

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

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(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 twinings 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 feldspars, so that interesting structural relations with the feldspar 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 $NaAlSi_2O_6 \cdot H_2O$ (*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 feldspars 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 zeolite⁴⁾ 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

4) 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 feldspars, 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 \AA . 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 departur e 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 Gr uner. 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:

$$(111)_{00} (1\bar{1}\bar{1})_{\frac{1}{2}\frac{1}{2}} (11\bar{1})_{\frac{1}{2}0} (1\bar{1}\bar{1})_{0\frac{1}{2}}$$

Two-fold rotation axes:

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

Glide-Planes:

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

Symmetry Centres:

$$(000) (\frac{1}{2}\frac{1}{2}0) (\frac{1}{2}0\frac{1}{2}) (0\frac{1}{2}\frac{1}{2}) (\frac{1}{2}\frac{1}{2}\frac{1}{2}) (\frac{1}{2}00) (0\frac{1}{2}0) (00\frac{1}{2}) \\ (\frac{1}{4}\frac{1}{4}\frac{1}{4}) (\frac{3}{4}\frac{3}{4}\frac{1}{4}) (\frac{3}{4}\frac{1}{4}\frac{3}{4}) (\frac{1}{4}\frac{3}{4}\frac{3}{4}) (\frac{3}{4}\frac{3}{4}\frac{3}{4}) (\frac{1}{4}\frac{1}{4}\frac{3}{4}) (\frac{1}{4}\frac{3}{4}\frac{1}{4}) (\frac{3}{4}\frac{1}{4}\frac{1}{4})$$

We have to find places for 16*Na*, 16*Al*, 32*Si*, 96*O* and 16*H*₂*O*, in the unit cell; this is impossible unless the *Na* and *Al* atoms occupy the two 16-fold positions {000} 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 {000} 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 4.5  . 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.

