AUTHIGENIC ZEOLITES IN ZEOLITIC PALAGONITE TUFFS ON OAHU, HAWAII

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ABSTRACT

Authigenic zeolites including phillipsite, gismondine, chabazite, gonnardite, natrolite, analcime and faujasite are the principal minerals in the cement of palagonitized alkali basalt and melilite nephelinite tuffs of the Honolulu Series on Oahu, Hawaii. The results of DTA, X-ray, chemical and electron microprobe analyses are given here. The authigenic zeolites are chemically similar to zeolites commonly found in the cavities of mafic lava flows.

There is a regular succession of the zeolite formation: K zeolite→Ca·Na zeolites→Na zeolites. This is explained by gradual change in composition pf percolating groundwater through the tuffs deposits during palagonitization. A sodium contribution by wind-blown salt from seawater and rainfall on the oceanic island probably causes the latter occurrence of Na zeolites in even the uppermost zeolitic tuffs in the semi-arid coastal area.

INTRODUCTION

Tephra deposits of the Honolulu Series on Oahu are middle to late Pleistocene in age and range in composition from alkali basalt to melilite nephelinite (Winchell, 1947). Some of the deposits are fresh, but most of them are partly palagonitized. Authigenic zeolites occur commonly as cements, in vesicles, and in veinlets of the pyroclasts. They were formed by reaction of sideromelane, nepheline, melilite and plagioclase with percolating groundwater of meteoric origin at low temperature (Hay and Iijima, 1968a; 1968b). They precipitated in the following general sequence: phillipsite, gismondine, chabazite, faujasite, gonnardite, natrolite and analcime. The order is kept when any of these are lacking. Gismondine and faujasite are rare; the other zeolites are common.

The nature and origin of the zeolitic palagonite tuffs on Oahu is described and discussed in Hay and Iijima (1968a; 1968b). This paper provides the results of DTA, X-ray, chemical and electron microprobe analyses of the authigenic zeolites.

EXPERIMENTAL

Optical character was observed under the microscope. Specific gravities were determined by immersion of mineral grains into a mixture of bromoform and acetone. DTA was done on an M. R. K. auto-recording differential thermal analyzer at a heating rate of 10°C/min. X-ray powder diffractions were done on a Norelco diffractometer using Cu(Kα)Ni radiation.
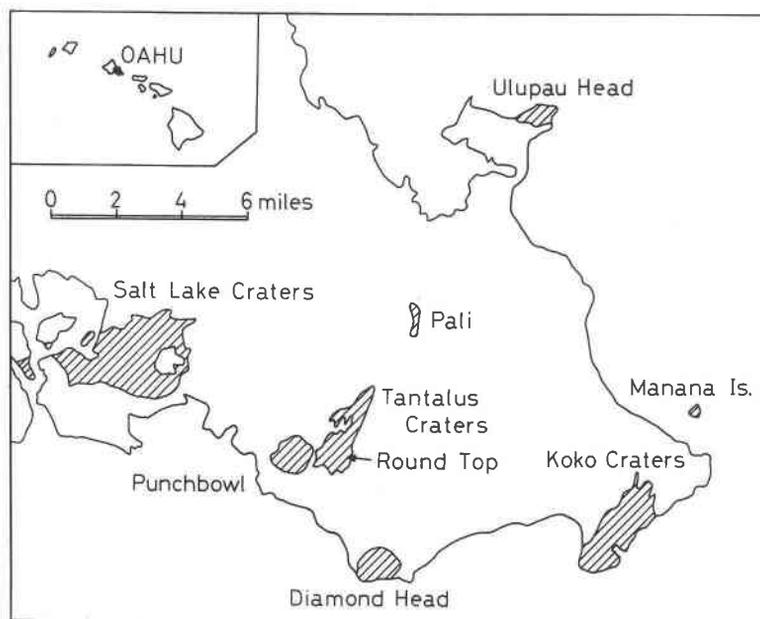
Fig. 1. Locality map of southeastern part of Oahu showing tuffs of the Honolulu Series from which zeolites studied were collected.

Chemical compositions were obtained by normal wet methods and electron microprobe. Microprobe analyses were made on an A. R. L. electron microprobe analyzer, model EMX, at the Department of Geology and Geophysics, University of California, Berkeley. Si, Ti, Al, Fe, Mg, Ca, Na and K were measured using alkali feldspar and plagioclase as comparison standards. The Ti and Mg in zeolites are negligible or present only in little amounts. Volatilization of lighter elements in zeolites was significantly accelerated by using small beams of high intensity. Therefore, sublimation was kept to a minimum by using a relatively large beam of low intensity at 15 kV, 0.01 mA and 20-second exposure. The countings of Na, K, Ca, Al and Si did not change systematically on twenty 2-second exposures at the same spot. The result obtained by 20-second exposure was identical to that of 50-second exposure. The water content may differ considerably from the theoretical content of H_2O, probably due to vaporization of zeolitic water during analysis. In this case, the numbers of atoms in the anhydrous cell unit are probably reasonably accurate although the percentage values are not. The Al reasonably balances the alkalies and alkaline earths. Two specimens of gismondine and gonnardite were analyzed both by wet methods and by the microprobe (Table 2, anal. 3, 4, 5; and anal. 7, 8). The exact comparison of those results are difficult on account of the heterogenity of zeolite crystals. The content of Fe in gismondine is much higher in the wet analysis than in microprobe analysis. The content of Ca is significantly lower but that of K is higher than in the probe analysis. The Si:Al ratio is considerably higher in the wet methods than in the microprobe. It is probable that these discrepancies are partly due to mixing small amounts of phillipsite and palagonite in the sample analyzed by wet methods, and partly due to insufficient numbers of probing spots. The content of Ca in gonnardite is larger and that of Na is less in the wet analysis than in

the probe. The Si:Al ratio is significantly lower in wet methods than in microprobe analysis. Insufficient numbers of probing spots probably result in these discrepancies.

PHILLIPSITE

Phillipsite was found in almost all zeolitic palagonite tuffs on Oahu. It occurs commonly as a thin crust on pyroclastic grains and as prismatic crystals in vesicles of palagonitized glass and tholeiite fragments. Small white spherulitic aggregates are abundant in porous tuffs on the southwest side of Round Top. Fourling twinned crystals with a rhombohedral shape are common in extensively altered tuffs in rainy areas of Pali and the summit of Round Top. Plant remains are sometimes replaced by white aggregates of very minute grains of phillipsite. Crystals are commonly less than 0.1 mm long and rarely as long as 0.5 mm.

Refractive indices of phillipsite are related to the types of original host

TABLE 1. REFRACTIVE INDICES OF PHILLIPSITE IN PALAGONITE TUFFS ON OAHU

Locality	Type of original rock	α	γ
Koko Craters	alkali basalt	1.466–1.497	1.467–1.499
Salt Lake Craters	melilite nephelinite and tholeiite	1.486–1.500	1.488–1.502
Pali	nepheline basalt	1.488–1.497	1.488–1.504
Punchbowl	nephelinite	1.482–1.503	1.482–1.505
Round Top	melilite nephelinite	1.486–1.504	1.488–1.508

rocks. They increase from alkali basalt tuffs of Koko Craters to melilite nephelinite tuffs of Round Top, as given in Table 1. Zonal structure is common, and refractive indices and birefringence are always lower in the outer shell.

Phillipsite replacing plant stems in the Lower Salt Lake Tuff was analyzed by wet methods (Table 2, anal. 1), and the structural formula recalculated from the result is $(Ca_{2.00}Mg_{0.16}Na_{0.81}K_{0.63})_{3.60}(Fe^{3+}_{0.06}Al_{6.01}Si_{10.00})_{16.07}O_{32} \cdot 15.23H_2O$. The unit cell dimensions are $a = 9.96$, $b = 14.30$, and $c = 14.30$, all ± 0.01 Å.

Chemical composition of the phillipsite of Oahu is clearly controlled by the compositions of original host rocks (Fig. 2). Phillipsite deposited in melilite nephelinite tephra of Round Top has higher Ca:Na and lower Si:Al ratios than that of the Salt Lake Tuff which contains abundant altered tholeiite fragments. The Si:Al ratio ranges from 1.06 to 1.55 in phillipsite of Round Top and from 1.56 to 1.93 in phillipsite of the Salt Lake Tuff. Slightly lower refractive indices of phillipsite in alkali basalt tephra from Koko Craters suggest that the phillipsite is either more sodic or more silicic, or both than that of the Salt Lake Tuff.

TABLE 2. CHEMICAL ANALYSES OF AUTHIGENIC ZEOLITES ON OAHU, HAWAII

wt. %

	1[a]	2	3[b]	4	5	6	7[a]	8	9	10	11
SiO_2	43.95	46.4	39.61	41.1	38.3	50.1	42.19	40.3	44.0	53.2	50.8
TiO_2	—	0.03	—	—	—	0.00	—	—	—	0.00	—
Al_2O_3	22.42	23.8	24.69	29.6	28.0	22.3	28.36	25.6	25.7	23.7	18.2
Fe_2O_3	0.38	0.20	2.28	0.76	0.72	0.15	0.40	0.83	1.10	0.12	0.48
MgO	0.46	0.00	tr.	—	—	0.30	0.00	—	—	—	—
CaO	8.22	7.4	9.27	12.2	12.3	5.4	3.98	2.4	1.2	1.14	4.3
Na_2O	1.83	1.9	1.76	2.1	1.0	5.1	12.82	13.4	14.3	12.7	4.0
K_2O	2.17	6.4	1.33	1.1	1.2	2.1	0.00	0.00	0.00	0.02	1.7
H_2O^+	15.80	—	20.91	—	—		0.00				
H_2O^-	4.28	—		—	—		12.60				
Total	99.51	86.13	99.85	86.86	81.52	85.45	100.35	82.53	86.30	90.88	79.48

Numbers of ions in anhydrous cell unit

Si	10.00	9.98	18.40	17.40	17.27	23.70	5.56	5.67	5.88	1.97	25.45
Ti	—	0.00	—	—	—	0.00	—	—	—	0.00	—
Al	6.01	6.03	13.52	14.78	14.83	12.43	4.41	4.24	4.05	1.03	10.73
Fe^{3+}	0.06	0.03	0.80	0.25	0.24	0.06	0.04	0.08	0.11	0.00	0.18
Mg	0.15	0.00	0.00	—	—	0.20	0.00	—	—	—	—
Ca	2.00	1.70	4.64	5.55	5.93	2.27	0.57	0.36	0.17	0.04	2.32
Na	0.81	0.79	1.60	1.73	0.87	4.69	3.28	3.65	3.70	0.91	3.88
K	0.63	1.75	0.80	0.59	0.95	1.28	0.00	0.00	0.00	0.00	1.08
H_2O	15.23	—	32.32	—	—	—	5.04	—	—	—	
O	32	32	64	64	64	72	20	20	20	6	72
Si/Al	1.66	1.66	1.36	1.18	1.16	1.90	1.26	1.34	1.45	1.91	2.37
S. G.	2.25		2.28				2.25				

[a] Wet chemical analysis, analyst: Ken-ichiro Aoki.

b Wet chemical analysis, analyst: K. Nagashima and K. Nakao. Others are electron microprobe analyses, analyst: A. Iijima.

1. Phillipsite replacing plant remains in lithic palagonite tuff of the Lower Salt Lake Tuff; from the cliff along Puuloa Road near the junction to Moanalua Road.
2. Phillipsite in cement of lithic palagonite tuff of the Salt Lake Tuff.
3. Gismondine spherules in cement of porous palagonite tuff of the Tantalus Crater group; from a quarry on the southwest side of Round Top.
4. The outer shell of a gismondine spherule of the same sample as No. 3.
5. The core of the same gismondine spherule as No. 4.
6. Mosaic chabazite in cement of dense palagonite tuff on the south side of Koko Crater.
7. Gonnardite in veinlet in palagonite tuff of Punchbowl; from the cliff of Stevenson Schoolyard on the east side of Punchbowl.
8. Gonnardite in the same veinlet as No. 7.
9. Natrolite growing on the same gonnardite as No. 8.
10. Analcime in vesicles of palagonitized glass in porous analcimic tuff on the south side of Koko Crater.
11. Faujasite in cement of lithic palagonite tuff of the Salt Lake Tuff.

Electron microprobe analyses were made for three zoned crystals in the prismatic direction, as shown in Figure 3. The Si:Al ratio roughly increases outward in the direction of growth. The distribution of cations tends to have a reverse relation to the Si:Al ratio in the lower part, and a parallel relation in the upper part.
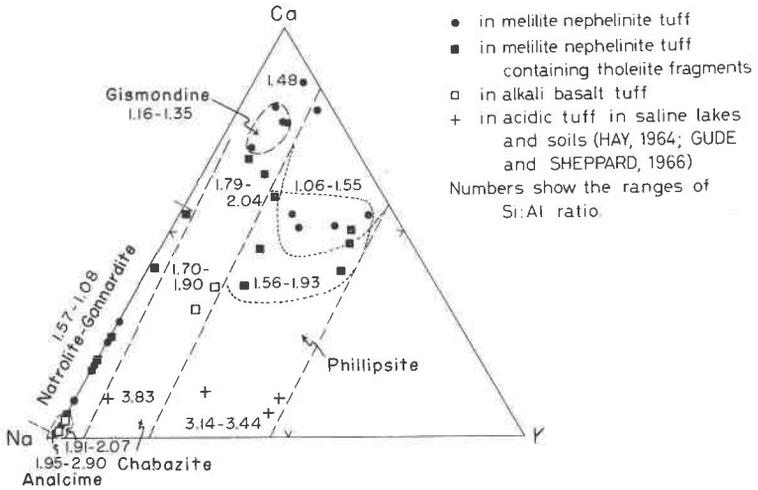
FIG. 2. Ca-Na-K diagram of authigenic zeolites of the Honolulu Series. Silica-rich phillipsite (Hay, 1964) and chabazite (Gude and Sheppard, 1966) are plotted for comparison.
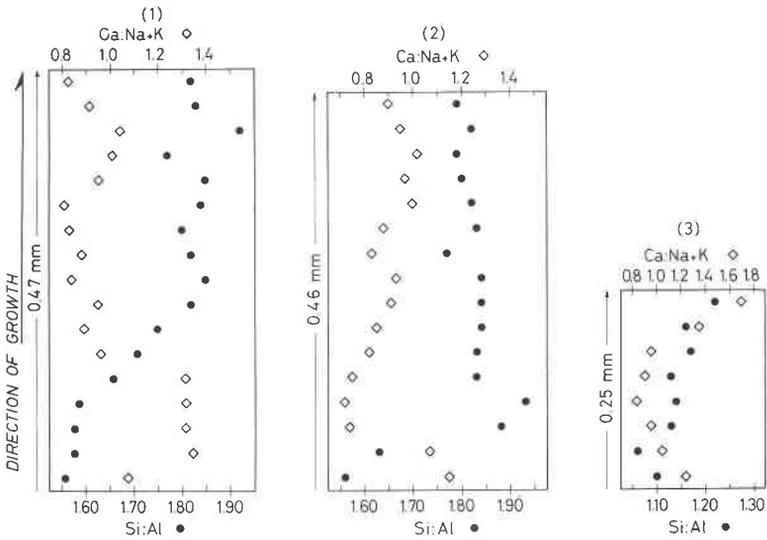

FIG. 3. Change of chemical composition within single crystal of phillipsite by electron microprobe analyses. The length and growing direction are shown on the left side of each figure.

(1) rim in vesicle of basalt block in the Salt Lake Tuff. Refer to No. 4 in Table 2.

(2) ditto. Refer to No. 5 in Table 2.

(3) prismatic crystal in vesicle of palagonite at Round Top. Refer to No. 9 in Table 2.

GISMONDINE

Gismondine was collected only from the lower half of 80-foot quarry face in melilite nephelinite tuffs on the southwest side of Round Top. It occurs as a cement of the pyroclasts and in vesicles of palagonitized glass. Crystals are spherulitic aggregates less than 0.5 mm in diameter. The core of the spherule is length-slow, having $\alpha = 1.500$–1.520 and $\gamma = 1.503$–1.522. The outer two-thirds or three-fourths is length-fast, having $\alpha = 1.520$–1.521 and $\gamma = 1.522$–1.525. The two parts are separated by an optically isotropic zone of about 0.005 mm thick. Optically is the core phillipsite and the outer part is gismondine. However, electron microprobe reveals that there is no regular difference in chemical compositions between them but slightly higher content of potassium in the core (Table 2, .anal. 4, 5). Any peaks of phillipsite were not discriminated from X-ray powder diffraction pattern of the spherules.

The DTA curve of gismondine is distinct. It has two endothermic peaks at 125°C and 215°C, and an exothermic one at 790°C (Fig. 4).

The X-ray powder diffraction pattern of gismondine is identical to previous data (Walker, 1962; Fischer, 1963). The indexing of reflections on the basis of space group $P2_1/c$ is a new contribution, as shown in Table 3. The unit cell dimensions are $a = 10.02$, $b = 10.63$, $c = 9.83$, all ± 0.02 Å; and $\beta = 92°42' \pm 15'$.

The result of wet chemical analysis of hand-picked gismondine spherules is given in Table 2, anal. 3, and is recast in terms of structural formula:

$$(Ca_{0.58}Na_{0.20}K_{0.10})_{0.88}(Fe^{+3}_{0.10}Al_{1.69}Si_{2.30})_{4.09}O_8 \cdot 4.04H_2O.$$
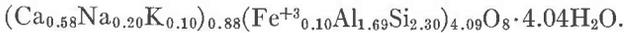
CHABAZITE

Chabazite is the next in abundance to phillipsite on Oahu. It is the principal cement of the upper dense palagonite tuffs of Koko Crater.

Chabazite occurs as a cement and in veinlets of tuffs and in vesicles of palagonitized glass and basalt fragments. Crystals are present in clear transparent rhombohedra and mosaic aggregates. They are as much as 0.8 mm long, and many of them are zoned. Refractive indices are always higher in the inner part than on the outer rim. Chabazite grows on phillipsite whenever associated with it, but never replaces it.

The results of electron microprobe analyses of five samples are illustrated in Figure 2. Chemical composition of the chabazite is a function of the original compositions of the host rocks. Chabazite in melilite nephelinite tuffs is characterized by abundant Ca and a low Si:Al ratio of 1.48. Moderate Ca and a Si:Al ratio of 1.86 to 1.89 characterize chabazite in the Salt Lake Tuff. Chabazite in alkali basalt tuffs of Koko Crater has a Si:Al ratio of 1.70 to 1.90 and a moderate content of Na.

TABLE 3. X-RAY DIFFRACTION POWDER DATA FOR GISMONDINE

I(obs.)	d(obs.)	d(calc.)	hkl	I(obs.)	d(obs.)	d(calc.)	hkl
56	7.26	7.285	110	12	2.032	2.031	$\bar{1}$43
		7.285	$\bar{1}$10	39	1.981	1.980	$\bar{3}$33
10	5.96	5.941	$\bar{1}$11	15	1.914	1.914	511
10	5.79	5.779	111			1.913	$\bar{1}$15
59	4.93	4.916	002	24	1.881	1.884	115
15	4.67	4.672	021			1.883	$\bar{5}$02
17	4.46	4.461	012	12	1.852	1.853	$\bar{5}$12
71	4.25	4.267	$\bar{1}$21			1.850	234
37	4.17	4.174	$\bar{2}$11			1.822	324
24	4.07	4.054	211	24	1.820	1.821	440
17	3.44	3.450	$\bar{2}$21			1.821	$\bar{4}$40
		3.435	202			1.801	512
		3.428	$\bar{1}$22	12	1.800	1.801	125
51	3.40	3.396	212			1.801	$\bar{4}$41
		3.382	221	12	1.777	1.779	215
39	3.32	3.331	031			1.776	$\bar{3}$43
34	3.28	3.277	003	22	1.746	1.748	153
		3.269	212	15	1.727	1.728	522
68	3.19	3.184	310			1.727	531
		3.184	$\bar{3}$10	12	1.709	1.708	225
61	3.13	3.147	131			1.708	433
		3.131	013	10	1.675	1.671	352
10	3.03	3.065	$\bar{3}$11			1.644	235
		3.024	$\bar{1}$13	10	1.642	1.644	315
19	2.968	2.970	$\bar{2}$22			1.642	$\bar{3}$25
12	2.779	2.789	023			1.641	261
		2.779	$\bar{1}$32	10	1.615	1.615	611
54	2.738	2.742	$\bar{3}$21	10	1.585	1.585	$\bar{5}$04
		2.723	$\bar{3}$12			1.566	026
100	2.706	2.708	302	10	1.565	1.564	360
		2.704	$\bar{2}$13			1.564	$\bar{3}$60
34	2.644	2.655	040	10	1.539	1.540	361
		2.566	140			1.538	206
10	2.556	2.566	$\bar{1}$40	22	1.488	1.487	036
		2.563	041			1.485	$\bar{4}$44
32	2.488	2.488	$\bar{3}$22			1.437	$\bar{1}$72
15	2.417	2.413	322	10	1.436	1.436	453
17	2.407	2.405	033			1.436	064
22	2.373	2.374	$\bar{3}$32			1.435	551
		2.345	240			1.413	640
24	2.344	2.345	$\bar{2}$40	12	1.413	1.413	$\bar{6}$40
		2.342	411			1.411	711
12	2.332	2.331	$\bar{3}$13			1.411	236
12	2.281	2.285	$\bar{1}$42			1.394	046
12	2.191	2.193	402	12	1.393	1.393	435
15	2.103	2.103	323			1.392	017
		2.101	242				

(Diffractometer, copper radiation, nickel filter, $\lambda = 1.5405°$)
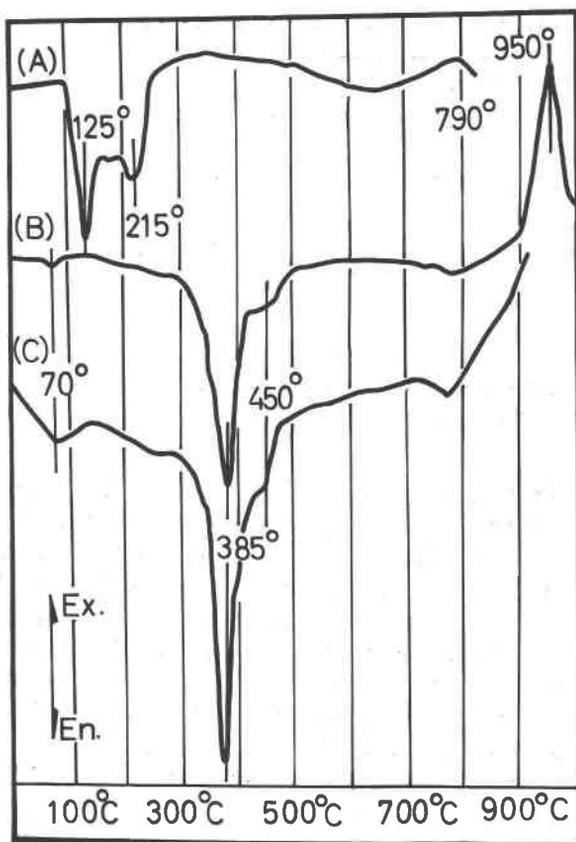
Fig. 4. DTA curves of gismondine and gonnardite. Heating rate 10°C/min.; reference junction 0°C; thermocouple Pt/Pt+13% Rh; reference material Al_2O_3; in atmosphere. (A) Gismondine from Round Top, Oahu; (B) Gonnardite from Punchbowl, Oahu; and (C) Gonnardite from Maze, Japan.

The Si:Al ratio within a single crystal of chabazite roughly increases outward in the direction of growth. The Ca:Na+K ratio also roughly increases outward (Fig. 5).

GONNARDITE AND NATROLITE

The low-silica fibrous zeolites constitute the dominant minerals in cement of nephelinite tuffs of Salt Lake Craters, Ulupau Head, Diamond Head, Punchbowl and Manana Island. They are very sparse in alkali basalt tuffs of Koko Craters.

Gonnardite occurs as white fibrous aggregates as large as 5 mm long in cements and veinlets of the pyroclasts, and in vesicles of palagonitized

TABLE 4. ASSOCIATIONS OF AUTHIGENIC ZEOLITES IN PALAGONITIZED TUFFS ON OAHU

| A. Alkali basalt tuff	B. Nephelinite and melilite nephelinite tuff
Ph	Ph
Ph-Ch	Ph-Ch
Ph-Ch-Go or Na	Ph-Gi-Ch-Fa
Ph-Ch-Na-An	Ph-Ch-Go-Na
Ph-Ch-An	Ph-Ch-Go or Na
Ph-An	Ph-Ch-Fa-Go-Na
	Ph-Go-Na-An
	Ph-Go-An
	Ph-An

Abbreviation: Ph phillipsite, Ch chabazite, Gi gismondine, Fa faujasite, Go gonnardite, Na natrolite, and An analcime.

glass and tholeiite blocks. It sometimes replaces plagioclase and plant remains. It grows on phillipsite or chabazite when associated with them. A film or crust of natrolite less than 0.1 mm thick usually fringes the gonnardite fibres with a sharp optical contact. Small rods or needles of natrolite are sparsely found in tuffs of the Koko Crater group, not associated with gonnardite. Natrolite replaces phillipsite in a few samples of the tuffs of Ulupau Head.

Chemical composition of gonnardite collected from the Stevenson Schoolyard on the east side of Punchbowl was determined by wet methods. The chemical composition falls into the compositional range of gonnardite proposed by Meixner *et al.* (1956) and Foster (1965). Refractive indices are also compatible with the previous data. Elongation is length-slow which is inconsistent with generalization by Deer, Howie and Zussman (1963, vol. 4, p. 374). In another paper (Hay and Iijima, in press), the gonnardite is described as "thomsonite" on the basis of elongation character. However, the X-ray diffraction pattern is identical to that of gonnardite (Meixner *et al.*, 1956; Harada *et al.*, 1967). The occurrence of thomsonite on Oahu is probably doubtful.

The result of differential thermal analysis of the gonnardite from Punchbowl is slightly different from that reported by Eva and Vela (1966). The gonnardite from Punchbowl shows three endothermic peaks at 70°C, 385°C and 450°C, and an exothermic one at 950°C, all of which agree well with those of gonnardite from Maze, Niigata, Japan (Harada *et al.*, 1967) (Fig. 4).

The fibrous zeolites on Oahu form an isomorphous series of solid solution; that is, gonnardite

$$Ca_{1.24-0.36}Na_{1.72-3.65}Al(Fe^{3+})_{4.57-4.17}Si_{5.40-5.80}O_{20} \cdot xH_2O$$
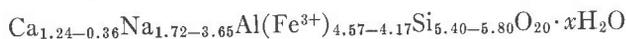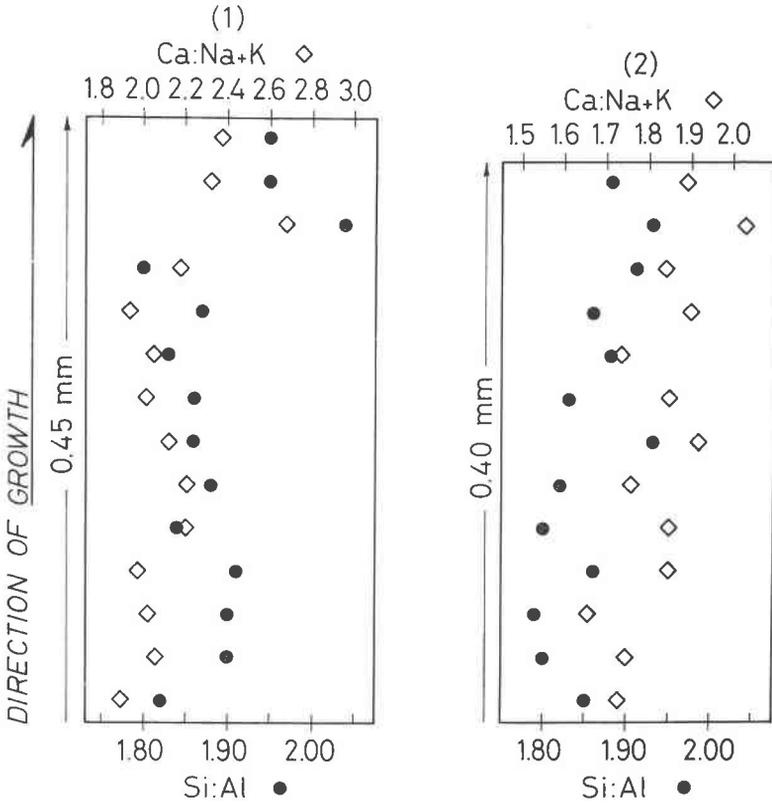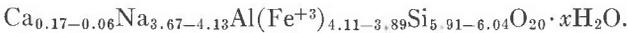
FIG. 5. Change of chemical composition within a single crystal of chabazite by electron microprobe analyses. The dimension and growing direction are shown on the left side of each figure.

(1) Prismatic crystal growing on phillipsite rim in vesicle of basalt block in the Salt Lake Tuff. Refer to No. 3 in Table 5.

(2) Rhombohedral crystal growing on (1). Refer to No. 4 in Table 5.

and natrolite

$$Ca_{0.17-0.06}Na_{3.67-4.13}Al(Fe^{+3})_{4.11-3.89}Si_{5.91-6.04}O_{20} \cdot xH_2O.$$

Refractive indices of gonnardite increase from $\gamma = 1.504$ to 1.528 with the increase of Ca and Al.

Electron microprobe analyses of single crystals of the fibrous zeolites show that the compositions change abruptly at the contact of gonnardite with natrolite. The Si:Al ratio in the gonnardite that is not associated with a natrolite rim increases near the outer end, whereas the Ca:Na+K ratio roughly decreases outward in the direction of growth (Fig. 6).
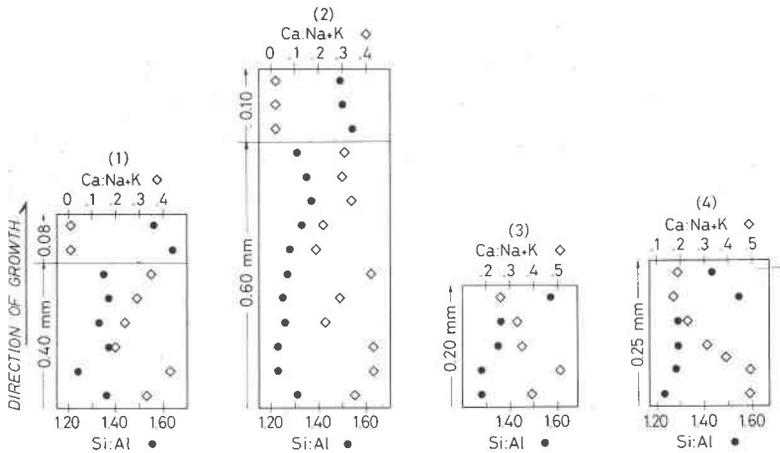
FIG. 6. Change of chemical composition within single crystal of gonnardite and natrolite. The length and growing direction are shown on the left side of each figure.

(1) and (2) Natrolite on gonnardite fibre from Ulupau Head. Refer to Nos. 5, 10 in Table 6.

(3) and (4) Gonnardite in the Salt Lake Tuff. Refer to No. 4 in Table 6.

FAUJASITE

Faujasite, a rare species of zeolite, was recognized in palagonitized tuffs at three localities: the cliff along Puuloa Road near junction to Moanalua Road on the east side of Salt Lake Crater; a roadcut along Puuloa Road at the junction to Peltier Avenue; and a quarry 0.4 mile southwest of Round Top. It occurs as small clear octahedra with rounded edges in cement of the pyroclasts. The largest crystal is 0.17 mm in diameter. Faujasite also occurs as white aggregates of very minute grains which replace plant stems in the Lower Salt Lake Tuff. Refractive index of faujasite is 1.471 ± 0.002 and isotropic.

X-ray diffraction powder data are very similar to those of synthetic C-faujasite (Barrer *et al.*, 1956). The unit cell dimension is $a = 24.69 \pm 0.02$ Å. The result of electron microprobe analysis is recast in terms of the structural formula:

$$(Ca_{2.32}Na_{3.88}K_{1.08})_{7.28}(Fe^{+3}_{0.18}Al_{10.73}Si_{25.45})_{36.36}O_{72} \cdot xH_2O.$$

ANALCIME

Analcime was found in rather extensively palagonitized tuffs of all localities except Manana Island and the Tantalus Crater group. It is common as a cement of tuffs of Koko Craters and Diamond Head.

Analcime rarely occurs as clear trapezohedra as large as 0.15 mm in

diameter, but is commonly rounded grains less than 0.05 mm in diameter. Crystals are isotropic with refractive indices $n = 1.489–1.494$. Analcime characteristically forms a coating on palagonite or other zeolites, but it replaces phillipsite in several samples and gonnardite in at least one sample (Hay and Iijima, 1968b). It rarely replaces plagioclase.

Three samples of analcime from Koko Craters were analyzed by microprobe (Table 2, anal. 10). They are of the low-silica variety with the Si:Al ratio of 1.91, 1.94 and 2.07, averaging 1.97. This is consistent with the Si:Al ratio as determined by the $(\overline{6}39)$ d spacing method (Saha, 1961; Coombs and Whetten, 1967). The values range from 1.68 to 2.30, averaging 1.98 in 15 samples from Koko Craters. Potassium occurs only in trace amounts. The content of CaO may be as much as 1.14 percent. Analcime in nephelinite tuffs may have the lower Si:Al ratio than that in alkali basalt tuffs. The Si:Al ratio as obtained by X-ray result ranges from 1.64 to 2.11, averaging 1.81 in six samples.

ASSOCIATIONS OF AUTHIGENIC ZEOLITES

Among the authigenic zeolites in palagonite tuffs of the Honolulu Series, the following associations were distinguished and are arranged in order of precipitation (Table 3). Phillipsite containing the most abundant potassium is always the initial zeolite. Chabazite, the next common in potassium, generally deposited after phillipsite. The next is gonnardite, which is followed by natrolite. Analcime is the latest. Gismondine probably precedes chabazite, and faujasite possibly follows it. The general sequence of precipitation is K zeolites→Ca·Na zeolites→Na zeolites (in ultramafic tuff), and K zeolites→Na zeolites (in mafic tuff). This corresponds well with the general sequence of zeolite formation, K zeolites→ analcime, in silicic tuff in saline-lake deposits (Hay, 1966). The change of chemical compositions of these successive zeolites are well illustrated schematically on a Ca-Na-K diagram in Figure 7, based on Figure 2. Ca:Na and Si:Al ratios of K zeolites are strongly affected by the compositions of original host rocks. Low-silica fibrous zeolites are restricted in nephelinite tuffs, exclusive of very sparse occurrence in tuffs of Koko Craters. The fibrous zeolites of Koko Craters are limited to the area along coastal line, suggesting addition of some cations from sea waters.

The leached Al, Si and K and high proportions of the Na and Ca from altering sideromelane were fixed as zeolites on or near the palagonitized sideromelane (Hay and Iijima, 1968b). Hence chemical compositions of the zeolites depend on the original compositions of host rocks. Precipitation of zeolites at the surface condition is controlled by the nature of solution such as pH, the activity of silica, the concentrations of alkalies and alkaline earths, etc. (Hess, 1966; Hay, 1966). The regular sequence of
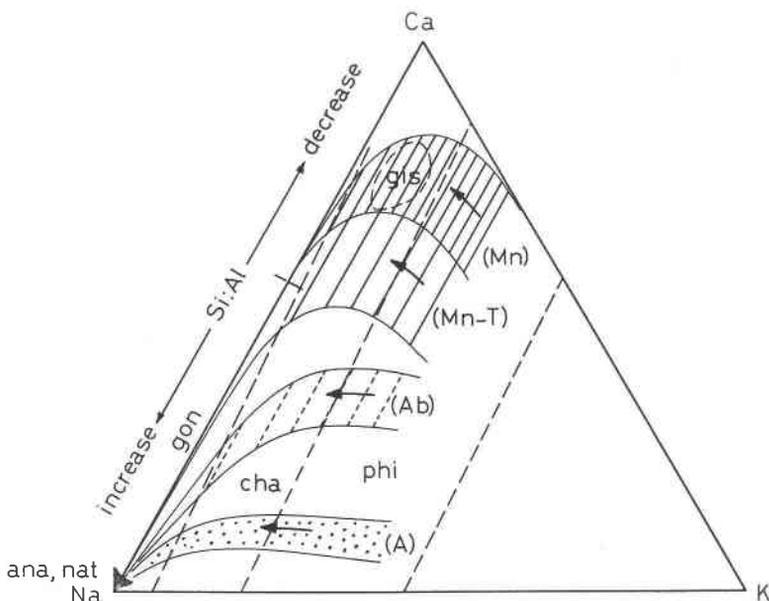
FIG. 7. Trends of the succession of authigenic zeolite formation in different types of original rocks during alteration of volcanic glass, dranw on the basis of Fig. 2. (Mn)—in melilite nephelinite tuff, (Mn-T)—in melilite nephelinite tuff containing abundant tholeiite fragments, (Ab)—in alkali basalt tuff, and (A)—in acidic tuff in saline lakes and soils. Ca:Na and Si:Al ratios of earlier-formed K-zeolites are strongly controlled by the types of original rocks. However, the final zeolite is analcime in all the tuffs.

zeolite formation should be explained by successive compositional change of percolating groundwater through porous tephra deposits as reacting with the pyroclasts.

The concentration of K^+ or $K/(Ca+Na)$ ratio would be sufficient to precipitate phillipsite at the initial stage of zeolitization. The concentration of Na^+ should increase downward, for an appreciable amount of excess Na^+ is dissolved and migrated with percolating water through porous tuffs. As the K:Ca+Na ratio decreases, chabazite begins to crystallize. Then gonnardite forms under a low-silica environment as long as Ca:Na ratio is favourable. The concentration of Na^+ eventually becomes to the point to deposit Na zeolites. Analcime is more abundant than natrolite. Natrolite is universally rare in sediments and altered vitric tuffs on account of a kinetic condition (Senderov and Khitarov, 1966). Almost all of the natrolite of Oahu grows on gonnardite as a film following the fibrous structure. Analcime would be more stable and easier to form than natrolite. The vertical zonation of zeolitic palagonite tuffs of Koko Crater and parts of Salt Lake Craters, Manana Island and Ulupau Head may be explained by the above hypothesis.

Na zeolites occur in even the uppermost zeolitic tuffs in the southwest part of the Koko Crater group and Diamond Head which are situated in semi-arid coastal lowland (Fig. 1). Wind-blown salt from seawater and rainfall on the oceanic island would contribute sufficient Na^+ to increase the Na: K ratio to the point of producing Na zeolites as the supply of K^+ from altering sideromelane diminishes. Relatively high salinity of water due to evaporation would result in zeolite formation even near under the surface.

Most of the Oahu phillipsite, chabazite and gonnardite are zoned. The Si: Al ratio increases outward in the direction of growth. This phenomenon is specifically remarkable in phillipsite which grows on pyroclasts. The rate of diffusion of aluminum ions that leach from sideromelane would be more sluggish than that of silicic ions. The difference in the rate of diffusion causes a chemical gradient of the Si: Al ratio which decreases outward. Hence the zoned crystals may form. The distribution of cations is complicated by large capacities of cation exchange of zeolites. The change of Ca: Na+K ratio is not always compatible with that of the Si: Al ratio in terms of the type of substitution $Si(Na, K) \rightleftharpoons AlCa$. This is significant in phillipsite and chabazite which have more open structures than gonnardite and natrolite.

COMPARISON WITH OTHER ZEOLITES

Authigenic phillipsite of Oahu is characteristic in low Si: Al and Na: Ca ratios, as compared with other analysed "sedimentary" phillipsite (Hay, 1964; 1966). It has rather very similar chemical compositions to the phillipsite commonly found in the cavities of mafic lava flows (Dunham, 1933; Harada *et al.*, 1967). For purposes of comparison, phillipsite in altered silicic tuffs of saline-lake deposits (Hay, 1964) are plotted on the Ca-Na-K diagram of Figure 2. It is remarkable that authigenic phillipsite comprises nearly the same content of potassium ranging from 17 to 43 percent of the total cations. The Si: Al and Na: Ca ratios are strongly affected by the original compositions of host rocks.

Gismondine of Round Top on Oahu is the first occurrence of authigenic origin. It has similar chemical composition to the low-potash gismondine which occurs in the cavities of basalt lavas in Ireland and Iceland (Walker, 1962).

Chabazite of Oahu is characterized by much lower Si: Al and Na: Ca ratios than those of authigenic chabazite in altered rhyolitic tuff of the Barstow Formation of Southern California (Gude and Sheppard, 1966), as illustrated in Figure 2. It shows the chemical similarity to the chabazite forming in cavities and veins of mafic lava flows (Majer, 1953; Kihara and Negishi, 1967).

Chemical compositions of authigenic gonnardite and natrolite of Oahu

are identical to the gonnardite and natrolite commonly found in the cavities of mafic lavas (Foster, 1965).

The Oahu analcime has a lower Si: Al ratio than most of the analcime in sedimentary rocks (Coombs and Whetten, 1967). Chemical compositions of the Oahu analcime are rather similar to the analcime occurring in the cavities of mafic lava flows (Saha, 1959). The low silica and rather high calcium contents may reflect the relatively low silica and high calcium contents of the original host rocks. However, very low potash content in the analcime of Oahu is different from the igneous analcime which sometimes contains high K_2O as much as 4.48 percent (Peters *et al.*, 1967). Authigenic analcime in altered silicic tuffs of saline-lake deposits always replaces potash zeolites (Hay, 1966). Most of the analcime of Oahu was directly precipitated as a cement and in vesicles.

In conclusion, the authigenic zeolites of Oahu show chemical similarity to the zeolites commonly found in the cavities of mafic lava flows. However, the sizes of crystals are much less than the latter.

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