66. *Hydrothermal Chemistry of the Silicates. Part XI.** *Habit and Surface Topography in Synthetic Crystals of the Analcite Group.*

By R. M. Barrer and I. S. Kerr.

Synthetic analcites prepared under different conditions with different cations have been examined by an electron-microscope replica technique. Both single crystals and spherulites were found. The crystals were 42-, 30-, or 24-hedra in the case of Na-, Cs-, K,Rb-, and Tl,Rb-analcite, and usually had rather featureless plane faces. Ca-analcite grew in octahedra with heavily stepped and truncated faces. The face indices agreed, in the main, with previous observations on the corresponding natural minerals. Spherulites with {211} facets occurred in Na-, Cs-, and Rb-analcite, whilst those containing thallium had {100} facets. The spherulites were measured carefully, so that the number and average density of crystal nuclei could be estimated. From this an instantaneous density of nuclei was postulated and shown to vary approximately as the inverse square of the radius. The successive growth layers on Ca-analcite and the frequent emergence of spherulites suggested that many of the samples grew under conditions of high supersaturation.

Comparison of the morphology of natural aluminosilicates and their synthetic counterparts is of interest for two reasons. First, the synthetic products often differ optically and chemically, and sometimes even in crystal symmetry from the naturally occurring analogues (reflecting differences in crystallising magmas and growth conditions); and, secondly, the variables in laboratory syntheses may be better known (pressure, temperature, composition, and time). Accordingly, in this paper, we report observations on the topology and morphology of synthetic phases of the analcite group. Naturally occurring members of this group are analcite (Na), wairakite (Ca), leucite (K), and pollucite (Cs), but by synthesis this range of compounds has been extended considerably (Table 1).

Crystalline aluminosilicates synthesised hydrothermally in these laboratories have been observed as single crystals, cruciform, and interpenetrating twins,[1] multiple twins,[2] rosettes,[1] overgrowths,[3] needles or whiskers,[4] clusters and spherulites.[5] Crystals have also appeared to be anhedral, or where one species was subsequently transformed into another the new species was occasionally a pseudomorph of the old; in other cases the species being metamorphosed was etched and corroded. Sometimes nucleation of a crystalline phase appeared to have occurred within a matrix of gel rather than by precipitation from solution. Of the two modes of growth, by deposition in successive layers and by spiral growth about dislocations, examples of the first,[6] but not of the second, have so far been noted. This supports the view that there is usually a comparatively high degree of supersaturation in the mother-" liquor " with respect to the crystallising species. However, growth of some needles may have been by the spiral dislocation mechanism, possibly when the supply of chemical " nutrients " from the magma was nearing exhaustion and the degree of supersaturation was becoming low.

The crystals grown have normally been quite small, and so far we have made little examination of surface detail by replica techniques. Difficulties of examining such small crystallites in this way have, however, been largely overcome in the case of certain clay

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* Part X, *J.*, 1961, 983.

[1] *E.g.*, Barrer and White, *J.*, 1951, 1267, Plate IV.
[2] *E.g.*, Barrer and White, *J.*, 1952, 1561, Plates II and III.
[3] Ref. 2, Plate IV.
[4] Ref. 2, Plate VII.
[5] Ref. 2, Plate I.
[6] Gard, Barrer, and Baynham, *J.*, 1955, 2480.

minerals,[7–9] for which topographical details of great interest have been revealed. We have now extended the method used in this work to synthetic tectosilicates of the analcite group.

TABLE 1.

Synthetic analcite-type species examined.

Specimen no.	Type	Ref.	Preparation
1	Na-analcite	*a*	Hydrous gel $Na_2O,Al_2O_3,8{\cdot}2SiO_2$, 2 days at 216° with 2N-Na_2CO_3. Analcite main product.
2	Na-analcite	*b*	Hydrous gel from $NaAlO_2 + Na_2SiO_3$ with $Al_2O_3 : SiO_2 = 1 : 4$, 1 day at 200°, with H_2O. Analcite ~100%.
15	Na-analcite	*c*	Similar to 2.
16	Na-analcite	2	Hydrous gels $Na_2O,Al_2O_3,nSiO_2$, hydrothermally treated for several days. High yield analcite. Particular prepn. not identified.
	Cs-analcite	*d*	Hydrous gels $Cs_2O,Al_2O_3,4{\cdot}5SiO_2$:
26			at 340° for 3 days
27			at 340° for 4 days
28			at 300° for 4 days
29			at 300° for 6 days
	Rb-analcite	10	Hydrous gels $Rb_2O,Al_2O_3,4SiO_2$:
22			at 300° for 64 hr.
23			at 350° for 43 hr.
24			at 400° for 21 hr.
25	Tl-analcite	*e*	Hydrous gel $Tl_2O,Al_2O_3,4SiO_2$ heated at 300°
19	Ca-analcite	*f*	Hydrous mixture $CaO,Al_2O_3,3SiO_2$ with water for 32 days at 300°. Tetragonal Ca-analcite in good yield (with some anorthite, and its hexagonal dimorph).
9	Rb,K-analcites	10, 11	Hydrous gel $(K_{0{\cdot}4}Rb_{0{\cdot}6})_2O,Al_2O_3,4SiO_2$ heated with water at 400° for several days.
10	K,Rb-analcites	10, 11	Hydrous gel $(K_{0{\cdot}6}Rb_{0{\cdot}4})_2O,Al_2O_3,4SiO_2$ heated with water at 400° for several days.
12	Tl,Rb-analcites	10, 11	Hydrous gel $(Tl_{0{\cdot}8}Rb_{0{\cdot}2})_2O,Al_2O_3,4SiO_2$ with excess aq. RbOH at 250° for several days. Two analcites with *n* 1·62 and 1·54, respectively.
13	Rb,Tl-analcites	10, 11	Hydrous gel $(Tl_{0{\cdot}2}Rb_{0{\cdot}8})_2O,Al_2O_3,4SiO_2$ with excess aq. RbOH at 350° for several days. Two analcites with *n* 1·62 and 1·54, respectively.

a, Prep. by R. M. Barrer. *b*, Prep. by Imperial Chemical Industries Limited. *c*, Prep. by L. M. Clark. *d*, Prep. by D. Marshall. *e*, Taylor, *J.*, 1949, 1253. *f*, Barrer and Denny, *J.*, 1961, 983.

EXPERIMENTAL AND RESULTS

A range of analcite-type compounds was selected from available synthetic materials. These included analcite-type phases in which Na, K, Rb, Cs, Tl, Ca, and Sr were the only cations present, as well as mixed phases where the cations were (K,Rb) and (Tl,Rb). In such " mixed " phases limited mutual solid solubility of the end members has been demonstrated,[10,11] and two crystalline phases may be so precipitated, one rich in the first of the two cations and the other rich in the second. The pure Rb-analcite crystals also consist of domains of two crystalline phases, both tetragonal, in intimate intergrowth in each crystal.[10] Some relevant details of the experimental materials are given in Table 1.

Preparation of Replicas.—The method is a modification of that described by Comer and Turley,[7] the main difference being the stage at which carbon is evaporated.

An aqueous suspension was made from the analcites, which were in the form of fine to moderately coarse powders, and drops were spread evenly on a microscope slide so as to cover a square centimetre. On drying, the particles adhere to the glass, and the specimen is shadow-cast at an angle of 45°. On account of the roughness of the deposit, greater inclination to the shadow-casting beam is of no further advantage. The first specimens were shadowed with a

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[7] Comer and Turley, *J. Appl. Phys.*, 1955, **26**, 346.

[8] Comer, 1959, Contribution No. 58–91, College of Mineral Industries, Penn. State Univ., Pa.

[9] Bates, " Selected Electron Micrographs of Clays and other Fine-grained Materials," 1958, Circular No. 51, Mineral Industries Expt. Station, College of Mineral Industries, Penn. State Univ., Pa.

[10] Barrer and McCallum, *J.*, 1953, 4029.

[11] Barrer, Baynham, and McCallum, *J.*, 1953, 4035.

mixture of gold and palladium, but later pellets containing equal weights of carbon and platinum were employed, after description of their use by Krantz and Seal.[12] Improved resolution was then obtained, and there was a notable absence of graininess due to recrystallisation.

For embedding, a small quantity of granulated polystyrene was placed on a slide and fashioned into a circle about 3 mm. thick. On gentle heating, a clear disc of the plastic was formed. When the disc was of moderate softness, the specimen was inverted and pressed on top of the disc. After cooling, the microscope slides were removed and the analcites dissolved in 20% hydrofluoric acid; 18 hours usually sufficed, at the end of which time the replica was inspected at magnification 150 for any remaining pieces. Next, carbon evaporation was carried out, and to fill the cavities left by the dissolving analcite this was done from two directions at 15° to the normal. Finally, the replica was marked out into 3 mm. squares, which on immersion in chloroform quickly became free from polystyrene. These pieces were washed and mounted on fine copper mesh microscope grids.

Examination of Replicas.—Replicas were taken from synthetic species of the analcite group prepared under different conditions or with different cations (Table 1). Seventeen produced successful micrographs, but on six replicas no areas were found which differentiated themselves from the general background as recognisable crystal surfaces. As these six were prepared from material of small crystal size (0·01—0·005 mm.) failures were probably due to the crystals' not making contact at the embedding stage.

The replicas, having large void areas, were scanned in a Phillips 100 electron microscope, to locate the places showing crystalline detail where the crystals had made contact with the polystyrene. Exposures were usually taken at magnification 1000 or 2000, so as to include the impressions of a whole crystal or conglomerate of crystals in the field of view. Great help in interpretation was afforded by taking stereographic photomicrographs for which a tilt of 6° between exposures proved sufficient. The results and references to the diagrams are presented in Table 2, and are further discussed below.

TABLE 2.

Summarised results.

		Single crystals					
Specimen no.	Prepn.	24-hedra {211}	30-hedra {211}, {100}	42-hedra {211}, {100}, and {110}	Octahedra {111}	Prisms	Spherulites
1	Na-analcite	—	+	—	—	—	+
2	Na-analcite	—	+	—	—	—	—
15	Na-analcite	—	+	—	—	—	—
16	Na-analcite	—	+	+	—	—	+
26—9	Cs-analcite	+	—	—	—	—	+
22—4	Rb-analcite	—	—	—	—	—	+
25	Tl-analcite	—	—	—	—	—	+
19	Ca-analcite	—	—	—	+	—	—
9	2 : 3,K : Rb-analcite	—	+	—	—	—	—
10	3 : 2,K : Rb-analcite	—	+	+	—	+	—
12	4 : 1,Tl : Rb-analcite	—	+	—	—	—	+
13	1 : 4,Tl : Rb-analcite	—	+	+	—	+	—

Na-*Analcite.*—Four specimens were examined, having a range in crystal sizes from 0·02 to 0·06 mm. A polyhedral and a spherulitic crystal habit were observed. The polyhedral form was present to a greater or less extent in all the specimens (Plate 1a). It consisted of plane-faced polyhedra with predominating {211} faces and truncations exposing {100} facets. The principal faces formed an icosatetrahedron, which with its truncations became a 30-hedron (Fig. 1a). The [110] axis was in one instance observed to be truncated. No detail, such as a steps or spiral, was observed on any face. Goniometric measurements, which were possible only on the largest crystals, served to confirm the {211} index. Face indices in the other samples were assigned on a morphological basis.

Spherulites were observed in two of the specimens, one of which was composed almost entirely of them. They were spheres, 15—30 μ in diameter, and frequently occurred as pairs or strings joined firmly together. The replicas (Plate 1b) showed their surfaces to be composed

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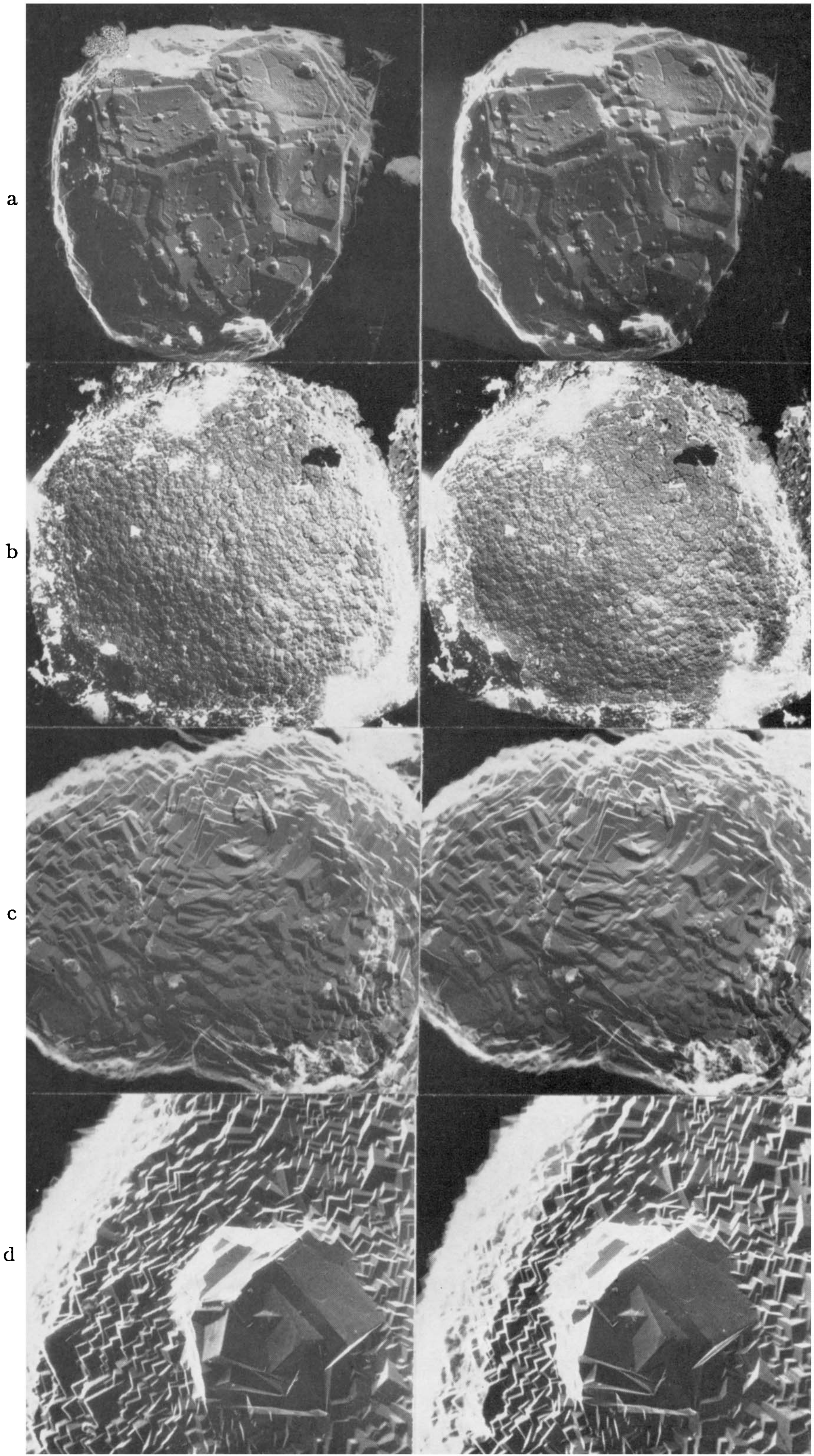
[12] Krantz and Seal, *Brit. J. Appl. Phys.*, 1961, **12**, 589.

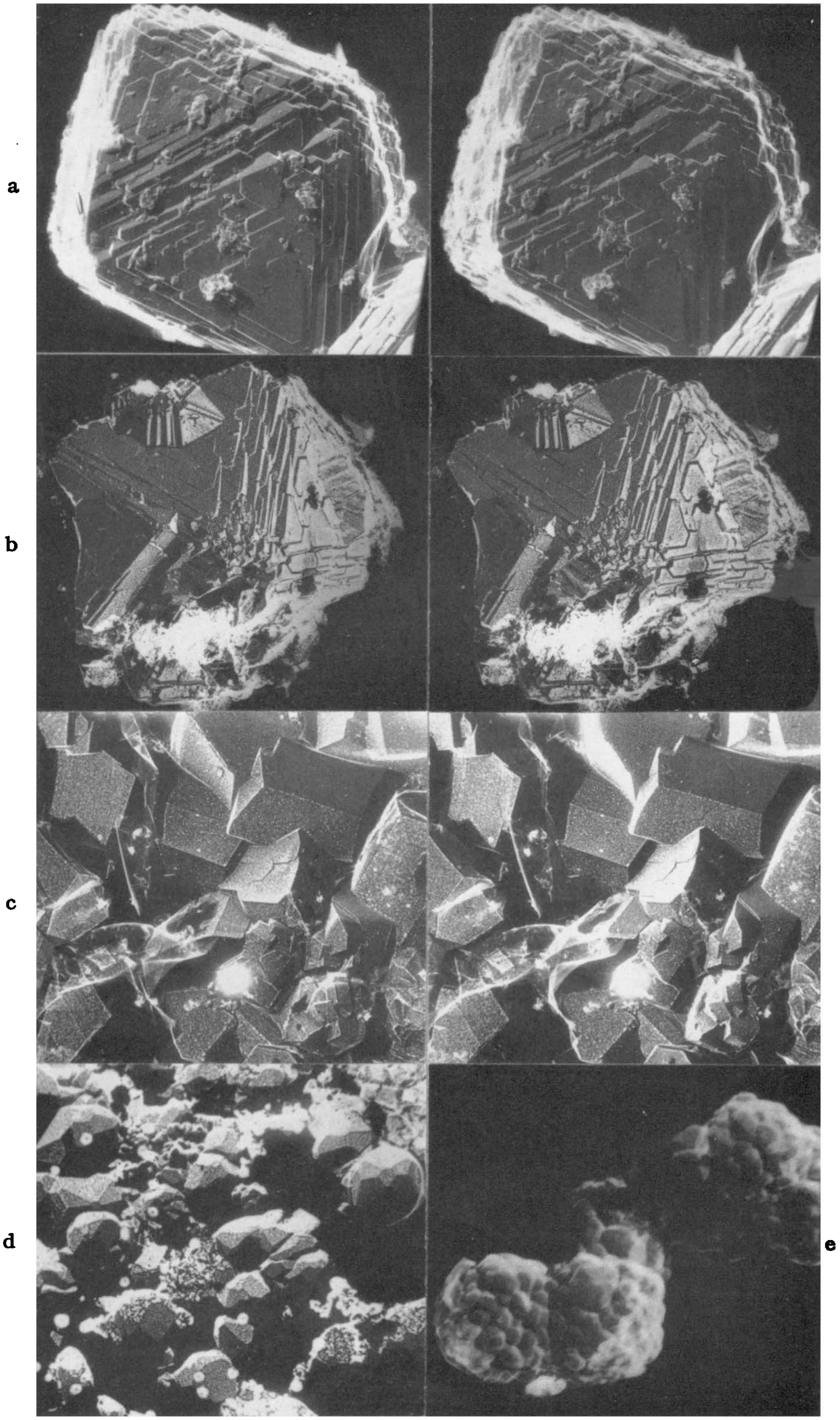
PLATE I.



a, 2125 × Na-analcite crystal from sample 2.
b, 1800 × Na-analcite spherulite from sample 16.
c, 5500 × Rb-analcite sample 23; a pair of intergrown spherulites.
d, 5500 × Tl-analcite spherulite from prep. 25; the outgrowth may possibly be a thallium compound analogous with kalsilite or kaliophilite.

All may be seen in three dimensions through a pocket stereographic viewer.

PLATE II.



a, 3700× } Ca-analcite octahedra from sample 19.
b, 2750× } The former shadowed with C–Pt, the latter with Au–Pd.
c, 2750× K,Rb-analcite No. 10. The prismatic form.
d, 2600× Tl,Rb-analcite sample 13, showing several examples of 42-hedra.
e, 14,500× Cs-analcite sample 29, the smallest spherulites found.

Photographs a, b, and c may be seen in three dimensions through a pocket stereographic viewer.

of groups of three {211} facets around a 3-fold axis such that the [111] axis was always directed radially outwards. Neighbouring groups were crystallographically independent of one another, while the sizes of individual facets were between 0·4 and 0·7 μ, the largest occurring on the largest spherulites.

Natural Na-analcites have been reported in the form of cubes with corners truncated by a group of three small faces and also to a less extent as rhombic 12-hedra truncated at the 3-fold apex.[13] Niggli[14] observed two main habits which were, first, deltoid 24-hedra with {211} as principal faces, with or without {332} bevels meeting at the 3-fold apices, and, secondly, cubes with corners truncated by a group of three {211} or {332} faces. {111} and {210} faces were also observed. Recently also, a synthetic analcite was prepared which under the microscope was seen to contain the 24-hedra.[15] It is of interest that natural leucite was also found to have grown in 24-hedra composed of {211} faces, sometimes with {110} facets, while cubes and 12-hedra were minor forms.[13,14] We were, however, unsuccessful in observing satisfactory crystallographic detail, using sintered synthetic leucite, for comparison with these natural habits.

Cs-*Analcite* (*Pollucite*).—Four specimens of cæsium analcite were examined, all of which showed a preponderance of small spherulites (Plate 2e) with diameters 0·5—1 μ. The facets on the smallest spherulites were less than 0·1 μ and, as this was near the limit of resolution of the replicas, the indices could only be assumed. However, on the larger spherulites the faces were identified as {211}.

Polyhedra were also present singly, or as a mass on intergrown crystals, both with {211} faces. Single crystals were therefore icosatetrahedra, and showed no truncations. Spherulites and single crystals appeared side by side in some photographs. Although growth may have taken place in different parts of the autoclave and on mixing subsequently, during washing and filtration, it seems likely that conditions for formation of spherulites and of single crystals are not widely different.

Naturally occurring pollucite is also described by Dana[13] as " cubic having trapezohedral faces like analcite," *i.e.*, {211} faces.

Rb-*Analcite*.—This material was formed as medium-sized spherulites (Plate 1c), whose diameters were 3—10 μ and whose facets varied between 0·1 μ on the smaller to 0·5 μ on the larger spherulites. The groups of facets protruded a little more than those of the sodium analcite, exposing, not only three {211} facets at the apex, but also three {100} facets at the base of each triangular pyramid. Some were so large that they appeared as small single crystals embedded in the surface. The relative importance of the two types of face seemed nearly equal. No isolated single crystals were found in any of the three samples examined.

Tl-*Analcite*.—Thallium analcite occurred mainly as large spherulites with sharply pointed apices (Plate 1d). The diameters of the spherulites were in the range 20—30 μ, whilst the facets varied between 0·2 and 0·6 μ; the latter were quite smooth and were identified as {100} faces, in contrast to those of other analcites studied. No single crystal was found, but one spherulite had a large protuberance consisting of several intergrown crystals.

Ca-*Analcite*.—Synthetic wairakites were also exceptional in that the predominating faces were {111} (Plates 2a and b). Large octahedra, 12—15 μ across, were evident from the photomicrographs. The {111} faces were heavily terraced, and {100} facets appeared at the corners of each triangular raised area. Since the shadowing angle on any one face was not known, step heights could not be directly determined. However, with the help of stereomicrographs, heights of different steps have been estimated as 0·05—0·4 μ. Ramps and small misalignments of different areas of the same face were observed. Intergrowths were clearly present.

Naturally occurring wairakites have been described by Coombs[16] as octahedra with small, modifying 24-hedron-like faces, and also as small, incomplete 24-hedra. With an optical goniometer it was possible to confirm {111} and {211} faces.

Mixed K,Rb-*Analcites*.—Two samples were examined and two crystal habits were noted in each. There was the now familiar 30-hedron (Fig. 1a), composed of {211} and {100} faces, and found here in rather an irregular form as if the rates of growth of different faces had got out of step. Secondly, there was a prismatic habit (Plate 2c and Fig. 2a), but this form was so

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[13] Dana, " System of Mineralogy," Wiley, New York, 1868, pp. 432, 334, 249.

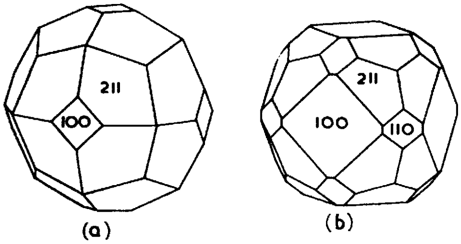
[14] Niggli, " Lehrbuch der Mineralogie," Kümmerly, Berlin, 1929, p. 209.

[15] Barrer, *Trans. Brit. Ceram. Soc.*, 1957, **56**, 155.

[16] Coombs, *Min. Mag.*, 1955, **30**, 699.

heavily intergrown that it was not clear whether the crystals in their simplest form were pentagonal or hexagonal prisms. Both habits had plane, rather featureless faces, showing no sign of steps.

Mixed Tl,Rb-*Analcites.*—Of two specimens of Tl,Rb-analcite both showed single crystals 1—3 μ in diameter (Plate 2d), which were identified as 30- and 42-hedra (Fig. 1) with the faces {100}, {211}, and {110} in order of diminishing size. Thus the relative importance of the {100} and the {211} faces was reversed as compared with Na-analcite. A simple explanation of this may be that the Tl-cation produces a tendency towards {100} faces, so that Tl-analcite is composed entirely of cube faces, whilst in mixed analcites the {100} truncations become enlarged. The {110} facets appeared frequently, producing small elongated hexagonal truncations.



(a) (b)

FIG. 1. (a) 30-Hedron. (b) 42-Hedron.

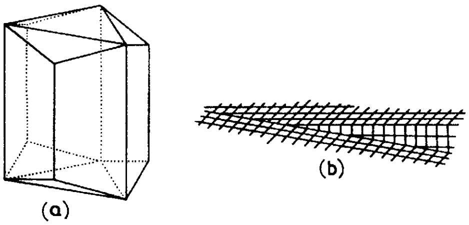

(a) (b)

FIG. 2. (a) Suggested "ideal" crystal of the prismatic form. (b) Join of two slightly misaligned crystals.

A prismatic habit was also observed, similar to that already noted in K,Rb-analcites. This form was only seen in analcites containing rubidium, and since a tetragonal structure for Rb-analcite has been found,[10] the prismatic form may possess tetragonal symmetry.

DISCUSSION

Habit and Growth.—The single crystals examined could all be subdivided into polyhedra derived respectively from the icosatetrahedron (24-hedron) and the octahedron. This applied also to intergrown crystals which are developments of the single crystals.

Icosatetrahedra, which have only {211} faces, were sometimes observed, but oftener than not {100} and {110} truncations produced the 30-hedron and 42-hedron of Figs. 1a and b. In general, the descriptions of analcite by Dana[13] and by Niggli[14] agree with the present observations, but some differences also arise, since we have noticed no {111}, {332}, or {210} facet. Faces were plane and gave little indication of the mechanism of crystal growth.

For the Ca-analcites, crystals based on the octahedron were the only ones observable, with heavily terraced faces and small {100} facets. The {111} faces were also predominant in natural wairakite, but Coombs[16] gives the minor faces as {211}. Misalignments of different triangular areas of the same face of the synthetic crystals have suggested a mechanism of crystal growth. Measurements from the micrographs indicated inclinations of different adjacent areas between 2° and 10°. There seems no way in which these misaligned areas could have grown from a perfect underlying crystal. Originally there must have been mis-orientations in the crystal, associated with which there would be dislocations along the boundaries (Fig. 2b). Growth steps which, if only a single unit cell in height would not be resolved in shadow-casting, might move outwards from the boundaries, so possibly accentuating the apparent misalignment of the surface. Owing to the tetragonality of wairakite, twinning on a (101) or (011) plane would produce a mis-orientation of 2° 10′ in the (111) planes, and repeated twinning could account for larger angles.

Spherulites.—The spherulites were roughly spherical, polycrystalline masses composed of many single crystals (see Plates) and orientated with a certain direction parallel to the radius; here the [111]. Each single crystal can be imagined as a cone with the vertex towards the centre of the spherulite and terminating in a "head" consisting of three or more facets, which are visible on the surface. To obtain an estimate of the depth at which a cone may be expected to originate and hence to throw some light on the history of spherulites, the diameters of the single crystal " heads " and the spherulites themselves were measured.

The smallest spherulites were found in Cs-analcites, the diameters being ~0·5 μ. The size increased through Rb- to Na- and Tl-analcites, where the diameter was as much as 30 μ. For the smaller spherulites, average particles were selected from photomicrographs showing several, and their dimensions were measured. Larger spherulites were less uniform, and accordingly as many as possible were measured individually. A small range in the size of " heads " on each spherulite was found, so that to estimate the number of " heads " one had to know what fraction of the surface area of the spherulite was covered by each size of " head." From inspection of several photomicrographs it appeared that this fraction of the total area was related to the size of the facets in a roughly linear way. This being the case, an average of the reciprocals of the " head " diameters should lead to the correct result. Such an average was used, where in Table 3 the ratio columns give spherulite diameter divided by average " head " diameter. If each nucleus is assumed to give rise to a " head," the total number and hence the density of nuclei can be evaluated (Table 3); the latter varies widely being greatest for the smallest spherulites.

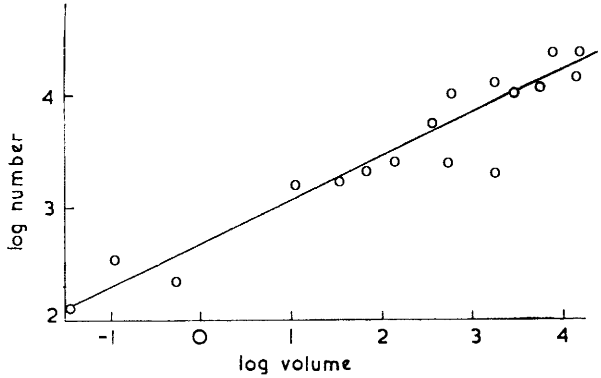


FIG. 3. The log of the volume of each spherulite plotted against the log of the estimated number of nuclei.

TABLE 3.

Measurements on spherulites.

	Diam. of spherulites (μ)	Vol. of spherulites (μ^3)	Diam. of facets (μ)	Ratio	Average ratio	No. of crystals in each spherulite	Density of nuclei per μ^3
Na·Analcite-16......	18	3,050	0·26—0·56	32—70	51	10,400	2·4
	30	14,140	0·35—0·85	35—85	60	14,400	1
	15	1,770	0·4—1·7	9—36	22·5	2,030	1·1
	15	1,770	0·18—0·5	30—84	57	13,000	7·4
	24·8	7,990	0·2—0·8	31—124	77·5	24,000	3
Tl,Rb-Analcite-12	6·5	144	0·17—0·52	13—38	25·5	2,600	18
Rb·Analcite-23 ...	5	65·5	0·15—0·35	14—33	23·5	2,200	34
-24 ...	4	33·5	0·15—0·27	15—27	21	1,760	53
-23 ...	2·75	10·9	0·09—0·3	9—31	20	1,600	150
	10·5	606	0·15—0·4	26—70	50·5	10,200	17
	9	382	0·16—0·5	18—56	37	5,480	14
	10	524	0·25—1·0	10—40	25	2,500	4·8
Cs-Analcite-29	1	0·524	0·1—0·2	5—10	7·5	225	430
-27	0·4	0·034	0·06—0·09	4·5—6·7	5·6	125	3,740
	0·6	0·113	0·05—0·09	6·6—12	9·3	345	3,050
Tl-Analcite-25	22	5,580	0·25—1	22—88	55	12,100	2·2
	31	15,600	0·25—1	31—124	77·5	24,000	1·5

The number (N) of nuclei was plotted against the volume (V) of the spherulite, logarithmic scales being used on account of the range in numbers. This plot showed an expected spread in the results, but there was an unmistakable trend (Fig. 3). From the slope and the intercept of the best line drawn through the points, it was possible to derive the relation $N = 480V^{0 \cdot 37}$ for the lines representing an average value for the number of nuclei, although not fitting any particular case. The spherulites of the various different cations appeared to obey the same relation, but since they covered different ranges in V, this result is open to correction.

If we can assume that the morphology of a spherulite is determined primarily by its size, and not by the cation, so that a Cs- would resemble a Na-spherulite when this was passing through the same stage of growth, a further interesting result may be derived. By differentiation the instantaneous density may be obtained and expressed in terms of the radius, r. Thus $dN/dV = 72 \cdot 9r^{-1 \cdot 88}$ per μ^3, so that dN/dV is roughly proportional to the inverse radius squared. The concentration of nuclei is high near the centre and diminishes asymptotically outwards.

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