X-ray observations on wairakite and non-cubic analcime.

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Introduction.

Mr. A. Steiner has kindly invited the present writer to study by X-ray methods the new mineral wairakite described by him in the preceding pages. The material provided includes an incomplete octahedron 15 mm. across with small modifying icositetrahedron-like faces, and some smaller partial icositetrahedra. Faces are dull and give diffuse reflections on the optical goniometer, but, by attaching small pieces of glass cover-slip to improve the reflections, interfacial angles approximating to those of the cubic forms {111} and {211} were measured. As pointed out by Mr. Steiner, however, the mineral is birefringent, biaxial, and finely twinned. A preliminary small-diameter X-ray powder photograph taken by Mr. N. Wells of the Soil Bureau, Wellington, showed an apparently cubic, analcime-like pattern (personal communication).

Powder data.

X-ray photographs on a 19-cm.-diameter camera were taken of wairakite; birefringent analcime from Låven, Norway (Brögger, 1890; Stewart, 1941), provided by Mr. Steiner; birefringent analcime in a steam cavity in basalt from Flinders, Australia; and synthetic analcime provided by Professor R. M. Barrer. Doubling of many lines in the cases of wairakite and Låven analcime clearly indicate measurable departures from cubic symmetry (fig. 1 and table I) although the multiple lines are so closely spaced that they would probably not be resolved on a small-diameter camera or with thick specimen rods. A general structural similarity with analcime is confirmed.

In the wairakite pattern, reflections corresponding to the 400 and 800 reflections of analcime are doubled, indicating a cell with maximum and minimum dimensions of about 13·68 Å. and 13·56 Å. This represents a slight collapse compared with cubic analcime, in which a = 13·7 Å., and is presumably a result of the replacement of Na atoms by only half the number of Ca atoms.

TABLE I. X-ray powder data for wairakite and analcime.
(Camera 19 cm. diameter, Cu-$K\alpha$ radiation.)

	Analcime, Flinders.		Wairakite.		Analcime, Låven.	
*hkl.**	Int.†	*d* Å.	Int.†	*d* Å.	Int.†	*d* Å.
(200)	< 1	6·87	4	6·85	2	6·88
211	8	5·61	8	5·57	8	5·61
220	4	4·86	4	4·84	4B	4·85
321	2	3·67	3	3·64	3B	3·64–3·67
400	10	3·43	6	3·42	10	3·43
			10	3·39		
(411,330)		—	< 1B	3·21	< 1	3·24
420		—	1B	3·04–3·06	2	3·08
					< 1	3·06
332	8	2·925	5	2·909	7	2·929
			3	2·897	3	2·896
422	2	2·801	1	2·783	2	2·804
			1	2·770	1	2·779
431(510)	5	2·693	4	2·680	4	2·696
			1	2·67	2	2·673
521	5	2·505	< 1	2·50	5	2·506
			4	2·489		
440	3	2·426	3	2·418	2	2·434
—		—		—	2	2·412
(530,433)		—	< 1B	2·35	< 1B	2·36
(600,442)		—	1B	2·26–2·28	1	2·290
611,532	4	2·226	4	2·215	3B	2·217–2·229
620	< 1	2·168	< 1	2·17	1	2·170
			1	2·147		
541	< 1	2·115	1	2·115	1	2·125
			< 1	2·095	< 1	2·10
631	1	2·022	2	1·996	2B	2·015
543(550,710)	< 1	1·940	< 1B	1·93	< 1B	1·94
640	5	1·903	3B	1·886–1·895	3	1·906
					3	1·892
—		—	1	1·867		—
633,721,552	4	1·867	3	1·857	4B	1·869
—		—	1	1·844		—
642	< 1	1·833	< 1B	1·822		—
732,651	6	1·743	4B	1·722–1·732	5B	1·744–1·734
800	3	1·716	< 1	1·708	4	1·713
			< 1	1·696		
741(811,554)	4	1·689	2B	1·680	2	1·692
					2	1·679
820(644)	1	1·664	< 1B	1·66	2	1·663
822,660	2	1·618	1B	1·612	2	1·621
831,743(750)	3	1·596	< 1	1·595	2B	1·596–1·585
			2	1·586		
842	2	1·498	1	1·487	1	1·500

TABLE I (*contd.*)

	Analcime, Flinders.		Wairakite.		Analcime, Låven.	
*hkl.**	Int.†	*d* Å.	Int.†	*d* Å.	Int.†	*d* Å.
761,921,655	2	1·480	1B	1·465	2	1·480
664	1	1·463		—		—
754,851(930)	1	1·447	< 1B	1·437	1	1·449
932,763	4	1·415	2B	1·407	3B	1·416
941,853(770)	< 1	1·386		—	1	1·390
860(10.0.0)	1	1·372		—	1	1·375
10.1.1,772	4	$1{\cdot}358_6$	1 1	1·354 1·343	3B	1·359
10.3.1,952,763	1	1·308		—	2	1·309
871(855,774)	2	$1{\cdot}284_9$		—	1	1·288
—		—		—	1	1·277
10.3.3,961	2	$1{\cdot}263_2$		—	1	1·266
963, &c.	3	$1{\cdot}222_0$	2B	1·215	2B	1·224
—		—		—	1	1·214
677, &c.	1	$1{\cdot}185_1$		—	1B	1·187
11.4.1,875	1	$1{\cdot}167_9$		—	< 1B	1·169
10.5.5, &c.	1	$1{\cdot}120_2$		—	< 1B	1·122

* Indices in brackets are for cubic analcime reflections extinguished in the space group *Ia3d* inferred for the strictly cubic modification.

† Relative intensities estimated by eye in each case. B = Broad reflection, unresolved group.

In addition to the doubling of many lines, the wairakite powder pattern differs from that of typical analcime in the presence of additional reflections. For example, 200 and 411,330 are extinguished in the space group *Ia3d* to which cubic analcime appears to belong (discussed in next section), but corresponding lines occur with wairakite, 200 (6·85 Å.) in particular being relatively strong.

POLYMORPHISM OF ANALCIME.

Optical anomalies in analcime including fine twinning of birefringent units have been frequently reported, as discussed by Stewart (1941). Powder patterns of two analcimes showing such effects have been studied in comparison with the wairakite pattern. That of analcime from Låven, southern Norway, is particularly interesting. Brögger (1890, pp. 565–566) described this mineral and reported lamellar twinning parallel to the cubic cleavages and to a less extent parallel to the dodecahedral directions. The mineral was usually biaxial, but occasionally uniaxial and some parts were isotropic. A new partial analysis by the Dominion Laboratory (Steiner, 1955) reveals only traces of K and Ca. The optical anomalies are therefore not chemically controlled.

The Låven specimen available for the present work is optically negative, uniaxial or nearly so, and it shows very fine blotchy twinning. In the powder pattern (fig. 1*c*) most of the normal analcime lines are broadened or represented by resolved multiple groups, a notable exception being those of the form *h*00. This suggests that the cubic analcime structure has been distorted to trigonal or near-trigonal symmetry, one or other of the four cubic triads having become the only triad by change of length relative to the others, the *h*00 planes of the cube consequently having become rhombohedral planes. Each reflection or group of reflections in the Låven analcime pattern can therefore be allotted provisional indices based on a non-primitive body-centred rhombohedral cell by direct analogy with the corresponding lines in the pattern of cubic analcime. Thus cubic 440 is represented by two lines in the Låven analcime pattern, and these can be given the provisional rhombohedral indices 440 and $4\bar{4}0$. This leads to two possible sets of lattice constants, but by consideration of observed and calculated spacings for other clearly resolved lines, one of these can be discarded and the pattern indexed in terms of a body-centred rhombohedral cell having *a* 13·71 Å., α 90° 31′. The corresponding primitive cell has the constants *a* 11·91 Å., α 109° $42\frac{1}{2}$′, but the non-primitive form is the more useful for showing

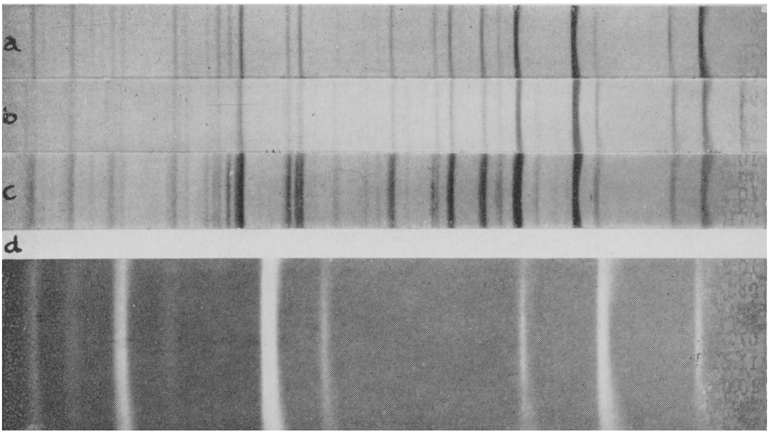

FIG. 1. X-ray powder photographs (lower θ region) of analcime and wairakite. Cu-$K\alpha$ radiation, Ni filter, camera 19 cm. diameter.

a, Analcime, Flinders, Australia. *b*, Wairakite, Wairakei, New Zealand. *c*, Analcime, Låven, Norway. *d*, Wairakite, enlargement of portion of the photograph (*b*) showing doubling of 400 (the strongest) and other reflections.

the relationship to cubic analcime for which a 13·64–13·75 Å. according to various authors (e.g. Gruner, 1928 *a*, *b*; Taylor, 1930; Lyons, 1944). Data for critical indexed reflections are set out below (table II).

TABLE II. Calculated and measured lattice spacings for Låven analcime.

(hkl)*	d_{hkl}calc.	d_{hkl}obs.	Int.
400	3·427 Å.	3·428 Å.	10
$3\bar{3}2$	2·933	2·929	7
$33\bar{2}$	2·926		
332	2·897	2·896	3
$4\bar{2}\bar{2}$	2·810	2·804	2
$42\bar{2}$	2·802		
422	2·777	2·779	1
$4\bar{4}0$	2·434	2·434	2
440	2·412	2·412	2
640	1·908	1·906	3
$6\bar{4}0$	1·893	1·892	3
800	1·713	1·713	4

* *hkl* indices for body-centred rhombohedral cell.

Birefringent analcime from Flinders, Victoria, Australia, is biaxial with variable optic axial angle. Determinations were made with the range $2V_\alpha$ 45–120°, but the majority of fragments observed gave $2V_\alpha$ 68–85°. The mineral being biaxial, the true symmetry can presumably be no higher than orthorhombic. Nevertheless the powder pattern consists of thin sharp lines with spacings consistent with cubic symmetry and a body-centred unit cell a 13·72±0·01 Å. A significant feature, however, is the presence of a weak line d 6·87 Å., corresponding to 200. This does not appear to have been present in previously recorded analcime powder patterns (e.g. Taylor, 1930; Konta, 1953), nor is it present in that of the synthetic analcime provided by Professor R. M. Barrer. This latter sample consists of crystals with a maximum diameter of 0·05 mm. Double refraction effects were not detected. It is interesting to note that Konta states that his material is strictly isotropic.

A 200 reflection is incompatible with the space group $Ia3d$ (O_h^{10}) which has as a requirement for reflections hhl, that $2h+l = 4n$, and for $0kl$ that k, $l = 2n$. This space group has been accepted for analcime by most workers (Gruner, 1928*a*; Hartwig, 1928; Jaeger, 1929; Taylor, 1930). On the other hand, Gruner (1928*b*) suggested that O_h^9 ($Im3m$) was more likely on account of the presence in oscillation photographs of certain rather doubtfully indexed reflections, and Schiebold (1930) considered the mineral to be tetragonal, space group D_{4h}^{20} ($I4_1/acd$). Taylor (1930, pp. 12–13) pointed out that the structure he determined for analcime (1930, 1938) is based on the cubic space group *Ia3d* with Si and Al ions occupying equivalent positions. Optical anomalies suggested that the mineral is only pseudo-cubic which would require non-equivalence (ordering) of the Si and Al atoms. The detailed arrangement has been further discussed by Beattie (1954).

In non-cubic sub-groups derived from *Ia3d* many limitations on possible reflections are removed. Thus reflections in positions corresponding to 200 and 411,330 and many other *Ia3d* extinctions are well represented in the wairakite and Låven analcime patterns. The presence of anomalous reflections in the patterns of Flinders and other birefringent analcimes does not mean that a disordered, strictly cubic, isotropic modification of analcime does not exist; in fact, the synthetic analcime appears to be of this type. It is suggested that weak reflections of the type *hhl* where $2h+l\neq 4n$, may appear when the true symmetry is non-cubic as indicated by the optical properties, even though the cell dimensions have not departed detectably from cubic requirements.

In the past the birefringence of analcime has been ascribed to loss of water (e.g. Náray-Szabó, 1938) although analyses at ordinary temperatures appear to show approximately the theoretical amount, or to strain during or after crystallization (Bannister, 1931; Stewart, 1941). Although Klein (1897, p. 350) found that the birefringence increased when analcime was heated in a dry atmosphere, the mineral usually became isotropic when heated to 250° in the presence of water vapour, becoming birefringent again on cooling.

The data appear to be consistent with an inversion process from a strictly cubic form existing in the presence of water vapour at moderately elevated temperatures to one or more forms of lower symmetry stable at ordinary temperatures. Evidence will be presented for a somewhat similar relationship in wairakite, and Wyart (1937) has clearly shown by X-ray methods the progressive and reversible transformation of a low-temperature tetragonal modification of the analogous mineral leucite to the cubic form at 625° C. The fact that analcime is shown to exist at ordinary temperatures with varying departures from cubic symmetry suggests that in its case the transformations tend to be more sluggish or complicated so that we see the products in various arrested states. Barrer, Baynham, and McCallum (1953) have recently discussed polymorphism among analcime-like structures with special reference to two modifications of synthetic Rb-analcime, both tetragonal. The sluggishness of the transition of these suggested a reconstructive process such as an order-disorder relationship of Si and Al ions rather than a displacive transformation as in leucite.

Tentatively, the following modifications of analcime may be recognized:

(i) Strictly cubic and isotropic, space group *Ia3d*. The synthetic specimen, hydrothermally prepared, appears to belong here.

(ii) Birefringent and biaxial, departures from cubic lattice dimensions not detectable although anomalous X-ray reflections may appear, e.g. Flinders analcime.

(iii) Trigonal or nearly trigonal with rhombohedral angle approximately $90\frac{1}{2}^\circ$, e.g. Låven analcime. Biaxial specimens from the same locality must be of lower symmetry.

The relation of these polymorphs to the high-pressure transition briefly reported by Morey (1953, p. 69) remains to be elucidated.

A systematic study of natural and synthetic analcimes in relation to their thermal history is beyond the scope of the present work. It is conceivable, however, that such a project could yield information of use in the lower temperature ranges of geothermometry, with applications in problems of diagenesis and incipient metamorphism as well as vein and amygdale deposition.

TWINNING, OPTICAL ORIENTATION, AND CELL DIMENSIONS OF WAIRAKITE.

An orientated thin section was cut through an octahedron perpendicularly to one of the tetrads. As in most grains of wairakite as seen between crossed nicols, the most obvious characteristic is the presence of fine, discontinuous lamellar twinning with conspicuous sets at right angles to each other. These are found to be parallel to (pseudo-)cubic {110} planes. Universal-stage examination reveals six sets of such dodecahedral twin lamellae in all. The extinction directions bisect, at least approximately, the angles between pairs of mutually perpendicular twin lamellae and hence remain closely parallel to the tetrads of the octahedron. The orientated section shows a very distinct cleavage parallel to the {100} directions as is the case with analcime. Oscillation photographs of twinned aggregates detached from the orientated section confirm that there is a repeat distance of about 13·6 Å. throughout, essentially parallel to each of the tetrads of the octahedron.

Twinning as here described recalls the secondary twinning so readily produced by inversion processes in anorthoclase, leucite, and other minerals. The indications are strong that wairakite crystallized in strictly cubic octahedra and icositetrahedra and on cooling inverted to a modification shown to be monoclinic. Any one of the (equivalent) *a*, *b*, and *c* cell-edges of the original cubic form could, in different parts of the crystal, become either *a*, *b*, or *c* (non-equivalent) of the lower-symmetry modification, giving rise to the complex twinning. In each case the new cell-edges remain essentially parallel to the cell-edges of the originally cubic modification. The twinning largely compensates for the strains caused by differential contraction along the different cell-edges, and the external apparently cubic morphology is retained, although with dulled faces.

Weissenberg photographs were taken about *a*, *b*, and *c* axes of a small fragment from the orientated section. The nature of the twinning makes interpretation complex, but on the basis of the fact that the larger part of the fragment has a single optical orientation, the following dimensions and orientation were determined. They are based on a body-centred cell to emphasize the relationship with analcime: *a* (near optical β) $13{\cdot}69 \pm 0{\cdot}02$, *b* (optical α) 13·68, *c* (near optical γ) 13·56 Å., β 90·5°. $8(CaAl_2Si_4O_{12}.2H_2O)$ per unit cell.

In regions showing two mutually perpendicular sets of twin lamellae, the short edge *c* is parallel to their direction of intersection and the lamellae are twinned on (110) and $(1\bar{1}0)$. The cell is seen to be pseudo-cubic and even more nearly pseudo-tetragonal.

A condition for reflections *hkl* is that $h+k+l = 2n$. In zero-layer Weissenberg photographs, very weak reflections were observed in positions closely corresponding to *h*0*l* where *h*, *l* are odd. However, in each case these were satisfactorily accounted for as 0*kl* reflections from that part of the crystal in twinned orientation across (110), and it is highly probable that a condition for reflections *h*0*l* is that $h = 2n$. In this case the space-group symbol for the chosen setting of wairakite is *Ia* or *I*2/*a*.

It is significant that reflections that do not accord with the extinction requirements for the cubic space group *Ia*3*d* tend to be weak or very weak. This is compatible with the view that the wairakite structure is derived from a cubic analcime-like structure by a non-reconstructive type of phase transformation. The fact that the observations were made on ejected fragments, presumably quickly cooled from near the crystallization temperature, suggests that the change may be of the rapid, displacive type as in leucite, but a decision on this point, as on the inversion hypothesis as a whole, must await experimental work performed at appropriate temperatures and pressures of water vapour.

STRUCTURE OF WAIRAKITE.

Beattie (1954) points out that although in terms of Taylor's structure for analcime there are 24 possible Na positions, each with an environment of 4 oxygen atoms associated with 2(Si,Al), only 16 of these groups can contain simultaneously one Al atom as well as Si. For valency reasons these are presumably the 16 sites occupied by the 16 Na ions in the unit cell. Beattie further suggested the possibility of an arrangement in which eight positions would have an environment of 4 oxygens associated with 2Al, and 16 positions with 4 oxygens and 2Si. Divalent calcium, as in wairakite, should favour the former of these last two types of site. A different and more specialized distribution of Si and Al atoms is thus implied as compared with that of Na-analcime. On this basis one might explain the failure to obtain pure Ca-analcime (wairakite) by base-exchange experiments with Na-analcime.

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