563. *Synthetic Chabazites: Correlation between Isomorphous Replacements, Stability, and Sorption Capacity.*

By R. M. Barrer and J. W. Baynham.

A study has been made, for synthetic and natural chabazites, of the influence of isomorphous replacements and of ion exchange upon the capacity to occlude water, oxygen, and argon. Exchanges $2Na \rightleftharpoons Ca$ in crystals of fixed Al : Si ratio represent a change in cation valency and density with little change in cation radius. After about two-thirds of the Ca had been replaced by Na there was a characteristic decrease in the amount of oxygen or argon sorbed in crystals having $Al_2O_3 : SiO_2 = 1 : 4{\cdot}9$. In some of the preparations a strong selectivity between oxygen and argon developed. This selectivity and the decrease in sorption capacity were influenced by the experimental conditions of the exchange.

Isomorphous replacements $LiAl \rightleftharpoons Si$, $NaAl \rightleftharpoons Si$, $KAl \rightleftharpoons Si$, $RbAl \rightleftharpoons Si$ and $(\frac{1}{2}Ca)Al \rightleftharpoons Si$ were obtained over a range in $Al_2O_3 : SiO_2$ ratios from 2·3 to 4·15. These are accompanied by changes in cation density and framework charge. Water was freely sorbed by all the crystals examined, and water retentivity was in the order Ca > Na > K, in any one crystal of fixed $Al_2O_3 : SiO_2$ ratio. K- and Rb-Chabazites did not occlude oxygen at 90° K, but the more siliceous Li- and Na-chabazites were good sorbents of oxygen and argon. Ca-Chabazites sorbed oxygen and argon still more copiously, and even in some aluminous crystals. Sorption was correlated with exchanges $Li \rightleftharpoons K$, $Na \rightleftharpoons K$, $K \rightleftharpoons Rb$ for fixed aluminosilicate framework charge. The dispositions of ions within the framework needed to explain these observations have been discussed.

In addition to the moderation of sorption capacity by ion exchange and isomorphous replacements, effects arise owing to salt occlusion, thermal instability, alkali extraction, and hydrogen-ion exchange. Metamorphosis of an aluminous chabazite into the nosean structure was observed under certain conditions.

In gas-sorbing zeolites, cations and occluded molecules co-exist together throughout porous aluminosilicate frameworks, and there is evidence that the cations may influence sorption in decisive ways. Using natural chabazite Rabinowitsch and Wood [1] found that sodium-rich crystals occluded little nitrogen but considerable hydrogen, but that potassium-rich crystals sorbed little of either gas. On the other hand, calcium-rich crystals are known to sorb many species, including molecules as large as *n*-heptane.[2] Kington and Laing (personal communication) found their Na-chabazite to be a poor sorbent of oxygen and hydrogen, although Addison and Barrer [3] observed a sorption capacity for oxygen of over 90 cm.^{3} at S.T.P./g. in another sodium-rich chabazite. These variable results, as well as the evidence of large effects of different ions upon sorption capacity, suggested the need for a systematic study of the relations between interstitial cations and gas-sorbing properties of zeolites.

Two other relevant investigations have been made.[3,4] In the first, mordenite crystals enriched by ion exchange in lithium, sodium, potassium, ammonium,* calcium, and barium were studied in relation to intracrystalline diffusion of permanent and inert gases. Diffusion was influenced strongly but in a complex manner by ionic radii and by ion valency. In the second research, sorption equilibria were measured in crystals of natural chabazites enriched in lithium, calcium, barium, and ammonium.* All these forms sorbed copiously the more condensable inert gases, but differences were noted in the affinity and

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* These ammonium forms may by loss of ammonia have changed in part, during outgassing, into the hydrogen forms.

[1] Rabinowitsch and Wood, *Trans. Faraday Soc.*, 1936, **32**, 947.

[2] Barrer, *Ann. Reports*, 1944, **41**, 31.

[3] Addison and Barrer, *J.*, 1955, 757.

[4] Barrer and Riley, *Trans. Faraday Soc.*, 1950, **46**, 853.

in the heat of sorption. Again the cations play a significant rôle in the sorption processes. A further moderating influence upon sorption and diffusion has been established in both mordenite and chabazite, an effect which brings into the picture the water affinity of the cations. Small polar molecules (H_2O, NH_3, NH_2Me) introduced in controlled amounts into the previously outgassed crystals may be immobilised at low temperatures (−183° c) and can then influence strongly and in a selective manner the intracrystalline diffusion of non-polar species.[5] In chabazite, heulandite, and stilbite, water retentivity among exchange forms is in the order [6] $Ca > K$, and more rigorous outgassing may be needed for calcium-rich than for potassium-rich crystals to reach a given stage of dehydration.

The variables which may be at our disposal in relating gas-sorption to intracrystalline cations are : (1) Cation density. This may be changed for the same cation by isomorphous replacements of the type $KAl \rightleftharpoons Si$. (2) Cation valency. This can be changed through simple ion exchanges such as $2Na \rightleftharpoons Ca$. Cation density and position and water retentivity may all be altered. (3) Cation radius. This may also modify cation position and water retentivity but for ions of the same valence does not change cation density.

Barrer and Baynham (unpublished work) discovered how to synthesise potassium chabazites and near-chabazites of varied $Al_2O_3 : SiO_2$ ratios, and Barrer and Bultitude (unpublished work) have synthesised the sodium form. Through further ion exchanges it has been possible, using these materials, to realise all three of the above variables. We now present the results of an investigation of the influence of these variables upon the gas-sorbing properties of chabazites, and attempt an explanation.

1. *Crystal Structure of Chabazite.*—Wyart [7] has made a structure determination of chabazite, which he considers to possess an anionic framework similar to that in the sodalite-nosean minerals. However, a slight distortion of the framework changes the crystal symmetry from cubic to rhombic. Some consequences of this structure from the view-point of sorption have been considered by Kington and Laing.[8]

From the structural viewpoint the important unit is a cage with 14 faces built from eight rings of six $(Al,Si)O_4$ tetrahedra, and six rings of four such tetrahedra. These cages are then stacked in eight-fold co-ordination by a sharing of each six-membered ring by two cages. This gives a near-cubic array of polyhedra. It is evident from the mode of stacking that each cage has eight " windows " (the six-membered rings) opening into eight other cages, so that a continuous criss-crossing network of channels exists. If we accept the Wyart structure the windows are not all of equal dimensions, those lying along and normal to the trigonal axes being slightly larger than the others. Kington and Laing have calculated a free diameter of ~3·2 Å for the larger windows and ~2·3 Å for the smaller. They show that the former, but not the latter, readily allow intracrystalline diffusion of argon of 3·8 Å diameter.

Although Wyart [7] made suggestions regarding the cation positions these are not settled, nor is there any evidence that in the water-free crystals the cations are placed as they are in the hydrated crystals. In a chabazite having base : $Al_2O_3 : SiO_2 = 1 : 1 : 4$ there are two univalent cations per cage, and it is possible to dispose of these so as to block the larger windows, while still preserving the crystal symmetry. Evidently it is fully possible in theory to eliminate the sorptive capacity of the crystals by cation dispositions and by changes in cation density. Some of the possibilities will be discussed below in relation to the experimental results.

2. *Isomorphous Series in Chabazite and Experimental Materials.*—Winchell [9] suggested that some zeolites could show isomorphous replacements such as $NaSi \rightleftharpoons CaAl$ more complex than those of simple ion exchange. This theory rested upon analyses of zeolites the composition extremes for chabazite being $Ca_7Al_{14}Si_{26}O_{80}$ and $Na_4Ca_3Al_{10}Si_{30}O_{80}$. Wyart [7] considered yet more complex replacements, for example, $AlNa_3 \rightleftharpoons SiCa$. Winchell's view requires a constant number of atoms per 80 oxygen atoms, but Wyart's

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[5] Barrer and Rees, *Trans. Faraday Soc.*, 1954, **50**, 989.
[6] Lowenstein, *Z. anorg. Chem.*, 1909, **63**, 69.
[7] Wyart, *Bull. Soc. franç. Miner.*, 1933, **56**, 106.
[8] Kington and Laing, *Trans. Faraday Soc.*, 1955, **51**, 287.
[9] Winchell, *Amer. Min.*, 1925, **10**, 88.

involves no such limitation. Wyart's suggestion represents the sum of two types of isomorphous replacement: NaAl $\rightleftharpoons$ Si and 2Na $\rightleftharpoons$ Ca.

The analyses listed by Winchell gave $Al_2O_3 : SiO_2 = 1 : 3·71$ for the most aluminous chabazites and 1 : 6·0 for the most siliceous; those given by Wyart indicated 1 : 3·26 for the former ratio. According to Lowenstein[10] the maximum substitution of aluminium for silicon in any framework based only on linked tetrahedra is 50%, giving the theoretical limiting ratio $Al_2O_3 : SiO_2 = 1 : 2$. Barrer and Baynham not only demonstrated by direct synthesis the correctness of the isomorphous replacement KAl $\rightleftharpoons$ Si but also extended the range of this replacement down to 1 : 2·3 or even less. The most siliceous synthetic chabazites made by Barrer and Bultitude had $Al_2O_3 : SiO_2 = 1 : 4·7$. There were thus available for the study of sorption many chabazite-like crystals in which the cation density is systematically varied. From these structures, by ion exchanges of the types Na $\rightleftharpoons$ K, Ca $\rightleftharpoons$ 2K, other forms were obtained, and all the variables mentioned in the introduction were realised.

In Table 1 are given some details of the K-chabazites used in this work. Although yields were normally high, in all the synthetic chabazites there is the possibility of simultaneous occurrence of small amounts of alumina and of uncrystallised gel. This can cause some variations in composition (*e.g.*, sample 2). All the crystallisations yielded products less siliceous than the parent gels. From these preparations many ion-exchanged forms were derived by procedures which, because it transpired that the exchange conditions could influence the behaviour, will be described later.

TABLE 1. *Crystallisation of some potassium chabazite-like phases.*

Sample no.	Gel compn. (oxide formula excluding H_2O)	Excess of KOH aq. added (%)	Ultimate compn. (excluding H_2O)
1	$K_2O,Al_2O_3,3SiO_2$	150	$2·5K_2O,Al_2O_3,3SiO_2$
2	$K_2O,Al_2O_3,4SiO_2$	140	$2·4K_2O,Al_2O_3,4SiO_2$
3	$K_2O,Al_2O_3,4SiO_2$	275	$3·75K_2O,Al_2O_3,4SiO_2$
4	$K_2O,Al_2O_3,5SiO_2$	310	$4·1K_2O,Al_2O_3,5SiO_2$
5	$K_2O,Al_2O_3,5SiO_2$	150	$2·5K_2O,Al_2O_3,5SiO_2$
6	$K_2O,Al_2O_3,6SiO_2$	150	$2·5K_2O,Al_2O_3,6SiO_2$

Sample no.	Crystalln. conditions	Refractive indices of product	Molar proportions in product				Ratio, H_2O : cations
			K_2O	Al_2O_3	SiO_2	H_2O	
1	3 days at 150°	$\alpha = 1·480$ $\gamma = 1·485$	0·92	1·00	2·30	3·40	1·85
2	4 days at 150°	$\alpha = 1·490$ $\gamma = 1·495$	1·11	1·00	2·56	2·62	1·15
3	2 days at 150°	$\alpha = 1·475$ $\gamma = 1·480$	0·99	1·00	2·65	3·72	1·88
4	4 days at 150°	$\alpha = 1·465$ $\gamma = 1·470$	0·95	1·00	2·72	3·94	2·08
5	4 days at 150°	$\alpha = 1·460$ $\gamma = 1·465$	1·00	1·00	3·91	4·63	2·32
6	1 day at 150°	$\alpha = 1·470$ $\gamma = 1·475$	1·03	1·00	4·15	4·38	2·13

An isomorphous series of chabazites with compositions in the range Na(0%),Ca(100%) to Na(100%),Ca(0%) was also prepared from natural chabazite having, when free from water, the initial composition $(Na_2,Ca)O : Al_2O_3 : SiO_2 = 1 : 1 : 4·9$, with Na = 20% and Ca = 80%. Pure Na-chabazite was obtained from these crystals by two treatments, of 7 days each, with saturated sodium chloride at ~100°. This was followed by percolation with 20% aqueous sodium chloride for eight hours at ~100°. Pure Ca-chabazite was made by three treatments of seven days each with concentrated aqueous calcium chloride at 100°. Both sodium and calcium forms were thoroughly washed and their cationic purity checked by chemical analysis. From these stock materials a series of equilibrium (Na,Ca)-chabazites was made by further treatments with solutions of sodium or calcium chloride, or their mixtures, as indicated in Table 2. Although the times allowed for equilibration were long, subsequent experience showed that very much shorter reaction times would also have given equilibrated products.[11]

3. *Investigation of Crystals.*—A Hilger HRX *X*-ray unit, using filtered Cu-*K*α radiation and 9-cm. powder cameras, was used to characterise and compare the various ion-exchanged forms.

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[10] Lowenstein, *ibid.*, 1954, **39**, 92.

[11] Barrer and Sammon, *J.*, 1955, 2838.

Optical examination was made with a Leitz polarisation microscope. Chemical analysis of the solid or of the equilibrium solutions was by standard procedures.[12]

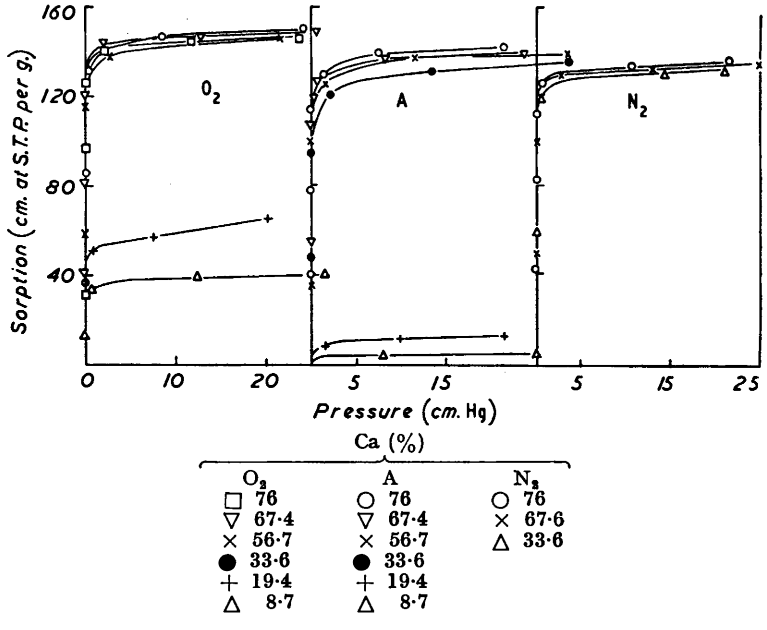
TABLE 2. *Preparation of mixed* Na,Ca-*chabazites.*

Prep. no.	Conditions of exchange (0·5N-solutions)	Calcium exchange (%)
1	0·607 g.; 5 ml. $CaCl_2$; 0·5 ml. NaCl; 14 days at 75°	8·7
2	0·5517 g.; + 1 ml. $CaCl_2$; 4 ml. NaCl; 14 days at 75°	19·4
3	0·4035 g.; 2 ml. $CaCl_2$; + 5 ml. NaCl; 14 days at 75°	33·6
4	0·5001 g.; + 5 ml. NaCl; 14½ days at 75°	56·7
5	0·5054 g.; 5 ml. $CaCl_2$; >7 days at 75°	67·4
6	0·1814 g.; 2 ml. NaCl; 2 ml. $CaCl_2$; 28 days at 75°	75—77 *
7	0·1055 g.; 1 ml. NaCl; 5 ml. $CaCl_2$; 28 days at 75°	
8	0·1078 g.; 5 ml. $CaCl_2$; >7 days at 75°	
9	0·2420 g.; 5 ml. $CaCl_2$; 14 days at 75°	

Nos. 1—3, 5, 8, 9: Na-chabazite. Nos. 4, 6, 7: Ca-chabazite. * Products 6, 7, 8, and 9 were combined to give one sorbent, taken as 76% exchanged to Ca.

The gas-sorbing properties of the isomorphous series of crystals were investigated, for oxygen, nitrogen, hydrogen, helium, and argon supplied in the pure state. Liquid oxygen (−183°), liquid nitrogen (−195°), and solid carbon dioxide (−78°) were used as low-temperature baths. Sorption was conveniently measured by the gas volumetric method. To remove intracrystalline water the crystals were outgassed for about 16 hours at temperatures up to 350°, before being used as sorbents. They were also thoroughly outgassed between sorption runs, under the same conditions.

FIG. 1. *Modifications in the oxygen, nitrogen, and argon isotherms at* −183° *in a natural chabazite, due to the exchange* 2Na $\rightleftharpoons$ Ca.



Ca (%)

O_2	A	N_2
□ 76	○ 76	○ 76
▽ 67·4	▽ 67·4	× 67·6
× 56·7	× 56·7	△ 33·6
● 33·6	● 33·6	
+ 19·4	+ 19·4	
△ 8·7	△ 8·7	

4. *Sorption in Relation to Cation Exchanges* 2Na $\rightleftharpoons$ Ca.—In the exchange 2Na $\rightleftharpoons$ Ca we have two ions of almost the same radius. The direct effects upon occlusion of change in valency are then measured. They may be associated with change in cation density, and may involve other factors such as re-siting of cations following exchange. The crystals of Table 2 were employed, and in addition crystals containing either 100% sodium or 100% calcium. In Figs. 1*a*, *b*, and *c* are shown isotherms obtained for oxygen, nitrogen, and argon at −183° in the Na,Ca-chabazites of Table 2. They show that some of the sodium-rich sorbents have a much diminished sorption capacity. Isobaric sorptions at −183° and at 20 cm. pressure are shown as functions of the cationic composition in Fig. 2. A

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[12] Groves, " Silicate Analysis," Allen and Unwin, London, 1951.

rapid drop in sorptive capacity occurs in crystals <35% exchanged to Ca, and moreover the crystals then show a marked selectivity for oxygen as compared with argon, in much the same way as mordenites and levynite.[3, 13] The time of equilibration over long intervals had little effect upon the amounts sorbed in this calcium-poor range, so that slow sorption processes, if present, are on a time scale inaccessible to experiment.

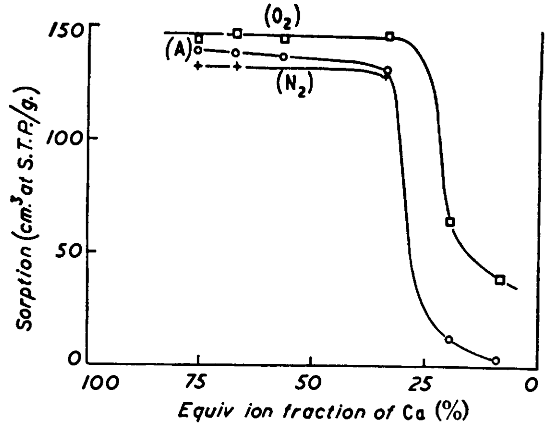

FIG. 2. *Influence of the exchange* 2Na $\rightleftharpoons$ Ca *on occlusion of oxygen, nitrogen, and argon at* —183° *and constant pressure of* 20 *cm.* Hg, *in a natural chabazite*

($Al_2O_3 : SiO_2 = 1 : 4{\cdot}9$).

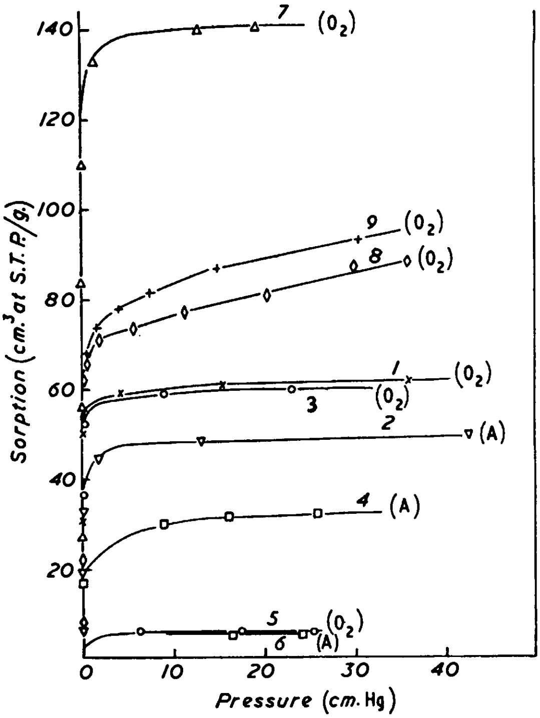

FIG. 3. *Isotherms of* O_2 *and* A *at* —183° *on various* Na-*chabazites, prepared by ion exchange from* Ca-*rich and* K-*forms. The behaviour differs as among different preparations. Curve* 7 *gives the occlusion of* O_2 *by* Ca-*chabazite re-converted from the* Na-*form.*

The attractive possibility of producing, by simple ion exchange, highly selective sorbents, as between oxygen and argon, was then investigated further with various Na-chabazites. The first of these was prepared much more rapidly than the selective sodium-rich forms of Table 2, but was derived from a chabazite with the same ratio $Al_2O_3 : SiO_2 = 1 : 4{\cdot}9$. The crystals of this natural chabazite ground to pass 200 mesh were given three two-hour treatments on the water-bath with 20% sodium nitrate solution. This time the selectivity between oxygen and

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[13] Barrer, *Trans. Faraday Soc.*, 1949, **45**, 363; *Nature*, 1947, **159**, 508.

argon had largely disappeared (Fig. 3, curves 1 and 2), while the occlusion of both gases was more copious.

Another Na-chabazite was then prepared from the stock of natural chabazite used for the previous specimen. Coarser crystals were used, but the treatment was more prolonged. Three treatments were given on the water-bath, each with 15% aqueous sodium nitrate, and were followed by percolation for 24 hr. with the hot reagent. A measure of selectivity had then appeared between oxygen and argon, the total sorption of argon being much reduced (Fig. 3, curves 3 and 4). The crystals from this experiment were removed and treated for 7 days with 10% aqueous sodium nitrate on the water-bath, since it was now suspected that the behaviour was being influenced by the time of contact of the crystals with hot solutions. This time the sorption of both oxygen and argon was reduced to a very small value indeed, in confirmation of the above view (Fig. 3, curves 5 and 6).

In order to demonstrate that even the inactive crystals could recover their sorptive capacity, given appropriate treatment, they were first ground, but without showing any recovery of sorptive power, and then reconverted into the calcium-rich form, by two treatments each of seven days with concentrated calcium chloride solution. Then the sorption of oxygen exceeded 140 cm.^{3} at S.T.P./g. (Fig. 3, curve 7). Finally, in order to show that the suppression of sorptive activity observed on longer exposure to hot solutions containing sodium was not due to more complete exchange, oxygen isotherms were determined for two synthetic sodium chabazites, one with an $Al_2O_3 : SiO_2$ ratio $\simeq 1 : 4{\cdot}7$ and entirely free from cations other than sodium, and the other also having a high alumina : silica ratio, with only sodium except possibly for a small contamination by potassium.* Both samples occluded oxygen freely, in larger amount than any of the earlier sodium-rich samples (Fig. 3, curves 8 and 9).

The foregoing observations show that ion exchange of sodium in place of calcium, combined with a second process [which might be a side reaction such as hydrolysis or salt occlusion (Section 5)], can yield from siliceous chabazites a variety of sorbents. These range from products which readily sorb both oxygen and argon to products which sorb oxygen but little argon, to products which sorb little of either gas. The synthetic sodium chabazites sorb oxygen more freely still, and the capacity for oxygen rises to about two-thirds of that shown by the Ca-form of chabazite. Moreover the loss of sorptive power which may be associated with the second factor in sodium exchange did not prevent recovery of very high sorptive power on grinding and reconversion into the Ca-form. *X*-Ray powder photographs gave no evidence of loss of crystallinity in any of these products.

5. *Isomorphous Replacements* $MAl \rightleftharpoons Si$ *and Sorbent Capacity.*—As the aluminium content of the anionic framework increases so do the framework charge and, therefore, the number of cations per unit cell. With compositions $M_2O : Al_2O_3 : SiO_2 = 1 : 1 : n$, the numbers of univalent cations per unit cell, for different values of *n*, are :

n	2	3	4	5
Ions M^+ per unit cell	6·0	4·8	4·0	3·4

From the structure given in Section 1 and the rhombic unit cell with $a \sim 8{\cdot}9$ Å and $\alpha \sim 94°$, it may be shown that there are two cages per unit cell, and in the silica-rich crystals discussed in Section 3 there were 1·74 Na^+ or 0·87 Ca^{++} ions per cage. This cation density increases to 2·57 Na^+ or 1·29 Ca^{++} ions per cage in the most aluminous product of Table 1 (where $0{\cdot}92 : 1 : 2{\cdot}3 = K_2O : Al_2O_3 : SiO_2$). Obvious possibilities exist for changing the gas-sorbing properties of the crystals by such increases in cation density. Not only may molecules diffuse less readily, but different numbers of ions must be arranged with molecules, such as water, in the cages. From the constancy of the unit-cell volumes among the crystals for different $Al_2O_3 : SiO_2$ ratios (Barrer and Baynham) we suspect that the cages also remain rather constant in dimensions.

From the compositions of the parent crystals (Table 1) and from the water contents of these and of their ion-exchanged forms, the numbers of water molecules per cage under

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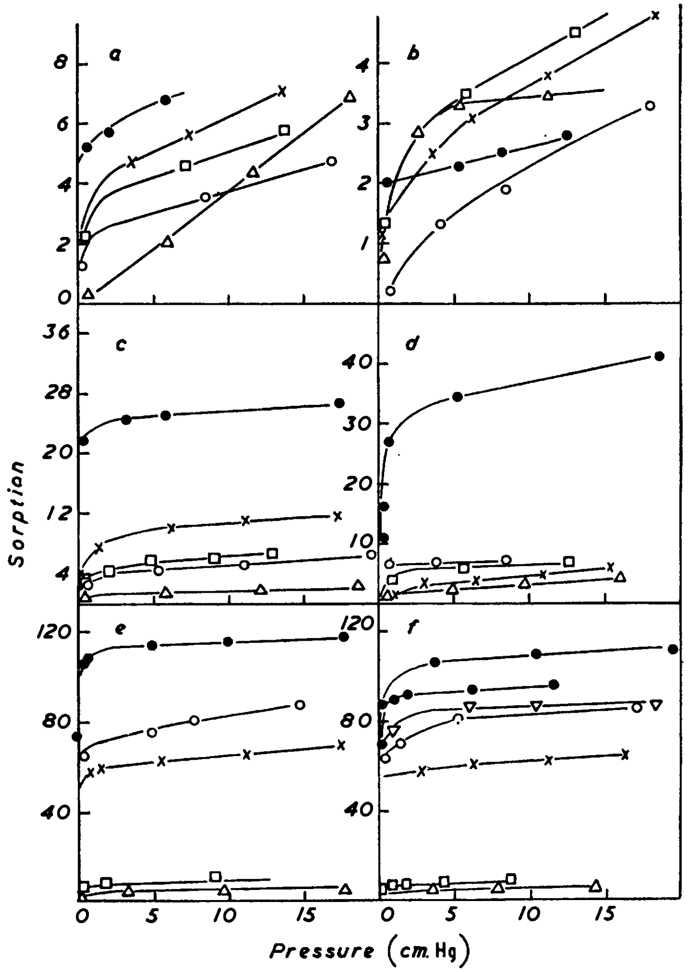
* The first of these materials was synthesised in these laboratories by Mr. F. W. Bultitude, who also measured the sorption isotherm of curve 8; the other was synthesised in the laboratories of Linde Air Products Co., by whom it was kindly supplied.

TABLE 3. *Water molecules per cage in chabazites of varied* $Al_2O_3 : SiO_2$ *ratios.*

$SiO_2 : Al_2O_3$ ratios	Univalent cations per cage	Water molecules per cage		
		K-form	Na-form	Ca-form
2·30	2·57	4·7	5·8	6·3
2·65	2·55	4·8	5·9	6·2
2·72	2·42	5·0	5·5	6·6
3·91	2·03	4·7	5·6	6·2
4·15	2·01	4·3	5·1	5·8
4·9 *	1·74	4·9	5·6	6·2

* Natural chabazite.

FIG. 4. *Isotherms for occlusion of oxygen at* −183° *for different ion-exchanged forms derived from various synthetic* K-*chabazite-like crystals. In Fig. 4a the* $Al_2O_3 : SiO_2$ *ratio of the crystals is* 1 : 2·3; *in Fig. 4b,* 1 : 2·56; *in Fig. 4c,* 1 : 2·65; *in Fig. 4d,* 1 : 2·72; *in Fig. 4e,* 1 : 3·91; *in Fig. 4f,* 1 : 4·15. *Sorption units are cm.*[3] *at S.T.P. for a fixed number of unit cells, viz., that in* 1 *g. of* K-*form with* $SiO_2 : Al_2O_3$ = 4·15.



● Ca⁺⁺; ○ Na⁺; □ K⁺; × Li⁺; △ Rb⁺; ▽ H⁺. *In Fig. 4f, the upper* Ca *curve refers to material hydrothermally extracted at* 200°.

ordinary atmospheric conditions can be calculated (Table 3). The water content per cage is in the order Ca > Na > K. The greater cation concentration is associated, as noted above, with higher anionic framework charge. The water retentivity thus rises with the polarising power of the cations.

While water molecules readily penetrate K-chabazite crystals of all $Al_2O_3 : SiO_2$ ratios, this is not the case with small non-polar molecules such as oxygen and argon. The potassium and rubidium forms of the chabazites of Table 1 were in no case able to occlude appreciable amounts of oxygen at 90° K (Fig. 4). This was true also of the most aluminous of the sodium- and lithium forms (Figs. 4*a*, *b*, *c*, and *d*). However, for the most siliceous crystals (Table 1, samples 5 and 6) the latter two forms have become satisfactory sorbents of oxygen (Figs. 4*e* and *f*).

The Ca-forms of the two most aluminous crystals (Table 1, samples 1 and 2) were also rather poor sorbents of oxygen at 90° K, as shown in Figs. 4*a* and *b*. Ca-forms of samples 3, 4, 5, and 6 moreover showed an increasingly good capacity for occluding oxygen (Figs. 4*c*, *d*, *e*, and *f*). The cation density of the Ca-forms is only half that in the Li-, Na-, K-, and Rb-forms, and this clearly results in improved sorptive capacity for oxygen. The advantage is seen also in the argon isotherms in the Ca- compared with the Na-chabazites (Figs. 5*a* and *b*), and is shown for oxygen as a function of the $Al_2O_3 : SiO_2$ ratio in Fig. 6.

FIG. 5. *Isotherms for occlusion of argon at* —183° *in* Ca-*forms and* Na-*forms respectively of the preparations* 1—6 *of Table* 1. *Each isotherm is given the number of the preparation of Table* 1 *which was used. Sorption units are as for Fig.* 4.

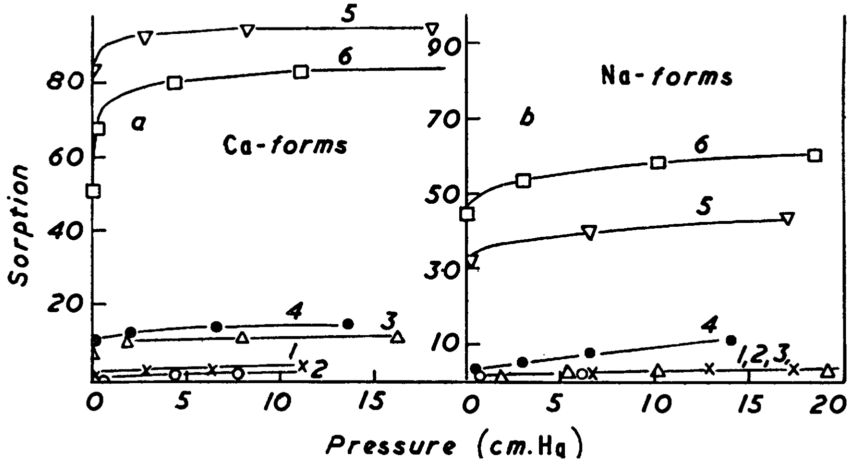
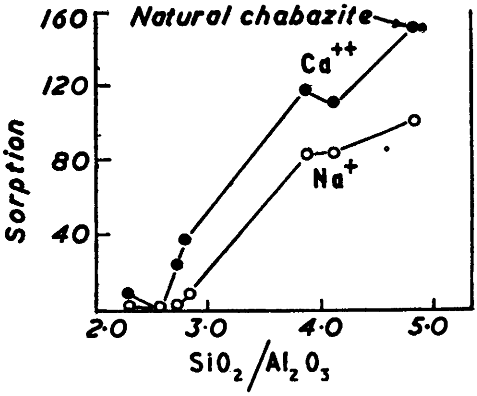


FIG. 6. *Influence of the replacements* (½Ca)Al $\rightleftharpoons$ Si *and* NaAl $\rightleftharpoons$ Si *on the sorption of oxygen at* —183° *and at* 20 *cm.* Hg *pressure in synthetic chabazites. Sorption units are as for Fig.* 4.



In preparing the above Li, Na, Rb, and Ca ion-exchanged forms we used a standard procedure : the parent potassium chabazites were heated with a saturated solution of lithium chloride, sodium chloride, rubidium chloride, or calcium nitrate at 200° for 4 hr. The chabazite crystals were then washed with hot water until free from the exchanging salts.

6. *Sorbent Modification by Factors Additional to Exchange.*—The isotherm results presented in Figs. 4, 5, and 6 establish clearly an influence on the sorption capacity, not

only of the isomorphous replacements LiAl $\rightleftharpoons$ Si, NaAl $\rightleftharpoons$ Si, KAl $\rightleftharpoons$ Si, RbAl $\rightleftharpoons$ Si, and ($\frac{1}{2}$Ca)Al $\rightleftharpoons$ Si, but also of the substitutions Li $\rightleftharpoons$ K, Na $\rightleftharpoons$ K, K $\rightleftharpoons$ Rb for crystals of fixed $Al_2O_3 : SiO_2$ ratios. Here the cation radius changes but not the cation density.

However, such isomorphous replacements and ion exchanges are not the only factors modifying the sorptive powers of the crystals. This is seen in the fluctuations in capacity among the different ion-exchanged forms shown in Fig. 4, where the sequence of sorption capacities is not always the same for crystals having different $Al_2O_3 : SiO_2$ ratios. Moreover, sometimes two preparations of the same exchanged product gave different sorption capacities. This is well seen in Table 4 which gives details of the preparation, ion exchange, composition, and sorption of oxygen and argon at 90° K, of a second group of synthetic chabazite-like phases. The product with $Al_2O_3 : SiO_2 = 1{\cdot}0 : 2{\cdot}50$ has developed a considerable capacity to occlude both gases, well above that shown for oxygen in Figs. 4*b* or *c*.

TABLE 4. *Sorption by a second series of chabazite-like crystals.*

Sample	Gel crystallised	Conditions of crystn.	Ion exchange conditions
7	$K_2O,Al_2O_3,3SiO_2$ + 110% molar excess of KOH + aq.	150° for 4 days	(i) 3 treatments of 12 hr. at 110° with $Ca(NO_3)_2$ aq.
			(ii) 2 further treatments, at 200° for 4 hr., with $Ca(NO_3)_2$ aq.
8	$K_2O,Al_2O_3,4SiO_2$ + 140% molar excess of KOH + aq.	150° for 2 days	(i) 2 treatments of 4 hr. at 200° with $Ca(NO_3)_2$ aq.
9	$K_2O,Al_2O_3,5SiO_2$ + 310% molar excess of KOH + aq.	150° for 4 days	(i) 2 treatments of 4 hr. at 200° with satd. $Ca(NO_3)_2$
10	$K_2O,Al_2O_3,5SiO_2$ + 150% molar excess of KOH + aq.	150° for 2 days	(i) 1 treatment of 12 hr. at 110°, followed by 2 treatments of 4 hr. at 200°, with satd. $Ca(NO_3)_2$

	Molar composition of product					
Sample	K_2O	CaO	Al_2O_3	SiO_2	H_2O	Sorption capacity * (cm.^{3} at S.T.P./g. at 30 cm. Hg)
7	—	0·63	—	—	—	37 (O_2); 30 (A)
	0·17	0·94	1·0	2·50	3·69	86 (O_2); 57 (A)
8	0·07	0·94	1·0	3·60	4·3	89 (O_2); 72·5 (A)
9	0·11	0·89	1·0	3·74	4·27	110 (O_2); 90 (A)
10	0·13	1·0	1·0	3·64	4·65	109 (O_2); 91 (A)

* Outgassing was for 16 hr. at 350°

TABLE 5. K *to* Ca *exchanges in sample* 1 ($K_2O : Al_2O_3 : SiO_2 = 0{\cdot}92 : 1 : 2{\cdot}3$).

Product and isotherm no.*	Mode of exchange †
1	Crystals heated with unsatd. $Ca(NO_3)_2$ soln. for 4 hr. at 200°
2	Crystals heated with satd. $Ca(NO_3)_2$ soln. for 4 hr. at 200° and extracted hydrothermally at 200°
3	Crystals heated with unsatd. CaI_2 soln. for 4 hr. at 200°
4	Product no. 1 further outgassed for 2 days at 350°
5	Crystals heated with satd. $CaCl_2$ soln. for 4 hr. at 200° and extracted with boiling water until free from Cl^-
6	Crystals hydrothermally extracted at 200° and then heated with unsatd. $Ca(NO_3)_2$ soln. for 4 hr. at 200°
7	Crystals heated with satd. solution of $Ca(NO_3)_2$ for 4 hr. at 200° and then hydrothermally extracted at 200°
8	Crystals heated with satd. $Ca(NO_3)_2$ soln. for 4 hr. at 200°
9	Crystals heated with satd. $Ca(NO_3)_2$ soln. for $\frac{1}{2}$ hr. at 200°

* Before use as sorbents, products were outgassed at 350° for ~16 hr., unless otherwise stated.

† Products were washed with hot water after exchanges, unless given alternative treatments as indicated.

The effect of the method of exchange upon the sorption capacity of the Ca-forms of sample 1 was then further studied. The forms were prepared as indicated in Table 5, and the isotherms to correspond are shown in Fig. 7. We were not able to develop a high capacity for oxygen sorption in any of these preparations, even though the cation density

(1·29 Ca^{++} ions per cage) was not excessive. There are, moreover, considerable fluctuations among the capacities, which could not be systematised.

Especially when treated with concentrated salt solutions the crystals tended to occlude salts, and such occlusion could impair the sorptive property. It was for this reason that hydrothermal extraction was sometimes used for removal of salt. For the aluminous crystals of sample 1 the isotherms given in Fig. 7 show that no significant improvement resulted, but for siliceous crystals it is seen from Fig. 4*f* that hydrothermal extraction of the Ca-form considerably increased its sorption capacity. Occlusion of salt probably modifies sorption, but it is not considered to be the only factor.

7. *Relation between Chemical Stability and* $Al_2O_3 : SiO_2$ *Ratio.*—To obtain further information about factors, additional to ion exchange, which can modify the sorptive power of chabazites, an examination was made of the chemical stability of chabazites of different $Al_2O_3 : SiO_2$ ratios.

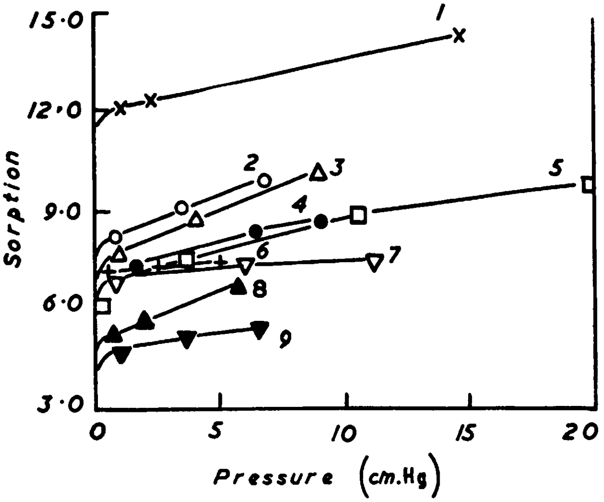


FIG. 7. *Sorptive capacity of* Ca-*chabazites all derived by ion exchange from the most aluminous* K-*chabazite of Table* 1. *The numbers on the isotherms correspond to the preparations of Table* 5. *Sorption units are as for Fig.* 4.

Various methods of obtaining the Ca-form from the most aluminous sample 1 were used (Table 5; Fig. 7). Even when the nitrate was used, the anion was noticeably occluded at 200°. When this occluded salt was removed by hydrothermal extraction, *X*-ray powder photographs of the product gave evidence of partial breakdown of the crystals. This breakdown was, however, not observed when the most siliceous chabazites were extracted. This tendency to breakdown of the crystalline structure was also observed when the most aluminous crystals were subject to prolonged outgassing at 350°.

Ammonium chabazites were then prepared by heating portions of the potassium chabazites of Table 1 with ammonium chloride vapour. The ammonium forms were then heated *in vacuo* at 250°, to yield the hydrogen zeolites ($NH_4Z \longrightarrow HZ + NH_3$). Ammonia was evolved, but with the aluminous chabazites the product had a nosean structure whereas the siliceous crystals did not recrystallise in this way, and the crystals were moreover good sorbents of oxygen at 90° K (Fig. 4*f*). A crystalline product of nosean structure was also obtained when the aluminous chabazite was heated with fused silver nitrate at 250°, in an attempt to obtain its silver form. It is of interest that according to the Wyart structure of chabazite (Section 1) this zeolite has an aluminosilicate framework which is a somewhat distorted nosean framework, so that interconversion may proceed easily.

When the original potassium forms of the aluminous samples of chabazite were repeatedly extracted with water under hydrothermal conditions, the pH of the mother-liquor did not drop below 8. This suggests the continued removal of alkali from the crystals, a process corresponding to their hydrolysis. After outgassing at 250—350° for ~16 hr., the *X*-ray powder photographs again showed the presence of some amorphous material. There is thus evidence of instability of the hydrogen forms of the aluminous chabazites. One reason for this is suggested below.

It is unlikely that the proton in the hydrogen forms of crystalline chabazite exists within the lattice as such. Since in zeolites where Al_2O_3 : base = 1 : 1 every oxygen is shared, hydroxyl groups also cannot be formed unless the oxygen becomes tervalent, which again is improbable. However, the protons will associate with any intracrystalline water molecules to form H_3O^+ ions. After exchange to the hydrogen form the aluminous chabazites, having the higher cation content, must contain a greater concentration of H_3O^+ ions than the siliceous chabazites. This greater inner acidity could result in a relatively greater tendency to decomposition of the aluminous crystals. Moreover, when the crystals are heated *in vacuo*, water is driven off and as soon as the $H_2O : H^+$ ratio drops below unity non-hydrated protons will be released and may rupture bonds in the anionic framework. In aluminous crystals, richer in H_3O^+ ions, the ratio $H_2O : H^+$ drops below unity for a smaller water loss than in the siliceous crystals, which have initially the lower H_3O^+ concentration. This factor will then contribute to the more ready breakdown on outgassing of aluminous as compared with siliceous chabazites.

It may be concluded from the results of Sections 4 and 5 that salt occlusion, alkali removal and so partial hydrogen-ion exchange, and instability during outgassing are at least some of the factors, additional to ion exchange and isomorphous replacements, which may modify the sorption capacity of chabazites.

8. *Sorption and Cation Radius and Position.*—In Section 4 it was pointed out that potassium and rubidium chabazites, however siliceous the crystals, did not occlude appreciable amounts of oxygen or argon at −183°, but that siliceous lithium and sodium chabazites were good sorbents. The cation density in any one crystal is unaltered by such exchanges as $K \rightleftharpoons Na$, but the cation radius does change.

We have to find whether any cation positions will explain the above behaviour. Consider a siliceous crystal having base : $Al_2O_3 : SiO_2$ = 1 : 1 : 4, where there are just two cations per cage. Each cage can be visualised as a sphere of free internal diameter ~7·3 Å. In accordance with Kington and Laing's discussion [8] of the chabazite structure proposed by Wyart,[7] molecule diffusion should occur only along the trigonal axis through the six-membered ring "windows" of ~3·2 Å free diameter. Cations could not be situated in these windows if diffusion is to occur. They could be in any of the remaining six six-membered ring windows of smaller free diameter (~2·3 Å), except that larger ions (K, Rb) could not lie right in the plane of these rings by reason of their size. However, contrary to the sorption results, distributing potassium ions as close to the ring centres as possible would still leave room for molecule diffusion in the case of the siliceous potassium chabazites. Instead, we will consider a model with the cations inside the cages, perhaps adhering to two of the six four-membered rings (Section 1), in positions diametrically opposed and so on opposite sides of the trigonal axis. These positions may vary with time, but the diametrical opposition of the cation pair is likely on energetic grounds, and also provides the best chance for molecule diffusion. For cages of 7·3 Å free diameter such as are found in chabazite, the unobstructed space at the centre of the cage has then the values given in Table 6. The limiting factor in the Li- and Na-forms is still the free diameter (3·2 Å) of the largest six-membered rings, so that molecule diffusion could occur readily. For K-, Rb-, and Cs-forms, however, the limiting factor is the small interionic spacing (2·0—0·78 Å) and diffusion would be inhibited. Thus for siliceous chabazites this ion distribution satisfies the sorption results, or alternatively a distribution where Li^+ and Na^+ lie in some of the smaller six-membered rings, but K^+, Rb^+, and Cs^+ are arranged as above.

TABLE 6.

Cationic form	Ionic diameter (Å)	Unobstructed distance (Å)
Li^+	1·56	(7·3 − 2 × 1·56) = 4·18
Na^+	1·90	3·50
K^+	2·66	2·0
Rb^+	2·96	1·38
Cs^+	3·26	0·78

As the $Al_2O_3 : SiO_2$ ratio changes from 1 : 4 to the limiting value of 1 : 2, the number of univalent cations per cage rises from 2 to 3. With three cations per cage, any clustering of cations inside a cage becomes energetically unfavourable, and the cations will tend to move apart and so to enter the planes of six of the eight six-membered rings in each cage. This just satisfies the requirement of electrical neutrality, since each cation belongs equally to two cages. At least six of eight possible channels to and from each cage are blocked. This arrangement is only possible for Li^+ and Na^+; the larger K^+, Rb^+, and Cs^+ must for steric reasons be displaced to a smaller or greater degree to either side of the planes of the rings.

When $1:2 > Al_2O_3:SiO_2 > 1:4$, and so the cation density falls, only a diminishing number of Li^+ and Na^+ in the planes of six-membered rings is possible. This is true also of the still smaller number of Ca^{++} required for electrical neutrality for *all* $Al_2O_3:SiO_2$ ratios. A purely random ion distribution among all eight six-membered rings would still make diffusion difficult, if we accept Kington and Laing's conclusion [8] that molecule diffusion is only possible along the trigonal axes passing through the two widest six-membered rings. This is because any ion sited in the plane of one of these rings would block diffusion. Even if ions were freely interchanging their positions at room temperatures, such jumps will inolve an activation energy, and ion mobility would almost certainly be frozen out at 90° K. Since however Ca-, Li-, and Na-forms of intermediate $Al_2O_3:SiO_2$ ratios have been shown to be sorbents it appears that any statistical distribution for small ions would have to be confined primarily to the six smaller six-membered rings per cage. Such a distribution ceases to be statistical when the number of cations per cage reaches three, which occurs when $Al_2O_3:SiO_2 = 1:2{\cdot}0$.

The wide range of replacements of the type $NaAl \rightleftharpoons Si$ found in chabazite suggests a statistical distribution of silicon and aluminium in the framework. However, as the ratio $Al_2O_3:SiO_2$ tends to $1:2$ the random character of substitution should disappear for, according to Lowenstein,[10] direct Al–O–Al links cannot occur in a framework of tetrahedra. Randomness can arise increasingly for more siliceous chabazites so that, subject to the above limitation, the aluminium content of any one cage and the associated cation density may vary from cage to cage. In the hydrothermal syntheses the crystals may not all have been precipitated at once, and the first crystals formed could have a somewhat different $Al_2O_3:SiO_2$ ratio from the last. Thus some crystals, or some parts of one crystal, might have sodium-ion densities sufficient to impair the sorption capacity relative to the much smaller total-cation density of the calcium form. We have in fact observed that even the most siliceous Na-chabazites sorb only about two-thirds as much oxygen or argon as their calcium counterparts.

The purpose of this discussion has been, first, to show from simple considerations that cation positions in chabazite should vary according to cation radius and to cation density, with combinations of both effects; secondly, to indicate that cation positions are possible which explain the results we have obtained, and that statistical fluctuations in Al : Si ratios in any one crystal or between successively deposited crystals are possible and must be considered in the interpretation of our observations. These remarks refer not to the hydrated but to the outgassed crystals. We have made numerous *X*-ray measurements on the ion-exchanged dehydrated crystals of different Al : Si ratios, but have not so far succeeded in locating ion-positions in terms of the Wyart structure. This is probably because ion positions change with cation size and with changing Al : Si ratios, and because at least some of the distributions are statistical in character.

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