

THE KAOLINITE STRUCTURE OF AMESITE,
 $(\text{OH})_8(\text{Mg,Fe})_4\text{Al}_2(\text{Si}_2\text{Al}_2)\text{O}_{10}$, AND
ADDITIONAL DATA ON
CHLORITES

JOHN W. GRUNER, *University of Minnesota,
Minneapolis, Minnesota.*

ABSTRACT

An investigation of amesite with x -rays discloses that the mineral cannot be a simple chlorite. It has essentially a kaolinite structure, with which a few chlorite units are interstratified. As chlorites increase in Al at the expense of Si, there is a shrinkage normal to the basal cleavage. Reasons for this decrease as well as for the instability of the chlorite structure when the ratio of trivalent ions to Si reaches a certain value are suggested.

INTRODUCTION

Amesite has been reported from only one locality, namely, Chester, Mass. On account of its unusual chemical composition and properties, it has attracted wide-spread attention. It has commonly been regarded as a chlorite. Tschermak, in 1890, called it the chlorite end member of an isomorphous mixture of chlorites and serpentines. McMurchy (3) determined the structure of the chlorites in the writer's laboratory in 1934 and x -rayed, among others, amesite. It was noticed then that there was sufficient difference between its structure and that of the chlorites proper so that it could not be included with the latter. In connection with the study of other layer structures, the writer has investigated amesite recently and has come to the conclusion that it has a kaolinite structure. He is indebted to the Graduate School of the University of Minnesota for aid in this study, and to Dr. W. F. Foshag for the specimen of amesite from the type locality.

PROPERTIES AND CHEMICAL COMPOSITION

Amesite occurs in close association with diaspore, magnetite, and co-rundophilite. Since the specimen used is the identical one described and analyzed by Shannon (2) in 1921 (U. S. National Museum #80715) his description is given below:

The specimen consisted of a large flat mass of diaspore showing pale grayish-pink cleavages several inches broad where broken and containing small cavities filled with interlacing needle-like crystals of diaspore. One side of the specimen is completely coated with a layer of flat amesite crystals of a pale green color somewhat iron stained. Scattered through the mass of the diaspore there are variously oriented crystals of amesite, large octahedrons of magnetite, and crystals of dark red to black rutile. The amesite occurs in tabular hexagonal crystals with dull prismatic faces. They reach an extreme diameter of 1 cm. with a thickness of 3 to 5 mm. By breaking up the diaspore, clean crystals were

readily secured and these, when ground, were used for analysis. The material was perfectly homogeneous and free from impurities as shown by optical study.

The amesite has a uniform pale bluish-green color. The luster is pearly to somewhat metallic on cleavage surfaces. In thick pieces the mineral is translucent to almost opaque. Thin fragments are transparent. The powder is white with a very faint tinge of green. The mineral has a micaceous basal cleavage which, however, is not nearly so perfect as in most crystallized chlorites. Laminae are rather brittle and break in a manner suggesting a very imperfect prismatic cleavage. The hardness is about 2.3, as it scratches gypsum readily, but is scratched with great ease by calcite. The specific gravity as determined on approximately 3 grams of coarse fragments in a pycnometer is 2.77.

Under the microscope cleavage plates of the amesite are dark in all positions between crossed nicols. Examined in convergent light a black cross is obtained, which separates slightly on rotation of the stage indicating that the mineral is biaxial with the axial angle, $2V$, very small, acute bisectrix normal to the perfect cleavage. The optical character is positive. The mineral is colorless as seen under the microscope. The refractive indices measured by the immersion method were found by Dr. E. S. Larsen to be as follows:

$$\alpha = 1.597 \pm .003, \beta = 1.597 \pm .003, \gamma = 1.612 \pm .003, \gamma - \alpha = .015 \pm .003.$$

Heated before the blowpipe the amesite swells somewhat and exfoliates slightly, becoming silvery brownish-white in color. It is infusible. It does not become magnetic when roasted on charcoal. It yields considerable water in the closed tube. The main portion of the water is basic, coming off only at a dull red heat. The mineral is partially decomposed by boiling in sulphuric, nitric, or hydrochloric acid with separation of flocculent silica.

The observations of the writer agree closely with those of Shannon. His chemical analysis is included in Table 1.

TABLE 1. CHEMICAL COMPOSITION AND IONIC DISTRIBUTION OF AMESITE

	1	2	3	4	5	6	7
		Mol. ratio	Oxide ratio adjusted	+ ions	+ charges	Occupied + positions	Theoretical anions positions
SiO ₂	20.95	.3488	16.00	16.0	64.0	32 tetrahedral 47.5 octahedral	80 O
Al ₂ O ₃	35.21	.3454	15.84	31.7	95.1		
FeO	8.28	.1152	5.28	5.3	10.6		
CaO	0.58	.0103	0.47	0.5	1.0		
MgO	22.88	.5674	26.03	26.0	52.0		
MnO	tr.						
H ₂ O+	13.02	.7225	33.14	66.3			64 OH
H ₂ O-	0.23						
Total	101.15				222.7		224 - charges
Mol. W.			4628				

Since amesite is unquestionably a layer silicate of pseudo-hexagonal or hexagonal unit cell and has an x -ray period of 14.03 Å, or a multiple of

this value, normal to the layers, its structure must be either that of chlorite, kaolinite, antigorite, or a combination of two of the three. Its chemical composition corresponds to any one of the three, of course, since they have the same number of ionic positions in their lattices. If we make the unit cell twice as large as the accepted one for chlorite, we have 80 O, 64 (OH), 32 (Si,Al) tetrahedral and a maximum of 48 (Mg,Al,Fe) octahedral positions. In columns 3 and 4 of Table 1, it is assumed that Si occupies 16 positions. The other 16 tetrahedral ones are filled by Al. This leaves a total of 47.5 cations to occupy the 48 octahedral positions. The positive charges of column 5 balance the negative charges of column 7, especially if a slight adjustment be made in the number of (OH) and O ions. The formula is: $(\text{OH})_{64}(\text{Mg, Fe}'')_{31.8}\text{Al}_{15.7}(\text{Si}_{16}\text{Al}_{16})\text{O}_{80}$. The molecular weight of this unit cell is 4628. Its volume is $2(5.30 \times 9.20 \times 28.06) = 2738 \text{ \AA}^3$. The theoretical density then is 2.789, in excellent agreement with the observed value (Table 3). All determinations, unless otherwise stated, were made in Thoulet solution. McMurchy's specific gravities were determined with the pycnometer and agree well with the new densities of Table 3.

X-RAY DATA

It was not intended to go into an exhaustive study of the space group and atomic coordinates of amesite in this investigation. It is probably

TABLE 2. THEORETICAL AND OBSERVED RELATIVE INTENSITIES OF BASAL REFLECTIONS OF AMESITE AND CHLORITE STRUCTURES. FE AND CU RADIATION. 57.3 MM. CAMERA RADIUS

Order of reflection	002	004	006	008	0010	0012	0014	0016	0018	0020	0022	0024	0026	0028	0030	0032
Theor. I. Kaolinite structure with amesite composition	0	74	0	82	0	22	0	3	0	13	0	17	0	14	0	15
Obs. I. Amesite	0	64	8	80+	6	24	very faint	8	0	16	0	24	0	24	0*	24*
Theor. I. Chlorite structure with amesite composition	7	43	51	53	18	3	10	0	1	13	0	15	0	16	0	9
Obs. I. Chlorite-corundophilite	13	54	48	80	40	0	20	0	0	20	0	20	0	26	**	**
Theor. I. Kaolinite layers with amesite composition, facing one another	2	58	12	59	18	7	1	1	7	0	12	15	0	9	7	0

* Observed with Cu radiation.

** Outside of range of Fe radiation.

not practical to do so as the mineral seems to have random shifts along the b axis as was shown for talc and related structures by Hendricks (4, p. 536). In order to determine whether amesite is a chlorite or kaolinite it is sufficient to thoroughly investigate the basal reflections of the minerals.

This was done by rotating small thin cleavage pieces of the minerals in the x -ray beam. Filtered Cu and unfiltered Fe radiations were used with cameras of 57.3 mm. radius. The arrangement was such that reflections of 14 Å spacing would easily register on the film. The observed intensities are recorded in Table 2. Since the unit of spacing normal to the cleavage is about 28 Å in chlorites, the first visible reflection near 14 Å would be 002. This is the spacing also assumed for amesite, though it may be too large by a factor of 2. For comparison, the observed basal intensities for corundophilite have been listed in Table 2. This is the chlorite which occurs with amesite at the type locality at Chester, Mass. A good specimen of it was available for this investigation. Its chemical analysis and other properties were described by Shannon (2). It is possible that his and the writer's corundophilite differ slightly in composition, as suggested by the small difference in theoretical and observed densities (Table 3). No x -ray data on powders are included here, though they were carefully studied. They have been previously recorded by McMurchy (3) and later by Hallimond and Bannister (6).

Pauling (1), McMurchy (3), and the writer (5) have shown the stacking of single layers of kaolinite, talc, pyrophyllite, and brucite which lead to structures with kaolinite-chlorite formulas. If one excludes the serpentine structures described by Warren and Bragg, there are only three possibilities:

1. The chlorites proper (1) and (3).
2. The kaolinites proper (1) and (5).
3. A structure of kaolinite layers in which adjacent layers would not be pointing in the same direction but would be turned 180° with respect to each other, in other words, would be facing each other.

The theoretical intensities of the basal reflections of each of these have been computed for the chemical formula of amesite and are recorded in Table 2. It may be mentioned here that the observed intensities of chemically quite different chlorites seem to be about the same. In other words, leuchtenbergite, sheridanite, corundophilite, and others fairly high in iron show about the same intensities though the theoretical ones differ considerably.

Examination of Table 2 shows that amesite cannot have the structure of 3, for no reflections are observed for 0018, 0022, and 0030. Also, 0032, which should be absent, is quite strong. Structure 1, that of the chlorites proper, is not possible because 002 is not observable on any of the films.

0012, which should be practically absent is quite strong, and 006, 0010, and 0014, which should be strong, are weak, and 0014 is extremely weak.

There remains only the kaolinite structure for which agreement would be very good if it were not for the presence of weak reflections at 006 and 0010. The latter is not visible in powder photographs. At first it was thought that possibly a little chlorite was in parallel intergrowth with amesite proper. This is not possible for three reasons: (a) Regardless of the place on the specimen from which the four samples for examination were taken, the intensities in all were alike; (b) The unit cells of amesite and corundophilite (or any other chlorite) are sufficiently different in size so that a mechanical mixture of the two would have been readily detected; (c) The optical properties of different specimens of amesite are quite constant.

PROBABLE STRUCTURE

Pauling (1, p. 578) in 1930 was of the opinion that a kaolinite structure with a large amount of Mg in place of Al is not possible because a Mg octahedral layer would be too large for the Si_4O_{10} tetrahedral layer. Distortion and warping would result. In amesite this tetrahedral layer has the formula $\text{Si}_2\text{Al}_2\text{O}_{10}$, and, therefore, is considerably larger. This case is quite analogous to that of cronstedtite described by Hendricks (4) where the tetrahedral layer is $\text{Si}_2\text{Fe}'''\text{O}_{10}$. The corresponding dimensions of the three minerals are as follows:

	a_0	b_0	Normal to (001)
kaolinite	5.14	8.90	7.14
amesite	5.30	9.20	7.015
cronstedtite	5.48	9.49	7.08

The contraction of amesite in the direction normal to the base is conspicuous but probably not much greater in proportion than in cronstedtite with its larger Fe''' ions. The contraction is distributed over the whole length of c , though probably the largest proportion occurs between the layers for which the distance between centers of O ions and (OH) ions was assumed, as 2.68 Å instead of 2.78 Å in kaolinite. The forces which hold adjacent layers in the actual mineral together are certainly greater than in talc or kaolinite, as may be demonstrated by splitting the mineral.

The weak reflections for 006 and 0010 and the very faint one for 0014 which do not belong to the kaolinite structure call for some explanation. If a unit of chlorite structure were inserted between packets of 10 to 16 layers of kaolinite structure, all the reflections could be accounted for. The individual chlorite layers could be of the same dimensions as the amesite units under these conditions. They may be considered essential to the structure to counteract any stresses otherwise present in a struc-

TABLE 3. LATTICE CONSTANTS AND DISTRIBUTION OF POSITIVE IONS IN CHLORITE AND KAOLINITE STRUCTURES

	Spacing 002	a_0	b_0	Number of + ions in 80 positions						Densities	
				Octahedral and brucite layers				Tetrahedral layers		Theor.	Observed
				Mg+Ca	Fe''	Fe'''	Al	Si	Al		
Leuchtenbergite, Philipsburg, Mont.*	14.21	5.30	9.19	41.4			6.6	23.2	8.8	2.636	2.606
Sheridanite, Miles City, Mont.*	14.20	5.32	9.21	36.6	0.2	0.8	10.4	20.9	11.1	2.664	2.668
Chlorite, Burra Burra, Tenn.*	14.18	5.32	9.21	31.1	5.6		11.3	20.5	11.5	2.705	2.756
Prochlorite, Trumbull, Conn.*	14.14	5.35	9.27	24.6	18.3		8.1	19.4	12.6	2.812	2.941 ³
Chlorite, ¹ Bolivia,*	14.12	5.37	9.30	10.1	25.7		12.2	19.7	12.3 ¹		
Corundophilite, Chester, Mass.	14.12	5.35	9.26	27.8	8.9	2.1	9.2	18.4	13.6	2.816	2.852
Kaolinite, Brooklyn, N. Y. (5)	14.28	5.14	8.90				32	32.0		2.589	2.585
Amesite, Chester, Mass.	14.03	5.30	9.20	26.5	5.3		15.7	16.0	16.0	2.789	2.782
Cronstedtite, Cornwall (4) ²	14.16	5.48	9.49	1.4	35.8	7.7	1.1	16.8	Fe''' 15.2	²	3.445

* Specimens used by McMurphy (3) were reexamined under the same conditions as amesite and corundophilite. The densities were found with Thoulet solution.

¹ The formula of the chlorite from Bolivia is only approximate since no accurate density was available and the analysis is incomplete, adding up to 91.17% and 4.28% insolubles.

² The formula for cronstedtite was adjusted by the writer on the basis of a density of 3.445 determined by Gossner (4).

³ The formula is based on the observed density. See Table 4.

ture of amesite composition complying with the space group requirements of a true kaolinite. If this interpretation is accepted, amesite has a superlattice cell of large dimensions in the direction of the c axis.

In an effort to find a reason for the fact that amesite and cronstedtite do not form chlorite structures, Table 3 was prepared. Wolf von Engelhardt (7) has prepared a similar one of chlorites for the purpose of showing the changes in lattice dimensions with changes in composition. He has included the chlorites which are very high in iron, as thuringite and bavalite. Since the analyses of these iron chlorites were not made on exactly the same material as the x-ray photographs, the writer felt they should not be included in Table 3. Engelhardt comes to the conclusion

that increases in Fe cause most of the shrinkage along c and expansion parallel to a and b . This can be only part of the explanation, for it does not account for the shrinkage in corundophilite and amesite. The writer has arranged the minerals in the order of the lengths of the 002 spacing. It will be noticed that corresponding to a decrease in 002, there is an increase in substitution of Al (Fe''' in cronstedtite) for Si. The chlorite from Bolivia seems to be the only one not in agreement. Since the analysis of this specimen is only a partial one (see footnote under table) the discrepancy may not be real. It is reasonable to expect the attraction between adjacent layers to rise as the $+$ charges in the tetrahedral layers decrease, as they would with an increase of Al in them. That the resulting shrinkage is not proportional to the percentage of Al is due to other substitutions taking place simultaneously.

As Al or Fe''' increases in the tetrahedral layers of the talc units, there must be a corresponding Al increase in the brucite layers between them. In other words, if amesite had a chlorite structure, all of the Al ions not substituting for Si should be concentrated in the brucite layers. Three-fourths of the divalent ions would be in the octahedral layers of the talc units. This segregation of di- and trivalent ions into separate layers should cause unstable structures. The kaolinite structure is not subject to this instability for it possesses only one type of layer in which all these ions are lodged.

SOME DISCREPANCIES IN CHLORITES

It is unusual to have several analyzed chlorites at one's disposal, on which x-ray and density determinations can be made. It may be proper, therefore, to call attention to certain discrepancies between calculated and observed densities of the prochlorite from Trumbull, Conn. (see Table 3). This mineral was carefully analyzed by Shannon (8, p. 473), who called particular attention to the relatively large amount of CaO in it. The writer obtained a part of this analyzed material from Dr. W. F. Foshag and made three density determinations on it. One with a fused silica pycnometer on 0.4 grams resulted in 2.95, and two with Thoulet solutions were 2.939 and 2.948. Inspection of Table 4 shows that this density is considerably higher than the theoretical one of 2.812. In column 3, Table 4, the 80 cations required to fill the unit cell are listed. It will be observed in column 4 that they have only 217.2+ charges instead of the usual 224. Also, instead of about 64 (OH) ions, only about 40 are present. An adjustment to reach agreement with the observed densities results in columns 5, 6, and 7. It will be noticed that there are about 83 cations for 80 positions. It takes 92 O and 42 (OH) to neutralize them. In other words, 12 (OH) positions are occupied by O, while 10 OH posi-

tions are vacant. If the chemical analysis is correct—and there is no reason to doubt it—three cations, probably the Ca ions, must be in new and unusual positions between the talc units and the brucite ones. They would correspond to the K or Ca ions in micas or brittle micas respectively. A total of eight such positions would be available, but only three would be filled. The Ca ion is small enough to fit in the hexagons of SiO_4 tetrahedra, as in margarite. Since some OH would be replaced by O coordinate valencies would be balanced.

This possible explanation must be considered merely as a suggestion to be followed, if future analyses of chlorites show similar discrepancies. If they are small as those of the chlorite from Burra Burra, Tenn. (Table 3), other explanations, like random interstratifications of occasional heavy talc units with chlorite units, might possibly be called upon. In the case of the Trumbull mineral this would not be a plausible explanation.

TABLE 4. ANALYSES, IONIC DISTRIBUTION, AND DENSITIES OF PROCHLORITE FROM TRUMBULL, CONN. E. V. SHANNON, *analyst*.

	1	2	3	4	5	6	7
		M. R.	+ ions	+ charges	Adj. + ions	Adj. + charges	Adj. anions
SiO_2	23.69	.3944	18.75	75.0	19.4	77.6	} O 92
TiO_2	tr.						
Al_2O_3	21.26	.2086	19.82	59.4	20.7	62.1	
FeO	26.52	.3692	17.55	35.1	18.3	36.6	
CaO	3.32	.0592	2.81	5.6	2.9	5.8	
MnO	.43	.0061	.29	0.6	0.3	.6	
MgO	17.60	.4365	20.75	41.5	21.7	43.4	
Total			79.97 (OH)	217.2	83.3 (OH)	226.1	} (OH) 42
$\text{H}_2\text{O}+$	7.63	.4234	40.26		42.1		
Total	100.45						134
Mol. Weight			4776		4993		
Theor. Density			2.812		2.942		
Obs. Density					2.944		

CONCLUSIONS

Amesite has the formula $(\text{OH})_8(\text{Mg}, \text{Fe})_4\text{Al}_2(\text{Si}_2\text{Al}_2)\text{O}_{10}$ and, contrary to earlier opinions, has a structure which is more like that of kaolinite than that of chlorite. It differs from a true kaolinite structure in this,

that a chlorite unit is interlayered with kaolinite units in the ratio of about one 14 Å chlorite unit to between 10 to 16 kaolinite units each 7 Å high. This results in a superlattice of considerable dimensions along the *c* axis. This interstratification is probably essential to keep the kaolinite units from curving.

There is a considerable shrinkage normal to 001 in amesite when compared to true kaolinite or to regular chlorites. It can be shown that such shrinkage, which also occurs in the chlorites, is connected with a substitution of Al for Si in the tetrahedral layers. Increase in this substitution causes decrease in the length of the *c* axis. Finally, when the limiting case of amesite is reached, the chlorite structure becomes unstable for reasons stated above. The same holds true for the mineral cronstedtite, which also has a kaolinite structure, in which about half of the Si has been replaced by Fe⁺⁺⁺.

A discrepancy in the theoretical and observed densities of chlorites, particularly in prochlorite from Trumbull, Conn., suggests that more ions are in the structure than are ordinarily thought possible. A place for these additional cations may possibly be found in the centers of the hexagonal rings of SiO₄ tetrahedra, that is, in positions similar to Ca in brittle mica.

REFERENCES

1. PAULING, LINUS, The structure of the chlorites: *Proc. Nat. Acad. Sci.*, **16**, 578-582 (1930).
2. SHANNON, E. V., Analyses and optical properties of amesite and corundophilite from Chester, Massachusetts, . . . : *Proc. U. S. Nat. Mus.*, **58**, 371-378 (1921).
3. McMURCHY, R. C., The crystal structure of the chlorite minerals: *Zeits. Krist.*, **88**, 420-432 (1934).
4. HENDRICKS, S. B., Random structures of layer minerals as illustrated by cronstedtite (2FeO · Fe₂O₃ · SiO₂ · 2H₂O): *Am. Mineral.*, **24**, 529-539 (1939).
5. GRUNER, J. W., The crystal structure of kaolinite: *Zeits. Krist.*, **83**, 75-88 (1932).
6. HALLIMOND, A. F., On the relation of chamosite and daphnite to the chlorite group: *Mineral. Mag.*, **25**, 441-465 (1939).
7. ENGELHARDT, WOLF VON, Die Strukturen von Thüringit, Bavalit und Chamosit und ihre Stellung in der Chloritgruppe: *Zeits. Krist.*, **104**, 142-159 (1942).
8. SHANNON, E. V., Some minerals from the old tungsten mine at Long Hill in Trumbull, Conn.: *Proc. U. S. Nat. Mus.*, **58**, 469-482 (1921).