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ZEOLITE STUDIES IV: Na-P ZEOLITES AND THE ION-EXCHANGED DERIVATIVES OF TETRAGONAL Na-P[1]

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ABSTRACT

A group of synthetic zeolites, the "P group," has been defined and an attempt has been made to determine the compositional extent of this group. New analyses of Na-P zeolites are given, and the analyses available to date show that the $Al_2O_3:SiO_2$ ratio ranges from at least 1:3.18 to 1:5.26. The effect of ion-exchange on the structure of Na-P_t (Na_2O, Al_2O_3, $3.63SiO_2$, $4.31H_2O$; tetragonal, $a=10.11$ Å $c=9.83$ Å) is considerable; a maximum range of 7% exists in the c-dimension of the tetragonal unit cells of the ion-exchanged forms. Three main structural divisions were distinguished at room temperature and $P_{H_2O}=7$mm Hg.

(1) Primitive cell, $a \geq c$: tetragonal Li, Na; cubic Mg, Co, Ni, Cu
(2) "Body-centered" cell, $a>c$: tetragonal K, Rb, Cs, Ag
(3) Body-centered cell, $c \geq a$: tetragonal Ca, Sr, Ba, (Pb); Cubic Cd.

A study of six dicationic zeolite systems containing Na, K, Ca and Ba-ions revealed that solid solution gaps exist at room temperature in the systems Na, K; Na, Ba and possibly K, Ca; a reaction point exists in the system K, Ba. Only in the Ca, Ba system was no evidence found against complete solid solution.

Hydrothermal treatment of Na-P_t and the Li, K, Mg, Ca, Ba ion-exchanged froms, at $P_{H_2O}=1000$ bars and temperatures up to 400° C, showed that K-P_t and Ca-P_t were more resistant to breakdown than the parent Na-P_t zeolite. The Li, K and Ba-P_t forms could be converted to lower symmetry (orthorhombic, monoclinic) H zeolites. The tetragonal dicationic P zeolites transformed more readily to H zeolites on hydrothermal treatment, than did the monocationic forms. The K_2Ca-H zeolite so prepared had an x-ray powder pattern identical with a natural phillipsite.

INTRODUCTION

In this study[2] of the Na-P zeolites we have considered them as members of a large group of structurally related zeolites—the "P group" of zeolites. The object of this paper is to demonstrate the possible extent, composition-wise, of this zeolite group and to present x-ray and other data for the known zeolite members. A subsequent paper (Zeolite Studies V) will deal with the complex dehydration behavior and the accompanying structural changes that occur on heating a P zeolite in the atmosphere, and under conditions of controlled partial water vapor pressure. A summation and evaluation of these data will thus delineate the extent of certain structural states of a P zeolite with respect to the

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[2] Details on the experimental procedure and extensive numerical data may be obtained in the Ph.D. dissertation of A. M. Taylor, Pennsylvania State University, Geochemistry 1962.

variables of composition, temperature and partial water vapor pressure.

The Na-P zeolites are of widespread occurrence in the system Na_2O-Al_2O_3-SiO_2-H_2O and have been reported crystallized at temperatures ranging from 60° to 250° C. and pressures from saturated water vapor up to at least 2000 bars. These zeolites are known to have variable composition and to exhibit different symmetry forms. The first part of this paper is concerned with determining the maximum probable range in composition and whether the observed symmetry is dependent on composition or some other variable.

The scope of the investigation is greatly expanded by studying the structural effects on the Na-P zeolite, resulting from the partial or complete exchange of the sodium ions for monovalent and divalent cations of various sizes and polarizing powers. The physical and chemical properties recorded for these ion-exchanged P zeolites will be valuable for comparison with properties of other phases that may be synthesized directly from gels, etc., or found to occur in nature, with the object in mind of determining whether or not such phases may be P zeolites.

The study of the hydrothermal treatment of P zeolites results in the evaluation of their relative persistence or "stability"[1] under a given set of p,T conditions. The cationic forms having maximum stability may be the varieties of P zeolite most likely to be found in nature; conversely, the least stable cationic forms are unlikely to be found. The p, T conditions of the hydrothermal breakdown of these zeolites, the process of breakdown, and the nature of the products—whether new zeolites are formed or anhydrous phases, all constitute valuable data in the attempt at the evaluation of phase relations in the many chemical systems involved. The breakdown products of the cationic forms having maximum stability will give an indication of the type of natural mineral assemblage where P zeolites might be discovered.

The Na-P zeolites were initially investigated by Breck *et al.*, (1956) who use the name "zeolite B" for these phases. Their findings, including the method of synthesis, variation in composition, and some ion-exchange and absorbent properties have been published in the patent literature (Milton, 1961). In a study by Barrer *et al.*, (1959a) of the hydrothermal crystallization of hydrous gels of composition $Na_2O \cdot Al_2O_3 \cdot nSiO_2$ $(1 < n < 12)$ in the presence of excess NaOH, there is reported the synthesis of three polymorphs of species P (or Na-P), cubic, tetragonal and orthorhombic[2] symmetry; *x*-ray data are given for each polymorph. This report was followed by a more extensive study (Barrer *et al.*, 1959b) of the properties of the Na-P zeolites and some ion-exchanged forms. A

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[1] The term "stability" is thus not used here in its rigorous thermodynamic meaning.

[2] Not encountered in this investigation. Considered to be more probably a member of the H group of zeolites (see Nomenclature).

structure was proposed for the cubic polymorph and the relations between this structure and orthorhombic or monoclinic unit cells of harmotome and phillipsite are indicated. Unfortunately, the term "harmotome zeolites" is used instead of "P zeolites" for the group of synthetic phases under study.

Additional reports of the synthesis of Na-P zeolites have been by Hoss and Roy (1960), where they were called "phillipsite, or cubic phillipsite"; Saha (1960), "zeolite B"; and Regis *et al.*, (1960), "phases P_c, P_t, P_o or cubic, tetragonal and orthorhombic phillipsite" respectively. Reports of synthetic phases considered here to very probably be P zeolites, but containing exchangeable cations other than sodium, are listed as follows: Phase Na, K-P?, and calcium "harmotome"?, Barrer *et al.*, (1959b); phase CASH-II, Koizumi and Roy (1960), Ames and Sand (1958); a cubic alkylammonium zeolite analogous to cubic Na-P, Barrer and Denny (1961a); tetragonal Ca-harmotome and Na-harmotome, Barrer and Denny (1961b).

The use of natural mineral names to describe synthetic phases should be avoided when identity is not certain. The current practice of using harmotome and phillipsite for both high and low symmetry synthetic phases has rendered these names rather meaningless. That some sort of standard nomenclature of these zeolites should be proposed is evident from the list of confusing descriptive terms given above.

NOMENCLATURE

The "P zeolite group" is here defined as that group of zeolites composed of members having an aluminosilicate framework linked in a manner identical to that of the cubic Na-P zeolite. The P group, so defined, includes tetragonal Na-P, which is related to the cubic form by a reversible, displacive-type transition that occurs on heating Na-P_t in the atmosphere at temperatures below 100° C. (Zeolite Studies V, in prep.). Ion-exchange processes that occur when the cubic and tetragonal Na-P zeolites are brought into contact with aqueous salt solutions at room temperature and atmospheric pressure are not known to cause any reconstructive changes in the aluminosilicate framework, hence the ion-exchanged products of these zeolites are also considered members of the P zeolite group.

The variables of composition and symmetry must not be used in any scheme for the structural classification of zeolites into groups. Use of such variables should be restricted to the subdivision of groups into subgroups and species. Three subgroups of the P zeolite group have been recognized and these are characterized by certain physical properties of the Na, K and Ca endmember zeolites. The subgroups are designated by a superscript, *e.g.*, $P^1(Na)$, $P^2(K)$, $P^3(Ca)$. The symmetry of a phase is shown by a subscript (P_c, cubic; P_{sc}, pseudocubic; P_t, tetragonal). *E.g.*, the formula $K,Ba\text{-}P_t^3$ represents a tetragonal, dicationic zeolite belonging to the Ca-subgroup of the P zeolite group.

The exchangeable cation composition phase may be shown either qualitatively or quantitatively; the Al_2O_3: SiO_2 ratio is given as a number in parenthesis, e.g., qualitative, $Na,Ca\text{-}P_t$; quantitative, $(2Na)_{30}Ca_{70}\text{-}P_t^3(363)$, the latter phase has an Al_2O_3: SiO_2 ratio of 1:3.63. The P zeolites that contain exchangeable cations other than sodium have all been prepared by ion-exchange processes and none by direct synthesis. The formula given for a P zeolite thus represents the resultant state of the phase, after perhaps several ion-exchange treatments, *e.g.*, $2K,Ca\text{-}P_c$ is a cubic phase produced by two ion-exchange treatments of zeolite $Na\text{-}P_t$. In general usage, it is proposed that when it is desired to indicate specifically that a particular cation has in fact been introduced by exchange the superscript ^{ex} be used; thus $K_2^{ex},Ca^{ex}\text{-}P_c$.

The relationship between the synthetic Na-P zeolites and the harmotome-phillipsite group has been studied by Barrer *et al.*, (1959b). They conclude from a comparison of unit cell measurements that these zeolites must have similar aluminosilicate frameworks. However, from a recent structure determination of harmotome by Sadanaga *et al.*, (1961), it is apparent that the anionic framework of harmotome is linked differently from the way proposed by Barrer *et al.*, (1959b) for the structure of cubic Na-P. Thus the transformation of a "P type" framework to a "harmotome type" cannot take place without a reconstructive change occurring *i.e.*, involving a breaking and relinking of some Si-O-(Si, Al) bonds, and by our definition they cannot be considered as belonging to the same group.[1]

Hydrothermal treatment of P zeolites, especially dicationic types, readily converts them to phases having low symmetry *x*-ray powder patterns practically identical to those of harmotome or phillipsite (see Part III). None of these hydrothermal reactions have been demonstrated to be reversible. Many different structural changes have been observed to take place on dehydration of P zeolites in the atmosphere (Zeolite Studies V, in prep.), but on no occasion has any phase been formed that has an *x*-ray powder pattern resembling either harmotome,

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[1] A broad group classification of zeolites has recently been proposed by J. V. Smith (1963). Zeolite Na-Pl ($Na\text{-}P_c$) is included in the phillipsite group, along with phillipsite, harmotome, gismondine and garronite. All the structures of zeolites within this group are based on parallel four- and eight-membered rings of tetrahedra. In our nomenclature, the P-group of zeolites (including garronite) may be considered as belonging to the phillipsite *family* of zeolites, all of which have certain structural features in common.

phillipsite or their meta-phases. These observations indicate very strongly that the P zeolites must undergo a reconstructive-type change during their conversion to harmotome or phillipsite-like phases under hydrothermal conditions. For this reason, the synthetic phases that have low symmetry (orthorhombic, monoclinic) *x*-ray powder patterns comparable to harmotome or phillipsite are there designated "H zeolites" and are considered as a group to be structurally different from the P group.

Part I—The Na-P Zeolites

EXPERIMENTAL

The method of synthesis used was that described by Regis *et al.*, (1960). Solutions of NaOH, $NaAlO_2$ and Ludox (ammonia stabilized colloidal SiO_2) were reacted in glass jars at 100° C. for 1 to 4 days. The weight ratio, anhydrous solids: water, was kept constant at 1:6. A starting composition of $6Na_2O \cdot Al_2O_3 \cdot 8SiO_2$ produced well crystalline Na-P_t (samples 349, 363, 378) after 3–4 days. The composition $1.7Na_2O \cdot Al_2O_3 \cdot 3 \cdot 5SiO_2$ produced Na-P_c (352) after 1 day. The duration of a run is dependent on the kinetics of the reactions involved. During the first few hours, initial crystallization of Na-F[1] or Na-A[2] occurs, followed by a gradual conversion to Na-P (1 to 3 days) and finally analcime begins to crystallize.

To obtain a product containing a single zeolite phase the run must be terminated at the right time which is found by trial and error. The product consists of amorphous solids containing some crystalline zeolite, ranging in size up to 1 mm; aggregates of zeolite grains (30–200μ); and relatively free zeolite grains (2–15μ). A purified sample of zeolite was obtained by a sedimentation process. The impure zeolite was brought into suspension in a large beaker of distilled water by vigorous stirring. When the coarse material had settled to the bottom, the fine zeolite suspension was sampled and examined microscopically; if no amorphous particles were present, the top third of the suspension in the beaker was poured into a Buchner filter. The process was repeated until nearly all the free zeolite grains were separated from the larger zeolite aggregates and amorphous material. The purified zeolite was found to be better than 99% pure by microscopic examination. Batch amounts of from 5 to 150 grams of purified zeolite were prepared by the above methods.

COMPOSITION AND SYMMETRY VARIATIONS

Seven samples of purified Na-P zeolite were analyzed at the Japan Analytical Chemistry Research Institute (analyst M. Chiba) and one sample (363b) by one of us (A.M.T.). The two analyses 363a, 363b are of

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[1] Na-F = synthetic faujasite.

[2] Na-A = Linde Molecular Sieve, Type A.

the same material.[1] The composition and symmetry of each sample is given below in Table 1.

The $Al_2O_3:SiO_2$ ratio of the samples ranges from 1:3.18 to 1:4.46 and there is no obvious relation between symmetry and composition. Six analyses of Na-P zeolites published by Barrer *et al.*, (1959b) have values of $Al_2O_3:SiO_2$ ranging from 1:3.35 to 1:5.26. Thus the analyses available to date indicate a probable range of 1:3 to 1:5.5. This is comparable to the range of at least 1:3 to 1:6 found for synthetic analcimes by Saha (1959).

TABLE 1. COMPOSITION AND SYMMETRY VARIATIONS OF SPECIES Na-P

Sample	Na_2O	A_2O_3	SiO_2	H_2O	Symmtry	$\Delta 2\theta$ (310)[1]
318	0.89	1	3.18	4.62	tetragonal	0.57
352	n.d.	1	3.52	4.74	cubic	0.00
402	0.91	1	4.02	5.60	tetragonal	0.62
446	0.94	1	4.46	5.81	cubic	0.00
349	n.d.	1	3.49	4.22	tetragonal	0.74
363a	0.94	1	3.46	4.52	tetragonal	0.74
363b	(0.99)	1	3.63	4.31		
378	0.91	1	3.78	5.08	tetragonal	0.71

[1] 2θ (103) $-$ 2θ (310); CuK_α, $\frac{1}{4}°$ 2θ/min., cht. scale $4'' = 1°$ 2θ.

The polymorphism of the Na-P zeolites at room temperature may be characterized by the following two groups of structures:

(1) Body-centered cubic and pseudocubic (tetragonal)
(2) Primitive tetragonal

The axial ratio c/a of the Na-P unit cell may vary from unity for the cubic species to 0.975 or less for unit cells exhibiting maximum tetragonality. A measure of the noncubic nature of a unit cell is given by the degree of splitting of the strongest *x*-ray diffraction peak (310); values of $\Delta 2\theta(310) = 2\theta(103) - 2\theta(310)$ are listed for each sample in Table 1. Samples 349, 363, 378 have primitive tetragonal cells with $\Delta 2\theta(310) > 0.70$ and the absolute intensities of the (310) and other peaks appear to be greater, in some cases double, that of the corresponding peaks for samples 318, 352, 402, 446. The samples 318, 402, that have $\Delta 2\theta(310) < 0.70$ appear to have body-centered tetragonal unit cells and are thus more closely related to the body-centered cubic species, than to the species having primitive tetragonal unit cells further removed from cubic symmetry.

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[1] The value $3.63SiO_2$ is used to give the sample number 363 for this particular batch of zeolite on which two analyses were made.

Microscopic examination showed that both the tetragonal species 318, 402 and the cubic species 352, 446 occurred as relatively free, rounded grains (5–15μ), whereas the primitive tetragonal species 349, 363, 378 consisted of clusters of irregularly shaped grains (5–10μ). The refractive index of individual rounded grains varied over a considerable range for any one sample (Table 2). The mean refractive index for a particular sample, however, was found to decrease linearly with increase in silica content. If it is assumed that the inter-grain variation of refractive index reflects a corresponding variation in Al_2O_3:SiO_2 ratio, then for example, sample 402 may be composed of individual grains that have ratios ranging from 1:3.3 to 1:4.8. The unit cell dimensions will to a certain extent be affected by such variations in composition; a variation in unit cell dimensions from grain to grain would explain the broader and lower intensity *x*-ray diffraction peaks obtained from these samples.

TABLE 2. OPTICAL PROPERTIES OF SPECIES Na-P

Sample	Refractive Index	Birefringence
318	Range 1.476–1.481; mean 1.479	weak
352	Range 1.473–1.479; mean 1.476	none
402	Range 1.465–1.478; mean 1.472	weak
446	Range 1.464–1.472; mean 1.468	very weak
363	1.482±0.002	weak
378	1.482±0.002	weak

The refractive index of the primitive tetragonal species 363, 378 did not exhibit any extensive inter-grain variation, and the value measured $N_{av}=1.482$) is somewhat higher than that of the four body-centered specimens. *X*-ray powder data for cubic and tetragonal Na-P are given in Table 3.

A range in Al_2O_3:SiO_2 ratio of 1:3.18 to 1:5.26 has been demonstrated by actual analyses of Na-P zeolites, however, a greater range is indicated from refractive index measurements made by other investigators. Barrer *et al.*, (1959a) synthesized Na-P zeolites from $Na_2O \cdot Al_2O_7 \cdot nSiO_2$ gels for which n=2 to 12. Refractives indices of Na-P ranged from 1.493 for a sample grown from gel n=2, to 1.455 from gel n=8. A similar decrease of refractive index with SiO_2 content of zeolite "B" (cubic or pseudocubic Na-P) synthesized from glasses having the composition $Na_2O \cdot Al_2O_3 \cdot 2$-$6SiO_2$, has been reported by Saha (1961). Assuming the same trend of refractive index with composition as is listed in Table 1, the refractive index range reported by Barrer for Na-P would indeed correspond to a range in Al_2O_3:SiO_2 ratio of 1:2 to 1:6.

TABLE 3. *X*-RAY POWDER PATTERNS OF Na-P_t AND Na-P_c

Na-P_t (363)[1]			Na-P_c (352)		
$a=10.11$ Å, $c=9.82$ Å			$a=10.02$ Å		
hkl	dÅ	I	hkl	dÅ	I
110	7.132	85	110	7.10	55
101	7.047	83		—	
111	5.776	5		—	
200	5.048	51	200	5.01	35
002	4.914	26		—	
102	4.420	8		—	
211	4.108	94	211	4.10	55
112	4.049	22		—	
202	3.527	4		—	
212	3.328	18		—	
310	3.194	100	310	3.16	100
103	3.117	64		—	
311	3.036	10		—	
113	2.979	5		—	
302	2.776	3		—	
203	2.750	5		—	
321	2.694	46	321	2.67	55
312	2.679	28		—	
213	2.653	21		—	
400	2.531	6	400	2.52	5
322	2.435	5		—	
104	2.387	4		—	
	—		411, 330	2.36	7
420 402	2.257	2		—	
421	2.206	2		—	
214	2.159	2		—	
422	2.055	1	422	2.054	5
510	1.982	2	510, 431	1.965	10
413	1.966	2		—	
105	1.929	1		—	
521	1.844	1		—	
440	1.787	2	440	1.771	7
441	1.759	2		—	
530	1.734	1	530, 433	1.719	7
503, 433	1.720	2		—	
422	1.681	2	600, 422	1.667	7
610	1.664	1		—	
006	1.638	1		—	
106	1.616	1		—	
116	1.597	1	611, 532	1.623	5
612	1.576	1		—	
504 541	1.560	1		—	

[1] Unit cell formula for Na-P_t (363) is $Na_{5.7}Al_{5.7}Si_{10.3}O_{32}\cdot 12H_2O$.

Regis *et al.*, (1960) have published data on the Na-P polymorphs and report that "tetragonal phillipsite" had an average composition of $Na_2O \cdot Al_2O_3 \cdot 8SiO_2 \cdot 16\text{-}20H_2O$, and give refractive indices of $\omega = 1.491$ and $\epsilon = 1.495$. It is not definitely stated that these refractive indices are of tetragonal Na-P having the average composition stated; it is virtually certain, however, that such a siliceous P zeolite would have refractive indices within the range 1.45 to 1.46.

Part II—Structural and Compositional Effects of Cation Exchange

Experimental Procedures

Essentially monocationic, ion-exchanged forms of zeolite Na-P_t (363) were prepared by slow percolation of salt solutions through the zeolite at room temperature, or by repeated soaking of the zeolite in salt solutions at 80–90° C.; in some cases if the former method was found to be ineffective, the latter method was employed with success (*viz.*, Mg^{2+} and Ni^{2+}). Between 2 to 3 liters of solutions having salt concentrations of 5–20 wt% were used to treat 5 gm lots of Na-P_t. Percolating times of 2 to 5 days were required. The ion-exchanged samples were kept in a saturator ($CaCl_2$, saturated solution) at 22–25°, for at least 3 days prior to analysis. Water contents were determined on 500–700 mgm of zeolite by repeated ignition to about 800° C., until a constant weight loss was obtained. The extent of exchange was determined by analyzing for residual sodium utilizing a Beckman flame photometer. The

$$\% \text{ exchange} = \frac{\text{quantity of Na}^+ \text{ removed}}{\text{original quantity of Na}^+} \times \frac{100}{1}$$

and is listed as follows: K, Ag, Ba, Cd, Pb 100%, Li, Rb, Ca, Sr, Co, Cu 95–99%, Cs 93%, Mg 86%, Ni 82%.

Dicationic or partially ion-exchanged zeolites were prepared from 1 gm lots of Na-P_t (363) or its ion-exchanged forms, by soaking the material in dilute choride salt solutions (0.02–0.1N) at room temperature. The amounts of the exchanging cation present in the solution was controlled so as to equal, or partially equal the amount of the exchangeable cation present in the zeolite. The progress of the ion-exchange reactions were noted each day, or at shorter intervals of time, by temporarily removing a sample for *x*-ray examination. *X*-ray charts taken of the region 27°–32° 2θ at 1/2°/min recorded the (310), (301), (103) peak positions of the phases present, hence it was possible to observe progressive changes in cell dimensions and the conversion of one structural form to another.

The dicationic zeolites were analyzed at the Japan Analytical Chemistry Research Institute by Mr. M. Chiba. The analytical data were used to calculate the ratio of the exchangeable cations and the parameter A, which is defined as the ratio, Sum of Exchangeable Cations: Al_2O_3, ×100. The A values calculated for the 21 samples average 95.5, with a minumum of 90 and a maximum of 99. For the seven Na, K samples, A averages 97.0 but for K, Ca only 92.0. The lower value for the latter samples may be due to the presence of minor residual sodium which was not analyzed for. The overall low A values may be due to minor hydronium ion substitution resulting from the use of slightly acidic salt solutions in the ion-exchange process.

A Norelco high-angle diffractometer was used for all *x*-ray work. Water smear mounts of the ground zeolite powder and an internal standard of synthetic spinel ($MgAl_2O_4$) were dried in a saturator, and then *x*-ray powder patterns obtained at a scanning speed of $\frac{1}{2}^\circ$ 2θ per min. on a chart scale of $\frac{1}{2}^\circ$ 2θ per inch. The dependence of unit cell dimensions on temperature and water vapor pressure is considerable in some cases, *e.g.*, at room temperature the c-dimension of $K^{ex}Na\text{-}P_t$ has a temperature dependence of -0.002 Å per ° C. The unit cell dimensions obtained are for temperatures of 22°–25° and high humidity (Figs. 1 and 4).

The unit cell dimensions of the dicationic zeolites were determined as follows: immediately on removal of the samples from the saturator, the (310), (301), (103) and the (200), (002) peaks were scanned at $\frac{1}{4}^\circ$ 2θ per min. on a chart scale of $\frac{1}{4}^\circ$ 2θ per inch. The (111) and (002) spinel peak positions were used as standards. The cell dimensions were calculated from the Q_{hkl} values of the above mentioned peaks. An accuracy of ± 0.01 Å is estimated for all the unit cell measurements.

RESULTS (A) MONOCATIONIC ZEOLITES

Considerable variation in unit cell dimensions and water content are found to occur with the ion-exchanged products of the $Na\text{-}P_t$ zeolite. Both cubic and tetragonal structures exist, with either a body-centered or a primitive lattice. Three main structural divisions may be distinguished at room temperature:

Group 1.	Primitive cell, $a \geq c$; tetragonal Li, Na, cubic Mg, Co, Ni, Cu	(P^1)
Group 2.	"Body-centered" cell, $a > c$; tetragonal K, Rb, Cs, Ag	(P^2)
Group 3.	Body-centered cell, $c \geq a$; tetragonal Ca, Sr, Ba, (Pb) cubic Cd	(P^3)

The division between primitive and body-centered lattices is not clear cut; the K-group zeolites (P^2) have one or two very weak reflections at high angles for which $h+k+l=$ odd, however, many other features such as unit cell dimensions, water content and dehydration behavior support the structural division between the $Na\text{-}P_t$ and $K\text{-}P_t$ zeolites. $Pb\text{-}P_t$ has a primitive lattice, but is placed in Group 3 for convenience.

A plot of unit cell dimensions vs. size of the exchangeable cation is shown in Fig. 1, Ahrens' values of ionic radii are used. The maximum ranges in unit cell dimensions are as follows:

a-dimension	9.89 Å (Ca)	to 10.13 Å (Cs)
c-dimension	9.67 Å (K)	to 10.38 Å (Pb)

The *c*-dimension has a range of about 7% (three times greater than the *a*-dimension) and is also more susceptible to change than the *a*-dimension, during dehydration.

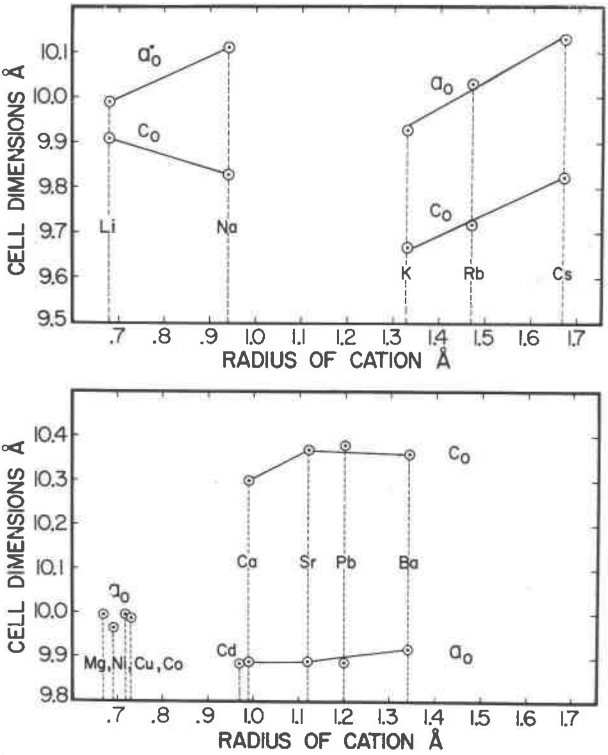

FIG. 1. Unit cell dimensions *vs.* radius of exchangeable cation.

The substitution of a smaller, more polarizing cation for Na^+, whether it be univalent or divalent, results in a cubic or pseudocubic structure. The structural effect of cations having equal size but different polarizing power is shown by the Ca-P_t and Cd-P_c zeolites, the former has an expanded tetragonal structure and the latter a contracted cubic structure. The Na-P zeolite itself, may exist at room temperature as the body-centered cubic polymorph.

The substitution of a larger cation for Na^+ tends to result in the change from a primitive to a body-centered lattice, there being two types of structures which separate the univalent and divalent ion-exchanged forms. The K-group (2) and the Ca-group (3) are distinguished by the former having $a>c$ and the latter $c>a$. It is important to note that the above structural division exists only near room temperature. Due to certain phase transitions that occur on dehydration it so happens that an increase in temperature to 65°, could place Li-P_t, Ba-P_t and Na-P_t in the body-centered group 2 (Zeolite Studies V).

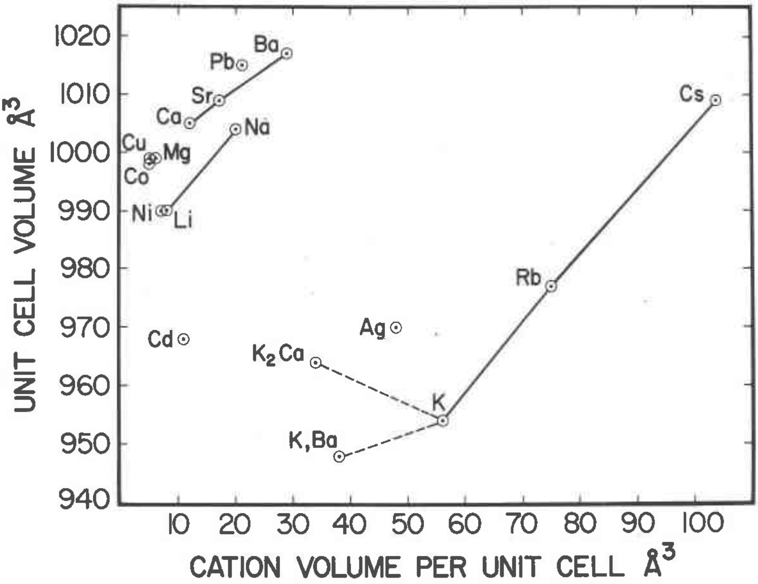

FIG. 2. Unit cell volume *vs*. volume of exchangeable cations.

The water content of a zeolite having a rigid anionic framework should be correlatable with the free volume, *i.e.*, the volume of the structural cages and channels not occupied by cations, and available for occupation by water molecules. The water contents of ion-exchanged faujasites are known to decrease, with increase in cation volume, there being a separate series for the transition metal, univalent and divalent ion-exchanged forms (Barrer and Bratt, 1959a). A similar correlation exists with the ion-exchanged forms of chabazite (Barrer and Langley, 1958). However, with the P zeolites, which have a non-rigid framework, a different situation arises. Within a structural group an increase in the volume of the exchangeable cations results in a corresponding increase in unit cell volume and water content is not greatly affected (Fig. 2 and 3). The unit cell volumes in the series Li, Na; K, Rb, Cs and Ca, Sr, Pb, Ba all increase with increase in cation size. Whereas the unit cell volumes of the cubic group Mg, Co, Ni, Cu are approximately equal. The number of water molecules per unit cell vs. the free volume is shown in Fig. 3 for each ion-exchanged form. The free volume is the unit cell volume minus the volume of the enclosed exchangeable cations, minus a constant volume occupied by the 32, 0 and 16 (Al, Si) atoms of the structural framework (estimated at 337 Å³).

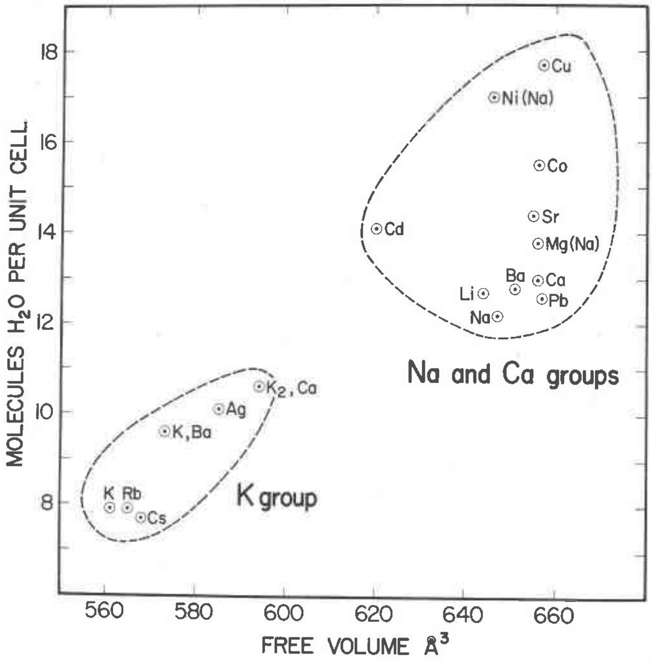

FIG. 3. Number of water molecules per unit cell *vs.* the free volume. (Free volume = unit cell volume minus the volume of enclosed exchangeable cations, minus the volume of enclosed exchangeable cations, minus a constant volume occupied by 32, 0 and 16 (Si, Al) atoms.)

Although the major factor determining the water content of a zeolite appears to be the free volume, the ionic potential of the cation should exert some effect as well. Cations having a high ionic potential may exist with compact hydration spheres of co-ordinately linked water molecules, e.g., Co^{2+}, Ni^{2+}, Cu^{2+} and thus directly affect the water content; or the presence of a strongly polarizing action may result in the zeolite having a contracted structure with a small free volume, thus indirectly affecting the water content, *e.g.*, Cd^{2+} *cf.* to Ca^{2+}.

The water contents in the K, Rb, Cs series are approximately constant with slightly less than 8 molecules per unit cell, which is considerably lower than the 12–13 molecules per unit cell for the Li, Na group. In the group Mg, Ca, Sr, Ba; Cd, Pb which have from 12.5 to 14.5 water molecules per unit cell, the Sr-P_t zeolite has the highest water content for reasons unknown. The Co, Ni, Cu group, with 15 to 18 water molecules per unit cell, have the highest water contents of all. Much of this water is probably linked in 6-coordination to the metal ions, as the fully hydrated zeolites are colored pink, green and blue, respectively.

In Tables 3, 4, 5 and 6 are given *x*-ray data, water contents, refractive indices and densities of Na-P_t (363) and certain ion-exchanged forms.

TABLE 4. DATA OBTAINED FOR Na-P_t (363) AND SOME ION-EXCHANGED FORMS AFTER THEIR EQUILIBRIUM OVER SATURATED $CaCl_2$ SOLUTION AT ROOM TEMPERATURE (25°–27° C.)

P (363)	wt % H_2O	Unit Cell	Dimensions	RI (+0.002)	d_{calc}	d_{meas} (+0.02)
Li	18.7	*a* 9.99	*c* 9.91	1.489	2.05	2.02
Na	16.9	10.11	9.83	1.482	2.16	2.15
K	10.8	9.93	9.67	1.504	2.30	2.28
Ca	18.0	9.89	10.30	1.505	2.15	2.16
Ba	14.6	9.92	10.36	1.531	2.57	2.57
K_2, Ca	14.5	9.88	—	1.507	2.26	2.07
K, Ba	11.9	9.89	9.69	1.530	2.56	2.56

These data will be useful for future identification of P zeolites by other investigators. The *x*-ray data of Table 5 indicates that the phase CASH-II synthesized by Koizumi and Roy (1960) is most probably Ca-P_t.

RESULTS (B) DICATIONIC ZEOLITES

Extension of the three structural divisions of the P zeolites into dicationic systems has been studied and it was found that either solid-solution gaps or reaction points exist between unlike structures. The solid-solution gaps are identified as two phase regions existing during the course of the ion-exchange process; the extent of the gap is, in most cases, determined from analyzed samples that consist very predominantly of one or the other limiting solid-solutions (Fig. 4). These phase relations exist at 25° C. and for water vapor pressures ranging from saturated, down to at least 5 mm Hg. Further work has shown that these solid-solution gaps probably do not extend above 45° at $P(H_2O)=7$ mm Hg. (Zeolite Studies V, in preparation).

It seems evident that the exchangeable cations in each of the P^1, P^2, P^3

TABLE 5. *X*-RAY POWDER PATTERNS OF Ca-P_t (363), GARRONITE AND CASH-II

Ca-P_t (363) $a=9.88$ Å; $c=10.30$ Å			Garronite Barrer *et al.* (1955b)		CASH-II Koizumi and Roy (1960)	
hkl	dÅ	I	dÅ	I	dÅ	I
101	7.13	82	7.15	ms	7.11	42
200	4.95	62	4.95	ms	4.942	33
112	4.15	71	4.12	s	4.133	42
211	4.07	51	4.07	m	—	
103	3.240	40	3.22	m	3.225	25
301	3.140	100	3.14	s	3.132	49
222	2.893	3	2.88	w	—	
213	2.708	9	2.68	vw	—	
312	2.674	62	2.66	s	2.663	35
321	+	sh	—			
004	2.573	7	2.54	vw		
411	2.334	8	2.34	w		
420	2.211	3	2.22	w		
332	2.125	3	2.12	vw		
224	2.072	5	2.05	vw		
422	2.030	2	2.03	vvw		
314	1.985	6	1.970	w		
431, 501	1.940	5	1.938	w		
512 521	1.811	4	1.805	w		
404	1.782	6	1.770	mw		
305	1.746	5	1.745	uw		
503, 433	1.713	4	1.730	vw		
	—		1.705	mw		
244	1.674	2	1.665	vw		
600	1.647	3	1.645	mw		
523 532	1.612	2	1.605	mw		
316	1.505	2				
613 631	1.463	3				
604	1.387	4				
525	1.367	3				
633	1.353	1				

structures must occupy a different set of lattice positions, each set presenting the lowest energy configuration for cations within certain limits of size and charge. Of special interest in this connection is the process of Ca-exchange on K-P_t. Very little Ca-exchange resulted with 0.1N solutions of $CaCl_2$. It was discovered, however, that treatment of K-P_t with saturated $CaCl_2$ solution at room temperature always produced a cubic

TABLE 6. INDEXED *X*-RAY POWDER PATTERNS FOR SOME ION-EXCHANGED FORMS OF ZEOLITE Na-P_t (363)

Mg-P_c $a=9.99_6$ Å			K-P_t $a=9.93$; $c=9.67$ Å			$Ca_{52}(2K)_{48}$-P_c $a=9.88$ Å		
hkl	dÅ	I	hkl	dÅ	I	hkl	dÅ	I
110	7.092	76	101	6.943	70	110	7.00	64
200	5.008	48	200	4.966	25	200	4.95	34
210	4.477	27	211	4.037	32	211	4.04	65
211	4.084	62	112	3.983	27	310	3.13	100
300, 221	3.331	14	202	3.473	4	222	2.853	11
310	3.161	100	301	3.132	100	321	2.643	43
311	3.015	10	103	3.066	47	411, 330	2.333	13
222	2.887	2	222	2.842	16	420	2.206	2
320	2.772	6	321	2.649	13	332	2.105	1
321	2.673	44	312	2.634	25	422	2.018	6
400	2.496	3	213	2.609	9	510, 431	1.936	9
410, 322	2.424	6	411	2.337	11	521	1.807	4
411, 330	2.356	2	303	2.310	4	440	1.746	4
331	2.292	2	204	2.175	2	530, 433	1.693	9
420	2.234	1	323	2.094	1	600, 442	1.649	7
421	2.182	4	422	2.016	3	611, 532	1.603	6
332	2.131	2	431	1.943	4	541	1.525	4
422	2.041	1	314	1.918	4	631	1.457	3
500, 430	1.998	1	105	1.898	3	710, 500, 543	1.397	1
510, 431	1.960	6	512	1.806	2	640	1.371	1
520, 432	1.856	4	404	1.733	1	721, 633, 552	1.344	5
521	1.825	1	305	1.669	3	651	1.255	6
440	1.767	4	600	1.653	4			
522, 441	1.740	2	610	1.609	4			
530, 433	1.714	4	523	1.604	4			
531	1.690	2	620	1.568	3			
600, 442	1.666	4	206	1.533	2			
610	1.643	1	514	1.517	3			
611, 532	1.622	1						
621, 540, 443	1.561	3						
541	1.542	1						
533	1.525	1						
622	1.505	1						
630, 542	1.490	2						
631	1.474	2						
700, 632	1.427	1						
640	1.386	1						
720, 641	1.373	1						
721, 633, 552	1.360	2						
730	1.313	1						
731, 553	1.302	1						
650, 643	1.280	1						
732, 651	1.270	2						

phase having a composition almost exactly at the halfway mark, *v.z.*, $K_2Ca\text{-}P_c$. To obtain at room temperature, Ca, $K\text{-}P_t$ phases richer in Ca-ions, it was necessary to treat $Ca\text{-}P_t$ with dilute KCl solution. If there are two sets of cation positions only half occupied, each separately by K^+ and Ca^{2+} ions, then the cubic phase $K_2,Ca\text{-}P_c$ which resists further Ca-exchange, may owe its stability to a maximum value of the configurational entropy of the system. It is interesting to note that the natural polycationic zeolite, phillipsite, frequently has a composition near $(K_2,Ca)\ Al_2Si_4O_{12},\ 4\cdot5H_2O$, which is almost identical to that of $K_2,Ca\text{-}P_c$ (see Part III for discussion on inter-conversion).

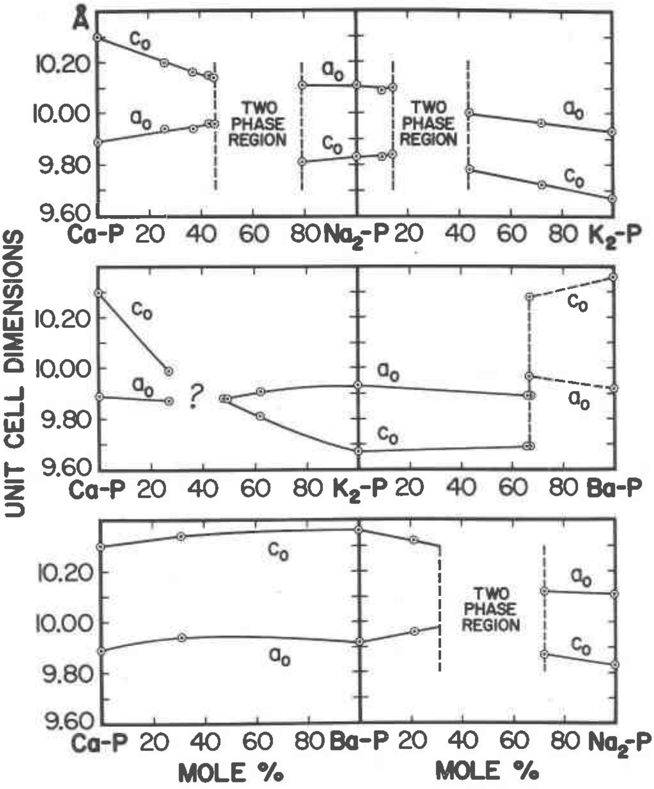

FIG. 4. Unit cell dimensions *vs.* composition.

Two samples containing both K^+ and Ba^{2+} were prepared (KBa1, KBa2). At the time of preparation, KBa1 (prepared by K-exchange of $Ba\text{-}P_t$) consisted of a mixture of approximately equal amounts of two phases (P^2+P^3), whilst KBa2 (prepared by Ba-exchange of $K\text{-}P_t$) was a single phase (P^2). The analyses showed that both samples had the same cation composition, *viz.*, $Ba_{66}(2K)_{33}-P_t$.

An *x*-ray examination of these samples several months after their preparation showed that while KBa2 still existed as a single P^2 phase, the sample KBa1 was almost completely converted to an identical P^2 phase, with only a trace of P^3 remaining. These data indicate, that at this unique composition, a reaction occurs whereby the phase, K,Ba-P_t^3 transforms to K,Ba-P_t^2. The unit cell volume of the former phase is 1021 Å^3, and the latter 948 Å^3 (these values represent the largest and smallest unit cell volumes known, for fully hydrated P zeolites at room temperature), hence the volume decrease is 73 Å^3 per unit cell, which must be accompanied by a correspondingly large water loss. This collapse reaction is analogous to the structural collapses that occur during the dehydration of most P zeolites, but in this case the temperature remains constant and the stability of the Ba-P_t phase is changed by substitution of $2K^+$ for Ba^{2+} (N.B., at 55°, the Ba-P_t^3 phase transforms to a semicollapsed phase having an *x*-ray pattern comparable to that of K,Ba-P_t^2, (Zeolite Studies V, in preparation).

The different results of Ca^{2+} and Ba^{2+} exchange of K-P_t may perhaps be explained as follows: The P^2 (K) and P^3 (Ca,Ba) structures are assumed to have different sets of positions for the exchangeable cations. The Ca^{2+} ion is considerably smaller than K^+ and very likely does not substitute for K^+ on the K^+ lattice positions, but on some other sites related to those existing in the P^3 structure. On the other hand, the Ba^{2+} ion is the same as the K^+ ion in size, and probably does substitute for it on the K^+-lattice sites, as far as the composition ($2K^+$, $2Ba^{2+}$, 2*) per unit cell (assuming a total of six K^+ sites per unit cell for K-P_t). Further substitution of Ba^{2+} would require the existence of the unit cell ($3Ba^{2+}$, 3*)P_t^2, *i.e.*, three Ba^{2+} ions distributed over six former K^+ sites, which is an unstable configuration relative to that of the Ba-P_t^3 structure, to which there is ready conversion.

It is apparent from Fig. 4 that there is somewhat more solid-solution of the cations Na^+, K^+, Ca^{2+}, Ba^{2+} in the P^2 structure than the P^3 and that P^1 exhibits the least solid-solution. Na-P_t (363) has 5.7 Na^+ per unit cell of 32 oxygen atoms. Complete replacement of one Na^+ by K^+ per unit cell is possible, but replacement of two Na^+ without nucleating a more K-rich P^2 phase is not possible. Complete replacement of $2Na^+$ by Ca^{2+} or Ba^{2+} per unit cell was not quite achieved, and it appears that the P^1 structure must be stabilized by having a certain proportion of the unit cells occupied entirely by Na^+ ions. Solid solution in the P^2 struc-

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* Asterisk denotes vacant lattice site.

ture extends to approximately 45K,55Na; 50(2K),50Ca and 33(2K), 66Ba; it should be remembered however that the extent of solid solution is greatly dependent on temperature and water vapor pressure.

It is appropriate here to consider the natural zeolite "garronite" which has recently been discovered in Northern Ireland and Iceland by Walker (1962). This zeolite has an average composition of $Ca_{2.5}NaAl_6Si_{10}O_{32}$; $13.5H_2O$ and its *x*-ray powder pattern (Table 5) is essentially indentical to that of Ca-P_t (as noticed by Barrer *et al.*, 1959b).

A study of Antrim garronite in this laboratory has shown it to have a tetragonal unit cell with $a = 9.8_5$ Å, $c = 10.3_2$ Å. Samples ground to −200 mesh were treated with saturated solutions of NaCl and KCl at 100° C. Almost complete cation-exchange occurred and both products had tetragonal unit cells with $a > c$, as is the case with the P zeolites (Na^{ex}garronite $a = 10.0_4$ Å, $c = 9.8_3$ Å; K^{ex}garronite $a = 9.9_6$ Å, $c = 9.6$ Å). The *x*-ray powder pattern of Na^{ex}garronite is identical to that of the body-centered tetragonal variety of Na-P (*e.g.* samples 318, 402) and K^{ex}garronite to K-P_t.

There is little doubt therefore, that garronite belongs to the P zeolite group. It may thus be represented by the formula $Ca_{85}(2Na)_{15}\text{–}P_t^3$ (333). The ability of this zeolite to undergo cation-exchange suggests that P^1(Na) or P^2(K) type zeolites might occur in association with garronite, or as a complete replacement of it.

DISCUSSION

The ability of a zeolite to undergo ion-exchange with univalent and divalent cations depends largely on the degree of openness of the anionic framework, and hence on the minimum free diameter of the channels; the maximum free diameter may also be critical when an exchange process involves assymetrical ions or molecules. Barrer and Kerr (1959) record a minimum free diameter of 3.5 Å, and a maximum of 4.4 Å for the non-planar 8-membered rings in the cubic Na-P structure. The tetragonal polymorph should have critical dimensions closely similar. A minimum channel diameter of 3.5 Å indicates that a cation as large as Cs^+ (r = 1.67 Å) should be exchangeable for Na^+, and this was found to be so.

The cation selectivity of the Na-P_t zeolite at room temperature may be recorded as K,Li > Rb > Cs and Ba,Sr > Ca > > Mg. The reverse nature of these series shows that cation selectivity is not simply related to the degree of cation hydration of the salt solutions employed for the ion-exchange process. A complex selectivity behavior may be expected if the anionic framework of the zeolite is not rigid and if more than one set of lattice positions exists for the exchangeable cations and the structural water (Ames, 1961).

The structural effects of cation-exchange on the Na-P_t zeolite are greater and more diversified than those found to occur with other zeolite species. The maximum range in unit cell dimensions of the ion-exchanged forms of Na-P_t is about 7%, which is comparable to that for analcimes (6% Barrer *et al.*, 1953), but somewhat greater than the range observed for zeolites that have very open structures, *e.g.* 3% for faujasites (Barrer *et al.*, 1956).

The P zeolite group and the analcime group of zeolites exhibit certain features in common. The univalent ion-exchanged forms of analcime, like the P zeolites, exhibit an isostructural grouping that is largely dependent on cation size. The Li^+, Na^+, K^+ forms of analcime are hydrated and have cubic symmetry, but with the larger ions K^+, NH_4^+, Tl, Rb^+ the structure is anhydrous and tetragonal. The K^+ ion is an inbetween size and both types of structure exist, *i.e.*, K-analcime and leucite (Barrer *et al.*, 1953). With divalent cations however, analcime does not undergo extensive exchange. The existence of solid-solution gaps in the dicationic analcime systems Na,K; K,Rb; K,Tl; Na,Rb has been demonstrated by Barrer and Hinds (1953); Barrer (1958). A detailed investigation of the extent, with respect to temperature and water vapor pressure, of the solid-solution gaps in these and other zeolite groups may do much to increase our understanding of the variety of zeolite species found in nature.

To obtain a reasonably complete picture of the phase relationships existing in the P zeolite group one must study a quinary system such as Na_2O-K_2O-CaO-X-H_2O (where $X = SiO_2/Al_2O_3$) with temperature and water vapor pressure as the variables. The data so far presented for this system have been for $X = 3.63$; $T = 25°$ C., $P_{H_2O} = 7$ mm Hg. A variation of X from 2 to 6 may be possible but no data are yet available of the effect of this component variable on the phase relations. Zeolite Studies V will deal with the effect of temperature and P_{H_2O} on mono- and dicationic P zeolites having $X = 3.63$.

Part III—Hydrothermal Stability and Reactions

EXPERIMENTAL PROCEDURES

The starting materials used consisted of partially or completely ion-exchanged samples of zeolite Na-P_t (363), which have been described in Part I. The usual techniques were employed to make the hydrothermal runs (Roy and Tuttle, 1956). Samples, with or without distilled water, were sealed in gold tubes and subjected to an outside pressure of 1000 bars, at temperatures within the range 150°–400° C. for 10 days. The products were identified from their *x*-ray powder patterns, and in most cases these results were checked microscopically.

RESULTS

The results of 140 runs are summarized in Table 7. The data do not necessarily represent equilibrium conditions as none of the reactions were demonstrated to be reversible. On the other hand, it must be made clear that the direction of equilibrium and the relative stabilities of the phases concerned are unequivocally indicated by the data.

TABLE 7. SUMMARIZED RESULTS OF HYDROTHERMAL TREATMENT OF P (363) ZEOLITES OF 10 DAYS DURATION AT 1000 BARS

Starting Material	1. Conversion Temp. ° C.	Phases Formed	2. Conversion Temp. ° C.	Phases Formed
Predominnantly wet runs:				
Na-P_t	200	analcime+P_t, 260 analcime		
Li-P_t	220	(P_t+Mt), 260 H+LASH-1	335	β-spodumene+eucryptite
K-P_t	310	(H)	320	leucite+P_t, 340 leucite
Mg-P_c	<200	montmorillonite	>400	
Ca-P_t	295	wairakite+P_t, 310 Wk	375	anorthite
Ba-P_t	<200	H	300	celsian+H, 345 celsian
Dry runs:				
$Na_{56}K_{64}$	220	H+analcime	330	analcime+leucite
$Na_{28}K_{72}$	255	H+analcime	335	analcime+leucite
$2Na_{79}Ca_{21}$	215	analcime+P_t, 240 analcime		
$2Na_{37}Ca_{63}$	215	P_t+analcime	250	wairakite
$2K_{62}Ca_{38}$	220	H, 315 H+wairakite	335	leucite+wairakite
$2K_{48}Ca_{52}$	220	H, 315 H+wairakite	335	feldspar[1]+wairakite
$2K_{27}Ca_{63}$	220	H, 290 H+wairakite	335	feldspar[1]+wairakite
$2K_{34}Ba_{66}$	<150	H	250	feldspar
$2Na_{72}Ba_{28}$	<200	H+analcime	320	feldspar+analcime
$2Na_{21}Ba_{79}$	<200	H	320	feldspar
$Ca_{69}Ba_{31}$	<150	H	>350	

[1] Sanidine-like feldspar.

Phases in parentheses were not reproducible.

Many dry zeolite samples were reacted in order to see if lack of water would retard the progress of reconstructive transformations (*e.g.* P zeolite→analcime). The retarding effect was much less than was expected (not more than 20° in favorable cases), which shows that reconstructive phase transformations are achieved at very low temperatures with only zeolitic water acting as an ionizing medium.

The Na-P_t zeolite is partly converted to analcime after 10 days at 200° and 1000 bars, and completely converted at 260°. In highly alkaline solutions such as are used in the synthesis of Na-P the reaction to form analcime is well progressed after one week, at 100° and water vapor pressure. No orthorhombic Na-H phase was encountered.

Between 260°–335°, the Li-P_t zeolite converted to fine-grained Li-H and larger aggregates of the Li-zeolite LASH-1 (Ruiz Menacho, 1959), also recorded as species A (Barrer and White, 1951). LASH-1 occurred as fibrous, radial and fanlike crystal growths, maximum diameter 110 μ, having straight extinction, length slow, low birefringence and $n_{av} = 1.530$. Strongest x-ray diffraction peaks attributed to this phase are at d 6.42, 4.29, 3.13, 3.04 Å. At temperatures above 335°, it was found that similar radial crystal growths consisted of α-eucryptite, having straight extinction, length slow, birefringence, and $\omega = 1.572$, $\epsilon = 1.587$, both ± 0.002. These properties are identical with those of α-eucryptite, as defined by Roy, Roy and Osborn (1950). The major phase above 335° was β-spodumene, which occurred as weakly birefringent crystals (15–20 μ), having tetragonal bipyramidal habit.

The zeolite K-P_t converted to K-H (not reproducibly) between 310°–320°, but at slightly higher temperatures leucite formed. The x-ray powder pattern of K-H is comparable to that of species K-M (Barrer *et al.*, 1956, 59a); for x-ray data, see Table 8.

Mg-P_c remained unaltered after 3 months hydrothermal treatment at 100° and w.v.p. The ready conversion to montmorillonite at 1000 bars and more elevated temperatures is what would be expected from the phase diagram for the system MgO-Al_2O_3-SiO_2-H_2O (Roy and Roy, 1955). The montmorillonite had a basal spacing varying between 12.5 and 13.6 Å; glycolation increased this to 17.7 Å.

Ca-P_t converted to wairakite[1] in both wet and dry runs between 295° and 375°. The zeolite Ba-P_t readily converted to the lower symmetry Ba-H zeolites; however the products from the wet and dry runs were not identical. A Ba-H phase closely resembling harmotome, was produced mainly from wet runs between 200°–330°, whereas the Ba-H (2) phase formed in dry runs between 300–400° (X-ray data, see Table 8).

In general, the dicationic P_t zeolites more readily convert to H zeolites on hydrothermal treatment, than the monocationic zeolites. The substitution of Na^+ for K^+ in K-P_t lowered its stability and resulted in the formation of the assemblage analcime + K,Na-P_t, the latter phase presumably richer in K^+ than the parent K,Na-P_t zeolite. The x-ray powder

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[1] An "analcime-type" phase containing Ca^{2+} as the predominant cation is referred to an wairakite irrespective of whether the weak (200) reflection is present or not. When an additional phase is present, this reflection is not always detectable.

patterns of the K,Na-H phases differ slightly in intensity from K-H, but are identical to the K,Na-M phases reported by Barrer *et al.*, (1959a).

The result of hydrothermal crystallization of a series of gels $(Na,K)_2O \cdot Al_2O_3 \cdot 4SiO_2$, at 2000–3500 bars, in the temperature range 150°–500°, is shown in Figure 5. The phase K,Na-H crystallized readily from compositions richer in K than 80Na,20K, and was in most cases accompanied by another phase, either analcime or leucite; the indications are that the cation composition of K,Na-H was nearly always in the range 60–80%K. Analcime+K,Na-H were produced in short runs of 20 hours, at 350° and 3000 bars, longer runs produced analcime+leucite. At temperatures below 300°, there was no evidence of K,Na-H converting to leucite+analcime. The assemblage analcime+K,Na-H was also formed from a 50Na,50K gel at 100° and 1 atm., by treatment for 3 weeks in a refluxing solution of dilute alkali having the same Na,K ratio.

TABLE 8. *X*-RAY POWDER DATA FOR SELECTED H ZEOLITES FORMED BY HYDROTHERMAL TREATMENT OF P (363) ZEOLITES

$(2K)_{48}Ca_{52}$-H $a=9.90$ Å $b=14.29$ Å $c=14.29$ Å			Phillipsite Hoss & Roy (1960)		K-H		$K_{72}Na_{28}$-H		Ba-H (1)		Ba-H (2)		$(2K)_{33}Ba_{67}$-H	
hkl	d Å	I	dkX	I	d Å	I	d Å	I	d Å	I	d Å	I	d Å	I
110	8.12	17	8.04	vw	9.8	1	9.5	1	8.12	5	10.0	1	8.12	8
111	7.13	85	7.14	vst	8.27	4	8.19	3	7.20	6	7.10	7	7.14	7
020					7.14	6	7.14	10	6.37	6	5.66	10	6.37	7
021	6.40	15	6.37	w	5.37	4	5.37	3	4.98	5	4.98	4	5.01	5
121	5.37	27	5.37	w	5.04	3	5.01	4	4.29	6	4.44	4	4.29	5
022	5.05	35	5.04	m	4.74	1	—		4.15	10	4.31	2	4.08	10
200	4.96	56	4.96	m	4.48	2	4.46	1	4.08	8	4.04	6	3.92	4
130	4.29	20	4.27	vw	4.29	2	4.29	2	3.92	3	3.96	7	3.24	5
131	4.12	52	4.11	st	4.11	1	4.10	2	3.65	1	3.79	1	3.15	10
220	4.05	30	4.08	m	3.66	2	3.68	1	3.48	2	3.56	1	3.08	2
032	3.93	8	3.95	w	3.44	3	3.43	2	3.24	6	3.33	2	2.92	2
040	—		3.58	vw	3.25	10	3.25	5	3.19	7	3.27	3	2.73	4
041	—		3.45	m	3.18	9	3.20	10	3.13	10	3.14	7	2.68	9
230	—		3.42	w	2.96	4	2.95	3	2.91	1	3.03	8	2.53	3
141	3.27	33	3.28	m	2.73	4	2.74	3	2.71	7	3.00	8	2.36	2
310	—		3.23	st	2.67	1	2.70	3	2.67	9	2.73	2	2.32	2
042	3.20	100	3.19	vst	2.55	2	2.57	2	2.52	2	2.67	7	2.23	1
311	3.14	76	3.13	st	2.17	1	—				2.64	5	2.15	1
223	—		3.09	vw							2.39	2	2.06	1
321	2.93	23	2.92	st							2.23	2		
240	—		2.89	vw							2.16	2		
050, 043	2.86	3	2.87	vw										
143	2.75	22	2.74	st										
242	2.69	39	2.69	st										
052	2.65	18												

The *x*-ray powder patterns of K,Na-H produced by hydrothermal treatment of K,Na-gels and K,Na-P_t zeolites, are identical for phases having approximately the same cation composition.

Only the Na,Ca-P_t dicationic zeolites failed to yield H zeolites on hydrothermal treatment. The stability of Ca-P_t is lowered by the partial substitution of $2Na^+$ for Ca^{2+}; complete conversion to wairakite occurred as low as 260°. At lower temperatures, down to 235°, analcime was produced together with a Ca,Na-P_t phase richer in Ca^{2+} than the original zeolite (after hydrothermal treatment, the c-dimension of the Ca,Na-P_t phase had increased to a value approaching that of Ca-P_t, thus indicating a composition change).

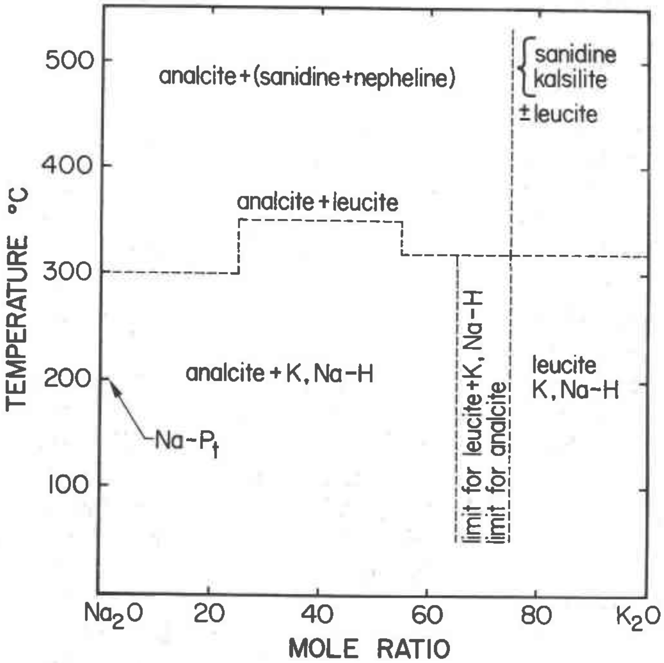

FIG. 5. Phases formed by hydrothermal crystallization at 2000–3500 bars of a series of gels having the compositions $(Na,K)_2O \cdot Al_2O_3 \cdot 4SiO_2$.

The K,Ca-P_t zeolites readily converted to H zeolites having *x*-ray powder patterns essentially identical to those of natural K,Ca-bearing phillipsites. The phase K_2Ca-H occurred as faintly birefringent grains (10–15 μ), having $n = 1.495$. The *x*-ray powder pattern could be indexed on the orthorhombic unit cell $a = 9.90$, $b = 14.29$, $c = 14.29$ Å (Table 8). A similar type unit cell proposed for phillipsite by Steinfink (1962) has $a = 9.96$, $b = 14.25$, $c = 14.25$ Å; space group *B2mb*.

The Ba-bearing P_t zeolites all formed well crystalline H zeolites on hydrothermal treatment, even from the Na-rich composition $(2Na)_{72}Ba_{28}-P_t$.

DISCUSSION

The above results indicate that the order of "stability" of the monocationic P zeolites to hydrothermal treatment is $K > Ca >> Li, Na > Mg, Ba$. Of the six zeolites investigated, the Ba-P_t zeolite is the least stable and readily converts to the harmotome-like phase Ba-H at temperatures below 200°. The presence of Ba in the dicationic P zeolites results in a considerable lowering of stability. It is also apparent that the assymetric charge distribution in the dicationic zeolites can result in a lowering of the stability of the zeolite to such an extent that it is less stable than either end member *e.g.*, KCa and probably KBa, CaBa systems. The H zeolite structure, having orthorhombic or monoclinic symmetry, should be more compatible with unlike cations, and these zeolites are the breakdown product of all except the Na,Ca-dicationic P zeolites. Except for the Ba-H phase, the monocationic H zeolites are not readily synthesized.

The process of breakdown of both the P and H zeolites is of interest. The K,Na-H and K,Ca-H phases reacted to give analcite and wairakite respectively, plus an H phase presumably richer in K^+ ions. Similarly the zeolite $2Na_{37}Ca_{63}$-P_t reacted to form analcite plus Ca-P_t. The possibility is discounted of an exsolution process occurring, such as Na, Ca-$P_t^3 \rightarrow$ Na(Ca)-P_t^1 + Ca(Na)-P_t^3 followed by independent decomposition of the Na and Ca-rich domains. A study of such an exsolution process (Zeolite Studies V) has shown it to be confined to the water-vapor region. The other alternative is for a complete breakdown of the P or H structure to occur, at least to the extent of multiple units of (Si,Al)-0 tetrahedra, followed by reorganization of those units to form two zeolite structures, each containing a different ratio of the two exchangeable cations, compared to the original zeolite.

The recrystallization of a P or H zeolite having a composition different from the original is an indication that such phases could be synthesized directly from gels or glasses of the right compositions, or formed in nature. This appears to be the case with Ca-P_t and many of the dicationic H zeolites.

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References

AMES, L. L. (1961) Cation sieve properties of the open zeolites chabazite, mordenite, erionite and clinoptilolite. *Am. Mineral.* **46,** 1120–1131.

——— AND L. B. SAND (1908) Hydrothermal synthesis of wairakite and calcium-mordenite. *Am. Mineral.* **43,** 476–480.

BARRER, R. M. (1958) Tilden Lecture, Crystalline ion-exchangers *Proc. Chem. Soc.* **99.**

——— J. W. BAYNHAM, F. W. BULTITUDE AND W. M. MEIER (1959a) Hydrothermal chemistry of the silicates. Part VIII. Low temperature crystal growth of aluminosilicates, and of some gallium and germanium analogues. *Jour. Chem. Soc.* 195–208.

——— J. W. BAYNHAM AND N. MCCALLUM (1954) The hydrothermal chemistry of the silicates. Part V. Compounds structurally related to analcite. *Jour. Chem. Soc.* 4035–4041.

——— AND G. C. BRATT (1959) Non-stoichiometric hydrates I. Sorption equilibria and kinetics of water loss for ion-exchanged near faujasites. *Jour. Phys. Chem. Solids* **12,** 130–145.

——— F. W. BULTITUDE AND KERR, I. S. (1959b) Some properties of, and a structural scheme for, the harmotome zeolites, *Jour. Chem. Soc.* 1521–1528.

——— W. BUSER, AND W. F. GRUTTER (1956) *Helv. Chim. Acta.* **39,** 518.

——— AND P. J. DENNY (1961a) Hydrothermal chemistry of the silicates. Part IX. Nitrogeneous aluminosilicates. *Jour. Chem. Soc.* 971–982.

——— AND P. J. DENNY (1961b) Hydrothermal chemistry of the silicates. Part X. A partial study of the field CaO-Al_2O_3-SiO_2-H_2O. *Jour. Chem. Soc.* 983–1000.

——— AND L. HINDS (1953) Ion-exchange in crystals of analcite and leucite. *Jour. Chem. Soc.* 1879–1886.

——— L. HINDS AND E. A. D. WHITE (1953a) The hydrothermal chemistry of the silicates. Part III. Reactions of analcite and leucite. *Jour. Chem. Soc.* 1466–1475.

——— AND I. S. KERR (1959) Intercrystalline channels in levynite and some related zeolites. *Trans. Faraday Soc.* **55,** 1915–1923.

——— AND D. A. LANGLEY, (1958) Reactions and stability of chabazite-type phases. Part III. Intercrystalline water. *Jour. Chem. Soc.* 3817–3824.

——— AND E. A. D. WHITE (1951) The hydrothermal chemistry of the silicates. Part I. Synthetic lithium aluminosilicates. *Jour. Chem. Soc.* 1167–1178.

BRECK, D. W., W. G EVERSOLE AND R. M. MILTON (1956) New synthetic crystalline zeolites. *Jour. Am. Chem. Soc.* **78,** 2338.

HOSS, H. AND R. ROY (1960) Zeolite studies III. on natural phillipsite, gismondine, harmotome, chabazite, and gmelenite. *Beitr. Mineral. Petrogr., Bd* **7,** 389–408.

KOIZUMI, M. AND R. ROY (1960) Zeolite studies I. Synthesis and stability of the calcium zeolites. *Jour. Geol.* **68,** 41–53.

MILTON, R. M. (1961) Crystalline zeolite B. U. S. Patent No, 3,008,803.

REGIS, A. J., L. B. SAND, C. CALMON AND M. E. GILWOOD (1960) Phase studies in the portion of the soda-alumina-silica-water system producing zeolites. *Jour. Phys. Chem.* **64,** 1567–1574.

ROY, D. M. AND R. ROY (1955) Synthesis and stability of minerals in the system MgO-Al_2O_3-SiO_2-H_2O. *Am. Mineral.* **40,** 147–178.

Roy, R., D. M. Roy and E. F. Osborn (1950) Compositional and stability relationships among the lithium alumino-silicates, eucryptite, spodumene and petalite. *Jour. Am. Ceram. Soc.* **33,** 152.

——— and O. F. Tuttle (1956) Investigation under hydrothermal condition. *Physics and Chemistry of the Earth* **1.,** Pergammon Press, London.

Ruiz Menacho, C. M. (1959) Subsolidus studies of the system Li_2O-Al_2O_3-SiO_2-H_2O. M. S. Thesis, College of Mineral Industries, Penn. State Univ.

Sadanaga, R., F. Marumo and Y. Takeuchi (1961) The crystal structure of harmotome, $Ba_2Al_4Si_{12}O_{32}\cdot 12H_2O$. *Acta. Cryst.* **14,** 1153.

Saha, P. (1959) Geochemical and *x*-ray investigation of natural and synthetic analcites. *Am. Mineral,* **44,** 300–313.

——— (1961) The system $NaAlSiO_4$ (nepheline)-$NaAlSi_3O_8$ (albite)-H_2O. *Am. Mineral.* **46,** 859–884.

Smith, J. V. Structural classification of zeolites, *Mineral Soc. Am. Spec. Paper* **1,** 281–290.

Steinfink, H. (1962) The crystal structure of the zeolite, phillipsite. *Acta Cryst.* **15,** 644.

Walker, G. P. L. (1962) Garronite, a new zeolite, from Ireland and Iceland. *Mineral Mag.,* **33,** 173–186.

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