

MISERITE FROM ARKANSAS; A RENAMING OF NATROXONOTLITE*

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ABSTRACT

A reinvestigation of a pink silicate mineral, occurring with and formed from wollastonite in a contact metamorphosed shale at Potash Sulphur Springs, Ark., has shown that the original analysis is in error. Because of the high sodium content ($4\frac{1}{2}\%$ Na₂O) reported and the supposed relation of the pink mineral to xonotlite, the name natroxonotlite was suggested by J. Francis Williams in 1891 in the famous volume 2 of the Arkansas Geological Survey. New analyses show that the dominant alkali is potassium, and not sodium, and dehydration and x-ray studies indicate that the mineral is not a xonotlite. The name natroxonotlite, therefore, is "glaringly false in signification" and the mineral is renamed miserite after Dr. Hugh D. Miser, geologist of the U. S. Geological Survey.

The original analysis indicated that miserite was intermediate in composition between wollastonite and pectolite, but the present investigation shows that this is not so. The formula of miserite is $\text{KCa}_4\text{Si}_5\text{O}_{13}(\text{OH})_3$ or $\text{K}_2\text{O} \cdot 8\text{CaO} \cdot 10\text{SiO}_2 \cdot 3\text{H}_2\text{O}$. Indices of refraction 1.58 to 1.59. $G=2.84$. Biaxial, positive, 2V small. The dehydration curves of miserite and of xonotlite are not similar. X-ray powder patterns of miserite are different from those of wollastonite, pectolite, and xonotlite.

INTRODUCTION

Some years ago, while compiling the available published information on wollastonites containing small but appreciable amounts of manganese or of iron, in order as far as possible to complete the data on the wollastonite-bustamite series, I noted the analysis of a white wollastonite from Arkansas, with 2.03 per cent of FeO and 2.08 per cent of MnO, published by Williams (1891, p. 356) and listed in the Supplement to Dana's System of Mineralogy, 6th ed., page 1052.¹ Associated with this white wollastonite was a pink calcium silicate (miserite), reportedly with less iron and manganese but with more water and nearly $4\frac{1}{2}$ per cent of soda. Williams called it a pink variety of wollastonite, related to xonotlite, the best-known hydrated calcium silicate at that time; and because of the sodium supposed to be present, he suggested the name natroxonotlite for it. An analysis, by R. N. Brackett, placed the mineral halfway between wollastonite and pectolite in composition.

The published description of the pink mineral suggested a number of intriguing relationships between these minerals, and as no specimen of it could be located, I welcomed an opportunity in November 1937 to visit the Arkansas locality in company with Hugh D. Miser and Clarence S. Ross. Abundant material was collected, and on return to Washington, some of its properties were determined. These were found not to be inter-

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¹ I am still looking for wollastonites containing 1 to 3 per cent MnO.—W.T.S.

mediate between the similar properties of wollastonite and pectolite. A reexamination of the pink mineral showed that the old analysis was in error. The pink mineral is not intermediate between wollastonite and pectolite, it is not a sodium (natro) compound, and it is not a xonotlite. The name natroxonotlite is, therefore, "glaringly false in signification"² and so grossly misleading as to be untenable and a new name is called for. No name could be more appropriate than miserite,³ after Dr. Hugh D. Miser, born in Pea Ridge, Ark., geologist of the U. S. Geological Survey since 1907, who has contributed so much to our knowledge of the geology and mineralogy of his native state. According to Dr. Miser, practically all of the available specimens of miserite have now been collected and deposited in the U. S. National Museum in Washington.

New analyses show that potassium and not sodium is the essential alkali, and the formula derived for miserite is $\text{KCa}_4\text{Si}_5\text{O}_{13}(\text{OH})_3$ or $\text{K}_2\text{O} \cdot 8\text{CaO} \cdot 10\text{SiO}_2 \cdot 3\text{H}_2\text{O}$. Through the courtesy of Prof. James D. Burfoot, Jr., of the Department of Geology, Cornell University, I was able to examine Williams' type specimen of his pink wollastonite or natroxonotlite, with which our material is identical. Blowpipe tests on many fragments of the type material gave the characteristic violet flame coloration of potassium. Only an occasional small fragment of the pink mineral gave a strong yellow sodium flame, but every such piece was seen to contain inclusions of aegirite. Similar results were obtained on our material.

OCCURRENCE

Miserite occurs at Potash Sulphur Springs (now called Wilson Mineral Springs) about halfway between Hot Springs and Magnet Cove, Ark. It is a constituent of the (quoting Williams) "very beautifully banded metamorphosed shales"⁴ in which "occur the beautiful pink [miserite] and white wollastonite crystals which were exposed when the rock was blasted open in building the road" [from Lawrence Station to the Springs hotel. The boulders in the creek bed from which we collected are undoubtedly pieces resulting from this blasting. The masses of white wollastonite probably represent calcareous portions of the original shale—W.T.S.]. The metamorphosed and indurated shale, now composed essentially of orthoclase, aegirite, wollastonite, and miserite, is in the contact band crossing the road about 700 yards south of the hotel, and was

² Dana, E. S., *System of Mineralogy*, 6th ed., 1892, Introduction, IV. Nomenclature. 13. Limitations of the Law of Priority, b. "When it [the name] is glaringly false in signification," p. xliii.

³ Pronounced my'-ser-ite.

⁴ This rock polishes well; and the contrasting pink miserite, white wollastonite, and greenish aegirite present a very attractive appearance. It is to be regretted that more material is not available.

“formed by the intrusion of a vertical dike of eleolite syenite 30 feet wide, cutting the shales in a nearly east and west direction. The shale on both sides of this dike is of a greenish gray color and but little decomposed while the igneous dike has almost disappeared.”

“Near the line of contact the shale has entirely lost its shaly, laminated structure and has the appearance of a glassy igneous rock. It is cut by numerous small sheets and masses of pink [miserite] and white [wollastonite] minerals which present a strong contrast to the greenish color of the rock. . . . This white mineral [wollastonite] is generally covered with a layer of the pink scales [miserite]. . . . The pink variety of wollastonite [miserite] occurs in thin plates and scales. The color is apple-blossom-pink to pale rose color and is characteristic of the thin scales of this mineral.⁵ It [miserite] might be considered as a xonotlite in which one-tenth of the lime (CaO) is replaced by soda (Na₂O) and in which the ratio of the normal silicate to the water is as 5:1 in place of 4:1 as in xonotlite. In view of this fact, the name *natroxonotlite* is suggested for this variety. . . . The natroxonotlite is formed by a decomposition of wollastonite. . . .”

Williams' description of miserite would indicate that it is in plates or scales, whereas it is fine-grained fibrous, and only the compact aggregates form slightly curved, scaly masses several inches in diameter but rarely more than a quarter of an inch thick. It commonly is in the white wollastonite, at many places forming a border zone between the wollastonite and the greenish host rock, which is much seamed with veinlets of wollastonite with or without miserite, and of aegirite.

An examination under the microscope of the wollastonite fragments (100 mesh), separated from the miserite by heavy solution, leaves little doubt as to the derivation of miserite from wollastonite, as stated by Williams. Many of these fragments of wollastonite are penetrated to a varying degree by long, extremely slender prisms of miserite, which are heterogeneously oriented or roughly parallel to the elongation of the wollastonite fragments and hence, when abundant, form aggregate pseudomorphs after wollastonite. Very rarely are the single long prisms of miserite wide enough to permit satisfactory optical observations. Disseminated small particles of orthoclase may be considered as evidence of the source of the potassium in the miserite. The ratio of Na₂O to K₂O in miserite is similar to that in orthoclase in general. A few fragments of miserite, carried down by the wollastonite, in the purification of the sample by use of bromoform, contain inclusions of smaller fragments of wollastonite, considered to be residual.

⁵ On surfaces of the rock which have been exposed to the weather for half a century, the miserite has taken on a more lavender hue.

OPTICAL PROPERTIES

The fineness of the fibers of miserite make it difficult to determine the optical properties satisfactorily. Most of the short prismatic pieces, as observed in crushed fragments, are compact aggregates of fine fibers, only approximately parallel. Occasional single unit fibers have parallel extinction with negative elongation; some of them are slightly more pinkish normal to the elongation. The axial plane is parallel to the elongation with an apparently centered acute bisectrix, with $2E$ measured about 60° . The sign is positive and the weak dispersion is $r > v$. Parallel to the elongation the index of refraction is close to 1.580 and normal thereto close to 1.590. Apparently orthorhombic.

Ignited miserite has indices of refraction of about $1.60\text{--}1.61 \pm$. Undetermined crystals (pseudowollastonite?), heterogeneously oriented in the fibers of ignited miserite, have developed. Ignition seems to produce a two-phase product.

The separated silica, resulting from HCl decomposition, without gelatinization, retains the size and shape of the original grains. This separated silica is weakly birefringent, has parallel extinction with positive elongation, and indices of refraction of about $1.41 \pm$.

CHEMICAL COMPOSITION

Selected pieces of the metamorphosed shale, richest in miserite, were ground to 100 mesh, washed dust free, and run through the Frantz isodynamic separator to remove the aegirite. Most of the orthoclase and wollastonite were removed by the use of proper heavy solutions (bromiform). The analyzed sample retained about 5 per cent of orthoclase and 3 to 5 per cent of wollastonite, as indicated by grain counts under the microscope.

Two analyses of the same sample of miserite were made, one by fusion with sodium carbonate and one by hydrochloric acid decomposition. The results of the analyses are shown in Table 1.

The recalculated values for the analysis by Na_2CO_3 fusion are obtained after deducting 5 per cent of orthoclase (the insoluble from the acid decomposition sample) and 1 per cent of sphene (based on the difference in percentages of TiO_2 in the two analyses) and recalculating to 100 per cent.

These results show several important differences from those obtained by Brackett (in Williams, 1891, p. 357). The most important one is that the essential alkali is potassium and not sodium, and hence the mineral name cannot be prefixed with "natro." Nearly twice as much water (all high temperature) as originally given is present. The percentages of FeO and of MnO earlier reported are much too high. If his deter-

TABLE 1. ANALYSES OF MISERITE FROM ARKANSAS

	By fusion with Na ₂ CO ₃		By acid decomposition	
	Analysis	Recalculated	Analysis	Recalculated
Insoluble	—	—	5.27 ³	—
SiO ₂	49.83	49.27	46.84	49.24
TiO ₂	0.84	0.46	0.38 ⁴	0.40
Al ₂ O ₃	1.62	0.74	0.84	0.88
Fe ₂ O ₃	0.42	0.45	0.36 ⁵	0.38
FeO	0.06	0.06	0.06 ⁶	0.06
MnO	0.26	0.28	0.26 ⁷	0.27
CaO	34.76	36.69	34.61 ⁸	36.38
MgO	None	None	None	None
Na ₂ O	0.91 ¹	0.97	0.89	0.94
K ₂ O	6.37 ¹	5.88	6.00	6.31
H ₂ O—	None	None	(None)	(None)
H ₂ O+	4.89 ²	5.20	4.89 ⁶	(5.14)
	99.96	100.00	100.40	100.00

G. 2.84.

¹ Average of three determinations by different chemists. See text.

² Ignition loss. Average of 4.91 and 4.87. Total loss found by Nutting in his dehydration determinations, stopping at 980° C. = 4.53. Penfield tube method was unsuccessful, only 1.23 per cent being obtained, but an additional 3.27 per cent loss was found by blasting the removed sample in a platinum crucible, giving a total of 4.50. On separate sample of a scaly mass of fibers, an ignition loss of 5.26 was found.

³ Probably slightly high (a few tenths of a per cent) as insoluble was dried only to 110° C for subsequent microscopic examination.

⁴ Average of 0.38, 0.37.

⁵ Average of 0.33, 0.39.

⁶ Values taken from those determined on the fusion sample.

⁷ Colorimetric. Average of 0.24, 0.26, 0.27.

⁸ Average of 34.63, 34.58.

minations of iron and manganese were made gravimetrically, it is possible that the undetermined alumina and titania may be the reason for his high results. Brackett did not report either TiO₂, Al₂O₃, or Fe₂O₃. The associated white wollastonite was found to contain 0.50 per cent of FeO and 0.68 per cent of MnO, values considerably higher than found for the pink miserite, suggesting that the pink color may be due to titanium rather than to manganese. Comparison of hand specimens shows the colors of miserite, particularly on weathered surfaces, and of dumortierite from Dehesa, Calif., to be similar. I had previously suggested (Schaller, 1905, p. 101) that the lavender color of the dumortierite from Dehesa was due to titanium.

The average of the two closely agreeing recalculated analyses of miser-

TABLE 2. AVERAGE OF TWO RECALCULATED ANALYSES OF MISERITE, WITH RATIOS

Average of recalculated analyses		Ratios		Calculated for $K_2O \cdot 8CaO \cdot 10SiO_2 \cdot 3H_2O$
SiO ₂	49.25	0.8333	10.04 or 10	50.16
TiO ₂	0.43			—
Al ₂ O ₃	0.81			—
Fe ₂ O ₃	0.42	—	—	—
CaO	36.53	0.6561	7.97 or 8	37.46
FeO	0.06			—
MnO	0.28			—
Na ₂ O	0.96	0.0802	0.98 or 1	—
K ₂ O	6.09			7.87
H ₂ O	5.17	0.2869	3.51 or 3	4.51
	100.00			100.00

ite given in Table 1, with the derived ratios, is shown below in Table 2.

Even if 5 per cent of wollastonite (a maximum) is considered to be present in the sample and deducted, the ratios become:

SiO ₂	10.12 or 10×1.01
CaO.....	7.85 or 8×0.98
(K, Na) ₂ O.....	1.03 or 1×1.03
H ₂ O.....	3.66 or 3×1.22

resulting in the same formula.

The derived formula of miserite is $K_2O \cdot 8CaO \cdot 10SiO_2 \cdot 3H_2O$ or $KCa_4Si_5O_{13}(OH)_3$. It is believed that the small excess of water found in this fibrous mineral is extraneous, owing possibly to the many washing operations to which the analyzed sample was subjected.

Finding that the dominant alkali present was potassium and not sodium was so surprising that I asked two of my colleagues in the Geological Survey to determine the alkalis in the same sample for confirmation of my results. The results obtained are as follows:

	R. E. Stevens	M. Fleischer	W. T. Schaller	Average
Na ₂ O	0.94	0.84	0.96	0.91
K ₂ O	6.33	6.38	6.39	6.37

A spectrographic determination of lithium by K. J. Murata indicated that lithium was of the order of 0.01 per cent.

The gross errors in Brackett's alkali determinations recall similar

gross errors in the reported values for Na_2O and K_2O in several micas by different authors, as already noted by Schaller and Stevens (1941), pp. 542-543). To emphasize the magnitude of these errors, the values may be repeated here.

<i>Mineral</i>	<i>Reported</i>		<i>Correct</i>	
	Na_2O	K_2O	Na_2O	K_2O
Polyolithionite	7.6	5.4	0.5	11.1
Hallerite	7.6	3.1	3.0	8.9
Muscovite	5.3	2.7	1.8	7.6
Euphyllite	3.6	4.6	5.6	1.7
Miserite	4.4	0.9	0.9	6.4

For polyolithionite and euphyllite the presence of lithium may have contributed to the errors but for the other minerals the errors are analytical. A possible explanation of the gross errors in Brackett's figures for the alkalis may be that in transcribing the results from his laboratory notebook, he inadvertently transposed the figures for Na_2O and K_2O .

I was much intrigued by the formula obtained from Brackett's analysis, as it agreed closely with that of a compound intermediate between the formulas of wollastonite and of pectolite, if the latter be considered as derived from that of wollastonite by the double substitution of one atom of sodium for one atom of calcium with compensatory substitution of one hydroxyl for one oxygen, as follows:

Wollastonite	Ca_6	Si_6	O_{18}
Intermediate	NaCa_5	Si_6	$\text{O}_{17}(\text{OH})$
Pectolite	Na_2Ca_4	Si_6	$\text{O}_{16}(\text{OH})_2$

A comparison (Table 3) of Brackett's analysis with the calculated composition of the intermediate formula shows close agreement.

TABLE 3. COMPARISON OF BRACKETT'S ANALYSIS WITH THE CALCULATED COMPOSITION OF THE INTERMEDIATE COMPOUND $\text{NaCa}_5\text{Si}_6\text{O}_{17}(\text{OH})$

	Brackett's analysis	Intermediate formula $\text{NaCa}_5\text{Si}_6\text{O}_{17}(\text{OH})$
SiO_2	50.96	52.93
CaO	36.72	41.19
FeO	1.69	—
MnO	1.40	—
MgO	0.57	—
Na_2O	4.41	4.55
K_2O	0.90	—
H_2O	2.74	1.33
	99.39	100.00

If the composition of miserite was that represented by Brackett's analysis, that is, intermediate between wollastonite and pectolite, then the specific gravity and indices of refraction likewise should be intermediate but they were found not to be so, as shown:

	<i>Specific Gravity</i>	<i>Indices of Refraction</i>
Wollastonite	2.91	1.620 to 1.634
Miserite	2.84	1.58 to 1.59
Pectolite	2.86	1.595 to 1.632

Miserite is not an intermediate compound between wollastonite and pectolite, either in composition or in its other properties, although Brackett's analysis suggested such a relation.

DEHYDRATION

Dehydration determinations, made by Dr. P. G. Nutting, on miserite and, for comparison, on xonotlite from Puebla, Mexico, show considerable differences. Xonotlite continuously loses a few tenths of a percent of water from 110°C to about 700°, when most of its total water (about 3 per cent) is given off. Total loss to 655° is 0.80 per cent; to 940° it is

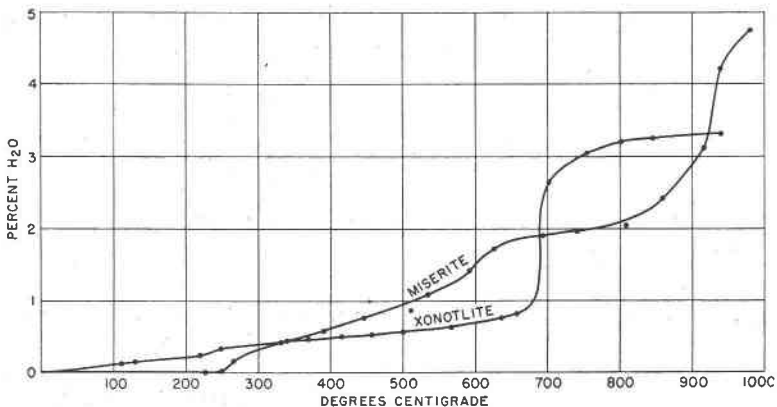


FIG. 1. Comparison of loss of water in miserite and xonotlite.

3.30 per cent. Miserite, on the other hand, loses no water until about 250° is reached. From here on to 980° there is a continuous loss. Total loss to about 800° is 2 per cent. Above 800° it loses an additional 3 per cent. When plotted the two dehydration curves are not similar, as shown in Fig. 1.

The loss of water by dehydration of miserite and xonotlite at increasing temperatures is given in Table 4.

TABLE 4. TOTAL LOSS OF WATER OF MISERITE AND XONOTLITE AT DIFFERENT TEMPERATURES

Temp. ° C.	Total loss		Temp. ° C.	Total loss	
	Miserite	Xonotlite		Miserite	Xonotlite
110	—	0.12	565	—	0.63
128	—	0.14	592	1.41	—
218	—	0.21	625	1.72	—
227	0.00	—	633	—	0.74
250	0.04	0.33	655	—	0.80
265	0.16	—	695	1.89	—
333	—	0.43	702	—	2.65
340	0.44	—	740	1.96	—
370	—	0.48	755	—	3.03
390	0.57	—	802	—	3.20
415	—	0.51	807	2.06	—
445	0.78	—	845	—	3.24
455	—	0.53	860	2.41	—
500	—	0.58	917	3.11	—
512	0.84	—	940	4.23	3.30
535	1.09	—	980	4.77	—

X-RAY PATTERNS

That miserite is not a xonotlite has already been suggested by the differences in the dehydration curves of the two minerals. The evidence is further substantiated by a comparison of the x -ray diffraction patterns. The pattern of miserite is different from the patterns of wollastonite, pectolite, and xonotlite. Those of wollastonite and of pectolite are closer to one another than those of any other pair of these minerals. The great similarity between the morphology of wollastonite and pectolite (both triclinic) has been shown by Peacock (1935, p. 110). Of these four minerals the greatest difference in x -ray patterns is shown by miserite. In no sense is the pattern of miserite intermediate between those of wollastonite and pectolite. The patterns of miserite and of yuksporite also are different. Some analyses of yuksporite, a mineral related to pectolite, show high K_2O . In an abstract (*Mineral. Abs.* (London), vol. 3, p. 112, 1926) of a paper on pectolite, yuksporite is said to be "related to Na-xonotlite."

The formula of miserite ($KCa_4Si_5O_{13}(OH)_3$) cannot be derived directly from that of wollastonite but it can be derived from that of xonotlite ($Ca_5Si_5O_{14}(OH)_2$) by substituting one atom of potassium for one atom of

TABLE 5. *d*-SPACINGS OF MISERITE AND RELATED MINERALS

Miserite 1	Wollastonite			Ignited xonotlite 3	Pectolite		Xonotlite			Pseudowol- lastonite 6	Ignited miserite 7
	2a	2b	2c		4a	4b	5a	5b	5c		
16.0 s	7.7 mw			7.8 w	7.8 w 7.0 mw 5.5 mw	7.7 2 6.9 2 5.4 2	7.0 s	7.06 7	7.10 6	5.7 w	
3.15 vs 3.07 m	3.85 ms 3.52 s	3.86 4 3.51 4	3.84 s 3.50 s	3.87 m 3.53 ms	3.90 ms 3.51 m	3.85 6 3.58 5	4.27 m 3.63 s	4.24 9 3.89 9 3.62 3	4.22 8 3.61 10	3.44 mw	3.85 mw 3.53 m
2.94 s 2.82 mw 2.78 mw	3.33 vs 3.09 ms	3.30 8 3.08 4 2.97 10	3.30 s 3.07 ms 2.97 vs	3.33 s 3.11 m 3.00 vs	3.32 s 3.28 s 3.09 vs	3.28 7 3.08 9	3.25 vs 3.09 ms	3.23 9 3.06 10	3.24 vs 3.07 8		3.33 m 3.24 vs 3.10 mw 2.99 s
2.68 m	2.30 m	2.54 4 2.46 4 2.33 6	2.54 mw 2.48 m 2.35 ms	2.49 mw 2.36 mw 2.31 mw	2.73 m 2.59 ms 2.30 s	2.89 10 2.72 6 2.58 6	2.82 m 2.70 ms	2.82 9 2.69 7 2.50 7	2.82 6 2.68 6 2.49 6		2.81 s
2.10 mw	1.759 mw	2.27 5 2.17 7 2.01 4	2.29 ms 2.18 ms 2.01 vw	2.20 mw	2.28 7 2.15 7		2.04 mw 1.945 m	2.03 9 1.938 9 1.827 7	2.03 8 1.940 8 1.826 6		2.00 m 1.981 s
1.672 m		1.821 7 1.751 4 1.710 8	1.826 mw 1.753 m 1.716 s	1.768 w 1.734 mw	1.749 mw	1.77 7 1.705 9 1.698 7	1.712 mw	1.702 7	1.705 6		1.982 s
		1.599 7 1.473 7 1.451 6	1.602 s 1.478 ms 1.453 ms		1.488 mw	1.539 7 1.477 6		1.512 7			

REFERENCES TO SPACINGS SHOWN IN TABLE 5

Miserite:

1. Analyzed sample. Arkansas.

Wollastonite:

2a. U. S. Geological Survey film 161. With strong preferred orientation. Kern County, California.

2b. A.S.T.M. Average.

2c. Neues Jahrb., 1948 A, p. 58.

Ignited xonotlite:

3. Puebla, Mexico. From same sample as xonotlite 5a.

Pectolite:

4a. U. S. Geological Survey film 164. With strong preferred orientation. New Jersey.

4b. A.S.T.M. Average. New Jersey.

Xonotlite:

5a. U. S. Geological Survey film 494. Analyzed sample. Puebla, Mexico.

5b. A.S.T.M. Puebla, Mexico.

5c. A.S.T.M. Isle Royal, Michigan.

Pseudowollastonite (synthetic):

6. From Geophysical Laboratory, Carnegie Institution.

Ignited miserite:

7. From same sample as miserite 1. Arkansas.

calcium, in the same way that the formula of pectolite can be derived from that of wollastonite:



But the differences in x -ray patterns of miserite and xonotlite are much greater than those of wollastonite and pectolite.

Ignited xonotlite gives a pattern similar to that of wollastonite. Ignited miserite gives a different pattern, and may be a two-phase product; if it is, the similarity between one of these phases and pseudowollastonite appears to be close.

The patterns of these minerals were taken by J. M. Axelrod, who also submitted the measurements of the d spacings (filtered Cu radiation) given in Table 5.

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