

STUDIES ON SCAPOLITE

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ABSTRACT

An x -ray method has been developed which permits the identification of the variety of scapolite more rapidly and with less skill than by optical methods.

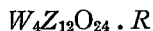
INTRODUCTION

During the course of a spectrochemical examination of a number of scapolites carried out at McMaster University by D. M. Shaw, it became evident that there were numerous uncertainties in the mineralogy of scapolites. For example, there is no indexed powder pattern available, there are uncertainties regarding the space group, chemical formula and various morphotropic properties of the scapolite family. These problems have been thoroughly discussed in a recent paper by Shaw (1960).

Eight completely analyzed scapolites as well as thirty partially analyzed specimens were obtained in order to attempt to resolve some of these problems.

HISTORICAL INTRODUCTION

The scapolites are an important group of silicate minerals about which relatively little information has been gathered. Almost none of this information is of modern quality. The name scapolite refers to a family of tetragonal aluminosilicates containing CO_3 , SO_4 , Cl, and other anions. The principal cations are Ca and Na. Shaw gives the following formula as provisionally suitable



where W is mainly Ca, Na, and K, but may include small amounts of other metals, Z is Si and Al, often with excess Si and deficient Al. R is (a) CO_3 , SO_4 , O_2H_2 , Cl_2 , or F_2 , for meionite components or (b) Cl, F, HCO_3 , HSO_4 , or OH for marialite. The nomenclature is accepted by Shaw as marialite $\text{Me}_0\text{-Me}_{20}$; dipyre $\text{Me}_{20}\text{-Me}_{50}$; mizzonite $\text{Me}_{50}\text{-Me}_{80}$, meionite $\text{Me}_{80}\text{-Me}_{100}$. So far as is known pure marialite does not occur in nature and 80% of the marialite molecule is the maximum found.

Early structural studies were those of Gossner & Brückle (1928), who, as a result of single crystal investigations, were of the opinion that the space group was one of three possibilities, *viz.*

$$C_{4h}^5(I4/m); C_{4h}^2(P4_2/m); \text{ and } C_{4h}^4(P4_2/n).$$

Later Schiebold & Seumel (1932) again as a result of single crystal measurements decided that the point group must be either $C_{4h}(4/m)$ or $S_4(\bar{4})$. They also tested their crystals for piezoelectricity and obtained no effect. Similarly, Hettich & Steinmetz (1932) were unable to obtain any indication of piezoelectricity. Greenwood (1935) tested two crystals from Mogok, Burma, of which one was colourless and the other pink; the colourless variety gave the piezoelectric effect and the pink variety did not. Greenwood considered that the point group of scapolite was, therefore, either $C_4(4)$ or $S_4(\bar{4})$ and that the impurity causing the pink colour suppressed the piezoelectricity.

Both Pauling (1930) and Scherillo (1935), as a result of preliminary structural analyses, considered the space group to be $I4/m$.

It can be seen from the foregoing that there is considerable doubt as to the correct space group or groups in which scapolite crystallizes, and indeed whether or not the crystals are centrosymmetric.

STUDIES ON CENTROSYMMETRY

To start the investigation an attempt was therefore made to test scapolite for centrosymmetry. Several recently devised statistical tests were not available to earlier workers.

Zero, first, and second layer Weissenberg photographs about the c axis of two scapolite crystals donated by the Royal Ontario Museum (Pianura R.O.M. M5432, Monte Somma R.O.M. M9122) were made. The cell dimensions and interaxial angles were measured from these photographs. The crystals were confirmed as tetragonal. The cell dimensions were $a = 12.25\text{\AA}$, $c = 7.548\text{\AA}$ (Pianura); $a = 12.11\text{\AA}$, $c = 7.600\text{\AA}$ (Monte Somma).

The intensity of the reflections in the $hk0$ layer were measured on a densitometer, and the Rogers $N(Z)$ test for centrosymmetry was applied. The results of this test are shown in Fig. 1, along with the two curves theoretically predicted for centrosymmetry and non-centrosymmetry. The experimentally determined curve varies somewhat from either of the theoretical curves. This is due to a number of reasons. Firstly because of experimental errors, and secondly because a crystal rarely meets the following necessary ideal conditions for the test: (a) that the unit cell should contain a large number of non-equivalent atoms; (b) that the positions of these atoms should be reasonably general; (c) that heavy atoms, if present, should not occupy true or apparent centres of symmetry, nor should they possess a considerable fraction of the total scattering power.

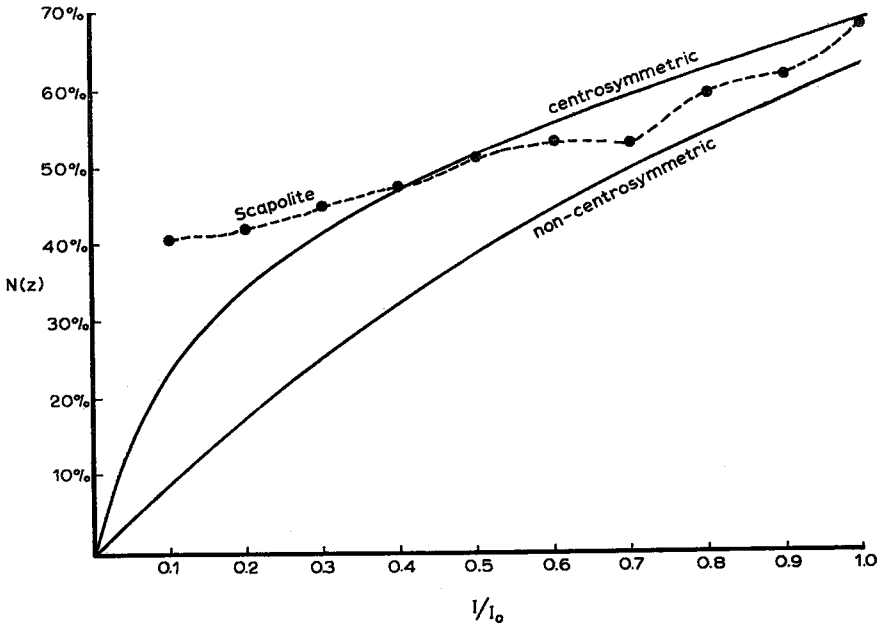


FIG. 1. Rogers $N(Z)$ test for centrosymmetry.

Generally speaking an approximation to the acentric distribution is regarded as an unambiguous indication of the absence of a centre of symmetry. The centric distribution may be formed either with true centrosymmetry or with pseudo-centrosymmetry (Kitajgorodsky, 1951), but in the latter case the distribution will ordinarily differ in type when evaluated for ranges of low and of high $\sin \theta$. The test was thus interpreted as indicating a centric distribution.

MORPHOTROPHISM

It was decided to make a study of the x -ray diffraction powder patterns of scapolites of different compositions. Eight completely analysed specimens plus a considerable number of unanalysed scapolites were obtained. The analyses of the eight completely analysed specimens (Table 1) were cast into the typical scapolite formula of the different scapolite end members as shown below (Table 2). The manner of doing this calculation has been explained by Shaw (1960).

The first six analyses were made by C. O. Ingamells, Rock Analysis Laboratory, University of Minnesota, the analysis of scapolite G was by Dr. O. Von Knorring the University of Leeds and scapolite JG by Dr. J. Gittins of the Pennsylvania State University.

TABLE 1. ANALYSES OF SCAPOLITE SAMPLES

	Q19D-S13A	Q87A	ON8	ON6A	M730	Q85	G	JG
SiO ₂	51.83	52.10	57.89	54.73	45.91	47.17	47.52	45.14
Al ₂ O ₃	24.29	23.79	21.62	22.85	28.19	26.29	25.21	27.83
TiO ₂	.03	.02	.01	.01	.07	.03	—	—
FeO							.30	.31
Fe ₂ O ₃	0.07 ^a	0.23 ^a	0.07 ^a	0.08 ^a	0.11 ^a	0.15 ^a	—	—
MnO	tr	tr	.01	1.00	.01	.01	.02	.00
MgO	.02	.18	.03	.03	.46	1.00	.14	.29
CaO	11.66	11.13	4.81	8.29	15.76	14.31	15.48	17.34
Na ₂ O	6.40	6.86	10.50	8.55	2.44	3.82	4.52	3.72
K ₂ O	1.16	.87	1.16	1.08	2.21	1.01	.10	.20
H ₂ O ⁺	.22	.07	.44	.13	1.12	.93	.22	.64
H ₂ O ⁻	.04	.10	.06	.00	.03	.50	.08	—
F	.02	.11	.00	.00	.01	.04	—	—
Cl	1.66	1.85	2.96	2.19	.05	.56	.06	.66
CO ₂	2.28	2.14	1.11	1.69	2.86	2.66	2.16	3.78
SO ₃	.72	.80	.03	.39	.94	1.42	4.17	.08
TOTAL	100.40	100.25	100.70	100.02	100.17	99.90	99.97	99.79

^aTotal Fe as Fe₂O₃.

The specific gravity of these analysed scapolites was determined on a Berman Balance by J. Weber as follows: ON8, 2.619; ON6, 2.660; Q87, 2.689; Q19D, 2.686; Q85, 2.705; M730, 2.703; G, 2.72. The density of scapolite JG was not determined because only a small amount of powder was available. Using these specific gravities and the known cell dimensions the cell content may be calculated and shown to be 2 formula units.

Using the approximate cell dimension data obtained from the single crystal studies, a powder pattern of scapolite Q85 estimated to contain 65.9% meionite was indexed and the cell dimensions refined by the $\sin^2\theta$

TABLE 2. ANALYSES CAST INTO SCAPOLITE END MEMBERS

Scapolite end members	Specimen number								
	ON8	ON6	Q87	Q19D	Q85	M730	G	JG	
MeCO ₃	17.0	30.0	46.2	49.5	53.8	44.3	45.4	72.0	
Me(OH) ₂	4.0	7.6			12.1	25.8			
MeSO ₄			1.0				20.3		
Ma*Cl	71.7	55.7	40.5	40.8	13.3	1.2	1.6	15.8	
Ma*F			4.4	0.9	1.6	.4			
Ma*HSO ₄	.3	5.0	7.9	8.9	16.9	11.5	27.8	2.2	
Ma*SO ₃									
Ma*HCO ₃	6.9	1.7			2.2	16.9		5.1	
Ma*CO ₃								4.9	
ΣMe	21.0	37.6	48.5	49.2	65.9	70.1	65.8	72.0	

N.B. Ma* signifies that K has been added to Na.

method to the values $a = 12.055\text{\AA}$ and $c = 7.51\text{\AA}$. An alternative dimension $a = 17.046\text{\AA}$ at 45° to the above a axes may be chosen to conform with the morphological axial ratios, but this does not conform to the smallest unit cell. Using $a = 12.055\text{\AA}$ and $c = 7.51\text{\AA}$ it was found possible to index all but one plane. The indexed pattern is listed in Table 3.

TABLE 3. INDEXED POWDER PATTERN OF SCAPOLITE
($a = 12.055\text{\AA}$; $c = 7.51\text{\AA}$; $\lambda = 1.5418\text{\AA}$)

I	$d_{\text{obs.}}$	$d_{\text{calc.}}$	hkl
13	5.961	6.001	200
31	3.797	3.811	310
15	3.532	3.541	301
100	3.434	3.426	112
80	3.051	3.054	321
44	3.013	3.014	400
6	2.831	2.838	330
15	2.723	2.725	411
66	2.675	2.675	312
5	2.365	2.364	510
15	2.299	2.295	501
4	2.270	2.270	213
5	2.194	2.190	422
15	2.148	2.145	521
23	2.130	2.125	303
8	2.070	2.067	530
16	2.008	2.009	600
16	1.919	1.922	522
28	1.908	1.907	620
15	1.883	1.882	540
5	1.829	1.834	423
6	1.815	1.811	532
6	1.751	1.752	612, 304
12	1.708	1.705	710
5	1.621	1.621	632
3	1.596	1.594	533
15	1.557	1.554	613
8	1.511	1.511	651
4	1.476	1.477	801
10	1.464	1.466	811
3	1.453	1.458	732, 215
10	1.425	1.427	652
4	1.413	1.416	225
4	1.407	1.406	305
7	1.376	1.377	751
20	1.368	1.369	325
3	1.352	—	—
4	1.344	1.344	405
4	1.336	1.366	415
6	1.319	1.319	832

Measurements were made using a Norelco high angle diffractometer with Cu radiation and Ni filter. Intensities were counted and background was subtracted.

The indices are compatible with a primitive lattice not a body centred

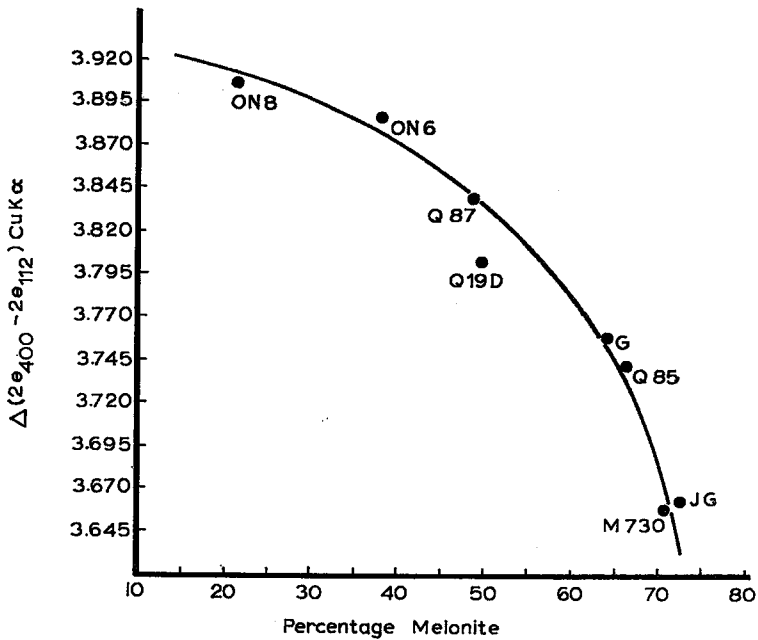


FIG. 2. Variation in lattice parameter $2\theta_{400}-2\theta_{112}$ ($\text{CuK}\alpha$) with composition.

lattice. Considering the centrosymmetry test and the previous discussion it is concluded that the most probable space group is $P4/m$.

All eight analysed scapolites were x -rayed and the patterns examined closely to seek any shift in the position of the reflections. It was observed that the angular distance between the reflections from the 400 and 112 planes varied sufficiently to be an easily measurable quantity. Accordingly, the x -ray diffractometer was set to oscillate between the 400 peak and the 112 peak. At least six patterns were run over this distance for each analysed specimen. The angular distance between the reflections was measured on a Norelco measuring vernier. This distance is accurate to about $\pm .010^\circ 2\theta$ for 95% confidence. The changes in this lattice parameter were thus measured directly on the six chart patterns, averaged and plotted against the compositional parameters in Fig. 2. Further the mean refractive indices $(N_o + N_e)/2$ of the eight analysed scapolites were available together with the refractive indices of a number of un-analysed specimens. These mean refractive indices are plotted against the angular distance $2\theta_{400}-2\theta_{112}$ in Fig. 3, and are tabulated in Table 4. The curves in Figs. 2 and 3 are drawn by eye. The specimen localities are given in Table 5.

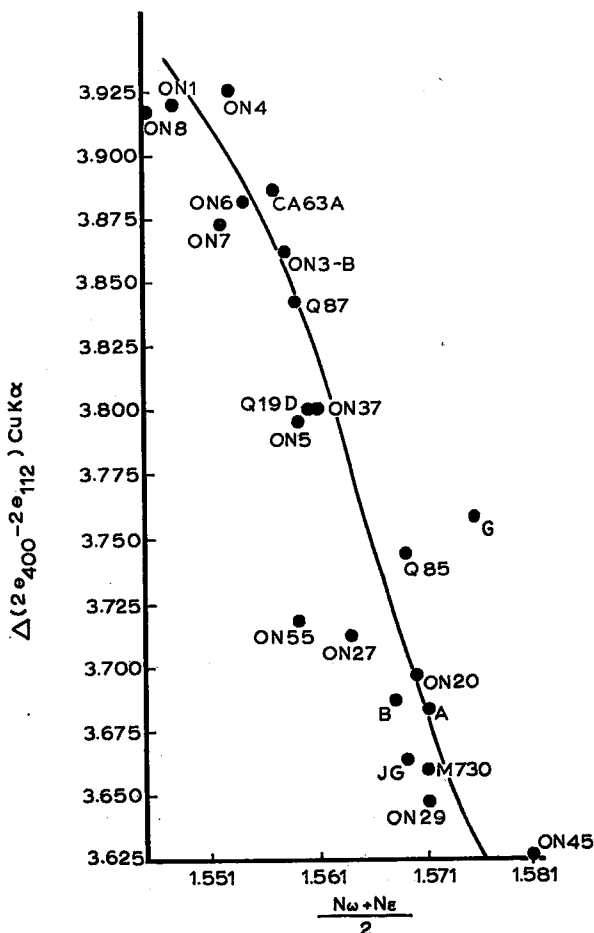


FIG. 3. Variation in lattice parameter $2\theta_{400} - 2\theta_{112}$ ($\text{CuK}\alpha$) with mean refractive indices.

DISCUSSION OF FIGURES

There is a considerable scatter of points along the curves. Some of the more important reasons for this scatter are as follows:

(a) The complexity of the chemical composition of the scapolites with so many theoretical end members makes it impossible to represent a number of analyses in the form of a variation of two components, for example, as a percentage of meionite. This has been recently discussed by Shaw (1960).

TABLE 4. LIST OF REFRACTIVE INDICES AND $\Delta 2\theta_{400} - 2\theta_{112}$

Scapolite	$(N_o + N_e)/2$	$\Delta(2\theta_{400} - 2\theta_{112})$
A	1.571	3.680
B	1.568	3.688
ON1	1.550	3.921
ON3B	1.558	3.862
ON4	1.553	3.925
ON5	1.559	3.798
ON7	1.552	3.872
ON20	1.570	3.695
ON27	1.564	3.707
ON29	1.571	3.648
ON37	1.561	3.801
CA63A	1.557	3.885
ON8	1.545	3.915
ON6	1.554	3.879
Q87	1.559	3.841
Q19D	1.560	3.800
Q85	1.569	3.767
M730	1.571	3.658
JG	1.569	3.633
ON55	1.559	3.718
ON45	1.580	3.626
G	1.576	3.758

TABLE 5. LOCALITIES OF SCAPOLITES MENTIONED IN THE TEXT

M730	Grenville Province, Quebec.
Q85	Lot 26, Range IV, Huddersfield Twp., Quebec.
Q19D	Lot 22, Range V, Huddersfield Twp., Quebec.
Q87A	Lots 16/17, Range V, Huddersfield Twp., Quebec.
ON6A	Lot 13, Con. XVI, Monmouth Twp., Ontario.
ON8	Highway No. 500, 2.4 miles E. of Gooderham, Glamorgan Twp., Ontario.
G	Shai Hills, Ghana.
ON4	Lot 25, Range XV, Lyndoch Twp., Ontario.
ON1	Lot 34, Range VIII, Brudenell Twp., Ontario.
CA63A	Lot 31, Range VI, Grand Calumet Twp., Quebec.
ON7	Lot 32, Range XVII, Monmouth Twp., Ontario.
ON3B	Lot 13, Range XVI, Lyndoch Twp., Ontario.
ON37	Lot 17, Range VI, Glamorgan Twp., Ontario.
ON5	Glendower Iron Mine, Bedford Twp., Ontario.
ON27	Olmsteadville, New York.
ON20	Lot 13, Range XVI, Monmouth Twp., Ontario.
B	Unknown.
A	Unknown.
JG	Monmouth Twp., Ontario.
ON29	Pargas, Finland.
ON45	Monte Somma, Italy, Royal Ontario Museum 5432.

(b) It is possible that the specimens have different thermal histories, since according to Shaw scapolites are reported from widely different environments occurring in every metamorphic facies; such a difference in thermal history could affect both optical and structural parameters, by reason of disorder of certain ions or actual polymorphism.

SYNTHESIS OF SCAPOLITES

The synthesis of scapolites has been attempted by a number of workers and with the exception of one, W. Eitel, these attempts have failed. Eitel (1925) reported the synthesis of meionite as a reaction rim on anorthite. The meionite reaction rim was identified by optical means. More recent workers, including Fyfe (1958), have failed to synthesize the mineral.

In order to clarify some of the problems outlined in the discussion above one of the authors (B. J. Burley) together with R. S. Stevens made a determined effort to synthesize the scapolites. Numerous different starting compositions were used over a range of temperature of 200° C to 800° C and a water pressure range of 10,000 psi to 35,000 psi. The experiments were conducted in the conventional test tube type bomb hydrothermal equipment. Experiments were also carried out under total CO₂ pressure and also under various partial pressures of CO₂ and H₂O. All these efforts met with failure. Regrettably, therefore, until such time as successful syntheses can be achieved, it is unlikely that the interesting problems raised in the discussion will be solved.*

CONCLUSION

Correlations between composition, cell dimensions, and mean refractive indices have been demonstrated for scapolites. The space group is shown to be $P4/m$, and the cell contains two formula-units.

ACKNOWLEDGMENTS

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REFERENCES

- EITEL, W. (1925): Die Synthese der Skapolithe auf Grund der Beobachtungen über ihre Vorkemmnisse, *Tschermaks Min. Petrogr. Mitteilungen*, **38**, 1-38.

*After this paper was completed it was learned from H. P. Eugster, Johns Hopkins University (personal communication), that he has succeeded in synthesizing nearly pure marialite at 1 atmosphere. Seeding with natural scapolite was however necessary and it is therefore uncertain whether equilibrium was attained (*Geol. Soc. America, Bull* **71**, 1859, 1960).

- FYFE, W. S. (1958): *Geological Soc. of America. Mem.*, **73**, 160.
- GOSSNER, B., & BRÜCKL, K. (1928): Untersuchungen über die Skapolithen, *Neues Jb. Mineral. Geol. Paläont.*, **34**, 349-384.
- GREENWOOD, G. (1935): Experiments on piezoelectricity, *Zeit. Kryst.*, **91**, 240-241.
- HETTICH, A., & STEINMETZ, H. (1932): Piezoelektrische Versuche nach der Methode von Giebe und Scheibe, *Zeit. Physik.*, **76**, 688-706.
- KITAJGORODSKY, A. I. (1951): A method of determining centrosymmetry in a crystal by x -ray structure analysis, *Zurnal fiz. khimii*, **25**, 127.
- PAULING, L. (1930): The structure of some sodium and calcium aluminosilicates, *Proc. of Nat. Acad. of Sciences*, **16**, 453-459.
- ROGERS, D. (1950): The probability distribution of x -ray intensities: new methods of determining crystal classes and space groups, *Acta. Cryst.*, **3**, 455.
- SCHERILLO, A. (1935): La meionite del Somma-Vesuvio, *Per. Mineral. Roma*, **6**, 227-239.
- SCHIEBOLD, E., & SEUMEL, G. (1932): Über die Kristall Struktur von Skapolith, *Zeit. Kryst.*, **81**, 110-134.
- SHAW, D. M. (1960): The geochemistry of scapolites, *Jour. Petrology*, **1**, 218-260, 261-285.