I. The structure of analcite ($NaAlSi_2O_6 \cdot H_2O$).

By

W. H. Taylor, Manchester University.

(With 3 figures.)

Introduction.

The members of the zeolite family form an interesting series of crystals for analysis by X-ray methods, but up to the present the difficulties encountered have made it impossible to determine completely any of these structures.

The distinguishing features of this group are the variable composition, the special role played by the water of crystallisation, the highly-complicated nature of the twinning which occurs, and the ease with which the constituents sodium, potassium, calcium, etc., can be replaced by other atoms such as silver and caesium, without destroying the crystalline properties. The optical anomalies exhibited by zeolites have been investigated very completely by many workers, and would appear to be intimately connected with the twinnings observed, and to depend on the state of hydration of the specimen under examination. Mineralogists have also suggested that many zeolites may be regarded as hydrated felspars, so that interesting structural relations with the felspar group may be anticipated (1).

The same properties which make the various members of the group so interesting, are also responsible for the difficulties which confront the X-ray crystallographer in his attempt to determine their structures; in particular, the mimetic twinning, which gives to the external form of the compound crystal a symmetry much higher than that which belongs to the individual simple crystals, introduces an uncertainty in the choice of crystal class which would probably be fatal to any direct attempt at structure determination based strictly on the formal principles of space-group theory.

So far as I am aware, the only zeolites previously examined by X-ray methods are scolecite and analcite; in the case of scolecite, Rinne (2) has examined, by means of Laue photographs, the alterations produced when water is expelled, and in the case of analcite the unit cell and space-group have been determined by Grüner (3) and by Jaeger (4).

Schiebold (5) has suggested a structure for analcite, which we shall discuss in detail in a later paragraph, and Hartwig (6) has confirmed the results of the other investigators. The ultramarines have many properties similar to those which are characteristic of the zeolites, and it is therefore of great interest to note that Jaeger (7) has described a determination of the structure of one of these compounds.

Analcite appears to be very suitable for an attack on zeolite structures, because it possesses the definite composition $NaAlSi_2O_6H_2O$ (Ca replaces a small fraction of the Na), and because its external form displays holohedral cubic symmetry. The crystals nearly always exhibit weak birefringence, and are resolved under the microscope into sectors which do not extinguish together, so that the crystals must be really only pseudo-cubic. In the next section it will be seen that chemical and physical considerations of a general nature suggest that the feature which may be common to all zeolite structures, is a framework of linked tetrahedra of oxygen ions containing the aluminium and silicon ions; and in the following sections of the paper this idea is applied to determine the structure of analcite.

The chemical composition of the zeolites.

The problem of determining exactly the chemical formulae of the zeolites is still, to some extent, unsolved, because different specimens of the same material, derived from the same locality, often show large variations in composition. The composition of the felspars is equally variable, and it is generally accepted that the members of each group represent mixtures, in different proportions, of two "end-compounds" — as in the albite-anorthite series. It is possible that a similar hypothesis may serve to explain the composition of the zeolites. (In the case of analcite the chemical composition does appear to be perfectly definite in all specimens.)

In spite of the untrustworthiness of some of the chemical formulae attributed to zeolites, certain important generalisations seem to be permissible. In the first place, if all the water present is regarded as water of crystallisation, the numbers of aluminium, silicon, and oxygen atoms in any zeolite[1]) are in the ratio $Al_xSi_yO_{2(x+y)}$, as e. g. in analcite $NaAlSi_2O_6 \cdot H_2O$, natrolite $Na_2Al_2Si_3O_{10} \cdot 2H_2O$, heulandite $CaAl_2Si_6O_{16} \cdot 5H_2O$. In the second place, for every two aluminium ions in the material, there are always either two monovalent positive ions

---

[1]) With the possible exception of Laubanite, which has a composition corresponding to $Ca_2Al_2Si_5O_{15} \cdot 6H_2O$. (Dana, Mineralogy, p. 588.)

such as sodium or potassium, or one divalent ion such as calcium or barium. The minerals above serve as illustrations.

These two generalisations are very striking (they have been discussed by various workers [8]) and have supplied the clue which enabled the analcite structure to be determined, and which is being used in investigating other zeolites. The fundamental guiding principle which we have adopted as an aid to analysis is that the zeolites are essentially silica-like structures, in which a portion of the silicon in the (SiO_2) material has been replaced by aluminium. If the silicon is supposed to be in the form of the ion Si^{+4}, and the aluminium to be the trebly-ionised Al^{+3}, the oxygen also being ionised (O^{-2}), then whenever one silicon atom is replaced by one aluminium atom, there will be one valency "to spare", and it is this "spare valency" which is satisfied by the one sodium ion (Na^{+1}) or other univalent positive ion which then enters the structure. If two aluminium ions replace two silicon ions, either one divalent ion (such as Ca^{+2}) or two univalent ions, may be added to the structure to satisfy the valencies. Machatschki (8a) has suggested that this type of linked-tetrahedra structure is the basis of the structures of the felspars, and has named it the "Feldspat-typus".

Assuming that this idea is correct, we expect to find both silicon and aluminium ions at the centres of tetrahedra of oxygen ions, the tetrahedra being arranged in such a fashion that they share corners everywhere — i. e. every oxygen ion is held in common by two adjacent tetrahedra. In this way the observed ratio $Al + Si : O = 1 : 2$ will be obtained; and it is to be expected that all corners of tetrahedra will be shared, rather than faces or edges, because in that type of sharing there is the greatest possible distance between neighbouring positive ions occupying the centres of the tetrahedra. The sodium or calcium ions may be expected to occupy positions within the arrangement of oxygen ions (which constitute the linked tetrahedra) where there is the necessary space, and probably near to the aluminium ions. These suggestions, of course, are based on a knowledge of previously-determined silicate structures; they are purely tentative, and are outlined with a view to simplifying the detailed account of the determination of the analcite structure.

The unit cell and space group of analcite.

Other workers who have examined analcite agree that the cubic unit cell with an edge of length 13.7 Å. contains sixteen molecules of $NaAlSi_2O_6 \cdot H_2O$, and that the space group is O_h^{10}, since the external symmetry of the crystal places it in the holohedral class of the cubic system. It has not been possible to detect, by X-ray methods, any departuré from truly cubic symmetry, though this might have been expected by reason of the optical anomalies exhibited by all analcite crystals.

We have confirmed these results, and have obtained a set of data giving the estimated relative intensities of reflection from a large selection of crystal planes, using the rotating-crystal method. Our relative intensities are estimated by eye, and correspond closely with those given by Grüner. The specimens used in our work were small clear crystals from the Cyclopean Islands, obtained from the British Museum through the generous help of Dr. L. J. Spencer, F.R.S.; in working with materials such as zeolites it is very desirable to have available trustworthy crystals, and we are happy to acknowledge our indebtedness to Dr. Spencer in this matter of securing suitable material.

The arrangement of symmetry elements in O_h^{10} is as follows (9): —
Four-fold rotation-reflection axes:

$(100)_{0\,\frac{1}{4}}$ $(100)_{\frac{1}{2}\,\frac{3}{4}}$ $(100)_{0\,\frac{3}{4}}$ $(100)_{\frac{1}{2}\,\frac{1}{4}}$ $(010)_{\frac{1}{4}\,0}$ $(010)_{\frac{3}{4}\,\frac{1}{2}}$ $(010)_{\frac{3}{4}\,0}$ $(010)_{\frac{1}{4}\,\frac{1}{2}}$
$(001)_{0\,\frac{1}{4}}$ $(001)_{\frac{1}{2}\,\frac{3}{4}}$ $(001)_{0\,\frac{3}{4}}$ $(001)_{\frac{1}{2}\,\frac{1}{4}}$.

Three-fold rotation axes:

$(111)_{0\,0}$ $(1\bar{1}1)_{\frac{1}{2}\,\frac{1}{2}}$ $(11\bar{1})_{\frac{1}{2}\,0}$ $(1\bar{1}\bar{1})_{0\,\frac{1}{2}}$.

Two-fold rotation axes:

$(1\bar{1}0)_{\frac{1}{4}\,\frac{1}{8}}$ $(1\bar{1}0)_{\frac{1}{4}\,\frac{5}{8}}$ $(1\bar{1}0)_{\frac{3}{4}\,\frac{3}{8}}$ $(1\bar{1}0)_{\frac{3}{4}\,\frac{7}{8}}$ etc. (24 altogether).

Glide-Planes:

$(100)_0$ $(100)_{\frac{1}{2}}$ etc. $(100)_{\frac{1}{4}}$ $(100)_{\frac{3}{4}}$ etc.
$(110)_0$ $(1\bar{1}0)_0$ etc. $(110)_{\frac{1}{2}}$ $(1\bar{1}0)_{\frac{1}{2}}$ etc.

Symmetry Centres:

$(0\,0\,0)$ $(\frac{1}{2}\,\frac{1}{2}\,0)$ $(\frac{1}{2}\,0\,\frac{1}{2})$ $(0\,\frac{1}{2}\,\frac{1}{2})$ $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ $(\frac{1}{2}\,0\,0)$ $(0\,\frac{1}{2}\,0)$ $(0\,0\,\frac{1}{2})$
$(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$ $(\frac{3}{4}\,\frac{3}{4}\,\frac{1}{4})$ $(\frac{3}{4}\,\frac{1}{4}\,\frac{3}{4})$ $(\frac{1}{4}\,\frac{3}{4}\,\frac{3}{4})$ $(\frac{3}{4}\,\frac{3}{4}\,\frac{3}{4})$ $(\frac{1}{4}\,\frac{1}{4}\,\frac{3}{4})$ $(\frac{1}{4}\,\frac{3}{4}\,\frac{1}{4})$ $(\frac{3}{4}\,\frac{1}{4}\,\frac{1}{4})$.

We have to find places for $16\,Na$, $16\,Al$, $32\,Si$, $96\,O$ and $16\,H_2O$, in the unit cell; this is impossible unless the Na and Al atoms occupy the two 16-fold positions $\{0\,0\,0\}$ and $\{\frac{1}{8}\,\frac{1}{8}\,\frac{1}{8}\}$, and the $32\,Si$ atoms must then be placed on the three-fold axes.

Now the 16-fold positions $\{0\,0\,0\}$ and $\{\frac{1}{8}\,\frac{1}{8}\,\frac{1}{8}\}$ are special points on the trigonal axes, so that in any structure obtained in this way all the positive ions Na^{+1}, Al^{+3}, Si^{+4}, are placed on the trigonal axes; it is easily calculated that the average distance between these ions cannot be greater than about 1.5 Å. Other arguments may be advanced which suggest that this type of structure is incorrect, but the crowding-together on the trigonal axes of all the positive ions is probably in itself sufficient to suggest that some alternative arrangement should be sought.

Schiebold (5) has already suggested a structure based on the above arrangement of positive ions, but points out that such a structure is improbable for various chemical and physical reasons. It is obviously necessary to approach the problem from some point of view other than the strictly formal one employed above.

The analcite structure.

The starting-point for our determination of the analcite structure has been the assumption that it is based on an arrangement of linked tetrahedra of oxygen ions, two thirds of the tetrahedra being occupied by silicon ions, and the remainder by aluminium ions. Every oxygen ion in such an arrangement is held in common by two tetrahedra, and the average distance between one silicon or aluminium ion and the nearest of the surrounding silicon or aluminium ions is of the order 3.0 Å to 3.3 Å. Further, considering silicon and aluminium ions alone, each such ion must have as its nearest neighbours four other similar ions, arranged about it in an approximately tetrahedral manner; otherwise it is impossible to obtain linked tetrahedra of oxygen ions.

Now the Al^{+3} and Si^{+4} ions are very similar, the Al^{+3} ion being only slightly the larger, so it is justifiable to consider the 32 silicon ions and the 16 aluminium ions in the unit cell as forming together one group of 48 equivalent points in the cubic space group. (The existence of optical evidence that analcite is not truly cubic but only pseudo-cubic, also suggests that this grouping of different atoms is not unreasonable.) Trial shows that there is only one way in which the group of 48 points can be arranged so that every point is surrounded tetrahedrally by four other points at a distance of about 3.0 Å; the points are then located on the digonal rotation-axes parallel to [110] $[1\bar{1}0]$ [101] $[10\bar{1}]$ [011] $[01\bar{1}]$. Assuming this arrangement of aluminium and silicon ions, it is an easy matter to place between them the 96 oxygen ions, in such a way as to build up nearly regular tetrahedra which are linked together at all the corners.

Supposing this part of the structure to have been determined correctly, it remains to find the positions occupied by the 16 sodium ions and the 16 water molecules in the unit cell. Schiebold (5) has supposed that the water molecules cannot occupy any fixed lattice position in the unit cell, since there was no 16-fold position available when the 32 Si^{+4} ions, the 16 Na^{+1} ions, and the 16 Al^{+3} ions had been fixed; in the analogous case of the ultramarines, too, Jaeger (7) considers it probable that certain constituents are "loose" and do not contribute to the regular diffraction of X-rays by the crystal planes. But if, in analcite, the 48 silicon and aluminium ions are placed in equivalent positions on the two-fold axes as we have suggested above, the 96 oxygen atoms will occupy a set of equivalent (general) positions, and there are the two special 16-fold positions $\{0\,0\,0\}$ and $\{\frac{1}{8}\,\frac{1}{8}\,\frac{1}{8}\}$ available. If the sodium atoms and the water molecules are placed in these positions, F-values can be calculated for reflections from planes of low indices, and there is, on the whole, fair agreement (of a qualitative nature, of course) between the F-values deduced in this way, and the observed relative intensities of reflection.

For two reasons this simple way of arranging the sodium atoms and water molecules has been rejected. In the first place, the environment of the sodium atoms, placed either at $\{0\,0\,0\}$ or at $\{\frac{1}{8}\,\frac{1}{8}\,\frac{1}{8}\}$, is quite different from what might reasonably be expected — each atom is at the centre of a space (empty of other atoms) larger than is needed to accommodate the atom if it is supposed to be ionised and to have the radius (1.0 Å.) usually attributed to the ion Na^{+1}. Again, although there is a fair agreement between calculated F-values and observed intensities, it was not possible to obtain much improvement in the agreement, by slight alterations of the atomic parameters. Examination of a model of the linked-tetrahedron arrangement showed that there is just room for a sodium ion (of radius 1.0 Å.) at each of the 24 points in the unit cell of which $(0\,\frac{1}{4}\,\frac{1}{8})$ is typical; a sodium ion placed in such a position is surrounded by four oxygen ions in a plane, and water molecules (of diameter 2.7 Å.) placed at the points $\{\frac{1}{8}\,\frac{1}{8}\,\frac{1}{8}\}$ touch the sodium ion at opposite ends of the diameter normal to the plane of the four oxygen

Table I.

Coordinates of atoms in unit cell of analcite.

Atom	No. in unit cell	$\frac{x}{a}$	$\frac{y}{a}$	$\frac{z}{a}$	$\theta_1 = 2\pi\frac{x}{a}$	$\theta_2 = 2\pi\frac{y}{a}$	$\theta_3 = 2\pi\frac{z}{a}$
$Si + Al$	48	0.161	0.089	0.625	58°	32°	225°
O	96	0.111	0.131	0.722	40	47	260
Na	16 $(= 24 \times \frac{2}{3})$	0	0.250	0.125	0	90	45
H_2O	16	0.125	0.125	0.125	45	45	45

The origin of coordinates is at a centre of symmetry; the arrangement of symmetry-elements in the space group O_h^{10} is described in an earlier section of the paper.

In calculating F-values $\frac{2}{3}\,Na^{+1}$ is placed at each of the 24 positions in the cubic unit cell, of which (0°, 90°, 45°) is typical.

The Na ions and H_2O molecules are fixed by symmetry, and the $(Si + Al)$ ions, on two-fold axes, have one degree of freedom, so that in the case above $\theta_1 = 60° - \alpha$, $\theta_2 = 30° + \alpha$, $\theta_3 = 225°$, where $\alpha = 2°$ to give the best agreement between observation and calculation. The O ions have three degrees of freedom.

Table II.

Comparison of Observed and Calculated Intensities.

Indices	sin θ	F_{hkl}	Observed Intensity
(211)	0.063	180	5 or 6
(220)	0.073	—105	4
(213)	0.097	45	1
(400)	0.103	—685	10
(420)	0.110	—20	nil
(233)	0.121	300	6
(422)	0.127	90	3
(413)	0.132	—100	3
(215)	0.142	—125	3
(440)	0.147	190	4
(235)	0.160	—85	2
(611)	0.160	—110	3
(620)	0.164	45	1 or 2
(415)	0.168	25	<1
(613)	0.176	—50	1
(444)	0.180	—30	<1
(435)	0.183	50	<1
(640)	0.187	215	4
(633)	0.190	—185	3 or 4
(255)	0.190	—50	nil
(217)	0.190	75	1 or 2
(246)	0.194	—30	<1
(237)	0.204	—190	4
(615)	0.204	110	2 or 3
(800)	0.207	460	8
(417)	0.210	115	3
(820)	0.214	—85	3
(660)	0.220	—145	3
(822)	0.220	—70	2
(831)	0.222	110	3
(840)	0.231	—30	nil
(248)	0.236	105	2
(219)	0.240	125	2
(655)	0.240	25	nil
(617)	0.240	—50	1
(466)	0.243	115	2
(457)	0.246	—85	1
(239)	0.251	—145	3
(637)	0.251	100	2
(844)	0.254	—75	1 or 2
(835)	0.256	—60	1
(860)	0.259	150	3
(10.1.1)	0.261	—165	4

Table II (continued).

Indices	sin θ	F_{hkl}	Observed Intensity
(277)	0.261	265	5
(10.2.0)	0.264	— 85	1 or 2
(10.3.1)	0.272	90	2
(817)	0.277	— 145	3
(10.4.0)	0.279	— 55	1 or 2
(10.3.3)	0.281	190	3 or 4
(837)	0.286	65	<1
(639)	0.290	160	3 or 4
(880)	0.292	145	nil
(677)	0.300	— 150	3
(10.3.5)	0.300	— 130	2 or 1
(10.6.0)	0.302	50	nil
(866)	0.302	— 110	2
(12.0.0)	0.311	— 65	<1
(488)	0.311	30	nil
(10.5.5)	0.317	— 210	3
(12.4.0)	0.328	— 30	nil
(10.8.0)	0.331	110	1 or 2
(299)	0.334	— 100	1 or 2
(12.6.0)	0.347	— 200	3
(888)	0.360	120	nil
(14.1.1)	0.365	115	2 or 3

The indices refer to the cubic unit cell with edge 13.7 Å., and θ is the glancing angle corresponding to these dimensions, and for the MoK_{α} wavelength $\lambda = 0.71$ Å.

The "observed intensities" are arranged on an arbitrary scale, in which 1 is very weak, 2 is weak, 3 or 4 medium, 5 or 6 strong, > 6 very strong. Most of the reflections quoted in the Table have been observed several times on different plates.

A modified atomic F-curve for the $(Si + Al)$ ions is deduced from the atomic F-curves for Si^{+4} and Al^{+3}. The scattering power of the water molecule H_2O is taken as equivalent to that of the oxygen ion.

ions. The sodium ion is thus surrounded by a distorted octahedron, consisting of four oxygen ions and two water molecules.

For the final calculation of F-values for comparison with observed relative intensities of reflection, we have then considered the arrangement of linked tetrahedra described above, with the 16 water molecules at the points $\{\frac{1}{8}\frac{1}{8}\frac{1}{8}\}$, and on the average $\frac{2}{3}\,Na$ at each of the 24 points $\{0\frac{1}{4}\frac{1}{8}\}$; for this is the simplest way of taking into account the fact that only $16\,Na^{+1}$ ions are available to occupy the 24-fold position to which they are assigned. (The real significance of this average distribution of Na^{+1} ions is discussed in the next section.)

The atomic parameters referred to the cubic space group O_h^{10} are given in Table I. In Table II are collected the calculated F-values and the observed relative intensities of a large number of reflections of all types; with few exceptions, the agreement is as good as can be expected.

The qualitative nature of the experimental data, and the fact that the assumptions made in the course of the analysis are rather novel, make it desirable to test the suggested structure as completely as possible.

Two tests have been carried out. In the first place, corresponding rotation-photographs have been taken, using the same single crystal of analcite before and after dehydration. Table III shows that, if the water molecules occupy the definite lattice-positions to which they are assigned in the structure described above, dehydration should produce marked

Table III.

Effect of dehydration on Intensity of Reflection.

Indices	sin θ	F_{hkl}	F'_{hkl}	Observed Alteration in Intensity
(211)	0.063	180	240	strengthened
(220)	0.073	— 105	— 105	none
(213)	0.097	45	100	strengthened
(400)	0.103	— 685	— 580	(not on plate)
(420)	0.110	— 20	— 20	none
(233)	0.121	300	250	weakened
(422)	0.127	90	90	none
(413)	0.132	— 100	— 100	none
(215)	0.142	— 125	— 170	strengthened
(440)	0.147	190	100	weakened
(235)	0.160	— 85	— 45	weakened
(611)	0.160	— 110	— 150	strengthened
(620)	0.164	45	45	none
(415)	0.168	25	25	none
(613)	0.176	— 50	— 85	strengthened
(444)	0.180	— 30	40	none
(435)	0.183	50	50	none
(640)	0.187	215	215	none
(633)	0.190	— 185	— 150	weakened
(255)	0.190	— 50	— 15	none
(217)	0.190	75	40	none

F_{hkl} is the F-value calculated for ordinary analcite for the plane (hkl), and F'_{hkl} the value for dehydrated analcite. For reflections with glancing-angle greater than $\theta = 0.190$, the alteration in F_{hkl} which results when the water is removed is not big enough to produce any detectable alteration in the blackness of the photographic image. With the exception of the reflection (400), all the reflections with glancing-angle less than $\theta = 0.190$ were observed on a pair of comparison photographs taken with ordinary and dehydrated analcite respectively.

alterations in intensity of reflection of X-rays only for a very few reflections with small glancing-angles. The photographs show precisely the predicted alterations in intensity. (Grüner (3) took powder-photographs of dehydrated analcite, but failed to observe any striking alterations in intensity of the lines: this is hardly surprising, since the calculations based on the structure show that the water contributes but little to the reflections from most lattice-planes.)

The second test affords direct evidence that the sodium ions are correctly placed in the structure suggested. For it is possible to replace the sodium in analcite by silver (by heating ordinary analcite with concentrated $AgNO_3$ solution for several days at 130°C—150°C), and to observe the changes in intensity of reflection which take place by reason of the much greater scattering-power of the silver ion. (It is reasonable to suppose that the silver ion occupies the lattice-position formerly occupied by the sodium ion which it replaces.) Corresponding rotation-photographs taken with the same single crystal of analcite, before and after treatment with silver, show the quite striking alterations in relative intensities of reflection by different planes to be expected if the silver ion displaces the sodium ion from the positions assigned above. The prolonged heating, however, causes the single crystal to splinter internally, and the spots on the rotation-photographs are indistinct and ill-defined. For this reason powder photographs of ordinary analcite and silver analcite have been taken, under identical conditions. They are reproduced in Fig. 1, and in Table IV is collected the data obtained from the first few lines of each photograph. The F-values for ordinary analcite and for silver analcite, calculated on the basis of the structure suggested, are also given in the Table. Bearing in mind that every line in the silver-analcite photograph is weakened owing to the strong absorption by the silver, and that the actual strength of any line in the powder-photograph depends both on the scattering power of the plane considered, and also on the total number of crystal planes

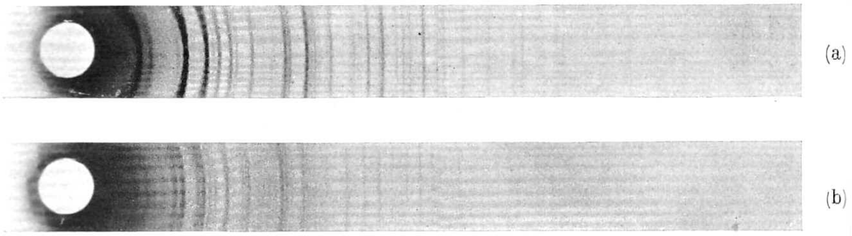


Fig. 1. Powder Photograph of ordinary analcite (a) and silver analcite (b).

which contribute to the reflection (e. g. six for the reflection (400), forty eight for the reflection (213)), the observed differences in intensity, due to the replacement of sodium by silver, agree with those predicted from the calculated F-values.

It is impossible that the sodium ions can occupy either of the two sets of 16 equivalent positions in the cubic unit cell ($\{000\}$ or $\{\frac{1}{8}\frac{1}{8}\frac{1}{8}\}$);

Table IV.

Data from powder photographs.

sin θ	Indices	Number of planes contributing to reflection	Observed Intensity		Calculated F-values	
			Ordinary Analcite	Silver Analcite	Ordinary Analcite	Silver Analcite
0.138	(211)	24	vs	m	180	0
0.159	(220)	12	m	m	— 105	— 285
0.211	(213)	48	vw	ms	45	215
0.226	(400)	6	vvs	s	— 685	— 515
0.253	(420)	24	vvw	ms	— 20	— 355
0.264	(233)	24	vs	s	300	465
0.276	(422)	24	w	w	90	250
0.286	(413)	48	ms	w	— 100	— 100
0.308	(215)	48	ms	s	— 125	— 280
0.320	(440)	12	mw	nil	190	35
0.346	(235)	48	m	m	— 90	— 235
	(611)	24			— 110	35
0.356	(620)	24	nil	nil	45	— 100
0.365	(415)	48	nil	nil	25	25
0.382	(613)	48	nil	w	— 50	— 185
0.393	(444)	8	nil	w	— 30	— 440
0.397	(435)	48	nil	nil	50	50
0.406	(640)	24	m	ms	215	490
0.414	(633)	24	m	m	— 185	— 320
	(255)	24			— 50	— 185
	(217)	48			75	210
0.420	(246)	48	nil	nil	— 30	100
0.443	(237)	48	ms	m	— 190	— 65
	(615)	48			110	235

The glancing angle θ corresponds to the wave-length $\lambda = 1.539$ Å., (CuK_α radiation). The length of edge of the cubic unit cell, deduced from the powder photographs, is $a = 13.68$ Å. ± 0.04 Å.

In the silver-analcite photograph one or two weak lines are present, to which indices cannot be assigned: they are probably due to impurities.

In the last two columns are collected the calculated F-values for ordinary analcite and silver analcite respectively. The F-values for silver analcite are calculated on the assumption that the sodium is completely replaced by silver. It is probable that in the actual specimen employed the substitution is not quite complete.

for if these ions are located at the points {000}, they contribute nothing to the reflections (211), (213), (420), (215), (640), which actually show considerable alterations in intensity when silver replaces the sodium; and if placed at the points $\{\frac{1}{8}\frac{1}{8}\frac{1}{8}\}$, they contribute nothing to the reflections (420), (640), while (440) should be very strong in silver-analcite, whereas it actually disappears.

The success of these tests makes it possible to state with confidence that the structure described is the correct average structure.

Discussion.

(a) The true symmetry of analcite.

The structure described is based on the cubic space group O_h^{10}, and is deduced by assuming that the 32 silicon ions and the 16 aluminium ions may be considered to form one group of 48 equivalent points in the unit cell, and that the 16 sodium ions occupy, uniformly on the average, a 24-fold position in the unit cell.

The first assumption is obviously not entirely justified, for the Al^{+3} ion is larger than the Si^{+4} ion, and will distort in some way the surrounding tetrahedron of oxygen ions-i. e., 16 of the tetrahedra will presumably be slightly different from the remainder of the 48 which are actually treated in the structure as identical.

Goldschmidt (9a) has shown that the effective interatomic distance is diminished when the coordination number is reduced, so the tetrahedron around the Al^{+3} ion is probably not distorted to any great extent.

Again, the structure suggested does not explain why the observed composition of analcite is so constant — it always corresponds very closely with $NaAlSi_2O_6 \cdot H_2O$ — for it would be expected that the $Al:Si$ ratio might vary within fairly wide limits without producing any marked alteration in structure, if all Al^{+3} ions and Si^{+4} ions were really structurally equivalent. At the same time, the Na-content would be expected to vary according to the proportion of Al present. There must be some reason why the composition is always the same in this particular member of the zeolite family.

The existence of the optical anomalies suggests that the crystal is not truly cubic, but only pseudo-cubic, and various explanations of these effects have been advanced by mineralogists (1), who assume either some type of twinning of tetragonal or orthorhombic individuals, or a mechanical lattice-strain connected in some way with the water-content. Bearing in mind the structure which we have derived, it seems probable that the pseudo-cubic nature of analcite may be due to either twinning of macroscopic individuals of lower than cubic symmetry, or twinning of microscopic (or sub-microscopic) individuals of this type, or local alterations in the arrangement of water molecules or sodium ions within a linked-tetrahedron structure which is continuous and coherent throughout the whole crystal. Various ways of obtaining the required average structure have been devised, but calculation shows that with the experimental data available it is improbable that the correct way of "averaging" could be chosen with any certainty. It will be sufficient if it can be shown that an explanation of the pseudo-cubic nature of analcite, on the lines suggested above, is also able to account for the constant composition of the mineral.

If the symmetry is reduced from cubic to tetragonal, the unit cell dimensions remaining unaltered, the 16 aluminium ions and the 32 silicon ions now occupy separate and distinct groups of equivalent points, instead of occupying together one group of 48 equivalent points. The 16 sodium ions may be disposed in either of two ways. If the tetragonal unit cell is centro-symmetric, then only two of the four oxygen ions round each sodium ion satisfy exactly Pauling's electrostatic valency principle (10) (they are connected to one silicon ion Si^{+4} and one aluminium ion Al^{+3} as well as to the sodium ion Na^{+1}), the other two oxygen ions being connected to two silicon ions as well as to the sodium ion. (The electrostatic valencies are of course satisfied on the average.)

If the tetragonal cell is supposed to be polar, then each of the four oxygen ions around eight of the sodium ions in the unit cell, obeys Pauling's rule exactly, while the oxygen-ion environment of the remaining eight is the same as when the cell is centro-symmetric.

These alternatives correspond to two different ways of putting the 16 sodium ions in two of the three groups of 8 equivalent points which are together equivalent to the group of 24 related points in O_h^{10}, supposed occupied uniformly "on the average" by the sodium ions.

The constant composition of analcite is thus explained if the symmetry of the individual unit cell is reduced from cubic to tetragonal, for the aluminium ions and silicon ions now occupy two different groups of equivalent points, and the sodium ions also occupy definite lattice positions. In view of the difficulty of devising any experimental way of deciding which is the correct way of building up the "average" cubic structure from the individual units of lower symmetry, we have not pursued these discussions. In any case, the most important point is that it may reasonably be supposed that both the constant composition of analcite, and the pseudo-cubic nature of the crystal, can be explained by assuming that the true symmetry of the individual unit cells is not higher than tetragonal.

(b) The principal features of the structure.

The continuous structure of linked tetrahedra can be regarded as built up of two kinds of tetrahedron rings, one kind containing four positive ions, the other kind containing six; this ring of six is a slight distortion of the tetrahedron-ring which forms the basis of the beryl structure, and the plane of the ring is normal to a trigonal axis of the cubic cell; both six-rings and four-rings are identical with those found in the ultramarine structure suggested by Jaeger. The shape and size of each type of ring is shown in Fig. 2. If the symmetry of the individual unit cell is reduced from cubic to tetragonal, as described in the preceding section, the aluminium ions are distinguished from the silicon ions, and it is perhaps significant that the whole structure is now built up from rings of four silicon tetrahedra, joined up by aluminium tetrahedra in such a way as to produce other rings of four tetrahedra (these consisting of two silicon- and two aluminium-

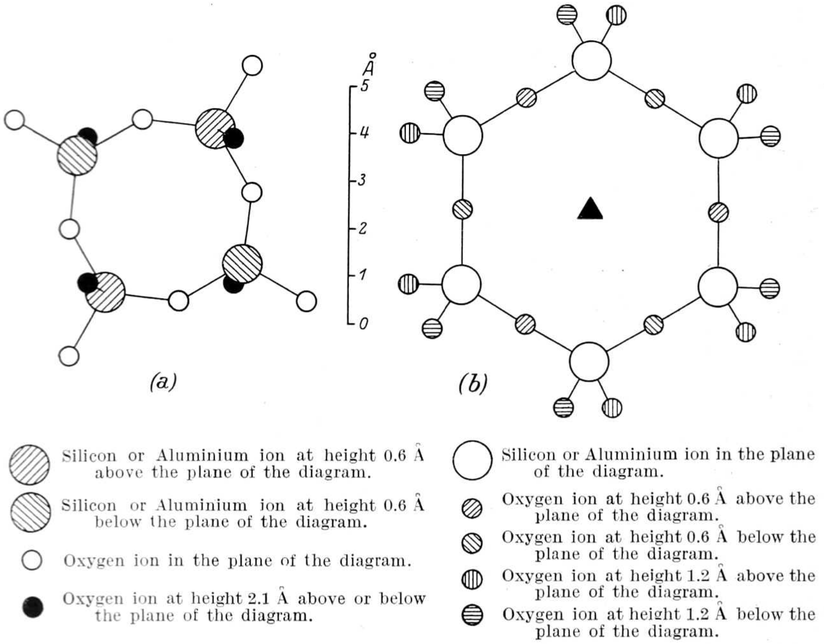


Fig. 2. Rings of four tetrahedra (a) and six tetrahedra (b), from which the analcite structure is built up. Every ring of six tetrahedra is normal to a trigonal axis of the cubic unit cell. The rings drawn above are slightly idealised, but the essential features are retained.

tetrahedra) and also rings of six tetrahedra (containing four silicon- and two aluminium-tetrahedra). These points are illustrated in Fig. 3, in which are reproduced photographs of a model of the unit cell of analcite built up to show tetragonal symmetry. The photographs show clearly the way in which the six-rings and four-rings are related.

The environment of the sodium ion is also seen clearly in Fig. 3. Each such ion has around it a group of four oxygen ions in an equatorial plane, and a water molecule at each end of the polar axis. The electrostatic valency rule enunciated by Pauling (10) is obeyed exactly if each of the four oxygen ions (O^{-2}) is linked to one silicon ion (Si^{+4}) and one aluminium ion (Al^{+3}), as well as to the sodium ion (Na^{+1}), since both silicon and aluminium ions are surrounded by tetrahedra of oxygen ions. In gypsum, which has recently been analysed (10a), there is almost exactly the same arrangement of four oxygen ions and two water molecules about each of the calcium ions.

The points occupied by the water molecules lie on the non-intersecting trigonal axes of the cubic space group; no other atoms lie on these axes, (around which the "beryl rings" of six tetrahedra are grouped) so that there are long channels passing through the structure parallel to all the cube-diagonals, wide enough to accommodate quite large atoms or molecules, and empty of everything but water molecules (see Fig. 3). There can be little doubt that these holes are in some way responsible for the ease with which the water may be removed from analcite and be replaced by other materials. In all probability they also facilitate the base-exchange which can so easily take place. It would be interesting to measure the rates at which ions of various sizes can be driven through analcite by electrolysis, (as in the case of quartz (11)) for the "holes" in the structure would probably provide the paths along which the ions could be driven. In the ultramarine structure suggested by Jaeger there are channels of the same size, but they intersect at the centre of the unit cube, whereas in analcite they are non-intersecting.

Each water molecule probably touches two sodium ions; if there were 24 sodium ions per unit cell, each water molecule would touch three of them, but as there are actually only 16, one of the three available positions will lack a sodium ion. The properties usually attributed to the water molecule suggest that it is more likely to be in contact with two sodium ions than in contact with three, and the hydrogen atoms may perhaps "occupy" in some way the "spare" hole similar to the two occupied by sodium ions.

It is also interesting to notice that the oxygen ions, which are everywhere common to two tetrahedra, do not lie midway between the

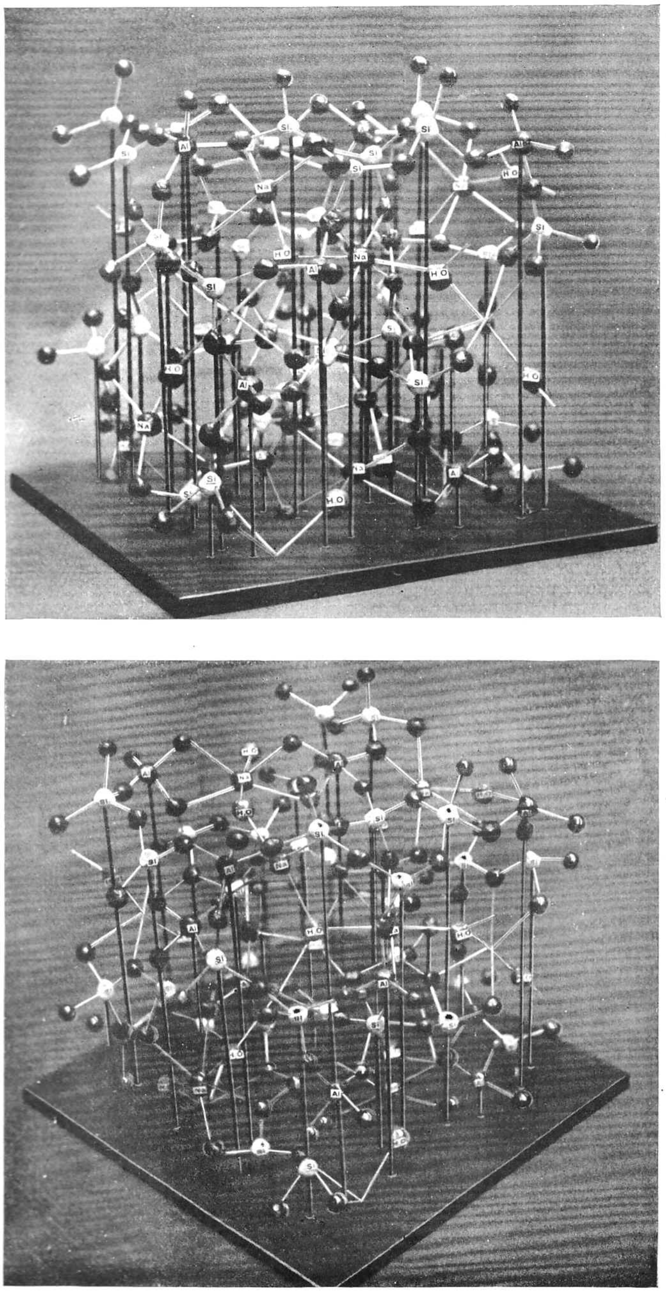
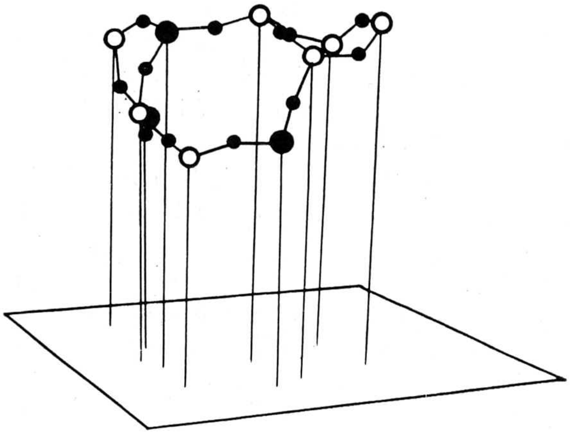


Fig. 3a. The unit cell of analcite.
The photographs show how the tetrahedron rings are linked together (in the Key two rings of four, and one ring of six, tetrahedra, are copied from the photographs); the environment of the sodium ion, and the existence of the large channels in which lie the water molecules, are also illustrated.

ions (Si^{+4} or Al^{+3}) which they touch, but the (oxygen to silicon or aluminium) bonds make an angle of about 140°. This is nearly the same as in the quartz structure, where the angle is 147° 30′ (12). Too much stress should not be laid on this point, since the determination of the analcite structure is only based on qualitative measurements, and is at best an "average" structure in which Si^{+4} and Al^{+3} are assumed to have an "average diameter" of about 0.9 Å., corresponding to the actual diameters 0.6 Å. and 1.1 Å., respectively.



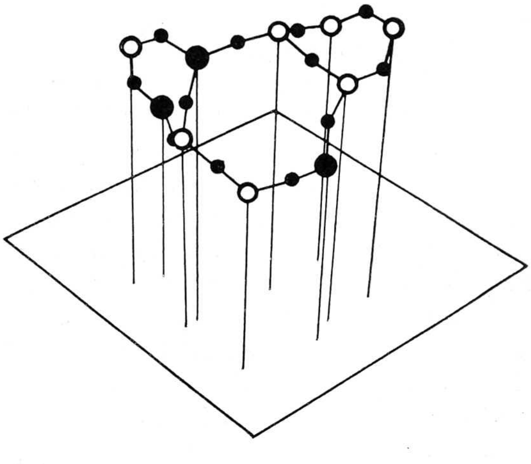


Fig. 3b. White circles represent silicon ions. Large black circles represent aluminium ions. Small black circles represent oxygen ions.

(c) Relationship with other crystals.

In the other zeolites we may expect to find the linked-tetrahedron arrangement as the basis of the structure, and their similar behaviour in regard to base-exchange and loss of water suggests that there may exist similar empty "channels" running through the structure. A number of these crystals are now being examined.

The felspars are anhydrous, but they show the same $Al + Si : O$ ratio as the zeolites, and we consider it probable that this series also will be found to be built up on a basis of linked tetrahedra containing the silicon and aluminium ions.

Leucite would also appear to be related to analcite in some way, but we have not yet been able to examine this crystal satisfactorily by X-ray methods.

The ultramarines form an extremely interesting group: a structure has been suggested by Jaeger, which is based on an arrangement of linked tetrahedra of oxygen ions. This forms the essential framework, within which places must be found for a number of atoms, such as sodium, and for some (SO_4) groups. The tetrahedra are occupied partly by silicon ions, partly by aluminium ions, and the whole framework of tetrahedra can be regarged as built up from rings containing four tetrahedra, and rings containing six tetrahedra; the rings are the same shape and size as in analcite (cf. Fig. 2), but are grouped differently so that the unit cell is a body-centred cube of edge about 9 Å. Jaeger considers it probable that some of the remaining constituents of the crystal do not occupy definite lattice positions, but are to be regarded as "wandering" in the large cavities formed by the intersection of the three-fold axes around which the rings of six tetrahedra are placed. It is interesting to find that the type of tetrahedron-linkage found in analcite is suggested by Jaeger as the basis of the structure of the ultramarines, which possess many zeolite-like properties (7).

I have to thank Professor W. L. Bragg, F.R.S., for constant help and advice throughout the course of the work. For assistance in obtaining suitable crystal specimens I am indebted to Dr. L. J. Spencer, F.R.S., and Mr. F. A. Bannister, of the British Museum; silver analcite was prepared for me by Mr. M. G. Evans (of this University) to whom I am also grateful for much information regarding the chemistry of the zeolites; Dr. A. J. Bradley and Mr. A. L. Roussin (also of this University) very kindly prepared for me the powder photographs which are reproduced in Fig. 1.

Received January 18th, 1930.

References.

1. For detailed references see, e. g., Mellor, "Inorganic Chemistry", **6.** — Dana, "Mineralogy", p. 595.
2. Rinne, N. Jb. Min. **48**, 240.
3. Grüner, Z. Krist. **68**, 363.
4. Jaeger, Trans. Faraday Soc. **25**, 334. 1929 and Akad. Amsterdam Versl. **36**, 483. 1928.
5. Schiebold, Trans. Faraday Soc. **25**, 411. 1929.
6. Hartwig, C. Min. A, No. 11, 380. 1928.
7. Jaeger, Trans. Faraday Soc. **25**, 320. 1929.
8. See for example, Winchell, Am. Mineralogist **10**, 65.
8a. Machatschki, C. Min., A. No. 3, 97. 1928.
9. Niggli, "Geom. Krist. des Diskont.", p. 399.
9a. Goldschmidt, Trans. Faraday Soc. **25**, 253. 1929.
10. Pauling, J. Am. chem. Soc. **51**, 1010. 1929.
10a. Ettore Onorato, Z. Krist. **71**, 277. 1929.
11. Joffé, Ann. Physik **72**, 461. 1923.
12. Gibbs, Pr. Roy. Soc. A, **113**, 351.
