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The fibrous zeolite erionite; its occurrence, unit cell, and structure.

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Summary. The type locality for erionite has been identified and specimens compared with Eakle's original material. New determinations of the physical properties and a chemical analysis have been made. Correlation of X-ray powder and fibre rotation data with electron diffraction of single crystals has shown that the unit cell is hexagonal with *a* 13·26, *c* 15·12 Å., space-group $P31c$, $P\bar{3}1c$, $P6_3mc$, $P\bar{6}2c$, or $P6_3/mmc$, giving a calculated sp. gr. of 2·07 and atomic cell contents $(Ca, Mg, Na_2, K_2)_{4\cdot5}Al_9Si_{27}O_{72}.27H_2O$. A structure is proposed for the aluminosilicate frame, with space-group $P6_3/mmc$, which gives satisfactory correlation between observed and calculated structure factors for the X-ray fibre rotation pattern.

In 1898 Arthur S. Eakle, then of Harvard University, and later at the University of California, Berkeley, reported receiving an unusual zeolite from Durkee, Oregon. This proved to be a new mineral for which he proposed the formula $NaK(Ca,Mg)Al_4Si_{12}O_{32}.12H_2O$, and which he named 'erionite' because of its woolly appearance. No description of the exact locality was given in his paper, and it is doubtful if Eakle was ever there. The only other reference to the locality is a statement by Lindgren (1901, p. 764) concerning the new zeolite examined by Eakle from a fire-opal quarry a few hundred feet from the Gold Hill mill. None of the present inhabitants of the Durkee or Baker regions had heard of the mineral, and one of the authors (L. W. S.) in the summer of 1953 set out to rediscover the locality. The reported association with fire-opal was a great help in locating the deposit. Fitzsimmons (1949), in a doctoral dissertation on the area, did not mention erionite but reported that although fire-opals were only a matter of hearsay to him, they were said to occur on Swayze Creek. When the locality was rediscovered, several hours' search were required before the first seams of erionite were found. Fire-opal is also difficult to find now.

X-ray investigation of Eakle's original material by L. W. Staples showed it to be identical with the newly collected material from Durkee. Information obtained from an electron-optical examination by J. A. Gard was correlated with the X-ray data, and indicated the unit cell and space-group.

Location and geology.

The erionite was found in Baker County, Oregon, at the site of the old Durkee opal mine, which was active in 1897 but which has not been worked in recent years. It is located in Sec. 36, Township 11 S., Range 43 E., which is reached by driving up Swayze Creek 1·6 miles from the junction of the road with U.S. Highway 30. A small quarry site lies on the north side of the road and a dump on the south side. No material was found in place because of the extensive slumping, but erionite was found in the waste rock on both sides of the road.

Fitzsimmons mapped the quarry area as Tertiary rhyolite tuff surrounded by pre-Tertiary foliated rocks, Tertiary lacustrine deposits, and basalt flows. The rhyolite tuff is actually an excellent example of a welded tuff with black glass shards appearing to flow around and through the contrasting lighter coloured matrix. The erionite is in seams, most of which are parallel to the flowage or bedding of the tuff, and the opal also occurs in similar fashion. The opal is later than the erionite and includes the latter in places, but it should not be concluded, as did Eakle, that the opal was formed from the zeolite. Opalitization in tuffs is well known and all stages in the opalitization of the pumice fragments of the tuff are in evidence. It is probable that the pumice fragments, which are now badly decomposed, yielded some of the material for the erionite. One part of the quarry contains a spherulitic phase of the tuff and cavities are lined with small crystals of heulandite. Zeolites other than erionite are rare in the quarry.

Erionite has been reported from other localities but the Durkee occurrence is the only one that has been confirmed by the writers. It was thought from an ambiguous statement by Fernquist (1937) that erionite occurred at the Oregon 'jade' mine on Shirttail Creek near Durkee 'in white, slender, wool-like fibres in cavities in the basalt' but careful search yielded no material and a subsequent communication from Fernquist stated, 'Nothing like erionite was found' (written communication, 3 December 1953). Reed (1937) reports the occurrence of erionite in layers or bands in amygdules in Columbia River lavas in Idaho. His collected material is no longer available and the writers are unable to confirm this occurrence.

Thugutt (1948, p. 31), in an interesting paper on the chemical relations and origins of the zeolites, mentions orthorhombic crystals of erionite as being found in Silesia near Klodzko, where they form a thin cover upon quartz, and in a rhyolite tuff at Teigarhorn, Iceland. Thugutt (personal communication, 1 June 1955) was unable to provide any further information concerning references or material from these localities, but the writers are continuing to search for them.

Recently, J. Regnier (1958, p. 80) reports finding erionite in altered Pleistocene tuffs of central Nevada, and he concludes it is the product of alteration of the vitric water-laid tuffs, possibly under the influence of mineralized lake waters.

Since this paper was submitted, K. S. Deffeyes (1959) has reported five other localities for erionite, of which three are in central Nevada, one in central Wyoming, and one in South Dakota. In each case it occurs in volcanic-rich Cenozoic sediments. B. Kamb and W. C. Oke (personal communication, 8 May 1959) have identified erionite in basalt dredged from the Columbia River at Rock Island Dam, near Wenatchee, Washington, D.C.; some of the crystals are hexagonal prisms. M. H. Hey (1959) has also identified as erionite two specimens collected in the Faroe Islands before 1824.

In all, there are nine confirmed localities for erionite; in at least eight it occurs in material of volcanic origin.

Physical and chemical properties.

Eakle's (1898) original description of erionite is for the most part accurate and needs additions rather than corrections. His observations concerning the loss of water on heating were checked, and in addition a differential thermal analysis was performed using an Eberbach portable unit. An endothermic peak, although not sharp, is obtained at 235–245° C., and a sharp break occurs at 920° C. Repeated heating and cooling experiments on 0·3 g. of erionite give substantially the same results obtained by Eakle. The erionite remains anisotropic nearly to 810° C., at which temperature the mineral is brittle, isotropic, and the index of refraction is 1·493. X-ray powder photographs for erionite heated to 825° C. show weak cristobalite lines, which become stronger for material calcined at 1000° C. The tendency for cristobalite to form during devitrification of glass has been noted by Warren and Biscoe (1938).

The first determination of indices of refraction for erionite was made by Larsen (1921) on material from the U.S. Geological Survey. He recorded α 1·438, γ 1·452, and probably on the basis of the mineral being optically positive, he noted β 1·44. These are the indices which are recorded in all reference books. A determination of the indices of refraction on Eakle's original material gives higher values than those recorded by Larsen. Through the kindness of Dr. G. Switzer, two small samples of erionite were obtained from the U.S. National Museum, one of which is probably the material worked on by Larsen. Likewise, new material obtained from the Durkee quarry was examined. All of these specimens, examined in sodium light, gave: ω 1·468, ϵ 1·473, ϵ–ω 0·005, within the usual limits of error. An exception to the above indices was obtained on one specimen which had come from the Roebling collection, although originally supplied by Eakle. This had indices ω 1·472, ϵ 1·476.

The determination of indices of refraction in fibrous materials is difficult and, as indicated by Morse and Donnay (1936), it may result in different values from those for the same substance in non-fibrous form, due in part to form birefringence. Water and opal are often the interstitial media. It is possible that variation in water content has been responsible for some of the variation observed in the indices of refraction. Heating erionite tends to raise its indices, although Hey (1932) in his studies of the zeolites noted in the case of thomsonite and other zeolites that dehydration in the initial stages can cause a drop in refractive index and density. The increase in refractive index of erionite heated to 810° C. has been noted above.

It is interesting that non-rotating fibre bundles of erionite, when placed with their length perpendicular to the X-ray beam, give a pattern similar to that produced by rotating a single fibre, which would seem to indicate that the fibres, often bound together in flat ribbons or bundles, have the slow ray direction in common, parallel to their length, but random orientation otherwise (electron diffraction results tend to confirm this).

The double refraction is not moderately strong as stated by Eakle. First-order yellow is seldom seen even in the thickest bundles of fibres.

The specific gravity of erionite is difficult to estimate because of its fibrous nature. Eakle recorded a value of 1·997 using methylene iodide and Thoulet solution. By the use of the Berman balance, and the Westphal balance with bromoform and alcohol, and various size bundles of erionite, results were obtained ranging from 1·80 to 1·97, most of which were above 1·90. In a further determination, a small fibre was immersed in a mixture of bromoform and benzene, which was boiled under reduced pressure to remove entrapped air; the specific gravity of the liquid was adjusted until the fibre remained suspended at the same level for several hours. This gave the highest value recorded, 2·02.

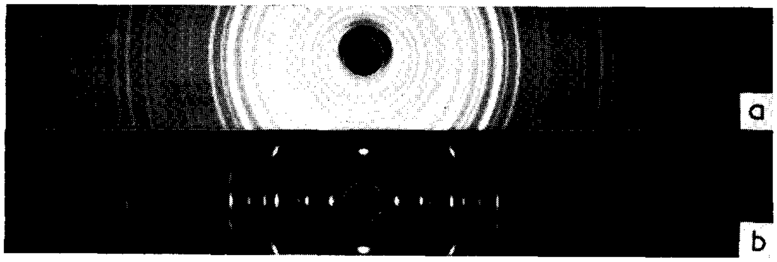


Fig. 1. *a*. Powder X-ray photograph of erionite. Cu-$K\alpha$ radiation in a 11·46-cm. diameter camera. *b*. X-ray photograph of a fibre bundle of erionite, rotated about the elongate axis.

X-ray data.

Although erionite is fibrous, powder photographs were obtainable which yielded fairly sharp lines (fig. 1*a*). A ball of fibres, rolled between the fingers to a spheroid about 1 mm. in diameter and mounted on a glass rod in the powder camera, also produced a pattern with lines almost as sharp as the usual type. Optimum results were obtained with an 8-hour exposure using copper radiation and a nickel filter. The results are listed in table I.

Natural fibre bundles oriented with the elongation direction of the fibres as the rotation axis were used in place of single crystals, identical patterns being produced both with and without rotation (figs. 1*b* and 2). Similar patterns were also obtained regardless of whether the X-ray beam was normal or parallel to the flat direction of the ribbon-like bundles of fibres. The same technique of using fibre bundles was adapted to the powder camera and aided in indexing the patterns. This use of the powder camera for single crystal work has been mentioned in the literature (Lindberg *et al.*, 1953, p. 1131), but it does not seem to be used as frequently as it might be, considering its usefulness and simplicity. One of its principal advantages is that the powder film and single crystal film are of the same size and can be superimposed for ready reference (fig. 1). The X-ray patterns could all be indexed on an orthorhombic lattice with parameters *a* 6·625, *b* 11·53, *c* 15·12 Å., but electron diffraction of single crystals later showed the unit cell to be a closely related hexagonal one.

Examination in the electron microscope.

Small fibres of the Durkee specimen were rubbed lightly with water on a clean glass slide and drops of the diluted suspension transferred to formvar-coated specimen grids. After drying in a desiccator, the specimens were shadow-cast with gold-palladium alloy at an angle of $\cot^{-1} 4$, and were examined with a Metropolitan-Vickers EM-3 electron microscope (Haine, Page, and Garfitt, 1950). This instrument can record electron-diffraction patterns from small selected areas of the specimen. The specimen stage may be tilted through a total angle of 10°; a method for calibration of the tilt device has been described elsewhere (Gard, 1956*a*).

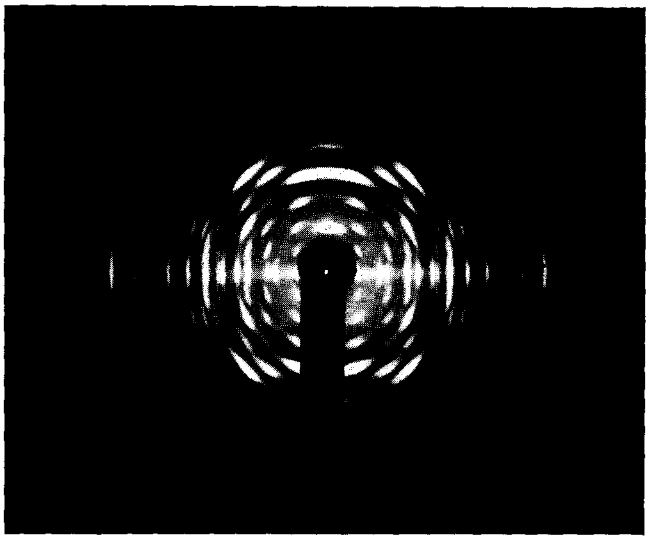


FIG. 2. X-ray photograph of a stationary natural fibre bundle of erionite. Cu-$K\alpha$ radiation in a 6-cm. diameter camera.

Fig. 3 shows a typical electron micrograph of erionite. Most of the specimen was in the form of long fibres, of mean width 550 Å. and mean thickness 300 Å., but some fine powder and larger particles were also present. Electron-diffraction patterns from individual fibres showed that they were single crystals. The spots in the patterns lie on rhombic networks, from which two unit-cell parameters in the plane of the supporting film can be estimated. Comparison with micrographs shows that in each pattern a row of spots lies parallel to the fibre direction, which will provisionally be called c, showing that c^* coincides with c. A few patterns have distinct circular Laue zones arising from rows of lattice points nearly parallel to the electron beam, the spacings of which were estimated by tilting the fibres around their axes, using a procedure described elsewhere (Gard, 1956*b*). Figs. 4 and 5 show examples from series of diffraction patterns recorded from two crystals lying at different orientations on the supporting film. In both series, rows of spots parallel to c in the odd-order Laue zones lie halfway between those in the even-order zones, indicating a C-centred lattice. Parameters estimated from the patterns of fig. 4 are 15·1 Å. for c, 22·4 Å. normal to c in the plane of the support, and 13·6 Å. for the row parallel to the beam. Corresponding

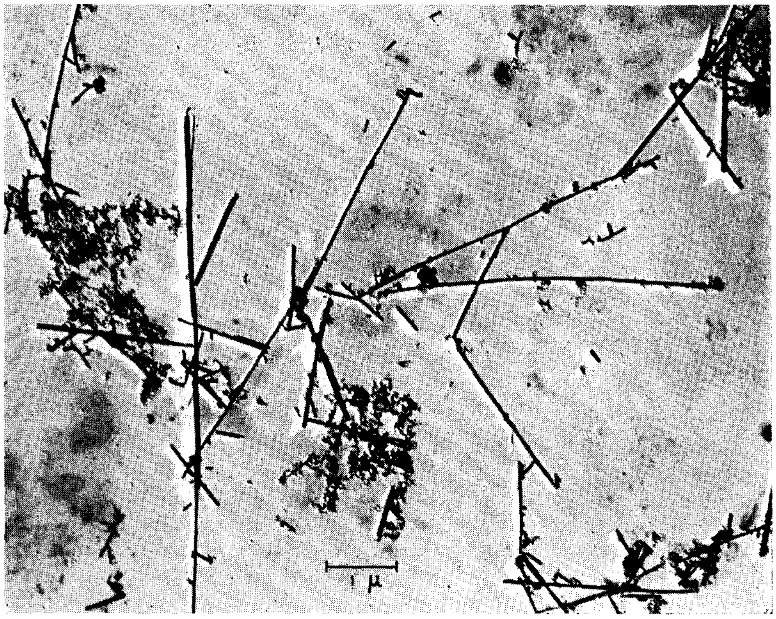


FIG. 3. Typical electron micrograph of erionite, shadowcast with Au-Pd at $\cot^{-1} 4$. The scale represents 1 μ.

parameters for the pattern of fig. 5 are 15·1, 13·3, and 23 Å., respectively. Clearly, the unit cell of the latter crystal is oriented about 90° around *c* with respect to that of the former. This suggests a unit cell that is, at least approximately, *C*-centred orthorhombic with *a* 13·3, *b* 22·4, *c* (elongation) 15·1 Å. This was confirmed by correlation with the X-ray powder and fibre data of table I, which gave the refined parameters of

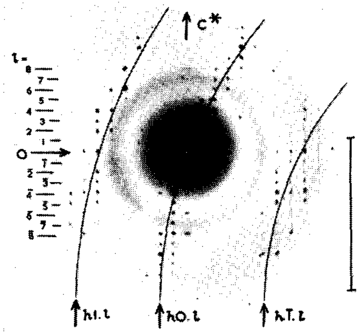


FIG. 4

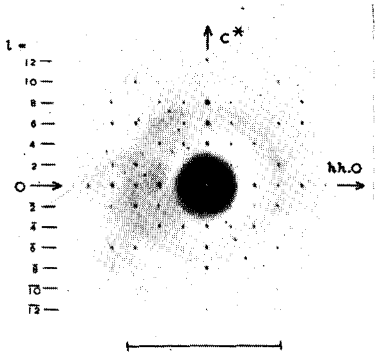


FIG. 5

FIG. 4. Electron-diffraction pattern from an erionite fibre with its $(11\bar{2}0)$ plane approximately normal to the electron beam. Rows of spots parallel to *c* in the first-order Laue zones, marked $h1.l$ and $h\bar{1}.l$, lie half-way between corresponding rows in the zero-order zone, marked $h0.l$, indicating a *C*-centred lattice. $000l$ reflections are missing for odd *l*-indices. The indices are for the hexagonal cell. The scale represents 1 Å.$^{-1}$

FIG. 5. An electron-diffraction pattern from an erionite fibre with its $(10\bar{1}0)$ plane normal to the electron beam. The fibre direction is marked *c**. Reflections with odd *l*-indices are completely absent. The scale represents 1 Å.$^{-1}$

a 13·26, *b* 23·08, *c* 15·12 Å. It is geometrically equivalent to a hexagonal cell with *a* 13·26, *c* 15·12 Å. Table I gives the X-ray data indexed on this unit cell; reflections with *l*-indices not confirmed by the fibre data are shown in parentheses. Indices have been inserted in the electron-diffraction patterns of figs. 4 and 5, and show that the crystals were lying with $(11\bar{2}0)$ and $(10\bar{1}0)$, respectively, normal to the electron beam.

There are no systematic absences of reflections with even *l*-indices. The only reflections with odd *l*-indices observed in the early X-ray patterns were $10\bar{1}1$, $10\bar{1}3$, $20\bar{2}1$, and $21\bar{3}1$. These were too few for derivation of the space-group, but indicate pseudo-halving of *c*. All electron-diffraction patterns (e.g. fig. 4) have $000l$ reflections missing for

TABLE I. X-ray powder data for erionite, indexed on a hexagonal unit cell with *a* 13·26, *c* 15·12 Å. All reflections have been confirmed on fibre rotation patterns, except those in parentheses which are not recordable. Indices are too numerous to be included for reflections with *d*-spacings less than 1·60 Å. Intensities were estimated visually. Cu-$K\alpha$ radiation was used in 6- and 11·54-cm. diameter cameras.

$d_{\text{obs.}}$	*I.*	*hkil*	$d_{\text{calc.}}$
11·57 Å.	**10**	$10\bar{1}0$	11·48 Å.
9·16	3	$10\bar{1}1$	9·16
7·56	5	0002	7·56
6·63	**8**	$11\bar{2}0$	6·63
6·30	1	$10\bar{1}2$	6·31
5·77	3	$20\bar{2}0$	5·74
5·37	4	$20\bar{2}1$	5·36
4·58	4	$20\bar{2}2$, $10\bar{1}3$	4·57, 4·61
4·34	7	$21\bar{3}0$	4·34
4·16	4	$21\bar{3}1$	4·18
3·80	**9B**	$30\bar{3}0$, $21\bar{3}2$ $20\bar{2}3$, 0004	3·83, 3·76 3·78
3·58	5	$10\bar{1}4$	3·59
	—	$30\bar{3}2$*	3·42
3·31	4	$22\bar{4}0$, $21\bar{3}3$ $11\bar{2}4$	3·31, 3·29 3·28
3·15	4B	$31\bar{4}0$, $31\bar{4}1$ $20\bar{2}4$	3·19, 3·12 3·16
2·92	1—	$31\bar{4}2$	2·91
2·84	**10B**	$40\bar{4}0$, $40\bar{4}1$ $21\bar{3}4$	2·87, 2·82 2·85
2·68	4	$40\bar{4}2$, $31\bar{4}3$	2·68, 2·69
2·50	7B	$41\bar{5}0$, $41\bar{5}1$, $32\bar{5}2$ $40\bar{4}3$, $22\bar{4}4$, $21\bar{3}5$	2·51, 2·47, 2·48 2·49
2·36	1—	$32\bar{5}5$	2·33
2·28	1—	$50\bar{5}0$, $50\bar{5}1$, $41\bar{5}3$ $40\bar{4}4$	2·30, 2·28, 2·25 2·28
2·21	4	$33\bar{6}0$, $50\bar{5}2$	2·21
2·12	2	$33\bar{6}2$, $30\bar{3}6$	2·12, 2·11
2·08	2	$51\bar{6}0$, $42\bar{6}2$, $50\bar{5}3$	2·06, 2·08, 2·09
2·04	1—	$51\bar{6}1$	2·04
1·99	1	$51\bar{6}2$, $32\bar{5}5$, $31\bar{4}6$	1·98, 1·99, 1·98

* Reflections observed on the fibre rotation patterns, but too weak to be seen on the powder patterns.

TABLE I (*cont.*)

$d_{\text{obs.}}$	*I.*	*hkil*	$d_{\text{calc.}}$
1·95Å.	1	$50\bar{5}4$	1·96Å.
	—	$51\bar{6}3$, $33\bar{6}4$, ($60\bar{6}0$ *	1·91
1·88	2	$43\bar{7}0$, $43\bar{7}1$, $40\bar{4}6$ (0008)	1·89, 1·87, 1·89 1·89
1·84	2	$52\bar{7}0$, $43\bar{7}2$, $51\bar{6}4$ $50\bar{5}5$	1·84, 1·83, 1·81 1·83
1·77	4	$43\bar{7}3$, $60\bar{6}3$, $41\bar{5}6$	1·77, 1·79, 1·78
1·75	1	$61\bar{7}0$, $40\bar{4}7$	1·75, 1·73
1·70	1	$61\bar{7}2$, $50\bar{5}6$	1·70
1·65	**7**	$44\bar{8}0$, $61\bar{7}3$, $52\bar{7}4$ $60\bar{6}5$, $33\bar{6}6$, $32\bar{5}7$	1·66, 1·65, 1·65 1·62, 1·66, 1·67

$d_{\text{obs.}}$	*I.*	$d_{\text{obs.}}$	*I.*	$d_{\text{obs.}}$	*I.*
1·59	5	1·37	3B	1·19	1
1·51	3B	1·34	3	1·14	2
1·46	2	1·27	3	1·06	1
1·43	1	1·24	2	1·04	1
1·41	1—	1·21	2		

* Reflections observed on the fibre rotation patterns, but too weak to be seen on the powder patterns.

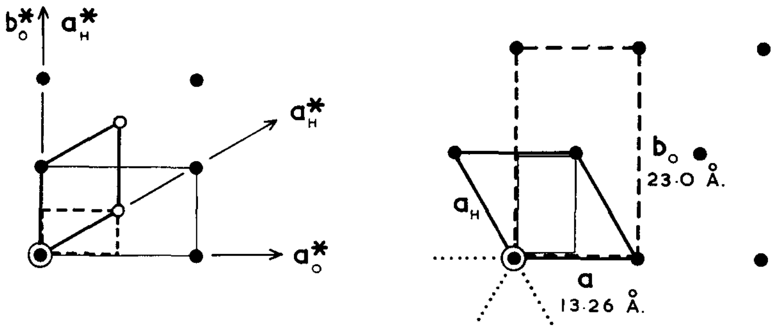
odd values of *l*. Reflections with odd *l*-indices are completely absent from the pattern shown in fig. 5, indicating a systematic absence of $hh\bar{2}\bar{h}l$ reflections for odd values of *l*. Other reflections with *l* odd, which have since been observed on fibre rotation patterns taken with much longer exposures, are in accord with this systematic absence, and have been interpolated in table I. $\{10\bar{1}0\}$ glide planes with component $c/2$ are therefore present, and the space-group is $P31c$, $P\bar{3}1c$, $P6_3mc$, $P\bar{6}2c$, or $P6_3/mmc$. The reciprocal and unit cells derived from the X-ray and electron data are summarized in fig. 6. It is interesting to note that whereas fibre rotation patterns do not distinguish between the apparent and true unit cells, single-crystal patterns are unequivocal. Fig. 5 also shows that $hh\bar{2}\bar{h}0$ reflections are much weaker for odd values of *h* than for even values.

Electron micrographs of fibres do not appear markedly hexagonal. It has already been stated that only a few electron-diffraction patterns show clear Laue zones. The angle between adjacent $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ planes is 30°, and in each case where Laue zones were present it was necessary to tilt the specimen stage up to 5° in order to centre the zero-order zone. This suggests that orientation of the fibres around their axes is random, and that there are no good cleavages in the zone parallel to *c*.

Chemical analysis and atomic cell contents.

A semi-quantitative spectrographic analysis of erionite gave: Si greater than 10 %; Al, Ca, Na, K, 10 to 1 %; Mg 1 to 0·1 %; Fe, Mn, Ba, Sr, 0·1 to 0·01 %; Cr, 0·01 to 0·001 %; and Zr, V, Cu, Ag, Ni, B, below 0·001 %.[1]

A new chemical analysis was made on 2 g. of selected and purified material. The results checked Eakle's analysis very closely, but with slightly higher water content and lower alkalis. Atomic cell contents were calculated for both analyses, assuming the highest experimental value for the specific gravity, 2·02. Results (table II) indicate the general formula $(\mathrm{Ca,Mg,Na_2,K_2})_{4\cdot5}\mathrm{Al_9Si_{27}O_{72}.27H_2O}$. The specific gravity calculated from this formula is 2·07, which is slightly higher than the experimental value. The formula differs from that suggested by other writers, but indicates the presence in the unit cell of 36 $(\mathrm{Si,Al})\mathrm{O_4}$ tetrahedra, which is more in accord with the hexagonal symmetry.



(a) (b)

FIG. 6. Parts of the *c*-faces of (*a*) reciprocal and (*b*) real lattices of erionite. In (*a*) black circles represent the reciprocal lattice points derived from the X-ray data, and open circles the extra points revealed by electron diffraction. In both (*a*) and (*b*) thin lines outline the orthorhombic cell indicated by the X-ray data, broken lines the larger *C*-centred orthorhombic cell indicated by electron diffraction, and heavy full lines the equivalent hexagonal cell. Dotted lines in (*b*) show the positions of the $[10\bar{1}0]$ glide planes.

After submission of this paper, K. S. Deffeyes (1959) has published a single-crystal X-ray study on erionite from Nevada that indicates a hexagonal unit cell, density, and atomic cell contents similar to those

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[1] Spectroscopist: T. C. Matthews, Oregon State Department of Geology and Mineral Industries, 9 Feb. 1954.

given above. $hh\overline{2h}l$ reflections were also missing for l odd. These data confirm those on which the crystal structure proposed in the following section is based.

Eakle noted that erionite contains ammonia and found 0·22 % present. Newly collected erionite was tested with freshly prepared Nessler reagent and gave a strong positive reaction, confirming Eakle's result. Ammonium ions may partly account for the small discrepancy (equivalent to 0·46 % NH_3) between the molar proportions of alumina and total alkalis and alkaline earths in the new chemical analysis. Ammonium zeolites have been prepared artificially (see Hey, 1955), but erionite is the only natural zeolite reported that contains a significant proportion of ammonia.

TABLE II. Atomic cell contents for erionite, calculated on the basis of a hexagonal unit cell with *a* 13·26, *c* 15·12 Å. (unit-cell volume 2300 Å^3) and specific gravity 2·02.

	1.	2.		3.	4.	5.	
SiO_2 ...	57·16	57·40	Si ...	26·68	26·80	27	36
Al_2O_3 ...	16·08	15·60	Al ...	8·82	8·57	9	
CaO ...	3·50	2·92	Ca ...	1·75	1·46		9†
MgO ...	0·66	1·11	Mg ...	0·45	0·77		
K_2O ...	3·51	3·40	K ...	2·09	2·02		
Na_2O ...	2·47	1·45	Na ...	2·23	1·31		
			O ... (not as H_2O)	71·0	70·3	72	
H_2O* ...	17·30	17·58	H_2O...	26·9	27·4	27	
	100·68	99·46					

† Calculated as monovalent ions.

* H_2O at 100° C., 7·69 %; H_2O at 400° C., 15·44 %; total H_2O at 820° C., 17·58 %.

1. Chemical analysis by A. S. Eakle (1898).
2. Chemical analysis by L. L. Hoagland, Oregon State Department of Geology and Mineral Industries (1954).
3. Atomic cell contents calculated from 1.
4. Atomic cell contents calculated from 2.
5. Idealized atomic cell contents.

Idealized cell contents $(Ca,Mg,Na_2,K_2)_{4\cdot5}Al_9Si_{27}O_{72}.27H_2O$.

Calculated specific gravity, 2·07.

Structure.

Zeolites contain anionic frameworks in which all the oxygen atoms are shared between two $(Si,Al)O_4$ tetrahedra, and which are traversed by channels large enough to accommodate the cations and water molecules. Erionite is unusual among the zeolites in having hexagonal, but not rhombohedral, symmetry. It also differs from the other fibrous zeolites (see A. F. Wells, 1950, p. 589), which have columns with a

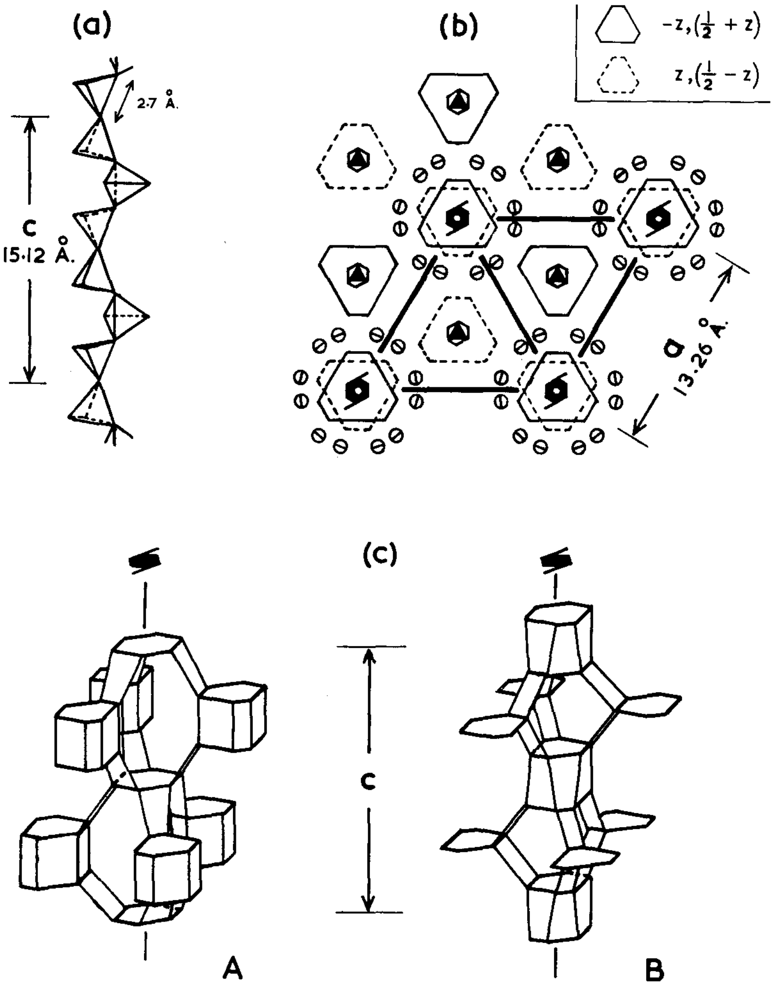

FIG. 7. (*a*) The 15·12 Å. *c*-spacing of erionite can accommodate 6 $(Si,Al)O_4$ tetrahedra, which form part of a continuous chain. (*b*) By suitable choice of *x*- and *y*-coordinates, the 24 general positions in the space-group $P6_3/mmc$ may be linked to form 6-membered rings. (*c*) The two possible ways of stacking six such rings. Comparison of calculated and observed structure factors shows that 'B' represents the correct structure.

repeating unit of five tetrahedra, cross-linked to give near-tetragonal symmetry; the fibre spacing is either about 6·6 or 13·2 Å., compared with 15·12 Å. for erionite. These distinctive characteristics of erionite make it interesting to speculate on its possible structure.

J. V. Smith (1954) has shown that the mean value for (Si,Al)–O bond lengths is 1·645±0·01 Å. for aluminosilicates in which the Al:Si ratio is 1:3, as in erionite, giving a mean value of 2·69 Å. for the edges of the $(Si,Al)O_4$ tetrahedra. The fibre spacing of 15·12 Å. could accommodate 6 such tetrahedra, each with one edge almost parallel to the *c*-axis, linked to form a continuous chain as in fig. 7*a*, in accordance with the fibrous nature of erionite; 6 such chains would be present in the unit cell. $P6_3/mmc$ appears to be the most probable space-group, as it would allow the maximum number, 24, of the 36 (Si,Al) atoms to occupy general positions, of which there are 6 in each plane normal to *c* at heights *z*, $(\frac{1}{2}-z)$, $(\frac{1}{2}+z)$, $-z$. Fig. 7*b* shows that suitable choice of *x* and *y*-coordinates would permit cross-linkage through oxygen bonds into rings containing 6 (Si,Al) atoms. Further bonding in the *c*-direction would give 'double-decker' rings, either with one centred on each of the $\bar{6}$-axes at (1/3, 2/3, *z*) and (2/3, 1/3, *z*), or with both centred on the 6_3-axis at (0,0,*z*). The remaining 12 (Si,Al) atoms must occupy special positions, and could form two 6-membered rings acting as links between the double rings. Thus, the two types of structure "A" and "B" shown in fig. 7*c* are possible; "B" is unambiguous, but the unit-cell parameters permit two variations of "A" differing only in orientation of the tetrahedra in the double rings. The X-ray powder pattern contains only 10 unambiguous reflections, too few to test the validity of the structures. Intensities were therefore estimated from the fibre rotation patterns by visual comparison with a standard exposure strip, and structure factors ($|F_0|$) were derived by application of polarization, Lorenz, and Cox and Shaw factors. Correlation with calculated structure factors ($|F_c|$) of *hki*0 reflections was poor for structures "A1" and "A2", but was satisfactory for "B", even when the comparison was extended to the other 8 recorded layer lines. The structure factors are shown in fig. 8 on a scale that represents values of $|F_c|$, but as no correction was made for absorption, comparison is only reliable within each layer, and values of $|F_0|$ have been adjusted therein so that $\Sigma|F_0| = \Sigma|F_c|$. The validity of structure "B" was confirmed by calculation of reliability factors $R = \Sigma(|F_0|-|F_c|) \div \Sigma|F_0|$, which are listed in table III. The rather poor correlation for *hki*1 reflections is due to an anomalously high value of $|F_c|$ for $10\bar{1}1$.

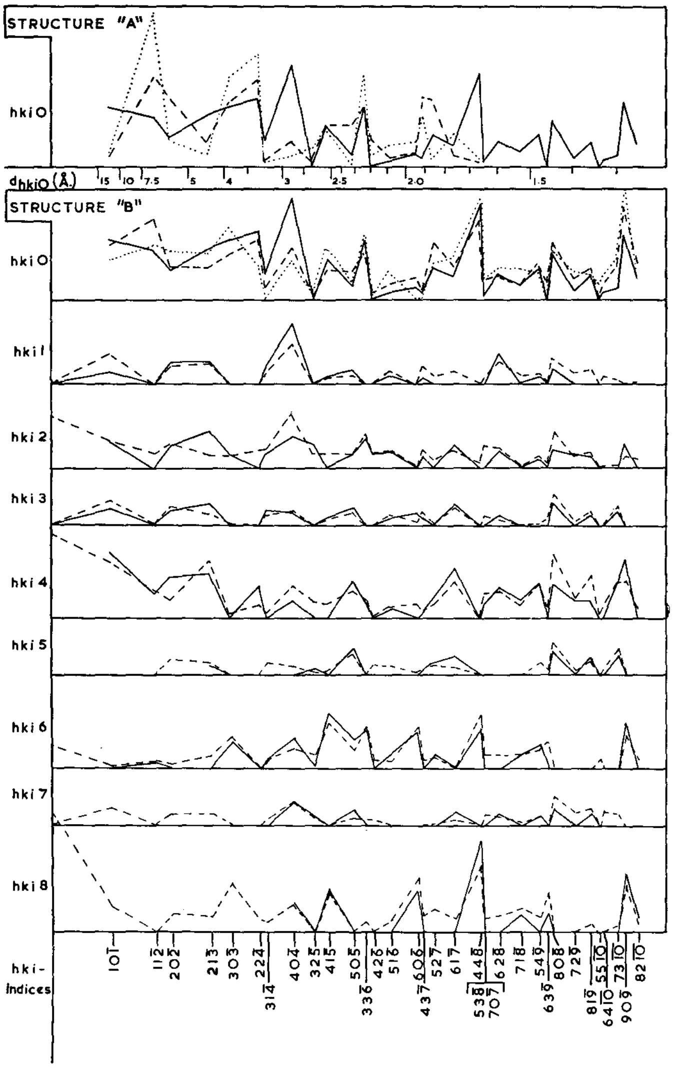

FIG. 8. Observed structure factors ($|F_0|$, represented by full lines) derived from the X-ray data, compared with those calculated ($|F_c|$, represented by broken lines) for the possible frame structures of erionite shown in fig. 7*c*. Correlation was poor for both of the minor variations of "A" (represented by broken and dotted lines in the upper graph), but was satisfactory for "B" for all recorded layer lines. The dotted line in the zero layer of "B" represents $|F_c|$ when the cations were assumed to be situated at (2/3, 1/3, z) and (1/3, 2/3, z). Correlation was slightly poorer than for the frame alone.

In an attempt to locate the approximate positions of the cations, they were provisionally assumed to be situated with random distribution on the principal axes of the cavities, i.e. at (2/3,1/3,z) and (1/3,2/3,z).

TABLE III. Reliability factors $R = \Sigma(|F_0|-|F_c|) \div \Sigma|F_0|$ for reflections observed in X-ray fibre rotation patterns of erionite and the two types of structure shown in fig. 7*c*. Value of $|F_0|$ were normalized so that $\Sigma|F_0| = \Sigma|F_c|$ within each layer. Correlation was so poor for structures A1 and A2 that values of F_c were not calculated for reflections with d-spacings less than 1·65 Å.

1.	2.	3.	4.
A1	0	19	0·80
A2	0		0·88
B	0	28	0·30
B+ cations*	0		0·34
B	1	12	0·46
B	2	19	0·31
B	3	15	0·35
B	4	21	0·36
B	5	8	0·28
B	6	12	0·25
B	7	8	0·34
B	8	9	0·30

1. Type of structure shown in fig. 7*c*.
2. l-index.
3. Number of reflections with calculated or observed structure factors above the observable minimum.
4. Reliability factor (R).

* The cations were assumed to be situated with random distribution on the principal axes of the cavities, i.e. at (2/3, 1/3, z) and (1/3, 2/3, z).

TABLE IV. Atomic coordinates for the aluminosilicate frame of erionite.

1.	2.	3.	x.	y.	z.
$\mathrm{Si_{I}}$	24	l	0·000	0·237	0·106
$\mathrm{Si_{II}}$	12	j	0·088	0·421	0·250
$\mathrm{O_{I}}$	24	l	0·017	0·350	0·162
$\mathrm{O_{II}}$	12	k	0·106	0·212	0·128
$\mathrm{O_{III}}$	12	k	0·123	0·246	−0·133
$\mathrm{O_{IV}}$	12	i	0	0·262	0
$\mathrm{O_{V}}$	6	h	0·217	0·434	0·250
$\mathrm{O_{VI}}$	6	h	0·450	0·900	0·250

1. Atoms, numbered as in fig. 9.
2. Number of equivalent atoms in one unit cell.
3. Type of atomic site (Wyckoff notation, International Tables for X-ray Crystallography, vol. 1, p. 304).

Structure factors were again calculated for the $hki0$ reflections, but correlation with $|F_0|$ values gave $R = 0·34$, rather higher than for the frame alone (table III), showing that the assumption was probably incorrect.

Projections of the structure of the erionite frame are shown in fig. 9, and atomic coordinates are listed in table IV. The mean (Si,Al)–O bond

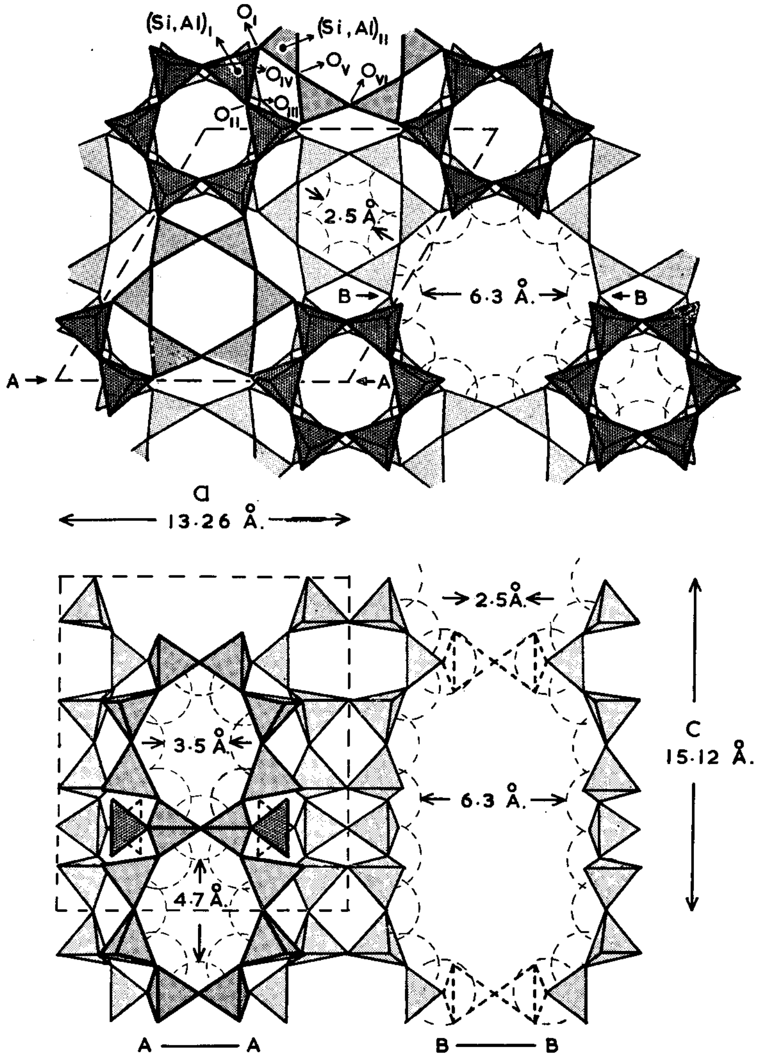

Fig. 9. Above, (0001) projection of erionite frame, showing the disposition of the $(Si,Al)O_4$ tetrahedra. Typical atoms are numbered as in Table III. Single rings are at $z = \frac{1}{4}$ (thin lines) and $z = \frac{3}{4}$ (heavy lines). Each has a 'window' with a free diameter of 2·5 Å.; one has been removed to show the free space at the centre of a cavity. Below, $(10\bar{1}0)$ projection, showing on the left the larger windows through 8-membered rings. These have been removed on the right to show a section of a cavity.

length is 1·635 Å., which is within the limits given by Smith (1954); Si–O–(Si,Al) bond angles vary between 137 and 170°. Fig. 10 shows views of a model of the aluminosilicate frame, in which the corners of polyhedra represent Si or Al atoms. It is characterized by columns in the *c*-direction, separated by cavities with a free diameter of about 6·3 Å., and a total length of 15·12 Å. Each column contains 6 chains of tetrahedra which are strongly cross-linked, but other bonds are comparatively few, explaining the fibrous nature of erionite and the absence of a distinct cleavage in the (*hki*0) zone. Each cavity is connected with six others through windows with a minimum free span of 3·5 Å., and with two others in the [0001] directions through smaller windows with a free diameter of 2·5 Å. The contents of each cavity thus have access to all others through the larger windows, suggesting that erionite should have a good capacity for base exchange, and that it could be used as a molecular sieve (see, for example, D. W. Breck and J. V. Smith, 1959).

Discussion.

Correlation between observed and calculated structure factors indicates that the structure shown in figs. 9 and 10 is substantially correct for the erionite frame. The presence of some anomalous values for F_c may be due to the effect of cations and water molecules, or to minor inaccuracies in the positions of the atoms of the frame. Fourier synthesis could assist in defining the complete structure. The X-ray data are adequate for refinement of the (0001) projection, but not of the *z*-coordinates. It has been shown (figs. 4 and 5) that electron-diffraction patterns can be recorded corresponding to $(11\bar{2}0)$ and $(10\bar{1}0)$ sections of the reciprocal lattice, raising the possibility of refinement of these projections, but the measurement of intensities presents a major difficulty. However, Burge *et al.* (1957) have described a modification to the electron microscope that spreads each spot into a rectangle of even optical density, which is claimed to facilitate accurate measurement of intensities.

Since this paper was read, L. S. Dent and J. V. Smith (1958) have proposed a new structure for chabazite, which makes an interesting comparison with that of erionite.[1] Chabazite is trigonal with a_H 13·78, c_H 15·03 Å. As in erionite, the *c*-spacing contains chains of 6 tetrahedra, and there are 6 rings in the unit cell each with 6 (Si,Al) atoms. In

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[1] The authors are grateful to Dr. J. V. Smith for indicating the resemblance between the structures of chabazite and erionite, and to Dr. I. S. Kerr for pointing out the relation between the unit cells of levyne and erionite.

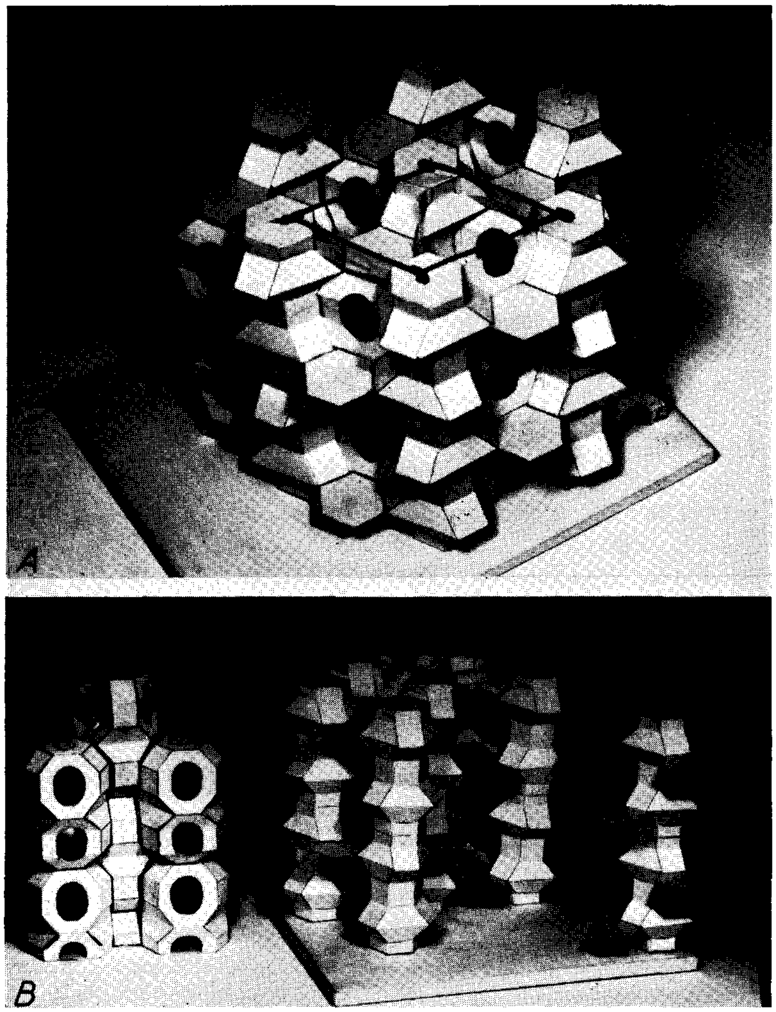

FIG. 10. Views of a model of the erionite frame, in which oxygen atoms are ignored, and corners represent (Si,Al) atoms. It is two unit cells high, with the fibre (*c*-) direction vertical, and the (0001) face on the base. The compact columns parallel to *c* are shown, and the cavities which carry the cations and water. Each cavity connects to six neighbouring ones through 'windows', and there are continuous channels in the $[11\bar{2}0]$ and approximate $[11\bar{2}1]$ directions. The compact columns are cross-linked by more widely spaced bonds, explaining the fibrous nature. In (*A*) the cavities are stacked in place between the compact columns; in (*B*) they are stacked separately, but in the same orientation, and one column has been detached from its neighbours.

chabazite, however, they are all linked in double rings situated at the corners of the rhombohedral cell. The cavities in chabazite are slightly smaller but more numerous, in the ratio 3:2, than those in erionite. Each cavity in both structures has windows formed from 8-membered rings. Levyne[1] (H. Strunz, 1956) is another zeolite that may have a structure related to that of erionite. It is hexagonal, with *a* 13·3, *c* 22·5 Å., so that the unit cell may contain nine 6-membered rings.

Synthesis of erionite is probably difficult to achieve, as it has only once been reported (Breck *et al.*, 1956; no details were given). It also occurs rarely in nature, which suggests that highly specific conditions are necessary for its formation. In order to explain the regular manner in which complex aluminosilicates crystallize, R. M. Barrer *et al.* (1959) have proposed that the first stage is the formation in solution of anionic units, comprising rings or polyhedra of linked $(Si,Al)O_4$ tetrahedra. Preservation of order during condensation of these complex units is easier to visualize than a similar process with tetrahedra as the building units. The simplest recurring unit into which the erionite frame can be divided is a polyhedron containing 18 (Si,Al) atoms, two of which occur between the (0001) unit-cell faces centred on the 6_3 axis (fig. 7*c*, "B"), and which in turn could be formed by condensation of the three 6-membered rings which lie roughly parallel to the *c*-axis. The unit of the chabazite structure could be the double 6-membered ring, formed by condensation of either two 6-membered or three 4-membered rings. The comparative simplicity of the repeat unit in chabazite may explain why that mineral is more abundant in nature and easier to synthesize than erionite.

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[1] See footnote on p. 278.

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