

X-RAY STUDY OF A NEW VARIETY OF SERPENTINE (ORTHO-ANTIGORITE)

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ABSTRACT

X-ray powder data show an ortho-hexagonal cell containing two structural layers. Close similarity with the data for amesite suggests a similar disposition of the layers within the unit cell. Evidence for a superlattice parameter is obtained indicating a structure similar to that discussed by Aruja and by Onsager.

INTRODUCTION

A full mineralogical study of a new variety of serpentine, named ortho-antigorite, has been submitted by the present writer and Dr. O. von Knorring for publication in the *American Mineralogist*. The work was undertaken in the University of Leeds, England. The following note summarizes those aspects of the x-ray analysis of this material which may be of interest to clay mineralogists. Since serpentine is the trioctahedral analogue of kaolinite, it is closely related to clay mineral structures. The material investigated forms irregular veins in a chromite-serpentine rock in the island of Unst, one of the Shetland Islands to the north of Scotland. It ranges in color from a greenish yellow to an olive green and has a massive resinous appearance without structural features. In thin section, the material is extremely fine grained and without significant texture. X-ray powder analysis was the only possible method of investigating the crystal structure.

X-RAY POWDER ANALYSIS

X-ray powder diagrams were taken using a 19 cm diameter Unicam instrument and a 20 cm diameter semi-focusing camera, with filtered $\text{CoK}\alpha$ and $\text{CuK}\alpha$ radiations. Some 50 reflections were recorded. The general pattern of the diagram (with one notable exception discussed later) showed marked similarity to the powder diagrams of amesite (Brindley, Oughton and Youell, 1951) and of orthorhombic chamosite (Brindley, 1951) and no difficulty was experienced in finding the unit cell dimensions. The following parameters were obtained taking $\lambda(\text{CoK}\alpha) = 1.79020\text{\AA}$:

$$\begin{aligned}a &= b/\sqrt{3} = 5.32_2\text{\AA} \\b &= 9.21_9\text{\AA} \\c &= 2 \times 7.265 = 14.53\text{\AA}\end{aligned}$$

The cell is ortho-hexagonal in shape and the structure is probably of hexagonal symmetry. To distinguish it from the more usual monoclinic varieties the name "*ortho-antigorite*" is suggested. In other respects discussed later the material resembles the antigorite rather than the chrysotile variety of serpentine.

The close resemblance of the *intensities* as well as of the *positions* of the x-ray reflections with the corresponding data for amesite leaves no doubt that the structures are essentially the same with two structural layers per unit cell arranged in the manner shown in Figure 1.

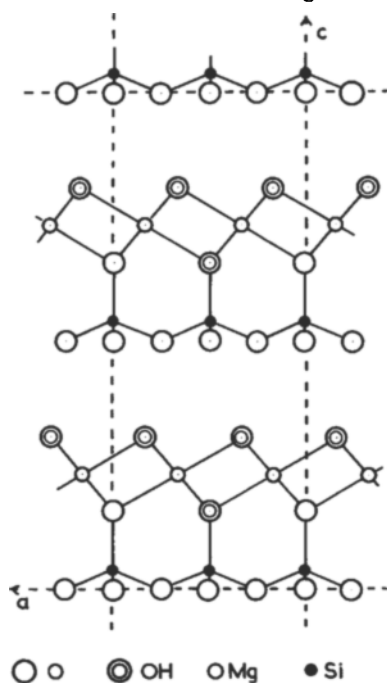


FIGURE 1.— Structure of amesite and of ortho-antigorite projected on the ac plane.

EVIDENCE FOR A SUPERLATTICE STRUCTURE

An outstanding feature of the powder diagrams was the existence of a closely and regularly spaced series of reflections extending from the 020 reflection ($d = 4.597\text{\AA}$) toward higher angles and having the general appearance of an optical band spectrum with the 020 line at the head of the band. The closeness of these lines can be explained only by the presence of a long spacing in the structure which is superimposed on the unit cell parameters already given. These reflections may be of the type H20 corresponding to a superlattice A parameter or of the type 02L corresponding to a superlattice C parameter. In either case, the reflections

will occur in accordance with a formula of the type $(1/d)^2 = (2/b)^2 + (N/S)^2$ where N takes integral values and S is the superlattice parameter. Close agreement is obtained with the observed data with $S = 43.8 \pm 0.2$ A.

The following interpretations may be considered:

- (i) $S = 3c = 43.5_9$ A
- (ii) $S = 8a = 42.5_8$ (c.f. Aruja, 1945)
- (iii) $S = 8\frac{1}{2}a = 45.2_4$ (c.f. Onsager, 1952)
- (iv) $2S = 16\frac{1}{2}a = 2 \times 43.91$

(i) is numerically acceptable. (ii) is the superlattice found by Aruja (1945) in x-ray studies of single crystals of antigorite, but it does not agree satisfactorily with the value found in the present work. (iii) is Onsager's (1952) recent interpretation of Aruja's data; it also does not fit the observed value. (iv) is a modified Onsager scheme with a periodicity of $16\frac{1}{2}a$ and with even values only of the index N . A clear distinction between (i) and (iv) is scarcely possible on the basis of powder data, but in the light of Aruja's results the interpretation is biased towards a superlattice along the a -axis.

SUMMARY

Serpentine from Unst (Shetland Islands, Scotland) is shown to have an ortho-hexagonal unit cell, which contains two structural layers arranged in the manner found in amesite. Evidence is found for a superlattice parameter $S = 43.8$ A which is consistent numerically with a superspacing along either a or c ; in the light of Aruja's results, the former is probably correct. The material is named "ortho-antigorite".

REFERENCES

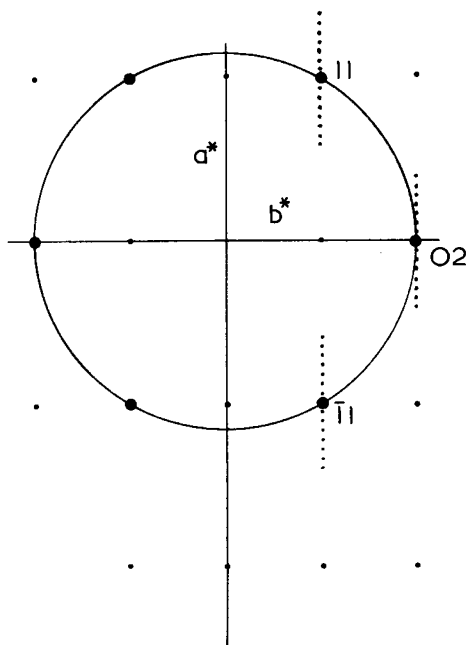
- Aruja, E. (1945) *An x-ray study of the crystal-structure of antigorite*: Mineral. Mag., v. 27, p. 65-74.
- Brindley, G. W. (1951) *The crystal structure of some chamosite minerals*: Mineral. Mag., v. 29, p. 502-525.
- Brindley, G. W., Oughton, B. M., and Youell, R. F. (1951) *The crystal structure of amesite and its thermal decomposition*: Acta Cryst., v. 4, p. 552-557.
- Onsager, L. (1952) See *Summarized proceedings of a conference on structures of silicate minerals—London, November 1951*, by K. Robinson and E. R. S. Shaw: Brit. J. App. Phys., v. 3, p. 277-282. See, in particular, p. 281-282.

DISCUSSION

W. F. Bradley. — For subparallel polycrystalline growths of antigorites these superlattice effects appear in the $h10$ reciprocal row line, exactly as in Aruja's single crystal work.

The superlattice is explicable as a result of the presence of brucite layers of two separate a -axis periodicities such that both traverse a nearly integral but different number of sub-units in one supertranslation.

G. W. Brindley. — I am not sure that the present observations “appear . . . exactly as in Aruja’s single crystal work”, though the apparent resemblances are clear enough as I have pointed out in the paper. For an ortho-hexagonal structure, the powder lines 110, $\bar{1}10$, and 020 are superimposed. A superlattice along a will tend to produce reflections of types H10, $\bar{H}10$ and H20, which may be represented in reciprocal space in the manner shown in the accompanying diagram; the small dots



represent the additional reflections arising from a modulation of the principal reflections shown by large dots. The correspondence of the 110, $\bar{1}10$ and 020 reflections from the main lattice is indicated by the circle. Superlattice lines will have d -spacings corresponding to circles passing through the small dots. Experimentally, I have observed the superlattice lines only on the large-angle side of the main reflection, which leads me to think that they are best indexed as H20 lines. Superlattice reflections would be likely to occur on both sides of a principal 110 or $\bar{1}10$ line. Admittedly Aruja observed superlattice reflections along an H10 line and he had the advantage of working with a single crystal. The material I used permitted only the powder method to be employed and the results are therefore less conclusive. I consider it better not to lean too heavily on Aruja’s conclusions when interpreting other data, since other structural varieties of antigorite may well exist.

Dr. Bradley's second point concerning the possible "presence of brucite layers of two separate *a*-axis periodicities" is interesting but not easily proved or disproved.

Bartholomew Nagy. — I wish to point out some of our data related to antigorite and chrysotile. In an attempt to explain the reason why chrysotile occurs in the form of tubes and antigorite in the form of flakes a suggestion came up some time ago that postulated the presence of Al^{3+} ions in the antigorite crystal lattice. Such an arrangement may reduce the strains that are responsible for the curvature of chrysotile. This hypothesis appears to be supported by certain evidence. A closer look at the picture implies, however, that this concept can not account for the flaky morphology of all antigorites. It is believed that pure Mg^{2+} antigorite also exists, together with the aluminous form. Certain chemical evidence supports the idea of a pure Mg^{2+} antigorite. In my opinion some of Dr. Brindley's statements and some of the literature he quoted may also imply that the existence of such a pure Mg^{2+} antigorite is possible.

Another point I would like to make is related to the differential thermal analysis curves of the serpentines. We have suspected for some time that the presence or absence of the high-temperature exothermic reaction may be due to a "textural" or particle-size effect. This idea is supported now by Dr. Brindley's observations and the results he quoted that have recently appeared in the literature.

G. W. Brindley. — The results quoted are those contained in the Doctoral Thesis of Ch. Kiefer, (Paris, 1951). In another publication, Kiefer refers to an article in *Rev. Mat. Const.*, B, nos 422-432, which may also contain his data on the serpentine minerals.

Duncan McConnell. — I should like to inquire whether or not the chemical analysis, for case number 2, was calculated on the basis of the simple assumption of an integer number of oxygens (that is 9) and the simultaneous assumption that the cations balance these charges in the ratios indicated by the analysis. Under these circumstances the charges of the cations (including hydrogen) should be summed to 18 and then the cations can be relegated to positions in the structure.

Further, I should like to inquire whether or not an attempt has been made to calculate part of the water as tetrahedral groups of hydroxyl ions substituting for SiO_4 groups.

Added later: Dr. Brindley has kindly made this entire paper available to me so that a note, which sets forth my interpretations, also can appear in the *American Mineralogist*.

G. W. Brindley. — The chemical analyses of these materials were carried out by Dr. O. von Knorring and are reported fully in the joint paper which is to appear in the *American Mineralogist*. The structural formulae were evaluated on the basis of 9 oxygen atoms, i.e., counting both oxygen atoms and (OH) radicals. The total cation charge (including hydrogen)

must sum to 18 since the calculation starts from electrically neutral oxides as given by the chemical analysis. On the basis of 9 oxygen atoms, the first material gave a normal serpentine composition, the second presented difficulties because it led to fewer than 2 (Si + Al) atoms, in fact 1.911 atoms. The formula was then re-calculated on the basis of 2 Si atoms per unit, and excess Mg attributed to brucite impurity.

In reply to Dr. McConnell's second question, we did not examine the possibility of 4(OH) replacing SiO_4 in the manner which he has discussed in relation to other minerals.