

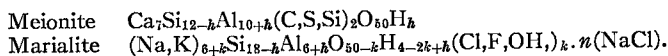
THE STOICHIOMETRY OF SCAPOLITE*

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ABSTRACT

Chemical analyses of scapolites have been evaluated by a formalized procedure, and it is concluded that natural scapolites may usually be represented as solid solutions of two end-members with the following formulae:

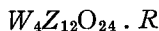


One unusual sample appears to have Cl and H₄ substituting for C in the meionite end-member. It is emphasized that these formulae represent the stoichiometry and might not be the structural formulae. The general procedure used in the evaluation of the analyses may prove of value in determining the stoichiometry of other mineral series, for which the structure is either unknown or imperfectly known. Caution is expressed about the validity of trace element determinations and it is suggested that many of these elements are present in sub-microscopic inclusions rather than in the scapolite structure. Electron micro-probe studies also suggest that such inclusions may even affect the major element composition in some cases. The method of calculation used serves as a check on the accuracy of the chemical analysis and in some cases indicates where analytical error lies together with the magnitude and sign of the error. Shaw's contention of a linear relation between mean refractive index and composition appears to be valid. Three new scapolite analyses are presented.

INTRODUCTION

Despite its rather widespread distribution in metamorphic terrains and the resultant petrological importance of scapolite relatively little is known about the crystal chemistry of the group.

After a careful appraisal of available scapolite analyses and structural data, Shaw (1960b) concluded that the general formula may be written:



where *W* is mainly Ca, Na, and K; *Z* is Si and Al; *R* is CO₃²⁻, SO₄²⁻, (OH)₂²⁻, Cl₂²⁻, or F₂²⁻ for meionite, and Cl⁻, F⁻, HCO₃⁻, HSO₄⁻, or OH⁻ for marialite. He noted that there is invariably an excess of hydrogen over the anion requirements and supposed that some of this may occur as OH replacing O, although pointing out that this would give rise to problems of valency satisfaction.

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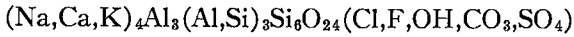
Deer, Howie & Zussman (1963) give the end members as



and



and the general formula as



Accurate chemical analyses of scapolite are not easy to obtain because of unusual analytical problems and the difficulty of separating clean material from coexisting minerals such as feldspar and nepheline. In addition to problems of mechanical separation careful consideration must be given to possible impurities contained as inclusions within the crystals. This is of course a problem common to the analysis of any mineral but while such inclusions may not generally be abundant enough to have a serious effect on the major element composition they may well have a strong bearing on the trace element composition, and evidence is presented later (Fig. 8) to show that in one case at least even the major element composition is affected. Electron microscope study of individual grains from the analyzed concentrates reveals many inclusions that are apparently in sub-microscopic cavities or healed fractures together with, in one case, minute cubic crystals that might be pyrite or halite (Fig. 1).

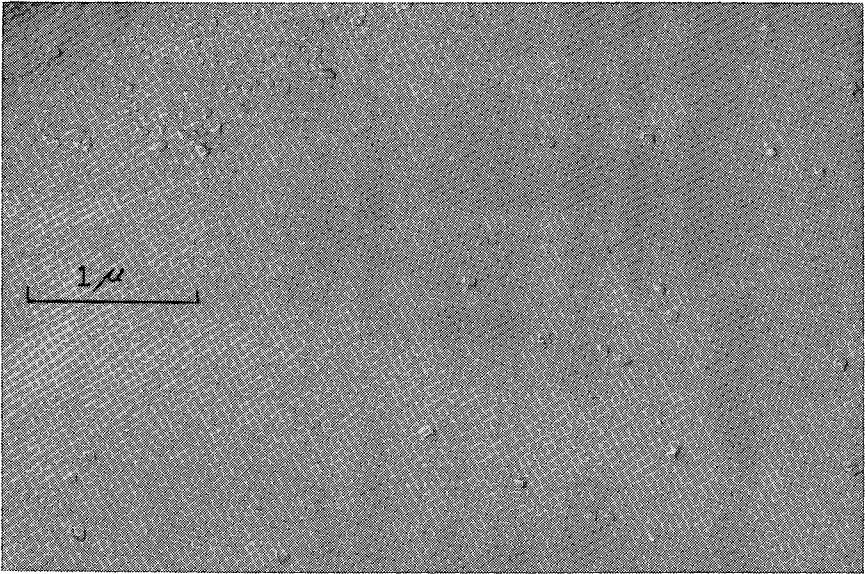


FIG. 1. Electron micrograph ($\times 22,500$) of the surface of scapolite grains from one of the analyzed concentrates, XXXIX showing cubic crystals within the scapolite host.

Crystals of pyrite could well be the repositories of many of the trace elements determined by Shaw and might account for the lack of correlation between either the various trace elements or between the trace and major elements.

Several properties of scapolites attract the analyst's attention and may usefully be considered for their bearing on scapolite structure and composition.

1. During grinding, some samples give a pronounced odor of sulphur compounds, which resembles that of carbon disulphide as much as hydrogen sulphide.

2. Most scapolites may be boiled in dilute hydrochloric acid without decomposition. Total carbon must be determined by combustion with a flux, or through solution in hydrofluoric or strong phosphoric acid. Some published analyses were conducted before it was generally realized that CO_2 is an essential constituent: that found by acid decomposition methods was assumed due to calcite contamination, and acid-insoluble CO_2 was left undetermined.

3. Water determination in scapolite presents many problems. The appearance of the material (usually brittle, hard, and difficult to grind in a mortar) would not lead one to expect high values for $\text{H}_2\text{O}-$ (110°C) in freshly prepared samples; yet in some cases there is as much $\text{H}_2\text{O}-$ as there is $\text{H}_2\text{O}+$.

Values for $\text{H}_2\text{O}+$ obtained by loss on ignition are so dependent on corrections for the behaviour of other constituents as to be completely unreliable: for example, undetermined acid-insoluble CO_2 will be counted as $\text{H}_2\text{O}+$; a sufficiently high temperature will certainly volatilize alkali chlorides.

Sulphur, chlorine, and fluorine interfere in many methods for total hydrogen in silicates, and even careful work may yield a value for $\text{H}_2\text{O}+$ which is unrelated to the combined hydrogen in the mineral. An added complication is the probable bi- or tri-fold role of hydrogen in the scapolite structure. Obvious possibilities are hydroxyl ion, hydronium ion, water of crystallization, absorbed water, and interstitial water.

GENERAL METHOD FOR DETERMINING STOICHIOMETRY

A general formula for a crystalline mineral showing solid solution between two end members, may be written

$$(1) \quad (1 - m)A_aB_bC_c \dots Z_z + m A_{a'}B_{b'}C_{c'} \dots Z_{z'}$$

In the process of normalization, one of the subscripts, or an arithmetic combination of two or more of them, is placed equal to a whole number,

the value of which is often known with some certainty from x -ray data, since it is related to the unit cell content. For convenience in calculation, this number may be made equal to unity: a factor will then convert the empirical formula to correspond with the physical data.

Formula (1) may be rewritten as follows:

$$(2) \quad A_{a(1-m)+a'm} B_{b(1-m)+b'm} C_{c(1-m)+c'm} \dots Z_{z(1-m)+z'm}$$

—and if the element Z is used for normalization, i.e. N_z is made equal to unity, the formula becomes

$$(3) \quad A \frac{a(1-m) + a'm}{z(1-m) + z'm} B \frac{b(1-m) + b'm}{z(1-m) + z'm} C \frac{c(1-m) + c'm}{z(1-m) + z'm} \dots Z$$

If the numbers $a, b, c \dots$ and $a', b', c' \dots$ are to be dealt with as constants, it is often necessary in any specific case to let the letters $A, B, C \dots Z$ stand for groups or combinations rather than for single elements. Which elements to group together depends on considerations of ionic radius, electronic charge, electronegativity, etc., and on a knowledge of crystal structure. In dealing with an incompletely known material, preliminary assumptions may have to be made and tested for validity. One assumption which cannot be avoided is that the subscripts z and z' of the normalizing element or group of elements, though not necessarily equal, are indeed constants. With minerals of known structure, selection of a normalizing element presents little difficulty: for most silicates, oxygen (or $O + OH + F + Cl$) is often used, despite the fact that oxygen is never determined directly, but is calculated from assumed stoichiometric relationships.

From formula (3), an expression for m may be obtained using any one of the elements, A for example. If N_A is the number of atoms of the element in the formula normalized to $N_z = 1$,

$$N_A = \frac{a(1-m) + a'm}{z(1-m) + z'm},$$

$$(4) \quad \text{whence } m = \frac{N_A z - a}{a' - N_A z' + N_A z - a}.$$

For any other element W , m may now be eliminated, and

$$(5) \quad N_W = N_A \frac{w'z - wz'}{a'z - az'} + \frac{a'w - aw'}{a'z - az'}.$$

Now, if values of N_W from a series of chemical analyses are plotted against corresponding values of N_A , and if a linear relation exists between

N_W and N_A from (5) the slope (S) and intercept (I) of the line will have the following values:

$$(6) \quad S_W = \frac{w'z - wz'}{a'z - az'} \quad (7) \quad I_W = \frac{a'w - aw'}{a'z - az'}$$

If the normalizing element is present atom for atom in each end member, that is $z = z' = 1$:

$$(8) \quad S_W(z = z') = \frac{w' - w}{a' - a} \quad (9) \quad \text{and} \quad I_W(z = z') = \frac{a'w - aw'}{a' - a}$$

If the normalizing element is present in only the primed end member, i.e. $z = 0$:

$$(10) \quad S_W(z = 0) = \frac{w}{a} \quad (11) \quad I_W(z = 0) = w' - \frac{w}{a} a'$$

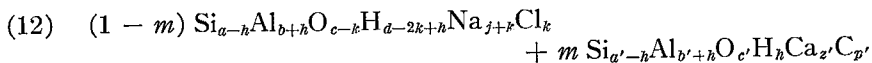
SCAPOLITE STOICHIOMETRY

This general method was then applied to a selection of scapolite analyses chosen as follows: all those analyses conducted by Ingamells and Gittins, those by Hooper reported by Gibbs & Bloss (1961), the four high carbon (sulphur) analyses by Kalinin in Shaw (1960a, nos. 1, 2, 4, VI), those in Shaw's collection with $N_{\text{Si+Al}}$ in the range 10 to 16 (used because this range is otherwise unrepresented), and one analysis (no. XII in Shaw) with a low value for $N_{\text{Si+Al}}$ (used for the same reason). Using all available analyses produces unnecessarily cluttered graphs. To avoid 'prejudging the issue' (to use Shaw's phrase) we have not been guided by Shaw's classification of "dubious" and "satisfactory" analyses in this selection.

Each analysis was calculated to cation proportions and normalized to $\text{Ca} = 1.00$. The calcium-normalized values for various groups of elements were then plotted against $N_{\text{Si+Al}}$ and the results are shown in Figs. 2 to 5.

(Si + Al) was selected as the m -determining element after trying both Si and Al alone, because a much closer approach to linear relationships is thus obtained. In all calculations it is assumed that K is equivalent to Na, F is equivalent to Cl, and that S is equivalent to C.

A general formula was written as follows:



in which $a, b, c, d, j, a', b', c', z'$ are expected to be constants, and h, k to be numbers which may vary from one sample to another. The value of p' may or may not be constant, and receives special attention in what

follows. It seems unnecessary to discuss the logic behind the selection of subscripts, except to point out that there is usually no possible way of assigning hydroxyl ion affecting (or affected by) the Si:Al ratio (H_h) to one end member or the other on the basis of chemical analysis alone, and it has been found in most cases convenient to assign it equally to both.

Table 1 gives the expressions for slopes and intercepts from equations (10) and (11) and formula (12), and also their numerical values (all based on $Ca = 1.00$) taken from the graphs. Other relationships to be derived are also included in Table 1. The following process was used to calculate numerical values for the subscripts in formula (12).

$$(13) \quad \text{From Fig. 2, } \frac{j}{a+b} = -0.25(a' + b') = -0.785$$

$$(14) \quad \text{From Fig. 3, } \frac{c}{a+b} = c' - 2.08(a' + b') = 0.606$$

$$(15) \quad \text{From Fig. 4, } \frac{a+d}{a+b} = a' - 0.93(a' + b') = -1.17$$

TABLE 1. SLOPES, INTERCEPTS, AND OTHER RELATIONSHIPS
($Ca = 1.00$; $N_A = N_{Si+Al+\dots}$)

W	S_w	I_w
Na + K - Cl - F	$\frac{j}{a+b} = 0.25$	$-j\left(\frac{a'+b'}{a+b}\right) = -0.785$
O + Cl + F	$\frac{c}{a+b} = 2.08$	$c' - c\left(\frac{a'+b'}{a+b}\right) = 0.606$
Si + H + 2Cl + 2F	$\frac{a+d}{a+b} = 0.925$	$a' - \frac{a+d}{a+b}(a'+b') = -1.17$
C + S	0	$p' = 0.29$

$$m = \frac{24}{7N_{Al+} + 2} \quad \text{or} \quad \frac{24}{7N_{Al+} + 7N_{(C+S)}}$$

$$h = 7mN_{Al+} \dots + 14mN_{Mg+\dots} - 4m - 6 \quad h_H = 7mN_H - (4 - 2k)(1 - m)$$

$$k = 7N_{Na+K} \frac{m}{1-m} - 6 \quad \text{or} \quad k = 2.00 \quad k_X = 7N_{Cl+F} \frac{m}{1-m}$$

$$x = 2 - 7N_{C+S}$$

$$H = 4 - 2k + h$$

$$H_X = 4 - 2k_X + h_H$$

$$O_{Me} = 50 - 2x$$

$$O_{Ma} = \frac{m}{1-m} (N_{(O+F+Cl)} - O_{Me})$$

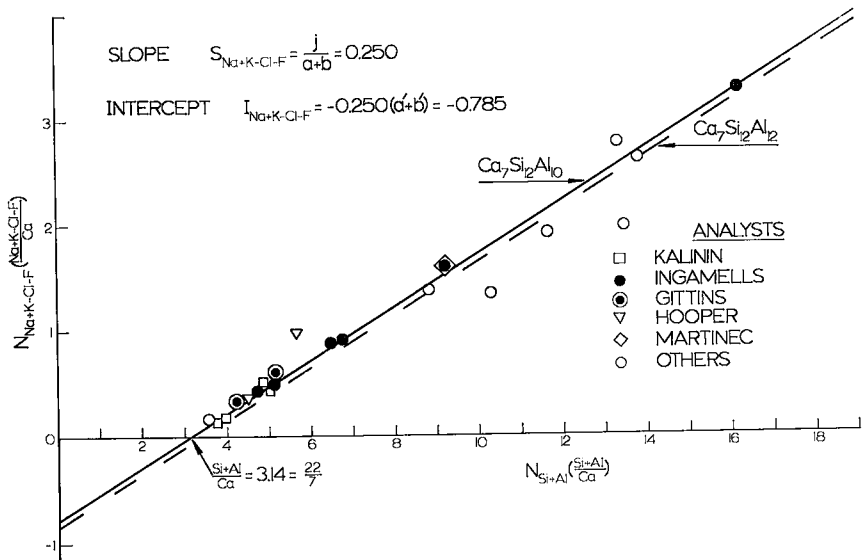


FIG. 2. Plot of $N_{Na+K-Cl-F} \left(= \frac{Na + K - Cl - F}{Ca} \right)$ against $N_{Si+Al} \left(= \frac{Si + Al}{Ca} \right)$

From Fig. 5, $p' = 0.29$ (if p' is indeed constant): from (13), $a' + b' = 3.14$: from (14), $c' = 7.14$: from (15), $a' = 1.74$ and $b' = 1.40$. If it is assumed that $c = c'$, then, from (13) and (14), $j = 0.86$. For charge balance it is necessary that $a = 2.57$ and $b = 0.857$.

In order to obtain nearly whole numbers for these values throughout, it is necessary to make $z' = 7$, when $a = 18$, $b = 6$, $c = 50$, $d = 4$, $j = 6$, $a' = 12$, $b' = 10$, and $p' = 2$.

This suggests that calcium and carbon are ideally present in the atomic ratio 7:2, and to test this deduction all analyses for which carbon and sulphur determinations are available are plotted in Fig. 6. There can be no reasonable doubt that many of the analyses do lie along the line corresponding to $Ca/(C + S) = 7/2$, but it is equally clear that there is a considerable scatter on each side of the line.* Several analysts are distinguished on this graph and at least some of the scatter appears to be due to analytical errors characteristic of the individual analysts (or persons who prepared the sample). This corresponds to the known difficulties of carbon determination in scapolites, already referred to, in which the various methods tend to give results that are systematically high or low. In Fig. 7, two histograms are presented, which show that determinations of $Ca/(C + S)$ in scapolite are no more scattered than

*Some of the scatter may be due to calcite impurity as suggested by the calculations in which the analysis is normalized to $(Ca-C-S) = 5.00$ (p. 225).

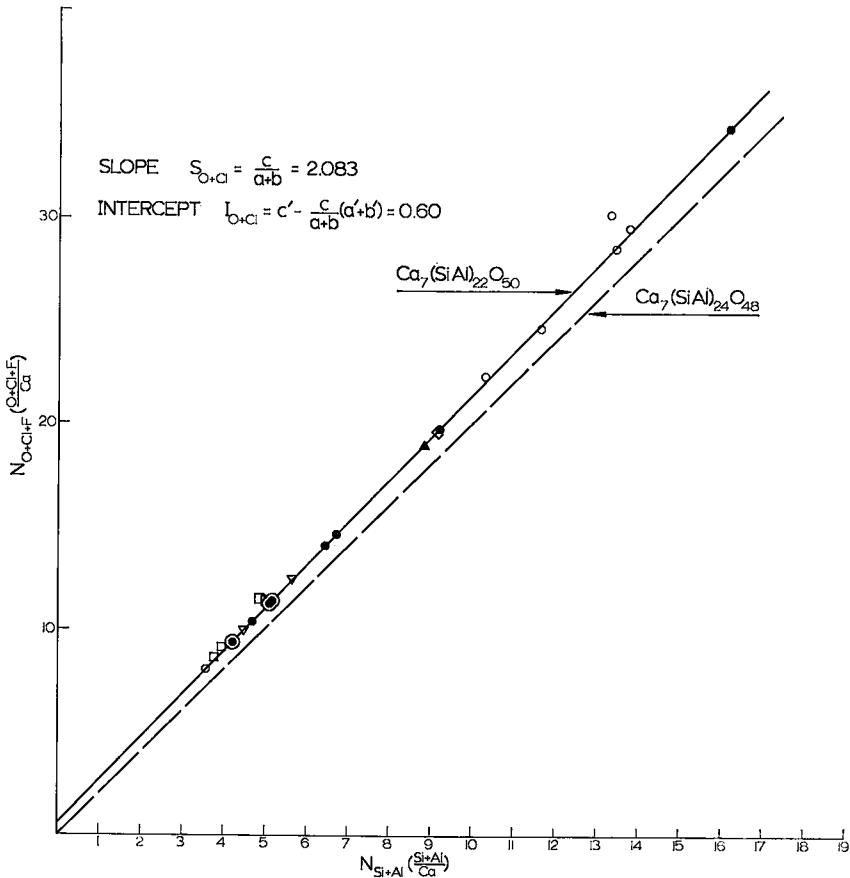


FIG. 3. Plot of $N_{O+Cl+F} \left(= \frac{O + Cl + F}{Ca} \right)$ against $N_{Si+Al} \left(= \frac{Si + Al}{Ca} \right)$

determinations of ferric iron in the standard geochemical sample G-1. The latter was selected for the comparison because, like the determination of carbon in scapolite, it is subject to two common possible errors of opposite sign.

There are, however, scapolites which almost certainly do not contain sufficient $(C + S)$ to give $Ca_7(C,S)_2$ (Fig. 6). Analyses XXX, XXXI, (Table 5) XXXVI, XXXVII, (Table 4) XXXVIII, XXXIX and XL (Table 3) plot on both sides of the line and the carbon value in each was obtained by methods known to give accurate results.

We conclude that in the ideal case the ratio $Ca/(C + S)$ approaches $7/2$ and that where there is a deficiency in $(C + S)$ it is made up by

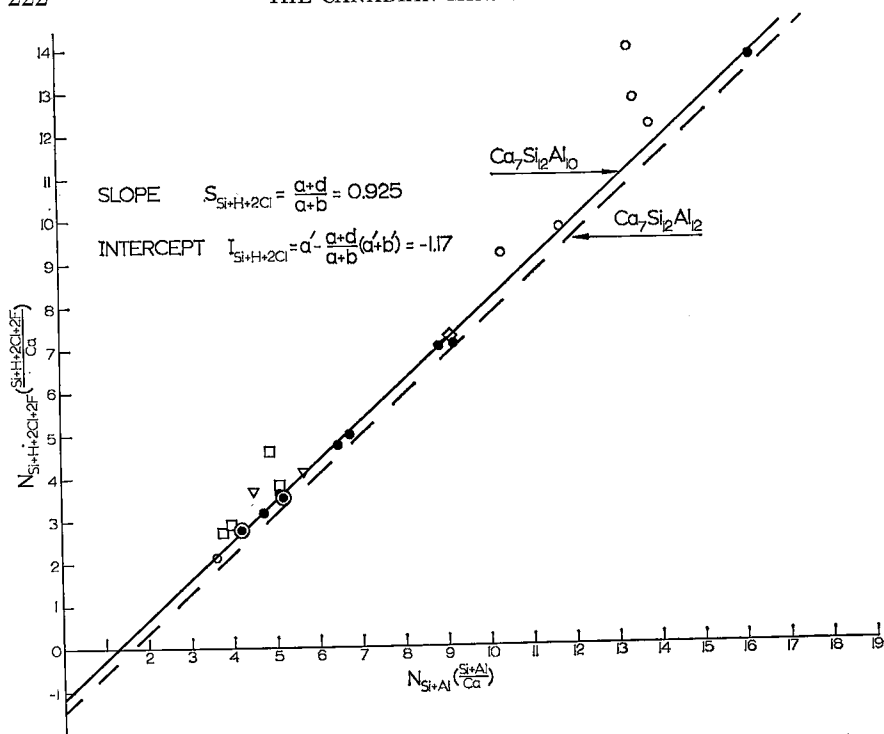
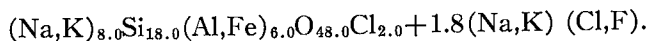


FIG. 4. Plot of $N_{Si+H+2Cl+2F} \left(= \frac{Si + H + 2Cl + 2F}{Ca} \right)$ against $N_{Si+Al} \left(= \frac{Si + Al}{Ca} \right)$

hydrogen, chlorine or silicon. For example in the very pure, almost gem quality scapolite from the Malagasay Republic (no. XXXVIII, Table 3) carbon is deficient and chlorine and hydrogen are in excess. The analysis recalculates best if the carbon deficiency is made up by silicon.

Calculation of Gibbs & Bloss' Grenville scapolite (XXXVII, Table 4) suggests that 4 H⁺ may substitute for C⁴⁺. Evidence that chlorine may make up a carbon deficiency is found in Gibbs & Bloss' Arendal scapolite (XXXVI, Table 4), which shows a very large excess of sodium (potassium) and chlorine (fluorine). The Ca/C ratio is much higher than 7:2. However, if after normalization to Ca = 7.00, Ca₇Si₁₂(C,Cl)₂Al₁₀ is taken out, the balance calculates to



There seems to be no other way to rationalize this analysis within the same framework as the majority of the others. It is, of course, important to keep in mind the fact that arithmetical exercises of this kind need physical substantiation before they may reasonably be accepted.

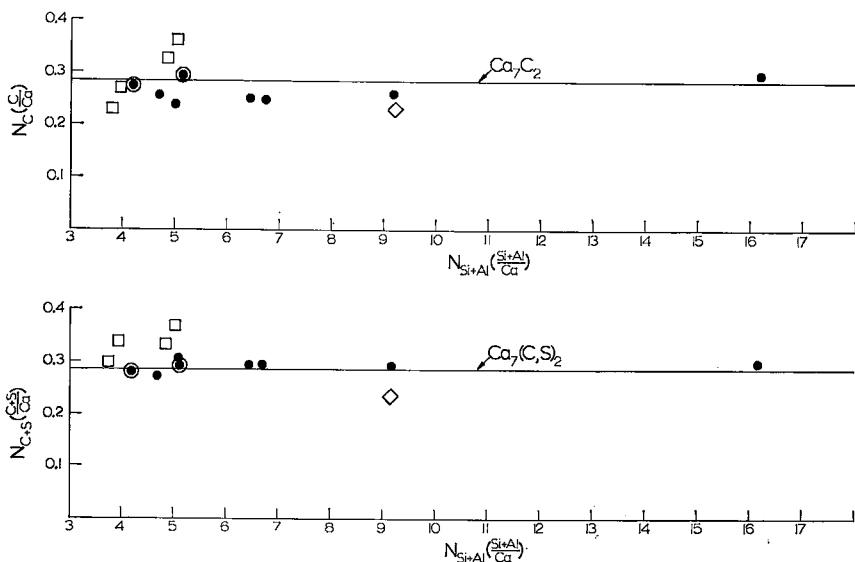
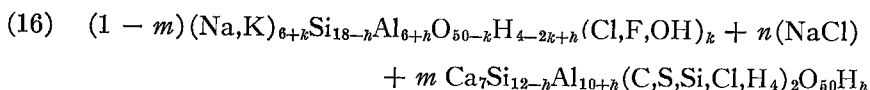


FIG. 5. Plot of $N_C \left(= \frac{C}{Ca} \right)$ against $N_{Si+Al} \left(= \frac{Si+Al}{Ca} \right)$ and of $N_{C+S} \left(= \frac{C+S}{Ca} \right)$ against $N_{Si+Al} \left(= \frac{Si+Al}{Ca} \right)$

PROPOSED FORMULA FOR NATURAL SCAPOLITE

On the basis of the above, we propose that natural scapolite may be represented by a general formula



in which h , k and n may vary widely from one sample to another, and in which substitution of Si, Cl, H_4 for C, S is perhaps doubtful or at least unusual and n is normally zero. It should be noted that this formula has been derived without reference to any physical measurements of scapolites, and is subject to such confirmation. In writing the formula, hydrogen has as far as possible not been equated to hydroxyl, and the presence of anionic groups (CO_3^{2-} , SO_4^{2-} , HCO_3^- , HSO_4^- , etc.) is neither confirmed nor denied. Only the stoichiometry of the mineral has been deduced.

It must be pointed out that the above argument does not unequivocally yield the end-member formulae given. Certain assumptions have been made: if these are false, the results are not valid. The most

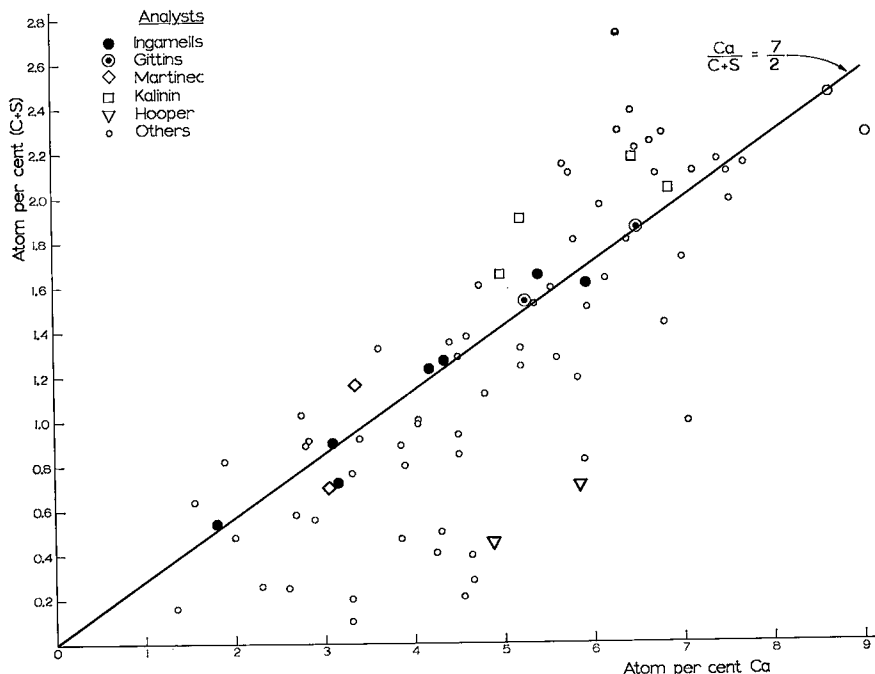


FIG. 6. Plot of atomic per cent Ca vs. (C + S) for all scapolite analyses listed by Shaw and the new ones given in this paper. Individual analysts are distinguished as far as possible. Many of the most recent analyses group along the line representing $\text{Ca}/(\text{C} + \text{S}) = 7/2$ while a few do not. The majority, but not all of the scatter, probably represents poor determinations of C and/or S and there is a suggestion that some analytical errors are characteristic of individual analysts.

significant assumption is that the number of atoms of (O+OH+Cl+F) is the same in both end-members, i.e. that $c = c'$. There is no way of confirming this with certainty without physical measurements. The stoichiometry of $\text{Ca}_7\text{Si}_{12}\text{Al}_{10}\text{C}_2\text{O}_{50}$ is not sufficiently different from that of $\text{Ca}_8\text{Si}_{12}\text{Al}_{10}\text{O}_{48}^{4+} \cdot 2(\text{CO}_3^-)$ to distinguish the two with complete assurance from the analyses alone. The atomic percentage composition of these two species and also of $\text{Na}_8\text{Si}_{18}\text{Al}_6\text{O}_{48}\text{Cl}_2$ is given in Table 7. Table 8 gives the atomic percentage composition of some of the analysed scapolites.

As previously indicated, it appears that Ca_7 etc. is more likely than Ca_8 etc. However, other possibilities are not excluded. There may, for example, be eight sodium and eight calcium positions, neither of which is always filled.

CALCULATION OF SCAPOLITE ANALYSES

The following method (illustrated in Table 2) was used to calculate the formulae of scapolites from their analyses.

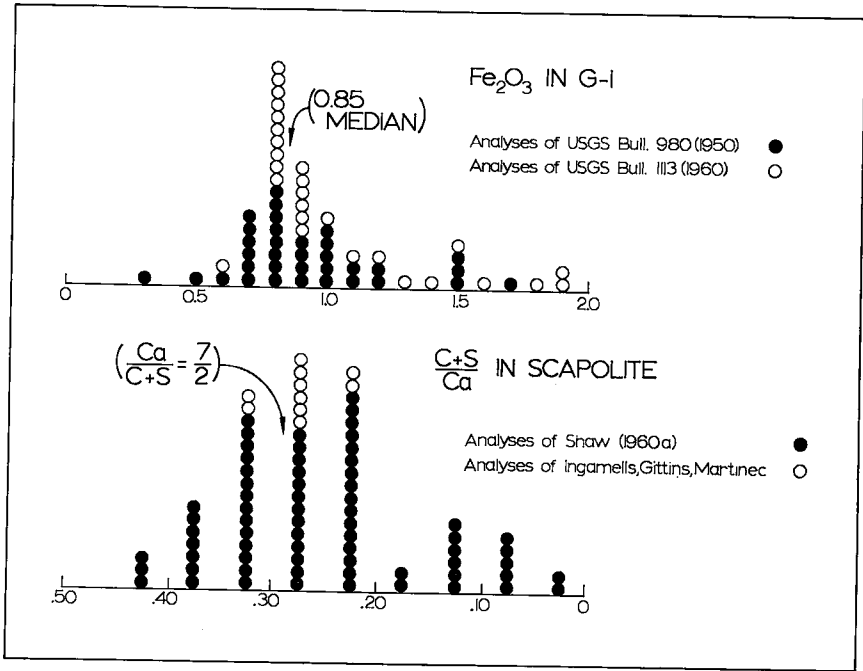


FIG. 7. Comparison between the scatter of (C + S)/Ca in scapolite analyses, and Fe₂O₃ in the standard granite G-1.

1. Calculate atomic proportions
2. Normalize to Ca = 7.00, or, if calcite is present, to (Ca - C - S) = 5.00, thereby obtaining values for 7N_{Si}, 7N_{Al}, etc.
3. Calculate *m*, *h* and *k* from equations (4) and (5), with *z* = 0:

$$(17) \quad m = \frac{24}{7N_{Si+Al} + 2} \quad \text{OR} \quad \frac{24}{7N_{Si+Al} + 7N_{C+S}}$$

$$(18) \quad h = 7mN_{Al} - 4m - 6$$

$$(19) \quad k = 2.00 \quad \text{OR} \quad 7N_{Na+K} \frac{m}{1-m} - 6$$

The quantity *m* corresponds to the fraction of meionite in the sample, and may be compared to Shaw's

$$\text{Atomic per cent Me} = \frac{\text{Ca} + \text{Mg} + \text{Fe} + \text{Mn} + \text{Ti}}{\text{Na} + \text{K} + \text{Ca} + \text{Mg} + \text{Fe} + \text{Mn} + \text{Ti}}$$

4. Subtract calcite if present.*

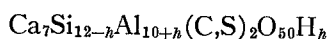
*Calcite impurity is another reason why some points on Fig. 6 do not lie on the line representing Ca/(C + S) = 7/2.

TABLE 2. CALCULATION OF SCAPOHITE STOICHIOMETRY
(Example—Shaw No. XXXIV; analyst, C. O. Ingamells)

Wt. %	Atomic Proportions	Atomic props. calculated to Ca = 7.0	Remainder			Departure from Ideal Composition (wt. percent of residuals)	
			Meionite Composition	Remainder	$x \frac{1-m}{m}$ (i.e. marialite composition)		Ideal Marialite* Composition
SiO ₂	54.73	9.108	43.13	31.37	17.75	17.76	
Al ₂ O ₃	22.85	4.482	21.22	10.98	6.21	6.24	
Fe ₂ O ₃	.08	.010	.05	.05	.03		
TiO ₂	.01	.001	.00				
MgO	.03	.007	.03	.03	.02	+0.03	
MnO	.00						
CaO	8.29	1.478	7.00				
Na ₂ O	8.55	2.758	13.06	13.06	7.39	8.00	
K ₂ O	1.08	.229	1.08	1.08	.61		
H ₂ O+	1.13	.144	.68	.44	.25	.24	
CO ₂	1.69	.384	1.82	.05	.03	0.05	
SO ₃	.39	.048	.23				
Cl	2.19	.617	2.93	2.93	1.66	2.00	
	100.02	29.183	138.19	88.19			
less O = Cl	.49						
	99.53				O _{Me} = 50.00	O _{Ma} = 49.84	
						O _{Ma} = 50.00	
$m = \frac{24.00}{43.13 + 21.22 + 0.05 + 2.00}$			$\frac{m}{1-m} = 0.361$			$h = m(21.22 + 0.05 - 4.00) - 6.00 = 0.24$	$h_H = 0.25$
$k = 2.00$			$x = +0.05$			H = 0.34	H _x = 0.93

*Calculated from h and k , based on formula (16). Compare with previous column which gives values calculated from the analysis.

5. Calculate and subtract the meionite formula



6. Multiply the remainder by $\frac{m}{1-m}$. This gives the marialite composition plus sample impurity and analytical errors. If there was insufficient (C + S) to meet the supposed requirements of meionite, residual atoms of H or Cl may be assigned accordingly.

The calculations sometimes serve to indicate where analytical error lies together with the magnitude and sign of the error; e.g. the value for chlorine in analysis XXXIV is probably low (see Table 2).

The values for h and k obtained through equations (18) and (19) do not depend on the analytical results for $\text{H}_2\text{O}+$ and (Cl+F). We may calculate quantities defined by the relations

$$(20) \quad h_{\text{H}} = 7mN_{\text{H}} - (4 - 2k)(1 - m)$$

$$(21) \quad \text{and } k_{\text{X}} = 7N_{(\text{Cl}+\text{F})} \frac{m}{1-m} - n$$

where the subscripts refer to hydrogen (H) and halogen (X) which should ideally be identical to h and k respectively. In view of the analytical difficulties of determining $\text{H}_2\text{O}+$, and the possibility that Cl^- may replace OH^- and vice versa, it seems that h and k , rather than h_{H} and k_{X} , may legitimately be used in the calculations.

Other quantities may be calculated, *viz*

$$(22) \quad x = 2 - 7N_{(\text{C}+\text{S})}$$

which represents a deficiency of carbon and sulphur, and, from formula (16),

$$(23) \quad \text{H} = 4 - 2k + h,$$

the number of hydrogen atoms (exclusive of those in OH^- replacing Cl^-) in the marialite, calculated without reference to either the $\text{H}_2\text{O}+$ or the Cl, F determinations. It may be compared to H_{X} calculated from equations (20) and (21)

$$(24) \quad \text{H}_{\text{X}} = 4 - 2k_{\text{X}} + h_{\text{H}}$$

The (O+Cl+F) content of the two end members thus calculated is

$$(25) \quad \text{O}_{\text{Me}} = 50.00 \text{ or } 50 - 2x$$

$$(26) \quad \text{and } \text{O}_{\text{Ma}} = \frac{m}{1-m} [7N_{(\text{O}+\text{F}+\text{Cl})} - \text{O}_{\text{Me}}]$$

These calculations are illustrated in Table 2, using an analysis (Shaw No. XXXIV) which shows a low total (99.53 per cent). The calculation indicates that the error is probably a low chlorine determination.

Calculations for three new analyses are given in Table 3, and the unusual scapolites of Gibbs & Bloss are evaluated in Table 4. Three 'normal' scapolites are calculated in Table 6.

Scapolite XXXIX (Table 3) presents an interesting problem in that the analysis appears to have too much lime and carbon dioxide. Normalizing to $(Ca-C-S) = 5.00$ and the consequent subtraction of 1.46 wt. % $CaCO_3$, however, brings the analysis into agreement. Accordingly a careful re-examination was made both of the grains from the analyzed concentrate and a thin section of the crystal from which the concentrate was prepared but no trace of calcite could be seen. Finally the grains were examined by electron micro-probe, and calcium-rich stringers, about 10 microns in width, presumed to be calcite, were discovered. (Fig. 8) It is not possible to make an estimate of the amount of such calcite in the grains but the figure of 1.46% does not seem unreasonable. Again the problem arises of the effect of sub-microscopic amounts of a second phase on the analysis. In this case even the major element composition appears to be affected.

A further example from the recent literature, Gib Lake scapolite, (Shaw, Schwarz & Sheppard, 1965) is given in Table 9. In this case the scapolite contains minute inclusions of calcite and a complete mechanical separation was impossible even though a high degree of purity was obtained. Normalizing to $(Ca-C-S) = 5.00$ suggests the amount of $CaCO_3$ that must be removed to bring the analysis into conformity with the proposed formula.

OPTICAL PROPERTIES

In Fig. 9 the birefringence Δn and the mean refractive index n_m are plotted against m . The result is similar to that of Shaw (1960a) who plotted against an expression believed to represent the percentage of meionite. In both cases there is an essentially linear relation for the more reliable analyses.

THE ROLE OF MAGNESIUM IN SCAPOLITE

We suggest that most of the minor constituents which have not thus far been taken into account, may usually be considered as impurities, except in unusually clean samples. The iron, titanium, etc. in most samples are insufficient in amount to make any meaningful difference to calculations. Magnesium, however, is an exception and its role is not entirely clear.

TABLE 3. THREE NEW SCAPOOLITE ANALYSES
(Analysts: XXXVIII; C. O. Ingamells; XXXIX, XL; E. Martinec)

No.	XXXVIII				XXXIX				XL				
	Wt. %	Composition of Me		Ma	Wt. %	Composition of Me		Ma	Wt. %	Composition of Me		Ma	
SiO ₂	55.06	Si	11.75	17.82	SiO ₂	54.06	Si	11.90	SiO ₂	54.84	Si	11.69	17.73
CO ₂	1.35	C	1.30	2.00	CO ₂	2.12	C	1.61	CO ₂	1.50	C	1.61	2.00
SO ₃	.37	S	.31		SO ₃	.66	S	.39	SO ₃	.05	S	.03	
Al ₂ O ₃	22.61	Al	10.25	5.99	Al ₂ O ₃	21.62	Al	10.10	Al ₂ O ₃	22.81	Al	10.31	6.17
B ₂ O ₃	.06	B	.05	.05									
Fe ₂ O ₃	.24	Fe	.08	.08	Fe ₂ O ₃	.26	Fe		Fe ₂ O ₃	.10	Fe		.03
TiO ₂	.02	Ti	.01	.01	TiO ₂	.01	Ti		TiO ₂	.02	Ti		.01
BeO	.02	Be	.02	.02									
MgO	.02	Mg	.01	.01	MgO	.10	Mg		MgO	.08	Mg		.05
Li ₂ O	.01	Li	.02	.02									
MnO	.00				MnO	.04	Mn		MnO	.00			
CaO	8.65	Ca	7.00		CaO	9.02	Ca	7.00*	CaO	8.33	Ca		
Na ₂ O	8.05	Na		8.01	Na ₂ O	8.78	Na		Na ₂ O	8.83	Na	7.00	
K ₂ O	1.51	K			K ₂ O	1.04	K		K ₂ O	1.06	K		8.30
H ₂ O+	.16	H	.25	.33	H ₂ O+	.16	H	.10	H ₂ O+	.26	H		.60
Cl	2.73	Cl		2.11	Cl	2.57	Cl		Cl	2.48	Cl		1.88
less	100.36	O + Cl	50.00	50.11	less	100.44	O + Cl	50.00	less	100.46	O + Cl	50.00	50.22
O = Cl	.61				O = Cl	.58			O = Cl	.56			
	100.25**				99.86**				99.80				
	<i>m</i> = 0.377				<i>m</i> = 0.365				<i>m</i> = 0.364				
	<i>h</i> = 0.25				<i>h</i> = 0.10				<i>h</i> = 0.31				
	<i>x</i> = 0.40								<i>x</i> = 0.36				
	<i>n</i> = 0.01				<i>n</i> = 0.41				<i>n</i> = 0.30				
Optical Properties													
	<i>ε</i> = 1.546				<i>ε</i> = 1.543				<i>ε</i> = 1.544				
	<i>ω</i> = 1.560				<i>ω</i> = 1.561				<i>ω</i> = 1.558				
XXXVIII Gem quality scapolite from Tarrasotra, near Ankarobe, Malagasy Republic (formerly Madagascar), University of Chicago Museum specimen no. M18199. XXXIX Bluish coarsely crystalline scapolite; locality unknown, Grenville Province, Quebec, Canada, Royal Ontario Museum, Mineralogy Collection, specimen no. M-27269. XL White, coarsely crystalline scapolite from calcareous gneiss, Lot. 32, Con. XVII, Monmouth Township, Ontario, Canada. This is no. ON7 of Shaw (1960b, table 5, p. 270). *Analysis normalized to (Ca—C—S) = 5.00; 1.46 per cent CaCO ₃ subtracted. **Totals are too high because sulphur is reported as SO ₃ and Fe as Fe ₂ O ₃ whereas their true state is unknown. In calculating (O + Cl), sulphur was taken as SO ₄ .													

TABLE 4. GIBBS AND BLOSS' SCAPOFITES*
(Analyst: R. E. Hooper, U.S. Bureau of Mines, Norris, Tenn.)

XXXXVI (Arendal)		XXXXVII (Grenville)					
No.	Wt. %	Composition of Me	Ma	No.	Wt. %	Composition of Me	Ma
SiO ₂	50.38	Si	12.00	SiO ₂	44.46	Si	11.00
Al ₂ O ₃	24.18	Al	10.00	Al ₂ O ₃	29.14	Al	11.00
Fe ₂ O ₃	0.29	Fe	.15	Fe ₂ O ₃	.23	Fe	6.82
CaO	13.06	Ca	7.00	CaO	16.36	Ca	.18
MgO	0			MgO	0		
Na ₂ O	7.09	Na		Na ₂ O	2.43	Na	7.58
K ₂ O	0.51	K		K ₂ O	2.23	K	
CO ₂	0.94	C	.64	CO ₂	0.95	C	.84
SO ₂	0	S		SO ₂	1.07	S	
Cl	4.32	Cl	1.36	Cl	0.35	Cl	1.06
F	.31	F		F	0.15	F	
H ₂ O+	n.d.	H	3.82	H ₂ O+	2.66	H	2.62 ¹
	101.07				100.14		
less				less			
O = Cl,F	1.08			O = Cl,F	.14		
	99.99				100.00		
	%						
	h						
	x						
	%						
	O _{Me}						
		0.577					0.715
		0.000					1.00
		1.36					1.16
		1.83					—
		49.98					50.03

¹H₂O+ equivalent to 0.16 weight per cent subtracted since the total reported by the analyst was 100.16 per cent.

*Gibbs & Bloss (1961, pp. 1495, 1496).

TABLE 5. MAGNESIUM-BEARING SCAPOLITES
(Analysts: XXX, XXXI, C. O. Ingamells; 26, Serdyuchenko)

XXX			XXXI			26			
Wt. %	Composition of Me	Ma	Wt. %	Composition of Me	Ma	Wt. %	Composition of Me	Ma	
SiO ₂	45.91	Si	47.17	Si	16.02	SiO ₂	45.54	Si	14.95
TiO ₂	.07	Ti	.03	Ti	.02	Al ₂ O ₃	—	Al	7.99
Al ₂ O ₃	28.17	Al	26.29	Al	7.19	P ₂ O ₅	28.51	B	.59
B ₂ O ₃	—	—	—	—	—	Fe ₂ O ₃	.80	P	.01
P ₂ O ₅	—	Fe	.15	Fe	.08	FeO	.49	Fe ²⁺	.16
Fe ₂ O ₃	.11	—	—	—	—	MgO	.11	Fe ²⁺	.04
FeO	—	Mg	1.00	Mg	1.10	—	—	Mg	2.07
MgO	.46	—	—	—	—	—	—	—	—
	23.96				{ 24.00				{ 24.00
	—				.41				1.72
MnO	.01	—	—	—	—	MnO	.04	Mn	.01
BaO	—	—	—	—	—	BaO	.15	—	—
CaO	15.76	Ca	14.31	Ca	7.00	CaO	7.91	Ca	7.00†
Na ₂ O	2.44	Na	3.82	Na	5.49	Na ₂ O	2.59	Na	2.15
K ₂ O	2.21	K	1.01	K	.95	K ₂ O	5.88	K	3.21
H ₂ O+	1.12	H	.93	H	4.59	H ₂ O+	2.34*	H	4.18
H ₂ O-	.03	—	—	—	—	H ₂ O-	.46	—	—
CO ₂	2.86	C + S	2.66	C + S	2.00†	CO ₂	1.76	C + S	2.00†
SO ₃	.94	—	—	—	—	SO ₃	.42	—	—
Cl	.05	—	—	—	—	Cl	.13	Cl	.09
F	.01	—	—	—	—	F	.04	F	.05
less	100.15	O + Cl + F	99.90	O + Cl + F	50.00	less	100.43	O + Cl + F	50.00
O = Cl,F	.02	—	—	—	—	O = Cl,F	.05	—	—
	100.13		99.76		100.38				
		<i>m</i> = 0.685		<i>m</i> = 0.612				<i>m</i> = 0.330	

*0.38% H₂O+ subtracted in subsequent calculations so as to be based on a total of 100.00.

†Normalized to (Ca + Ba - C - S) = 5.00.

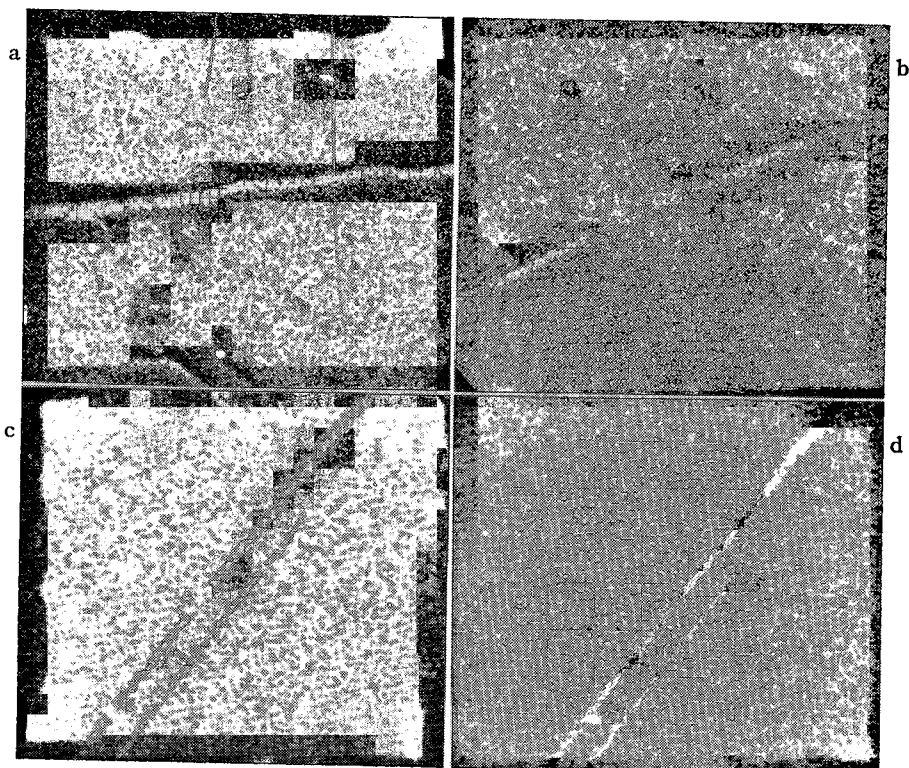


FIG. 8. Electron microprobe photographs of scapolite XXXIX. (a), (b) electron back scatter; calcite lamella are light coloured. (c) CaK_α with calcite lamellae light coloured (d) SiK_α with calcite lamellae dark.

TABLE 7. ATOMIC PERCENTAGE COMPOSITION OF POSSIBLE SCAPOLITE END-MEMBERS

	$\text{Ca}_7\text{Si}_{12}\text{Al}_{10}\text{C}_2\text{O}_{50}$	$\text{Ca}_8\text{Si}_{12}\text{Al}_{12}\text{O}_{48} \cdot 2\text{CO}_3$	$\text{Na}_8\text{Si}_{18}\text{Al}_6\text{O}_{48}\text{Cl}_2$
Ca	8.64	9.09	
Na(K)			9.76
Si	14.82	13.63	21.95
Al	12.35	13.63	7.32
C	2.47	2.27	
Cl			2.44
O	61.73	61.37	58.53
	100.0	100.0	100.0
Si + Al	27.16	27.27	29.27
Si + Al + C	29.64	29.54	29.27

TABLE 8. SCAPOLITES CALCULATED TO ATOM PER CENT

	XIV	XXX	XXXI	XXXII	XXXIII	XXXIV	XXXV
Ca	6.51	5.92	5.39	4.34	4.17	3.10	1.79
Mg	.15	.24	.54	.01	.10	.02	.02
Fe	.08	.03	.04	.01	.06	.02	.02
Na	2.54	1.65	2.59	4.33	4.66	5.77	7.04
K	.09	.99	.45	.51	.39	.48	.52
Si	15.81	16.05	16.55	18.07	18.21	19.06	20.01
Al	11.49	11.61	10.87	9.97	9.80	9.36	8.80
OH	1.50	2.60	2.17	.51	.16	.30	1.01
Cl	.38	.03	.34	.97	1.10	1.61*	1.72
F		.01	.04	.02	.12	.90	.54
C + S	1.86	1.61	1.65	1.27	1.23	59.38	58.53
O	59.60	59.22	59.39	59.99	60.02		
	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Si + Al	27.30	27.66	27.42	28.04	28.01	28.42	28.81
Si + Al + C + S	29.16	29.27	29.07	29.31	29.24	29.32	29.35
Si + Al + C + S + Mg	29.31	29.51	29.61	29.34	29.34	29.34	29.37
Si + Al + C + Mg	29.26	29.26	29.24	29.13	29.13	29.24	29.36
O + OH + F + Cl	61.48	61.86	61.94	61.39	61.40	61.29	61.26
Na + K + Ca	9.14	8.56	8.43	9.18	9.22	9.35	9.35
Na + K + Ca + Mg + Fe	9.37	8.83	9.01	9.20	9.38	9.39	9.39
S	.05	.25	.37	.19	.21	.10	.01
C	1.81	1.36	1.28	1.08	1.02	.80	.53

*Revised from originally reported figure to make the analysis total 100.000 per cent.

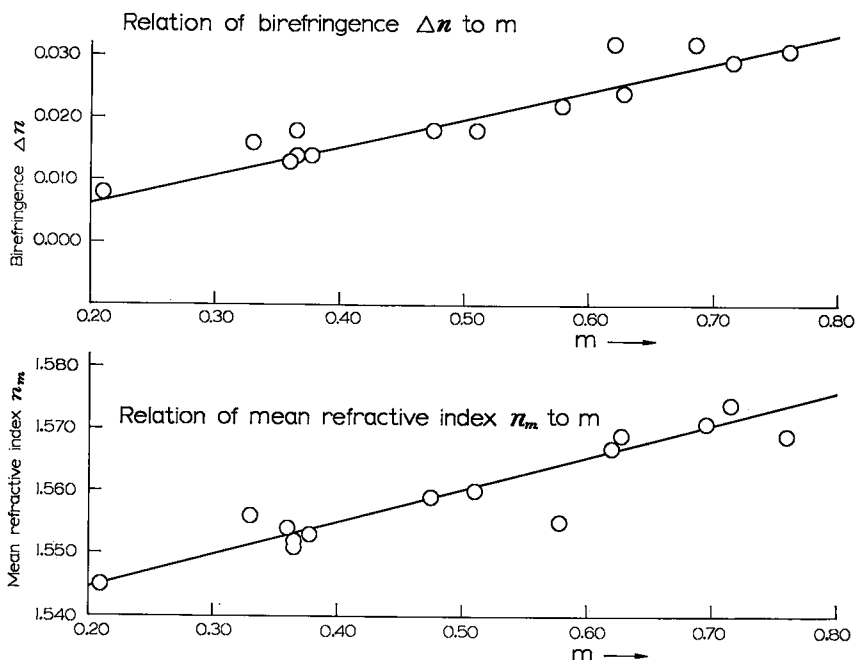


FIG. 9. Variation of birefringence and mean refractive index with composition (expressed as calculated fraction of meionite, m) for scapolite.

In view of the correlation between H_2O and MgO noted by Middleton (1964), and with the known behaviour of magnesium in other minerals in mind, it seems reasonable to group this element with aluminum in considerations of stoichiometry. Calculation on the basis of two samples (Nos. XXX and XXXI of Shaw, 1960a) with appreciable magnesium seems to support this grouping (Table 5). On the other hand, the very complete analysis of Serdyuchenko (Table 5, and Shaw 1960a, Table 4, Anal. 26), which shows 3.24 per cent MgO , will calculate satisfactorily only if part of the Mg is taken as replacing Na . In the Gib Lake scapolite of Shaw (Table 9), however, it is not clear where the magnesium belongs.

In Table 5, modifications of formulas (20) to (26) have been used to take into account the bivalence of magnesium. Where Mg replaces Al , an equivalent amount of OH^- must replace O^{2-} , and where it replaces Na , O^{2-} must replace OH^- , in order that charge balance be retained.

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TABLE 9. SCAPOLITE, GIB LAKE QUEBEC
(Analyst: J. Muysson)

	Weight Per Cent		Composition of Me Ma	
SiO ₂	55.44	Si	11.64	17.63
TiO ₂	Tr	Ti		
Al ₂ O ₃	22.89	Al	10.36	6.36
Fe ₂ O ₃	.00	Fe		
MnO	.00	Mn		
MgO	.30	Mg		.16*
CaO	7.72	Ca	7.00	
Na ₂ O	9.36	Na		
K ₂ O	.22	K		7.76
P ₂ O ₅	.05	P		
H ₂ O ⁺	.22	H	.36	.44
H ₂ O ⁻	.03			
CO ₂	1.85	C	2.00	
SO ₃	.18	S		
Cl	2.30	Cl		1.62
F	.00	F		
	100.37	O + Cl		49.71
less O = Cl	.48			
	98.89			
<i>m</i>	.318	<i>k</i>	1.76	
<i>h</i>	.36	CaCO ₃	.32	

*residual, not included in Ma composition.

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