundant clinoptilolite, but the greenish portion has only a trace. Both red and green parts contain detrital grains of quartz, feldspar, rock fragments, rare pyroxene, and traces of calcite and pyrogenic biotite; red areas contain significantly more plagioclase than green areas. Sample UT–85–5g is a sandy altered tuff that is predominantly smectite with abundant detrital quartz and feldspar and traces of clinoptilolite. Samples UT–85–5c and UT–85–5h are vitric tuffs that have altered chiefly to clinoptilolite. Sample UT–85–5c has a spectacular vitroclastic texture characterized by clinoptilolite pseudomorphs of originally vitric shards. Sample UT–85–5h has more quartz, smectite, plagioclase, biotite, and calcite than UT–85–5c, with many shards altered to smectite or to clinoptilolite with a smectitic border.

Sample UT–85–6 is an altered vitric tuff that was collected from a roadcut adjacent to the Four Corners Monument. Clinoptilolite has replaced originally vitric shards that

Table 1. Localities and descriptions of samples collected from the Brushy Basin Member of the Morrison Formation.

Sample[1]	Locality	Color[2]	Description
UT–85–1a	South side of Sleeping Ute Mountain, sec. 10, T. 33½ N., R. 18 W., lat 37°10'30"N., long 108°47'35"W.	Dusky yellow (5Y 6/4)	Silicified tuff; base of exposed Brushy Basin Member
UT–85–1b		Pale olive (10Y 6/2)	Silicified tuff; irregular patches of dark-green chalcedony; 0.5 m above **1a**
UT–85–1c		Pale olive (10Y 6/2)	Altered tuff; 1 m above **1b**
UT–85–2a	Coyote Wash, west edge of Reservation, SE¼ sec. 33, T. 34 N., R. 20 W., lat 37°15'N., long 109°00'W.	Light greenish-gray (5GY 8/1)	Sandy tuff; base of exposed Brushy Basin Member
UT–85–2b		Grayish yellow-green (5GY 7/2)	Sandy tuff; red veinlets; base of exposed Brushy Basin Member
UT–85–3a	McElmo Canyon, southeast side of Cannon Ball Mesa, SE¼ sec. 29, T. 36 N., R. 19 W., lat 37°20'50"N., long 108°56'10"W.	Pinkish gray (5YR 8/1)	Lowest altered tuff; reddish-brown streaks
UT–85–3b		Greenish gray (5GY 6/1)	Tuff; irregular red areas
UT–85–3c		Dusky green (5G 3/2)	Dense nodule in tuff; 3 m above **3b**
UT–85–3d		Light greenish-gray (5GY 8/1)	Altered tuff; well-indurated; sparse irregular red streaks
UT–85–3e		Grayish olive-green (5GY 3/2)	Altered tuff; well-indurated
UT–85–3f		Pale olive (10Y 6/2)	Altered tuff; highest tuff
UT–85–4a	West end, north side of McElmo Canyon, SE¼ sec. 31, T. 36 N., R. 20 W., lat 37°20'N., long 108°57'50"W.	Dark reddish-brown (10R 3/4)	Clinoptilolite-rich tuff; well-indurated
UT–85–4b		Pale reddish-brown (10R 5/4)	Clinoptilolite-rich tuff
UT–85–5gn	Reentrant, north side of San Juan River valley, NE¼ sec. 22, T. 32 N., R. 20 W., lat 37°00'05"N., long 109°02'40"W.	Grayish olive-green (5GY 3/2)	Multicolored altered tuff just above Westwater Canyon Member
UT–85–5rd		Pale reddish-brown (10R 5/4)	
UT–85–5a		Light brown (5YR 6/4)	Clinoptilolite-bearing tuff; 6 m above **5rd**
SJ–85–2a		Grayish orange-pink (5YR 7/2)	Tuffaceous sandstone; 7 m above **5a**
UT–85–5aa		Pale red (10R 6/2)	Clinoptilolite bands in gray shale above organic-rich zone
UT–85–5b		Grayish green (10GY 5/2)	Well-indurated tuff; red streaks
UT–85–5c		Pale reddish-brown (10R 5/4)	Clinoptilolite-bearing tuff; 6 m above **5b**
UT–85–5d		Grayish green (10GY 5/2)	Sandy altered tuff; 3 m above **5c**
UT–85–5e		Grayish orange-pink (5YR 7/2)	Altered tuff; chalky
UT–85–5f		Grayish orange-pink (5YR 7/2)	Altered tuff
UT–85–5g		Grayish orange-pink (5YR 7/2)	Altered tuff
UT–85–5h		Moderate orange-pink (10R 7/4)	Altered tuff; just below contact with Cretaceous rocks; 1 m above **5g**
UT–85–6	Roadcut at entrance to Four Corners Monument, T. 32 N., R. 21 W., lat 37°00'02"N., long 109°02'36"N.	Moderate reddish-brown (10R 4/6)	Clinoptilolite-rich tuff

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[1] Number in third term denotes sample-collection site indicated in figure 1.

[2] Colors are from the rock-color chart (Goddard, 1948).

Table 2. Mineralogical composition of tuffaceous samples of the Brushy Basin Member of the Morrison Formation, as estimated from x-ray diffractograms of bulk samples.

[Ni-filtered $CuK\alpha$ radiation. Numbers are 2-theta peak heights in chart units for the peaks in brackets; n.d., not detected]

Sample	Clinoptilolite [020]	Quartz [100]	Clay Minerals[1] [001]	Plagioclase [202]	Other[2]
UT–85–1a	n.d.	40	6	11	n.d.
UT–85–1b	n.d.	54	4	10	n.d.
UT–85–1c	n.d.	90+	7	34	n.d.
UT–85–2a	n.d.	58	21	55	Gypsum (4,[020])
UT–85–2b	n.d.	78	32	38	n.d.
UT–85–3a	3	76	21	39	n.d.
UT–85–3b	22	45	7	19	n.d.
UT–85–3c	n.d.	90+	4	37	Vermiculite (7,[001])
UT–85–3d	n.d.	51	12	14	n.d.
UT–85–3e	n.d.	90+	3	34	Vermiculite (3,[001])
UT–85–3f	n.d.	90+	2	10	Illite (7,[001]); kaolinite (7,[001])[3]
UT–85–4a	36	77	4	38	n.d.
UT–85–4b	34	42	7	23	n.d.
UT–85–5gn	2	48	3	17	Kaolinite (9,[001])[3]
UT–85–5rd	48	58	4	27	n.d.
UT–85–5a	68	39	23	73	n.d.
UT–85–5aa	13	33	11	40	n.d.
UT–85–5b	5	89	3	trace	Authigenic sanidine (59,[220])
UT–85–5c	25	39	6	17	Authigenic sanidine (18,[220])
UT–85–5d	2	90+	10	77	Analcime (19,[400]); kaolinite (10,[001])[3]
UT–85–5e	9	31	21	20	n.d.
UT–85–5f	14	81	26	40	n.d.
UT–85–5g	5	38	18	28	n.d.
UT–85–5h	38	68	24	83	n.d.
UT–85–6	50	42	4	16	n.d.

[1] Unknown mixture of 10–14Å mixed-layer clay minerals.

[2] Potassium feldspar and calcite occur in all samples.

[3] May include [002] 14Å clay mineral.

are embedded in a smectitic matrix containing volcanic(?) lithic fragments and biotite. Isolated patches of calcite have replaced the smectite.

CLINOPTILOLITE

DESCRIPTION AND IDENTIFICATION

Clinoptilolite is monoclinic and is a member of the heulandite structural group (Gottardi and Galli, 1985). It is distinguished from heulandite by a higher Si:Al ratio (>4.0) (Boles, 1972), a higher Na+K:Na+K+Ca+Mg ratio (>0.6) (Mason and Sand, 1960), a lower mean index of refraction (<1.485) (Mason and Sand, 1960), and thermal stability above 450°C (Mumpton, 1960). Clinoptilolite is generally stable up to 700°C, whereas heulandite either decomposes or converts to a different structure at 450°C (Alberti, 1975). Many clinoptilolite-heulandite minerals exhibit intermediate chemical and physical properties and thermal behavior (Alietti, 1972); the Brushy Basin samples are no exception.

Chemical and physical data collected during this study indicate that the heulandite-group zeolite in the Brushy

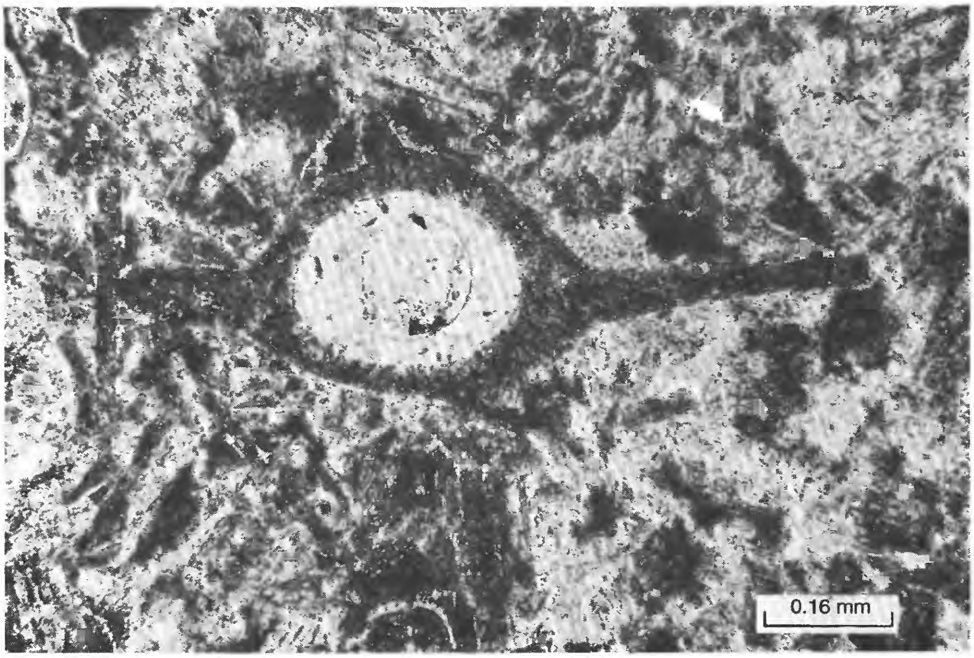

Figure 2. Clinoptilolite pseudomorph of a glass shard in a smectitic matrix of altered tuff. Sample UT–85–4a from the Brushy Basin Member of the Morrison Formation. Plane-polarized light.

Basin Member is clinoptilolite. The average Si:Al ratio of eight zeolite crystals in sample UT–85–4a is 4.3 based on measurements of eight crystals; values ranged from 4.1 to 4.8. Samples UT–85–4a and UT–85–5a retained their structures after heating for 15.75 hours at 450°C, although UT–85–5a showed a 40 percent loss in intensity of the [020] reflection. SEM examination of samples revealed crystal forms dominated by [010] lamellae characteristic of clinoptilolite (Gottardi and Galli, 1985) (fig. 3). On the other hand, the mean indices of refraction of representative samples of Brushy Basin clinoptilolite crystals are relatively high, ranging from 1.484 to 1.492 (table 3), which may be due in part to the presence of ferric oxide and a high calcium content. A high index of refraction in heulandite-group minerals is generally attributed to calcium substitution for potassium and sodium (Shepard and Starkey, 1966) or to a lower Si:Al ratio (Boles, 1972). The cation ratios could not be used for identification because of the impurity of the samples.

Clinoptilolite is characteristic of low-temperature, near-surface, silicic tuffaceous sedimentary deposits, whereas heulandite occurs chiefly in hydrothermal or deeply buried deposits (Gottardi and Galli, 1985) and commonly in mafic volcanic rocks, regardless of burial depth. Based on Si:Al and cation ratios, Bell (1983) identified all heulandite-group zeolite species (with the exception of one sample) collected from the Brushy Basin Member in the southeastern part of the San Juan basin as clinoptilolite.

In the present study, the largest prismatic clinoptilolite crystals (up to 170 μm in length) have parallel extinction and are length slow (fig. 4). The tips of these cloudy, orange-red crystals are commonly clear. The salmon-orange to red-orange colors of clinoptilolite-bearing beds in the Brushy Basin Member (as opposed to the white-gray colors of most

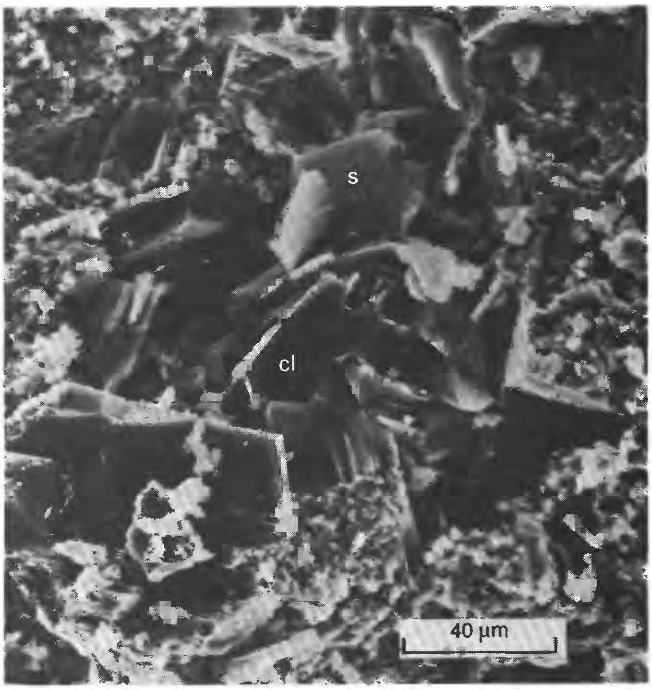

Figure 3. Scanning electron micrograph of clinoptilolite (**cl**) crystals filling a vug in the smectitic (**s**) matrix of altered tuff. Sample UT–85–4a from the Brushy Basin Member of the Morrison Formation.

Table 3. Mean index of refraction for selected samples of clinoptilolite in the Brushy Basin Member of the Morrison Formation. All crystals are length slow.

Sample	Mean index of refraction
SJ–85–2a	1.485
UT–85–4a	1.492
UT–85–5a	1.484
UT–85–5c	1.490
UT–85–6	1.489

clinoptilolite-rich beds) are due to the presence of ferric oxide. Hydrothermal clinoptilolite that has a similar red color and contains 0.75 weight percent structural ferric oxide has been reported from Italy (Alberti, 1975; Gottardi and Galli, 1985). In the Brushy Basin samples, it is unknown whether ferric iron has substituted for aluminum in the clinoptilolite structure or whether the iron is present as submicroscopic inclusions that exsolved from original structural positions in the zeolite. Examination of large crystals in transmitted plane-polarized light under high magnification, however, did not reveal a separate ferric-oxide phase.

CHEMICAL COMPOSITION

The chemical composition of clinoptilolite [$Ca_x(Na,K)_{6-2x}(Al_6Si_{30}O_{72})\cdot 24H_2O$] is approximated by bulk analyses of samples containing the most clinoptilolite (table 4). Estimates of the amount of clinoptilolite in these samples can best be obtained by using the water content as a guide, because clinoptilolite averages 14 percent water (Gottardi and Galli, 1985). Assuming that all the water is in the clinoptilolite, sample UT–85–4a contains 49 percent clinoptilolite, and sample UT–85–6 contains 55 percent. However, the amount of clinoptilolite in sample UT–85–5a cannot be determined in this manner because of its high clay content. High silica contents in all three samples reflect the proportions of detrital and authigenic quartz. Sodium is the dominant cation in sample UT–85–5a but calcium is dominant in the others. Not all of the sodium and calcium are contained in the clinoptilolite; some sodium is in plagioclase and some calcium is in calcite. Sample UT–85–5a is higher in Al_2O_3 because of a higher clay mineral content. Fe_2O_3 contents of these samples are higher than for most clinoptilolites (or heulandites) inasmuch as the highest Fe_2O_3 content in clinoptilolite reported by Gottardi and Galli (1985) is only 1.75 weight percent.

A comparison of the chemical analysis of sample UT–85–4a with the SSQ analysis of clinoptilolite crystals from the same sample (table 5) gives a clearer picture of the composition of clinoptilolite. Although the normalized analytical totals are anhydrous, the relative amounts of oxides are meaningful. SSQ results show that the Fe_2O_3 content is consistently less than 1 percent, suggesting that some iron in the bulk sample is contained in clay minerals or iron oxides. Al_2O_3 values are 13–16 percent, typical of clinoptilolite. MgO is 0.4–3.8 percent; clinoptilolite crystals having the

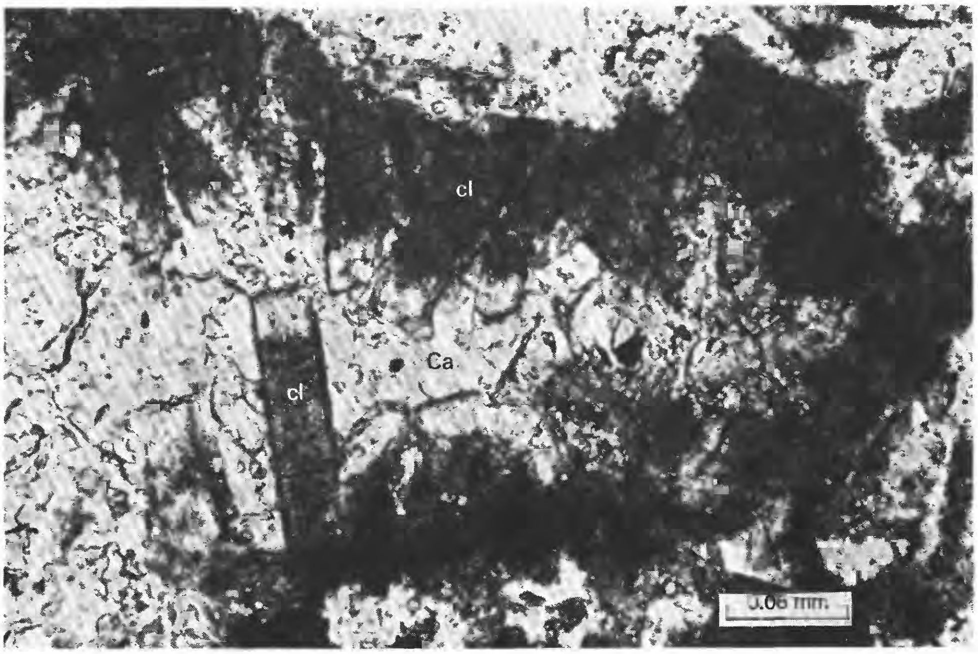

Figure 4. Clinoptilolite (cl) crystals lining a calcite-filled (Ca) vug in altered tuff. Sample UT–85–4a from the Brushy Basin Member of the Morrison Formation. Note transparent tips of cloudy clinoptilolite crystals. Plane-polarized light.

Table 4. Chemical analyses of three clinoptilolite-rich tuffs in the Brushy Basin Member of the Morrison Formation.

[Numbers represent composition in weight percent. X-ray fluorescence analyses by A.J. Bartel, K. Stewart, and J. Taggart, analysts]

Major oxide	Sample		
	UT–85–4a	UT–85–5a	UT–85–6
SiO_2	76.5	66.8	74.1
Al_2O_3	8.82	14.3	10.0
Fe_2O_3	1.76	2.29	1.87
MgO	0.51	1.24	0.74
CaO	1.98	1.22	1.73
Na_2O	1.52	2.56	1.33
K_2O	1.46	1.97	1.53
TiO_2	0.24	0.28	0.1
P_2O_5	<0.05	<0.05	<0.05
MnO	0.07	0.02	0.04
LOI[1]	6.89	8.89	7.67
Total	99.80	99.62	99.16

[1] LOI: Loss on ignition (H_2O) at 900°C.

highest MgO contents have the lowest Si:Al ratios. K_2O is 0.9–2.56 percent, and Na_2O is 0.46–1.9 percent. Low Na_2O values are probably due to absorption. The CaO contents of the analyzed crystals in sample UT–85–4a are consistently high, ranging from 5.16 to 5.59 percent; thus, this clinoptilolite is calcium rich inasmuch as most clinoptilolites average only 1–3 percent CaO (Gottardi and Galli, 1985).

NH_4^+-EXCHANGE CAPACITY

The NH_4^+-exchange capacity of clinoptilolite-bearing tuffs from the Brushy Basin Member was determined because many commercial or potential uses of clinoptilolite are based on this property. The exchange capacity of a zeolite is directly related to the amount of aluminum that substitutes for silicon in the zeolite structure (Flanigen and Mumpton, 1981), because substitution of aluminum for silicon results in a charge deficiency that is balanced by incorporation of monovalent or divalent cations. The NH_4^+-exchange capacities of six samples from three tuffs relatively rich in clinoptilolite range from 0.33 to 0.51 meq/g (table 6). Even taking into consideration the fact that these values represent the NH_4^+-exchange capacities of impure bulk samples, the values are low compared to the average cation-exchange capacity (2.3 meq/g) of pure clinoptilolite (Flanigen and Mumpton, 1981).

Table 5. Semiquantitative analyses of clinoptilolite crystals from sample UT–85–4a from the Brushy Basin Member of the Morrison Formation.

[Values are average normalized compositions in weight percent based on 3–5 analyses per crystal; totals represent anhydrous samples. Analyses made with the Tracor Northern Semiquantitative Analysis System (SSQ) attached to a Cambridge 250 Mark 2 scanning electron microscope: accelerating potential, 20 kV; beam diameter, 1 μm; count time, 30 sec; take-off angle, 56.5°; corrected for atomic number, absorption, and fluorescence; pure elemental standards used by SSQ program]

Major oxide	Clinoptilolite crystal number							
	1	2	3	4	5	6	7	8
SiO_2	75.03	76.67	76.23	74.23	72.25	71.96	72.64	79.25
Al_2O_3	14.71	15.02	14.70	15.33	15.49	15.10	14.93	13.92
Fe_2O_3	0.61	0.27	0.45	0.47	0.63	0.83	0.89	0.12
MgO	1.62	1.06	1.10	1.71	2.34	2.70	2.44	0.23
CaO	5.28	5.16	5.60	5.59	5.50	5.22	5.19	5.19
Na_2O	1.00	0.58	0.60	1.14	1.78	2.15	1.96	0.03
K_2O	1.78	1.20	1.31	1.57	2.01	2.04	2.02	1.29
Total	100.30	99.96	99.99	100.04	100.00	100.00	100.07	100.03

Table 6. NH_4^+-exchange capacity of three clinoptilolite-bearing tuffs from the Brushy Basin Member of the Morrison Formation.

[Analytical method after Busenberg and Clemency (1973); D. Eberl, analyst]

Sample	NH_4^+-exchange capacity (meq/g)
UT–85–4a	0.33
UT–85–4a	0.34
UT–85–4a	0.51
UT–85–5a	0.39
UT–85–5a	0.44
UT–85–6	0.49

ECONOMIC POTENTIAL OF CLINOPTILOLITE-BEARING TUFFS ON THE UTE MOUNTAIN UTE RESERVATION

Based on the data presented in this report, the economic potential of clinoptilolite-bearing tuffs in the Brushy Basin Member is low. Although the samples collected for analysis were taken from tuffs containing the most clinoptilolite, this zeolite constitutes no more than 55 percent of any sample. The other mineral phases present in these samples detract from the economic value of the clinoptilolite because of the difficulty and high costs of purification. In addition, the low NH_4^+-exchange capacity of the clinoptilolite-bearing tuffs and the presence of relatively thick post-Jurassic overburden on the Morrison Formation would render mining of clinoptilolite prohibitively expensive.

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