

ERIONITE FROM CENOZOIC TUFFACEOUS SEDIMENTS, CENTRAL NEVADA

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ABSTRACT

The mineral erionite, a zeolite known previously from only one locality, has recently been identified from six different areas in Wyoming, Nevada, and South Dakota. In each case it occurs in volcanic-rich Cenozoic sediments. A re-examination of the properties of the mineral shows that the original and subsequent descriptions have been incorrect in placing the mineral in the orthorhombic system. Single-crystal x -ray photographs show that the mineral has hexagonal symmetry and the optical properties observed are consistent with an assignment to the hexagonal system.

INTRODUCTION

Erionite was defined by A. S. Eakle in 1898 from material sent to Harvard for identification from Durkee, Oregon. The mineral occurred as white wooly fibers associated with opal in cavities in rhyolite tuff. On the basis of chemical properties, Eakle placed the mineral in the zeolite family and assigned the species to the orthorhombic system because the fibers exhibited parallel extinction and, "The acute bisectrix lies parallel to the fibers, since an axial figure normal to the obtuse bisectrix can be seen in the fibers" (1898, p. 68). Since that time the mineral has been regarded as extremely rare and no additional occurrences have been noted. In 1957 Staples reported that he had found the type locality and he published optical and x -ray measurements which were consistent with orthorhombic symmetry.

In 1956 the author and F. B. Van Houten found a material from Nevada and from Wyoming which had optical properties and diffraction spacings corresponding to no known mineral. Van Houten referred some of the samples to the Geochemistry and Petrology Branch of the U. S. Geological Survey and a comparison of the x -ray powder pattern of the specimens with the U.S.G.S. collection of powder patterns was made by F. A. Hildebrand who suggested that the material was erionite (Rept. IWX 799, Feb. 21, 1957). During this time an optical and x -ray diffraction study carried out by the author showed that the material from Wyoming and Nevada did not correspond to the crystallographic properties which had been published for erionite. Through the courtesy of Dr. C. S. Hurlbut of Harvard University, a portion of the type specimen (Harvard specimen no. 86532) was made available. This material did correspond in optical properties and x -ray pattern to the materials from Nevada and Wyoming, so a redescription of the properties of erionite is necessary.

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PHYSICAL PROPERTIES

The name erionite was derived from the Greek word for wool (*ἐριον*) because of the crinkly white appearance of the mineral fibers. Although this texture is duplicated in one small specimen from Nevada, more commonly the mineral occurs as fine-grained fibers or small radiating crystal groups in beds which were formed by partial or complete alteration of acidic vitric ash which fell into Cenozoic lakes. The beds composed dominantly of zeolite are thin bedded, massive, or blocky and they are white or light orange in color. In the specimens studied fine-grained mixtures of erionite and heulandite are about as common as beds of nearly pure erionite.

The measurements reported in this study were all made on crystals which were separated with heavy liquids (tetrabromethane and carbon tetrachloride) and a magnetic separator, from a sample of a tuff bed in Jersey Valley, Nevada. A full description of the outcrop is included in the discussion of localities.

The density was determined by the use of a centrifuge, heavy organic liquids, and a liquid density balance using the method described by Bass (1957). The mineral concentrate was pure except for flakes of volcanic glass which were included in about one-fourth of the grains. Since the glass is heavier than the zeolite, the density sufficient to float the first 20% of the sample is taken as the correct value: $2.070 \pm .01$ grams/cm.³ Eakle's original description (1898, p. 68) reported a specific gravity of 1.997.

OPTICAL PROPERTIES

Eakle's original description of erionite stated that the interference figure viewed in the direction perpendicular to the fiber axes was the obtuse bisectrix (1898, p. 68). This inference that the two optic axes were not coincident with each other and with the fiber axis has led later investigators to search for and to report variations in refractive index of about 0.002 in the directions perpendicular to the fibers (Larsen, 1921, p. 72; Staples, 1957). It is suggested that the differences reported between the least and intermediate indices has resulted from accepting the variations between grains as variations due to differences of orientation.

If the mineral were biaxial its optical behavior could be demonstrated by determinations of refractive indices of light vibrating perpendicular to the fiber axes and by locating the optic axes on the universal stage. In this study measurements of refractive index were made using a water cell for temperature control, a sodium monochromator, and a refractometer for measuring the indices of the immersion oils. The small variation from grain to grain of the least index of refraction was no greater

than the corresponding variation in the greatest index. Since variations in the greatest index (vibration direction parallel to the fibers) cannot be due to differences in orientation, it is concluded that the refractive indices were not observed to depart measurably from uniaxial behavior.

By placing unusually thick mounts of loose grains in plastic on a universal stage it was possible to tilt some grains until the fiber axis was vertical. The crystals showed no birefringence when viewed along the fiber axis and in all other positions the fibers were length slow. A check on the magnitude of the birefringence was made by determining directly the thickness and retardation of grains on the universal stage using a micrometer eyepiece and a Berek compensator. The optical properties of the material from Jersey Valley, Nevada are:

$$\begin{aligned} n_z & 1.4740 \pm .0005 \\ n_x & 1.4711 \pm .0005 \\ \text{birefringence} & .003 \\ \text{uniaxial, positive } Z=c & \end{aligned}$$

These values are close to those observed by Staples (1957) but they are considerably higher than the observations quoted in standard mineralogy textbooks which were taken from the determinations of Larsen (1921, p. 72).

X-RAY STUDY

The crystal system and approximate unit cell dimensions were determined from rotation and Weissenberg photographs of a single fiber rotated parallel to the fiber axis. A rotation photograph showed a layer spacing of 15 Å and a symmetry of C_{2v} . The even layer lines have considerably greater intensities than the odd layer lines. The positions and intensities of spots on a Weissenberg photograph of the zero layer line of the same crystal indicated a symmetry of C_{6v} (Buerger, 1942, p. 483) indicating a hexagonal lattice with an a_0 spacing of 13.1 Å.

The rotation photograph was used to index peaks on diffractometer traces. The precise cell dimensions were determined with a Norelco diffractometer using a nickel filtered copper radiation and silicon metal as an internal standard. Because of the fibrous habit of the mineral the intensities observed are strongly influenced by preferred orientation. The only systematic absence noted is that peaks having the indices $hh2\bar{h}l$ are present only when l is even. The only $000l$ peak present is 0002 but the weakness of the basal series is at least partially explained by selective orientation of the fibers. The information is insufficient for the assignment to a space group but the diffraction information indicates that erionite has a primitive hexagonal lattice with $a_0 = 13.200 \pm .005$ Å and $c_0 = 15.07 \pm .01$ Å. Diffractometer traces of the type specimen from

TABLE 1. X-RAY DIFFRACTION DATA FOR ERIONITE FROM JERSEY VALLEY, NEVADA, OBTAINED WITH A NORELCO DIFFRACTOMETER. Cu K α , Ni FILTER

<i>hkl</i>	2θ (obs)	2θ (calc)	<i>d</i>	I
10·0	7.7	7.73	11.43	100
00·2	11.7	11.72	7.54	3
11·0	13.4	13.41	6.60	60
10·2	14.0	14.00	6.32	4
20·0	15.4	15.45	5.73	28
20·1	16.5	16.54	5.35	15
20·2	19.4	19.44	4.56	8
12·0	20.5	20.52	4.32	90
12·1	21.3	21.35	4.16	30
30·0	23.3	23.34	3.81	60
12·2	23.7	23.69	3.75	45
10·4	24.8	24.81	3.58	12
22·0	26.9	27.02	3.30	40
12·3	27.1	27.17	3.28	8
31·0	28.1	28.11	3.17	25
20·4	28.4	28.30	3.15	25
31·1	28.7	28.74	3.10	12
31·2	30.5	30.55	2.924	8
10·5		30.59	2.920	
40·0	31.2	31.27	2.858	75
12·4	31.4	31.44	2.843	25
40·1	31.8	31.84	2.808	40
40·2	33.5	33.50	2.673	14
41·0	36.0	36.00	2.493	22
32·2	36.2	36.23	2.477	12
50·0	39.4	39.39	2.287	4
33·0	41.0	40.98	2.200	12
33·2	42.8	42.77	2.112	7
42·2	43.5	43.52	2.078	4
51·1?	44.5	44.47	2.035	1
51·2	45.8	45.73	1.981	4
50·4	46.5	46.37	1.956	1
43·0	48.3	48.37	1.880	2
52·0	49.8	49.76	1.831	10
41·6	51.6	51.54	1.772	5
61·0	52.4	52.42	1.744	2
61·2	53.9	53.91	1.699	5
44·0	55.6	55.65	1.650	30
62·0	58.3	58.13	1.585	10
62·1	58.5	58.49	1.576	10
62·2	59.5	59.53	1.551	2
71·0	61.1	61.15	1.514	3
54·0	63.5	63.50	1.464	8
62·4		63.60	1.462	
80·0	65.2	65.23	1.429	4
90·0	74.6	74.65	1.270	12

Durkee, Oregon showed peaks which were broader and less distinct but otherwise the spacings and intensities were identical.

Staples (1957) reported that "The optical properties of erionite indicate that it is orthorhombic, and all x -ray patterns may be indexed on an orthorhombic lattice of the dimensions: $a_0=6.625 \text{ \AA}$, $b_0=11.53 \text{ \AA}$, and $c_0=15.12 \text{ \AA}$." His unit cell has a simple relationship to the cell selected in this study and multiplication of Staples' a_0 and b_0 dimensions by the factors shown indicates that the sizes of the cells are similar.*

Staples (1957)		This study
a_0	$6.625 \times 2 = 13.25$	$a_0 = 13.20$
b_0	$11.53 \times 2/\sqrt{3} = 13.31$	$b_0 = 15.07$
c_0	15.12	

The x -ray observations can be adequately explained by a hexagonal lattice, and the following two observations indicate that there is no measurable deviation from hexagonal symmetry: (1) Certain of the diffrac-

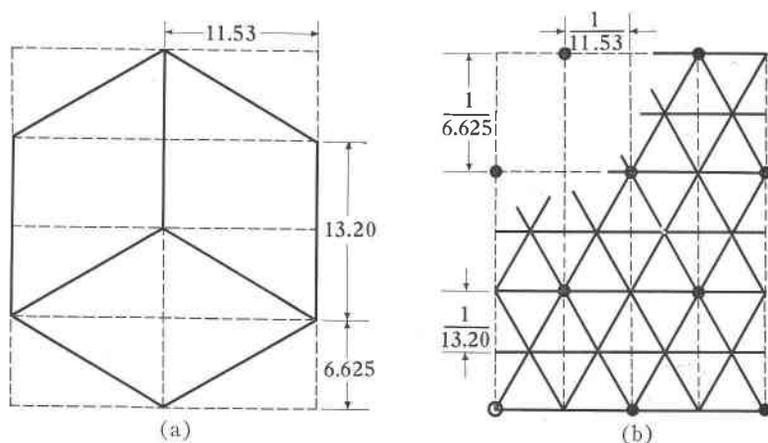


FIG. 1. Comparison of orthorhombic (dashed lines) and hexagonal (solid lines) lattices for erionite. (a) Direct lattice. (b) Reciprocal lattice. Heavy dots indicate those reciprocal lattice points which have two sets of orthorhombic indices approaching the same d spacing.

tion peaks have one set of hexagonal indices and two independent sets of orthorhombic indices. (An example is hexagonal 20·0 which is both 020 and 110 in the orthorhombic lattice.) The splitting or broadening of these peaks on the diffractometer traces would indicate an orthorhombic symmetry, but none of the dozen peaks of this type which were observed showed any sign of broadening or splitting. (2) The intensities as well as

* After the completion of this study, Staples and Gard stated in an abstract for the June 5, 1958 meeting of the Mineralogical Society that electron diffraction data on material from the type locality indicated a hexagonal unit cell of very nearly the same size as the one suggested in this report.

the positions of spots on the Weissenberg photograph show a sixfold symmetry which can be explained only by a hexagonal lattice or by nearly perfect pseudohexagonal twinning in which exactly equal amounts of each member of the twin is present.

CHEMICAL COMPOSITION

Considerable labor was expended in an unsuccessful attempt to concentrate a sample of erionite of sufficient size and purity for a chemical analysis. The agreement between the mole fraction of aluminum and the mole fraction of total alkalis and alkaline earths is frequently used as a check on the quality of zeolite analyses, and since Eakle's original analysis shows an excellent agreement it has been used in the calculation of unit cell contents:

	wt. %	moles/100 grams	atoms/unit cell	
SiO ₂	57.16	.953	Si	27.00
Al ₂ O ₃	16.08	.158	Al	8.95
CaO	3.50	.062	Ca	1.76
MgO	0.66	.017	Mg	0.48
K ₂ O	3.51	.039	K	2.21
Na ₂ O	2.47	.040	Na	2.26
H ₂ O	17.30	.960	H ₂ O	27.2
			O	71.9

The unit cell is probably composed of 36 tetrahedrally coordinated silicon and aluminum atoms linked into chains by sharing of the oxygen atoms at the corners of the tetrahedra. The alkali and alkaline earth atoms and water molecules occupy open spaces within the framework.

The unit cell composition proposed by Staples (1957) contains 16 Al and Si atoms in a cell having half the volume of the one suggested in this study. A calculation based on his unit cell dimensions and cell contents gives a density of 1.825 grams/cc., a result which seems too low to be considered reasonable.

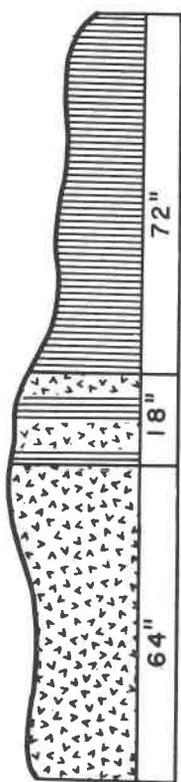
ION EXCHANGE

Potassium, silver, and thallium ions were substituted for the alkali ions in erionite by heating finely ground crystals in a low melting salt of the heavy metal. The exchanged zeolites have refractive indices considerably greater than the natural product and *x*-ray diffractometer observations show that the intensities of the peaks are greatly changed but the cell dimensions remain constant, indicating a substitution which does not affect the structural framework.

OCCURRENCES

At the type locality erionite is found in association with opal in fractures in rhyolite tuff. Thus far, in addition to the type locality, erionite has been found in sediments of late Cenozoic age in Nevada and in early Cenozoic sediments from Wyoming and South Dakota.

An outcrop near the center of sec. 8, T.27N., R.40E. in northern Jersey Valley in the Sonoma Range Quadrangle, Nevada, has been the source of the material used for the mineralogical studies in this report. For this reason a relatively complete description of the outcrop is included. The outcrop is near the top of a thick sequence of Miocene and early Pliocene sediments. The nearest fossils are early Pliocene in age and are about 700 feet lower in the sequence. Figure 3 is a photograph of the tuff bed and a description is included in Fig. 2. A small quarry at this site has been a source of building stone.



The uppermost part of the erionite bed is thin-bedded and fissile with fish fossils preserved along the bedding planes. The lower part is bedded but it is not fissile. Two well-developed sets of joints perpendicular to the bedding direction break the rock into equant blocks roughly one foot in size. Diffusion bands of orange color alternating with a gray background are present parallel to the joint surfaces and the bands are continuous across the bedding planes. The entire unit is composed of a mass of extremely fine erionite fibers with occasional grains of glass and plagioclase.

Alternating beds of tuff and erionite, similar respectively to the beds below and above.

Silver-gray rhyolite tuff, composed of well-sorted glass shards with a refractive index of 1.503. Plagioclase, zircon, quartz, and magnetite are present in very small amounts. The rock contains about 5% of radiating groups of erionite crystals about $\frac{1}{4}$ mm. long which were used for the measurements in this report. The tuff is soft but not friable. Ripple marks and disturbed bedding are occasionally present in the upper half of this unit.

Fig. 2. Section through beds composed of vitric tuff and erionite, Jersey Valley, Nevada.

In central Nevada erionite has been found in early Pliocene sediments in the Shoshone Range (T.27N., R.44E., Sec. 1) and in the valley of the Reese River (T.24N., R.43E., Sec. 26). In both localities erionite is found both as relatively pure beds and as mixtures with clinoptilolite. Erionite has been found by Regnier (personal communication) in lacustrine beds of Blancan (Plio-Pleistocene) age in Pine Valley south of Carlin, Nevada.



FIG. 3. Photograph of outcrop of unit described in Fig. 2. The beds composed of erionite begin about a foot above the head of the hammer.

In central Wyoming a mixture of erionite and clinoptilolite has been found by Van Houten (1954, personal communication, 1957) in thin bedded light gray altered tuff in the upper and middle Eocene rocks along the Beaver Divide east of Sand Draw. Samples of the White River (Oligocene) formation from South Dakota in the Princeton University collection which have been described by Wanless (1922) as mordenite, were re-examined by α -ray techniques and were found to contain a mixture of erionite and clinoptilolite.

A synthetic preparation of erionite has been reported by Breck et al. (1956).

SUMMARY

On the basis of a detailed mineralogical analysis it is concluded that erionite has erroneously been assigned to the orthorhombic system and that the optical properties and x -ray measurements are consistent with hexagonal symmetry. The mineral has the distinction of being the only known hexagonal fibrous zeolite.

Most frequently erionite has been formed by the alteration of acidic volcanic material, especially vitric ash which was deposited in lacustrine environments; moreover present knowledge of its distribution shows it is much less rare than it was formerly thought to be.

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