822. *Hydrothermal Chemistry of Silicates. Part V.* Compounds structurally related to Analcite.*

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Sodium, potassium, rubidium, thallium, and cæsium aluminosilicates based on the analcite structure can be synthesised directly from gels, and Li, NH_4, Ag, and PbOH forms can be made indirectly. These compounds have been considered as a group, and a number of properties compared, including limited solid solubility of some end-members of the family, polymorphism and optical behaviour, relative stabilities in comparison with felspars, and variations of hydration, ion-exchange power, and unit-cell dimensions with radius of the interstitial cation.

Considerable study has been made in this laboratory of analcite and related structures. We present the results of studies of the properties of end-members of what is now shown to be a stable and rather extensive family of structurally related compounds, and where relevant summarise briefly some previously discovered features of the group (Barrer, *J.*, 1950, 2342; Barrer and Hinds, *J.*, 1953, 1879; Part IV*).

A structure has been proposed for the cubic mineral, analcite ($Na_2O,Al_2O_3,4SiO_2,2H_2O$), by W. H. Taylor (*Z. Krist.*, 1930, **74**, 1) and it is also clear that pollucite [$(Na_xCs_{1-x})_2O,Al_2O_3,4SiO_2,2xH_2O$] has a unit cell of the same size as, and is virtually isostructural with, analcite (*e.g.*, Barrer and McCallum, *Nature*, 1951, **167**, 107; Barrer, *loc. cit.*). Leucite, which changes on heating from a low-temperature tetragonal to a high-temperature cubic variety (Wyart, *Bull. Soc. franç. Min.*, 1940, **63**, 5), is also based on an aluminosilicate framework closely allied to that of analcite (*idem, ibid.*; Naray-Szabo, *Z. Krist.*, 1942, **104**,

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* Part IV, preceding paper.

39). Many syntheses of each of these naturally occurring variants of analcite have now been effected (Barrer, *Discuss. Faraday Soc.*, 1949, **5**, 326; Part II, Barrer and White, *J.*, 1952, 1561; Barrer, *J.*, 1950, 2342; Barrer and Baynham, in preparation; Barrer and McCallum, Part IV *). In addition, purely synthetic Ag, NH_4, Li, Tl, and Rb structures of the same type have been prepared (H. F. Taylor, *J.*, 1949, 1253; Barrer, *J.*, 1950, 2342; Barrer and McCallum, Part IV; Barrer and Hinds, *loc. cit.*). Some members have proved more stable than corresponding felspars, and in certain directions the analcite group shows a remarkable range in properties.

Immiscibility Gaps in Analcite Crystals containing two Cations.—The procedure described in Part IV (*loc. cit.*) was adopted to investigate mutual solid solubility in the systems $Tl_2O,Al_2O_3,4SiO_2–Rb_2O,Al_2O_3,4SiO_2$; $Tl_2O,Al_2O_3,4SiO_2–Na_2O,Al_2O_3,4SiO_2,2H_2O$; $Na_2O,Al_2O_3,4SiO_2,2H_2O–Cs_2O,Al_2O_3,4SiO_2$; $Rb_2O,Al_2O_3,4SiO–K_2O,Al_2O_3,4SiO_2$; and $Rb_2O,Al_2O_3,4SiO_2–Na_2O,Al_2O_3,4SiO_2,2H_2O$. Gels containing two cations were crystallised hydrothermally and the crystals studied optically and by *X*-ray powder photography.

The gels of different cationic compositions are summarised in Table 1. In all these gels the ratio of total bases : alumina : silica = 1 : 1 : 4 as in analcite. Typical results of the hydrothermal crystallisations of the gels in Table 1 are given in Table 2. From the gels containing the cation pairs Na–Tl, Rb–Tl, and Na–Rb the end-products of crystallisation frequently contained analcite-type structures of two kinds, as assessed by the refractive indices and the *X*-ray powder patterns. For example, in the mixture of crystals grown from the Tl–Na-containing gels two types of diffraction pattern were sometimes superimposed. One of these was very similar to the pattern of the end-member $Tl_2O,Al_2O_3,4SiO_2$, and the other closely resembled the pattern of the end-member $Na_2O,Al_2O_3,4SiO_2,2H_2O$. The refractive indices of the crystals were, however, intermediate between those of the pure end-members. Accordingly, there is limited solid solubility of each end-member in the other.

TABLE 1. *Cationic composition and nomenclature of mixed gels.*

Na_2O	K_2O	Rb_2O	Cs_2O	Tl_2O	Nomenclature
0·2	—	—	—	0·8	TNA
0·4	—	—	—	0·6	TNB
0·6	—	—	—	0·4	TNC
0·8	—	—	—	0·2	TND
—	—	0·2	—	0·8	TRE
—	—	0·4	—	0·6	TRF
—	—	0·6	—	0·4	TRG
—	—	0·8	—	0·2	TRH
0·2	—	0·8	—	—	NRA
0·4	—	0·6	—	—	NRB
0·6	—	0·4	—	—	NRC
0·8	—	0·2	—	—	NRD
0·2	—	—	0·8	—	CNA
0·4	—	—	0·6	—	CNB
0·6	—	—	0·4	—	CNC
0·8	—	—	0·2	—	CND
—	0·4	0·6	—	—	KRB
—	0·6	0·4	—	—	KRC

Limits of solubility were estimated by measurement of refractive indices, a linear relation being assumed between refractive index and cationic composition. The refractive indices of the end-members are given in Table 3, and were determined on specimens grown from gels containing only one cation. The actual refractive indices of the crystals grown from the gels of mixed cationic composition then give by simple proportion the cationic compositions of the crystals.

In the Tl–Rb series those products rich in rubidium gave *X*-ray patterns which indicated that the crystals were composed of domains of the polymorphic forms B and H of rubidium analcite described in Part IV. For these crystals a R.I. of 1·508 was taken. On the other hand, the *X*-ray powder photographs of the Tl-rich crystals were those of polymorph B, so that a value of the R.I. of 1·521 was used in calculating the Rb content of Tl-analcite.

The limits of solid solubility are then given in Table 5 for various pairs. The limits of solubility of the Tl–Rb analcites are here particularly interesting because Rb and Tl have virtually identical univalent ionic radii. Accordingly, ion size alone does not govern the effect.

Products from the Na–Rb aluminosilicate gels consisted of mixtures of analcitic crystals. Those rich in Rb were again composed of domains of B and H of mean R.I. ~1·508. An immiscibility gap arose between Rb-rich and Na-rich crystals (cf. Table 5) and often a characteristic zoning was observed. In crystallisations of Na-rich gels above 350° albite and other species tended to replace analcite. The Na–Cs aluminosilicate gels gave only crystals of uniform refractive indices ranging in different preparations between 1·503 and 1·521. This shows that continuous solid solutions were obtained over a substantial composition range. Cæsium was concentrated relative to sodium in the crystals rather than in the solution.

TABLE 2. *Crystallisation of gel preparations containing* Tl *and* Na *or* Rb.

Nomenclature of parent gel	Temp.	Conditions of expt.	Optical examination	*X*-Ray examination
TNA	200°	Excess NaOH; pH>10	Tl-analcite, R.I. 1·596	Tl-analcite
TNA	350	Excess NaOH; pH>10	Tl-analcite, R.I. 1·596	—
TNA	400	H_2O; pH ~8	Tl-analcite, R.I. 1·607	Tl-analcite
TNA	450	Excess NaOH; pH>10	Tl-analcite, R.I. 1·596	—
TNB	350	Excess NaOH; pH>10	Tl-analcite, R.I. 1·594, and cancrinite	Tl-analcite and cancrinite
TNC	200	Excess NaOH; pH>10	Na-analcite, R.I. 1·501, and compound B of H. F. Taylor (*loc. cit.*) ($Tl_2O,Al_2O_3,2SiO_2$)	Na-analcite
TNC	250	Excess NaOH; pH>10	Na-analcite, R.I. 1·501, and compound B of H. F. Taylor (*loc. cit.*)	—
TNC	350	Excess NaOH; pH>10	Cancrinite $\varepsilon = 1·51$, and Na-analcite, R.I. 1·501	Cancrinite
TNC	450	Excess NaOH; pH>10	Cancrinite $\varepsilon = 1·51$	Cancrinite
TND	200	H_2O; pH ~10	Cancrinite $\varepsilon = 1·50$	Cancrinite
TND	250	Excess NaOH; pH>10	Na-analcite, R.I. 1·51	Na-analcite
TND	400	Excess NaOH; pH>10	Cancrinite $\varepsilon = 1·503$	Cancrinite
TRE	250	Excess RbOH; pH>10	Analcite, R.I. 1·62, and analcite, R.I. 1·54	—
TRE	350	Excess RbOH; pH>10	Analcite, R.I. 1·62, and analcite, R.I. 1·54	—
TRF	350	Excess RbOH; pH>10	Analcite, R.I. 1·62, and analcite, R.I. 1·54	—
TRG	350	Excess RbOH; pH>10	Analcite, R.I. 1·54, and analcite, R.I. 1·62	—
TRH	250	Excess RbOH; pH>10	Analcite, R.I. 1·535, and analcite, R.I. 1·625	—
TRH	350	Excess RbOH; pH>10	Analcite, R.I. 1·535, and analcite, R.I. 1·62	—
TRH	250	H_2O; pH ~10	Analcite, R.I. 1·525	—

TABLE 3. *Refractive indices of some analcitic compounds.*

Crystals	R.I.	Crystals	R.I.
$Na_2O,Al_2O_3,4SiO_2,2H_2O$	1·486	$Rb_2O,Al_2O_3,4SiO_2$ (domains of B and H)	1·508 (mean)
$K_2O,Al_2O_3,4SiO_2$ (leucite)	1·512		
$K_2O,Al_2O_3,4SiO_2,2H_2O$	1·490	$Rb_2O,Al_2O_3,4SiO_2$ (H)	1·481
$Rb_2O,Al_2O_3,4SiO_2$ (B)	1·521	$Cs_2O,Al_2O_3,4SiO_2$	1·523
		$Tl_2O,Al_2O_3,4SiO_2$	1·637

The results on crystallisation of K–Rb analcites are not easy to interpret, owing to the occurrence of polymorphic forms of Rb-analcite (Part IV, and also next section). and because neither Rb-analcite B nor crystals consisting of domains of Rb-analcites B and H differ very greatly in refractive indices from leucite (cf. Table 3). However, analyses were made * of K and Rb in a number of crystalline K–Rb-analcites, which were also submitted to examination by *X*-ray powder photography. The results are presented in Table 4. In cols. 2 and 3 the initial and final cationic mole-fractions of potassium are given for the products referred to in col. 1. Finally, some, but by no means all, of the *d*-spacings are given.

It is first seen that neither cation was very greatly enriched at the expense of the other

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in the final analcitic crystals as compared with the original gel. This result is in contrast to the enrichment of the reaction product in potassium when mixed Rb–K-felspar crystals are formed (Part IV, and also preparation No. 6 of Table 4). The *X*-ray data of Table 4 contain some spacings which are nearly constant for all preparations (*e.g.*, that at 2·65 Å), together with others which show a steady change as the potassium content increases, such as that at 1·815 Å for Rb-analcite B. Finally, some spacings vary in a rather irregular way, for instance that at 5·40 Å for leucite. In preparation No. 5 the crystals are closer in their pattern to Rb-analcite H rather than to B, so structures based on either polymorph of Rb-analcite can appear in mixed K–Rb–analcites.

TABLE 4. *Cationic composition and d-spacings in* Rb–K-*analcites.*

Preparation from gel	Initial mole-fraction of K in gel	Final mole-fraction of K in crystals	Some typical *d*-spacings, in Å				
1. Pure Rb-analcite (B)	0	0	—	—	3·61 (s)	3·40 (s)	3·31 (s)
2. KRB and aq. RbOH at 300°	0·40	0·32	5·40 (vw)	4·79 (vvw)	—	3·42 (s)	3·33 (vs)
3. KRB and aq. KOH at 400°	0·40	0·36	5·49 (vw)	4·76 (vw)	3·59 (s)	3·44 (s)	3·31 (vs)
4. KRB and water at 400°	0·40	0·51	5·47 (vw)	—	3·59 (s)	3·43 (s)	3·31 (vs)
5.* KRC and water at 400°	0·60	0·58	5·51 (w)	4·83 (vw)	3·61 (ms)	3·45 (s)	3·32 (vs)
6.† KRA and aq. KOH at 250°; then heated to 1250°	0·20	0·63	5·48 (ms)	4·77 (vvw)	3·59 (ms)	3·37 (vs and diffuse)	
7. KRC and aq. KOH at 400°	0·60	0·66	5·48 (vw)	4·77 (vvw)	—	3·43 (vs)	3·30 (vs)
8. Leucite (K-analcite)	1·00	1·00	5·40 (ms)	4·72 (vvw)	—	3·43 (vs)	3·22 (vs)
9. Pure Rb-analcite (H)	0	0	5·55 (w)	4·84 (vvw)	3·62 (m)	3·38 (vs)	

	Some typical *d*-spacings, in Å								
1.	3·16 (s)	2·98 (m)	2·87 (vs)	2·65 (s)	2·38$_1$ (s)	2·16$_8$ (s)	1·96$_8$ (m)	1·85$_5$ (w)	1·815 (m)
2.	3·16 (vw)	2·97 (ms)	2·86 (vs)	2·65 (m)	2·38 (s)	2·16$_6$ (ms)	1·96$_3$ (vw)	1·84$_8$ (w)	1·812 (mw)
3.	3·13 (vvw)	2·97 (s)	2·86 (vs)	2·65 (m)	2·38 (s)	2·16$_0$ (s)	1·95$_9$ (w)	—	1·811 (ms)
4.	—	2·97 (ms)	2·86 (s)	2·65 (m)	2·38$_6$ (s)	2·15$_6$ (ms)	1·95$_0$ (vw)	1·84$_2$ (vw)	1·814 (w)
5.	—	2·99 (ms)	2·87 (s)	—	2·38$_8$ (ms)	2·16$_3$ (m)	1·95$_1$ (vw)	1·82$_7$ (vw)	1·802 (m)
6.	3·17 (vvw)	2·97 (w)	2·86 (vs)	2·64 (w)	2·38$_3$ (s)	2·17$_3$ (w & diffuse)	1·94$_9$ (vvw)	1·83$_4$ (w)	1·802 (w)
7.	3·12 (vw)	2·95 (m)	2·85 (s)	2·65 (w)	2·42$_0$ (ms)	2·15$_3$ (ms)	1·93$_9$ (vw)	—	1·801 (m)
8.	—	2·90 (s)	2·81 (s)	2·64 (m)	2·36$_8$ (s)	2·14$_0$ (ms)	1·94$_9$ (w)	1·85$_8$ (w)	1·778 (mw)
9.	—	2·89 (s)	2·76 (vvw)	2·65 (mw)	2·38$_6$ (ms)	2·19 (m)	1·94$_4$ (vvw)	1·83$_6$ (ms)	—

* These crystals are closer to Rb-analcite (H), the polymorphic form, than to Rb-analcite (B).

† This product initially consisted of crystallites of a Rb–K-felspar. Heating at 1250° converted it into Rb-analcite (B). The $Al_2O_3 : SiO_2$ ratio in this gel was not 1 : 4 as in analcite, but 1 : 4·5 (Part IV).

TABLE 5. *Approximate solid solubility limits in analcitic compounds.*

Pair of compounds	Mean solid solubility limits,	%
$Tl_2O,Al_2O_3,4SiO_2$–$Rb_2O,Al_2O_3,4SiO_2$	Tl- in Rb-compound	20
	Rb- in Tl-compound	11
$Tl_2O,Al_2O_3,4SiO_2$–$Na_2O,Al_2O_3,4SiO_2,2H_2O$	Tl- in Na-compound	10
	Na- in Tl-compound	27
$Rb_2O,Al_2O_3,4SiO_2$–$Na_2O,Al_2O_3,4SiO_2,2H_2O$	Rb- in Na-compound	30
	Na- in Rb-compound	30
$Cs_2O,Al_2O_3,4SiO_2$–$Na_2O,Al_2O_3,4SiO_2,2H_2O$	Continuous solid solubility	

In none of the *X*-ray powder photographs, of which Table 4 includes only a fraction, was there evidence of the co-existence of two types of pattern such as that of Rb-B or -H together with that of leucite. Although the very close similarity of the patterns of Rb-B and of leucite may obscure this evidence, the data are compatible with continuous solid solubility between Rb-analcites and leucite. This view is supported by the approximately equal affinity for Rb and for K shown by the analcite frame-work during its formation in the presence of both these ions (*loc. cit.*).

Ion-exchange experiments at temperatures not above 110° have also demonstrated immiscibility gaps for the pairs $Na_2O,Al_2O_3,4SiO_2,2H_2O$–$K_2O,Al_2O_3,4SiO_2$; $Na_2O,Al_2O_3,4SiO_2,2H_2O$–$Tl_2O,Al_2O_3,4SiO_2$; $K_2O,Al_2O_3,4SiO_2$–$Tl_2O,Al_2O_3,4SiO_2$ (Barrer and Hinds, *loc. cit.*). Thus limited solid solubility is rather general and has been observed over a range at least of 300°.

Polymorphism among Analcitic Structures.—In Part IV two rubidium compounds B and H were prepared both based upon the analcite structure. These hydrothermal crystallisations occurred from gels $Rb_2O,Al_2O_3,nSiO_2$ where $3<n<10$. The refractive index of the crystals depended upon the conditions of formation, the most important of which was the value of n. Average R.I.'s for different values of n are tabulated below.

n	3	4·05	6	7
R.I.	1·507—1·512	1·504—1·509	1·495—1·500	1·500—1·504

The lowest refractive indices occurred for $n = 6$.

Although the crystals appeared under the microscope to be well developed, practically all gave *X*-ray powder photographs with very diffuse lines. When the crystals were heated above 1200° sharp lines characteristic of species B were obtained and the R.I. changed to 1·521. The speed of this reaction increased markedly with rising temperature. On the other hand, if the crystals were heated below about 1050° they very slowly approached an R.I. of 1·481. The higher the refractive index of the initial material the more sluggish was the reaction. At an R.I. of 1·50 or less, the *X*-ray pattern characteristic of species H became dominant. It seems that any crystal of Rb-analcite prepared hydrothermally consists of very small domains of both compounds B and H.

Typical changes of refractive index following heat treatment of domain crystals are shown in Table 6. Identical treatments may transform different crystals of the same preparation from B into H at different rates, some crystals scarcely changing at all. Both forms of Rb-analcite could also be prepared by sintering Rb-felspar. Species H resulted between 910° and 1070°, and species B above 1070°. The sluggishness of the transition between B and H suggests that it is of the reconstructive rather than the displacive type (Smoluchowski, Mayer, and Weyl, " Phase Transformations in Solids," 1951, Wiley, p. 183) exhibited by the change of leucite from tetragonal to cubic habit at 625° (Wyart, *loc. cit.*). A possible reconstructive process might be an order–disorder transformation of the Si and Al ions in the aluminosilicate framework. Both R.I. and unit-cell dimensions show that the species B is more compact than the species H.

Rb-analcite, prepared by ion exchange from synthetic Na-analcite by Barrer (*J.*, 1950, 2342), also appeared from its *X*-ray pattern to consist of crystals which were a mixture of domains of B and H. Similarly prepared Tl-analcite was extremely close to this mixed Rb-analcite in its *X*-ray powder photograph, and may comprise two polymorphic forms of the same type. For this reason no attempt to index the pattern to give a unit cell of the Tl-analcite of Table 7 has been made. Pollucite ($Cs_2O,Al_2O_3,4SiO_2$) also gave evidence of variable refractive index in different preparations, without however showing corresponding changes in *X*-ray pattern (Part IV).

TABLE 6. *Changes of refractive index of* Rb-*analcites on heating.*

Heat treatment	Initial R.I.	Final R.I. (average)
1400° for 2 days	1·504	1·521
1600° for 1 day	1·504	1·521
1230° for 2 days	1·504	1·521
1400° for 2 days	1·497	1·521
880° for 7 days	1·512	1·505
880° for 1 day	1·497	1·493
880° for 10 days	1·497	1·481 (uniform)
1230° for 1 day and then 880° for 2 days	1·521	1·514—1·521
1230° for 1 day and then 880° for 21 days	1·521	1·492—1·516
500° for 6 days	1·497	1·483

A further example of polymorphism was observed with crystals of potassium analcite composition. Potassium analcite obtained from synthetic analcite by exchange of Na with K (Barrer, *J.*, 1950, 2342; Barrer and Hinds, *loc. cit.*) and also directly from gels (Barrer and Baynham, in preparation) was identical with leucite ($K_2O,Al_2O_3,4SiO_2$). However, direct syntheses in the range 200—450° also resulted under certain conditions in the formation of a true potassium analcite ($K_2O,Al_2O_3,4SiO_2,2H_2O$). The product obtained at 200° had an R.I. of 1·490 and was cubic with a unit-cell of edge $13{\cdot}7_9$ Å. Heating this product for 4 days at 250° caused it to lose 5·09% by weight of water; at 350° this loss increased to 6·2%. On heating at 450° for 6 days the R.I. dropped to ~1·420 but was not uniform in all crystals. These were still cubic and indexed to give $a = 13{\cdot}7_1$ Å.

When the crystals were sintered at 800° some potash felspar spacings began to appear. At the same time the R.I., which was not uniform, rose to 1·502—1·514. Heating the crystals to 1000° and quenching converted the potassium analcite into potash felspar as the only crystalline product. In contrast to the rubidium analcites B and H, the compounds $K_2O,Al_2O_3,4SiO_2,2H_2O$ and $K_2O,Al_2O_3,4SiO_2$ (leucite) are not interconvertible. The change of the former into potash felspar is paralleled by a similar conversion of analcite into albite (Barrer and White, *J.*, 1952, 1561).

Relative Thermal Stability of Analcites and Felspars.—As noted above, analcite and hydrated potassium analcite are converted into albite and potash felspar by heat. These felspars are accordingly more stable to heat than are the corresponding analcites. However, leucite is stable to heat, while orthoclase melts incongruently at about 1150° to leucite and a glass, from which it is re-formed on cooling. It has, moreover, been shown (*loc. cit.*) that the low-temperature polymorph of Rb-analcite is changed by heat, not to Rb-felspar, but to the high-temperature form of Rb-analcite, which remains stable up to the m. p. of about 1675°. On the other hand, heating Rb-felspar converts it into the high or low polymorph of Rb-analcite (and glass), according to the temperature. Cs-analcite (pollucite) was thermally stable under all conditions, and Cs-felspar could not be synthesised at all (Part IV). Thus several of the analcites are more stable structures than are the corresponding felspars.

It seems likely from the above stability relations that if Rb or Cs were abundant elements the corresponding analcites would be the geochemically significant species, rather than the felspars. Leucite is already known as a major constituent of certain magmas (Shand, " Rocks for Chemists," 1952, Allen and Unwin, p. 85).

Interstitial Cations.—The cations Li^+, Na^+, K^+, and Cs^+, and also Ag^+, Tl^+, NH_4^+, and $(PbOH)^+$, have all been introduced into aluminosilicate frameworks of analcite type (Barrer, *J.*, 1950, 2342; Barrer and Hinds, *loc. cit.*). The ability of this structure to accommodate univalent ions exceeds that of the felspar framework which has been obtained only in Na, K, and Rb forms. On the other hand, only small amounts of bivalent ions can be introduced into analcite, whereas Ca^{++}, Sr^{++}, Ba^{++}, and Pb^{++} at least can occur in high proportion in the felspar framework.

Simple relations between the unit cells of cation-exchanged forms of analcite can be correlated with ion size (Table 7). With Li^+, Na^+, and Ag^+, the three smallest ions, the structures contain zeolitic water, and the crystals have all the properties of zeolites. With the potassium ion, one of two things may happen : either a crystal is formed with zeolitic water and with appreciable expansion of the unit cell, or there is some collapse to give the anhydrous tetragonal leucite structure. An anhydrous tetragonal structure appears also with NH_4^+, Rb^+, and Tl^+. These ions, though larger than K^+, are still not so large as Na^+,H_2O, considered as a space-filling unit. Accordingly, as with leucite, these unit cells are slightly collapsed relative to that of the hydrated Na-form, but as expected the unit cells are slightly larger than that of leucite. The largest ion, Cs^+, considered as a space-

TABLE 7. *Some properties of members of the analcite group.*

Cation	Radius (Å)	Unit cell	Hydrated	Ion-exchange
Li^+	0·78	Cubic; $a = 13{\cdot}5$ *	Yes	Yes
Na^+	0·98	Cubic; $a = 13{\cdot}6_6$ †	Yes	Yes
Ag^+	1·13	Cubic; $a = 13{\cdot}7$ †	Yes	Yes
K^+	1·33	(*a*) Cubic; $a = 13{\cdot}7_9$ ‡	Yes	Yes
		(*b*) Tetragonal; $a = 12{\cdot}9_2$; $c = 13{\cdot}7_0$ ‡	No	Yes
NH_4^+	1·43	Tetragonal; $a = 13{\cdot}1_7$; $c = 13{\cdot}6_9$ †	No	Yes
Rb^+	1·48	(*a*) Tetragonal; $a = 13{\cdot}6_4$; $c = 13{\cdot}3_3$**	No	Yes
		(*b*) Tetragonal; $a = 13{\cdot}2$; $c = 13{\cdot}6$**	No	Yes
Tl^+	1·49	Tetragonal †	No	Yes
Cs^+	1·63	Cubic; $a = 13{\cdot}6_6$ †	No	No

* Barrer and Hinds (*loc. cit.*).
† Barrer, *J.*, 1950, 2342, or based on this work.
‡ Barrer and Baynham, in preparation.
** Part IV, *loc. cit.*

filling unit, is equal to Na^+,H_2O, so the unit cell is of identical dimensions in analcite ($Na_2O,Al_2O_3,4SiO_2,2H_2O$) and pollucite ($Cs_2O,Al_2O_3,4SiO_2$).

Among the anhydrous forms, those with K, NH_4, Rb, and Tl have the ion-exchange properties of nosean–sodalite felspathoids, but the Cs-form has lost even this property, each Cs^+ ion being locked in its own interstice. Accordingly, there is a remarkable range in properties from zeolites (Li, Na, Ag, and sometimes K) to a crystal which has neither zeolitic water nor ion-exchange power. These changes in properties, including the dimensional changes in the unit cells of the ion-exchange forms, are all correlated directly with cation size.

Isomorphous Replacement in the Aluminosilicate Anion.—Cation replacements can clearly be extensive in the analcite-type structures. However, replacements in the aluminosilicate framework are also known. Thus, Goldsmith (*J. Geol.*, 1950, **58**, 518) has prepared a gallium leucite, $K_2O,Ga_2O_3,4SiO_2$, in which Al^{34} is replaced by Ga^{34}. Viseite, according to McConnell (*Amer. Min.*, 1952, **37**, 609), has a structure remarkably close to that of analcite, but one in which some SiO_4^{4-} or AlO_4^{5-} tetrahedra are believed to be replaced by PO_4^{3-} in the aluminosilicate anion. Moreover, a compound $K_2O,MgO,5SiO_2$ has recently been prepared which gives an X-ray powder pattern very close to that of leucite, with which it exhibits complete miscibility (Roedder, *Amer. J. Sci.*, 1951, **249**, 224). There is also a ferrous analogue, $K_2O,FeO,5SiO_2$, which again appears similar in structure to leucite (*idem ibid.*, Bowen Volumes, 1952, 435). It is thus apparent that the analcite type of structural framework persists among a wide variety of species of very different chemical compositions.

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