

ANTIGORITE: SUPERLATTICE AND STRUCTURAL FORMULA

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It is the purpose of this note to comment on two topics occurring in *The American Mineralogist*, Vol. 39. Nos. 9 and 10, 1954. First, the discussion by Brindley and von Knorring (1954) of the possible nature of the superlattice in antigorites from Unst, (Shetlands) and from Mikonui (New Zealand.) Secondly, the derivation of structural formulae for antigorites from chemical analyses, a matter which was dealt with by the above authors and also by McConnell (1954) in a note on "Ortho-antigorite and the tetrahedral configuration of hydroxyl ions." A similar topic was the subject of a note by Brindley (1954) concerning an antigorite from Caracas, Venezuela. (The localities Unst, Mikonui and Caracas will be denoted *U*, *M*, and *C* respectively in the following paragraphs.)

THE SUPERLATTICE

On the powder photographs of antigorite (*U*) examined by Brindley, in addition to lines corresponding to an orthorhombic cell $a=5.322$, $b=9.219$, $c=14.53$ Å, some were noted which were consistent with a super-lattice parameter $S=43.8$ Å similar to that which occurs for antigorite (*M*) where $S=43.5$ Å. In the latter instance Onsager (1952) had suggested that the superlattice resulted from an undulating sheet structure containing $8\frac{1}{2}$ sub-cells in each large repeat distance in the "*a*" axis direction. This is one possible explanation in the case of antigorite (*U*) which Brindley rejects since $8\frac{1}{2}$ times the sub-cell dimension is considerably greater than 43.8 Å ($8\frac{1}{2} \times 5.322$ Å = 45.24 Å). It is here suggested that this fact does not rule out the undulating sheet possibility, for such a structure possessing $8\frac{1}{2}$ repeats of the small cell along its curved surfaces would in fact result in a smaller repeat distance measured along straight lines parallel to the true cell axis. This concept fits well with the single crystal data obtained for antigorite (*M*) by Aruja (1945).

There is the important difference between the two cases however, that in antigorite (*M*) reflections cannot be indexed using a cell dimension $a=5.32$ Å. If along reciprocal lattice row a^* , the 17th order reflection for the superlattice is taken as 2nd order of a sub-cell, then the latter has dimension $a=5.12$ Å. If the 16th order is taken then the sub-cell has $a=5.44$ Å. This is to be expected if the simple cell with $a=5.32$ Å (i.e., $b/\sqrt{3}$) repeats only along a curve and not strictly in the true cell edge direction. Since the index *H* of strong superlattice reflections is sometimes a multiple of 16 and sometimes of 17 or of other integers, the value $a=5.42$ KX, for antigorite (*M*) quoted by Brindley from Aruja's work has no special significance as a sub-cell parameter.

In the case of antigorite (*U*) reflections did occur precisely at points of a reciprocal lattice corresponding to $a = 5.32 \text{ \AA}$ although at the same time other reflections were indexed for a super-cell with $S = 43.8 \text{ \AA}$. Assuming that the superlattice is related to the "a" parameter and not to "c" [it certainly is so in antigorite (*M*)], then since reflections of the sub-cell can only occur at large cell reciprocal lattice points, this implies that the true value of S is $4 \times 43.8 \text{ \AA}$ (approx. $33 \times 5.32 \text{ \AA}$). If this is so then there is no indication of sheet curvature, since 5.32 \AA is the normal repeat distance and occurs strictly along a straight line. It also means that for some reason reflections were observed only where H (the superlattice index) is a multiple of 4.

An alternative explanation of the Unst powder photograph is that it is in fact a superposition of two, one from a small cell serpentine mineral with $a = 5.322 \text{ \AA}$ and a second from a large cell variety similar to antigorite (*M*); i.e. that two differently crystallized serpentine minerals are present in the specimen. A varying proportion of large cell variety may account for the different relative intensities of superlattice and normal lattice lines in photographs from different specimens.

The Antigorite Formula

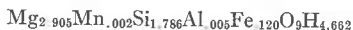
The analysis by von Knorring of antigorite (*U*) No. 2 gave a structural formula, derived on the basis of $9(\text{O}, \text{OH})$, which did not accord very well with the ideal serpentine composition $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$. A closer approximation to this composition was obtained on the basis of 2 Si atoms and by assuming the presence of approximately 10% of brucite impurity. An alternative interpretation of the chemical data was suggested by McConnell which involves the assumption that all the water including $(\text{H}_2\text{O})-$, which formed 1.26% of the sample, was essential to the crystal structure. Neither of these two assumptions would appear to be justified by experimental evidence and it is shown here that a reasonable interpretation of the analysis may be made without them.

In his note McConnell describes the use of von Knorring's analysis of antigorite (*U*) No. 2 to provide "further indirect evidence of the occurrence of hydrogens in substitution for silicon (i.e. tetrahedral hydroxyls)." The writer feels that since no agreed structural model has yet been adopted for ortho-antigorite the case chosen is not particularly suitable for this purpose. In the absence of data such as the measured density and the number of formula units per cell, in addition to the measured cell volume, a chemical analysis can give only atomic proportions. These may be used according to a structural concept to give numbers of atoms occupying the different atomic sites, and even this may be done in many different ways. As an example there is the case of antigorite

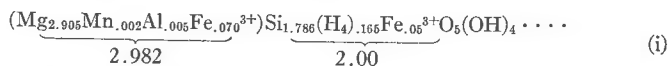
(C) for which Hess, Smith and Dengo (1952) derived two possible formulae, Brindley (1954) obtained a third, and a fourth based on a modified crystal structure was suggested by Zussman (1954).

A feature of several chemical analyses of antigorite has been that the ratio of octahedral to tetrahedral ions is less than that of the ideal formula, 1.5:1.0. This occurs again in antigorite (*U*) No. 1 described by Brindley and von Knorring, and may well be a necessary consequence of the crystal structure of certain antigorites. If therefore, a redistribution of ions similar to that suggested by McConnell results in a ratio nearer to 1.5:1.0 this need not be taken as evidence in favor of the new arrangement.

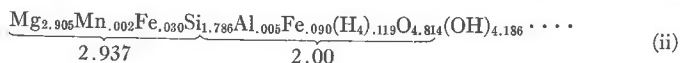
Even if this ratio is deemed desirable there is no need to make the assumption that (H₂O)− is structural water in order to achieve it. For the numbers of ions obtained by von Knorring are:



and using McConnell's suggestion of tetrahedral hydroxyls the various ions may be grouped in the following manner:

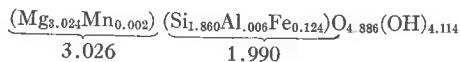


One should also consider the possibility that extra hydrogen atoms may occur in the structure as (OH)[−] replacing O^{−−}. This alternative and the dual role of trivalent ions in octahedral and tetrahedral positions, makes it possible to derive many different formulae from one set of atomic proportions. As a further example, if some of the extrahydrogens in antigorite No. 2 occur in hydroxyl ions replacing O^{−−} and some as 4 (OH)[−] in otherwise empty tetrahedral sites, the following formula may be obtained:



This is "designed" to be very similar to that given for antigorite (*U*) No. 1. It should be noted that formulae (i) and (ii) are obtained from the analysis without treating (H₂O)− as structural water, and without the assumption of brucite impurity.

By making a different and hardly less justifiable assumption, i.e. that 2.3% of the 15.03% (H₂O)+ should be regarded as impurity, and calculating on the basis of 9 anions the following formula may be obtained:



This contains an appreciable amount of trivalent iron in tetrahedral positions, more than there is in antigorite (*U*) No. 1, but very little extra

hydrogen to be allocated an unusual role in the structure.

These examples illustrate that unless the weight of the unit cell content is known there is scope for a variety of interpretations of a chemical analysis taken as it stands, and still further variety if changes are made which have no strong experimental justification.

Finally I should like to point out that the method of calculation adopted by McConnell in his Table 1 (1954) has no essential new feature. McConnell's treatment differs from von Knorring's only in the assumption about (H_2O)—. If this is excluded and the number of cationic charges is made 18 following the scheme of Table 1 pg. 830, the last column gives exactly the numbers of cations first obtained by von Knorring. This must be so since any formula based on an analysis expressed in terms of neutral oxides must itself be charge balanced. Therefore the assumption of 18 cationic charges per cell is equivalent to the assumption of 18 negative charges, i.e. 9 oxygen ions in the present case.

I am grateful to Dr. G. W. Brindley for providing opportunity to discuss some of the x -ray results prior to their publication.

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COMMENT ON DR. J. ZUSSMAN'S NOTE

Dr. Zussman has kindly allowed me to see the text of his note prior to publication. I agree with many of his points. There is undoubtedly a difficulty in understanding the superlattice parameter $S=43.8$ and a normal pattern which indexes very well with $a=b/\sqrt{3}=5.32$ Å. The possibility that the material examined by x -rays may contain two kinds of structure was not seriously considered by the writer, although it was noted that the intensity of the entire group of superlattice lines varied from one sample of antigorite to another. It may be significant that the specimen showing the superlattice lines most clearly also showed in thin section the wavy thread-like bands which are illustrated in figure 1, plate 1, of the original paper (*Am. Mineral.*, **39**, p. 796, 1954). Dr. Zuss-

man's comments on structural formulae are apposite. Von Knorring and I assumed a brucite impurity but admitted the slender nature of the evidence, McConnell invoked tetrahedral hydroxyl groups and Zussman now shows this concept can be variously applied; he also considers "a different and hardly less justifiable assumption" that 2.3% of the 15.03% of $\text{H}_2\text{O}+$ should be treated as an impurity. This later suggestion appears to be just about as arbitrary as our brucite suggestion and it is scarcely strengthened by the Fe atoms going wholly into tetrahedral positions. What emerges most clearly from these discussions is that structural formulae are difficult to determine reliably when departures from normality arise. Under such circumstances, it is obviously desirable to survey the problem from a variety of points of view before attaching much weight to an unusual formula arrived at from one set of assumptions.

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NOVACEKITE FROM THE WICHITA MOUNTAINS, OKLAHOMA

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Novacekite, $\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$, described by Frondel (1951) from Schneeberg, Saxony, has been identified from the Wichita Mountains in Southwest Oklahoma. This member of the torbernite group was first found in October 1952 by Earl Smith, in Permian Red Beds and recent sedimentary deposits in SE $\frac{1}{4}$, SE $\frac{1}{4}$ Sec. 23, T. 3 N., R. 14 W., when the writer accompanied him in selecting a problem for his Master's thesis in the Wichita Mountains. Later, in April 1953 novacekite was again found in a friable red sandstone, $\frac{1}{2}$ mile northwest of Twin Mountain, while the writer undertook the investigation of the Wichita Mountains igneous complex. Small cavities of the sandstone are filled with novacekite crystals along with limonite, malachite, calcite and quartz grains. The occurrences of novacekite in sandstone are reminiscent of that recently described by Stern and Ansell (1954). They found the same mineral from the Woodrow area, Laguna Reservation, Valencia County, New Mexico. The novacekite coats a somewhat iron-stained friable sandstone in the Westwater Canyon sandstone member of the Morrison formation of Jurassic age.

Novacekite forms a series with saléeite, $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$, its phosphate analogue. Frondel divides this phosphate-arsenate series and applies the species names saléeite and novacekite to the halves of the series with $\text{P} > \text{As}$ and $\text{As} > \text{P}$, respectively, in atomic per cent. The speci-

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