

**GEOLOGY, MINERALOGY, AND MINING OF THE  
BOWIE ZEOLITE DEPOSIT,  
GRAHAM AND COCHISE COUNTIES, ARIZONA**

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**INTRODUCTION**

The Bowie deposit is probably the most commercially important zeolite deposit in the United States. It is the largest known body of chabazite in the country, and although only about 12,000 tons of material has been mined from this body since 1962, the value of the high-grade chabazite ore has been about \$40,000,000. Most of the mined ore has been pelletized for use in the removal of CO<sub>2</sub> from low BTU natural gases, the drying of acid gases, and the extraction of radioactive cesium and strontium from contaminated waters. The Bowie deposit is also significant in that it demonstrates that beds of zeolitic tuff as thin as 10–20 cm can be mined and processed economically.

The Bowie deposit has been claimed by Union Carbide Corporation and other industrial organizations since 1961. Because of its ease of access, flat-lying nature, and abundant exposures in outcrop and mining pits, the Bowie deposit has been visited numerous times by organized field trips, beginning with ZEOLITE '76, the International Conference on the Occurrence, Properties Utilization of Natural Zeo-

lites, held in Tucson, in 1976. Geologically, the Bowie deposit well illustrates many of the mineralogical and sedimentological features characteristic of zeolitic tuffs formed from precursor volcanic ash in saline, alkaline lakes. Much of the present report is taken or expanded from the field guide to that trip prepared by Sheppard et al. (1978) and from later reports by Eyde (1978, 1982).

**LOCATION**

The Bowie zeolite deposit is located in the San Simon valley of southeastern Arizona, about 155 km east of Tucson. San Simon Valley is a northwest-trending intermontane basin in the Mexican Highland section of the Basin and Range physiographic province. The valley is about 120 km long, extending from Rodeo, New Mexico, northward to Safford, Arizona. It is about 35 km wide at its central part near Bowie (Figure 1)

The San Simon River flows northwestward through the valley to join the Gila

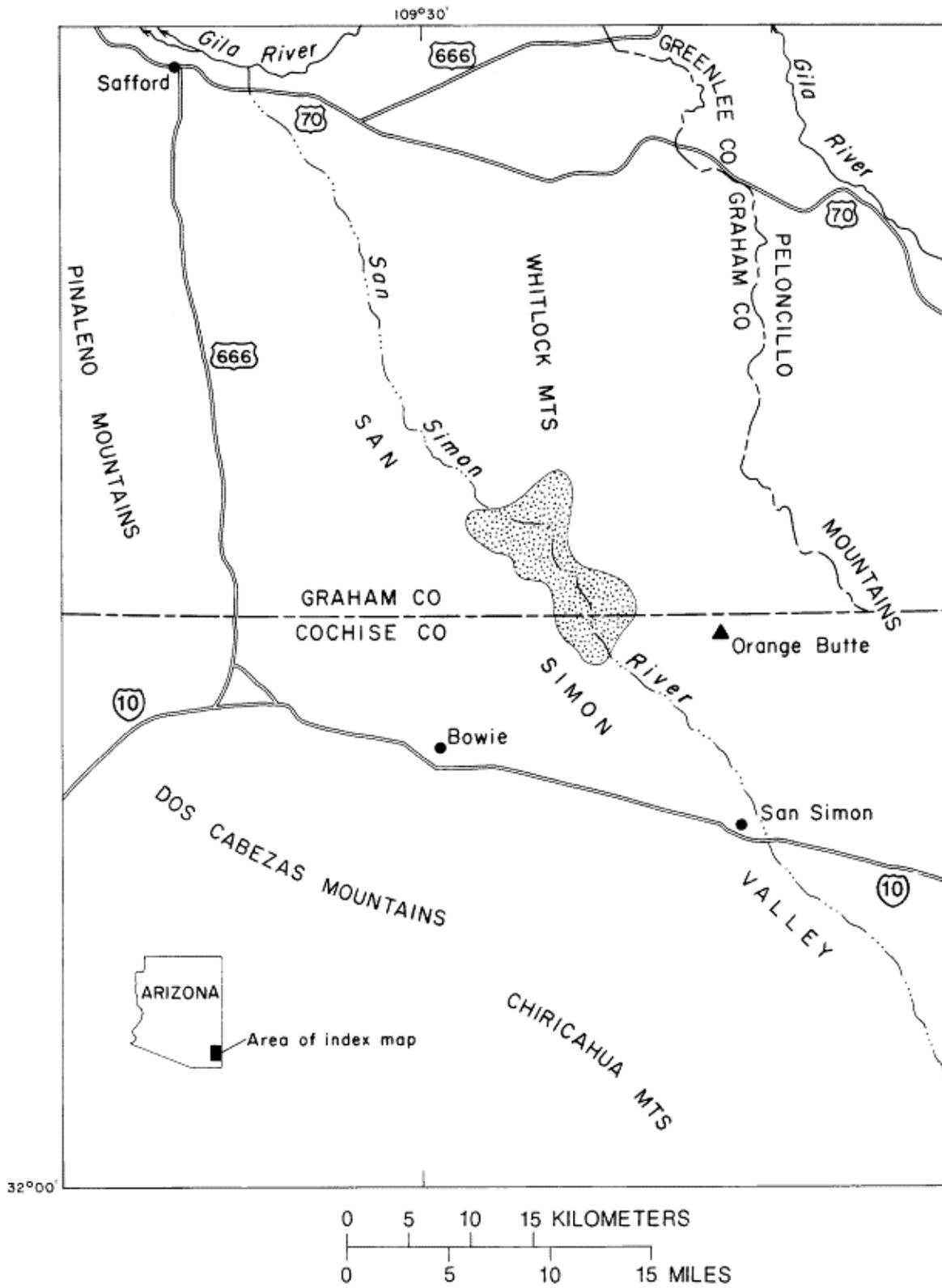


Figure 1. Index map of southeastern Arizona showing Bowie zeolite deposit (shaded) in San Simon Valley.

River near Safford. The San Simon Valley is bounded on the east by the Whitlock and Peloncillo Mountains and on the west by the Pinaleno, Dos Cabezas, and Chiricahua Mountains. The town nearest to the zeolite deposit is Bowie, located just north of Interstate Highway 10. Improved dirt roads provide access northward from Bowie to the deposit, a distance of about 21 km (13 mi.). Although the land immediately north of Bowie is intensely farmed for cotton and contains numerous pecan orchards, the desert north of the Graham-Cochise County line is open range and virtually unpopulated.

Zeolite ore is hauled by truck from pits at the deposit to warehouses at Bowie, where it is shipped on the Southern Pacific Railroad to processing plants in Alabama and other locations.

#### HISTORY OF THE DEPOSIT

The report of Loew (1875) is probably the earliest reference to a bedded zeolite deposit in the United States. He described an outcrop of what apparently is the chabazite-bearing "marker" tuff (vide infra) of the Bowie deposit, about 6.5 km south of Whitlock Cienga (see Sheppard et al., 1978), however, no evidence exists that Lowe's report was ever common knowledge, and the exact site of Lowe's discovery cannot be located today. As reported by Eyde (1978), in the late 1950s, Ernest Baugher, a retired railroad engineer from Buffalo, New York, discovered outcrops of soft tuff in the area of the present deposits while mineral collecting in the area. Although he was unaware of the zeolitic nature of the tuff, he recognized the potential of these lightweight "tuffa stones" and convinced Frank Meadows and Paul Sanger, both of whom worked for the Southern Pacific, that the deposit was valuable. In the Spring of 1959, they staked together the BMS claims covering outcrops of the tuff in the central and northwestern parts of the deposit. At about this same time, Frank Clark, a butcher in Bowie and part-time prospector, staked with Gus Fernstrom the Tuffa Tex claims covering outcrops in the southeastern part of the deposit. Both Baugher and Clark quarried the lower, massive bed of the variegated tuff and fabricated bookends, lamp bases, paperweights, and pencil holders from it. These souve-

nirs, made of so-called "Arizona Tuffa-Tex", were sold at stores and shops along the Tucson-El Paso highway during the late 1950s and 1960s.

In 1959, geologists employed by Union Carbide Corporation evaluated the deposit following the submittal of a sample of the zeolitic tuff by K. G. Bell, chief chemist of Kennedy Minerals Company (see Mumpton, 1984). Chabazite and erionite were identified in the samples by Xray powder diffraction (XRD) at Carbide's Linde Division in Tonawanda, New York, but low XRD peak heights suggested that only minor quantities of these zeolites were present. Because of its apparent large areal extent and flat-lying, near-surface nature, the deposit was re-examined in early 1960, and several dozen samples were submitted to the Linde laboratory. Once again, only minor amounts of chabazite and erionite were indicated by the XRD patterns; however, no other crystalline materials nor glass, for that matter, were indicated either. To establish unequivocally the zeolite content of the Bowie tuff, oxygen adsorption analyses were made, a procedure routinely employed by Linde to evaluate materials that, from XRD analyses, contained major percentages of zeolite minerals. Oxygen adsorption values as high as 22 wt. % O<sub>2</sub> were found for many of the samples, equivalent to a chabazite content of 80-90% (see Mumpton, 1984). A re-evaluation of the XRD data later disclosed that the very fine grain size (about <0.1-1 vide infra) of the chabazite in the tuff was probably responsible for the broad, weak peaks that had been interpreted earlier as indicative of a low zeolite content.

In April 1961, the Linde Division of Union Carbide Corporation located 249 placer claims covering about 4980 acres and filed for prospecting permits covering an additional 2640 acres on State land (see Eyde, 1978). This land position covered most of the deposit behind the outcrops, which were already covered by the BMS and Clark-Fernstrom claims. In 1965, the Davison Chemical Division of W. R. Grace acquired 1450 acres of placer claims and State prospecting permits covering lands in the southeastern part of the deposit that had been released by Union Carbide. In subsequent years, Norton Company, Letcher and Associates, NRG Incorporated, Filtrrol Corporation, and Anaconda Minerals Company

acquired claim groups and State lands which either had not been acquired or had been dropped by Union Carbide following the completion of an exploratory drilling program in 1963.

Significantly in 1982, Union Carbide reacquired 620 acres of State mineral leases covering reserves of chabazite having a high sodium content, and in 1985 it relocated 34 claims which had been dropped by Anaconda. In 1986, East-West Minerals Inc. acquired the State mineral leases held by Anaconda, and GSA Resources Inc. bought the State mineral leases held by W. R. Grace. Currently, the following organizations and individuals hold property positions on the Bowie, Arizona, zeolite deposit: Union Carbide Corporation, Letcher and Associates, NRG Incorporated, Norton Company, East-West Minerals, Inc., GSA Resources, Inc., T. E. Higgins, and J. M. Phillips.

#### **GEOLOGIC SETTING**

The mountain ranges bounding the San Simon Valley contain a wide variety of sedimentary, igneous, and metamorphic rocks (see Drewes et al., 1985). The Whitlock and Peloncillo Mountains are chiefly Tertiary volcanic rocks of rhyolitic to basaltic composition. The Pinaleno Mountains are Precambrian granodiorite to granite, granitic gneiss, and schist overlain by Tertiary volcanic rocks on the southern flank. The Dos Cabezas Mountains consist of Precambrian granite, granitic gneiss, and schist, Paleozoic to Tertiary sedimentary rocks, and Tertiary volcanic rocks. similar variety of lithologies makes up the Chiricahua Mountains; however, Tertiary volcanic rocks and Tertiary granitic intrusive rocks comprise most of the southern part of this range.

The nearly flat-lying alluvial and lacustrine deposits of the San Simon valley have a maximum thickness of 2500 m (Drewes et al., 1985) and are probably late Miocene to Holocene in age. The thickness and character of the valley fill is known mainly from drillers' logs of water wells and several relatively deep wells for petroleum (B. B. Hauser, U.S. Geological Survey, Denver, Colorado, oral communication, 1987). Natural exposures of the sedimentary deposits are poor, and the maximum thickness ex-

posed is typically no more than several meters. A conspicuous zeolitic tuff, herein termed the "marker tuff", is part of a unit mapped as "older alluvial fill" by Cushman and Jones (1947). The older alluvial fill consists mainly of claystone, siltstone, sandstone, and gravel, and Cushman and Jones concluded that some of the fine-grained detrital sediments of the San Simon valley were deposited in a closed lake basin. The lower part of the older alluvial fill contains water under artesian pressure and is the source of most of the ground water in the valley (White, 1963).

Although the detailed stratigraphy of the older alluvial fill is unknown, a hole drilled by the U.S. Geological Survey (Edson, 1977) in the central part of the Valley about 3.3 km northwest of Field Trip Stop 3 (see Figure 2) penetrated the marker tuff and about 50 m of the underlying lacustrine claystone. Another zeolitic tuff (65 cm thick) was intersected by the drill hole about 23.5 m beneath the marked tuff. A hole drilled for Anaconda Minerals Company about 3 km northeast of Field Trip Stop 4 intersected a chabazite-rich tuff (15 cm thick) about 12.2 m beneath the marker tuff. These stratigraphically lower tuffs do not crop out in the Valley.

The marker tuff is part of a fine-grained unit of the Gila Conglomerate (upper Miocene to Pleistocene) that was mapped in the northwestern part of San Simon Valley (Drewes et al., 1985). Where mapped and studied south and southeast of Safford by Houser et al. (1985), this unit is considered to be equivalent to lacustrine and fluvial beds of 111 (one-eleven) Ranch of Pliocene age. The lacustrine sediments were deposited in Tertiary Lake Graham, which at its maximum may have extended from Pima, near Safford on the northwest, to Bowie on the southeast (Houser et al., 1985).

#### **MARKER TUFF**

The marker tuff is the most conspicuous and resistant unit in the lacustrine sediments. Even so, natural exposures are rather scarce, and the tuff crops out discontinuously near the 3450-foot contour for about 15 km along both sides of the Valley (Figure 2). The marker tuff has also been recognized in the subsurface to a distance

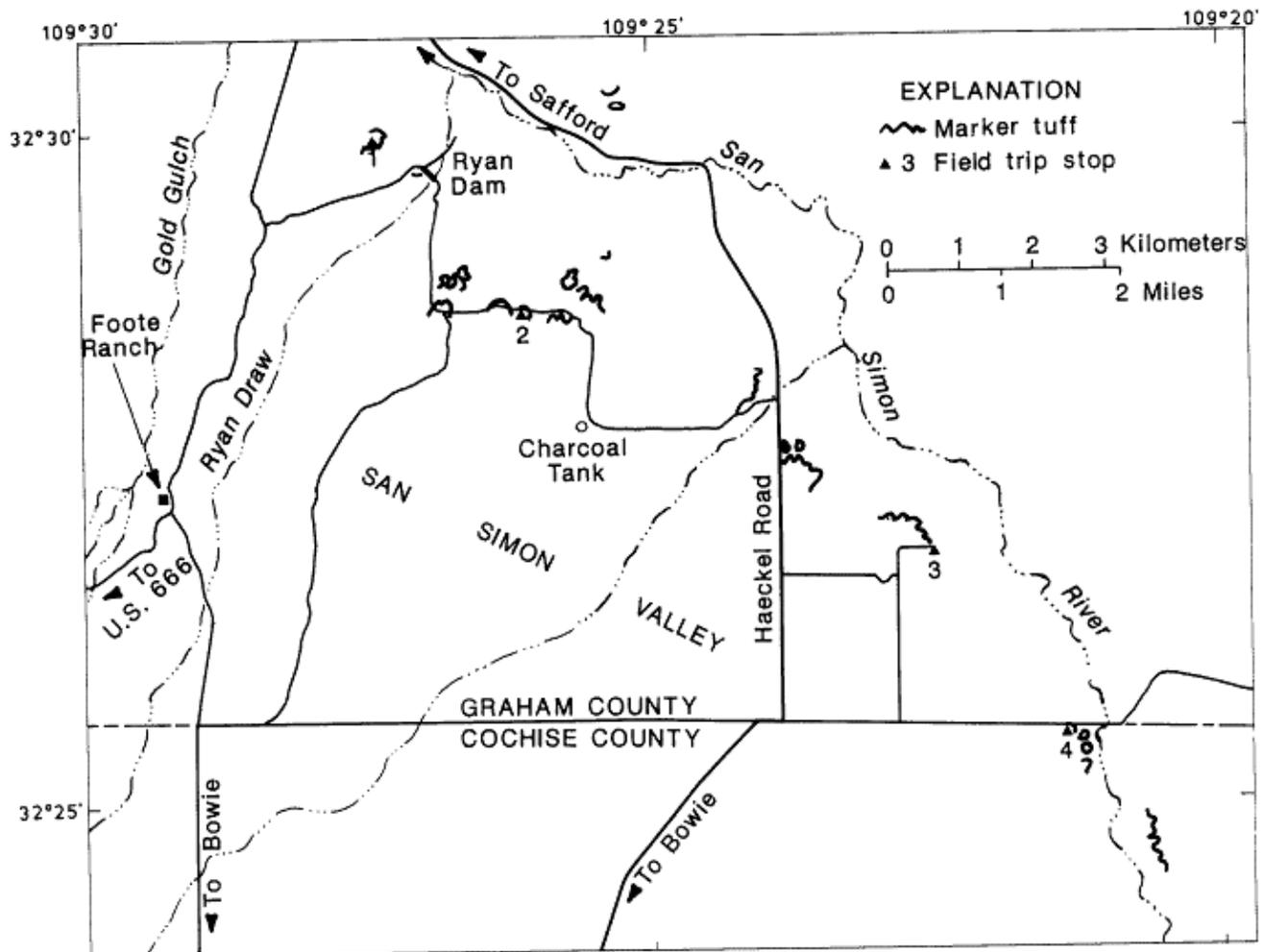


Figure 2. Map showing outcrop distribution of marker tuff and field trip stops at the Bowie zeolite deposit.

of about 1.5 km southeast of the southernmost outcrop. Most of the outcrops and the areas being mined, however, are along the southwestern side of the Valley. Unpublished data from more than 3000 drill holes by mining companies suggest that the marker tuff originally was distributed over an area of about 280 km<sup>2</sup> in the central part of the basin (Eyde, 1982). Its present areal distribution, however, is probably not more than about 20 km<sup>2</sup>

The present limited and discontinuous nature of the marker tuff is due chiefly to removal by erosion. Some of the tuff was eroded after the original glass altered to zeolites, as shown by the rounded fragments of the zeolitic tuff which occur in unconsolidated sand and gravel of fluvial channel deposits. Furthermore, the tuff is still being eroded. Other areas of the

tuff may have been eroded prior to zeolitization. Eyde (1982) suggested that a network of small streams flowed into, the shallow northwestern part of the lake. These freshwater streams locally eroded and reworked the vitric ash prior to zeolitic alteration. Channel deposits of these streams consist of fine-grained sand and unaltered vitric material and can be recognized in the zeolitic marker tuff in pits at the northwestern part of the deposit. Closely spaced drilling prior to the stripping and mining operations has been necessary to locate these channels. Although difficult to prove, the discontinuous character of the marker tuff may be due, in part, to local areas of non-deposition of the original vitric ash, controlled by the topography of the lake bottom.

Where observed in shallow pits and

natural outcrops, the marker tuff is 22–155 cm thick. This tuff characteristically consists of a basal massive bed, ranging from 10 to 20 cm thick, overlain by 4–135 cm of thin to very thin beds (Figure 3). The thin-bedded part of the marker tuff is thickest near Field Trip Stop 3 and thins to the northwest and southeast. Only the basal bed is mined, and it is commonly termed the "high-grade" bed or the "ore" bed. The overlying thin-bedded tuffs are known as the "thin-bedded" unit or the "low-grade" bed. The color of the marker tuff is white, gray, yellow, or orange, but pastel shades of yellow seem to be most common. The ore bed seems to be especially orange and variegated southeastward from Field Trip Stop 3.

The zeolitic marker tuff has a dull or earthy luster, and it commonly breaks with a hackly or subconchoidal fracture. The original vitroclastic texture and sedimentary structures, such as tipple marks, are generally preserved in the zeolitic tuff. Convolute structures are especially common in the ore bed, and ripple marks are especially common in the overlying thin-bedded unit. Casts of llama and camel tracks have been recognized locally at the base of the ore bed in the northwestern part of the deposit, southwest of the San Simon River (Eyde, 1978, 1982). The tracks attest to

the shallowness of the northwestern part or the ancient lake prior to, at least, the deposition of the vitric ash of the marker tuff.

#### MINERALOGY OF THE MARKER TUFF

Parts of the marker tuff still locally contain relict glass shards. A particularly striking example is at Field Trip Stop 1 (see Figure 2), where most of ore bed and much of the overlying thin-bedded tuffs consist of unaltered glass. Those parts of the marker tuff that are chiefly fresh glass are gray and friable. The vitric particles are very fine grained to fine grained and are of two types: (1) platy bubble-wall shards formed from the walls of relatively large, broken bubbles, and (2) pumice shards that contain small elongated bubbles. Platy bubble-wall shards predominate in the marker tuff. The index of refraction of the unaltered glass is 1.506–1.512 and indicates a silicic composition. Even if relict glass were not recognized in the marker tuff, the generally well-preserved vitroclastic texture (Figure 4) is convincing evidence that volcanic glass was the parent material for the zeolites.

In addition to vitric material, the



Figure 3. Exposure of marker tuff in pit at Field Trip Stop 3. Ore bed (at hammer) is 13 cm thick and is overlain by thin-bedded tuffs that are 112 cm thick.

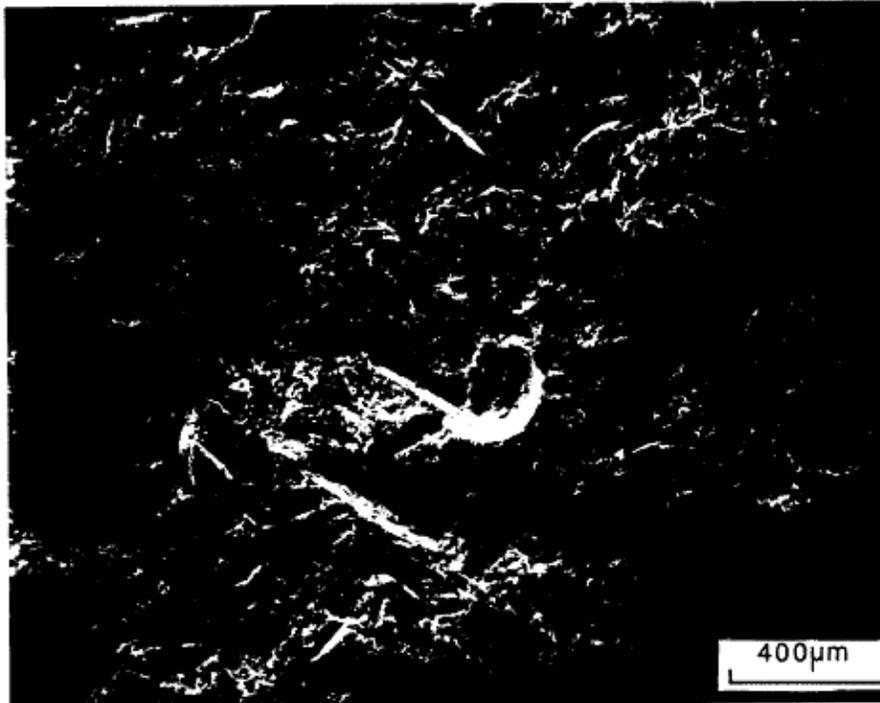


Figure 4. Scanning electron micrograph of ore bed showing excellent preservation of vitroclastic texture. Tuff consists chiefly of chabazite.

marker tuff contains <1–20% crystal fragments of quartz, sodic plagioclase, hornblende, clinopyroxene, and zircon. These crystals, unlike the relatively unstable glass, are generally unaltered in the zeolitic tuff. Hornblende and clinopyroxene, however, are intensely etched.

The mineralogy of the zeolitic marker tuff was determined from XRD data of bulk samples; some representative analyses are given in Table 1. The tuff commonly contains three zeolites, less commonly two zeolites, and rarely one or four zeolites. The most common zeolite assemblage is chabazite, erionite, and clinoptilolite. Small amounts of analcime have been identified in the marker tuff in the southern part of the deposit. In addition to zeolites, the marker tuff commonly contains minor smectite, calcite, quartz, and plagioclase, and locally, minor halite, gypsum, or thenardite.

The relative abundance of chabazite, clinoptilolite, and erionite in the marker tuff is variable from bed to bed and from locality to locality within the same bed. Perhaps the most consistent mineralogical aspect of the marker tuff is the relatively high chabazite content of the ore bed. Al-

though the chabazite content of the ore bed ranges from (5 to 90%, it is commonly in the range 70–80%. Inasmuch as chabazite is the principal zeolite being sought at the Bowie deposit, it is understandable that only the ore bed is mined. Erionite seems to be most abundant in the ore bed from the central part of the deposit.

Analcime has been recognized only in that part of the ore bed from the southeastern part of the deposit. Analcime makes up (10% of the lower part of the ore bed from about Field Trip Stop 3 southeastward. Core from a drill hole about 3.5 km southeast of Field Trip Stop 4 shows that the basal centimeter of the ore bed there consists of about 50% analcime.

#### Chabazite

The zeolites in the marker tuff are generally finely crystalline, and their crystal size, morphology, and grain relationships were determined using a scanning electron microscope. Chabazite commonly occurs as aggregates of minute rhombohedral crystals that form ragged, thin plates (Figures 5–7), 2–25  $\mu\text{m}$  in their longest dimension. The plates are commonly ar-

Table 1. Mineralogical composition of marker tuff and associated rocks at the Bowie zeolite deposit.

Field trip

Stop

(Figure 2) Sample Stratigraphic position

Of sample in cm above

(+) or below (-) base

of marker tuff Xray diffraction analysis of bulk samples

(in parts per ton

			Glass	Mi	Sm	Ch	Cp	Er	An	Qtz	Pl	Gp	Other
1	F	+34, marker tuff, thin bed	7	-	tr	tr	-	1	-	1	1	-	-
	E	+22, marker tuff, thin bed	2	-	1	6	---	1	---	tr	tr	---	---
	D	+16, marker tuff, ore bed	8	-	1	1	---	tr	-	-	-	-	-
	C	+10, marker tuff, ore bed	9	-	1	tr	-	-	-	-	-	-	-
	B	+2, marker tuff, ore bed		-	-	9	1	tr	-	-	-	-	-
	A	-75, siltstone		-	tr	2	---	1	---	4	3	---	---
2	E	+74, siltstone		---	1	1	1	3	tr	---	2	---	---
	D	+20, marker tuff, thin bed		-	-	8	1	1	---	---	---	tr	---
	C	+14, marker tuff, ore bed		---	---	tr	9	1	tr	---			
	B	+4, marker tuff, ore bed		---	---	1	8	tr	1	---	---	tr	---
	A	-2, siltstone		---	1	2	---	tr	---	4	3	---	---
3	F	+165, mudstone		---	2	2	-	-	1	3	2	---	---
	E	+65, marker tuff, thin bed		---	---	tr	-	2	7	-	-	-	1
	D	+23, marker tuff, thin bed		---	---	tr	4	3	2	-	-	-	1
	C	+8, marker tuff, ore bed		---	---	tr	6	2	2	---	-	-	-
	B	+5, marker tuff, ore bed		---	---	tr	5	3	1	1	-	-	-
	A	-5, mudstone		---	tr	4	-	-	1	1	1	1	2
4	D	Spoil pile, unknown interval above ore bed							-	-	tr	1	2
-	tr	-											
	C	+8, marker tuff, ore bed		-	-	tr	8	2	tr	-	tr	-	tr
	B	+1, marker tuff, ore bed		-	-	-	7	2	tr	1	-	-	tr
	A	-10, mudstone		-	tr	4	-	-	2	3	1	-	-

<sup>1</sup>Mi = muscovite, biotite, illite; Sm = smectite; Ch = chabazite; Cp = clinoptilolite; Er = erionite; An = analcime, Qtz = quartz; Pl = plagioclase; Gp = gypsum; Other = halite, except in sample A from Field Trip Stop 3, which contains calcite; --- = looked for but not found.

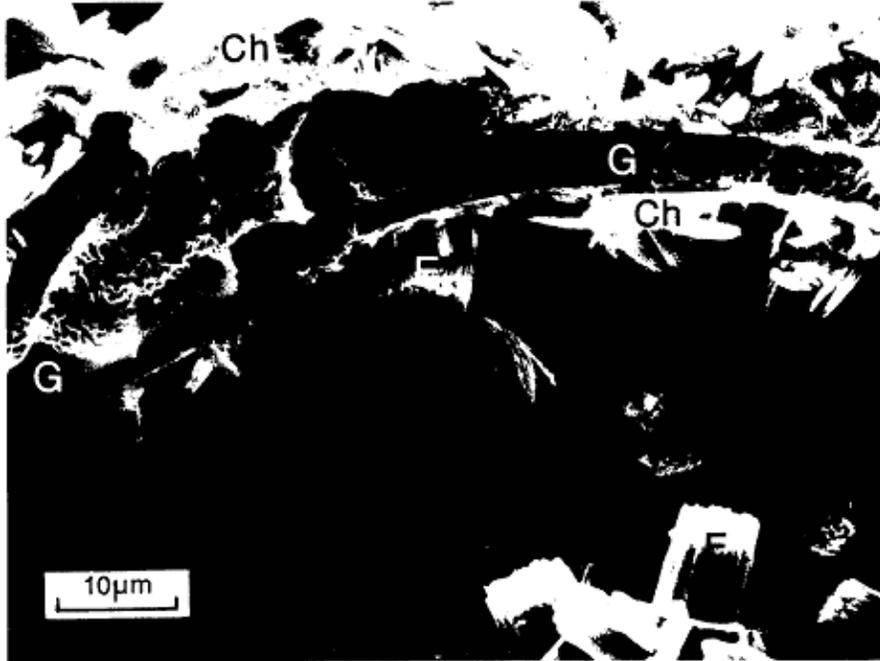


Figure 5. Scanning electron micrograph of ore bed showing an early stage in the alteration of bubble—wall shard. Glass (G) is pitted, and both surfaces of shard are encrusted with ragged plates of chabazite (Ch) and bundles of erionite (E).



Figure 6. Scanning electron micrograph of ore bed showing well-formed tablets of clinoptilolite (Cp) perched on ragged plates of chabazite (Ch). Some clinoptilolite has crystallized in pores formed by the plates of chabazite.

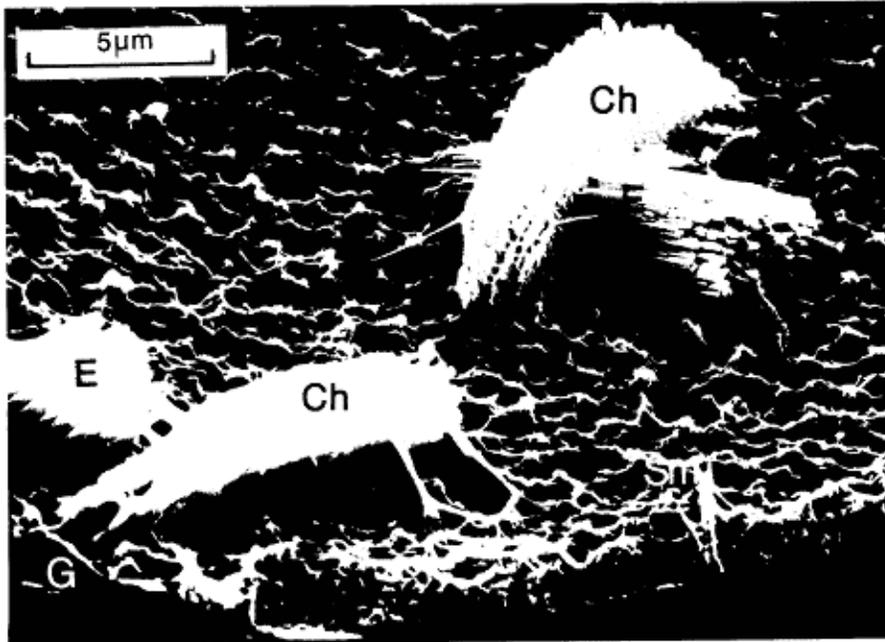


Figure 7. Scanning electron micrograph of ore bed showing ragged plates of chabazite (Ch), bundles of erionite (E), and crenulated aggregate of smectite (Sm) on concave surface of a vitric, bubble-wall shard (G). The smectite has covered much of the surface and has lapped onto the chabazite and erionite.

ranged in fan-like and radial groups as large as 65  $\mu\text{m}$  in diameter. Individual chabazite crystals of the plates range from  $<0.1$  to  $0.8 \mu\text{m}$  in size, and the smaller crystals are typical of the partly altered tuff from the northwestern part of the deposit. The very small crystal size is probably responsible for the consistently low intensity and relatively broad nature of the peaks on XRD records (*vide supra*). Chabazite also occurs as well-developed twinned crystals (Figure 8),  $1\text{--}6 \mu\text{m}$  on an edge, in inter-shard pores, on inter-shard pore casts, and in shard molds in the lower  $10\text{--}15 \mu\text{m}$  of the ore bed.

#### Erionite

Erionite (Figures 5 and 7) occurs as bundles of rod-like or acicular crystals that are  $2\text{--}60 \mu\text{m}$  long, with most being  $10\text{--}40 \mu\text{m}$  long. In partly altered tuff, erionite typically occurs in stubby, barrel-shaped bundles, only  $29 \mu\text{m}$  long, which are oriented at large angles to shard walls or perpendicular to chabazite plates. In other parts of the deposit, erionite bundles commonly occur in open spaces among stacks of chabazite plates. Rarely, erionite occurs as single crystals.

#### Clinoptilolite and analcime

Clinoptilolite occurs as well-formed tabular crystals,  $2\text{--}135 \mu\text{m}$  in length, with most being  $10\text{--}30 \mu\text{m}$  long (Figure 6). Clinoptilolite typically occurs in clusters of intergrown, single and twinned crystals which fill pores among aggregates of chabazite plates. Analcime occurs as well-formed trapezohedra, as much as  $40 \mu\text{m}$  in diameter (Figure 9). The analcime appears to be perched on chabazite platelets and clinoptilolite tablets.

#### Clay minerals

Authigenic clay minerals are common in the partly altered marker tuff near Field Trip Stop 1 and at some outcrops of the ore bed near Field Trip Stop 2, but clay minerals are scarce in the remainder of the marker tuff. The clays are predominantly smectites that have first-order basal reflections of  $12.4\text{--}15.0 \text{ \AA}$ , with most being  $13.0\text{--}14.5 \text{ \AA}$ , for oriented, air-dried samples or that have basal spacings of  $17.0\text{--}17.6 \text{ \AA}$ , averaging  $17.1 \text{ \AA}$ , for glycolated samples. Results of the Green-Kelley test and median positions of the 060 reflection of about  $1.499\text{--}1.515 \text{ \AA}$  indicate that the

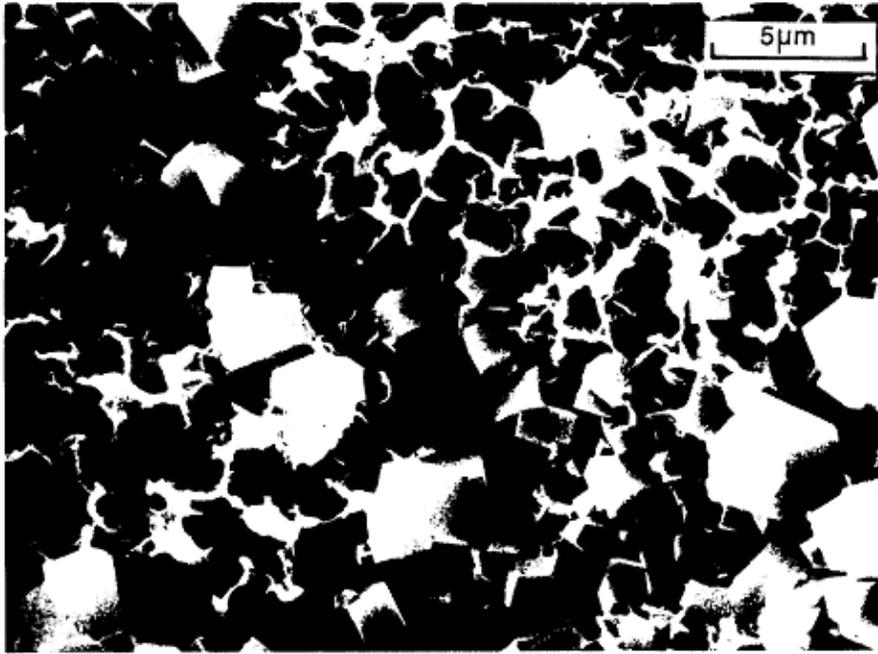


Figure 8. Scanning electron micrograph of ore bed showing relatively large, twinned rhombohedra of chabazite, partly encrusted by crenulated smectite.



Figure 9. Scanning electron micrograph of ore bed showing well-formed trapezohedra of analcime perched on ragged plates of chabazite and tablets of clinoptilolite.

smectite belongs to the beidellite-nontronite series. Smectite is randomly inter-stratified with illite and contains 60–100% expandable layers.

In partly altered tuff of the ore bed in the northwestern part of the deposit, smectite occurs as thin, scaly coatings on glass shards and on zeolites that project from shard surfaces. It also forms blankets of frothy, crenulated, platy aggregates on the inner, concave walls of bubble-wall shards (Figure 7), on shard molds, and on inter-shard pore casts. Smectite also partly fills secondary pores formed by the zeolites. A distinctive feature of some smectite is its occurrence in circular or elliptical, rosette-like aggregates on surfaces of relict shards (Figure 10). The diameter of the individual rosettes is about 3–33  $\mu\text{m}$ , with most being 20–25  $\mu\text{m}$ .

#### Paragenetic relations

The paragenetic relationship between the zeolites and smectite that formed by alteration of silicic glass at the Bowie deposit is different from that described by Hay (1966) and from that shown for other saline, alkaline lake zeolite deposits (Sheppard and Gude, 1968, 1973). Results of these earlier studies suggest that clay mineral alteration of glass preceded zeo-

litization. Unpublished studies by one of us (C.S.V.B.) of the partly altered marker tuff from the northwestern part of the deposit by scanning electron microscopy show that the smectite was clearly not the first authigenic mineral to form. At the Bowie deposit, the early-formed authigenic minerals are chabazite and erionite. In the partly altered tuff, most erionite seems to have grown on polycrystalline chabazite plates and probably began to form after the chabazite. In partly altered tuff near Field Trip Stop 1 and in more completely altered tuff near Field Trip Stop 2, smectite encrusts both chabazite and erionite (Figure 11) and, therefore at least here, formed after these zeolites.

Clinoptilolite crystallized later than chabazite and erionite and probably later than smectite. Where clinoptilolite occurs with the other zeolites and smectite, the chabazite and erionite are coated with smectite, but the clinoptilolite is uncoated. Analcime seems to have been the last authigenic silicate mineral to form in the marker tuff. Other studies of analcime in tuffs from saline, alkaline lacustrine deposits indicate that it generally formed by the reaction between early-formed zeolites and interstitial fluids (see Sheppard and Gude, 1973). The Bowie analcime probably formed in a similar manner, but no

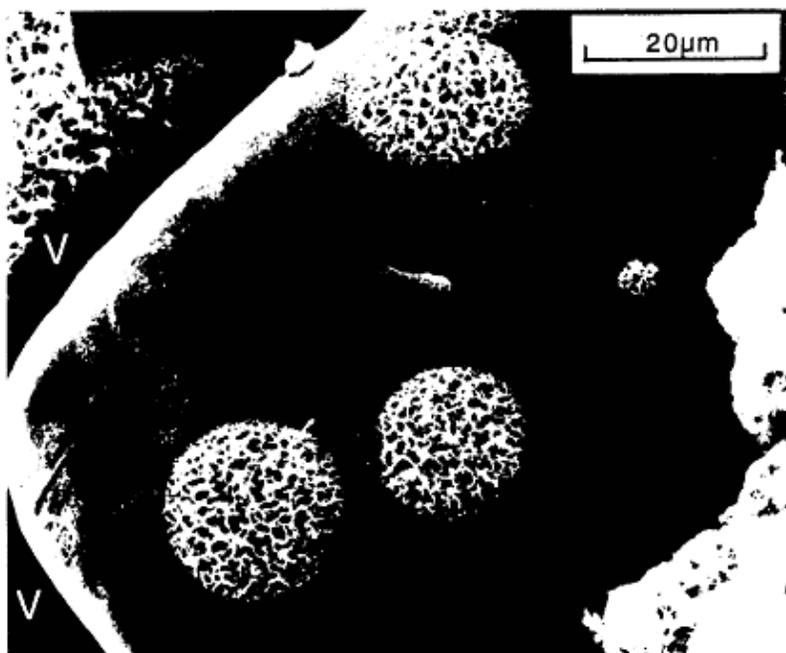


Figure 10. Scanning electron micrograph of ore bed showing rosettes of smectite on an inter-shard pore cast. Void (V) represents site of now-dissolved shard.

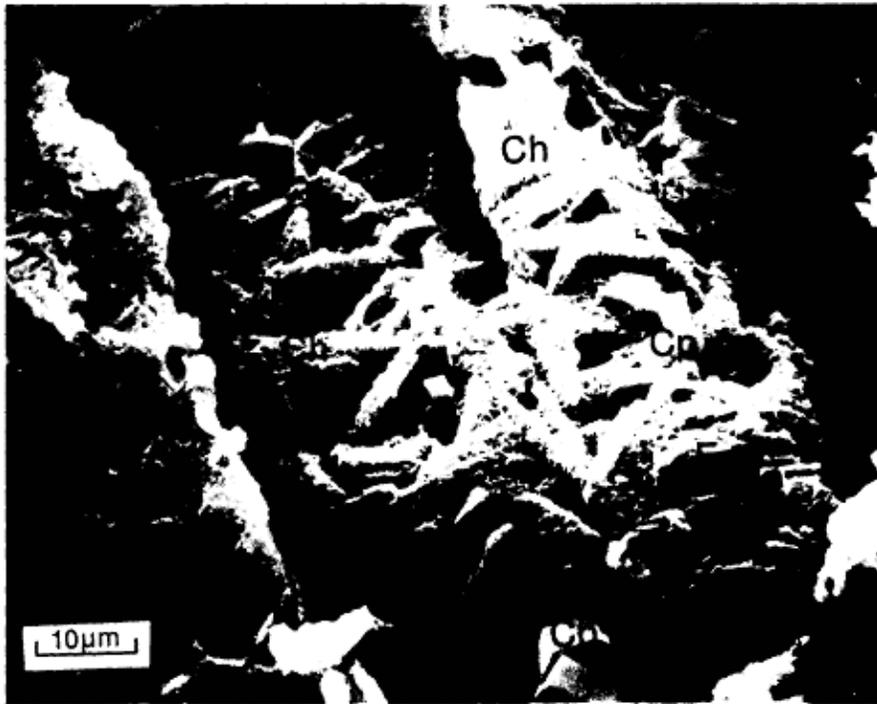


Figure 11. Scanning electron micrograph of ore bed showing crenulated smectite coating ragged plates of chabazite (Ch) and bundles of erionite (E). Relatively large tabular crystals of clinoptilolite (Cp) are uncoated.

textural evidence has been recognized.

#### CHEMISTRY OF THE MARKER TUFF

Chemical analyses of two bulk samples of the ore bed are given in Table 2. Both samples are mineralogically similar, consisting chiefly of chabazite with minor erionite, clinoptilolite, and smectite. Sample A was collected in the northwestern part of the deposit, near Field Trip Stop 2 (Figure 2), and sample B was collected in the southeastern part of the deposit, at Field Trip Stop 4. The analyses are similar, except that sample A shows a much higher CaO:Na<sub>2</sub>O ratio than sample B. Additional unpublished analyses (C. S. V. Barclay and R. D. Hettinger, U.S. Geological Survey, Denver, Colorado, written communication, 1975) suggest that a decrease in the CaONa<sub>2</sub>O ratio from north to south is characteristic for the ore bed west of the San Simon River. Because chabazite is the major constituent of the ore bed, the same chemical trend is suggested for the chabazite.

Chemical analyses and the unit-cell compositions of chabazite separated from the two previously mentioned bulk samples are given in Table 3. These data show that chabazite from sample A has significantly higher calcium and lower sodium contents than chabazite from sample B. These data support the conclusion of Regis and Sand (1976) that a southward decrease in the Ca:Na ratio of the chabazite exists. As shown in Table 3, both chabazites are siliceous, having Si:(Al + Fe<sup>3+</sup>) ratios of 2.86 and 2.76, respectively. Relatively small unit-cell dimensions and low indices of refraction of the Bowie chabazite are consistent with its siliceous character (Sheppard, 1973).

#### GENESIS OF THE ZEOLITES

The zeolites and associated authigenic silicate minerals in the marker tuff crystallized after the accumulation of the original silicic vitric ash in Tertiary Lake Graham. Alkaline and moderately saline pore water, trapped during sedimenta

Table 2. Chemical analyses (wt. %) of two ore-bed samples'.

	A	B
SiO <sub>2</sub>	55.3	54.6
Al <sub>2</sub> O <sub>3</sub>	13.2	14.9
Fe <sub>2</sub> O <sub>3</sub>	3.40	2.28
MgO	0.98	0.60
CaO	3.25	0.22
Na <sub>2</sub> O	2.85	6.67
K <sub>2</sub> O	1.15	0.90
LOI	19.1	19.4
Total	99.23	99.57

A = Lab. No. D159477; locality = SW 1/4, NW 1/4, Sec. 13, T15S, R28E, Graham County, Arizona. B = Lab. No. D161834; locality = NE 1/4, NW 1/4, Sec. 2, T12S, R19E, Cochise County, Arizona.

<sup>1</sup>SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> determined colorimetrically by G. T. Burrow; total Fe as Fe<sub>2</sub>O<sub>3</sub>; MgO, CaO, Na<sub>2</sub>O, and K<sub>2</sub>O determined by atomic absorption by Violet Merritt and Wayne Mountjoy; loss on ignition (LOI) determined at 900°C for 1 hr by G. D. Shipley. From Sheppard et al. (1978).

Table 3. Chemical analysis (wt. %) and composition of unit cell of chabazite<sup>1</sup>.

	Chemical analyses	
	A	B
SiO <sub>2</sub>	51.9	52.1
Al <sub>2</sub> O <sub>3</sub>	12.0	14.2
Fe <sub>2</sub> O <sub>3</sub>	5.30	2.81
MgO	1.17	0.88
CaO	3.46	0.11
Na <sub>2</sub> O	3.68	6.71
K <sub>2</sub> O	0.38	0.68
H <sub>2</sub> O	22.11	22.51

	Unit-cell composition <sup>2</sup>	
Si	26.64	26.63
Al	7.26	8.56
Fe <sup>3+</sup>	2.05	1.08
Mg	0.89	0.67
Ca	1.90	0.06
Na	3.66	6.65
K	0.25	0.44
H <sub>2</sub> O	37.85	38.38
Si/(Al + Fe <sup>3+</sup> )	2.86	2.76

A = Lab. No. D160295; separated from sample A of Table 2. B = Lab No. D161678; separated from sample B of Table 2.

<sup>1</sup>SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> determined colorimetrically by G. T. Burrow; total Fe as Fe<sub>2</sub>O<sub>3</sub>; MgO, CaO, Na<sub>2</sub>O, and K<sub>2</sub>O determined by atomic absorption by Violet Merritt and Wayne Mountjoy; H<sub>2</sub>O calculated by difference. From Sheppard et al. (1978).

<sup>2</sup>Unit-cell composition on basis of 0=72.

tion in a lacustrine environment, dissolved the original vitric material, thereby providing the chemical constituents necessary for the formation of these minerals. The zeolites, then, precipitated directly from the solution provided by the dissolved glass shards.

Eyde (1982) reported a northwest-to-southeast mineralogical zonation in the marker tuff of unaltered glass to glass + chabazite + clinoptilolite + erionite to chabazite + clinoptilolite + erionite to chabazite + clinoptilolite + erionite + analcime. The zones are gradational and are attributed to a lateral compositional variation in the water of ancient Lake Graham. In the northwestern part of the Bowie deposit, where the marker tuff is still vitric, the lake water was probably fresh, near-neutral pH, and calcium bearing. This area was probably closest to the major inlet and tributary streams that delivered relatively fresh water to the lake. Farther basinward (southeastward), the water increased in pH, salinity, and sodium. Calcite is common in the northwestern part of the deposit, but halite and thenardite are common in the southeastern part. Also, the gradation of calcic chabazite to sodic chabazite from northwest to southeast was probably controlled by the southeastward increase of sodium in the lake water.

The crystallization of smectite later than chabazite and erionite but before clinoptilolite in the marker tuff in the northwestern part of the Bowie deposit may have been caused by a temporary, localized decrease in salinity and alkalinity of the pore water that was due to an increased influx of fresh water to the ancient lake. The paragenetic sequences of the authigenic minerals suggest that when the volcanic ash was deposited, the lake was too alkaline for the formation of smectite, and chabazite and erionite crystallized with the dissolution of the silicic glass. Subsequently, all but the most alkaline and saline parts of the lake freshened, and, in these areas of reduced alkalinity and salinity, smectite precipitated within the tuff. Clinoptilolite then crystallized in the tuff when the lake once again returned to its alkaline and saline condition.

## MINING TECHNIQUES

The Bowie zeolite deposit is strip-mined, and the overburden is removed to the top of the marker tuff using scrapers. To produce the highest purity chabazite possible from the ore bed, all the overlying thin-bedded tuffs and the underlying clay or siltstone must be removed. A smaller self-loading scraper is often used to remove most of the entire thickness of the overlying thin-bedded tuff without disturbing the ore bed. A grader is then used to remove the lowest several centimeters of the low-grade beds. A road broom sweeps the top of the ore bed, and remaining pockets of unaltered ash are removed with hand tools. The ore bed is picked up in large pieces using a backhoe, and any clay that adheres to the bottom of the ore bed is scraped off with hand tools (Figure 12). Blocks of the crude high-grade chabazite are stockpiled in the pit until the mining cycle is completed (Figure 13) and then hauled to Bowie where it is stockpiled in warehouses and allowed to dry.

The crude ore is presently shipped by truck or rail to the Milwhite grinding plant at Riverside, Texas. There, the chabazite is ground to <200 mesh, bagged, and shipped to processing facilities at Chickasaw, Alabama, for Union Carbide Corporation, or at Chattanooga, Tennessee, for Norton Company. The ground chabazite is mixed with an attapulgite (palygorskite) binder, extruded, "activated" by heating to 425°C, and then packed in sealed drums.

Accurate production information is not available for the Bowie chabazite deposit. Estimates based on Arizona Land Department records, production data provided by some producers, and the size of mined areas indicate that about 12,300 short tons of crude chabazite was produced from 1961 to 1986. Union Carbide Corporation probably accounted for about 80% of that production.

The selling price of the Bowie chabazite depends on the purity, mineralogy, processing required for specific end use applications, and quantity produced. Crude lump chabazite sells for \$0.10 to \$0.35/lb, and unactivated, ground chabazite products

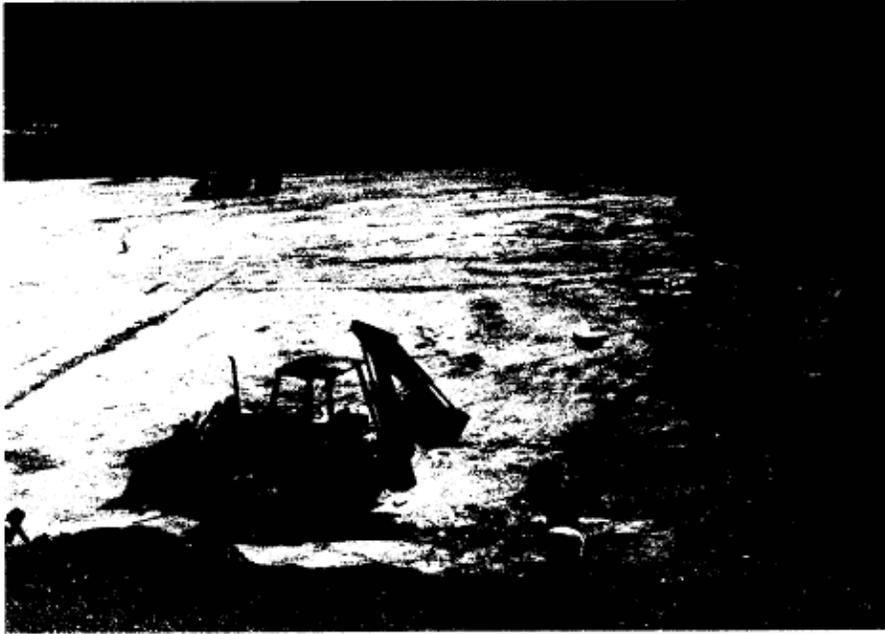


Figure 12. Mining the chabazite-rich ore bed of the marker tuff at the Bowie zeolite deposit. Backhoe in foreground has been used to dislodge large blocks of the ore bed, and workers are removing adhering clay at the bottom of the bed. Top of ore bed was swept clean by road broom shown in background.

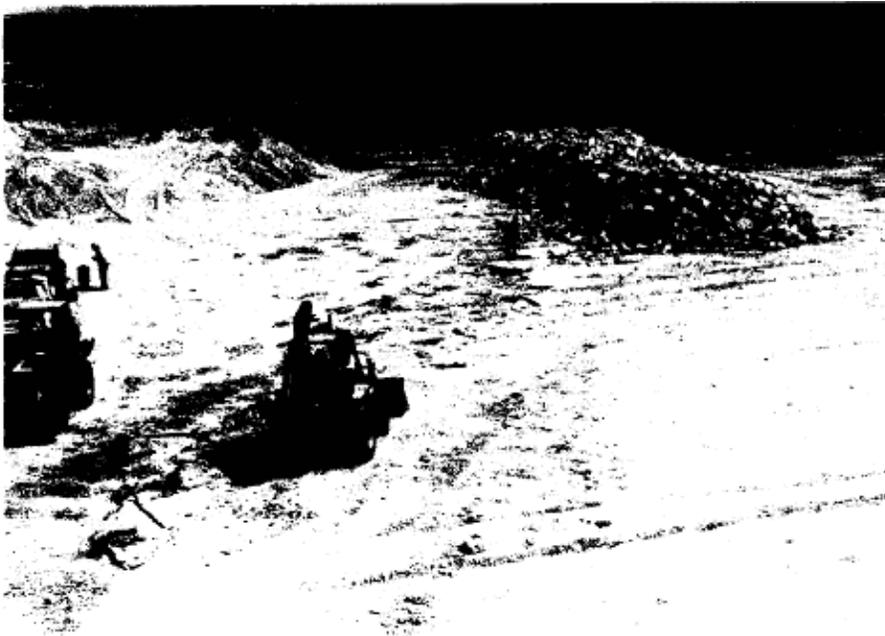


Figure 13. Mining chabazite-rich ore bed of marker tuff at Bowie zeolite deposit. Front-end loader in foreground carries cleaned blocks of ore bed to stockpile shown in background.

sell for \$0.40 to \$0.75/lb. Activated extrudates sell for about an estimated \$2.50/lb. for specialty adsorbents, and crushed extrudates used in ion-exchange applications for radioactive waste treatment sell for about \$7.50/lb. After deducting moisture, mining, and processing losses, the estimated market value of chabazite sold since production began at Bowie is probably about \$40,000,000, at present prices. Most of the production has been sold as activated extrudates.

#### **UTILIZATION OF THE BOWIE ZEOLITE**

The zeolite tuff mined at the Bowie deposit has numerous industrial applications that are based chiefly on the ion-exchange, adsorption, and acid-stability properties of the chabazite; however, information on some uses or potential uses is not available because the companies mining the zeolite consider the data proprietary. The properties of the Bowie zeolite are apparently superior to those of many synthetic zeolites for certain specialized adsorption applications.

A major use of the Bowie zeolite is in the drying and purification of gases. By appropriate pressure-swing adsorption processes, the zeolite is used to remove H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O from acidic natural gas streams. Casing-head gas at the Salt Lake oil field near Los Angeles, California, is upgraded in this manner to make the gas acceptable to pipelines and public utilities (Eyde, 1982). The Bowie zeolite is used to purify methane produced by the decomposition of organic waste material at the Palos Verde landfill near Los Angeles (Mumpton, 1983). Mumpton (1983) suggested that the Bowie zeolite could be similarly used to remove CO<sub>2</sub> and H<sub>2</sub>S from methane gas produced during anaerobic digestion of sludge at municipal sewage-treatment plants and of animal wastes from farms and feedlots. Bowie zeolite, marketed by the Linde Division of Union Carbide Corporation as AW500, is claimed to be capable of removing HCl from reformer hydrogen streams, drying chlorine, purifying certain chlorinated hydrocarbons, drying and purifying certain fluorinated hydrocarbons, and purifying stack gases (Union Carbide Corporation, 1962). Walker Mufflers recently introduced

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Figure 14. View westward at Field Trip Stop 1 showing natural exposure of partly altered marker tuff. Man at right is standing on the marker tuff that here contains much unaltered silicic glass. Pinaleno Mountains are in background.



Figure 15. Zeolitic marker tuff in pit at Field Trip Stop 2. Man at right is standing on the top of the ore bed, which here is 15 cm thick and consists mainly of chabazite.

cm) and overlying thin-bedded tuffs (32 cm). The light-gray ore bed locally contains much unaltered glass, but the basal 1-3 cm is light yellow and consists chiefly of chabazite and minor to trace amounts of clinoptilolite and erionite. Thin-bedded tuffs above the ore bed are 1-4 mm thick and consist mainly of varying amounts of relict glass, smectite, chabazite, and erionite. Brown mudstone and siltstone

underlie and overlie the marker tuff. Irregular, gray, calcareous concretions are common in the siltstone beneath the tuff.

#### Stop 2

The pit at Field Trip Stop 2 is mined by Norton Company and exposes about 24 cm of the light-yellow zeolite marker tuff, most of which (16 cm) is the ore bed at the

base (see Figure 15). No relict glass has been found in the marker tuff here; however, the original vitroclastic texture is well preserved, especially in the ore bed which consists mainly of chabazite. Calcareous concretions occur locally in the lower part of the ore bed. Thin-bedded tuff above the ore bed shows ripple marks and consists of chabazite and minor amounts of erionite and clinoptilolite. Brown siltstone underlies the marker tuff and contains minor clinoptilolite; grayish-brown siltstone overlies the marker tuff and consists of 40–50% authigenic zeolites in addition to the detrital constituents. The zeolite fraction consists of varying proportions of chabazite, clinoptilolite, and erionite.

### Stop 3

The pit at Field Trip Stop 3 is operated by NRG Incorporated and exposes about 125 cm of the zeolite marker tuff (Figure 3). A relatively new pit adjoins this pit to the north and is operated by Union Carbide Corporation. The orange, white, and yellow-green ore bed is 13 cm thick and consists of major chabazite and minor clinoptilolite and erionite. Irregular segregations in the ore bed have a sugary texture and consist of relatively large clinoptilolite crystals as much as 125  $\mu$ m long. The ore bed locally contains minor analcime in the lower part and a white efflorescent coating of halite and thenardite. Gypsum is locally common at the top and bottom of the ore bed. The overlying thin-bedded tuffs are yellow-gray to yellow-green, locally show ripple marks, and consist of varying proportions of chabazite, clinoptilolite, and erionite. Clinoptilolite and erionite, rather than chabazite, commonly are the major zeolites in the thin-bedded tuffs. Green mudstone, underlying and overlying the marker tuff, contains about 10% authigenic analcime.

### Stop 4

The pit at Field Trip Stop 4, originally opened about 1967 by W. R. Grace and Company but now operated by GSA Resources Incorporated, exposes mainly the ore bed of the marker tuff. The orange and white bed is 10 cm thick and consists of major chabazite, minor clinoptilolite, and trace quantities of erionite. The basal part of the ore bed commonly contains about 10% anal-

cime. A white, efflorescent powder of halite and thenardite commonly coats weathered exposures of the ore bed. Although the thin-bedded tuffs that overlie the ore bed have been stripped at this pit, samples of the material from the spoil pile show varying proportions of chabazite, clinoptilolite, and erionite. Green mudstone beneath the marker tuff contains 10–20% authigenic analcime.

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