

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 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 Laubandite, which has a composition corresponding to $Ca_2Al_2Si_5O_{15} \cdot 6H_2O$. (Dana, Mineralogy, p. 588.)

