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The Structure of Analcite and Ion-Exchanged Forms of Analcite

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From a consideration of the accepted structure of analcite it is shown that this mineral need not necessarily be considered as having an averaged lattice. The structure of leucite, and other ion-exchanged forms of analcite, is discussed in relation to the known data on pollucite, leucite and analcite. The importance of the degree of hydration of the various ion-exchanged analcites is mentioned.

Analcite and pollucite give almost identical spacings of the diffraction arcs obtained by means of X-ray powder photography, since the alumino-silicate network is essentially the same for each of these minerals. Their symmetry is cubic O_h^{10}, and the length of the unit cell is 13·7 Å. The structure of analcite originally proposed by Taylor (1930) placed the sodium ions in the positions (0·125, 0, 0·25), of which there are 24 in the unit cell. Since only 16 sodium ions are available to fill these 24 positions Taylor regarded the resultant lattice as an averaged structure with the 16 sodium ions arranged statistically among 24 sites. Náray-Szabó (1938) on the other hand suggested that the sodium ions in analcite occupied the same lattice points as the caesium ions in pollucite. The positions of the caesium ions in pollucite, namely (0·125, 0·125, 0·125), were not disputed.

Taylor (1930) studied the effect of dehydration of analcite on the X-ray diffraction patterns obtained from single crystals. In a discussion of the observations of Náray-Szabó (1938), Taylor (1938) pointed out that his experiments showed that the changes observed in line intensities on dehydration of analcite were of the same order as those calculated using the Taylor model as a basis. The alterations predicted for the Náray-Szabó structure were however in several cases the opposite of those observed in practice. Further, the water molecules in Taylor's structure are tetrahedrally bonded to two sodiums and two oxygens, in agreement with the known properties of the water molecule (Taylor, 1934). The Náray-Szabó structure results in the water molecules being surrounded by six nearest neighbours, four oxygens and two sodiums completing the octahedral group.

The formula of anhydrous analcite is $Na_2O, Al_2O_3, 4SiO_2$. From an examination of the structure proposed by Taylor, it is easily seen that each sodium ion is surrounded by four oxygens, the whole array being approximately situated in one plane. The four oxygens are made up of two pairs, both oxygens in each pair being attached to the same adjacent silicon or aluminium. This is shown in Fig. 1, which may then be said to represent the formula of analcite if the sodiums are taken to be present in only two-thirds of the possible positions. This may be written $\frac{2}{3}$Na, 2(Si or Al), 4O, or more accurately as $\frac{2}{3}$Na, $\frac{2}{3}$Al, $\frac{4}{3}$Si, 4O. In

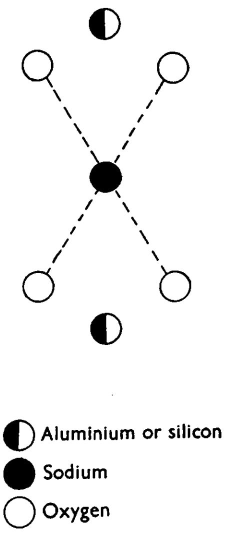

Fig. 1. Representation of the lattice position of a sodium ion in analcite.

other words, since there are 24 of these positions given by Fig. 1 only 16 of them can contain an aluminium as well as a silicon, the other eight containing two silicons. It is a logical next step to assume that the 16 sodium ions would be associated with the 16 aluminiums. The unit cell would then consist of 16 Na, Al, Si, 4O and eight 2Si, 4O. From this discussion it is clear that although there are 24 crystallographically equivalent positions (0·125, 0, 0·25) it is impossible to obtain more than 16 positions that are energetically equivalent, since the silicons and aluminiums cannot be considered to be interchangeable. The sodium positions adjacent to an aluminium represent potential energy minima due to the net negative charge on the network, so that there are 16 fixed lattice points for the sodium ions. The resultant structure is not therefore a statistically averaged array, except in so far as the aluminiums and silicons may themselves be distributed at random in the 48-fold site which they fill.

It is possible to arrange the atoms in the unit cell so that there are eight positions Na, 2Al, 4O, eight Na, 2Si, 4O, and eight 2Si, 4O. This would result in averaged positions for only eight of the 16 sodiums, the other eight being in positions adjacent to two aluminiums, and in a low energy state. Allowing for a completely random distribution of the silicons and aluminiums amongst the lattice points, any stoichiometrically correct combination between the two extremes mentioned is possible, but a consideration of the structure makes it seem more probable that the first interpretation is the correct one.

Although the sodium ions in analcite are in only the 16 positions adjacent to an aluminium and surrounded by four oxygens in the same plane as the sodium, the caesium ions in pollucite are in cages of 12 oxygens. This is made clear by Fig. 2, which shows the caesium ions in pollucite at the centre of a cage of three sets of four oxygens. It is probable that two aluminiums and four silicons will be associated with each caesium position, so that all the 16 positions would then be equivalent.

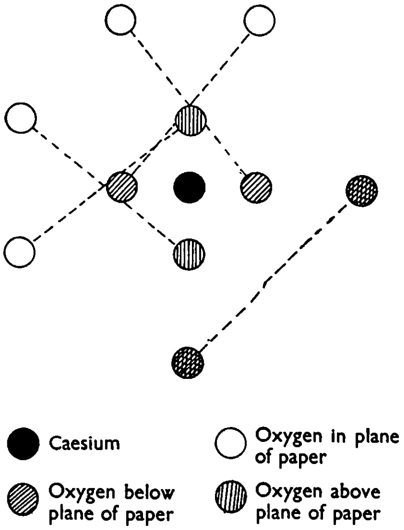

Fig. 2. Representation of the lattice position of a caesium ion in pollucite.

Additional evidence, in favour of the Taylor structure, was produced by an examination of the X-ray diffraction patterns obtained from single crystals of analcite in which approximately 50% of the sodium ions had been replaced by silver ions (Taylor, 1938). The intensities observed were in excellent agreement with those which had been calculated assuming the correctness of the Taylor structure. The basic assumption made in these calculations was that the silver ions occupied the same positions in the analcite lattice as the sodium ions they replaced.

The Na–O distance in Fig. 1 is 2·6 Å, leaving only 1·2 Å for the cationic radius if the oxygen is taken to have an ionic radius of 1·4 Å. Hence, although the silver ion of ionic radius 1·13 Å can replace a sodium, repulsion forces would not allow the potassium ion to do so. This means that the potassium ion will be forced away from the sodium position towards the position normally occupied by caesium in pollucite (0·125, 0·125, 0·125). The potential energy minimum for such an ion will then lie in some position intermediate between that of the caesium and that of the sodium. The structure will no longer possess cubic symmetry and it is clearly possible for a contraction in the lattice to occur, despite the fact that a larger ion has been substituted for the sodium ion.

Barrer (1950) has shown that the sodium ions in analcite may be readily exchanged for potassium, ammonium, thallium$^{\mathrm{I}}$ or rubidium ions. The X-ray powder photographs of these ion-exchanged minerals indicated that they were all based on a similar alumino-silicate framework, although none of these forms is cubic at normal temperatures. Further, the spacings of the diffraction arcs for rubidium and thallium$^{\mathrm{I}}$ analcites, and potassium and ammonium analcites, were nearly identical.

If now a similar type of reasoning to that given above for potassium is applied to any of the other exchanging ions, to suggest their positions in the lattice, it becomes apparent that ionic radius will be one of the main factors influencing the location of the resultant potential energy minimum for a monovalent ion. It is therefore to be expected that rubidium and thallium$^{\mathrm{I}}$, with ionic radii of 1·50 Å and 1·49 Å, will have almost identical positions for their potential energy minima. Similarly, potassium and ammonium will also have nearly the same positions for minima. This will clearly result in very similar spacings of the X-ray diffraction arcs, as found in practice.

Leucite undergoes a gradual transition to cubic as the temperature is raised. The transition is completed at approximately 620° C., when the unit cell edge is still only 13·4 Å (Wyart, 1938). Since a contraction in the unit cell of leucite, compared with that of analcite, is still apparent when the symmetry is cubic, the potassium ion has presumably moved across to the normal caesium-ion position in pollucite. If this reasoning is correct, then rubidium analcite, and thallium$^{\mathrm{I}}$ analcite if stable, may also show a similar high-temperature transition.

The importance of the degree of hydration of the mineral must be stressed. Although the potassium, rubidium, thallium, ammonium and caesium forms of analcite may not be completely anhydrous, they do not contain interstitial water to anything like the same extent as the sodium and silver forms, which may be written M_2O, Al_2O_3, $4SiO_2$, $2H_2O$. This is due to the fact that the water molecules normally occupy the positions (0·125, 0·125, 0·125), which are, of course, the caesium positions in pollucite. Presumably the repulsion forces due to the potassium, rubidium, thallium$^{\mathrm{I}}$ and ammonium ions in the anhydrous forms make these positions untenable. Since the potassium and ammonium ions are only slightly too large for them to fit into the normal sodium positions in analcite, it seems possible that a very strongly sorbed gas might convert these into a cubic form. There appears to be no experimental evidence in favour of this suggestion.*

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* *Note added in proof*, 13 *March* 1954.—Barrer, Baynham & McCallum (1953) have recently reported the synthesis of a *hydrated* form of leucite which is cubic.

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The (*hki*0) Reflexions of Graphite

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Some quantitative data are presented for the shape and position of the *hki*0 reflexions of graphite, in the intermediate region between a random-layer structure and a true three-dimensional structure. With increasing perfection the reflexion rapidly becomes symmetrical but the displacement of the peak decreases more slowly.

In an earlier note (Bacon & Franklin, 1951) it was pointed out that the variation of the *a* dimension for fairly well crystallized graphites (Bacon, 1950) could be explained by an extension of Warren's (1941) treatment of the two-dimensional reflexions of random-layer structures. This study has now been carried further, giving a quantitative picture of the transition, with increasing crystalline perfection, from the displaced and asymmetrical two-dimensional reflexion band to the normal centred and symmetrical three-dimensional peak. A numerical error in the earlier note has emerged, although this does not affect the qualitative conclusions of the latter.

Following, for example, Wilson's (1949) treatment of diffraction using the reciprocal lattice, the intensity distribution in the neighbourhood of the (*hk*) reflexions may be derived from a consideration of Fig. 1, which illustrates the intersection of the *hk* spike in reciprocal space by the powder reflecting sphere. The changes of reflecting density across and along the spike, i.e. horizontally and vertically, are indicated at (i) and (ii). The intensity diffracted at any angle θ, corresponding to the radius s, is obtained by carrying out a summation over the area which appears in section as the path QPQ'. To a very close approximation for the purpose of this summation the sphere may be replaced by a cylinder with the same centre, O, and with its axis

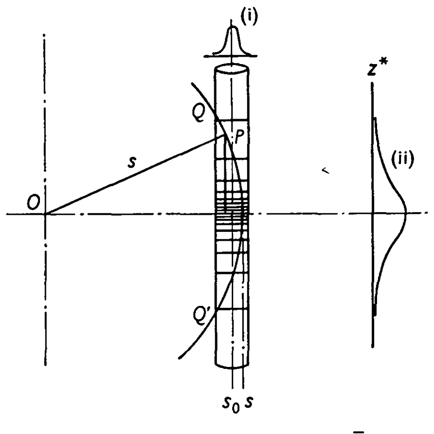

Fig. 1. Calculation of the contour of the 11$\bar{2}$0 reflexion from the reciprocal-lattice diagram for an *hk* spike.