821. *Hydrothermal Chemistry of Silicates. Part IV.* Rubidium and Cæsium Aluminosilicates.*

By R. M. Barrer and N. McCallum.

Hydrothermal crystallisation of rubidium aluminosilicate gels, in the temperature range 160—450° and over the composition range $Rb_2O,Al_2O_3,nSiO_2$ where $1 < n < 10$, has yielded six new mineral type species. These included two modifications of the rubidium counterpart of analcite, and also the rubidium form of potash felspar. Crystallisation of the corresponding cæsium aluminosilicate gels under the same conditions yielded two compounds of which one was a pure cæsium pollucite while the other has no naturally occurring analogue. Two of the rubidium compounds were hydrated and one of these at least was probably a zeolite.

The mutual solid solubility of several pairs of crystal species with allied structures was studied by crystallisation of the appropriate aluminosilicate gels containing various proportions of two cations. It was found that thallium can replace rubidium in the rubidium felspar over a wide but not complete range of cationic composition, while it is likely that rubidium and potassium felspars are miscible in all proportions. The structurally similar compounds $Cs_2O,Al_2O_3,2SiO_2$ and $Rb_2O,Al_2O_3,2SiO_2$ form a continuous range of solid solutions.

Rubidium and cæsium are often concentrated together during magmatic differentiation. However, probably owing to their chemical similarity to potassium, they do not form species of their own but instead give isomorphous replacement of potassium, sodium, and one or two other elements. So much is this the case that no natural rubidium aluminosilicates are known, and only one cæsium aluminosilicate. This is the mineral pollucite which may be formulated as $(Cs_xNa_{1-x})_2O,Al_2O_3,4SiO_2,2(1-x)H_2O$ (Barrer and McCallum, *Nature*, 1951, **167**, 1071). Early in the present programme H. F. Taylor (*J.*, 1949, 1253) synthesised a number of relatively stable thallium aluminosilicates, thus demonstrating that failure to observe such aluminosilicates in mineralogy is a result only of insufficient concentration of this element in crystallising magmas. Barrer and White (Part I, *J.*, 1951, 1267) similarly added several purely synthetic lithium aluminosilicates to the small total of such species known to occur naturally. It may then be expected that a variety of rubidium and cæsium aluminosilicates could be grown under laboratory conditions provided there is no intrinsic difficulty in accommodating these larger cations within framework structures. The comparable ionic radii of some of these cations are: K^+, 1·33; Rb^+, 1·49; Tl^+, 1·48; Cs^+, 1·63 Å; and can explain known associations of K–Rb, Rb–Tl, and Rb–Cs. The occurrence of Rb and Cs in lepidolite, a lithium-rich mica, can be understood because all these ions occur between sheets which may move apart to accommodate cations of different dimensions. Such accommodations cannot always be made in rigid three-dimensional frameworks. Schiebold (*Neues Jahrb. Min. Geol.*, Beilage-Bd., 1931, **64**, *A*, 251) nevertheless considered on theoretical grounds that rubidum and cæsium felspars could be formed, but no experimental work has yet been offered in test of this. The present paper is therefore concerned with synthetic rubidium and cæsium aluminosilicates.

Experimental

Hydroxides of rubidium and cæsium were prepared by the reaction $M_2SO_4 + Ba(OH)_2 = 2MOH + BaSO_4$, where M = Rb or Cs. The alkali hydroxide was then stored in absence of carbon dioxide. Aluminium hydroxide was obtained by the action of water upon lightly amalgamated aluminium. Silica gel was supplied by British Drug Houses Ltd. Hydrothermal extraction of a sample of the gel at 200° gave a mother-liquor neutral in reaction and free from common inorganic anions. The series of gels of composition $M_2O,Al_2O_3,nSiO_2,mH_2O$ $(1 < n < 10)$ were made by mixing the constituents in the correct proportions and evaporation to dryness on a steam-bath.

---

* Part III, *J.*, 1953, 1466.

The gels were crystallised hydrothermally in silver test-tubes placed inside stainless-steel autoclaves of a type described in Part I (*loc. cit.*). The crystallisations were investigated between 160° and 450°. After the autoclaves had been kept at a fixed temperature for a chosen time they were quenched in cold water. The products were then examined optically and by *X*-ray examination, and the pH of the cold mother-liquor was measured to the nearest 0·2 unit.

Pyrolytic investigations * were carried out between 850° and 1800°. Below 1500° a furnace tube of ΔRR crystallised alumina was wound with platinum tape. Temperatures were measured with a Pt–(Pt + 13% Rh) thermocouple. The compositions prepared for investigation were wrapped in platinum envelopes and placed in a ΔRR alumina crucible. Equilibrium in the investigated compositions was approached for each temperature in two ways : by heating a crystallisation previously made hydrothermally, and by heating an intimate mixture of M_2CO_3, Al_2O_3, and SiO_2 (M = Rb or Cs) in the same proportions, in separate envelopes. In each case heating was continued until the same end-product was obtained. The crucible, after being heated for a given time, was air-quenched. Above 1500° a molybdenum-wound furnace was employed, the temperature being measured by optical pyrometer.

Results.—Species obtained hydrothermally in major or considerable yields are given in Table 1, and the experiments are summarised in Table 2. Species A (Plate 1) and F (Plate 2) have, according to the *X*-ray data of Table 4, the same aluminosilicate framework, the cæsium compound being slightly expanded relative to the rubidium one. There is also a less striking similarity between A and F and the species $Tl_2O,Al_2O_3,2SiO_2$ (H. F. Taylor, *loc. cit.*). Refractive indices of A and F were respectively 1·531 and 1·574. The rubidium compound appeared as very small apparently isotropic crystals. It gave no evidence of exchange with saturated aqueous potassium chloride or cæsium sulphate at 110° during 4 days. The melting points of both A and F were above 1750°.

TABLE 1. *Synthetic rubidium and cæsium aluminosilcates.*

Ref. letter	Oxide formula	Name	Ref. letter	Oxide formula	Name
A	$Rb_2O,Al_2O_3,2SiO_2$	—	D	$Rb_2O,Al_2O_3,2SiO_2,H_2O$	—
B	$Rb_2O,Al_2O_3,4SiO_2$	Rb-analcite I *	E	$Rb_2O,Al_2O_3,6SiO_2,H_2O$	—
H	$Rb_2O,Al_2O_3,4SiO_2$	Rb-analcite II *	F	$Cs_2O,Al_2O_3,2SiO_2$	—
C	$Rb_2O,Al_2O_3,6SiO_2$	Rb-felspar	G	$Cs_2O,Al_2O_3,4SiO_2$	Pollucite

* See following paper (Part V).

TABLE 2. *Hydrothermal crystallisations of hydrated gels under alkaline conditions.*

(1) $Rb_2O,Al_2O_3,nSiO_2$.

Value of *n*	Crystallisation temperatures							
	165°	180°	200°	250°	300°	350°	400°	450°
1	—	A + D	A	A	A	A	A	A
2	D	D	A	A	A	A	A	A
3	—	D	B + A	B + A	B + A	B + A	B + A	B + A
4	—	D	B	B	B	B	B	B
5	—	B	B	B	B	B	B	B
6	E	E	H	H	C	C	C	C
7	—	E	H	H + quartz	C + quartz	C + quartz	C + quartz	C + quartz
8	—	E	H	H + quartz	C + quartz	C + quartz	C + quartz	C + quartz
9	—	E	H	H + quartz	C + quartz	C + quartz	C + quartz	C + quartz
10	—	—	H	H + quartz	C + quartz	C + quartz	C + quartz	C + quartz

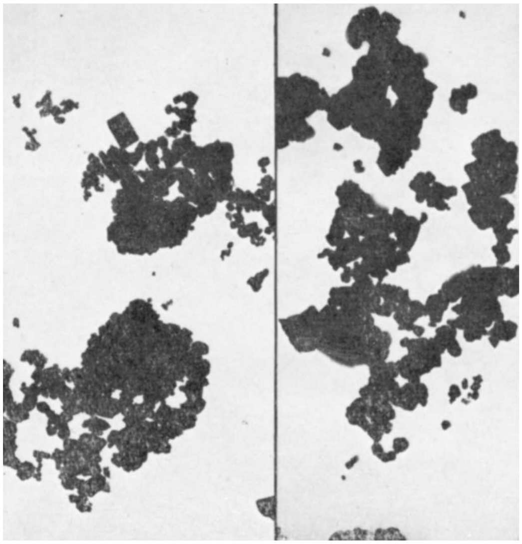
(2) $Cs_2O,Al_2O_3,nSiO_2$.

	160°	200°	250°	300°	350°	400°	450°
1	G + F	F	F	F	F	F	F
2	G	G	F + G	F	F	F	F
3	—	G	G	F + G	F + G	F + G	F + G
4	G	G	G	G	G	G	G
5	G	G	G	G	G	G	G
6	G	G	G + quartz	G + quartz	G + quartz	G + quartz	G + quartz
7	G	G	G + quartz	G + quartz	G + quartz	G + quartz	G + quartz
8	G	G	G + quartz	G + quartz	G + quartz	G + quartz	G + quartz
9	—	G	G + quartz	G + quartz	G + quartz	G + quartz	G + quartz
10	G	G	G + quartz	G + quartz	G + quartz	G + quartz	G + quartz

---

* Experiments above 1500° were carried out in the laboratories of Dr. L. R. Barrett, Chemical Engineering Dept., Imperial College of Science and Technology, London.

Plate 1.

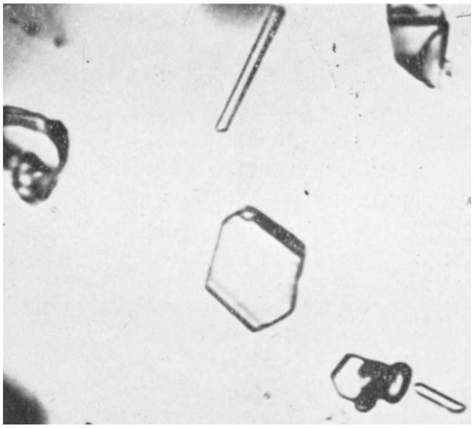


Species A.
$(Rb_2O,Al_2O_3,2SiO_2)$
from gel (1 : 1 : 2) + *excess* RbOH (pH = 10·5) *at* 350°.
Electron micrographs are at magnifications of 6500 (*left*) *and* 7000 (*right*).

Plate 2.

Interpenetration twin (*left*) *and a typical preparation* (*right*) *of*
Species F.
$(Cs_2O,Al_2O_3,2SiO_2)$
from gel 1 : 1 : 2 *at* 400°. *Electron micrographs are at magnifications of* 8000.

PLATE 3.



Species C.

($Rb_2O, Al_2O_3, 6SiO_2$)

as central felspathic crystal, together with some quartz.

The mutual solid solubility of A and F was studied by crystallising gels $(Rb,Cs)_2O,Al_2O_3,2SiO_2$ of several cationic proportions. In each crystallisation only optically uniform crystals were formed, and *X*-ray *d*-spacings increased in an approximately linear manner with the refractive indices (Table 3). The R.I.'s and therefore the *X*-ray spacings may be assumed proportional to the molar compositions, and the data indicate continuous solid solubility of the two end members.

TABLE 3. *Relation between typical* X-*ray spacings and refractive indices of solid solutions * of A and F.*

Crystals	Pure A	Solid soln., 1	Solid soln., 2	Pure F
n	1·531	1·540	1·557	1·573
d-Spacings	3·18$_3$ (vs)	3·19$_0$ (vs)	3·22$_6$ (vs)	3·23$_3$ (vs)
	2·90$_1$ (w)	2·91$_0$ (w)	2·93$_1$ (w)	2·95$_1$ (w)
	2·77$_5$ (w)	2·78$_0$ (w)	2·80$_2$ (w)	2·81$_2$ (w)
	2·66$_5$ (s)	2·67$_8$ (s)	2·69$_2$ (s)	2·70$_9$ (s)

* The gels of all cationic compositions were crystallised at 350°. The pH's of cold mother-liquors after crystallisation were all between 7 and 8.

Species B and H both appeared, according to the *X*-ray data of Table 4, to be tetragonal. Spacings for B were indexed to give for the unit cell a = 13·2 and c = 13·6 Å, and those of H gave a = 13·6$_4$ and c = 13·3$_3$. The mean R.I. of species B was 1·52, and its m. p. was 1675° ± 15°. That of H was 1·48$_1$, and the mineral was stable up to about 1070°, but above this temperature it was transformed into species B.

Compound G has, according to the *X*-ray data, similarities to B and H and especially to the latter (Table 4). It is a pure cæsium pollucite, isotropic, having m. p. >1700°, with unit cell edge 13·7 Å and with R.I. = 1·523. Different crystallisations of this mineral showed refractive indices ranging between 1·512 and 1·523; when it was heated above 1250° the R.I.

TABLE 4. X-*Ray* d-*spacings for some species of Table* 1.

$Rb_2O,Al_2O_3,$ $2SiO_2$		$Cs_2O,Al_2O_3,$ $2SiO_2$		$Rb_2O,Al_2O_3,$ $4SiO_2$		$Rb_2O,Al_2O_3,$ $4SiO_2$		$Cs_2O,Al_2O_3,$ $4SiO_2$		$Rb_2O,Al_2O_3,$ $2SiO_2,H_2O$	
(A)		(F)		(B)		(H)		(G)		(D)	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
4·63$_7$	w	4·72$_2$	w	—	—	5·53	vw	5·64	w	7·95	m
3·18$_3$	vs	3·23$_3$	vs	—	—	4·03	vvw	—	—	3·71$_5$	m
2·90$_1$	w	2·95$_1$	w	3·61	s	3·63	m	3·65	s	3·48$_8$	vw
2·77$_5$	w	2·81$_2$	vw	3·40$_2$	s	3·39	vs	3·43$_4$	vs	3·25$_8$	vs
2·66$_5$	s	2·70$_9$	s	3·31	vs	—	—	—	—	3·11$_0$	s
2·29$_5$	w	2·34$_7$	vw	3·16	s	—	—	—	—	2·96$_5$	s
2·27$_0$	ms	2·31$_3$	mw	—	—	—	—	3·05$_4$	vw	2·41$_8$	vw
2·17$_6$	ms	2·21$_7$	w	2·97$_6$	m	—	—	—	—	2·35$_4$	v
2·10$_9$	w	2·15$_4$	vw	2·86$_6$	vs	2·89$_1$	s	2·91$_2$	s	1·90$_2$	vw
2·04$_0$	w	2·09$_2$	w	2·65$_0$	s	2·65$_6$	vw	2·68$_0$	vw	1·79$_4$	mw
1·978	m	2·002	ms	—	—	2·51$_8$	mw	2·49$_6$	m	1·74$_5$	vw
1·191	w	1·956	vw	2·38$_1$	s	2·39$_8$	m	2·41$_4$	s	1·63$_4$	vw
1·799	ms	1·839	m	2·29$_1$	vvw	—	—	—	—	1·58$_6$	vw
1·740	vvw	—	—	2·25$_8$	vw	2·197	w	2·219	s	1·54$_9$	vw
1·705	ms	1·743	m	2·168	s	1·999	vw	2·013	mw		
1·685	w	—	—	2·108	vvw	1·962	vvw	1·976	w		
1·650	vw	1·685	vw	1·968	m	1·828	w	1·862	s		
1·618	ms	1·649	m	1·855	w	1·702	mw	1·737	s		
1·584	m	1·614	mw	1·815	m	1·695	vvw	1·710	vw		
1·557	m	1·588	w	1·733	w	1·545	vvw	1·681	vvw		
1·535	m	1·570	vvw	1·695	m	1·395	vvw	1·659	vvw		
1·492	m	1·524	w	1·658	vw	1·340	vvw	1·634	vw		
1·451	mw	1·486	w	1·616	mw	1·290	vvw	1·591	vw		
1·387	w	1·410	w	1·584	vw	1·268	vvw	1·550	w		
1·331	w	—	—	1·557	w			1·529	mw		
1·316	w	1·345	vvw	1·527	vvw			1·475	w		
1·276	ms	1·299	m	1·493	vvw			1·411	w		
1·266	m	1·289	mw	1·457	vvw			1·396	vw		
1·227	m	1·249	vvw	1·390	vw			1·354	mw		
1·201	m	1·225	w	1·361	vw			1·305	m		
				1·329	vw			1·283	vvw		
				1·263	w			1·258	vw		
								1·219	w		
								1·181	w		
								1·116	w		

$Rb_2O,Al_2O_3,$ $6SiO,H_2O$	
(E)	
d	*I*
4·32	vs
3·34$_5$	vs
3·10$_0$	m
2·51$_4$	s
2·35$_4$	mw
2·22$_2$	m
1·55$_1$	ms
1·45$_2$	m

always changed to 1·523. There was no significant difference in *d*-spacings between crystals of lower and higher refractive indices.

Compound C (Plate 3) showed moderate birefringence with $\gamma = 1{\cdot}529$ and $\alpha = 1{\cdot}524$. Crystal habit and the *X*-ray data of Table 4 indicated that this substance belonged to the felspar group. Between 910° and 1070° it recrystallised to species H and glass, while above 1070° it changed to Species B and glass.

Compound D appeared as small isotropic crystals of R.I. = 1·49; *d*-spacings are given in Table 3. This substance was examined for ion-exchange with saturated thallous sulphate solution at 85° for 10 days. The R.I. changed to 1·615, indicating considerable exchange. Similarly, on treatment with saturated cæsium sulphate solution at 110° for 7 days, the R.I. rose to 1·510, again indicating an exchange reaction. This compound is almost certainly a zeolite, because a potassium analogue was subsequently prepared (by J. W. Baynham in this laboratory) which proved to be a zeolitic compound.

Yields of Species E were not high, and on this account there is some doubt as to its water content as given in Table 1. The species was precipitated as minute, apparently isotropic crystals of R.I. = 1·48 and gave the *d*-spacings shown in Table 3.

Solid-solubility Relations in Synthetic Felspars.—Solid solubilities of end-members in the important felspar group of minerals have been studied in a number of cases (*e.g.*, Tuttle and Bowen, *J. Geol.*, 1950, **58**, 572; Laves, *ibid.*, 1952, **60**, 436; Donnay and Donnay, *Amer. J. Sci.*, 1952, **250**, 115). It was in this connection of considerable importance to find the extent of mutual replaceability of Rb and K and of Rb and Tl in the synthetic rubidium felspars. This was particularly so because of the known association of these pairs of elements in some minerals. The solid solubility was investigated by crystallising hydrothermally the gels of Table 5, with additions of aqueous rubidium or potassium hydroxide instead of water in many systems. The products were characterised optically, by *X*-ray powder photography, and in some cases by analysis * (Table 6).

TABLE 5. *Compositions of some mixed gels in molar proportions.*

Rb_2O	Tl_2O	K_2O	Al_2O_3	SiO_2	Nomenclature
0·2	0·8	—	1	6	TRA
0·4	0·6	—	1	6	TRB
0·6	0·4	—	1	6	TRC
0·8	0·2	—	1	6	TRD
0·8	—	0·2	1	4·5	KRA
0·2	—	0·8	1	4·5	KRD
0·8	—	0·2	1	6	KRE

Crystallisation processes from gels containing thallium are rather complex, various species appearing over a considerable range of compositions (cf. H. F. Taylor, *loc. cit.*). Rubidium felspars did not crystallise below 300° from gels of felspar composition containing only rubidium as cation. Instead, compounds B and H and quartz appeared (Table 6). The thallium compound E in gels of mixed cationic composition occurred very frequently as inclusions in crystals of analcite type. Limits of solid solubility in the Tl–Rb felspar series were computed

TABLE 6. *Hydrothermal crystallisation of the mixed gels of Table* 5.

Gel	Temp.	Conditions	Optical examination	*X*-Ray examination and three strongest *d*-spacings	Initial K : Rb ratio in gel	Final K : Rb ratio in crystals
TRA	250°	Aq. RbOH added; pH 10	Rb-analcite, R.I. 1·535; Tl-compound E, R.I. 1·70	Tl-cpd E + Rb-analcite	—	—
TRA	350	As above	Rb-analcite, R.I. 1·535; Tl-compound E, R.I. 1·70	Tl-compound E + Rb-analcite	—	—
TRA	400	As above	Rb-felspar, $\gamma = 1{\cdot}61$, $\alpha = 1{\cdot}605$; Tl-compound E, R.I. 1·70	Rb-felspar + Tl-compound E	—	—
TRA	450	As above	As above	As above	—	—
TRB	250	As above	Rb-analcite, R.I. 1·54; Tl-compound E, R.I. 1·70	Rb-analcite + Tl-compound E	—	—

---

* Spectrochemical analyses of Rb and K were carried out by Dr. R. L. Mitchell of the Macaulay Institute for Soil Research.

TABLE 6. (*Continued.*)

Gel	Temp.	Conditions	Optical examination	*X*-Ray examination and three strongest *d*-spacings	Initial K : Rb ratio in gel	Final K : Rb ratio in crystals
TRB	350	As above	Rb-felspar, $\gamma = 1{\cdot}59$, $\alpha = 1{\cdot}585$; Tl-compound E, R.I. 1·70	Rb-felspar + Tl-compound E	—	—
TRB	400	As above	As above	As above	—	—
TRB	450	As above	As above	As above	—	—
TRC	250	As above	Rb-analcite, R.I. 1·54; Tl-compound E, R.I. 1·70	Rb-analcite + Tl-compound E	—	—
TRC	350	As above	Rb-felspar, $\gamma = 1{\cdot}57$, $\alpha = 1{\cdot}565$; Tl-compound E, R.I. 1·70	Rb-felspar	—	—
TRC	400	As above	Rb-felspar, $\gamma = 1{\cdot}57$, $\alpha = 1{\cdot}565$; Rb-analcite, R.I. 1·54	Rb-felspar	—	—
TRC	450	As above	Rb-felspar, $\gamma = 1{\cdot}57$, $\alpha = 1{\cdot}565$	Rb-felspar	—	—
TRD	250	As above	Rb-analcite, R.I. 1·525, and Rb-analcite, R.I. 1·575	Rb-analcite	—	—
TRD	350	As above	Rb-felspar, $\gamma = 1{\cdot}539$, $\alpha = 1{\cdot}534$, and Rb-analcite, R.I. 1·526	Rb-felspar and Rb-analcite	—	—
TRD	400	As above	Rb-felspar, $\gamma = 1{\cdot}539$, $\alpha = 1{\cdot}534$, and Rb-analcite, R.I. 1·525	As above	—	—
TRD	450	As above	Rb-felspar, $\gamma = 1{\cdot}539$, $\alpha = 1{\cdot}534$, and Rb-analcite, R.I. 1·52	As above	—	—
KRA	250	11d. Aq. KOH added; pH 9·5	Crystals weakly birefringent; some with R.I. $<1{\cdot}514$, most with R.I. $>1{\cdot}519$. Felspar and analcite	Felspar (3·34, 2·87, 3·00)	0·25	1·71
KRA	300	3d. Aq. RbOH; pH 8	—	Rb-analcite (3·38, 2·89, 1·714)	—	—
KRA	350	6d. Aq. KOH; pH 10	Crystals with R.I. slightly $>1{\cdot}526$. Also crystals with isotropic centres, but birefringent outgrowths	Felspar (3·33, 2·88, 3·00)	—	—
KRA	400	2d. Aq. KOH + RbOH; pH 10	Crystals with R.I. ~1·526	Felspar	—	—
KRA	400	6d. Aq. KOH; pH 10	Crystals with R.I. ~1·521	Felspar (3·34, 2·87, 3·00)	—	—
KRA	400	4d. Water only; pH 7·5	Felspar of R.I. ~1·521; very faint birefringence	Felspar	0·25	1·88
KRD	300	3d. Aq. KOH; pH 8	Felspar	Felspar	—	—
KRD	400	2d. Aq. KOH; pH 7·5	Felspar with R.I. ~1·523	Felspar	—	—
KRD	350	6d. Aq. KOH; pH 10	Crystals of R.I. ~1·529 and others of R.I. ~1·523 (latter not identified)	Felspar (3·31, 3·27, 3·00)	4·00	5·31
KRD	250	11d. Aq. KOH; pH 10	Very small crystals of R.I. ~1·52	Felspar (3·33, 3·23, 3·81)	—	—
KRD	400	4d. Water only; pH 10	Two types of crystal, one of R.I. ~1·521, and others of R.I. ~1·529 in smaller amount	Felspar (3·31, 2·86, 3·44)	—	—
KRE	400	7d. Water only; pH 7	Felspar of R.I. ~1·525	Felspar (3·36, 3·23, 3·81)	—	—
KRE	400	5d. Aq. KOH + RbOH; pH 10	Felspar of R.I. ~1·525	Felspar	0·25	1·88
KRE	330	12d. Water only; pH 7	Felspar of R.I. ~1·524	Felspar and analcite	0·25	0·94
KRE	330	2d. Aq. KOH; pH 10	Felspar of R.I. ~1·521	Felspar (3·35, 3·24, 3·00)	0·25	4·09

by assuming a linear relation between the R.I.'s of both end-members and all intermediate compositions. The pure rubidium felspar (*loc. cit.*) has $\gamma = 1{\cdot}529$ and $\alpha = 1{\cdot}524$, and the thallium end-member was taken to have a mean R.I. of 1·70, which is the value for the near-felspar $Tl_2O,Al_2O_3,6SiO_2$ (H. F. Taylor's Compound E). On this basis about 47 atomic % of Rb can be replaced by Tl in Rb-felspar. On the other hand, no replacement of Tl by Rb could be detected in Taylor's Compound E.

The pure rubidium and potassium felspars do not differ greatly in their refractive indices, so optical methods of studying solid solubility were not satisfactory. The analyses recorded in Table 6 for various mixed K–Rb-felspars cover a considerable composition range. The proportion of K : Rb has increased in the crystals over that in the parent gels for all crystallisations. Some important *d*-spacings for the analysed specimens are given in Table 7, most of which show little change in passing from pure potassium to pure rubidium felspars. When, however, a change was observed, this change was progressive, allowing for minor fluctuations. In no crystallisation was a line characteristic of a rubidium-rich felspar observed alongside that of a potassium-rich felspar. It therefore seems probable that potassium and rubidium felspars form a continuous range of solid solutions.

TABLE 7. *Felspars* $(Rb,K)_2O,Al_2O_3,6SiO_2$.

Mol.-fraction of K in crystal	Mean R.I.	Typical *d*-spacings				
0	$\alpha = 1{\cdot}524$ $\gamma = 1{\cdot}529$	—	—	3·61 (s)	3·40 (s)	3·31 (vs)
0·48	$1{\cdot}52_4$	4·24 (m)	3·79 (ms)	3·60 (vw)	3·44 (s)	3·29 (vs)
0·63	$>1{\cdot}51_9$	4·29 (m)	3·80 (s)	3·62 (s)	3·43 (m)	3·34 (vs)
0·65	$1{\cdot}52_1$	4·28 (m)	3·79 (s)	3·58 (ms)	3·46 (m)	3·34 (vs)
0·80	$1{\cdot}52_1$	4·28 (s)	3·79 (s)	3·62 (m)	3·46 (ms)	3·35 (vs)
0·84	$1{\cdot}52_3$ $(1{\cdot}52_9)$	4·25 (s)	3·79 (s)	3·62 (m)	3·45 (ms)	3·31 (vs)
* 1·00	$\alpha = 1{\cdot}517$ $\gamma = 1{\cdot}523$	4·23 (s)	3·78 (s)	3·61 (vw)	3·45 (mw)	3·30 (vvs)
0	$\alpha = 1{\cdot}524$ $\gamma = 1{\cdot}529$	3·16 (s)	$2{\cdot}97_6$ (m)	—	$2{\cdot}86_8$ (vs)	
0·48	$1{\cdot}52_4$	—	2·99 (w)	$2{\cdot}92_3$ (w)	2·84 (mw)	
0·63	$>1{\cdot}51_9$	3·21 (s)	$2{\cdot}99_6$ (s)	$2{\cdot}87_4$ (s)	$2{\cdot}76_4$ (w)	
0·65	$1{\cdot}52_1$	3·21 (s)	$2{\cdot}99_6$ (s)	$2{\cdot}87_4$ (s)	$2{\cdot}76_3$ (ms)	
0·80	$1{\cdot}52_1$	3·24 (vs)	$3{\cdot}00_2$ (s)	$2{\cdot}90_1$ (ms)	2·77 (vw)	
0·84	$1{\cdot}52_3$ $(1{\cdot}52_9)$	3·27 (s)	$3{\cdot}00_0$ (s)	$2{\cdot}88_0$ (ms)	$2{\cdot}76_0$ (m)	
* 1·00	$\alpha = 1{\cdot}517$ $\gamma = 1{\cdot}523$	3·23 (vs)	2·99 (ms)	$2{\cdot}90_3$ (ms)	2·77 (m)	

* The synthetic pure potassium felspar was prepared by J. W. Baynham from gel of composition $K_2O,Al_2O_3,6SiO_2,xH_2O$ and water in 2 days at 400°. The powder pattern is nearer to that of sanidine than of orthoclase.

DISCUSSION

An interesting feature of these investigations into the chemistry of synthetic aluminosilicates has been a persistence and recurrence of structural types, observed usually when the cations are not too dissimilar in radius. Thus it has been possible to grow crystals of felspars (Na, K, Rb, and Ba forms) and near-felspars (Pb and Tl forms) (see Part II, *J.*, 1952, 1561, and Part III, *loc. cit.*, for albite; Part III for potassium, barium, and lead felspars or near-felspars; and H. F. Taylor, *loc. cit.*, and this paper, for thallium near-felspar). It also has proved possible to grow various cationic forms of the purely synthetic compound $M_2O,Al_2O_3,2SiO_2$ where M = Rb, Cs, or Tl (this paper and H. F. Taylor, *loc. cit.*). Again, the synthetic zeolite $M_2O,Al_2O_3,2SiO_2,xH_2O$ has been grown where M = K or Rb and where $x = 1$ for the Rb form and 3 for the K form (this paper). In Part V (following paper) we have considered minerals and mineral type compounds based on analcite. Here the small size of some cations (*e.g.*, Li or Na) is compensated as against the larger cations (*e.g.*, Rb, Tl, Cs) by incorporation of water molecules into Li or Na analcites, so that the aluminosilicate framework persists largely unaltered for many cationic forms. Simplification of the chemistry of synthetic aluminosilicates may be effected by trying to classify them into a smaller number of recognisable structural types rather than by considering them as individuals.

Although rubidium yielded a variety of crystalline aluminosilicates, cæsium appeared in these experiments in two structures only. The reason for this is not yet clear, for it has been demonstrated that cæsium can by ion-exchange readily enter open-framework structures (*e.g.*, compound D of Table 1; and also chabazite, Barrer, *J.*, 1950, 2342). Similarly, during growth it may be incorporated up to 100% of the cationic composition, as in compounds F and G. Schiebold's theoretical prediction (*loc. cit.*) that a cæsium felspar should be formed has not been substantiated, and it therefore seems likely that this framework is too compact to contain such ions. The upper limit of cation size which can be accommodated in the felspar framework is probably about that of Rb or Tl. The wide ranges of replacement of Rb by Tl or K in felspars are clearly in line with the tendency of Rb and Tl, and of K and Rb to be associated in some aluminosilicates. The association of Rb and Cs is similarly illustrated by the analogy in structure of the compounds A and F of Table 1, and also of the compounds B and H with pollucite (species G).

Under the alkaline conditions we have employed the main species formed are framework structures rather than layer lattices. This has proved to be the case for nearly all of the synthetic aluminosilicates of Li, Na, K, Rb, Cs, Tl, Pb, or Ba which have been grown in the present programme (Parts I to V and H. F. Taylor, *loc. cit.*). The polarising power of the cations varies greatly over the above series, but this property under alkaline conditions has apparently little influence upon the crystal chemistry of the resultant aluminosilicate ion, which is nearly always of framework type.

Our thanks are due to Imperial Chemical Industries Limited for the loan of a Hilger HRX *X*-ray diffraction unit, and to the Royal Society for a grant to purchase a Leitz research microscope. One of us (N. McC.) acknowleges the award of a Carnegie Senior Research Scholarship during the tenure of which this work was carried out. We are indebted to Mr. J. Gard, B.Sc., of this Department, for the electron micrographs shown in Plates 1 and 2.

THE UNIVERSITY, ABERDEEN.

[*Received, July* 17*th*, 1953.]