

ERIONITE, PHILLIPSITE AND GONNARDITE IN THE
AMYGDALES OF ALTERED BASALT FROM MAZÉ,
NIIGATA PREFECTURE, JAPAN

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ABSTRACT

Erionite, phillipsite and gonnardite have been found in the amygdales of altered basalt, Mazé, Niigata Prefecture, Japan. Chemical, physical, optical and X-ray data are provided. Erionite is hexagonal, $P6_3/mmc$.

INTRODUCTION

Offretite, described by Gonnard in 1890 (see Dana's System, 6th Ed., p. 1043), was examined by Hey and Fejer (1962) who stated that it was identical to erionite. Bennett and Gard (1967, personal comm.) and the present writers found at the same time but independently that erionite and offretite were both valid species. This paper deals with erionite in some detail together with phillipsite, gonnardite, natrolite and analcime.

There are many descriptions of zeolites and associated minerals in the amygdales of thoroughly weathered and altered olivine basalt and in the andesite exposed along the seashore of Mazé in the Iwamura district, Niigata Prefecture. They include apophyllite (Jimbo, 1907), chabazite (Shimazu and Kawakami, 1967), analcime (Shimizu, 1915), natrolite, thomsonite (Mumeikai Group, 1948), heulandite (Harada, Tomita and Sudo, 1966), iron-rich saponite (Miyamoto, 1957). It is the first discovery of erionite in Japan. One other occurrence of erionite in altered basalt was described by Kamb and Oke (1960) with type paulingite.

ZEOLITE ASSEMBLAGES

The above-mentioned zeolites and associated minerals in the amygdales of olivine basalt resemble those of the amygdales of the Antrim basalts reported by Walker (1951, 1959, 1961*a* and 1961*b*), although levyne, gmelinite and scolecite are absent at Mazé.

The following zeolites are often recognized in zonal zeolite assemblages in amygdales (1–10 cm. in diameter) in sequences from the outer wall to central parts, which probably correspond to earlier and later stages of crystallization:

a) Thomsonite ($\alpha=1.507$, $\beta=1.520$, $\gamma=1.531$, $\gamma-\alpha=0.024$ and (+) $2V=68^\circ$) and/or gonnardite ($\alpha=1.500$, $\gamma=1.504$, $\alpha=0.004$, $c\Delta X=O^\circ$) followed by natrolite ($\alpha=1.476$, $\beta=1.486$, $\gamma=1.487$, $\gamma-\alpha=0.013$ and (+) $2V=60^\circ$) followed by analcime ($n=1.487$). This sequence might be explained by decreasing Ca^{++} and increasing Na^+ in the host solution during crystallization.

X-ray powder data for gonnardite, which has been misidentified as natrolite due to the similarity of its X-ray powder pattern, is identical to that of Meixner, *et al.* (1956). Chemical compositions and features of this zeolite assemblages are shown in Figure 1 and Table 1.

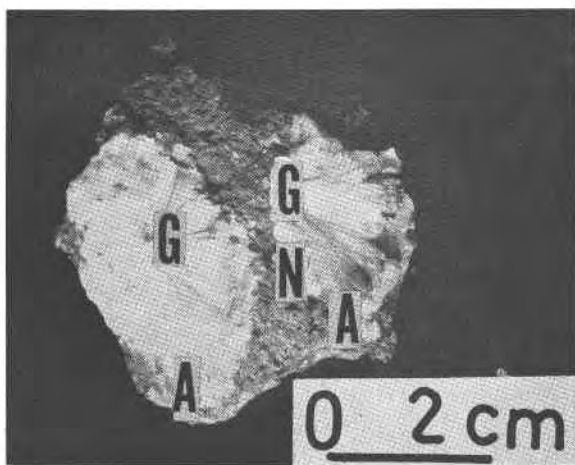


FIG. 1. Zonal arrangements of zeolites in an almond-shaped amygdale of basalt.

Note: A, analcime; N, natrolite and G, gonnardite.

b) Heulandite followed by phillipsite followed by natrolite. c) Heulandite followed by chabazite followed by erionite (Fig. 2). This sequence may be explained by the similarity of the crystal structures (Strunz, 1960) and chemical compositions (Hay, 1964). Mineral assemblages of this type were described also by Hey (1959). d) Heulandite followed by analcime.

Yellow calcite is abundant throughout the zeolite assemblages, and quartz is always absent in the amygdales, as well as in the basalt host rocks. These zeolite assemblages are silica-poor species, which may indicate that silica activity was notably low (Hay, 1964) during crystallization.

In andesitic rocks, ordinary silica-rich zeolite assemblages, as clinoptilolite-heulandite-mordenite-analcime assemblages were observed, sometimes with quartz. Stilbite and laumontite have not been found at Mazé.

TABLE 1. CHEMICAL ANALYSES OF GONNARDITE, NATROLITE, ANALCIME, ERIONITE AND PHILLIPSITE

	1	2	3	4	5
SiO ₂	42.71	46.82	55.86	54.72	46.03
TiO ₂	none	none	none	none	none
Al ₂ O ₃	27.43	31.02	22.29	15.24	21.43
FeO+Fe ₂ O ₃	0.14	0.16	0.16	1.04	0.99
MnO	none	none	none	none	none
MgO	none	0.64	0.15	1.17	none
CaO	5.28	0.55	0.47	4.32	5.73
K ₂ O	none	none	0.07	2.46	5.59
Na ₂ O	11.12	15.00	12.21	1.00	3.13
H ₂ O ⁻	}13.91	0.46	0.39	}19.12	}17.22
H ₂ O ⁽⁺⁾		5.74	8.06		
Total	100.69	100.39	99.66	99.07	100.12

1. Gonnardite, this corresponds to structural formula:



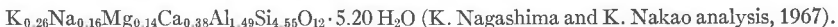
2. Natrolite, this corresponds to structural formula:



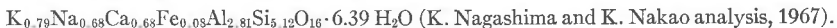
3. Analcime, this corresponds to structural formula:



4. Erionite, this corresponds to structural formula:



5. Phillipsite, this corresponds to structural formula:



* (Nos. 1-3 correspond to the specimen shown in Fig. 1).

PHYSICAL AND OPTICAL PROPERTIES

The erionite specimens described in this paper are those of Shimazu and Kawakami (1967). Some reference specimens including offretite from another locality came from Dr. Sakurai of the National Science Museum, Tokyo.

The erionite-bearing materials occur in intensely deuterically altered and weathered basalt soil. They contain woolly white radial aggregates of fibrous erionite and anhedral chabazite, as shown in Figure 2. Erionite fibers 2×0.05 mm terminate with a needle-like appearance or with a rectangular profile suggesting the possible development of weak basal cleavage.

Under the petrographic microscope, this mineral is colorless, with

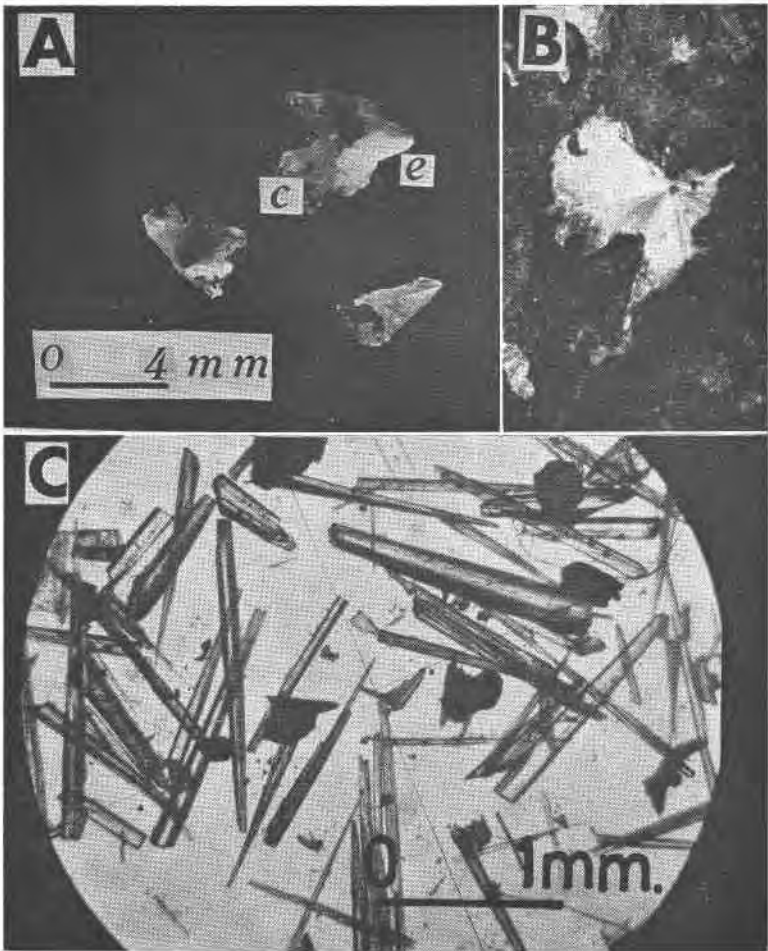


FIG. 2. Erionite. (A) Fibrous erionite closely associated with chabazite. Note; *c*, chabazite and *e*, erionite. (B) Erionite in thoroughly weathered basalt soil. (C) Photomicrograph of erionite; the fibrous figures terminate with needle-like appearance or rectangular profile, and possible development of weak basal cleavage was suggested (Polars not closed).

parallel extinction and positive elongation. It is uniaxial positive and the refractive indices measured by the immersion method using Na light at 18°C are $\epsilon = 1.477 \pm 0.002$, $\omega = 1.480 \pm 0.002$ and $\omega - \epsilon = 0.003$. These values are somewhat higher than those hitherto reported for this mineral (Deffeyes, 1959, Staples and Gard, 1959, Kamb and Oke, 1960 and Sheppard, *et al.*, 1965). The specific gravity measured by pycnometer is

2.08 as the average of three measurements. Calculated specific gravity but with (Si+Al) adjusted to 36.0, based on chemical analyses (Table 1), gave 2.13.

Eakle's analysis (Eakle, 1898) leads to a calculated specific gravity of 2.07 (observed specific gravity 2.02) but with (Si+Al) adjusted to 3.60. The higher density of Mazé erionite is due to the higher water content.

Phillipsite, deposited at Geological and Mineralogical Institute, Tokyo University of Education, was collected by Mr. N. Miyamoto in 1956. This mineral occurs as interpenetrating twin or single crystals (rare) up to 3×4 mm, closely associated with heulandite. It is optically biaxial, zoned, with $(+)2V = 63^\circ$, $c\Delta Z = 23^\circ$, $\alpha = 1.483 \pm 0.002$, $\beta = 1.485 \pm 0.002$,

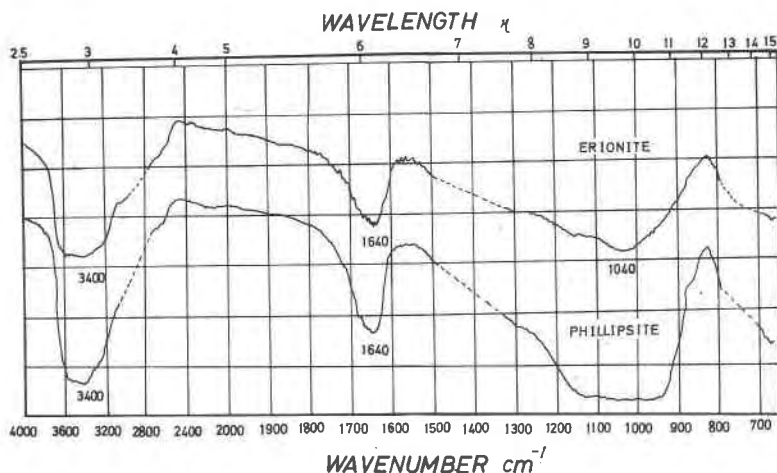


FIG. 3. Infrared absorption spectra for erionite (upper) and phillipsite (lower). Note: Dotted line indicates elimination of the peaks due to Nujol.

$\gamma = 1.487 \pm 0.002$, $\gamma - \alpha = 0.004$ in Na light, and specific gravity (mean) = 2.19.

Under the petrographic microscope, single crystals of phillipsites are always zoned. Refractive indices increase progressively away from the central parts of the crystals. A phillipsite gives $\gamma = 1.488 \pm 0.002$ in the rim.

INFRARED ABSORPTION SPECTRA

Infrared absorption spectra for erionite and phillipsite were obtained using a Nippon Bunkō DS-401-G grating-type spectrophotometer and the Nujol paste method (Fig. 3). The spectra are similar and have absorption bands at 1040 cm^{-1} , 1640 cm^{-1} and 3400 cm^{-1} . The bands at

1040 cm^{-1} are attributed to Si-O stretching vibrations (Milkey, 1960).

When closely examined, absorption bands at 3400 cm^{-1} in the water-stretching region are broad and spread toward higher frequencies. This phenomenon has also been described in gonnardite, phillipsite and stilbite by Eva and Vela (1965) and Harada and Tomita (1967). It may be explained if part of water in these zeolites is structurally bound.

X-RAY DATA

Approximate unit-cell dimensions were determined for erionite from rotation and zero-layer, normal beam, Weissenberg photographs. A

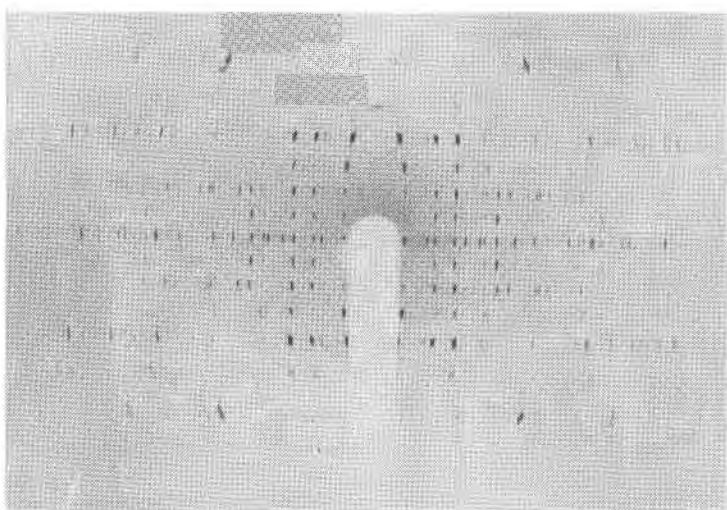


FIG. 4. Rotation photograph for erionite, with crystal rotated about the c -axis. $\text{CuK}\alpha$ radiation with Ni-filter. Camera diameter 57.3 mm.

clear transparent crystal, 0.1×0.3 mm, was rotated parallel to the longer axis. The rotation photograph (Fig. 4) gave a lattice spacing as 15.2 ± 0.2 Å based on accurate measurements of high-level spots, which were obtained with Ni-filtered $\text{CuK}\alpha$ radiation, camera diameter 57.3 mm, exposure up to 8 hours. The even-layer lines have considerably greater intensity than odd-layer lines and have a symmetry of C_{2h} , which agrees well with X-ray data by Deffeyes (1959). The 15.2 Å spacing is assumed to be c .

The rotation photograph establishes an important point. The weak, odd-layer lines result from the AABAACAABAAC stacking in erionite, where A, B, C are the stacking positions of a 6-membered ring of (Si, Al) O_4 tetrahedra. Recently, J. A. Gard (personal communication, 1967)

has shown that the unit-cell of offretite from Montbrison, France is hexagonal, with $a=13.31$, $c=7.59$ Å, i.e., with c half that of erionite. X-ray powder pattern for offretite disagree with erionite in detail. Offretite has a stacking of AABAABAABAAB. Mixtures of the two stackings lead to streaks in the c^* direction on the rotation photograph (Bennett and Gard, 1967).

The same crystal was used in the zero- and first-layer Weissenberg photograph with the crystal oscillating about c . Exposures up to 48

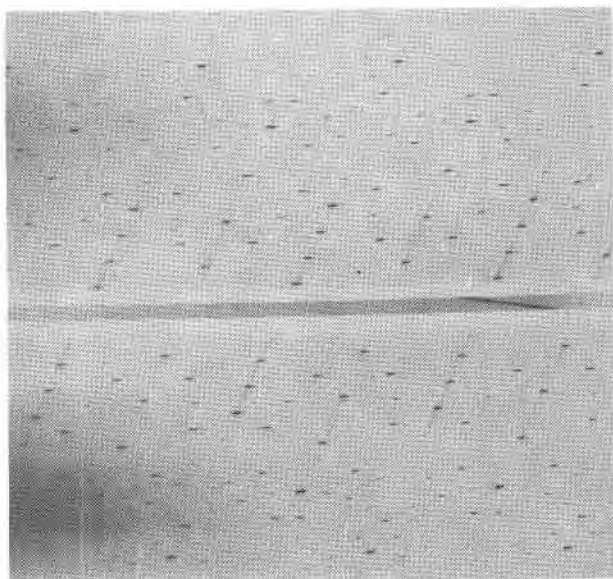


FIG. 5. Zero-layer, normal beam Weissenberg photograph of erionite, with crystal oscillated about the c -axis. $\text{CuK}\alpha$ radiation, Ni-filter. Camera diameter 57.3 mm.

hours were required in Ni-filtered $\text{CuK}\alpha$ radiation with camera diameter 57.3 mm (Fig. 5). The positions and intensity of the spots on the film gave both zero- and first-level symmetry which corresponds to D_{6h} (Buerger, 1942, p. 474 and p. 483). An observed a spacing gave 13.1 ± 0.2 Å from zero-level spots.

There are no systematically absent spots on the zero-level Weissenberg photograph and the only systematic absences on the 1st-level Weissenberg photograph are $h.h.2h.l$ when l is odd. No pyroelectric effect was detected when crystals were placed on an aluminium foil and soaked in liquid air. The mineral is probably centrosymmetric with space group confirmed as $P6_3/mmc - D_{6h}^3$.

TABLE 2. PHILLIPSITE: X-RAY POWDER PATTERN
pseudorhombic: $a=9.96$, $b=14.23$ and $c=14.23$ Å

d (meas.)	d (calc.)	hkl	I
8.19	8.17	101	5
7.19	7.13	020, 002	100
6.41	6.37	012	12
5.37	5.37	121	10
5.06	5.04	022	25
4.98	4.98	200	17
4.69	4.70	210	3
4.31	4.29	103	10
4.13	4.11	131, 113	40
4.07	4.08	202, 220	13
3.96	3.95	032	6
3.70	3.67	123	3
3.54	3.54	222	6
3.47	3.46	014	6
3.26	3.26	141	30
3.19	3.19, 3.18	024, 042, 123	85
3.14	3.15	311	34
2.930	2.946	321	14
2.893	2.898	240, 204	6
2.857	2.850	034	4
2.754	2.740	143, 105	21
2.698	2.691	151, 115	34
2.667	2.674	331, 313	9
2.577	2.578	125	6
2.542	2.543	323	8
2.389	2.295	341	8
2.309	*	*	2
2.259	2.253	062, 026	4
2.160	2.163	343, 305	4
2.136	2.139	315, 351	3
2.053	2.053	262, 226	6
2.001	2.007	344	3
1.981	1.976	064, 046, 155, 117, 171	8
1.964	1.963	424, 442	7
1.910	1.915	361	3
1.834	1.837	264, 246	7
1.810	1.814	452	3
1.787	1.782	080, 008	17
1.733	1.736	307	4
1.721	1.723, 1.719	355, 371, 317, 460, 406	7
1.680	1.680, 1.677	066, 208, 280	4
1.652	*	*	7
1.644	1.645	183	4
1.600	1.599	365	4
1.548	1.548	464, 446	4

* Unidentified.

With the obtained space group and cell dimensions, X-ray powder diffraction peaks are indexed; they conform well to previous data (Staples and Gard, 1959, and Deffeyes, 1959). Then, using this indexing, accurate values of hexagonal lattice dimensions were obtained using quartz as an internal standard: $a=13.24$ and $c=15.12$, both ± 0.02 Å, which are very close to the data of Staples and Gard (1959).

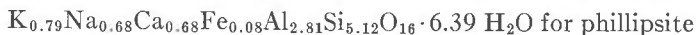
Diffraction peaks of phillipsite were indexed using cell dimensions and space group proposed by Steinfink (1962) (Table 2) and pseudo-rhombic lattice dimensions were obtained from powder data: $a=9.96$, $b=14.23$ and $c=14.23$, all being ± 0.02 Å. These values agree well with the data by Steinfink (1962).

CHEMICAL DATA

About 2 g of pure samples for erionite and phillipsite were separated by hand picking and were carefully analysed chemically by normal wet methods (Table 1). Recast in terms of structural formulae, they correspond to:



and



These formulae conform well with previous analyses. The Ca, Mg are higher, and Na, K lower than for Eakle's (1898) and Hoagland's (Staples and Gard, 1959) analyses of erionite from the type locality. An erionite from Central Nevada (J. A. Gard, personal comm.) had $(\text{Ca}, \text{Mg})=0.27$, $(\text{K}, \text{Na})=7.57$ and $\text{O}=72$. Wide variations are expected in the cations, as discussed by Hay (1964, p. 1379).

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