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SILICA-RICH CHABAZITE FROM THE BARSTOW FORMATION,
SAN BERNARDINO COUNTY, SOUTHERN CALIFORNIA¹

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The Barstow Formation of middle and late Miocene age (Lewis, 1964) is a thick sequence of fluvial and lacustrine rocks. Mudstones and sandstones are dominant, but locally more than 30 relatively thin tuffs are recognized. Recent work by the authors on the alteration of the tuffs has shown that much of the vitric material is replaced by zeolites, potash feldspar, opal and (or) montmorillonite. These authigenic minerals are generally so finely crystalline that positive identification can be made only by x-ray techniques. Routine examination of x-ray diffractometer traces of bulk samples of an altered tuff from the upper part of the formation indicated that some samples consist mainly of a zeolite having a diffractometer pattern similar to chabazite. Detailed study of the diffrac-

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tometer traces and optical determinations indicate that the authigenic zeolite differed from "normal" chabazites thus far reported.

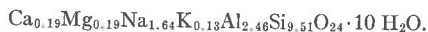
The chabazite-bearing tuff crops out in the vicinity of Fossil Canyon, approximately 10 miles north of Barstow, San Bernardino County. Although the tuff is displaced by several northwest-trending faults, it can be traced along strike for about a mile. The altered tuff is white to light gray and 2 to 4.5 feet thick.

Thin section study of the altered tuff shows that the chabazite occurs as a mosaic or as aggregates of anhedral crystals replacing vitric material. Individual crystals average approximately 20 microns in size. Locally, the altered tuff consists almost entirely of silica-rich chabazite, but generally crystal fragments and relict glass or clinoptilolite, erionite, or montmorillonite are associated with the chabazite. Crystal fragments of plagioclase (An₃₂), sanidine, quartz, biotite, hornblende, zircon, and apatite, generally constitute less than 10 per cent of the tuff.

The mean index of refraction of the authigenic chabazite ranges from 1.461 to 1.468 (± 0.001), and the birefringence is very low. This compares with the range of 1.470 to 1.494 given by Deer *et al.* (1963, p. 387) for chabazite from nonsedimentary environments. Most of these chabazites have a mean index of refraction near 1.48.

A sample of the chabazite-rich tuff, selected to avoid as many impurities as possible, was separated for chemical analysis. The altered tuff was first crushed and then ultrasonically disaggregated. Then the -100+270 mesh fraction was concentrated by repeated centrifuging in a heavy liquid mixture (sp. g. ≈ 2.2) of bromoform and acetone. The final separation contained approximately 99 per cent chabazite and 1 per cent impurity, mainly montmorillonite and calcite.

The chemical analysis and content of the unit cell based on 72 oxygens is given in Table 1. The ideal formulas for chabazite and herschelite are $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 12\text{H}_2\text{O}$ and $\text{Na}_4\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 12\text{H}_2\text{O}$, respectively, and there are three such formula units per unit cell (Mason, 1962, p. 985). The calculated formula for the zeolite from the Barstow Formation is



A comparison of this formula with that of ideal chabazite and herschelite shows marked differences in the cation content and the Si/Al ratio. Although the Barstow zeolite is alkali-rich, it has only slightly more than half of the cations of ideal herschelite. Charge balance is maintained by the high content of Si which is in excess of that for ideal chabazite or herschelite. Ideal chabazite and herschelite have a Si/Al ratio of 2, but the Barstow zeolite has a ratio of 3.86.

Natural chabazite shows considerable variation in cation content and

Si/Al ratio (Deer *et al.*, 1963, p. 365). Departures from the ideal formula can be explained by replacement of the type $\text{Na}(\text{K})\text{Si} \rightleftharpoons \text{CaAl}$ and the type $\text{Na}_2(\text{K}_2) \rightleftharpoons \text{Ca}$. The chabazite-herschelite series is characterized by $\text{Na}_2(\text{K}_2)$ replacement of Ca (Mason, 1962), whereas the Barstow chabazite can be derived from ideal chabazite by mainly $\text{Na}(\text{K})\text{Si}$ replacement of $\text{Ca}(\text{Mg})\text{Al}$. A small amount of $\text{Na}_2(\text{K}_2)$ replacement of Ca also is necessary to account for the composition of the Barstow zeolite.

TABLE 1. CHEMICAL COMPOSITION AND UNIT CELL CONTENTS OF AUTHIGENIC CHABAZITE FROM THE BARSTOW FORMATION

	1		2
SiO_2	59.68	Si	28.53
Al_2O_3	13.11	Al	7.39
Fe_2O_3	.13	Fe^{3+}	.05
FeO	.02	Fe^{2+}	.01
MgO	.79	Mg	.56
CaO	1.13	Ca	.58
Na_2O	5.30	Na	4.91
K_2O	.62	K	.38
H_2O^+	10.25	H_2O^+	16.34
H_2O^-	8.76	H_2O^-	13.97
TiO_2	.04	O	72.00
P_2O_5	.02	$\text{Si} + \text{Al} + \text{Fe}^{3+}$	35.97
MnO	.00	$\text{Si}/\text{Al} + \text{Fe}^{3+}$	3.83
CO_2	.01		
Total	99.86		

1. Serial No. D100593; analyst: E. S. Daniels. Locality: tributary to Fossil Canyon, NE1/4SE1/4 sec. 15, T. 11 N., R. 2 W., Opal Mountain quadrangle, San Bernardino County, Calif.
2. Atoms per unit cell, recalculated on the basis of $\text{O} = 72$. Ti, Mn and P were omitted in the calculation. Analysis uncorrected for CO_2 and its equivalent of Ca.

The water content of the Barstow zeolite may be low compared with ideal chabazite. In her study of the fibrous zeolites, Foster (1965) found that the water content is lower for Na members than for Ca members. Barrer and Sammon (1955) also noted a similar relationship in ion exchanged chabazite: the univalent ions produce a less hydrated condition than the bivalent ions. Perhaps part of the low water value in the Barstow zeolite is due to loss of weakly held water during storage in the low humidity of the Denver laboratory prior to analysis.

X-ray diffraction powder data for herschelite, normal chabazite, and the chabazite from the Barstow Formation are presented in Table 2. The

TABLE 2. X-RAY DIFFRACTION POWDER DATA FOR HERSCHELITE AND CHABAZITE
(DIFFRACTOMETER; COPPER RADIATION, NICKEL FILTER)

1 Herschelite				2 Chabazite				3 Silica-rich chabazite			
Calculated		Observed		Calculated		Observed		Calculated		Observed	
hkl	d _{hkl}	d _{hkl}	I	hkl	d _{hkl}	d _{hkl}	I	hkl	d _{hkl}	d _{hkl}	I
*		11.89	8								
101	9.3711	9.361	51	101	9.3569	9.351	50	101	9.2819	9.263	70
110	6.8994	6.894	22	110	6.8930	6.894	10	110	6.8558	6.846	22
102	6.3833	6.379	3	102	6.3705	6.384	5	102	6.3053	6.298	8
201	5.5560	5.555	15	201	5.5497	5.555	9	201	5.5146	5.514	32
*		5.127	8								
003	5.0339	5.032	40	003	5.0216	5.021	30	003	4.9606	4.959	38
202	4.6855	4.679	6	202	4.6784	4.677	6	202	4.6409	4.643	4
*		4.500	3								
211	4.3273	4.322	67	211	4.3227	4.324	76	211	4.2970	4.293	100
113	4.0666	4.109	9	113	4.0588	4.044	1	113	4.0189	4.020	5
300	3.9834	3.976	8	300	3.9796	3.976	2	300	3.9582	3.957	5
212	3.8762	3.877	23	212	3.8710	3.870	28	212	3.8432	3.844	20
104	3.6000	3.600	21	104	3.5918	3.590	23	104	3.5503	3.549	47
220	3.4497	3.448	18	220	3.4465	3.448	13	220	3.4279	3.427	21
311	3.2373	3.235	11	311	3.2341	3.235	6	311	3.2156	3.217	10
204	3.1917	3.193	7	204	3.1853	3.190	5	204	3.1526	3.152	11
303	3.1237	3.125	2	303	3.1190			303	3.0940	3.056	2
312	3.0349	3.031	2	312	3.0313	3.033	2	312	3.0116	3.011	1
*		2.981	18								
401	2.9307	2.930	100	401	2.9278	2.925	100	401	2.9113	2.911	62
105	2.9283			105	2.9214			105	2.8871	2.885	22
214	2.8967	2.897	29	214	2.8915	2.890	30	214	2.8643	2.864	34
223	2.8456	2.852	9	223	2.8416	2.842	3	223	2.8201	2.820	6
402	2.7780	2.7775	5	402	2.7748	2.7759	4	402	2.7573	2.7575	3
321	2.6974			321	2.6948			321	2.6797	2.6812	2
205	2.6955	2.6953	11	205	2.6898	2.6898	7	205	2.6608	2.6619	6
410	2.6077	2.6062	18	410	2.6053	2.6048	10	410	2.5912	2.5909	11
322	2.5769	2.5758	4	322	2.5741	2.5743	2	322	2.5582	2.5565	3
006	2.5170			006	2.5108			215	2.4805	2.4806	12
215	2.5107	2.5108	12	215	2.5058	2.5067	11	006	2.4803		
314	2.4908			314	2.4868			314	2.4660		
116	2.3645	2.3635	2	116	2.3592	2.3611	2	501	2.3452		
501	2.3606			501	2.3584	2.3575	2	116	2.3324		
404	2.3428			404	2.3392			404	2.3205	2.3224	1
413	2.3155	2.3160	7	413	2.3126	2.3098	3	413	2.2968	2.2979	2
330	2.2998	2.3001	5	330	2.2976	2.2996	4	330	2.2853	2.2855	2
502	2.2786			502	2.2762	2.2767	1	502	2.2625	2.2629	4
421	2.2335			421	2.2314	2.2333	1	421	2.2190		
315	2.2324	2.2275	1	315	2.2285			315	2.2082		
324	2.2184			324	2.2151			324	2.1980		
422	2.1637	2.1631	2	422	2.1614			422	2.1485	2.1493	1

1. Herschelite; AMNH No. 12987. Locality: Aci Reale, Sicily.

2. Chabazite. Locality: North Table Mountain near Golden, SE $\frac{1}{4}$ sec. 22, T. 3 S., R. 70 W., Jefferson County, Colorado.3. Silica-rich chabazite ($\text{Ca}_{0.19}\text{Mg}_{0.19}\text{Na}_{1.61}\text{K}_{0.12}\text{Al}_{2.46}\text{Si}_{9.51}\text{O}_{24} \cdot 10\text{H}_2\text{O}$); No. D100593; Barstow Formation. Locality: tributary to Fossil Canyon, NE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 15, T. 11 N., R. 2 W., San Bernardino County California.

* Reflections due to intergrown gmelinite.

calculated d values are those resulting from the least-squares refinement procedure (Evans *et al.*, 1963). All the diffraction data are compatible with space group $R\bar{3}m$. The d values for both herschelite and normal chabazite are slightly larger than those for the silica-rich chabazite. The (401) reflection is the most intense peak for herschelite and normal chabazite, but the (211) reflection is the most intense peak for the authigenic chabazites. This difference may be partly due to differences in composition and differences in crystal size or orientation.

Cell constants and indices of refraction for these same specimens are compared in Table 3. The cell of the chabazite from the Barstow Formation is noticeably smaller than that of either herschelite or normal chabazite and probably reflects the relatively high Si content in the alumin-

TABLE 3. CRYSTALLOGRAPHIC AND OPTICAL DATA FOR HERSCHELITE, NORMAL CHABAZITE, AND SILICA-RICH CHABAZITE FROM THE BARSTOW FORMATION

	Herschelite 1	Normal chabazite 2	Silica-rich chabazite from the Barstow Formation 3
a (Å)	13.799±0.001	13.786±0.002	13.712±0.001
c (Å)	15.102±0.002	15.065±0.004	14.882±0.002
Cell volume (Å ³)	2490.2±0.5	2479.5±0.8	2423.1±0.4
α (±0.001)	1.479	1.494	1.460
γ (±0.001)	1.481	1.496	1.462

silicate framework. The relatively low indices of refraction of the Barstow zeolite also may be due to the high Si content, although the exchangeable cations and degree of hydration also are known to affect the optical parameters of zeolites. Relatively small cell constants and low indices of refraction, similar to those of the Barstow chabazite, were found for authigenic chabazites from altered rhyolitic tuffs of the Oligocene and Miocene John Day Formation in Oregon and the Miocene and Pliocene(?) Belted Range Tuff in Nevada.

The relationship between the chabazite of the Barstow Formation and normal calcium-rich chabazite is analogous to that between clinoptilolite and heulandite. Clinoptilolite is alkali- and silica-rich and has lower refractive indices than heulandite (Mumpton, 1960; Mason and Sand, 1960). The analogy can be carried even further inasmuch as silica-rich chabazite and generally clinoptilolite form from rhyolitic volcanic glass in a sedimentary environment, whereas most chabazite and heulandite occurs in fractures and cavities of more basic igneous rocks. Authigenic

analcime (Ross, 1928) and phillipsite (Hay, 1964) from sedimentary rocks originally rich in rhyolitic vitric material also are more siliceous than their counterparts occurring in basic igneous rocks. The availability of relatively large amounts of silica and alkalis in rhyolitic volcanic glass probably explains the high silica and high alkali content of authigenic zeolites from sedimentary environments (Mumpton, 1960).

Other occurrences of authigenic chabazite doubtlessly will be found when the mineralogy of rhyolitic tuffs of Cenozoic age in the desert areas of the southwest are studied in detail. Rather than propose a new name for this zeolite from the Barstow Formation, the authors prefer to term it "silica-rich chabazite." This terminology implies a structural relationship to chabazite and serves to set it apart from herschelite. Perhaps additional analyses of chabazites from rhyolitic tuffs will more clearly define the compositional variation at the high Si end and warrant selection of an end member name.

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