American Mineralogist, Volume 58, pages 81-92, 1973

Crystallographic Data and Refractive Indices of Scapolites

HORST H. ULBRICH, *Department of Geology and Geophysics,*
University of California, Berkeley, California 94720

Abstract

Scapolites of intermediate composition show sharp b-reflections ($h + k + l \neq 2n$), in addition to the a-type ($h + k + l = 2n$), thus establishing $P4_2/n$ as a possible space group. $I4/m$ was found at both sodic and calcic end members. New cell parameters, determined with Guinier methods, and refractive indices are reported. Determinative charts based on cell dimensions, d-spacings and refractive indices allow estimation of meionite content within about ±7 percent. Regression of cell parameters on chemical data reveals several possible regression models. Treating the whole group as a single population works best for refractive indices, which can be predicted mostly within ±.002. On the other hand, cell parameter regression on composition is best treated assuming two different populations, one on each side of 65–66 percent meionite; predicted cell dimensions are usually within ±.003 Å. The possibility of limited miscibility gaps in intermediate scapolites is discussed. P-group specimens, at least, cannot be considered an ideal solid-solution series.

Introduction

The structure of scapolites has been described by numerous investigators (Gossner and Brückl, 1928; Pauling, 1930; Schiebold and Seumel, 1932; Scherillo, 1935). The model proposed by Schiebold and Seumel and by Pauling has been confirmed recently by Papike and Zoltai (1965) and Papike and Stephenson (1966). Cell parameters of scapolites have been reported by Scherillo (1935), Burley, Freeman and Shaw (1961), Gibbs and Bloss (1961), and Eugster, Prostka and Appleman (1962). A large amount of chemical information on the group is available—for example, Gossner and Brückl (1928), Shaw (1960a, 1960b), Hietanen (1967), Ingammells and Gittins (1967) and bibliography therein—but only recently has an acceptable stoichiometric model been proposed (Evans, Shaw and Haughton, 1969). Optical properties of the group are discused by Shaw (1960a, 1960b).

Scapolites change their composition according to two replacement schemes (Evans *et al.*, 1969). From the end member marialite, $Na_4Al_3Si_9O_{24}Cl$, a replacement of Na_3Si_2Cl by $Ca_3Al_2CO_3$ takes place. From 25 percent marialite to the end member meionite, $Ca_4Al_6Si_6O_{24}CO_3$, the substitution is NaSi by CaAl, as in plagioclases.

Several space groups have been proposed for scapolites. Gossner and Brückl (1928) proposed $P4_2/m$ or $P4_2/n$ as possibilities, and ruled $I4/m$ out. Burley, Freeman and Shaw (1961) reported space group $I4/m$, the same with which Papike *et al.* (1965, 1966) refined the structures of two scapolites. Primitive space groups ($P4_2/n$) were recently reported as being the most commonly observed in scapolites (Lin and Burley, 1971; Ulbrich, 1971). Electron diffraction patterns of one sample of intermediate composition lead Phakey and Ghose (1972) to propose $P4/m$ or $P4$.

Scapolites are framework silicates with two formula units in the cell. Structural refinements on two body-centered scapolites (Papike *et al.*, 1965, 1966) and preliminary refinements of a Monte Somma meionite (this author) indicate that aluminum occupies the T-2 site (multiplicity: 16) up to a maximum Si-Al ratio of one. Excess Al (from 33 percent meionite on to the calcic end member) is located in the T-1 site (multiplicity: 8). The structural formula for body-centered scapolites is then:

$$Ca_xNa_yK_z({Si^{I}}_{4-xx}Al^{I})_{xx} \cdot ({Si^{II}}_{8-yy}\,{Al^{II}}_{yy})O_{24} \cdot (CO_3)_uCl_v(SO_4)_w$$

where $x + y + z = 4$; $xx \geq 0$ if $yy = 4$; and, as a charge-balance requirement, $2x + y + z = xx + yy + 2u + v + 2w$. In practice there is a slight deficiency in anions or cations (Evans *et al.*, 1969), possibly due to errors in chemical analysis.

Ideal solid solutions between end members in a

---

[1] Present address: Mineralogisch-petrographisches Institut, Bernoullianum, Basel, Switzerland.

TABLE 1. SPACE GROUPS OF SCAPOLITE SPECIMENS

Specimen and locality	Percent meionite[1]	Space group	Remarks
Bishop Tuff Bishop, Calif.	14-20[2]	I4/m	"Hydrothermal" environment
ON 8 Gooderham, Ontario	21.3	I4/m	Space group from Papike-Zoltai 1965.
17122 Mineville, Ontario	32.5	$P4_2/n$	Skarn?
17120 Gouvernor, N. Y.	37.0	$P4_2/n$	Skarn? Some weak violations to n-glide plane (see text)
17139 Hastings Co., Ontario	48.2	$P4_2/n$	Skarn?
Q 85 Huddersfield Twp., Quebec	65.2	$P4_2/n$	
17141 Impilahti, Finland	67.4	$P4_2/n$	Strongly deformed; pegmatite
17161 Bucks Co., Pa.	71.1	$P4_2/n$	Granulite?
M 730 Greenvile, Ontario	74.8	I4/m	Space group from Papike-Stephenson 1966.
M 9122 Monte Somma, Italy	92.7	I4/m	"Hydrothermal" environment

[1] Compositions according to Evans *et al.*, 1969.

[2] Evans, 1971, personal communication.

binary system give rise to simple linear relations between composition and crystal parameters. Although scapolites have a rather complicated substitution scheme—two binary systems with a common link at the composition of 75 percent meionite—they provide excellent material to investigate the relations between chemical composition and physical properties.

Scope of Investigation and Material

The present investigation was carried out to: a) determine changes in the space group symmetry of the series; b) add new optical data; c) determine cell parameters; d) investigate the relationship between cell dimensions and optical properties with chemical composition by means of regression techniques. A partial report was published as an abstract elsewhere (Ulbrich, 1971).

The scapolites analyzed by Evans *et al.* (1969) were available to the author. Part of the material (the 17000 series) is from the collection of the Department of Geology and Geophysics, University of California, Berkeley; it consists mostly of large crystals and cleavage pieces from Eastern USA, the Canadian Shield, and Finland (see listing in Evans *et al.*, 1969). As far as can be judged from the mineral specimens, the parent rocks are probably all skarns, granulites or pegmatites. One sample, M9122, is a high temperature, "hydrothermal" specimen from Monte Somma, Italy, with clear, idiomorphic crystals without cleavage, growing from a substrate as a multicrystalline aggregate (specimen in the Royal Ontario Museum; see also Scherillo, 1935). Another sample, the Bishop Tuff scapolite, consists of very small well-crystallized prisms, presumably formed from circulating fluids flowing through a small "hydrothermal" vent in the Bishop Tuff Formation, near Bishop, California. The rest of the samples are from the collections of McMaster University (*cf.* Shaw, 1960a, 1960b).

Experiments and Results

Space group symmetry

In the present study, precession photographs were taken of several scapolites (Table 1). The orientation is such that a_0 and c_0 are close to 12 and 7.5 Å, respectively. The Laue symmetry of all specimens is $4/m$. Both body-centered and primitive space groups were found. A distinction is made between *a*-reflections ($h + k + l = 2n$) and *b*-reflections ($h + k + l \neq 2n$).

The diffraction symbol for the body-centered

TABLE 2. HEAT TREATMENT OF SOME SCAPOLITES

Specimen	Temperature (°C)	Duration (days)	Cell dimensions[1] c_0	a_0	Vol.	Space group	N[2]
17120	untreated		7.5811(5)	12.0904(5)	1108.19(9)	$P4_2/n$	48
	900	9	-	-	-	$P4_2/n$	
	1000	14	7.5579(8)	12.1253(9)	1111.19(17)	-	23
17161	untreated		7.5636(7)	12.1512(8)	1116.8(1)	$P4_2/n$	34
	900	9	-	-	-	$P4_2/n$	
	1000	14	7.5561(5)	12.1609(6)	1117.45(11)	-	28
17141	untreated		7.5632(6)	12.1451(6)	1115.6(1)	$P4_2/n$	43
	900	9	-	-	-	$P4_2/n$	
	1000	14	7.5580(8)	12.1564(9)	1117.47(8)	-	21

[1] Least squares refinement using Guinier film data.

[2] Number of reflections from which cell parameters were calculated.

scapolites is $4/mI-/-$, and by analogy with results listed in the literature (*e.g.,* Papike *et al.,* 1965, 1966), the space group $I4/m$ *is* assigned. In addition to precession studies, intensity data for the M9122 meionite were collected on a Picker automated diffractometer. Reflections were considered unobserved when $I_{obs} \leq 3\sigma(I)$, where $\sigma(I)$ is the standard deviation of intensity counts. By this criterion, all but one or two *b*-reflections have to be considered unobserved; the exceptions are, however, barely above background level. It can therefore be safely concluded that the scapolite M9122 is body-centered; in fact, preliminary refinements with $I4/m$ symmetry converged after several trials to a conventional *R*-factor of less than 5 percent. The sodic Bishop Tuff scapolite is variable in composition (Table 1), and the crystals were rather small. No *b*-reflections were observed, even in long precession runs of 70 to 100 hours.

The diffraction symbol for scapolites of intermediate composition is $4/mP4_2/n$ and the space group is therefore uniquely determined as $P4_2/n$ (Table 1). Although *b*-reflections are prominent, they are on the whole much weaker and less numerous than the *a*-type. One of the specimens (no. 17120) showed two weak violations of the *n*-glide plane condition in the *hk*0 layer, most probably due to multiple reflection effects.[1]

Three primitive scapolites were heated to different temperatures, in order to investigate changes in cell dimensions and possible variations in symmetry (Table 2). The heating was performed under atmospheric conditions in a common laboratory furnace, followed by air-quenching. Fresh material was used each time a new experiment was started, so as to avoid uncertainties arising from the effects of reheating the same specimen. Precession photos were taken of the heated specimens 17120 and 17161; although the results are still fragmentary, a tendency towards weakening of *b*-reflections is observed.

Cell parameters

The cell parameters were determined using a Jagodzinsky-Guinier camera, with quartz monochromator and FeKα_1 radiation(lambda = 1.93597 Å). Forward reflections were recorded on single-coated films. Silicon (a = 5.43054 Å) was used as internal standard. Exposure times were usually 24 hours. All strong reflections are of the *a*-type, and the indexing is on the whole consistent with the list given in Gibbs and Bloss (1961). Cell parameters from 35 or more reflections were calculated using a combination program (Wilde, 1969) which corrects the measurements taken on a Guinier film for direct input into a least-squares program (Burnham, 1962). For results, see Table 3 and Figure 1; following Evans *et al.* (1969) meionite content refers to the ratio Ca/(Ca + Na + K).

Cell parameters of some heated specimens (Table 2) were also measured. There is considerable variation between the dimensions of the heated and unheated samples. This difference is statistically significant, since there is no overlap at the 99 percent confidence intervals, as computed from the standard errors of cell dimensions in heated and unheated specimens (Table 2).

Refractive indices

Refractive indices (Table 3, Figure 2) of the scapolites from the Berkeley collection and the Monte Somma specimen were measured with sodium light, using various mixtures of the following liquids as immersion media: nitrobenzene, oil of cloves, 1-chloronaphthalene and mineral oil. Whenever necessary, the refractive indices of the immersion media were corrected to 25°C; an average temperature coefficient of refraction of 3×10^{-4} deg^{-1} was taken (*e.g.,* Emmons, 1959, p. 56). Errors are estimated at ±.001.

Relation of optical properties and cell parameters to chemical composition

In scapolites, a description of the changes in optical and cell constants as a function of chemistry can be attempted by means of a multivariable linear model (see also Middleton, 1964). Such relations are depicted by equations of the form:

$$\bar{Y}(\pm y') = b_0 + b_1(\pm b_1')X_1 + b_2(\pm b_2')X_2 + \cdots + b_n(\pm b_n')X_n$$

---

[1] Phakey and Ghose (1972) propose $P4/m$ or $P4$ as the space group for the scapolite 17120 from electron diffraction studies. However, precession photographs of three different intermediate scapolites, exposed for longer periods of time (a week and over), failed to detect the additional reflections conforming to $P4/m$ symmetry. The reason may be that double reflection effects are recorded on electron diffraction patterns, or else that the greater intensity of the electron beam (650 kv) brings out reflections not detectable with photographic X-ray techniques.

TABLE 3. CELL PARAMETERS AND REFRACTIVE INDICES OF SCAPOLITES

	Me %	n_e	n_o	n_m	a_o (Å)	c_o (Å)	Cell volume	N^a
ON 8^c	21.3	1.541	1.549	1.545	12.060 $(3)^e$	7.572 $(3)^e$	1101.3 $(9)^e$	
ON 7	33.3	1.544	1.560	1.553	12.0636 (5)	7.5827 (5)	1103.51 (9)	45
GL	34.1				12.0544 (4)	7.5856 (5)	1102.24 (8)	37
ON 70	39.5				12.0807 (5)	7.5813 (5)	1106.4 (1)	45
ON 3B	42.5	1.550	1.566	1.558				
Q 30	42.7	1.549	1.567	1.558				
Q 87	42.8	1.550	1.568	1.559				
CA 63A	44.5	1.548	1.565	1.557				
Q 26	48.2	1.552	1.572	1.562	12.1106 (4)	7.5776 (4)	1111.38 (8)	44
Q 13A	51.3	1.551	1.571	1.561				
ON 27	59.3	1.550	1.577	1.564	12.1419 (2)	7.5673 (2)	1115.61 (4)	43
Q 85	65.2	1.557	1.581	1.569				
M 730^d	74.8	1.555	1.587	1.571	12.169 (4)	7.569 (3)	1121. (1.)	
ON 47	79.6	1.560	1.592	1.576	12.1654 (3)	7.5741 (3)	1120.95 (6)	46
M 9122	92.7	1.562	1.598	1.580	12.2008 (5)	7.5785 (4)	1128.13 (9)	35
17122	32.5	1.548	1.561	1.554	12.0670 (7)	7.5853 (7)	1104.5 (1)	45
17120	37.0	1.547	1.563	1.555	12.0904 (5)	7.5811 (5)	1108.19 (9)	48
17118^b	40.6	1.548	1.569	1.558				
17139	48.2	1.547	1.569	1.558	12.1184 (9)	7.5762 (9)	1112.6 (2)	41
17134	50.5	1.550	1.571	1.560	12.1206 (6)	7.5717 (5)	1112.4 (1)	37
17141	67.4	1.551	1.581	1.566	12.1451 (6)	7.5632 (6)	1115.6 (1)	43
17151	67.3	1.553	1.583	1.568	12.1478 (4)	7.5653 (3)	1116.40 (7)	43
17126	68.9	1.552	1.584	1.568	12.1497 (4)	7.5637 (4)	1116.53 (7)	43
17154	70.7	1.552	1.584	1.568	12.1502 (8)	7.5630 (8)	1116.5 (2)	43
17161	71.1	1.553	1.585	1.569	12.1512 (8)	7.5636 (7)	1116.8 (1)	34
17136	71.1	1.553	1.588	1.570	12.1564 (7)	7.5636 (7)	1117.7 (1)	46
17138	71.9	1.554	1.585	1.569	12.1596 (8)	7.5646 (7)	1118.5 (1)	34

a: number of reflections used for cell parameter calculations.
b: variable composition.
c, d: cell parameters from Papike and Zoltai (1965) and Papike and Stephenson (1966).
e: standard error, in terms of the last significant figure of the cell parameter.

Meionite content from Evans *et al.*, 1969. Optical data: 17000 series, own measurements; the rest from Shaw, 1960a. (errors are estimated at ± .001).

where $\overline{Y}$ is the predicted physical parameter (*e.g.*, cell dimension or refractive index), y' is the standard error of $\overline{Y}$, b_o is the constant of the equation, b_i are the coefficients and b_i' their standard errors, and X_i are the chemical predictors (*e.g.*, atomic proportions, or their squares or cross-products, *etc.*). Each predictor variable is assigned a significance level L_i (Iscol, 1969; Wenk, 1971). Conversely, one could set up a second set of equations in which the predicted magnitude would now be the chemical component (*e.g.*, atomic proportions) and the predictor variables would be the cell or optical parameters. This yields poor results for scapolites, and would do so in general for all tetragonal, hexagonal, and cubic silicates in which only one or two cell constants are available as predictors for rather complicated chemical substitutions.

Although both body-centered and primitive scapolites are included in this study, the structure of samples with primitive space groups is not known; hence no occupancy assignments can be attempted for them (*e.g.*, Al and Si content in the different tetrahedral positions). It is therefore convenient, for statistical purposes, to take the total atomic proportions (*e.g.*, total Al or total Si without site distinction) as chemical predictors.

Many possible combinations of independent predictor variables have been tried and only those with the fewest statistically significant parameters are recorded (Tables 4 and 5). Calculations of the

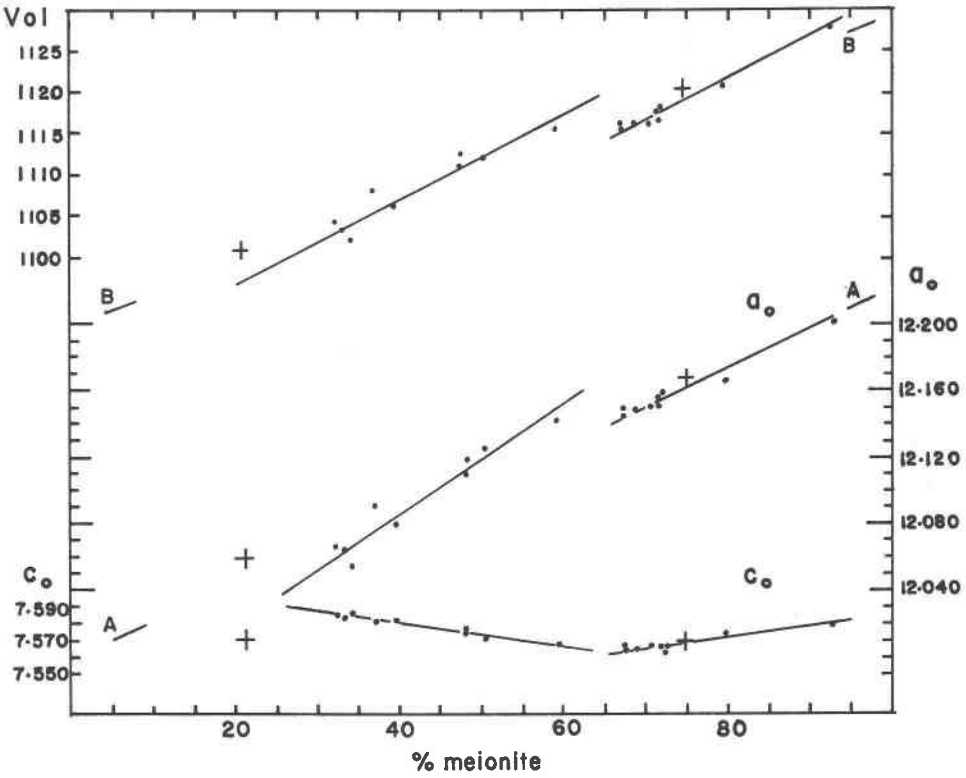

FIG. 1. Variation of cell parameters with meionite content. Cell edges in Angstroms, cell volume in cubic Angstroms. Dots indicate cell dimensions measured with Guinier camera; crosses are values from the literature (see Table 3). Traces AA and BB are plots of linear equations 3–4, Table 4, and may be used for estimating meionite content in specimens of unknown composition.

several regression equations were performed using a stepwise regression technique (Efroymson, 1960) with computer programs in the Ariel language available at Berkeley (Iscol, 1969). Chemical data were taken from Evans *et al.* (1969); analytical techniques and errors are discussed in the same paper.

Plots of cell parameters on meionite percentage show a simple correlation pattern, and an inspection of the data (Fig. 1) suggests several possible regression models: a) the whole group treated as one population and its properties represented as simple functions of chemical parameters; b) dividing the series into two binary solid solutions, with the 75 percent meionite as comon link (Evans *et al.,* 1969); c) selecting two populations, one at each side of 65–66 percent meionite, as suggested qualitatively by the plots in Figure 1 (S. Ghose, personal communication).

The single population assumption represents satisfactorily the variation of refractive indices with meionite percentage (Fig. 2; equations 3–4, Table 4). It also accurately describes the changes as a function of atomic proportions (equations 1–2, Table 4); plots of residuals for observed minus calculated refractive indices (Figs. 3a–3b) show that deviations from the 45-degree line are mostly within a ± .002 interval. Since this is the error usually associated with index measurements, the regression equations in Table 4 can be used with confidence to calculate optical properties from chemical data. The refractive index n_e of the extraordinary ray has a weaker correlation with composition (Fig. 2) and no regression was calculated. Furthermore, information about n_e is contained in the equations for n_o and for the average refractive index n_m where n_m equals $(n_o + n_e)/2$ (see Shaw, 1960a).

This model is, however, not entirely satisfactory for regressions of a_o, c_o and cell volume on compo-

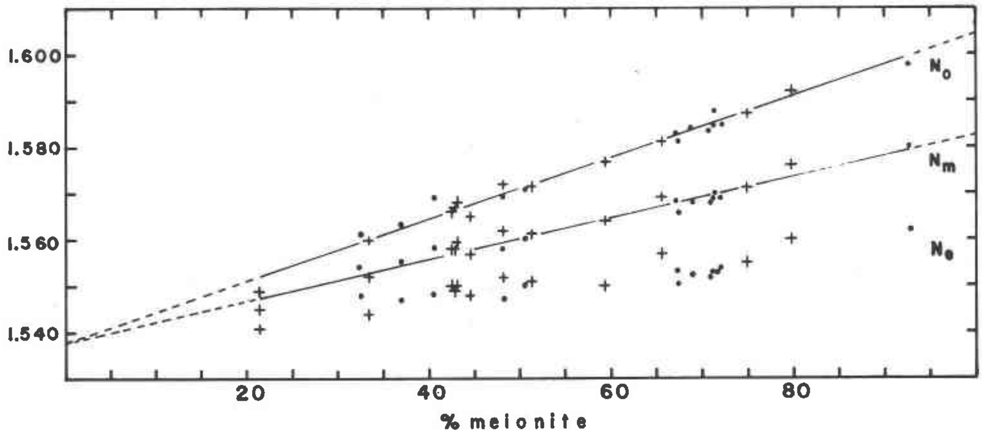

FIG. 2. Refractive indices of scapolites as a function of composition. Dots are measurements reported there, crosses are values taken from Shaw (1960a). n_o and n_e: indices of the ordinary and extraordinary rays. n_m: average of n_o and n_e. Regression lines are traces of equations 5–6, Table 4.

sition (either meionite percentage or atomic proportions). For instance, a_o can be represented as a function of Al, K, Cl and S, but the residuals (observed a_o minus predicted a_o) turn out to have larger deviations than expected from the accuracy of the data. Furthermore, simple linear regressions of cell parameters on meionite percentage describe the behavior as $\bar{Y} = a + bX$ (where $\bar{Y}$ is the predicted value and X the meionite percentage) and can be tested for linearity, *e.g.*, through a plot of residuals vs. $\bar{Y}$. In a strictly linear case, the scatter of points should conform to a "horizontal band" (*e.g.*, Draper and Smith, 1966, p. 90). A plot of the a_o residuals against $\bar{Y}$ (Fig. 4a) with departures from the "horizontal band" indicates that the underlying assumption of linearity for the whole group is not entirely correct. Square terms in the regression equation do not improve the results.

TABLE 4. LINEAR REGRESSION EQUATIONS*: SINGLE POPULATION MODEL

No.	$\bar{Y}$	y'	b_o	X_i	b_i	b_i'	L	N
1	N_o	.0019	1.5236	Al^{tot}	.0129	.003	0.	25
				K	.0136	.009	.15	
				Cl	-.0298	.007	0.	
2	N_m	.0014	1.5159	Al^{tot}	.0109	.002	0.	25
				K	.0077	.0077	.28	
				Cl	-.0140	.006	.02	
				S	.0110	.004	.02	
3	%me	4.02	-5350.4	a_o	445.6	21.7	0.	20
4	%me	4.20	-2917.2	Vol	2.671	.135	0.	20
5	%me	2.40	-2289.1	n_o	1488.8	42.7	0.	25
6	%me	3.20	-3340.9	n_m	2173.2	81.4	0.	25
7	%me	3.60	-6327.8	d_{321}	2077.6	103.6	0.	18
8	%me	3.80	-6245.0	d_{822}	4598.0	238.6	0.	18

*All regression equations are of the form:

$$\bar{Y}\ (\pm y') = b_o + b_1\ (\pm b_1')\ X_1 + b_2\ (\pm b_2')\ X_2 + \ldots + b_n\ (\pm b_n')\ X_n$$

where $\bar{Y}$ is the predicted physical parameter (e.g., cell dimension or refractive index), y' is the standard error of $\bar{Y}$, b_o is the constant of the equation, b_i are the coefficients and b_i' their standard errors, and x_i are the chemical predictors (e.g., atomic proportions or their squares or cross-products, etc.). L is the significance level and N is the number of observations used for the regression.

TABLE 5. LINEAR REGRESSION EQUATIONS*: DOUBLE POPULATION MODEL WITH "BREAK" AT 65-66% MEIONITE

No.	$\bar{Y}$	y'	b_o	X_i	b_i	$b_{i'}$	L	N
(A) Compositions up to 66% meionite								
1	%me	2.543	-3599.2	a_o	301.11	29.79	0.	9
2	%me	2.526	11180.0	c_o	-1469.5	144.4	0.	9
3	%me	2.894	-2086.3	Vol	1.9204	.2185	0.	9
4	a_o	.0063	11.308	Al^{tot}	.3551	.1089	.03	10
				Ca	-.2912	.1054	.05	
				K	.1819	.0421	.01	
				Cl	-.4806	.1620	.04	
				S	-.1056	.0704	.20	
5	c_o	.0032	7.7176	Al^{tot}	-.1336	.0550	.07	10
				Ca	.1638	.0533	.04	
				K	-.0715	.0213	.03	
				Cl	.3095	.0819	.02	
				S	.1262	.0356	.02	
6	Vol	.8541	983.02	Al^{tot}	45.703	14.693	.03	10
				Ca	-29.147	13.957	.09	
				K	22.839	5.588	.01	
				Cl	-41.597	18.909	.08	
(B) Compositions over 66% meionite								
7	%me	1.918	-5417.1	a_o	451.55	38.94	0.	10
8	%me	2.7895	-10043.0	c_o	1337.0	173.1	0.	10
9	%me	1.6579	-2144.9	Vol	1.9829	.1464	0.	10
10	a_o	.0009	11,894	Al^{tot}	.0523	.0014	0.	10
				K	.0746	.0142	0.	
				S	-.0076	.0039	.10	
11	c_o	.0011	7.4630	Al^{tot}	.0203	.0022	0.	10
				K	-.0326	.0175	.12	
				Cl	.0395	.0164	.06	
				S	.0296	.0073	.01	
12	Vol	1.658	1054.7	Al^{tot}	12.611	.4234	0.	10
				K	9.5852	3.3673	.04	
				Cl	5.8060	3.1430	.12	
				S	3.2423	1.4049	.07	

*See footnote, Table 4.

There is no indication of discontinuities in the reported data or changes in slope at 75 percent meionite, and so the second model is abandoned.

The third model is suggested by the spread of data as a function of meionite percentage; in Figure 1, a_o and c_o show different behavior above and below on 65–66 percent meoinite. Accordingly, two populations have been assigned to each cell parameter with the 65–66 percent meionite as the separating composition, and straight regression lines were computed as a function of meionite content (Fig. 1; equations 1, 3, 7 and 9, Table 5). A plot of a_o-residuals against $\bar{Y}$ (Fig. 4b) tests the linearity assumption for this regression model; the scatter conforms better to "horizontal bands" (compare with Fig. 4a). Further tests can be applied to the lines representing regression of cell parameters on meionite percentage. The methods described in Brownlee (1965, p. 349) have been followed. For n observations, the residual variance is

$$S_k^2 = 1/f \sum (y_i - \bar{Y}_i)^2$$

where $k = 1, 2$, refers to line 1 or line 2 (below or above 66 percent meionite); $f = n - 2$ are the degrees of freedom, y_i and $\bar{Y}_i$ are the individual observed and calculated values. The ratio S_1^2/S_2^2 follows an F-distribution with f_1, f_2 degrees of freedom and tests the hypothesis of a joint variance. If that hypothesis is accepted, a joint value can be calculated:

$$S_j^2 = (f_1 S_1^2 + f_2 S_2^2)/(f_1 + f_2)$$

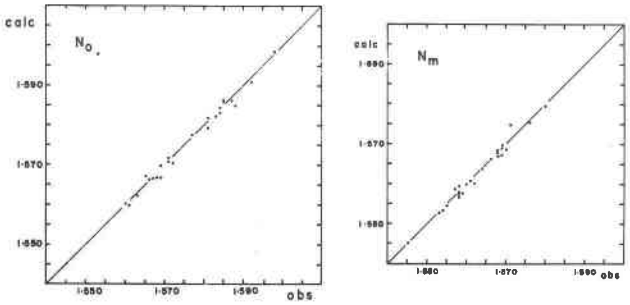

FIG. 3. Plots of refractive indices (observed vs. calculated). Calculated indices are estimated with equations 1–2, Table 4. The 45-degree line indicates perfect fit.

Next, the null hypothesis $H_0\colon b_1 - b_2 = 0$, can be tested against the alternative $H_1\colon b_1 - b_2 \neq 0$, where b_i = slopes of the regression lines. The difference between the two slopes follows a t-statistic:

$$t(\alpha/2;\, f_1 + f_2) = \frac{b_1 - b_2}{S_i\{[\sum (X_{1i} - \bar{X})^2]^{-1} + [\sum (X_{2i} - \bar{X}_2)^2]^{-1}\}^{1/2}}$$

X_{1i}, X_{2i}, are individual predictor values (meionite percentages) corresponding to lines 1 and 2; $\bar{X}_1$, $\bar{X}_2$ their corresponding averages. Results are as follows. Regression lines for c_0 (Table 5) yield values as quoted[1]: $b_1 = 1337.0$, $b_2 = -1469.6$, $n_1 = 10$, $n_2 = 9$, $S_1^2 = 7.78$, $S_2^2 = 6.37$, $S_i^2 = 7.12$. Variance ratio is 1.22, F(8, 7; .001) = 14.6, and so the hypothesis of a joint variance can be accepted at a rather low significance level. The t-value is $t(\alpha/2, 15) = 4.67$. From tables, $t(.005, 15) = 2.9$; the null hypothesis of equal slopes can be rejected at the 0.01 significance level.

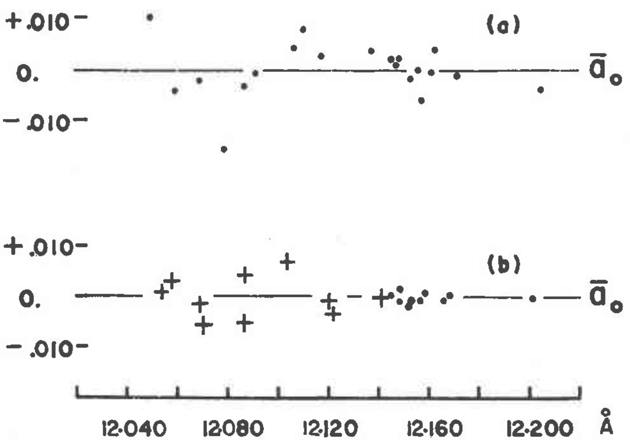

FIG. 4. Plots of residuals vs. a(calc) in Angstroms. a) Results for single-population model; b) Two populations with a "break" at about 66 percent meionite.

That is, the two lines are significantly different in slopes. Results for a_0 are: $b_1 = 301.11$, $b_2 = 451.55$, $S_1^2 = 6.44$, $S_2^2 = 3.70$, $S_i^2 = 4.99$, $n_1 = 9$, $n_2 = 10$. Variance ratio is 1.74, and so the hypothesis of a joint variance can also be accepted at a low significance level. The t-value is $t(\alpha/2, 15) = 1.31$. For $t(0.10, 15) = 1.34$, and the null hypothesis cannot be rejected at the 0.01 significance level. Results for the two lines representing the cell volume reflect their dependence on a_o and c_o.

The two population model can be further tested by calculating a_o, c_o and cell volume as functions of atomic parameters (Table 5). Residuals are drawn in Figure 5a (for a_o) and 5b (c_o), in the form of Y(obs) vs. Y(calc). A good agreement between observed and calculated parameters is shown by a clustering of points near the 45-degree line; deviations from it are in general less than ±.003 Å.

In conclusion, the two-population model is tentatively accepted, in spite of the poorer result given by the slope test for a_o.

Determinative curves

Meionite composition can be estimated from cell dimensions, interplanar spacings, and optical indices. Determinative charts have been presented by various authors, *e.g.*, with refractive indices as the entry (Tröger, 1959; Shaw 1960a, 1960b). The variation in $\Delta(2\theta_{400} - 2\theta_{112})$ CuKα with meionite content is reproduced in Burley *et al.* (1961).

Both a_o and cell volume are good estimators of meionite percentage. Unambiguous results are obtained with two estimator lines, one for a_o and another for cell volume (equations 3 and 4, Table 4); they are plotted as traces AA and BB in Figure 1. Prediction of meionite content from these lines involves uncertainties of about ±8 percent meionite at the 95 percent confidence interval.

Several strong reflections change markedly with composition; simple linear equations are sufficient as predictors and are plotted for two d-spacings in Figure 6 (equations 7 and 8, Table 4). In scapolites of unknown composition, the two reflections can be

---

[1] Scapolite ON 8 plots outside the scatter band for those specimens with compositions up to 65–66 percent meionite (Fig. 1); deletion of this sample reduces the number of observations to nineteen. The quoted values refer to this reduced set. Results similar in magnitude were obtained when a weighting scheme was set up—including ON8—in which each cell parameter was weighted according to its standard error.

located from tables given in Gibbs and Bloss (1961). Compositional estimates from these reflections are accurate to about ±7-8 percent meionite for the 95 percent confidence interval. No conspicuous inflection in slope is present in data plotted in Figures 2 and 6. The slope in c_0 as a function of meionite content is opposite to that of a_0 at the more sodic compositions (Fig. 1); consequently, "breaks" visible in plots of a_0 and c_0 may be partly smoothed out in representations of *d*-spacings versus composition.

Prediction can also be attempted by means of refractive indices (Fig. 2; regression equations 5 and 6, Table 4). The refractive index n_0 is not only easier to measure than the average refractive index n_m, but the slope of the regression line is also steeper. It should be used preferentially over n_m. In fact, prediction of meionite percentage from optical parameters is still the best and quickest procedure; estimation from the n_0 line, for instance, is accurate within ±5 percent meionite at the 95 percent confidence interval.

Discussion

Space Group Symmetry and the Possibility of Order-Disorder Relations

A change in space group symmetry in a solid-solution series, as in the scapolites, may result from 1) thermal or growth history, or 2) changes in chemical composition, where differing ratios of chemical elements alter the symmetry constraints.

The basic scapolite structure is not likely to change as a result of thermal and growth history, although order-disorder relations, especially of Si and Al, may become important. On a speculative basis, several types of Si-Al ordering could arise: a) Complete disorder, in which Al is randomly distributed throughout the tetrahedral sites of the framework. The "average" symmetry shown by X-rays would be $I4/m$. Such a case has yet to be reported. b) Partial ordering, with Si and Al as indistinguishable atoms but in a fixed ratio at a certain site. This is the case with the refinements reported previously, where Si and Al are present in site *T*-2 in a 1:1 proportion. c) Further ordering (for example, within *T*-2 itself), with destruction of the $I4/m$ symmetry.

The change of symmetry may also be a function of the constraints imposed on the structure by the Cl–CO_3 replacement (for a discussion, see Phakey and Ghose, 1972). Additional structural data are needed to decide which model is correct.

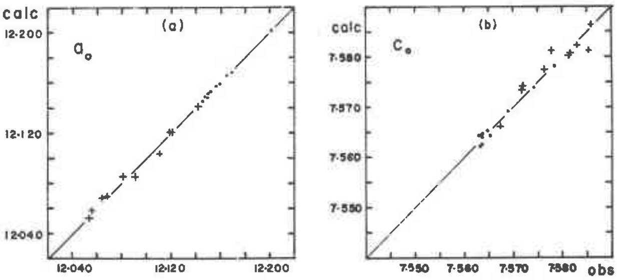

FIG. 5. Plots of cell edges (observed vs. calculated) in Angstroms. Calculated cell edges are from equations 4, 5, 10 and 11, Table 5. Crosses: compositions up to 66 percent meionite; dots: over 66 percent.

As to the effect of chemical composition on symmetry, recent work allows a better insight. Totally ordered meionites (the extreme of case c), having a Si:Al ratio of one (or close to one), would alternate Si and Al in such a way that some Al-occupied tetrahedra would be adjacent to one another (Papike and Stephenson, 1966, p. 1022). Such an arrangement violates the aluminum-avoidance principle (Loewenstein, 1954; Goldsmith and Laves, 1955; Papike and Stephenson, 1966) and is probably not stable. In fact, total ordering with alternating Si–Al tetrahedra would violate the avoidance principle as long as the scapolite has a Si–Al ratio of 7:5 or higher (about 66 percent meionite or higher).

Domain structures (Schiebold and Seumel, 1932, p. 124), where each domain could in itself be a totally or partially ordered structure (Papike and Stephenson, 1966, p. 1022), have been suggested for scapolites and shown to exist in intermediate specimens (Phakey and Ghose, 1972).

Regression Analysis and the Significance of "Breaks" in the Scapolite Series

The results derived from regression analysis do not always have a clear physical meaning (see discussion in Winchell, 1961; Winchell and Tilling, 1960), but in the case of scapolites certain conclusions can be drawn.

The predicted and observed cell parameters are numerically very similar for scapolites with meionite percentages over 66 percent, whereas a larger discrepancy is observed in samples of intermediate and sodic compositions (Figs. 4b and 5). This is also apparent in the fewer number of predictor variables needed to describe a_0 and c_0 at calcic compositions (Table 5, equations 4 to 6, 10 to 12). Reasons for this are not clear, and more structural data on inter-

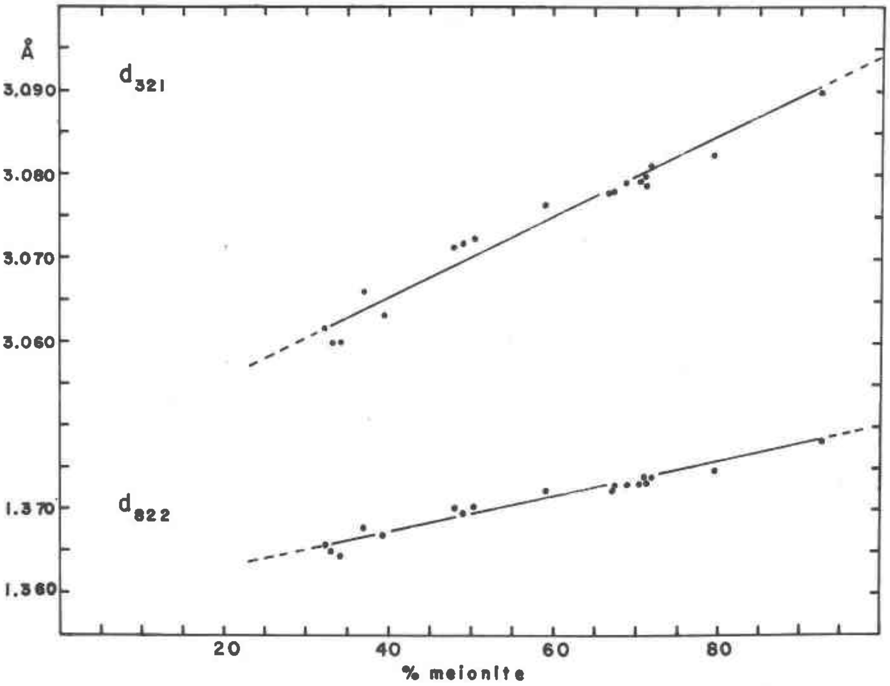

FIG. 6. Change of *d*-spacings with composition. Regression lines are those of equations 7–8, Table 4.

mediate scapolites are needed before any explanation is attempted.

In the regression equations predicting a_0 and c_0 that were derived from the double population model, the larger coefficients (in absolute values) are usually associated with the major independent variables: Al (total), Ca and Cl. Structural considerations on *I*-group scapolites can predict the relative influence of predictor variables. *T*-1 tetrahedra are joined, forming four-membered rings parallel to (001); *T*-2 tetrahedra are similarly arranged. Replacement of Si by Al increases the *M*-O distance and would also increase a_0. Mizzonites are structurally different from marialites in that the cation channels (parallel to c_0) are relatively compressed in the *a*-direction by rotation of *T*-1 and *T*-2 rings. Channel occupancy by Ca is an indication of increasing meionite content, and so Ca-filled channels are relatively shortened along a_0 (Papike and Stephenson, 1966). It is therefore to be expected that regression coefficients in equations predicting a_0 would be positive for Al, but of opposing sign for Ca. Potassium is a large cation and, though present in minor amounts, should counteract the shrinking along a_0 of the cation channels. Its influence on the prediction of c_0 is not clear. The CO_3 group in an "average" unit cell is planar, parallel to (001). Published data (Papike *et al.,* 1965, 1966) indicate that the distance from the origin to Ca is significantly larger than for Na. Hence, an increase in CO_3 and Al should have the same effect on a_0. On the other hand, the planar "average" CO_3 group has probably no effect on c_0, while chlorine substitution should increase it. Sulphur is known to be present as SO_4 groups (Lovering and Widdowson, 1968; Chappell and White, 1968); it is presumably in tetrahedral coordination and would therefore expand c_0. Its effect on a_0 is not clear.

It can now be seen that, as far as a_0 estimation is concerned, the regression coefficients behave as expected (*e.g.,* equation 4, Table 5: Al and K with positive coefficients, Cl and Ca with negative values). Some predictions also hold for c_0: for instance, Cl, S and Al have positive coefficients in equation 11, Table 5. The slope of a_0 is always positive in Figure 1, whereas the c_0-line is slightly negative up to 66 percent meionite. This fact would explain why the regression coefficients in equation 5, Table 5 (for a_0) have signs opposite to those of equation 6 (for c_0). It should be noted that the previous analysis can be carried over to scapolites with primitive space groups as well, since the overall structure is unlikely to be significantly different from that of body-centered specimens.

In general, the regression results strongly point out the overall importance of Si–Al replacement (and coupled substitutions) in the control of cell parameters. Changes in cell volume reflect the contrasting pattern exhibited by variations in a_0 and c_0.

Optical properties in scapolites are apparently not as sensitive to structural replacements as are cell parameters. Thus, the refractive indices have been satisfactorily regressed on a single-population model.

We now consider the physical significance of the inflection or "break" in the regression at 65–66 percent meionite (Si:Al ratio of about 7:5). No change in space group symmetry is observed; precession photographs of scapolites close to 66 percent meionite (ON 87 and 17141, respectively, with 65.2 and 67.4 percent meionite) fail to reveal any abnormal features. It is significant, however, that the inflection occurs at a composition beyond which, at least theoretically, the aluminum avoidance principle would prohibit any total ordering of Al and Si. On the other hand, that composition is not close enough to 75 percent meionite, where the change in the chemical substitution scheme occurs (Evans *et al.*, 1969). As suggested earlier, this inflection may be entirely a result of the control the structural replacements have on cell parameters.

Analyses reported as satisfactory (*e.g.*, Shaw, 1960a; Evans *et al.*, 1969) list few scapolites with compositions in the 50–65 percent meionite range. Indeed, only one specimen (a 1939 analysis with 64.3 percent meionite, from Slyudyanka, Russia) is cited in the interval 60–65 percent (see Shaw, 1960a, Table 5). Limited miscibility gaps in primitive scapolites may be a possible explanation for this scarcity. The present findings show that intermediate scapolites with a primitive space group cannot be regarded as an ideal solid-solution series.

Acknowledgments

The author is indebted to Professor B. W. Evans for encouragement, discussions, and loan of specimens. Discussions and advice provided by Professors H. R. Wenk and S. Ghose are gratefully acknowledged. Professor A. Pabst read an earlier version of the manuscript. Mr. D. Stickney kindly donated the Bishop Tuff specimen. The author is also indebted to the Computer Center at Berkeley for subsidized time on the CDC 6400. Most of the work was done with financial aid from NSF grants to Professor F. J. Turner.

References

BROWNLEE, K. A. (1965) *Statistical theory and methodology in Science and Engineering.* J. Wiley and Sons, New York. 590 p.

BURLEY, B. J., B. B. FREEMAN, AND D. M. SHAW (1961) Studies on scapolites. *Can. Mineral.* **6,** 670–679.

BURNHAM, C. W. (1962) Lattice constant refinement. *Carnegie Inst. Washington Year Book,* **61,** 132–135.

CHAPPELL, B. W., AND A. J. R. WHITE (1968) The X-ray spectographic determination of sulphur coordination in scapolites. *Amer. Mineral.* **53,** 1735–1738.

DRAPER, N. R., AND H. SMITH (1966) *Applied regression analysis.* J. Wiley and Sons, New York. 407 pp.

EFROYMSON, M. A. (1960) Multiple regression analysis. *In* A. Ralston, and H. S. Wilf, Eds. *Mathematical methods for digital computers.* J. Wiley and Sons, New York.

EMMONS, R. C. (1959) The universal stage. *Geol. Soc. Amer. Mem.* **8,** 205 p.

EUGSTER, H. P., H. J. PROSTKA, AND D. F. APPLEMAN (1962) Unit cell dimensions of natural and synthetic scapolites. *Science,* **137,** 853–854.

EVANS, B. W., D. M. SHAW, AND D. R. HAUGHTON (1969) Scapolite stoichiometry. *Contrib. Mineral. Petrology,* **24,** 293–305.

GIBBS, G. V., AND F. D. BLOSS (1961) Diffraction data for scapolites. *Amer. Mineral.* **46,** 1493–1497.

GOLDSMITH, J. R., AND F. LAVES (1955) Cation ordering in anorthite $CaAl_2Si_2O_8$ as revealed by Ga and Ge substitution. *Z. Kristallogr.* **106,** 213–226.

GOSSNER, B., AND K. BRÜCKL (1928) Untersuchungen über die Skapolithe. *Neues Jahrb. Mineral. Geol. Paläontol.* **34,** 349–384.

HIETANEN, A. (1967) Scapolites in the Belt Series in the St. Joe-Clearwater region, Idaho. *Geol. Soc. Amer. Spec. Pap.* **86,** 56 p.

INGAMELLS, C. O., AND J. GITTINS (1967) The stoichiometry of scapolites. *Can. Mineral.* **9,** 214–236.

ISCOL, R. (1969) G-2 Cal Regress Ariel program for stepwise multiple regression. Computer Center, University of California, Berkeley.

LIN, S. B., AND B. J. BURLEY (1971) The superlattice reflections and its relationship to the crystal structure of scapolites (abstr.) *Geol. Soc. Amer. Abstr. Programs,* **3,** 634.

LOEWENSTEIN, W. (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates. *Amer. Mineral.* **39,** 92–96.

LOVERING, J. F., AND J. R. WIDDOWSON (1968) Electron microprobe determination of sulphur coordination in minerals. *Lithos,* **1,** 264–267.

MIDDLETON, G. V. (1964) Statistical studies on scapolites. *Can. J. Earth Sci.* **1,** 23–34.

PAPIKE, J. J., AND N. C. STEPHENSON (1966) The crystal structure of mizzonite, a Ca-and carbonate-rich scapolite. *Amer. Mineral.* **51,** 1014–1027.

———, AND T. ZOLTAI (1965) The crystal structure of a marialite scapolite. *Amer. Mineral.* **50,** 641–655.

PAULING, L. (1930) The structure of some sodium and Ca aluminosilicates. *Wash. Proc. Acad. Sci.* **16,** 453–459.

PHAKEY, P., AND S. GHOSE (1972) Scapolite: direct observation of antiphase domain structure. *Nature,* **238,** 78–80.

SCHERILLO, A. (1935) La meionite del Somma-Vesuvius. *Period. Mineral.* **6,** 227–239.

SHAW, D. M. (1960a) The geochemistry of scapolites. Part I. Previous work and general mineralogy. *J. Petrology,* **1,** 218–260.

——— (1960b) The geochemistry of scapolites. Part II. Trace elements, petrology, and general geochemistry. *J. Petrology,* **1,** 261–285.

SCHIEBOLD, F., AND G. SEUMEL (1932) Uber die Krystallstruktur von Skapolith. *Z. Kristallogr.* **81,** 110–134.

TRÖGER, W. E. (1959) *Optische Bestimmung der gesteinsbildenden Minerale. Part 1: Bestimmungstabellen.* Schwesizerbart'sche, Stuttgart. 147 pp.

ULBRICH, H. H. (1971) Space groups, cell parameters and refractive indices of scapolites. *Geol. Soc. Amer. Abstr. Programs,* **3,** 736.

WENK, H. R. (1971) Variation of lattice constants in clinoamphiboles. *Z. Kristallogr.* **133,** 364–385.

WILDE, W. R. (1969) *Program Powcor* (unpublished). Department of Geology and Geophysics, University of California, Berkeley.

WINCHELL, H. (1961) Regression of physical properties on the compositions of clinopyroxenes. II: Optical properties and specific gravity. *Amer. J. Sci.* **259,** 295–319.

———, AND R. TILLING (1960) Regression of physical properties on the compositions of clinopyroxenes. I: Lattice constants. *Amer. J. Sci.,* **258,** 529–547.

Manuscript received, March 20, 1972; accepted for publication, September 21, 1972.