

## PAULINGITE, A NEW ZEOLITE, IN ASSOCIATION WITH ERIONITE AND FILIFORM PYRITE

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## ABSTRACT

A new zeolite, for which the name paulingite is proposed, has been found in vesicles in basalt from the Columbia River near Wenatchee, Washington. Paulingite is cubic, and occurs as perfect, transparent rhombic dodecahedra. The very large cubic cell has  $a_0 = 35.10 \pm .02 \text{ \AA}$ , and the space group is probably  $O_h^9 - Im\bar{3}m$ . Ca and K are the chief cations, but Ba and Na are also present. The atomic ratio of Si to Al is roughly 3. In association with the paulingite is the rare zeolite erionite. It occurs as relatively large acicular hexagonal prisms, and also as tufts of very fine fibers. The hexagonal unit cell has dimensions  $a = 13.27 \pm .02 \text{ \AA}$ ,  $c = 15.05 \pm .02 \text{ \AA}$ , and the space group is either  $D_{6h}^4$ ,  $C_{6v}^4$ , or  $D_{3d}^4$ . Erionite is a member of the chabazite group of zeolites. Also in association with the paulingite and erionite is pyrite of remarkable filiform habit.

## INTRODUCTION

In the course of deepening the channel of the Columbia River at Rock Island Dam, Washington, boulders of vesicular basalt containing a suite of hydrothermal minerals were dredged up. Samples of the basalt were sent to us by Walter Muffly, of Wenatchee, Washington. The minerals, which are found as well-formed crystals attached to the walls of the vesicles, include heulandite, phillipsite, calcite, and pyrite. Some of the pyrite displays a remarkable filiform habit, and is described in detail below. In association with these minerals occur two species that are not readily identifiable. The first occurs as fine, white, acicular crystals superficially resembling natrolite but distinguished from it by the hexagonal appearance of crystals large enough to be seen in cross section under the binocular microscope. The second is present as clear, perfect rhombic dodecahedra, and was thought at first to be analcite in an unusual habit. The occurrence and association of the two minerals, as well as their appearance, suggest that they are zeolites.

Optical examination fails to distinguish the isometric mineral decisively from analcite or faujasite. The acicular mineral is distinguished from natrolite by lower birefringence. X-ray powder diffraction patterns of the minerals suggest that they are distinct from the isometric and acicular zeolites for which powder data are available or for which we have obtained powder patterns—analcite, natrolite, thompsonite, and mordenite.

Examination of single crystals of the acicular mineral by x-ray diffraction indicates that it is the zeolite erionite, for which characterizing data have recently been obtained by Gard (Barret *et al.*, 1959) and by

Deffeyes (1959). Because erionite had, previous to the work of Deffeyes (1959), been known from only one locality in the world, we shall present the data obtained in our study of the mineral.

X-ray examination of single crystals of the cubic mineral shows decisively that it is a new species, and semi-quantitative chemical tests confirm its assignment as a zeolite. We propose the name *paulingite* for it.

#### OCCURRENCE

The rock in which the zeolites occur is a microporphyritic basalt containing abundant 0.05 to 0.4 mm. augite phenocrysts and abundant lath-like 0.1 to 0.5 mm. labradorite ( $An_{53}$ , assumed to be the high temperature form) phenocrysts having very ragged, forked ends. A few larger, less ragged phenocrysts of labradorite up to 1.0 mm. in length are present, usually showing a slight concentric compositional zonation. The groundmass, which makes up about 30 per cent of the volume of the rock (mesostasis), is a weakly devitrified glass displaying variolitic structure, and containing numerous well-formed dendritic aggregates of magnetite (?) cubes 0.005 to 0.01 mm. in size. In addition to the groundmass, a significant portion of the space interstitial to the phenocrysts, some 15 per cent of the volume of the rock, is filled with colloform layers of goethite (possibly with some lepidocrocite) which wrap around the phenocrysts and, less commonly, around the groundmass to a depth of .02 to .03 mm., filling the smaller interstices but leaving voids at the centers of the larger ones, which are gradational in size with unmistakable vesicles 0.5 mm. and greater in diameter. The goethite coating consists usually of two distinct layers, each .01 mm. thick, and the goethite contains magnetite dendrites (in many cases small cruciform aggregates), indistinguishable from the dendrites of the groundmass. Some of the voids enclosed by the goethite layers are empty, while others are filled or partially filled with zeolitic spherulites.

As dredged from the bottom of the channel, the zeolite-bearing basalt forms large rounded boulders that appear to have been transported some distance, to judge from the roundness and smoothness of their surfaces. A large volume of boulders, all basalt, was dredged from the bottom, but most of the boulders are non-vesicular and unrounded, in contrast to the rounded vesicular boulders that contain the zeolites. Within the rounded vesicular boulders, only a small fraction of the vesicles contain the hydrothermal minerals. Several persons have searched portions of the Columbia River channel above the point where the minerals were discovered, but to date the original provenance of the material has not been found. The presence of erionite brings to mind the vicinity of the original locality of this mineral at Durkee, Oregon, as a possible source, but the drainage patterns rule out this possibility.

The zeolites are evidently the latest crystallization products in the rock, since they overlie the goethite coating. The coating itself displays seemingly contradictory features: on the one hand, the uniformity of the coating as an interstice-filling, and the apparent absence of a source for the iron (as would be exhibited in altered relicts) in the bulk of the rock, suggest a late-stage origin for the coating, as though it were deposited from solutions derived elsewhere; whereas the content of magnetite dendrites indistinguishable from the magnetite in the glassy groundmass suggests a close relation with the crystallization of the bulk of the rock. With these uncertainties of interpretation, even less can be inferred about the detailed conditions of genesis of the zeolites, and we shall not, therefore, pursue further this interesting aspect of the occurrence.

#### PAULINGITE

Paulingite occurs as perfect clear rhombic dodecahedra 0.1 to 1.0 mm. in diameter. Because of their attachment to the vesicle walls, the crystals are roughly hemispherical in shape, and exhibit usually only five or six of the dodecahedral planes. As seen in place on the vesicle walls, the crystals appear dark brown to black, but in fact they are clear and colorless, the apparent dark color being due to their clarity and secure attachment to the dark vesicle walls. The dodecahedral faces are smooth and planar, and display a bright vitreous luster. A few faint growth striations, parallel to the edges of the faces, are visible. The crystals appear to have no cleavage, and fragments seen under the binocular microscope remarkably resemble small chips of ice. No crystal forms other than the rhombic dodecahedron are present, even as narrow truncations or facets. The hardness is about 5. Figure 1 shows a typical paulingite crystal in place on a vesicle wall.

Under the petrographic microscope the crystals are seen to contain a scattering of minute bubble-like inclusions. These inclusions are prominent when the index of refraction of the mineral is nearly matched to that of the immersion liquid, but they evidently do not detract from the macroscopic clarity of the crystals. Paulingite is quite isotropic throughout, and only extremely rarely can faint, isolated, fuzzy, very weakly birefringent twinning (?) lamellae be found. This distinguishes paulingite from analcite, though not from faujasite.

The index of refraction, measured at 23° C. in sodium vapor light, by the immersion method, is  $n_D^{23^\circ} = 1.473 \pm .001$ . The immersion liquids (Cargille) were not calibrated, but were taken from previously unopened and sealed bottles purchased in September, 1957.

Single crystal  $x$ -ray diffraction study, using zero and upper level Weissenberg and precession photographs, provides the following data. Paulingite is cubic, and the cubic cell has edge length  $a_0 = 35.10 \pm .02$  Å.

A precise determination of this value was obtained from a rotation photograph using copper  $K\alpha$  radiation, nickel-filtered, with the film in self-calibrating (Straumanis-type) arrangement. The crystal used was rotated about a cubic axis, and the reflections were indexed with the help of a zero-layer Weissenberg photograph. Reflections of the type  $hkl$  for  $l=0$  to  $l=12$  have been examined with equi-inclination Weissenberg photographs, and only reflections having  $h+k+l$  even are observed, indicating a body-centered lattice. No other systematic extinctions are

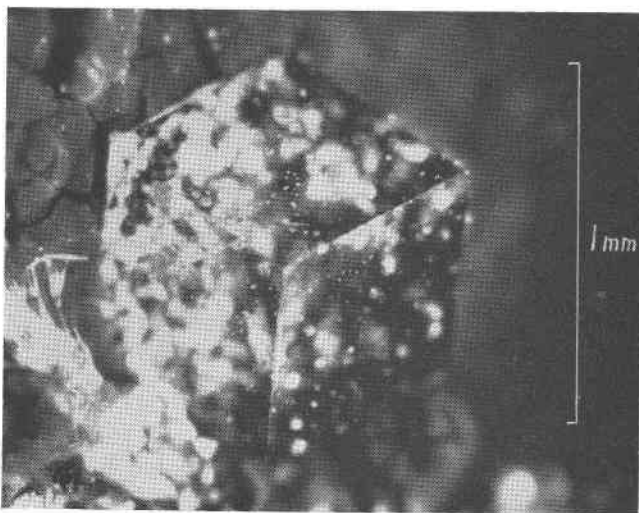


FIG. 1. Crystal of paulingite, in place on vesicle wall. The dodecahedron is viewed in the direction [111]. The bright spots are caused by light reflected at the under side of the crystal.

present. The Laue group is  $O_h$ , and the diffraction symbol is  $m3m-I \dots$ . The possible space groups are therefore  $O_h^5-I432$ ,  $T_d^3-I\bar{4}3m$ , and  $O_h^9-Im3m$ . A prominent feature of the diffraction patterns for all observed values of  $l$  is the relative abundance of weak reflections as compared with reflections of intermediate intensity, suggesting a centrosymmetric structure. The space group is therefore probably  $O_h^9-Im3m$ .

In Fig. 2 is shown, full size, a portion of an oscillation photograph, obtained with unfiltered copper radiation, of a paulingite crystal rotating about an  $a$  axis, and in Fig. 3 is shown part of the zero level Weissenberg photograph (also full size) of the same crystal, obtained with  $CuK\alpha$  radiation.

The size of the paulingite unit cell is remarkable. In fact, the paulingite cell is, to our knowledge, the largest known unit cell of an inorganic

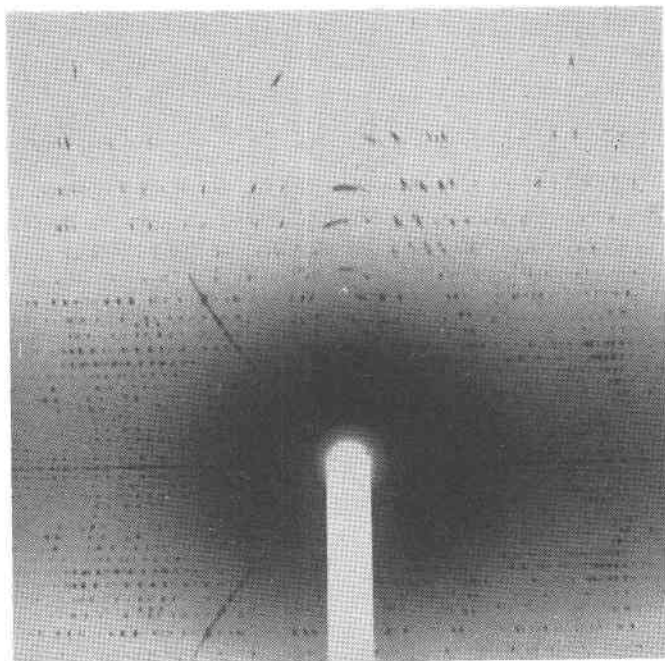


FIG. 2. 20° oscillation photograph of paulingite, reproduced at full scale. Oscillation axis [100]. Unfiltered copper radiation. Camera diameter 57.3 mm.

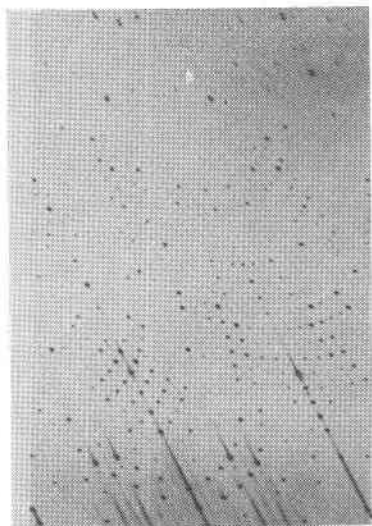


FIG. 3. Equatorial Weissenberg photograph of the  $(hk0)$  plane of paulingite, obtained with nickel-filtered copper radiation. Full scale; camera diameter 57.3 mm.

compound, exceeding in size the cells of the most complex intermetallic compounds, sulfosalts, and metallic sulfides, and surpassed only by the unit cells of crystallized proteins.

Because of the large observed size of the paulingite unit cell, we have examined the diffraction data carefully for any indication that the large cell might be accounted for by multiple twinning of a cell of smaller size and lower symmetry, or by syntactic intergrowth of cells of different sizes. Such phenomena have been found to explain diffraction patterns of some apparently large cubic lattices (Donnay *et al.*, 1958*a* and 1958*b*). However, the absence of any systematic extinctions other than those due to the body-centering translation preclude any such interpretation of the paulingite data, and the optical isotropy in addition makes unlikely the possibility of multiple twinning of individuals of lower symmetry.

Because of the very small amount of paulingite available, a complete wet gravimetric chemical analysis is not possible. But in any case a complete chemical analysis would not be of much help in characterizing such a structurally complex substance, or in establishing its identity from other minerals. We have, however, obtained semi-quantitative information on the composition. A batch of crystals (total weight about 15 mg.) was picked by hand from the vesicle walls, and hand sorted under the binocular microscope into two lots—(1) fragments bearing a visible incrustation of goethite derived from the vesicle walls, and (2) fragments appearing perfectly clean. The fragments of lot 1 were crushed gently in a diamond mortar, and resorted into lots 1 and 2, which then weighed respectively 2.9 mg. and 10.1 mg. The water content was determined by heating the samples to a dull red heat, which was sufficient to cause fusion, in platinum crucibles, and measuring the weight loss. The two dry samples were then analyzed semi-quantitatively by emission spectroscopy. The analyses were performed by Elisabeth Godijn in the spectrographic laboratory of the Division of the Geological Sciences, California Institute of Technology. Weights of the samples available for spectrographic analysis were 0.9 mg. (lot 1) and 7.7 mg. (lot 2).<sup>3</sup>

The results of the analyses are given in Table 1. The small amount of material in lot 1 allows only a qualitative interpretation of this analysis. The agreement between the two analyses is of the order expectable from the spectrographic method, except for the marked discrepancy in CaO content. The  $\text{Fe}_2\text{O}_3$  in lot 1 is doubtless due to the goethite impurity, and presumably the MgO is to be ascribed to the same source, although its high value casts doubt on the (optical) identification of the impurity as goethite. Here we restrict our consideration to the analysis of the larger, cleaner sample (lot 2).

The indicated composition is evidently that of a zeolite. The mag-

nesium reported doubtless derives from the goethite (?) incrustation, a small amount of which must have been present in lot 2, because a few small fragments in the sample became black upon heating. The Al/Si ratio of 0.15 given by the analysis conflicts with the cation composition in lot 2, which requires an Al/Si ratio of 0.47. Either the analysis is internally inconsistent, or else anions must be present outside the tectosilicate framework. Halogens are not detectable in the spectral

TABLE 1. SEMI-QUANTITATIVE ANALYSES OF PAULINGITE

	Lot 1 (dirty) (0.9 mg.)	Lot 2 (clean) (7.7 mg.)
H <sub>2</sub> O+ : % of total (hydrated) wt.:	24	22
Oxides: % of dry wt.:		
SiO <sub>2</sub>	40	67
Al <sub>2</sub> O <sub>3</sub>	6	9
CaO	1	7
BaO	2	2
SrO	—	—
Na <sub>2</sub> O	*	1
K <sub>2</sub> O	*	10
MgO	2	0.01
Fe <sub>2</sub> O <sub>3</sub>	0.5	—
Atoms (based on Si+Al=12):		
Si	11.0	10.4
Al	1.0	1.6
Ca	0.3	1.2
Ba	0.2	0.1
K	*	2.0
Na	*	0.4
H <sub>2</sub> O	?	14.3

Dashes indicate that the element was not detected.

\* Not observable in wavelength region employed.

range used for the analysis, but without further evidence it seems more likely that the discrepancy reflects the inherent inaccuracies of the spectrographic method.

We have not measured the density of paulingite, but to get an idea of the contents of the unit cell we may use the following very rough method, based on the index of refraction. From the equation of Lorentz and Lorentz

$$V_m \frac{n^2 - 1}{n^2 + 2} = \sum_i N_i \lambda_i$$

where  $V_m$  is the volume of one mole of the substance, and where there are  $N_i$  atoms or atomic groups of atomic refractivity  $\lambda_i$  ( $i=1, 2, \dots$ ) in one molecule, we calculate the refractivity  $\lambda_x$  for the tetrahedral groups  $\text{Si}_{1-x}\text{Al}_x\text{O}_2$  in the framework of various tectosilicates, by making use of the ionic refractivities for  $\text{Na}^+$ ,  $\text{Ca}^{++}$ ,  $\text{K}^+$ ,  $\text{Ba}^{++}$ , and  $\text{Cl}^-$  given by Wasastjerna (1923). The results, in Table 2, show a progressive increase in refractivity from about 7.4 for  $\text{SiO}_2$  to about 8.0 for  $\text{Si}_{1/2}\text{Al}_{1/2}\text{O}_2$ . The

TABLE 2. MOLECULAR REFRACTIVITIES  $\lambda_x$  FOR THE  $\text{Si}_{1-x}\text{Al}_x\text{O}_2$  TETRAHEDRAL GROUPS IN THE FRAMEWORKS OF VARIOUS TECTOSILICATES

Mineral	$x$	$\lambda_x$	Mineral	$x$	$\lambda_x$
Quartz	0	7.25	Celsian	$\frac{1}{2}$	8.05
Tridymite	0	7.5	Sodalite	$\frac{1}{2}$	7.9
Cristobalite	0	7.4	Gmelinite	$\frac{1}{3}$	7.7
Orthoclase	$\frac{1}{4}$	7.6	Chabazite	$\frac{1}{3}$	8.1
Albite	$\frac{1}{4}$	7.6	Levynite	$\frac{1}{3}$	7.5
Leucite	$\frac{1}{3}$	7.8	Analcite	$\frac{1}{3}$	7.8
Nepheline	$\frac{1}{2}$	8.1	Faujasite	$\frac{1}{3}$	7.8 ± 0.2
Artif. $\text{NaAlSiO}_4$	$\frac{1}{2}$	8.1	Natrolite	$\frac{2}{5}$	7.9
Kaliophilite	$\frac{1}{2}$	8.0	NaA (artif.)	$\frac{1}{2}$	7.9
Anorthite	$\frac{1}{2}$	7.9			

method may be applied to zeolites by assuming in addition the value 3.74 for the molecular refractivity of  $\text{H}_2\text{O}$ , intermediate between the values 3.71 for liquid water and 3.77 for ice. The results scatter more widely, but remain on the average in agreement with those for the anhydrous tectosilicates.

For a zeolite framework with  $x = \frac{1}{4}$ , which is of the order indicated by the analyses for paulingite, we may take  $\lambda_{1/4} = 7.7$ . Adjusting the total number of cations in Table 1 (lot 2) to fit  $x = \frac{1}{4}$ , we may then calculate the cell content of paulingite from its index of refraction and cell size. We find approximately 580 silicon plus aluminum atoms (plus the corresponding 1160 framework oxygen atoms), 690 water molecules, 40 calcium atoms, 65 potassium atoms, 15 sodium atoms, and 3 barium atoms. Of course, if the cations are in fixed positions in the structure, the number of barium atoms in the cell must be either 2, or 6, 8, etc., but the above numbers must be considered only the roughest approximation.

Table 3 gives x-ray powder diffraction data for paulingite.

Paulingite is named in honor of Linus Carl Pauling, Professor of Chemistry in the California Institute of Technology, in recognition of his outstanding contributions to the understanding of the complex structures of silicate minerals and other compounds.



TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR PAULINGITE<sup>1</sup>

<i>d</i>	<i>I</i> <sup>2</sup>	<i>hkl</i> <sup>3</sup>	<i>d</i>	<i>I</i>
12.37	1	220	2.983	8d
9.45	1	321	2.851	2d
8.29	10	411, 330	2.789	2
7.86	1	420	2.725	6
7.14	2	422	2.615	7
6.88	10	510, 431	2.574	1
6.21	4	440	2.520	2
5.86	5	600, 442	2.484	1
5.70	5	611, 532	2.448	1
5.42	3	541	2.046 <sup>4</sup>	3
4.96	5	710, 550, 543	2.010	3
4.78	9	721, 633, 552	1.774	6
4.68	3	642	1.290 <sup>5</sup>	3
4.385	4	800	1.286	1
4.25	4	820, 644	1.253	1
4.08	4	831, 750, 743	1.181	2
3.875	4	910, 833	1.168	1
3.694	2	930, 851, 754	1.068	2d
3.582	8	844	1.030	2
3.440	1	10·2·0, 862	1.017	1
3.346	8	10·3·1, 952, 765	0.979	2
3.261	9	10·4·0, 864		
3.176	2	11·1·0, 954, 873		
3.129	7	11·2·1, 10·5·1, 963		
3.078	9	11·3·0, 970		

<sup>1</sup> Data from self-calibrated (Straumanis-type) photograph obtained with manganese-filtered iron radiation.

<sup>2</sup> Intensities are visual estimates, not based on an intensity calibration scale; they are therefore sequential only, from 1="very weak" to 10="very strong." The suffix *d* indicates a diffuse line, resulting from near superposition of two or more reflections.

<sup>3</sup> Indices assigned on the basis of  $a_0 = 35.10 \text{ \AA}$  and  $\lambda_{\text{FeK}\alpha 1} = 1.936 \text{ \AA}$ . Indexing not carried out beyond  $d = 3.0 \text{ \AA}$ .

<sup>4</sup> Six very weak lines in the range  $2.448 > d > 2.046$  were not measured.

<sup>5</sup> Twenty one weak lines in the range  $2.010 > d > 1.290$  were not measured.

### ERIONITE

Erionite forms fine transparent acicular crystals, isolated and in radiating clusters, and white to brownish tufted masses of very fine fibers. The yellowish and brownish tufts are colored by a "limonite" stain; the individual crystals are clear and colorless. The crystals are up to 2 mm. in length, and occur in diameters ranging from a fraction of a micron up to 0.2 mm. Most of the crystals are very fine: in the tufted masses, the majority of the fibers are too narrow to be resolved clearly

in width under normal high power ( $\times 400$ ) magnification, and the largest crystals are about  $3\mu$  in width. The larger crystals, up to 0.2 mm. in diameter, are rare, and occur mostly as isolated individuals growing out from the vesicle walls. These large crystals appear to be hexagonal prisms, and the hexagonal character is confirmed on the optical goniometer, although the prism faces give very diffuse signals, probably because of the presence of numerous growth striations and vicinal faces parallel to the prism axis. The crystals show parallel extinction, length slow, and

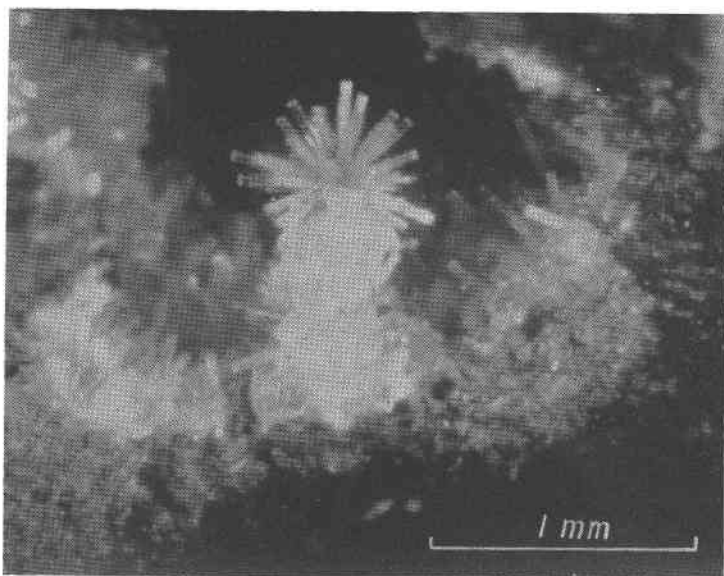


FIG. 4. Relatively large hexagonal prisms of erionite, forming a radiating cluster and lining the walls of a vesicle. The scale is indicated by the 1 mm. bar.

are doubtless uniaxial positive. The ordinary index  $\omega$  is  $1.474 \pm .001$ , measured by the immersion method in sodium vapor light at  $24^\circ$  C. The optical properties of the fine crystals from the tufted masses and of the coarser acicular crystals are identical, confirming that they are the same material. The birefringence is very low, and was measured with a Berek compensator upon a well-shaped hexagonal crystal 0.06 mm. in diameter. The result is  $\epsilon - \omega = 0.0014 \pm .0002$ . The hardness and density cannot readily be determined.

A cluster of the larger erionite crystals is shown in Fig. 4.

Single-crystal  $x$ -ray diffraction patterns were obtained from acicular crystals about 0.1 mm. in diameter, rotating about the needle axis. Zero

and upper layer Weissenberg photographs show strict hexagonal symmetry. The length of the hexagonal  $a$  axis, measured by the method described above for the paulingite  $a$  axis, is  $13.27 \pm .02$  Å. The  $c$  axis was measured from rotation photographs about [0001], and from  $hh \cdot l$  and  $h0 \cdot l$  precession photographs for which the film-to-crystal distance  $F$  was simultaneously calibrated by means of the  $a$  axial length on the photographs. The result is  $c = 15.05 \pm .02$  Å. The precession photographs show  $hh \cdot l$  present only for  $l = 2m$ , indicating a  $c$  glide plane. The Laue group is  $D_{6h}$ , and the diffraction symbol is  $6/mmm - P \cdot \cdot c$ . The possible space groups are therefore  $C_{6v}^4 - P6_3mc$ ,  $D_{3h}^4 - P\bar{6}2c$ , and  $D_{6h}^4 - P6_3/mmc$ .

The above single-crystal  $x$ -ray data are in good agreement with electron diffraction data obtained for erionite by J. A. Gard (given in Barrer et al., 1959), and with  $x$ -ray powder diffraction data obtained by K. Deffeyes (1959):

Source	$a$	$c$	Diffraction Symbol
Deffeyes	13.20	15.07	$6/mmm P \cdot \cdot c$
Gard	13.26	15.12	—
Kamb and Oke	13.27	15.05	$6/mmm P \cdot \cdot c$

The optical data given above agree reasonably with those obtained by Deffeyes.

The unit cell dimensions show that erionite is a member of the chabazite group of zeolites (the "würfel" zeolites), which embraces four members, whose space groups and cell dimensions (hexagonal cell) are:

chabazite	$R3m$ (nearly)	$a$ 13.78	$c$ 14.97	$Z=6$
gmelinite	$P6_3/mmc$	$a$ 13.72	$c$ 9.95	$Z=4$
levynite	(rhombohedral)	$a$ 13.31	$c$ 22.44	$Z=9$
erionite	$P6_3/mmc$	$a$ 13.27	$c$ 15.05	$Z=6$

The data for chabazite, gmelinite, and levynite are from Strunz (1956, 1958). The gmelinite space group is inferred from the ideal structure of Dent and Smith (1958).

The ideal "molecule" of the chabazite-group zeolites is  $(Ca, Na_2) Al_2Si_4O_{12} \cdot 6H_2O$ . The number of oxygen atoms in the erionite cell, determined by Deffeyes (1959) from the density and the original chemical analysis by Eakle (1898) agrees with this formula and with the structural relations inferred, although the number of water molecules appears to be about 4.5 rather than 6, and the mineral contains less aluminum than suggested by the formula.

Recently Dent and Smith (1958) have proposed a structural scheme for chabazite and gmelinite, according to which gmelinite is built by a stacking of double hexagonal rings of  $SiO_4$  and  $AlO_4$  tetrahedra in a

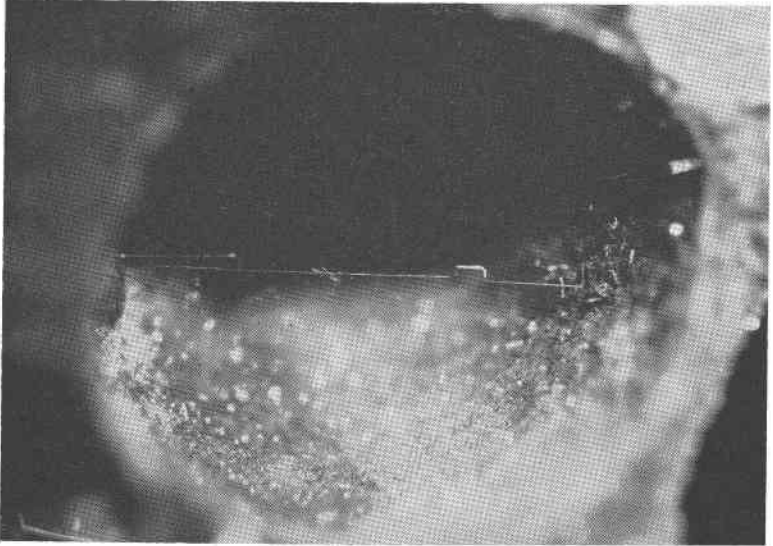


FIG. 5. Filiform crystals of pyrite growing from a pyrite cube in a vesicle. Note the right angle bends. The length of the long fiber is 6 mm.

hexagonally closest packed array, while in chabazite the same units are stacked in a sequence corresponding to cubic closest packing, thus resulting in a rhombohedral cell. It is interesting to note that erionite and levynite appear to be related in a manner analogous to the relation of gmelinite to chabazite, to judge by the ratio of  $c$  axial lengths, and the space group relations, to the extent that they are known. The kinship of erionite and levynite is further suggested by the  $a$  axial lengths, which contrast with the longer  $a$  axes of gmelinite and chabazite.

#### FILIFORM PYRITE

The minerals described above came to our attention because Walter Muffly asked if we could identify the fine "brass wires" in some of the vesicles. Microchemical study of the "wires" suggested that they are pyrite, and  $x$ -ray single crystal and powder diffraction study confirms this identification. The filiform crystals of pyrite are about 0.05 mm. in diameter, and vary from 1 to 4 mm. in length. Most of the crystals are square in cross section, but a few are flattened ribbons. Some crystals are simple straight needles, but most consist of several straight portions joined by right-angle bends. One crystal was noted with thirteen such bends, and some of the crystals form bizarre shapes.

The orientation of the pyrite wires has been determined by means of

an  $x$ -ray rotation photograph in which a single wire was rotated about its axis. The axis of the wire is parallel to one of the crystallographic  $a$  axes.

Typical pyrite crystals—cubes modified by octahedral facets—also occur in some of the vesicles, some of the crystals having pyrite needles growing out at right angles to the cube faces.

A vesicle containing several filiform pyrite crystals is shown in Fig. 5.

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#### REFERENCES

- BARRER, R. M., *et al.* (1959) Hydrothermal Chemistry of the Silicates. Part VIII: *J. Chem. Soc.* **36**, 195–208.
- DEFEYES, K. (1959): *Am. Mineral.* **44**, 501–509.
- DENT, L. N., AND SMITH, J. V. (1958) Crystal structure of chabazite, a molecular sieve: *Nature* **131**, 1794–1796.
- DONNAY, G., DONNAY, J. D. H., AND KULLERUD, G. (1958a) Crystal and twin structure of digenite,  $\text{Cu}_9\text{S}_5$ : *Am. Mineral.* **43**, 228–242.
- (1958b) “Bornite”: Ann. Rept. Dir. Geoph. Lab., Carnegie Inst. Wash. Yrb. 57 (1957–1958), p. 248.
- EAKLE, A. S. (1898) Erionite, a new zeolite: *Am. J. Sci.* **6**, 66.
- STRUNZ, H. (1956) Die Zeolithe Gmelinit, Chabasit, Levyn: *N. Jb. Min., Mh.* **11**, 250–259.
- (1958) *Mineralogische Tabellen*: Leipzig (3d. ed.), p. 344.
- WASASTJERNA, J. A. (1923) Soc. Sci. Fenn. Comm. *Phys. Math.* **1**, 37.

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