American Mineralogist, Volume 59, pages 837–842, 1974

Levyne-Offretite Intergrowths from Basalt near Beech Creek, Grant County, Oregon

RICHARD A. SHEPPARD, ARTHUR J. GUDE, 3D, GEORGE A. DESBOROUGH,
U.S. Geological Survey, Denver, Colorado 80225

AND JOHN S. WHITE, JR.
Smithsonian Institution, Washington, D. C. 20560

Abstract

Intergrowths of levyne and offretite occur in vesicles of the Picture Gorge Basalt near Beech Creek, Oregon. Levyne occurs as aggregates of thin, platy crystals, and the offretite occurs as white, silky, fibrous layers on the levyne. The offretite fibers grew normal to the (0001) of levyne, and, locally, replaced the levyne. Electron microprobe analyses of the zeolites yielded the formulas $Ca_{2.50}Mg_{0.00}Na_{0.58}K_{0.27}Al_{6.78}Si_{11.45}O_{36} \cdot nH_2O$ for levyne and $Ca_{1.79}Mg_{0.17}Na_{0.30}K_{1.00}Al_{6.08}Si_{12.11}O_{36} \cdot nH_2O$ for offretite. Hexagonal cell parameters for the levyne are $a = 13.356(3)$ Å, $c = 22.88(1)$ Å, $V = 3{,}535(2)$ Å^3; and for the offretite, $a = 13.348(2)$ Å, $c = 7.59(2)$ Å, $V = 1{,}172(3)$ Å^3. Offretite had previously been recognized only from the type locality near Montbrison, France. Thus, the identification of offretite from the Beech Creek locality, as well as from other similar occurrences associated with levyne in basalts, indicates that it is not so rare as previously supposed.

Introduction

Offretite was first recognized by Gonnard (1890) as a new zeolite in amygdaloidal basalt at Mount Simionse near Montbrison, Loire, France. Except for a possible occurrence in basalt from Palau Island, Caroline Islands (Dürrfeld, 1911), no other occurrence of offretite has been reported. Erionite, a closely related (Bennett and Gard, 1967) but much more common zeolite, has been reported from amygdaloidal basalts and especially from diagenetically altered vitric tuffs (Sheppard and Gude, 1969).

Shimazu and Mizota (1972) described intergrowths of erionite and levyne in amygdaloidal basalts from Chojabaru, Iki Island, Japan, and from a locality in the United States designated as Beech Creek, Oregon. The identification of the erionite from Japan is supported by X-ray, optical, and chemical data; however, the identification of the Beech Creek material is doubtful and is supported only by a chemical analysis and incomplete X-ray data. Even the chemical analysis of the Beech Creek material given by Shimazu and Mizota (1972, p. 420) seems closer to that of offretite than to that of erionite. Furthermore, we have been studying the zeolites from the Beech Creek locality since 1971 and have identified intergrowths of levyne and offretite. This occurrence of offretite at Beech Creek is the only documented occurrence other than that near Montbrison, France.

Occurrence of Levyne and Offretite

Our specimens were collected from the Miocene Picture Gorge Basalt by A. L. McGuinness in 1964. The zeolite-bearing basalt flow crops out in a small quarry about 0.2 km east of Beech Creek in the NW¼ SW¼ sec. 18, T. 12 S., R. 31 E., Grant County, Oregon. A preliminary geologic map of the Long Creek quadrangle (Thayer and Brown, 1967) shows that the Picture Gorge Basalt dips gently northward at this locality. The basalt is dark gray and vesicular, and most vesicles are in the range of 5–20 mm. Thin sections show that the basalt has an intersertal texture and consists of calcic plagioclase laths, subophitic clinopyroxene, dark-brown glass, and minor olivine.

Levyne occurs in vesicles of the basalt as thin, platy, single crystals parallel to (0001) or more commonly as parallel aggregates of platy crystals that are mostly 1–7 mm in longest dimension. Individual crystals of levyne are 0.01–0.2 mm thick, but the aggregates of platy crystals are commonly 0.2–1.0 mm thick. The levyne forms a boxwork within the vesicles (Fig. 1) and generally is separated from the vesicle wall by a thin film of an unidentified greenish-brown, 14 Å clay mineral.

Offretite occurs as a silky white coating on the levyne. Aggregates of the platy levyne, if broken normal to the plates, also show layers of fibrous offretite between the individual levyne plates. Under a hand lens, these broken crystals show an alternation of clear levyne and white offretite (Fig. 1). The offretite has grown perpendicular to (0001) of levyne (Fig. 2). Offretite layers are 2–80 μm thick and consist of compact fibers that show pointed terminations where they have grown on single crystals of levyne (Fig. 3).

Some vesicles in the basalt are filled with colorless chabazite. The chabazite generally fills the entire vesicle and nowhere has been found associated with the levyne-offretite intergrowths.

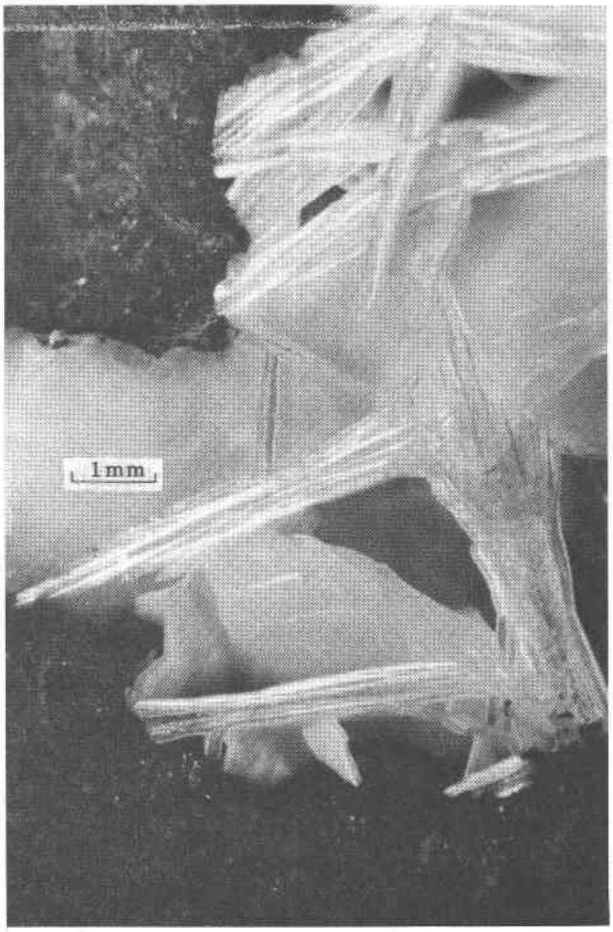

FIG. 1. Boxwork of levyne (pale gray) and offretite (white) in a large vesicle in the Picture Gorge Basalt.

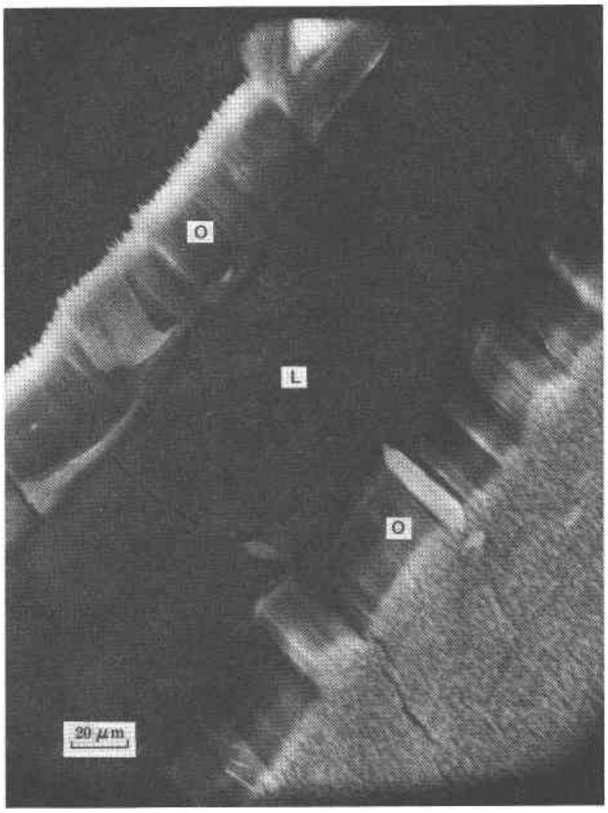

FIG. 2. Scanning electron micrograph showing fibrous layers of offretite (O) that grew normal to a single crystal of levyne (L).

Chemical Composition of Levyne and Offretite

Standard chemical analyses could not be performed on the levyne or the offretite because of the difficulty in obtaining sufficient quantities of pure separates. Both zeolites were, however, amenable to analysis by the electron microprobe. An ARL model EMX-SM microprobe was used, and the electron beam was defocused to a diameter of 25 μm to eliminate decomposition effects. Matrix corrections of X-ray intensities were not made.

The electron microprobe analyses and unit cell contents of the Beech Creek levyne and offretite (U.S. National Museum No. R15766) are given in Table 1. The mole ratio Al_2O_3: (Ca, Mg, Na_2, K_2)O for zeolites should be unity, but this ratio is 1.16 and 1.15 for levyne and offretite, respectively. Thus, both analyses show a slight excess of Al_2O_3 relative to the sum of the cation oxides. Divalent cations are in excess of monovalent ones for both zeolites, and the Si:Al ratio for levyne and offretite is 1.69 and 1.99, respectively.

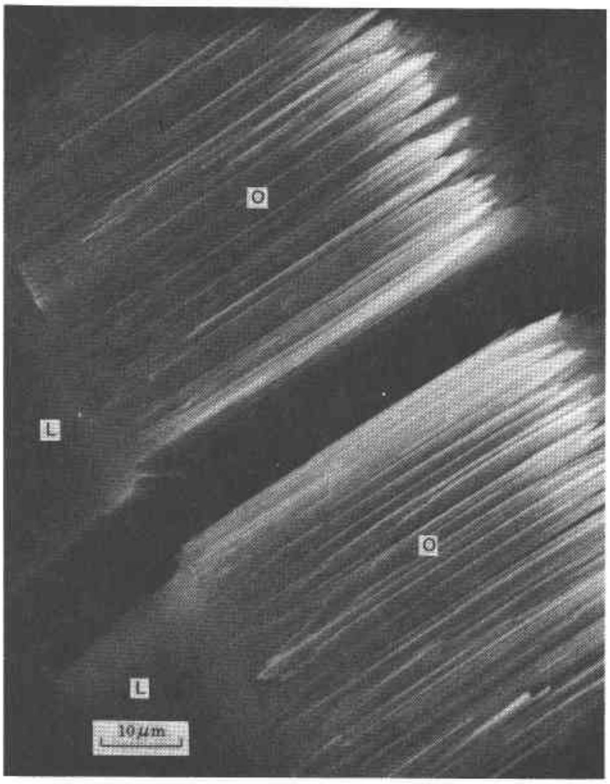

FIG. 3. Scanning electron micrograph showing the individual fibers of offretite (O) that grew normal to (0001) of levyne (L).

The reported compositions of erionites and offretites are represented in Figure 4. Erionites are more siliceous and alkali rich than offretites. Erionite generally has a Si:Al+Fe^{3+} ratio greater than 3 and a Na+K:Na+K+Ca+Mg ratio greater than 0.5, whereas offretite has a Si:Al+Fe^{3+} ratio less than 3 and a Na+K:Na+K+Ca+Mg ratio less than 0.5. Analysis 1 represents the offretite from the original locality near Montbrison, France. Analysis F is the Beech Creek offretite given in Table 1, and analysis C is a Beech Creek zeolite identified as erionite by Shimazu and Mizota (1972). Both analyses, F and C, clearly plot in the offretite field. Analysis D is an unidentified zeolite that was reported by Cross and Hillebrand (1885, p. 38) from the Table Mountain Shoshonite at Golden, Colorado. This zeolite is associated with levyne, and the brief published description and the analysis suggest that it is offretite.

Optical Properties and X-ray Powder Data

Levyne and offretite are uniaxial negative. Indices of refraction for the Beech Creek levyne are $\omega = 1.498$ and $\epsilon = 1.494$, and the indices for the offretite

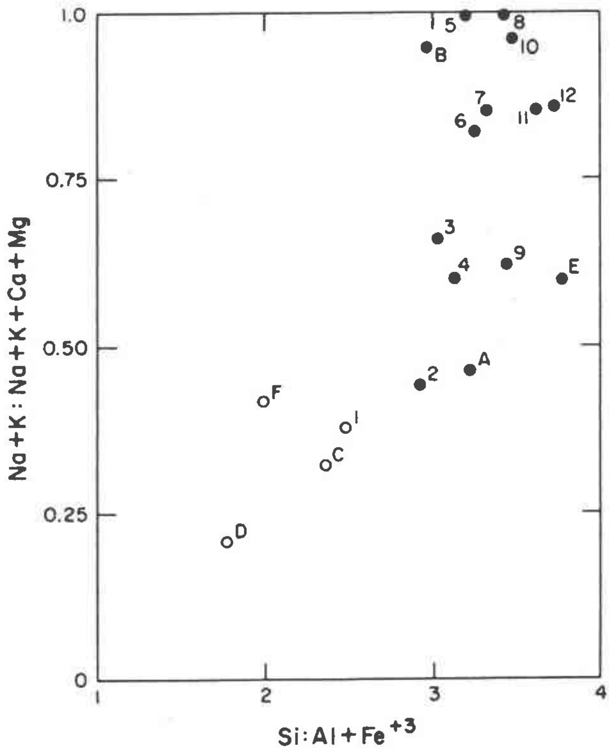

FIG. 4. Plot showing the compositional variation of erionite (black dot) and offretite (open circle). Source for the numbered analyses is Sheppard and Gude (1969). Sources for the lettered analyses are A, Batiashvili and Gvakhariya (1968); B and C, Shimazu and Mizota (1972); D, Cross and Hillebrand (1885); E, Sheppard and Gude (1973); F, this report.

TABLE 1. Electron Microprobe Analyses* and Unit Cell Contents of Levyne and Offretite from Beech Creek, Oregon

	Levyne	Offretite
	Electron microprobe analyses in weight percent**	
SiO_2	48.8 (0.8)	53.5 (0.5)
Al_2O_3	24.5 (1.6)	22.8 (0.6)
MgO	0.0	0.50 (0.01)
CaO	9.95 (0.40)	7.38 (0.36)
Na_2O	1.28 (0.15)	0.69 (0.50)
K_2O	0.90 (0.43)	3.77 (0.10)
	Unit cell contents on the basis of O = 36	
Si	11.45	12.11
Al	6.78	6.08
Mg	0.00	0.17
Ca	2.50	1.79
Na	0.58	0.30
K	0.27	1.09
Si + Al	18.23	18.19
Si : Al	1.69	1.99

*The elements were analyzed at three different operating conditions, with spectral lines and analyzing crystals as follows: (1) FeKα -LiF, BaLα -LiF, and KKα -ADP at 15 kV and 30 nA; (2) CaK_α -LiF, BaL_α -LiF, and NaKα -ADP at 10 kV and 25 nA; (3) SiKα -ADP, AlK_α -ADP, and MgKα -KAP at 6 kV and 30 nA. Reference standards included albite, benitoite, three synthetic glasses, microcline, quartz, corundum, periclase, and anorthite.
**Standard deviations are given in parentheses. FeO is less than 0.1 weight percent, and BaO is less than 0.05 weight percent.

are ω = 1.495 and ϵ = 1.491. All of the indices of refraction are ±0.001. Inasmuch as the Beech Creek offretite has grown normal to (0001) of the levyne, the *c* crystallographic axes of both zeolites are parallel. Offretite has negative elongation, a property that serves to distinguish it from erionite (Sheppard and Gude, 1969). In addition, the measured indices of refraction of the Beech Creek offretite are significantly higher than those of any reported erionite.

TABLE 2. X-Ray Powder Diffraction Data* for Levyne and Offretite

Levyne				Offretite			
hkl	d(calc) (Å)	d(obs) (Å)	I	hkl	d(calc) (Å)	d(obs) (Å)	I
100	11.57			100	11.56	11.56	100
101	10.32	10.36	11				
102	8.14	8.15	20				
003	7.63			001	7.59	7.58	15
110	6.68	6.69	24	110	6.67	6.69	79
103	6.37			101	6.35		
200	5.78			200	5.78	5.79	34
201	5.61	5.61	1				
202	5.16	5.17	11				
113	5.02	5.03	1	111	5.01		
203	4.609			201	4.599		
210	4.372			210	4.369	4.369	76
211	4.294	4.300	4				
105	4.256	4.253	15				
212	4.084	4.084	100				
300	3.855	3.854	18	300	3.853	3.852	65
006	3.814	3.811	4	002	3.797		
301	3.802	3.805	4				
213	3.793	3.786	7	211	3.787	3.787	13
302	3.654	3.655	1				
106	3.622			102	3.607	3.600	5
205	3.589	3.587	5				
214	3.474	3.471	7				
303	3.441	3.445	2	301	3.436		
220	3.339	3.338	16	220	3.337	3.338	35
116	3.312	3.308	2	112	3.300		
310	3.208			310	3.206	3.201	10
304	3.197	3.198	2				
206	3.184			202	3.174		
215	3.161	3.156	17				
312	3.089	3.089	7				
223	3.059			221	3.055		
313	2.957			311	2.954		
400	2.892			400	2.890	2.889	71
216	2.874	2.888	15	212	2.866	2.869	12
401	2.869	2.871	9				
207	2.846	2.838	10				
402	2.803	2.805	60				
306	2.712			302	2.705		
403	2.704	2.704	3	401	2.701	2.703	4
320	2.654			320	2.652		
315	2.627	2.626	2				
217	2.618	2.618	7				
322	2.585	2.583	2				
009	2.543			003	2.531		
410	2.524	2.522	10	410	2.523	2.522	31
226	2.512			222	2.507		
323	2.506	2.501	2	321	2.504		
413	2.396	2.397	4	411	2.394		
325	2.296	2.295	2				
1·0·10	2.245	2.241	2				
330	2.226	2.223	6	330	2.225	2.225	18
333	2.137	2.137	2	331	2.135		
309	2.123	2.121	2	303	2.116		
416	2.105	2.105	1	412	2.101		
423	2.101			421	2.099	2.097	3
514	1.953	1.952	1				
430	1.902	1.904	1	430	1.900		
507	1.888	1.889	2				
520	1.852	1.852	2	520	1.851	1.849	5
419	1.791	1.791	4	413	1.787		
440	1.669	1.668	7	440	1.668	1.669	20

* Diffractometer, nickel-filtered $CuK\alpha_1$ radiation, 1° divergence slit, 0.002-inch receiving slit, scanning speed of 1/2° 2 θ per minute, fluorite internal standard. Calculated d's less than 2.500 are reported only for observed reflections.

X-ray powder diffraction data for the Beech Creek levyne and offretite (Table 2) were obtained for pure separates hand picked from gently crushed levyne-offretite intergrowths. Because of the small quantities obtained by this method, the X-ray data were collected from collodion-membrane mounts of unoriented powder to which annealed fluorite had been added as an internal standard. Diagrammatic X-ray powder diffraction patterns for the Montbrison offretite, the Beech Creek offretite, and a typical erionite are shown in Figure 5. Although offretite and erionite have many lines in common, there are sufficient differences in the number and positions of the lines to distinguish the two zeolites. Figure 5 clearly shows that the Beech Creek zeolite studied here is offretite and not erionite.

Cell parameters for the Beech Creek levyne and offretite were obtained by a least-squares refinement of the X-ray powder diffractometer data utilizing the U.S. Geological Survey's FORTRAN IV computer program W9214. The resulting hexagonal cell parameters for levyne are $a = 13.356(3)$ Å, $c = 22.88(1)$ Å, and $V = 3{,}535(2)$ Å^3 and for offretite

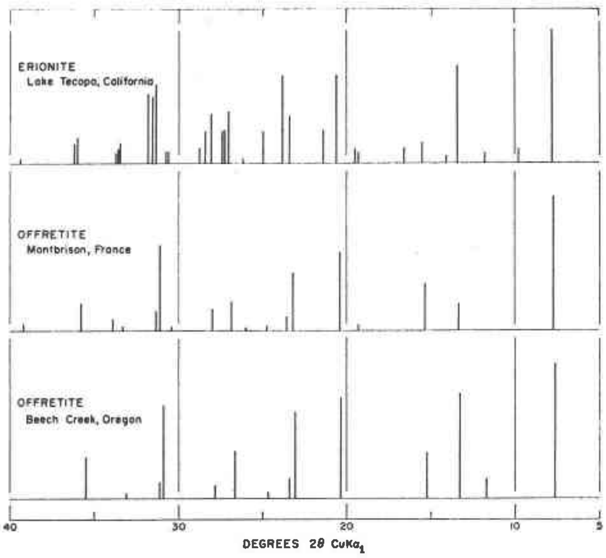

FIG. 5. Diagrammatic representation of X-ray powder diffractometer patterns for the Beech Creek offretite, the Montbrison offretite, and a typical erionite. Relative intensities are indicated by height of lines above baseline.

are a = 13.348(2) Å, c = 7.59(2) Å, and V = 1,172(3) Å^3. These values are close to published cell parameters for the two zeolites. The a dimension is nearly the same for both levyne and offretite, but the c dimension for levyne is about three times that for offretite.

Discussion

The offretite from Beech Creek has clearly formed later than the levyne, and, at least locally, has replaced the levyne. Most clay minerals and zeolites in the vesicles of Cenozoic basalts formed after crystallization and cooling of the basalts (Nashar and Basden, 1965). The Beech Creek zeolites are probably no exception, and the constituents necessary for the zeolites were probably dissolved from the Picture Gorge Basalt by cool meteoric water. Compositional differences in the zeolites probably reflect the compositional differences in the solutions from which the zeolites crystallized. The relatively late offretite crystallized from a solution characterized by a higher potassium and Si:Al ratio but lower calcium and, especially, sodium contents than that from which the earlier levyne crystallized.

In addition to the levyne-offretite intergrowths from Beech Creek and possibly from Table Mountain, Golden, Colorado, other published descriptions of zeolites in basalts suggest that this association may be relatively common. Walker (1951, p. 776) described a satiny, fibrous mineral that formed from levyne in Tertiary basalts of County Antrim, Ireland. Although the alteration mineral was not identified, the reported habit and optical properties suggest to us that it is offretite. More recently, Chatterjee (1971) described and illustrated an unidentified fibrous mineral associated with levyne in the Deccan basalts near Bhopal, India. Neither optical nor chemical properties for the unidentified mineral were given by Chatterjee, but the mineral is probably offretite or perhaps erionite as suggested by Shimazu and Mizota (1972, p. 423).

A search of levynes in the collection of the Smithsonian Institution by one of us (J.S.W.) located two additional specimens that have a silky, white, associated mineral. X-ray powder diffractometer and optical studies indicate that both are offretite. These levyne-offretite specimens occur in basalt, probably the Picture Gorge Basalt, near Spray, Wheeler County, Oregon, and near Ritter, Grant County, Oregon. The Ritter material was described by Hewett, Shannon, and Gonyer (1928, p. 7), who tentatively identified the levyne but not the silky, white mineral.

R. W. Tschernich and W. S. Wise (written communication, 1973) have identified levyne-offretite intergrowths from many localities in the basaltic terranes of Oregon, Washington, and British Columbia. A description of the localities and the zeolite mineralogy is in preparation by these workers. Thus, offretite is not so rare as previously supposed. Many additional occurrences will undoubtedly be discovered by careful examination of levyne occurrences in basalt.

Acknowledgments

We thank A. L. McGuinness (San Mateo, California) for providing the Beech Creek specimens and a description of the locality. We also greatly appreciate the unpublished data provided by R. W. Tschernich (Snohomish, Washington) and W. S. Wise (University of California, Santa Barbara) on additional occurrences of levyne-offretite intergrowths. Louise Hedricks (U.S. Geological Survey) prepared the photomicrograph, and W. R. Brown (Smithsonian Institution) prepared the scanning electron micrographs.

References

Batiashvili, T. V., and G. V. Gvakhariya (1968) Erionite found for the first time in Georgia. *Dokl. Akad. Nauk SSSR,* **179,** 122–124. [trans. *Dokl. Akad. Nauk SSSR,* **179,** 426–427 (1968)].

Bennett, J. M., and J. A. Gard (1967) Non-identity of the zeolites erionite and offretite. *Nature,* **214,** 1005-1006.

Chatterjee, A. C. (1971) Levyne in the Deccan traps. *Mineral. Mag.* **38,** 527–528.

Cross, Whitman, and W. F. Hillebrand (1885) Minerals from the basalt of Table Mountain, Golden, Colorado. *U.S. Geol. Surv. Bull.* **20,** 13–39.

Dürrfeld, V. (1911) Über einen offretitähnlicken Zeolith in Drusen eines Feldspatbasaltes von den Palau-Inseln (Carolinen). *Z. Kristallogr. Mineral.* **49,** 200.

Gonnard, M. F. (1890) Sur l'offrétite, espèce minérale nouvelle, *C. R. Acad. Sci (Paris),* **111,** 1002–1003.

Hewett, D. F., E. V. Shannon, and F. A. Gonyer (1928) Zeolites from Ritter Hot Spring, Grant County, Oregon. *U.S. Natl. Mus. Proc.* **73,** art. 16, 1–18.

Nashar, Beryl, and Ralph Basden (1965) Solubility of basalt under atmospheric conditions of temperature and pressure. *Mineral. Mag.* **35,** 408–411.

Sheppard, R. A., and A. J. Gude, 3d (1969) Chemical composition and physical properties of the related zeolites offretite and erionite. *Am. Mineral.* **54,** 875–886.

——— (1973) Zeolites and associated authigenic silicate minerals in tuffaceous rocks of the Big Sandy Formation, Mohave County, Arizona. *U.S. Geol. Surv. Prof. Pap.* **830,** 36 p.

Shimazu, Mitsuo, and Tadato Mizota (1972) Levyne and erionite from Chojabaru, Iki Island, Nagasaki Prefecture, Japan. *J. Jap. Assoc. Mineral. Petrol. Econ. Geol.* **67,** 418–424.

THAYER, T. P., AND C. E. BROWN (1967) Preliminary geologic map of the Long Creek quadrangle, Grant County, Oregon. *U.S. Geol. Surv. Open-File Rep.*

WALKER, G. P. L. (1951) The amygdale minerals in the Tertiary lavas of Ireland. I. The distribution of chabazite habits and zeolites in the Garron plateau area, County Antrim. *Mineral. Mag.* **29,** 773–791.

Manuscript received, December 18, 1973; accepted for publication, February 21, 1974.