283. *The Hydrothermal Chemistry of Silicates. Part I. Synthetic Lithium Aluminosilicates.*

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The formation of crystalline lithium aluminosilicates, and to a lesser extent of silicates and aluminates, has been studied by hydrothermal methods over the temperature range 150—450°.

Known species synthesised in this range include boehmite, α-petalite, α- and β-eucryptite, α- and β-spodumene, γ-alumina, and α-quartz. A lithium aluminate similar to but not identical with the spinel $LiAl_5O_8$ was found; and also a lithium silicate, Li_2O,SiO_2, previously grown elsewhere by pyrolytic methods. In the lithium aluminosilicate field, in addition to the minerals mentioned above, species of composition $Li_2O,Al_2O_3,2SiO_2,4H_2O$ (A), and $Li_2O,Al_2O_3,8SiO_2,5H_2O$ (H) were produced in major yields, together with lesser yields of two other species. These have been characterised by optical and, where possible, by *X*-ray studies.

Thermal stability of the minerals A and H was examined; ignition produced β-eucryptite and β-spodumene, respectively. The minerals A and H also showed the sorptive behaviour of zeolites, and underwent a variety of ion-exchange reactions involving Li^+, Ag^+, Na^+, K^+, Rb^+, Tl^+, NH_4^+, Ca^{++}, and Ba^{++}. These reactions were followed optically, chemically, and by *X*-ray methods.

A feature of the geochemistry of lithium is the limited number of naturally occurring lithium aluminosilicate minerals. Only three minerals composed entirely of lithia, alumina, and silica have been discovered: petalite ($Li_2O,Al_2O_3,8SiO_2$), spodumene ($Li_2O,Al_2O_3,4SiO_2$), and eucryptite ($Li_2O,Al_2O_3,2SiO_2$). These, with the lithia-containing micas lepidolite $[(HO,F)_2,(Li,K)_2,Al_2Si_3O_9]$ and zinnwaldite $[(HO,F)_2,(Li,K)_3,FeAl_3Si_5O_{16}]$, comprise almost all the naturally occurring species rich in lithium. The crystallisation of petalite, spodumene, and eucryptite by the pyrolytic method has been claimed by various workers (Hautefeuille and Perrey, *Bull. Soc. franç. Min.*, 1890, **13**, 145; Ballo and Dittler, *Z. anorg. Chem.*, 1912, **76**, 39; Winkler, *Acta Cryst.*, 1948, **1**, 27). Following an unsuccessful attempt at hydrothermal crystallisation by Hatch (*Amer. Min.*, 1943, **28**, 471), all three minerals have been recently synthesised in their low-temperature forms (Roy, Roy, and Osborne, *J. Amer. Ceram. Soc.*, 1950, **33**, 152). Pyrolytic crystallisations of melts containing lithia, alumina, and silica have been reported to give several synthetic species (Weyberg, *Centr. Min.*, 1905, 646; Hautefeuille and Perrey, *loc. cit.*; Ballo and Dittler, *loc. cit.*), and Thugutt (*Z. anorg. Chem.*, 1892, **2**, 64, 113) reported a hydrothermal preparation of crystals of composition $Li_2O,Al_2O_3,2SiO_2,2H_2O$. Too little information is given concerning these synthetic species, however, for their subsequent recognition. Work, often of a rather conflicting nature, has also been carried out in the lithium silicate and lithium aluminate fields (Hautefeuille and Margottet, *Bull. Soc. franç. Min.*, 1881, **4**, 175; Ballo and Dittler, *loc. cit.*; Noll, *Neues Jahrb. Min. Geol.*, Beil. Bd., 1935, **70**, 65; Kracek, *J. Amer. Chem. Soc.*, 1939, **61**, 2870; Hatch, *loc. cit.*; Austin, *J. Amer. Ceram. Soc.*, 1947, **30**, 219; Rustrum Roy and Osborne, *J. Amer. Chem. Soc.*, 1949, **71**, 2086).

The present investigation was undertaken, as part of a programme concerned with the synthetic hydrothermal chemistry of the aluminosilicates, to improve understanding of growth conditions and of diversity among such lithium compounds. A particular object was to find whether lithium zeolites can be crystallised from gels. Natural zeolites contain only sodium, potassium, calcium, and barium as interstitial cations, although a number, but not all of them (*e.g.*, chabazite and mordenite), can exchange considerable amounts of these cations for lithium under hydrothermal conditions. One may question whether the unusually open character of the aluminosilicate framework of zeolites is fully compatible during growth with the small size of the lithium ion, and attempt to answer this question by successful crystallisation of lithium zeolites.

The investigation also represents an attempt to determine whether the lack of diversity of natural lithium aluminosilicates can be attributed to the lesser amount of this element than of sodium or potassium in the lithosphere, resulting in a failure of natural processes to segregate lithium under mineralising conditions. If this is the only reason for such lack of diversity, then under laboratory conditions a good variety of aluminosilicates could be expected.

Knowledge of synthetic lithium aluminosilicates has been obtained mainly by the pyrolytic method. Until recently their hydrothermal chemistry has been little studied. Moreover, zeolites grow under alkaline hydrothermal conditions, which also favour the formation of well-developed crystals. For these reasons the hydrothermal method was used here as the normal method of synthesis and crystal growth.

EXPERIMENTAL.

Lithium hydroxide was prepared by the reaction $Li_2SO_4 + Ba(OH)_2 = 2LiOH + BaSO_4\downarrow$. The hydroxide was made and stored in absence of carbon dioxide. Aluminium hydroxide was obtained by the action of water on lightly amalgamated aluminium (Wislicenus, *Z. anorg. Chem.*, 1904, **17**, 805; Weiser and Milligan, *Chem. Revs.*, 1939, **25**, 1). The product was washed with alcohol and ether, and air-dried. Ignition loss corresponded to $Al_2O_3,3H_2O$. Silica gel was supplied by B.D.H. Ltd., as silicic acid containing ~15% of SiO_2. Hydrothermal extraction of a sample at 250° gave a mother-liquor neutral and free from common inorganic cations. *X*-Ray powder photographs of the aluminium hydroxide and silicic acid showed that both were amorphous.

The series of gels $Li_2O,Al_2O_3,nSiO_2,mH_2O$, in which n varied between 1 and 10, were made by mixing the constituents in the correct proportions and evaporating the mixtures to dryness at 120°. The dried products were ground and stored under carbon dioxide-free conditions. Hydrothermal crystallisations were carried out by mixing 2 g. of gel with 10 c.c. of water or ~N-lithia solution in stainless-steel autoclaves of ~20 c.c. internal capacity (Barrer, *J.*, 1948, 127). Autoclaves were then heated in air ovens with thermostatic control, operating up to 300°. For higher temperatures a specially designed thermostatted furnace was employed, capable of holding up to nine autoclaves. Most experiments were left for 36—60 hours for crystallisation to occur, although at the lowest temperatures (<150°) 3—4 days were given. In a few experiments carried out above 450° good yields of large crystals appeared in less than 2 hours.

After the crystallisation period, the autoclaves were quenched in cold water, the pH value of the cold mother-liquor was measured to the nearest 0·2 pH unit, and the insoluble reaction products were collected for further examination.

Examination of Products.—Optical examination was carried out by means of Vickers projection and Leitz polarising microscopes. Refractive indices (in sodium light) were measured in most cases to within ±0·002 unit; extinction angles were also observed; and in the case of favourably large crystals, interference figures were studied.

X-Ray powder photographs were taken of the products which were formed in high enough yields, a Hilger HRX unit operating with 9-cm. cameras being used. Nickel-filtered Cu-K_α radiation was used throughout. Where possible the probable unit-cell dimensions were determined by means of logarithmic Bjurstrom charts. This method carried out for synthetic quartz gave dimensions within 1% of the accepted values.

Investigation of the sorptive properties of the crystals was carried out in a simplified modification of Barrer and Ibbitson's apparatus (*Trans. Faraday Soc.*, 1944, **40**, 195, 206). Only crystals with water of constitution were so examined, the sample being first outgassed between 200° and 300° for 24 hours. Gases used in these experiments were: ammonia, propane, hydrogen, nitrogen, and helium. The last three were obtained from the British Oxygen Co., in the pure state; propane was taken from a cylinder, dried, and fractionated; and ammonia was prepared by warming quick-lime and ammonium chloride in an evacuated flask, drying the evolved gas by passing it through a column of quick-lime, and fractionating it.

Ion-exchange reactions were studied using chlorides, nitrates, or nitrites of Li, Na, K, Rb, Cs, Ca, Ba, Ag, Tl, and NH_4. Hydrothermal, fusion, and vapour-phase exchange procedures were employed (Barrer, *J.*, 1950, 2342). Hydrothermal exchanges involved heating the crystals with aqueous solutions of the desired salts (the salt being in excess) in sealed glass tubes at 120° for about 2 days. During exchange, the tubes were rotated continuously in a thermostatted air oven. Above 120° recrystallisation was frequently observed, but much below it the rates of exchange were often low. Exchange reactions by fusion were limited to silver nitrate and barium nitrite, since the lithium aluminosilicates showing exchange properties underwent irreversible thermal lattice changes at 300°. The fusion method was found very effective. Vapour-phase exchange was restricted to NH_4^+ (Clark and Steiger, *Amer. J. Sci.*, 1902, **13**, 27; *Z. anorg. Chem.*, 1902, **29**, 338). A preliminary outgassing of the specimens was needed to prevent evolved water from bursting the glass reaction tubes. The method, however, proved less successful with the lithium aluminosilicates than with most zeolitic species.

Ion-exchange products were washed free from exchanging salt, dried, and examined by *X*-ray, optical, and chemical methods.

Analytical results were in many cases difficult to interpret because of varying amounts of uncrystallised gel or of alternative species. Attempts were made to separate the required crystals by various methods, but only partial success was obtained. Accordingly, analytical data were collected primarily for species which appeared in nearly 100% yield. Standard methods were used for determination of silica, alumina, and metallic ions, decomposition of the minerals being effected by sodium carbonate fusion, or by treatment on a steam bath with 1 : 1 nitric or hydrochloric acid. Lithium was determined after removal of silica and alumina. The residual salts were converted into chlorides, and the lithium chloride extracted with *iso*amyl alcohol in a modified Soxhlet apparatus.

Results.

The Alumina Field.—In order to simplify the investigation in the field of compositions Li_2O–Al_2O_3–SiO_2–H_2O, preliminary study was made in the fields Li_2O–Al_2O_3–H_2O and Li_2O–SiO_2–H_2O. In this way it was hoped that products in these fields could be identified and thus recognised if again encountered among the lithium aluminosilicates. The results of experiments in the alumina field are given in Table I. It is seen that treatment of aluminium hydroxide with water or lithium hydroxide yielded boehmite, a lithium aluminate, and γ-alumina. Boehmite was found over the whole range 130—450°, its formation being favoured by lower pH values, although some boehmite appeared also in specimens treated with lithia water, especially at lower temperatures. Lithium aluminate appeared between 160° and 450°, with optimum yields at 300°. At 450° in media of high pH values γ-alumina crystallised in varying quantities.

TABLE I.

Reactants.	Temp.	Products.
$Al(OH)_3$ + LiOH, aq.	130°	Mostly *boehmite*, small crystals.
$Al(OH)_3$ + LiOH, aq.	160	*Boehmite*, with some *lithium aluminate.*
$Al(OH)_3$ + aq.	250	*Boehmite*, moderate yield, very small crystals.
$Al(OH)_3$ + LiOH, aq.	250	*Boehmite*, with some *lithium aluminate.*
$Al(OH)_3$ + LiOH, aq.	310	*Lithium aluminate*, good yield.
$Al(OH)_3$ + aq.	360	*Boehmite*, very good yield of large crystals.
$Al(OH)_3$ + LiOH, aq.	360	*Lithium aluminate*, moderate yield.
$Al(OH)_3$ + aq.	420	*Boehmite*, good yield.
$Al(OH)_3$ + Li_2SO_4, aq.	450	*γ-Alumina, boehmite*, some *lithium aluminate.*
$Al(OH)_3$ + LiOH, aq.	450	*γ-Alumina boehmite*, some *lithium aluminate.*
$Al(OH)_3$ + aq.	450	*Boehmite*, moderate yield of small crystals.

Some properties of the species crystallised in the alumina field are summarised below :

Synthetic boehmite (Plate I). The *X*-ray spacings of boehmite are recorded in Table IV, Noll's data (*loc. cit.*) being given for a second synthetic specimen. The crystals grew as irregular hexagonal plates up to 150 μ. in length. Birefringence moderate, straight extinction, negative elongation, biaxial positive, $\alpha = 1{\cdot}650$, $\beta = 1{\cdot}659$, $\gamma = 1{\cdot}670$. System orthorhombic. Optimum growth : $Al_2O_3 + H_2O$ at 400°. Analysis : Al_2O_3,H_2O. Recrystallised on ignition to α-Al_2O_3 (corundum). The refractive indices noted above are slightly higher than values in the literature (*e.g.*, Dana's " System of Mineralogy," 7th edn., Wylie & Sons).

γ-Alumina. The *X*-ray spacings of the γ-Al_2O_3 of Table I are compared in Table IV with those for γ-Al_2O_3 given in the " Alphabetical Index of *X*-Ray Diffraction Data." The crystals grew as cubes of indefinite outline up to 15 μ. long, isotropic, $n \sim 1{\cdot}70$. Conditions of growth : $Al(OH)_3 + H_2O$ at 450° ; usually mixed with boehmite.

Lithium aluminate (Plate II). *X*-Ray spacings in Table IV give over 20 lines in agreement with the spinel $Li_2O,5Al_2O_3$ (Kordes, *Z. Krist.*, 1935, **91**, *A*, 193), but there are some differences. The crystals grew as rectangular prisms up to 50 μ. long. Birefringence moderate ; straight extinction ; positive elongation, uniaxial, $\omega = 1{\cdot}620$, $\varepsilon = 1{\cdot}640$. System tetragonal. Optimum conditions of growth : $Al(OH)_3$ + excess LiOH, aq. at 300°. Usually mixed with boehmite. Hatch (*loc. cit.*) reported a product Li_2O,Al_2O_3, which is uniaxial negative, with $\omega = 1{\cdot}606$, $\varepsilon = 1{\cdot}624$.

TABLE II.

Reactants.	Temp.	Products.
$SiO(OH)_2$ + LiOH, aq.	160°	Masses of very small crystals of *lithium silicate.*
$SiO(OH)_2$ + aq.	250 (1 day)	Little or no crystallisation.
$SiO(OH)_2$ + aq.	250 (4 days)	Little or no crystallisation.
$SiO(OH)_2$ + LiOH, aq.	310	*Lithium silicate* in good yield.
$SiO(OH)_2$ + LiOH, aq.	360	*Lithium silicate*, moderate yield.
$SiO(OH)_2$ + aq.	450	*Quartz*, little *cristobalite.*
$SiO(OH)_2$ + Li_2SO_4, aq.	450	*Quartz*, good yield.
$SiO(OH)_2$ + LiOH, aq.	450	*Quartz*, good yield.

The Silica Field.—Silica gel, treated with excess of lithium hydroxide solution, crystallised to a lithium silicate (Li_2O,SiO_2) at 160° and 310°. The yield, however, decreased with rise of temperature until at 450° quartz became the primary phase. Treatment with water alone yielded no crystalline products at 250°, and at 450° small quartz crystals were formed together with small amounts of cristobalite. Table II records experiments in the silica field. The results in Tables I and II indicate that in the aluminosilicate field there will be little complication due to co-precipitation with aluminosilicates of either aluminates or silicates of lithium. The lithium silicate of Table II was crystallised also from aluminosilicate gels (Table III), but was readily identified. The properties are given below.

TABLE III.

*Summary of results in aluminosilicate field.**

(Compositions $Li_2O,Al_2O_3,nSiO_2$.)

Temp.	$n = 1$.	$n = 2$.	$n = 3$.	$n = 4$.	$n = 5$.
130°	Good A 10·5	Good A 10·5	Poor A 10·5	Poor A 10·5	—
150—160	Good A 10·5	Good A 10·0	Mod. A 10·0	Poor A 10·5	Poor H 10·5
190	Good A 10·5 (Poor A>11)	V. good A 10·5 (Mod. A>11)	Good A 10·5 (Some A & D>11)	Poor A 10·5 (Some A & D>11)	Poor A 10·5 (Mod. D>11)
220—230	Good A 10·3 (Good A>11)	Good A 9·8 (Good A>11)	Mod. A 10·0 (Poor A; some D>11)	Poor A 9·8 (Some A & D~11)	Poor A & D 8·7 (Poor H~11)
250	Good A~10 (Mod. A>11)	Good A~10 (Mod. A>11)	Mod. A 9·7 (Mod. A>12)	Poor A 10·0) (Mod. A>11)	Poor A Some H~10 (Mod. A~10)
275	Mod. A 9·0 (Mod. A & B >11)	Mod. A 7·4 (Some B~11)	Mod. A 7·4 (Some B & E ~11)	Poor A 7·7 (Some B 10·5)	Poor A 7·7 (—10·5)
300	Some A & B 10·5 (Mod. B~11)	Mod. A Some B 8·7 (Mod. B~11)	Mod. A Poor B 8·7 (Some A & B 10·5)	Poor A Some B 8·0 (Poor A & B 10·5)	Poor A Some B 8·0 (Poor A 10·5)
330—340	Mod. B 8·5 (Mod. B~11)	Mod. B 7·4 (Good B~11)	Mod. B 6·1 (Mod. B~11)	Poor B Some A 7·4 (Mod. B~11)	Poor B 9·3 (Poor B~11)
360	Mod. B 8·8 (V. good B~11)	Good B 9·0 (V. good B 10·5)	Good B 10·0 (Good B~11)	Good B 7·7 (Good B 10·0)	Mod. B 8·0 (Mod. B 10·0)
390	Mod. B 10·5 (V. good B~11)	Good B 8·3 (V. good B 10·5)	Mod. B 8·0 (Good B 10·5)	Mod. B 9·0 (Mod B 10·5)	Poor B & C 10·0 (Poor C 10·0)
450	Good B 10·0	Good B 10·0	Mod. B & I 8·7	Some B & I 8·7	Some B & I 10·0

Temp.	$n = 6$.	$n = 7$.	$n = 8$.	$n = 9$.	$n = 10$.
130	—	—	—	—	—
150—160	V. poor H 10·5	Poor H 10·5	Poor H 10·5	V. poor H 10·5	10·5
190	Poor H 10·5 (Mod. D>11)	Poor H 10·5 (Poor D>11)	Poor H 10·5 (Poor H & D>11)	Poor H 10·5 (Poor H & D>11)	—10·5 —>11
220—230	Some A & D 10·0 (Some H~11)	Poor A & D 10·0 (Poor H~11)	Poor H 10·0 (Mod. H~11)	Poor H 10·0 (Mod. H~11)	V. poor H 10·0 (Mod. H~11)
250	Some A & H~10 (Mod. A 10·5)	V. poor H~10 (Some A 10·5)	Poor H~10 (Some D 10·5)	Poor H~10 (Poor D 10·5)	V. poor H~10 (Poor D 10·5)
275	Some A 7·4 (—10·5)	V. poor H 7·4 (Poor D 10·5)	Poor H 7·4 (Poor D 10·5)	Poor H 7·4 (Some D~10·5)	Poor H 7·4 (Some D~10·5)
300	Poor A 7·7 (Some A 10·5)	Some A Poor H 8·0 (Some A 10·5)	Mod. H 7·7 (—10·5)	Mod. H 7·7 (—10·5)	Poor H 8·0 (—10·5)
330—340	V. poor B 7·7 (Some B & C~11)	Poor C 8·3 (Some B & C~11)	Poor C 6·4 (Poor C~11)	Poor C 10·0 (Mod. C~11)	Poor C 7·4 (Poor C~11)
360	Poor B Mod. C 7·1 (Poor B & C 10·0)	Good C Some G 3·5 (Poor B. Mod. C 10·0)	Mod. C 3·6 (Good C 10·0)	Poor C 6·7 (Mod. C 10·0)	Poor C 4·2 (Mod. C 10·5)
390	Mod. C 10·0 (Mod. C 10·0)	Mod. C 10·0 (Good C 10·0)	Good C 10·0 (Good C 10·0)	Mod. C 10·0 (Mod. C 10·5)	Mod. C 10·0 (Mod. C 10·5)
450	V. poor B & I 9·6	Good C Poor I, 8·7	V. good C Some I 8·7	V. good C 8·7	—

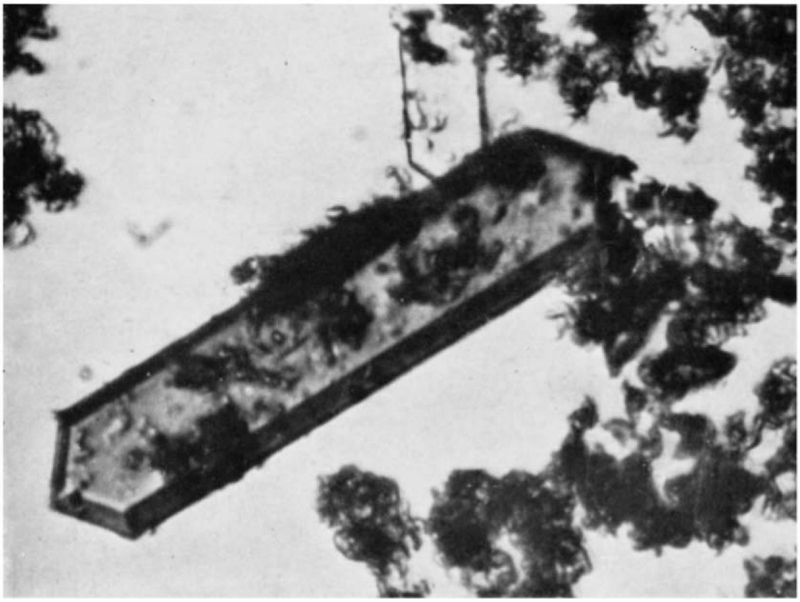
* Results recorded parenthetically are those of treatment of gels in presence of excess of LiOH solution.

Lithium silicate (Species D of Table III). *X*-Ray spacings in Table IV agree with those of the compound Li_2O,SiO_2 obtained by Austin (*loc. cit.*). Formed as radial clusters of long needle-like crystals up to 20 μ. in diameter, and also occurred as spherulites. Birefringent; straight extinction; positive elongation; probable system: tetragonal, $\varepsilon = 1{\cdot}599$, $\omega = 1{\cdot}587$. Unit cell dimensions $a = 9{\cdot}3_8$; $c = 5{\cdot}9_2$ A. Optimum growth: SiO_2 + excess LiOH, aq. at ~300°.

a-Quartz. Quartz was grown as hexagonal prisms up to 30 μ. long, showing moderate birefringence, straight extinction and being uniaxial negative; $\varepsilon = 1{\cdot}553$, $\omega = 1{\cdot}544$. Best condition of growth: SiO_2 + excess LiOH, aq. at 450°. Identified by *X*-ray spacings as *a*-quartz.

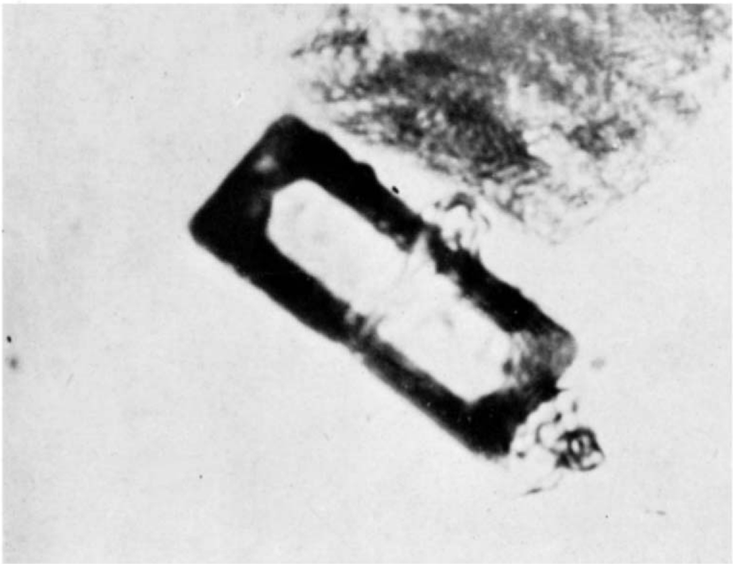
The Aluminosilicate Field.—Most of the work done with compositions $Li_2O,Al_2O_3,nSiO_2$ + aq. is summarised in Table III, in which the crystalline species are designated by letters A—J. The crystals

PLATE I.



Synthetic boehmite, × **1030**.

PLATE II.



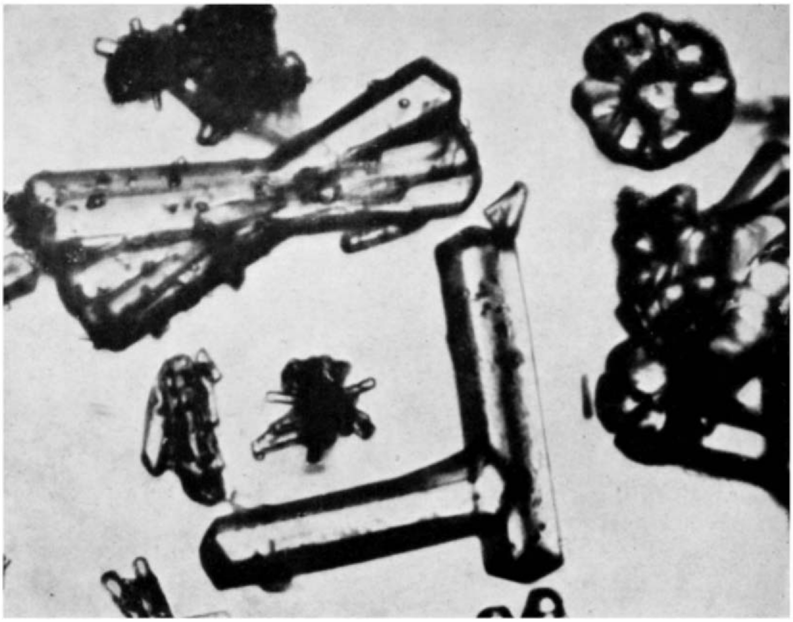
Lithium aluminate, × **1520**.

[*To face p.* 1270.

PLATE III.

Species A, × 1500.

PLATE IV



Species B (*α-eucryptite*), × 820.

Plate V.

Species C (*petalite*), × **640.**

Plate VI.

Species E, × **730.**

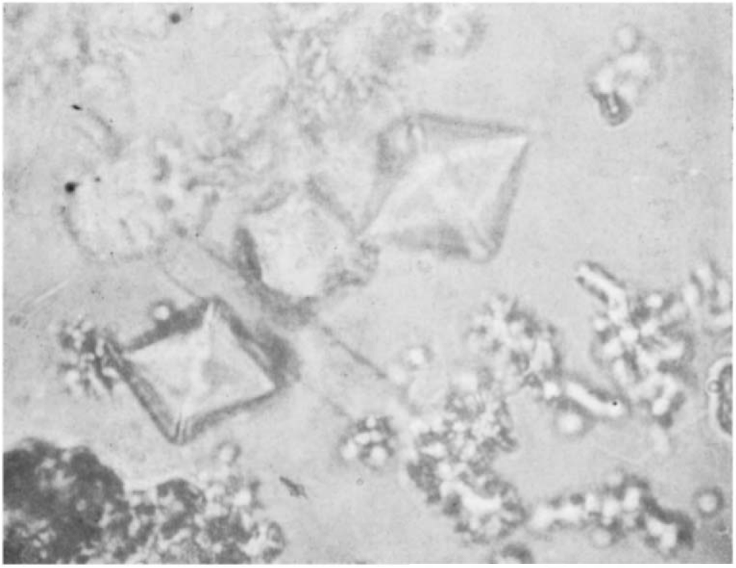


PLATE VII.

Species F (*β-eucryptite*), × 800.

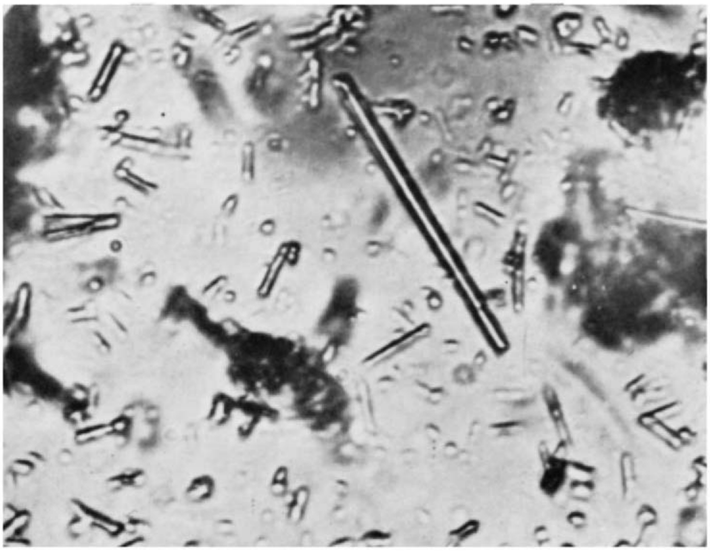


PLATE VIII.

Species H, × 1500.

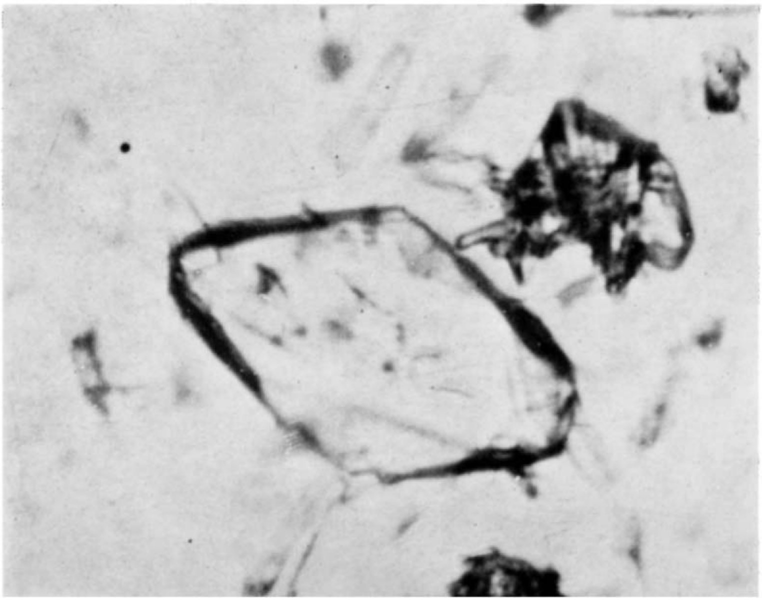


PLATE IX.

Species I (*β-spodumene*), × 1540.

TABLE IV.

X-*Ray data* (*spacings in* A.).

Species A.*		Species B * (α-eucryptite).		Species C (α-petalite).		Natural petalite.		Species D (lithium silicate).		Li_2O,SiO_2.†	
I.	*d.*	*I.*	*d.*	*I.*	*d.*	*I.*	*d.*	*I.*	*d.*	*I.*	*d.*
vs	6·42	s	6·92	w	5·48	w	5·45	—	—	0·02	5·32
mw	5·21	mw	4·32	mw	4·67	w	4·69	s	4·85	1	4·70
vs	4·29	vs	3·97	w	4·30	w	4·26	—	—	0·1	4·02
vw	4·06	w	3·59	m	4·02	—	—	s	3·39	0·72	3·32
vw	3·27	s	3·48	vvs	3·73	vvs	3·72	—	—	0·02	3·20
vs	3·15	s	3·37	ms	3·52	ms	3·54	s	2·74	0·74	2·72
vs	3·03	w	3·21	w	3·40	vw	3·36	—	—	0·13	2·66
s	2·490	w	3·14	vw	3·24	vvw	3·20	m	2·50	0·04	2·59
w	2·392	w	3·04	—	—	mw	3·11	s	2·35	0·19	2·35
m	2·326	s	2·74	m	3·00	m	2·99	w	2·11	0·05	2·10
vw	2·243	vs	2·55	mw	2·780	w	2·781	m	1·780	0·10	1·78
mw	2·173	vw	2·32	ms	2·578	m	2·576	m	1·663	0·12	1·66
w	2·042	m	2·25	vvw	2·503	vw	2·531	vw	1·625	—	—
mw	1·952	w	2·08	mw	2·408	mw	2·407	m	1·569	0·30	1·57
vw	1·868	vw	1·98	w	2·262	—	—	—	—	0·04	1·53
m	1·754	mw	1·946	ms	2·070	s	2·066	w	1·483	—	—
mw	1·725	ms	1·877	vvw	1·995	vvw	1·993	w	1·418	0·02	1·40
w	1·556	ms	1·803	s	1·939	ms	1·935	m	1·354	0·06	1·36
mw	1·524	m	1·635	m	1·899	m	1·895	m	1·300	0·12	1·30
m	1·474	mw	1·547	m	1·875	—	—	w	1·256	0·08	1·26
vw	1·445	w	1·526	vw	1·837	vvw	1·835	w	1·174	0·05	1·18
mw	1·405	m	1·490	w	1·807	w	1·803	w	1·137	0·05	1·14
vw	1·371	vw	1·441	vw	1·756	w	1·755	w	1·069	—	—
vw	1·348	vw	1·399	mw	1·726	w	1·722	w	1·022	—	—
vw	1·327	s	1·374	vw	1·632	m	1·629	w	1·001	—	—
vw	1·300	vw	1·348	w	1·640	—	—	—	—	—	—
w	1·270	m	1·321	—	—	vw	1·612	—	—	—	—
vw	1·244	m	1·295	vw	1·529	mw	1·522	—	—	—	—

Synthetic Li aluminate.		$LiAl_5O_8$.‡		Synthetic γ-Al_2O_3.		γ-Al_2O_3.*	
I.	*d.*	*I.*	*d.*	*I.*	*d.*	*I.*	*d.*
m	7·56	—	—	m	7·71	—	—
m	4·60	0·3	4·59	ms	4·64	—	—
m	4·05	—	—	m	4·09	—	—
m	3·85	—	—	m	3·87	—	—
vw	3·54	0·15	3·56	vw	3·15	—	—
m	2·80	0·5	2·81	s	2·82	0·6	2·80
m	2·70	0·1	2·67	m	2·72	—	—
vw	2·625	—	—	mw	2·63	—	—
vw	2·462	—	—	vw	2·54	—	—
s	2·383	1·0	2·388	vw	2·46	—	—
w	2·290	0·25	2·291	vvs	2·403	0·7	2·39
—	—	0·08	2·234	w	2·301	0·4	2·28
w	2·221	0·08	2·208	vs	1·989	0·8	1·98
s	1·980	0·7	1·982	vw	1·903	—	—
vw	1·890	—	—	vw	1·817	0·2	1·82
vw	1·807	—	—	mw	1·622	0·2	1·62
—	—	0·04	1·732	w	1·578	—	—
—	—	0·04	1·693	vs	1·530	0·5	1·52
w	1·620	0·36	1·619	vvs	1·405	1·0	1·40
w	1·568	0·01	1·586	w	1·302	—	—
s	1·525	0·6	1·527	w	1·256	0·2	1·24
vw	1·473	0·04	1·474	m	1·215	0·2	1·21
vw	1·444	0·05	1·446	m	1·143	0·5	1·14
vs	1·400	1	1·401	m	1·094	—	—
vw	1·343	0·12	1·342	—	—	0·4	1·06
w	1·321	—	—	s	1·033	0·2	1·03
vw	1·300	0·05	1·306	ms	0·992	0·5	0·991
—	—	0·05	1·285	m	0·936	—	—
w	1·255	0·18	1·254	ms	0·916	0·2	0·916
—	—	0·01	1·237	ms	0·887	0·5	0·885
—	—	0·01	1·227	vw	0·871	—	—
w	1·213	0·3	1·209	—	—	—	—
w	1·147	0·23	1·145	—	—	—	—
—	—	0·12	1·112	—	—	—	—
vw	1·062	0·2	1·060	—	—	—	—
w	1·033	0·38	1·032	—	—	—	—
m	0·992	0·3	0·991	—	—	—	—

* Mean of several photographs of good specimens. † After Austin (*loc. cit.*). ‡ After Kordes (*loc. cit.*).

TABLE IV—(*continued*).

Species H.*		Species J (α-spodumene).		Synthetic boehmite.		Boehmite.†	
I.	*d.*	*I.*	*d.*	*I.*	*d.*	*I.*	*d.*
m	9·84	m	6·24	m	7·14	10	6·86
mw	8·39	m	4·46	vs	6·14	10	6·10
w	8·10	m	4·28	w	4·47	—	—
ms	6·68	m	3·49	m	3·52	4	3·53
w	5·33	vw	3·23	vs	3·17	9	3·15
ms	4·88	vw	3·10	vw	2·57	5	2·60
vw	4·55	vs	2·96	vw	2·52	—	—
s	4·27	vs	2·83	w	2·44	—	—
vw	3·97	mw	2·70	vs	2·29	10	2·34
w	3·78	ms	2·48	m	1·98	6	2·04
mw	3·58	m	2·391	vw	1·91	3	1·98
w	3·49	vw	2·200	vs	1·85	10	1·84
mw	3·40	w	2·136	vw	1·82	—	—
mw	3·32	mw	2·085	ms	1·77	4	1·77
vw	3·08	w	2·024	s	1·66	6	1·66
w	2·97	w	1·906	vvw	1·63	2	1·61
w	2·80	vvw	1·869	m	1·53	5	1·53
w	2·66	mw	1·688	mw	1·492	—	—
m	2·52	m	1·623	s	1·452	8	1·45
vvw	2·38	mw	1·594	m	1·432	5	1·433
vw	2·02	w	1·555	vw	1·416	—	—
w	1·87	vvw	1·526	vw	1·402	—	—
		vw	1·502	s	1·383	6	1·380
		w	1·480	vs	1·309	8	1·306
		w	1·351	—	—	1	1·286
		vw	1·332	—	—	1	1·254
		vw	1·302	w	1·225	—	—
		vvw	1·279	w	1·208	2	1·207
		vw	1·234	m	1·176	4	1·176
		vvw	1·217	m	1·156	4	1·158
		vvw	1·193	ms	1·132	6	1·149
		vvw	1·021	mw	1·112	3	1·114
				mw	1·045	3	1·046
				vw	1·037	—	—
				w	1·027	3	1·022
				w	1·010	—	—
				vw	0·991	—	—
				w	0·982	1	0·980
				mw	0·950	5	0·949
				mw	0·930	3	0·931

* " Alphabetical Index of *X*-Ray Data " (American Soc. Testing Materials).
† After Noll (*loc. cit.*).

D are the lithium silicate already described. These crystals appeared in the presence of excess of lithia over the temperature range 200—275°. Table III shows the influence of several variables upon the yields of crystals—variables of pH, temperature, and composition, any of which can exercise a decisive influence on growth of the various species. The figures recorded in Table III are the pH values of the cold mother-liquors after crystallisation; compositions and temperatures are also shown. By keeping the ratio $Li_2O : Al_2O_3 = 1 : 1$, and varying the silica content, a considerable number of crystalline species has, then, been formed under hydrothermal conditions, of which some appear to be new aluminosilicates of lithium. Because of this, considerable attention has been given to their characterisation. Products occurring in major yields of $\geqslant 80\%$ were A, B (α-eucryptite), C (α-petalite), and H, and there is evidence that the species I (β-spodumene) becomes a primary phase above 450°.

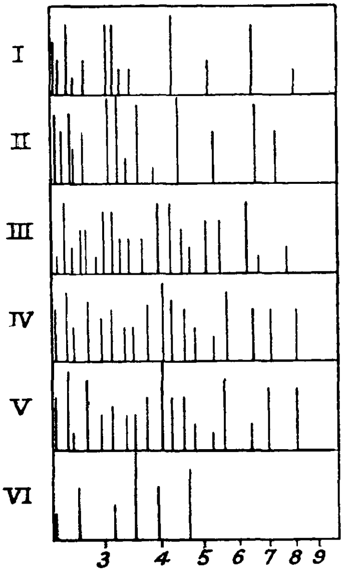
Species A (Plate III). *X*-Ray spacings are given in Table IV. The crystals grew as rods up to 30 μ. long, occurring singly and in radial clusters. Birefringence moderate; straight extinction; positive elongation; biaxial; system probably orthorhombic; $\alpha = 1{\cdot}535$, $\gamma = 1{\cdot}525$. Optimum growth: 250° from $Li_2O,Al_2O_3,2SiO_2$ compositions. Addition of small amounts of potassium fluoride had a marked mineralising action. Analysis: Li_2O, 8·30; Al_2O_3, 31·4; SiO_2, 39·8; H_2O, 21·2% ($Li_2O,Al_2O_3,2SiO_2,4H_2O$ requires Li_2O, 9·3; Al_2O_3, 31·5; SiO_2, 37·0; H_2O, 22·2%). This *silicate* exhibits sorptive and ion-exchange properties (*q.v.*).

Species B (Plate IV). *X*-Ray spacings (Table IV) identified the mineral as α-eucryptite. The crystals grew as hexagonal prisms occurring singly up to 150 μ. long, and also as radial clusters and spherulites. Cruciform twinning common; birefringent; positive elongation; interference pattern biaxial, therefore pseudo-hexagonal, probably orthorhombic; $\alpha = 1{\cdot}575$, $\beta = 1{\cdot}578$, $\gamma = 1{\cdot}586$. Optimum growth at 400° from $Li_2O,Al_2O_3,2SiO_2$ compositions at pH $>$ 10 (excess LiOH, aq.). Analysis: Li_2O, 11·4; Al_2O_3, 40·5; SiO_2, 46·8 (Calc. for $Li_2O,Al_2O_3,2SiO_2$: Li_2O, 11·9; Al_2O_3, 40·5; SiO_2, 47·6%). Crystals were anhydrous and without sorptive or ion-exchange properties. No changes in *X*-ray spacings were apparent after ignition over a Meker burner for 3 hours. Crystallographic properties are not entirely in agreement with published data (Brush and Dana, *Amer. J. Sci.*, 1880, **20**, 257; Roy, Roy, and Osborne, *loc. cit.*).

Species C (Plate V). *X*-Ray spacings given in Table IV identified the mineral as α-petalite. Crystals grew in prismatic, lath-like, and usually irregular form, both singly and in radial clusters up to 50 μ. long. Low birefringence; straight extinction; positive elongation. Biaxial; mean *n* 1·510; system monoclinic. Optimum growth at ~420°, from compositions $Li_2O,Al_2O_3,8SiO_2$, at high pH values (excess of LiOH). Analysis: Li_2O, 4·6; Al_2O_3, 16·5; SiO_2, 78·6 (Calc. for $Li_2O,Al_2O_3,8SiO_2$: Li_2O, 4·9; Al_2O_3, 16·7; SiO_2, 78·4%).

FIG. 1.

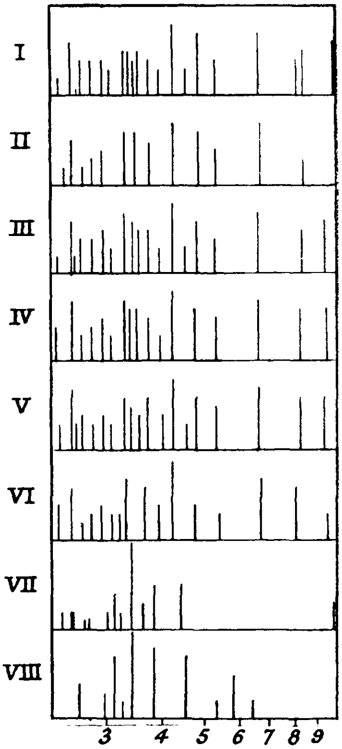
Change in principal lattice spacing on thermal treatment of species A.



I, *Species* A.
II, „ *heated at* 150°.
III, „ „ 200°.
IV, „ „ 250°.
V, „ „ 360°.
VI, „ „ ~800°.

FIG. 2.

Change in principal lattice spacings on thermal treatment of species H.



I, *Species* H.
II, „ *heated at* 200°.
III, „ „ 250°.
IV, „ „ 300°.
V, „ „ 350°.
VI, „ „ 420°.
VII, „ „ ~650°.
VIII, „ „ ~800°.

(*Horizontal scales in* A. *Vertical distances represent intensities.*)

Species E (Plate VI). Crystals grew as small, yellow-green needles, up to 20 μ. long. High birefringence; straight extinction; positive elongation; mean *n* ~1·79; probably monoclinic. Growth from $Li_2O,Al_2O_3,3SiO_2$ compositions at ~280°. Reproducibility uncertain. Probably a compound containing iron (from autoclave). Occurs together with species A and B as an alteration product in the hydrothermal recrystallisation of analcite with excess of lithium nitrate at 300°. No major yields obtained, so constitution unknown.

Species F (Plate VII). Formed as hexagonal bipyramids, 25 μ. long. Low birefringence; symmetrical extinction; uniaxial, $\varepsilon = 1{\cdot}522$, $\omega = 1{\cdot}518$. System hexagonal. Growth from compositions $Li_2O,Al_2O_3,1$—$4SiO_2$ at 450° and at high pH values. Major yields not obtained, but available data agree with corresponding data for β-eucryptite.

Species G. Small octahedra (~15 μ.). Isotropic; *n* 1·514. Cubic system. Growth from compositions $Li_2O,Al_2O_3,7SiO_2$, above 450°, and at high pH. No major yield and constitution unknown.

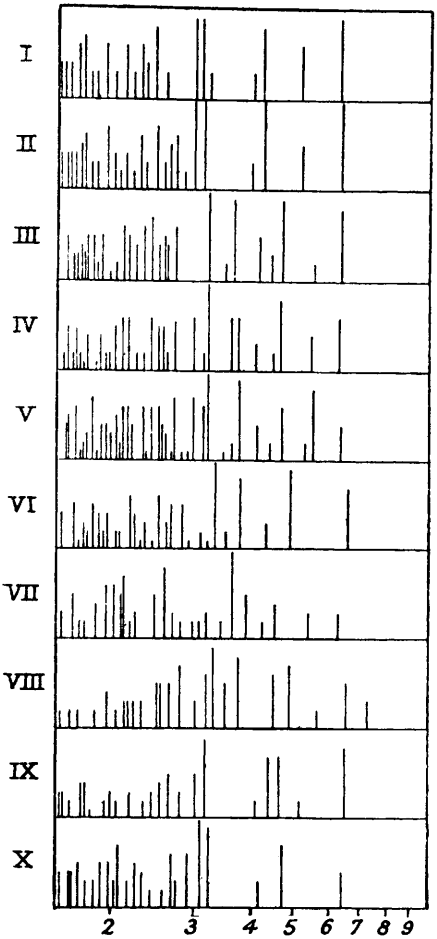
Species H (Plate VIII). *X*-Ray spacings in Table IV. Occurred as rods up to 30 μ. in length, singly and in irregular masses. Birefringence not detectable; *n* 1·480. System probably tetragonal.

Optimum growth from compositions $Li_2O,Al_2O_3,8SiO_2$ at 220° and with high pH values (excess of LiOH). Analysis: Li_2O, 4·3; Al_2O_3, 14·4; SiO_2, 66·0; H_2O, 13·4% ($Li_2O,Al_2O_3,8SiO_2,5H_2O$ requires Li_2O, 4·3; Al_2O_3, 14·6; SiO_2, 68·4; H_2O, 12·9%). Rarely obtained in yields >80%, but some degree of purification was achieved. This silicate showed ion-exchange and sorptive properties (*q.v.*).

Species I (Plate IX). Prismatic crystals of complex shape, up to 50 μ. long. Birefringence weak, symmetrical extinction; positive elongation; uniaxial; $\omega = 1{\cdot}519$, $\varepsilon = 1{\cdot}524$. Growth from compositions $Li_2O,Al_2O_3,3$—$8SiO_2$ at 450° and with pH ~10·0. Reproducibility good, but no major yields at 450°. Identified as β-spodumene.

FIG. 3.

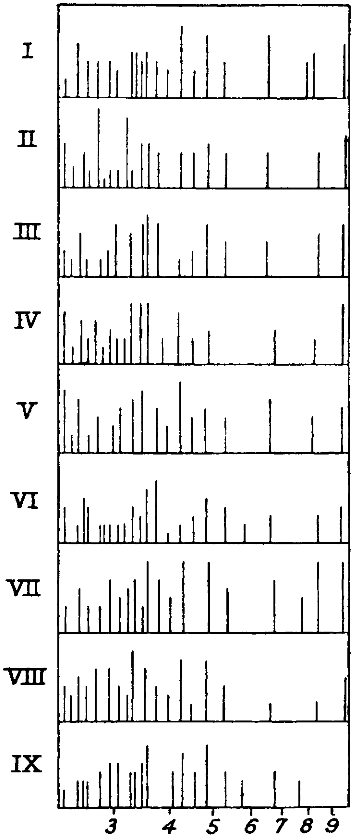
Principal lattice spacings of species A *ion-exchange products.*



I, *Species* A.
II, *Regenerated* Li–A.
III, Na–A.
IV, Ca–A.
V, Ag–A.
VI, K–A.
VII, Ba–A.
VIII, NH_4–A.
IX, Rb–A.
X, Tl–A.

FIG. 4.

Principal lattice spacings of ion-exchange products of species H.



I, *Species* H.
II, Na–H.
III, Ca–H
IV, Ag–H.
V, K–H.
VI, Ba–H.
VII, NH_4–H.
VIII, Rb–H.
IX, Tl–H.

(*Horizontal scales in* A. *Vertical distances represent intensities.*)

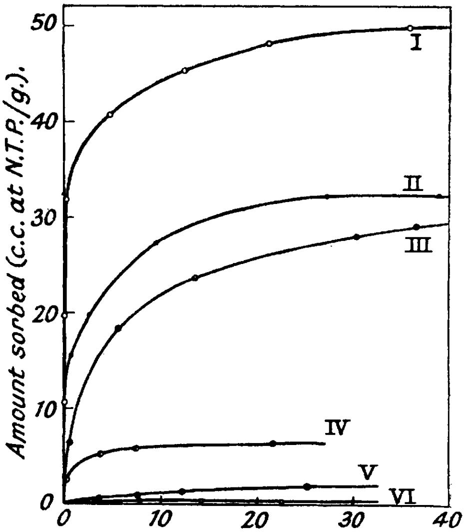
Species J. Lath-like crystals, up to 100 μ. long. Birefringence weak; straight extinction; negative elongation; *n* ~1·76. Grown from compositions $Li_2O,Al_2O_3,4$—$8SiO_2$ at ~360°; deposited on stopper and walls of autoclaves, but did not occur in major yields. Identified by *X*-ray data as α-spodumene.

The species A and H were examined further, for thermal stability, ion-exchange, and sorptive properties.

Thermal Stability of Species A *and* H.—Samples of each mineral were heated in air at temperatures between 150° and 450°, in 50° intervals, for about 2 days. The products were cooled in a desiccator

FIG. 5.

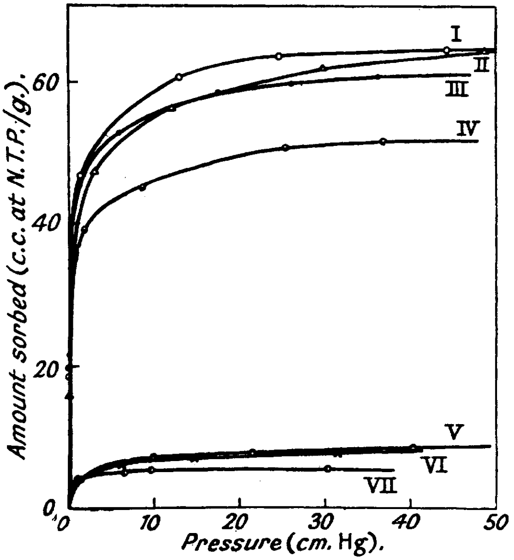
Typical sorption isotherms in species A.



I, NH_3 *at* 0°.
II, NH_3 *at* 0° (*outgassed at* 320°).
III, NH_3 *at* 150°.
IV, N_2 *at* −186°.
V, C_3H_8 *at* 0°.
VI, H_2 *at* −186°.

FIG. 6.

Typical sorption isotherms for species H *and its ion-exchange products.*



Curve no.	*Sorbent.*	*Sorbate.*	*Temp.*
I,	Tl–H	NH_3	0°
II,	Ag–H	NH_3	0°
III,	H	NH_3	0°
IV,	H (*outgassed at* 320°)	NH_3	0°
V,	Tl–H	C_3H_8	0°
VI,	H	C_3H_8	0°
VII,	H	N_2	−186°

and subjected to X-ray examination. Irreversible lattice changes were thus detected as changes in d-spacings. Finally, specimens were also ignited over Meker burners and re-examined.

Species A, $Li_2O,Al_2O_3,2SiO_2,4H_2O$ (Fig. 1), showed slight lattice changes at 200°, possibly due to loss of water. Further changes were noted at 250°, but above this temperature spacings remained constant until recrystallisation occurred on ignition, without chemical disproportionation. The new species consisted of ill-formed, weakly birefringent, irregular crystals, n 1·522. The X-ray powder photograph identified the material as β-eucryptite.

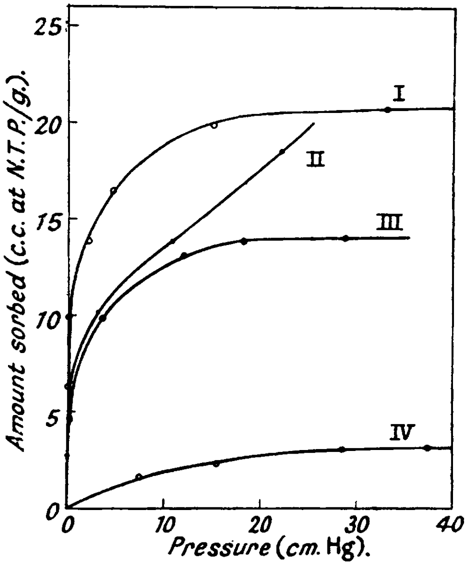
Species H, $Li_2O,Al_2O_3,8SiO_2,5H_2O$, showed little change in its X-ray powder photograph up to 350°, when heated in air. Considerable alteration was, however, observed at 430°. On ignition, a solid of amorphous appearance was obtained; it was homogeneous as regards refractive index (n 1·524) and gave a well-defined X-ray photograph which identified it as β-spodumene.

These experiments indicate the temperatures to which the two minerals may safely be subjected during outgassing, before investigation of their behaviour as sorbents.

Ion-exchange Reactions.—Both species A and H showed well-defined ion-exchange properties. Species B, which was also examined from this point of view, did not undergo ion-exchange. Both A and B, however, tended to recrystallise with NaCl,aq. at 150°, giving analcite, $Na_2O,Al_2O_3,4SiO_2,2H_2O$.

FIG. 7.

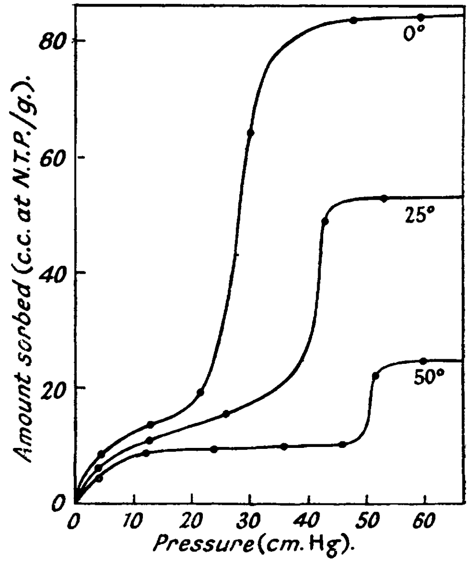
Some typical isotherms in an outgassed but otherwise untreated lithium aluminosilicate gel ($Li_2O,Al_2O_3,3SiO_2$).



I, NH_3 *at* 0°. III, N_2 *at* −186°.
II, NH_3 *at* 50°. IV, C_3H_8 *at* 0°.

FIG. 8.

Sigmoid isotherms obtained with NH_3 *on species* A, *converted into* Ag–A *and then reconverted into* A *by ion-exchange* $Li^+ \rightleftharpoons Ag^+$.



Silver ions readily replaced lithium ions in both A and H, on hydrothermal treatment with excess of silver nitrate at 110° for 2 days. The fusion method also introduced silver and barium ions on use of silver nitrate (m. p. 212°) and barium nitrite (m. p. 217°), but species A showed some decomposition. Other ion-exchange products were obtained by treatment of the silver compounds with solutions of metallic chlorides at ~110° (Tl^+, Ca^{++}, Ba^{++}, Na^+, K^+, Rb^+, and NH_4^+). Most of these exchange products were then entirely free from silver ions. However, with the ammonium compounds, whether prepared hydrothermally or by vapour-phase exchange (using ammonium chloride vapour), there was only limited exchange (~10%). The ease with which the silver cation exchanged forms were made is in accordance with the behaviour of some zeolites (*e.g.*, Taylor, *Proc. Roy. Soc.*, 1934, **145**, *A*, 80; Barrer, *J.*, 1950, 2342). The result with ammonium chloride vapour is, however, in contrast to the usual behaviour where ion exchange is frequently extensive (Clark and Steiger, *loc. cit.*; Barrer, *J.*, 1948, 2158; *loc. cit.*).

From crystals of Ag^+–A, treatment with excess of lithium chloride gave the species A with only minor difference in the X-ray powder photographs from the original sample of A, although the sorptive properties (*q.v.*) indicated that a change had occurred. In general, changes in both intensities and spacings were, however, apparent among the ion-exchanged forms (Figs. 3 and 4). Exchange was also followed by measurements of refractive indices, which were considerable for silver and thallous compounds. The birefringence in most cases decreased, exceptions being silver and thallous ion exchanged forms. Partial analyses of products were made to determine the degree of exchange, calculations being based on the formula $(R'', R'_2)O,Al_2O_3,2SiO_2,4H_2O$.

The species H could not be regenerated from its silver ion exchanged form by hydrothermal treatment with excess of lithium chloride or by fusion with lithium nitrate. Exchange was sometimes accompanied by increases in refractive indices, but not to the same extent as with the mineral A, and all products were isotropic. *X*-Ray diffraction patterns showed changes in intensity, but the spacings were constant within errors of measurement (Fig. 4). Specimens of H used in the ion-exchange experiments were not so pure as those of A, small amounts of unchanged gel being present in most cases. Partial analyses for the ion-exchanged products are therefore of uncertain value and are omitted. The presence of the exchanged ions was, however, demonstrated by analysis. Some ion-exchange data for both species are given in Table V.

TABLE V.

Ion-exchange data for species A *and* H.

Exchange cations.	Species A. R.I. (mean).	Species A. Exchange, %.	Species H.† R.I.
Li^+ (original)	1·53	—	1·48
Li^+ (regenerated from Ag^+–A)	1·53	100 *	—
Na^+	1·54	33·8	1·49
Ca^{++}	1·56	12·9	1·49
Ag^+	1·66	88·1	1·54
K^+	1·54	28·1	1·49
Ba^{++}	1·55	85·6	1·49
Tl^+	1·70	79·5	1·54
Rb^+	1·55	—	1·49
NH_4^+	1·54	11·1	1·49

* On basis of complete absence of Ag^+.

† Products and parent mineral isotropic; $Li^+ \longrightarrow Ag^+$ not reversible.

Sorptive Properties of A *and* H.—Several samples of A and H were tested as sorbents together with some cation-exchanged forms of these minerals, and a specimen of untreated dry gel of composition $Li_2O,Al_2O_3,3SiO_2$. The maximum amounts of several gases sorbed in our experiments are given in Table VI, and a number of characteristic isotherms in Figs. 5, 6, 7, and 8.

TABLE VI.

Sorptive behaviour of several lithium aluminosilicates.

Specimen.	Outgassing temp.	Gas.	Temp. of isotherm.	Max. sorption, obs., c.c. at N.T.P./g.	
A	220°	NH_3	0°	50	
	220	NH_3	150	30	
	220	N_2	−186	6·5	
	220	C_3H_8	0	2·0	
	220	H_2	−186	0·3	
	300	NH_3	21	3·3	
Regenerated Li–A	230	NH_3	0	84	
	230	NH_3	25	53	
	230	NH_3	50	25	
Ba–A	230	NH_3	0	~ 5·0	
Ag–A	230	NH_3	0	~ 6·0	(not true equilibrium)
	230	NH_3	0	2·0	
	230	NH_3	50	3·7	
	230	NH_3	100	~15	
H	230	NH_3	0	60	
	230	N_2	−186	5·4	
	230	C_3H_8	0	7·8	
	320	NH_3	0	52	
Ag–H	230	NH_3	0	65	
Tl–H	230	NH_3	0	65	
B	240	NH_3	0	3·2	
Gel $Li_2O,Al_2O_3,3SiO_2$	230	NH_3	0	21	(saturation not reached)
	230	NH_3	50	18·5	
	230	N_2	−186	14·2	
	230	C_3H_8	0	3·1	

The mineral A showed a moderate capacity to occlude ammonia at 0°, but uptake of propane at 0° and of nitrogen at −186° was limited. The behaviour of Ag^+–A was unusual; the crystals occlude more ammonia above 0° than at this temperature, so it is probable that intracrystalline diffusion of ammonia sets in freely only at higher temperatures, and isotherms do not represent true equilibrium. Similar behaviour has frequently been observed with zeolitic crystals, where activated diffusion may be very slow at lower temperatures (*e.g.*, Barrer, *Trans. Faraday Soc.*, 1949, **45**, 363). It is also found in crystals where the lattice is subject to expansion and contraction according to the content of interstitial water or other small polar molecules. Examples include fibrous and laminar zeolites such as natrolite and heulandite (Barrer, *Proc. Roy. Soc.*, 1938, *A*, **167**, 392, 406). The regenerated Li^+–A produced sigmoid ammonia isotherms (Fig. 8), the initial portion being largely due to sorption on external, easily accessible surfaces which become saturated. After an approximate threshold pressure, however, penetration began, with an approach to saturation of intracrystalline sorption sites at higher pressures. This behaviour is closely analogous to that observed in the ammonia–natrolite system (Barrer, *loc. cit.*), and is again indicative of a collapsing and expanding lattice. Outgassing of specimens above 250° seriously impaired the sorptive behaviour of the crystals.

Crystals of the species H also showed a considerable sorptive power towards ammonia. Base exchange ($Li^+ \rightleftharpoons Ag^+ \rightleftharpoons Tl^+$) did not alter this affinity very greatly (Table VI), and no anomalous effects characteristic of a swelling and shrinking lattice were observed. This contrast between A and H is entirely in accord with their lattice stabilities deduced from structural changes on ion-exchange and on thermal treatment. Specimens of H outgassed at 320° were not quite as active as those outgassed at ~220°, but the decrease was less marked than for species A.

The sorption of ammonia by the anhydrous species B was confined to a small amount of adsorption upon external surfaces of the crystallites. No evidence of intracrystalline sorption was obtained. Ammonia was, however, sorbed to a considerable extent by a sample of outgassed uncrystallised gel, though not so much as by species A and H (Table VI). At −186° nitrogen was, as might be expected, rather more strongly adsorbed on the gel than on the crystalline materials. However, since the samples of A and H used approached 100% purity, the sorption there observed cannot be ascribed to the presence of amorphous gel.

DISCUSSION.

The species A and H have the ratios $Li_2O : Al_2O_3 = 1 : 1$, contain crystal water replaceable by ammonia to give continuous sorption isotherms, and show ion-exchange properties. In all these ways they conform to the definition of a zeolite, and it is thus possible that two entirely synthetic new zeolites have been prepared. Of these species, one (mineral A) shows a tendency to lattice changes, partially reversible, on outgassing or ion exchange, and is to be compared therefore with the fibrous or laminar zeolites (*e.g.*, the natrolite group and heulandite). The other species (mineral H) is less prone to these lattice changes, and may be likened more nearly to the robust three-dimensional network zeolites (chabazite, gmelinite, analcite, harmotome, mordenite, or levynite).

This work has largely been carried out in a temperature range complementary to that investigated by Roy, Roy, and Osborne (*loc. cit.*), where crystallisation was studied mainly above 450°. Results are in good agreement, except for the formation of β-eucryptite at temperatures of *ca.* 450°; also the inversion of α-petalite to β-eucryptite was not observed on several hours' heating at ~800°.

There are interesting differences in physical properties between natural and synthetic α-eucryptites. As between synthetic and natural specimens, one finds appreciable variations in refractive indices, the synthetic crystals (this paper; and Roy, Roy, and Osborne, *loc. cit.*) having higher values of *n* than natural crystals (Brush and Dana, *loc. cit.*). There are also apparent variations in crystal habit and system between the synthetic minerals obtained by ourselves and by Roy, Roy, and Osborne. On the other hand, the *X*-ray photographs of both sets of synthetic crystals agree excellently *inter se* and with those of naturally occurring α-eucryptite.

α-Spodumene occurred only as a deposit on autoclave walls, considerably contaminated with ferric oxide; *X*-ray data were, however, obtainable and gave positive identification. Again, refractive indices were considerably in excess of values quoted for the natural mineral but were in better agreement with those for synthetic α-spodumene grown by Roy, Roy, and Osborne (*loc. cit.*).

As would be expected from the high density and refractive index of α-spodumene, this mineral was produced only at ~400°, and in small quantities. Species A and H, the open zeolitic crystals with a considerable content of water molecules, were, on the other hand, produced at low temperatures (Table III). The formation of β-spodumene and β-eucryptite would appear analogous to the hydrothermal formation of metastable cristobalite (*e.g.*, Wyart, *Bull. Soc. franç. Min.*, 1943, 479; H. F. W. Taylor, *J.*, 1949, 1253), when the stable phase (α-quartz) would be expected.

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