

THE INFRARED ABSORPTION SPECTRA OF SCAPOLITE

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ABSTRACT

The infrared absorption spectra of twenty-three scapolites covering a compositional range of $\text{Me}_{20}\text{-Me}_{90}$ were taken. The band located near 610 cm^{-1} yields a linear least squares function for compositions in the range $\text{Me}_{20}\text{-Me}_{75}$ of: $\% \text{ Me} = 2015.6 - 3.1928\sigma$, where σ is the wavenumber (cm^{-1}) of the band.

Certain of the absorption bands remain constant with change of composition. These bands fit a model for essentially decoupled $\text{Si}(\text{O}/2)_4$ and $\text{Al}(\text{O}/2)_4$ group vibrations. It is proposed that these be called Matossi modes. The remaining bands change position with change of composition. They are empirically treated by comparing the characteristics of the curves for each band with the tetrahedral substitutional scheme for scapolite proposed by Papike. They are tentatively explained by assuming that three structural units (each involving only $T_1\text{-O-T}_1$, $T_1\text{-O-T}_2$, or $T_2\text{-O-T}_2$ bonds) independently give rise to a set of vibrations whose positions are a function of the Al/Si ratios in the tetrahedral sites associated with the unit.

INTRODUCTION

Papike (1965, 1966) in his refinement of the scapolite structure has shown that it consists of two kinds of fourfold rings of tetrahedra linked together to form a framework structure. One ring, which he calls Type 1, is centered on tetrad axes, while the other ring (Type 2) is centered on tetrad screw axes. He has proposed a substitutional scheme of Al for Si in each of the rings, which might make it feasible to use shifts in infrared absorption bands which are due to compositional changes as a means of distinguishing bands which arise in one or the other ring sites or in the linkages between them. The purpose of this paper, other than examining the infrared spectra of scapolite in detail over a large compositional range, is to attempt to find a model through which the various bands can be assigned to certain subunits of structure and which is compatible with present knowledge of the structure and crystal chemistry of scapolite.

Previous work on the infrared spectra of scapolite is sparse. Two studies that should be mentioned are by Milkey (1960) and Schwarcz and Speelman (1965). Milkey's well-known work is of the reconnaissance kind in which the infrared spectra of the tectosilicates is broadly characterized. He includes several spectra of scapolites of different compositions and makes the suggestion that analysis of the spectra of a series of chemically analyzed scapolites should yield a curve giving the relationship of peak wavelength and aluminum content. The work by Schwarcz and Speelman will be discussed later in this paper. They investigated the role of carbon and sulfur in scapolite and were able to show that

carbon is coordinated in the scapolite structure as the carbonate radical which is placed in a low symmetry site.

EXPERIMENTAL METHODS

A Perkin-Elmer, model 337, grating infrared spectrophotometer with a two range span of 4000–400 cm^{-1} was used. Range 1 is between 4000–1200 cm^{-1} , and Range 2 is 1333–400 cm^{-1} .

The spectral trace of powdered samples was obtained by the KBr disc method. 0.75 mgm. of hand-picked sample was mixed with 250 mgm. KBr to give a disc 0.06 cm. thickness and 1.30 cm. diameter. The spectrophotometer was usually run using a normal slit control program with a slow scan time.

Values of wavenumbers were read to 5 cm^{-1} in Range 1 and to 1 cm^{-1} in Range 2. The reproductibility of wavenumber is within that of published specification (4 cm^{-1} for Range 1 and 1.3 cm^{-1} for Range 2). It is believed that the accuracy of values of wavenumbers are within published specifications ($\pm 6 \text{ cm}^{-1}$ for Range 1 and $\pm 2 \text{ cm}^{-1}$ Range 2) except in the 1100–1333 cm^{-1} portion of Range 2, where calibration with indene suggests an abscissa accuracy of $\pm 3 \text{ cm}^{-1}$.

SAMPLE PREPARATION

Samples from the McMaster University Collection had already been purified by methods described by D. M. Shaw (1960). It only remained to select the required grains under the microscope.

The rest of the samples were prepared by selecting individual single crystals and crushing them to <100 mesh. Magnetic impurities were removed by means of an isodynamic separator. The sample for use was selected by hand-picking under a microscope.

CONTROL OF CHEMICAL COMPOSITION

Of the 23 samples examined, 21 were controlled by chemical analysis, of which 5 had the further control of microprobe analyses (Table 1). Two of the chemically analyzed samples had a further control using index of refraction measurements based on the linear regression equation for mean index of refraction vs. percent Me given by D. M. Shaw (1960). The remaining samples were controlled only by index of refraction measurements. The determination of index of refraction was made using monochromatic sodium light. Matched liquids were checked immediately with an Abbe refractometer. Measurements of index of refraction are believed to be good to ± 0.001 .

A partial chemical analysis of sample 1928a, from Mt. Somma, Italy, gave the results:

| | |
|-------------------|-------|
| Na ₂ O | 2.07 |
| K ₂ O | 1.04 |
| CaO | 19.53 |
| <hr/> | |
| % Me | 79.7 |

analyst: J. H. Scoon

EXPERIMENTAL RESULTS

Figure 1 shows the infrared absorption spectra obtained for several representative powdered scapolites. A small spike locates two of the CO_3^{-2} bands at 669 cm^{-1} and 850 cm^{-1} . Arrows locate the Si tetrahedral

TABLE 1. COMPOSITIONAL CONTROL OF SAMPLES

| Source | Sample No. | Locality | %Me (conventional anal.) | %Me (Micro- probe anal.) | %Me (optical anal.) ^a | Indices of refraction ^b | |
|--------|------------|---|--------------------------------|-----------------------------------|--|------------------------------------|-------|
| (1) | ON-8 | Gooderham, Ontario | 19.4 ^b | 21.3 ^c | | | |
| (2) | 19702 | Libarens, near Mauleon Pyrenees | | | 26.4 | 1.554 | 1.542 |
| (3) | 2119 | Yerington, Nevada | | | 30.4 | 1.559 | 1.541 |
| (1) | ON-7 | Monmouth Twp, Ontario | 33.0 ^d | 33.3 | | | |
| (1) | GL | Gibb Lake, Pontiac Co., Quebec | 32.5 ^c | 34.1 | | | |
| (2) | 19701 | Arendal, Norway | | | 34.3 | 1.560 | 1.552 |
| (1) | On-6A | Monmouth Twp, Ontario | 33.5 ^b | 34.9 | | | |
| (1) | S-16-2 | — | 55.3 ^f | | 39.3 | 1.563 | 1.546 |
| (2) | T-123 | Craigmont Quarries Raglan Co., Ontario | | | 40.2 | 1.570 | 1.540 |
| (1) | Q-87A | Huddersfield Twp, Quebec | 46.2 ^b | 42.8 | | | |
| (1) | S-83-4 | — | 45.4 ^f | | | | |
| (1) | Q-19D | Huddersfield Twp, Quebec | 47.5 ^b | | | | |
| (2) | 2003 | St. Lawrence Co., New York | | | 50.1 | 1.571 | 1.542 |
| (2) | T-48 | Bronson, Near Bancroft, Ontario | | | 55.0 | 1.576 | 1.549 |
| (1) | S-43-5 | — | 56.3 ^f | | | | |
| (3) | 839 | New York State | | | 59.0 | 1.576 | 1.553 |
| (1) | S-55 | — | 60.5 ^f | | | | |
| (2) | 2004 | Laurinkari, Finland | | | 62.0 | 1.577 | 1.555 |
| (2) | 1939 | Bolton, Massachusetts | | | 62.9 | 1.582 | 1.551 |
| (1) | M730 | Grenville, Quebec | 70.1 ^b | 74.8 | | | |
| (2) | 1928a | Mt. Somma, Italy | 79.7 ^a | | 78.6 | 1.590 | 1.559 |
| (2) | 1928b | Mt. Somma, Italy | | | 87.3 | 1.599 | 1.561 |
| (2) | 1925 | Fosso Grande, Mt. Vesuvius, Italy | | | 90.6 | 1.599 | 1.562 |

(1) McMaster University Collection.

(2) University of Cambridge Collection.

(3) University of Montana Collection.

^a This work^b Conventional analyses by C. O. Ingamells in Shaw (1960).^c Conventional analysis by J. Muysson in Shaw, Schwarcz, and Sheppard (1965).^d Conventional analysis by E. Martinec in Ingamells and Gittens (1967).^e Microprobe analyses by E. W. Evans, D. M. Shaw, and D. R. Haughton (1969).^f Conventional analyses by E. L. Speelman.

fundamental modes at 1030 cm^{-1} and 988 cm^{-1} and the Al tetrahedral fundamental mode at 950 cm^{-1} .

Figure 2 gives the location of absorption maxima and shoulders as a function of percent meionite. The criteria for deciding whether a particular maximum or a shoulder on a strong peak should be considered in this study are: (1) all definite maxima were considered to locate the position of a band whether they were very strong and well-defined (as the

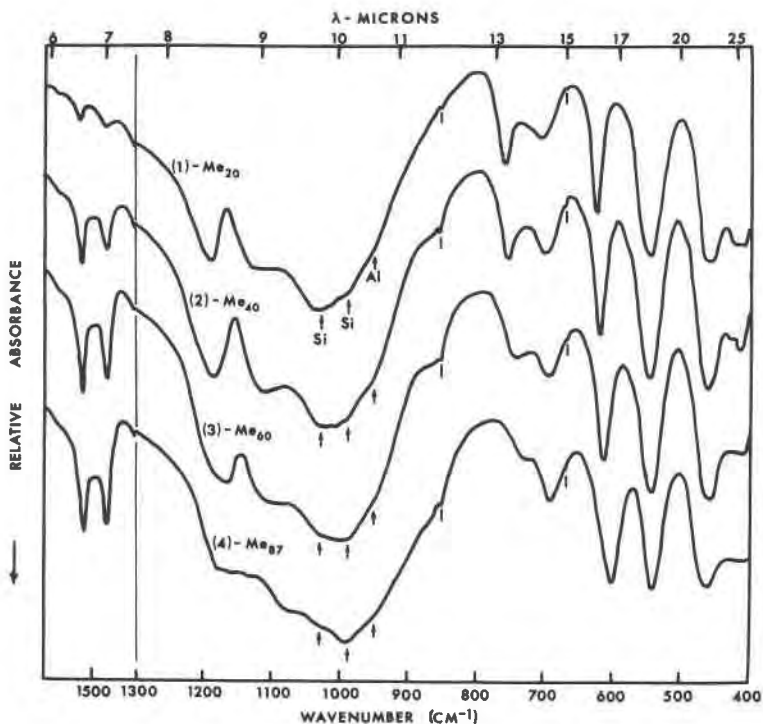


FIG. 1. Infrared absorption spectra for four typical scapolites. Arrows indicate position of the Si and Al fundamental Matossi modes. The ticks locate the position of CO_3^{2-} modes at 850 cm^{-1} and 669 cm^{-1} . Solid vertical line indicates change of scale.

band at 610 cm^{-1}), or were weak but highly persistent over a considerable range of composition (as at 850 cm^{-1}); (2) less well-defined maxima (as at 1060 cm^{-1}) were used if they were found in a number of spectra with a range of composition and were either invariant in wave-number with composition, or if they changed uniformly with a change of composition (as at 860 cm^{-1}); (3) if a well-defined change of slope occurred on the shoulder of a maximum, a band was inferred to be located at the point of break of slope if the shoulder was persistent and invariant in position in a number of spectra (as at 1215 cm^{-1}); (4) in some cases well-defined maxima passed into shoulders on an intermediate maximum (as in the region of $1160\text{--}1180 \text{ cm}^{-1}$). These shoulders were considered to be the extensions of the bands represented by the adjacent maxima.

These criteria obviously allow the inclusion of maxima and particularly of shoulders that may not be real bands. In some cases, these quasi-bands may be recognized; but in other cases, they can go unrecognized,

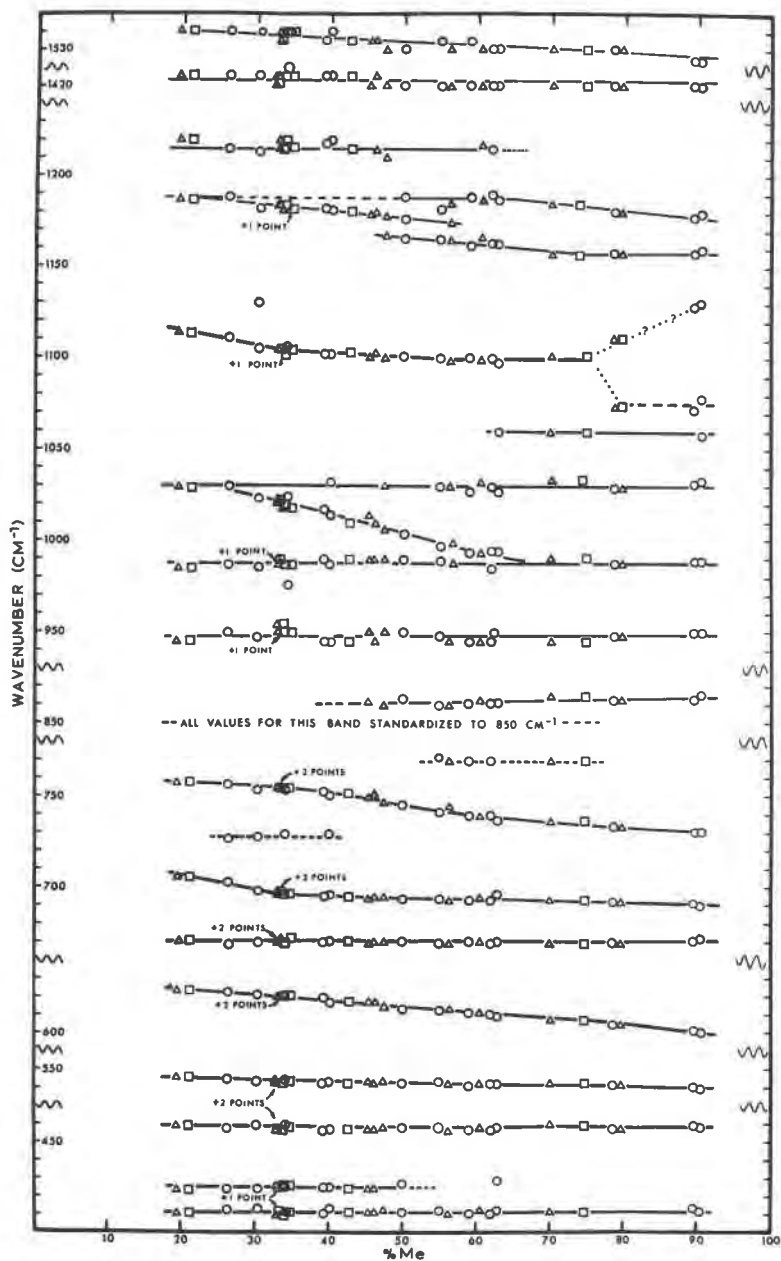


Fig. 2. Position of infrared absorption band for scapolite as a function of % Me. Triangles are for points controlled by standard chemical analysis, squares are for points controlled by microprobe analysis. (Both points are included if controlled by both methods of analysis). Circles are for points controlled by optical means.

particularly where over-lapping bands that are of asymmetric form give rise to false maxima (this may be the case for the band at 730 cm^{-1}). The advantage of this approach is that it offers a maximum amount of information for the construction of models, most of which must be accounted for by the "best" model or models, but a fair proportion of this useful information cannot be evaluated prior to the model building. An arbitrary selection of "good" bands before the models are made may forfeit the information that is required, not only for choosing the "best" models, but also to construct them. One criterion for the "best" model would be that it satisfactorily explains a maximum number of well-defined bands and at the same time can accommodate other bands that before evaluation might be placed in the doubtful category but which fit the model.

Where compositions of scapolite have been determined by microprobe analysis, as well as chemical analysis, both values for the sample are plotted in order to suggest the range of compositional uncertainty. With the exception of one point, there is good correlation between composition and position of bands. Sample S-16-2 ($\text{Me}_{55.3}$) falls well outside the distribution of the other points. Careful measurement of index of refraction on a single grain of this sample gave a value of $\text{Me}_{39.3}$, which falls in the range of the other samples. Because the sample was only a few milligrams in size and there is no reason to question the chemical analysis, the discrepancy must either be due to inhomogeneity of the original sample or to subsequent contamination. This point was not considered in further evaluation of the bands.

The overlapping of a great number of bands in the $900\text{--}1300\text{ cm}^{-1}$ region, together with the lack of information as to their shape, leads to a considerable uncertainty not only with respect to the position of absorption maxima, but also their physical meaning. The position of these bands can only be regarded as certain within $\pm 10\text{ cm}^{-1}$. The ability to discern a band shift between two samples of neighboring composition, however, is somewhat better because experience indicates band positions and band shapes do not change much with a small change of composition over most of the range of composition. The scatter of points for band maxima and shoulders from their respective curves generally lies within $\pm 4\text{ cm}^{-1}$, and so consistent band shifts that are greater than this value, over the range of composition, probably are significant.

The very sharp band at 850 cm^{-1} that occurs as a shoulder on the main absorption maximum was found to be invariant over a wide range of composition in spectra that were all obtained over the course of one day. Minor variations in this position were found upon cleaning and ad-

justment of the instrument, as well as minor secular changes that occurred from day to day. Calibration of the instrument with indene gave the best value for this band as 850 cm^{-1} and accordingly the wavenumbers in each spectrum were adjusted to this standard. The standard deviation of raw values from this standard value is $\pm .33\text{ cm}^{-1}$.

The interpretation of these data in terms of compositional variation of individual bands is shown in Figure 3. Capital letters to the right of the bands designate each band. The thickness of a given band is proportional to the peak or shoulder height of the band using the minimum absorption near 800 cm^{-1} as a base for bands that lie in Range 2. Shoulders or portions of bands that occur as shoulders are marked *S* adjacent to the band. Band *R* is the only one, which on absolute scale of absorption, remains most nearly constant and linear as a function of composition. It shows a small increase in peak height with increasing meionite content. All band intensities of a given spectrum were adjusted to this standard to correct for variations in peak heights due to sample preparation and instrumental factors.

USE OF THE INFRARED SPECTRUM TO DETERMINE THE COMPOSITION OF SCAPOLITE

Only one band, located near 610 cm^{-1} , is useful for the determination of percent Me throughout the compositional range of $\text{Me}_{20}\text{--Me}_{90}$. This band approaches a straight line as a function of wavenumber vs. percent Me, with a change in slope at Me_{75} .

The linear least squares function for compositions in the range $\text{Me}_{20}\text{--Me}_{75}$ using only points with chemical analytical control is:

$$\% \text{ Me} = 2015.6 - 3.1928\sigma$$

where σ is the wavenumber (cm^{-1}) of the 610 band. The standard deviation for this function is $\pm 0.74\text{ cm}^{-1}$. The standard deviation from this equation for points based on optical measurement of composition in this range is $\pm 1.11\text{ cm}^{-1}$. The uncertainty of measurement of values of meionite percentage at the 95 percent confidence level in this range is ± 4.8 percent.

A similar function for compositions greater than Me_{75} may be approximated by another linear function:

$$\% \text{ Me} = 1431.7 - 2.232\sigma$$

The standard deviation for all points in this range is $\pm 1.08\text{ cm}^{-1}$.

INTERPRETATION OF DATA

1. *The Carbonate Spectrum.* The carbonate spectrum of scapolite has been described by H. P. Schwarcz and E. L. Speelman (1965). They

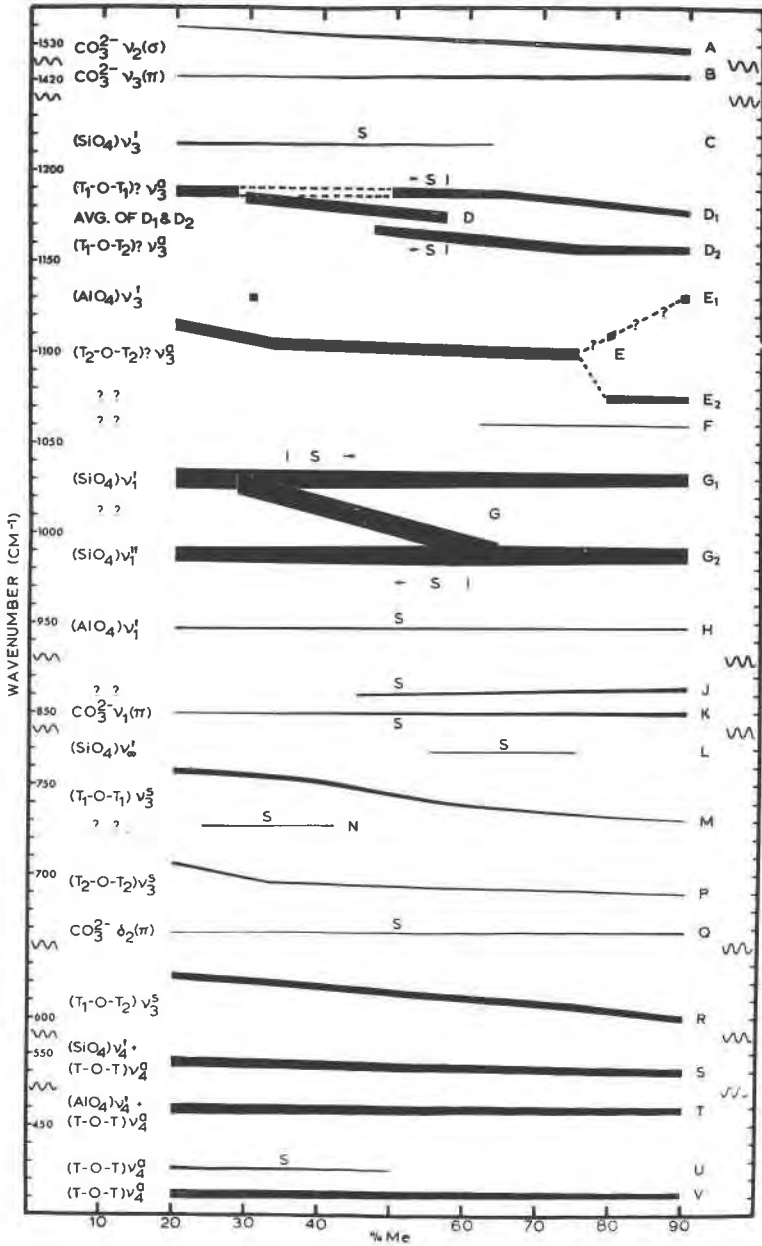


FIG. 3. Band intensity as a function of composition. S indicates presence of band as a shoulder. Capital letters to the right of bands designate the adjacent band. To the left of each band is its tentative interpretation.

showed that the carbon in scapolite occurs as the carbonate ion, and identified the mode species. They also suggested that the plane of the carbonate ion is perpendicular to the cation square, which lies in the (001) plane, and that it is parallel with one edge of the square.

The carbonate spectra of powdered scapolites in this study are similar to those of Schwarcz and Speelman except for these additional details: a small but persistent, sharp, invariant peak (Band *Q*) was found as a shoulder at 669 cm^{-1} . Its intensity increases with carbonate content and it is believed to be a carbonate band. Band *A* at about 1530 cm^{-1} decreases in wavenumber with increasing meionite content, while Band *B* (1420 cm^{-1}), within the precision of measurement, remains constant with change of composition.

Schwarcz and Speelman point out that the splitting of the ν_2 mode of the carbonate ion is due to the lowering of site symmetry (to C_{2v}). It may be useful to consider this to be a special case of an XZY_2 molecule in which the mass of *Z* equals that of *Y*. The bands accordingly may be assigned (Beckmann, Gutjahr, and Mecke, 1964):

| | | | | | | |
|------------|--------------|-----------------|--------------|--------------------|-----------------|----------|
| vibration | $\nu_1(\Pi)$ | $\nu_2(\sigma)$ | $\nu_3(\Pi)$ | $\delta_1(\sigma)$ | $\delta_2(\Pi)$ | γ |
| class | A_1 | B_1 | A_1 | B_1 | A_1 | B_1 |
| wavenumber | 850 | ~ 1530 | 1420 | — | 669 | — |

Wolfram and de Wames (1966) show that vibrations of the A_1 class are independent of geometrical changes (*i.e.*, purely mass dependent), while B_1 class vibrations are mass-geometry dependent. Because the mass of the carbonate ion remains constant, class A_1 bands remain constant over the range of scapolite composition; but class B_1 bands, of which only the one at 1530 cm^{-1} is observed, reflect the change of cation environment in the decreasing value of wavenumber toward the meionite end member.

The Framework Spectra of Scapolite, Invariant Bands. The curves in Figure 3 show that there are essentially two kinds of spectra—those that vary in wavenumber with composition and those that are invariant. A reasonable model for the invariant bands is that at least some of these are due to vibrational modes of individual tetrahedra as first suggested by Schaefer, Matossi, and Wirtz (1934). To clarify the character of this vibrational unit and to emphasize its relative independence, it shall be designated in this paper as a $T(O/2)_4$ unit. The half oxygen is used because in the central force model used below, the tetrahedron is essentially “decoupled” from neighboring tetrahedra by assigning half mass to the oxygens. Boillet (1962) interprets the splitting of the 1000 cm^{-1} ν_1

TABLE 2. GROUP FREQUENCIES AND CALCULATED FORCE CONSTANTS FOR $\text{Si}(\text{O}/2)_4$ AND $\text{Al}(\text{O}/2)_4$

| Group | ν_3 | ν_1 | ν_{90} | ν_4 | ν_2 | force constants ($\times 10^5$ dynes/cm) | | |
|--------------------------------|-------------|---------|------------|---------|---------|--|------|------|
| | | | | | | k_2 | k' | k |
| $\text{Si}(\text{O}/2)_4$ obs. | ~ 1215 | 1030 | 770 | 543* | — | | | |
| calc. | 1222 | 1030 | 762 | 540 | 252 | 5.0 | 0.0 | -0.3 |
| $\text{Al}(\text{O}/2)_4$ obs. | ~ 1130 | 948 | — | 458* | — | | | |
| calc. | 1129 | 950 | 701 | 450 | 206 | 4.25 | 0.0 | -0.2 |

* Overlapped with another band.

vibration of orthoclase as being due to constraint of the fundamental mode of the SiO_4 tetrahedron to two frequencies which arise out of the possible ways the tetrahedra can cooperatively vibrate in the feldspar ring. Langer and Schreyer (1969) suggest that the mode near 950 cm^{-1} in cordierite may be the fundamental mode for AlO_4 tetrahedra.

In the scapolite spectra, we find an invariant band (G_1) at 1030 cm^{-1} and another at 988 cm^{-1} (G_2) which probably correspond to the split ν_1 $\text{Si}(\text{O}/2)_4$ mode found in feldspar by Boillet (1010 cm^{-1} and 990 cm^{-1}). His single crystal spectra showed that the 990 cm^{-1} band is very weak in comparison to the 1010 cm^{-1} band. The strong modes are here designated ν' ; the weak modes are ν'' . The comparable scapolite modes associated with the 1030 cm^{-1} ν_1' mode are present, those associated with the 988 cm^{-1} ν_1'' mode are not observed. Using the central-force model for framework silicates derived by Matossi (1949), a good fit of calculated frequencies may be made with those of invariant bands for the strong modes of the $\text{Si}(\text{O}/2)_4$ and the $\text{Al}(\text{O}/2)_4$ tetrahedra (Table 2). The force constant k in this model is a/l where a is a linear term given in the equations relating the forces acting upon one oxygen due to the other oxygens in the tetrahedron and l is the oxygen-oxygen distance (Herzberg, 1945). The value of k for $\text{Si}(\text{O}/2)_4$ compares very well with the value of $-.26 \times 10^5$ dynes/cm. given by Matossi (1949) for quartz. The force constant k_2 relates the forces acting between the Si and O atoms and is that used by Saksena (1961). The force constant k' is usually chosen at about $.4-.7 \times 10^5$ dynes/cm (Matossi, 1949; Saksena, 1961), but the present model seems to suggest that the deformational interaction between neighboring oxygens in the tetrahedra approaches nil since $k'=0$.

With regard to the $\text{Al}(\text{O}/2)_4$ vibrations, in a preliminary scanning of the plagioclase spectra, an andesine (University of Cambridge Collection No. 3657) shows a marked dampening and smearing out of the

structural modes but the $T(O/2)_4$ modes are quite prominent, particularly the $Si(O/2)_4 \nu_1$ modes at 1032 cm^{-1} and 995 cm^{-1} and the $Al(O/2)_4 \nu_1'$ mode at 947 cm^{-1} as well as a band at 915 cm^{-1} . This last band might be the weak $Al(O/2)_4 \nu_1''$ mode corresponding to the equivalent Si mode at 995 cm^{-1} . Langer and Schreyer (1969) also observe a mode at $908\text{--}911 \text{ cm}^{-1}$ in cordierite, while analysis of the asymmetric tail of the absorption maximum for scapolites suggests the possibility of a minor invariant band at about 912 cm^{-1} , which might likewise be interpreted as the weak $Al(O/2)_4 \nu_1''$ mode.

In view of the fact that those modes have been sufficiently documented, it may be useful to distinguish them from other kinds of modes by designating them as Matossi modes, after Frank Matossi who did so much of the important pioneering work in deciphering the infrared spectra of silicate minerals.

Matossi modes are defined as those vibrational modes of a mixed crystal which are limited to the smallest subunits of structure that give rise to vibrational energy transitions in the crystal and whose frequencies are not dependent on compositional variation in the structure. They differ from the ordinary vibrational modes (structural modes as used in this paper) in that the latter embrace a larger subunit of structure in the mixed crystal and thus are affected by compositional changes in the crystal. At the present time they have been recognized in only a few of the silicates, principally tectosilicates. It will be interesting to see if this is a general phenomenon for those structures in which the oxygens are entirely shared between low coordination number cations.

We thus conclude that the fundamental Matossi modes in scapolite occur at 1030 cm^{-1} and 988 cm^{-1} for the silica tetrahedra and at 950 cm^{-1} and possibly 912 cm^{-1} for the alumina tetrahedra.

Variable Bands in the Framework Spectra of Scapolite. For the purposes of this paper, we shall designate Papike's Type 1 ring as the T_1 ring and the four corresponding tetrahedral sites as T_1 , and likewise his Type 2 ring is designated as T_2 .

The general aspect of the variable bands is that they shift toward lower wavenumbers with increasing Al substitution, as would be expected. If we consider these modes to arise exclusively from each of the fourfold rings, we find that the number of degrees of freedom are considerably greater than the number of modes observed. The T_1 ring (point symmetry C_{4h}) should give rise to 4 A and 6 E modes, while the T_2 ring (point symmetry S_4) gives rise to 11 A modes and 10 E modes. Considering that the low wavenumber end of the spectrum is cut off, and that it is likely that there is overlapping of bands but that ring linking

bonds are certain to contribute a fair number of modes of vibration, it is necessary to construct a highly degenerate model in order to account for so few bands in the actual spectrum.

We begin the construction of a working model by designating the variable bands occurring in the 1190–190 cm^{-1} region as the asymmetric ν_3 structural modes, the bands in the 760–600 cm^{-1} region as the symmetric ν_3 structural modes and bands from the 550–400 cm^{-1} as the asymmetric ν_4 modes. These latter modes appear to be nearly constant with change of composition and may overlap the Matossi modes in this region.

Because bands *M*, *P*, and *Q* are well resolved (see Fig. 1), an interpretation of the structural modes might best start with them. Band *P* shows an abrupt change of slope at about Me_{33} . According to the substitutional scheme of Al/Si in the scapolite structure found by Papike (1965), Al substitutes preferentially in the T_2 position until the number of Al atoms equals the number of Si atoms in that position (at $\text{Me}_{33.25}$). The behavior of this band is consistent with the concept that it arises out of vibrations originating in T_2 site structural units.

Band *M* has a double flexure at about Me_{40} and Me_{65} . According to the Papike scheme, the T_1 site should have no Al in it until the T_2 site is filled up at $\text{Me}_{33.25}$. The T_1 site will continue to fill up with continuing Al substitution until at a composition of about Me_{65} the T_1 ring will have, on the average, 1 Al per ring. At Me_{100} this will have increased to 2 Al per ring. I suggest that the double flexure of Band *M* might be explained by the following: the low slope in the Me_{0-40} part of the band is due to no essential change in composition of the T_1 ring at least to Me_{34} , but it does reflect minor changes in geometry within the ring, and changes in the environment about the ring. Substitution of Al in the ring in the ratio of one per four positions causes an abrupt decrease in band position of about 7 wavenumbers, and the region of high slope corresponds to the average band maxima created by mixture of the all Si T_1 rings with T_1 rings that have an Al/Si = $\frac{1}{4}$. The slope of band *M* in the region $\text{Me}_{>65}$ is very nearly that for the all Si T_1 ring. This plus the observation that the intensity of the band rapidly decreases at compositions of $\text{Me}_{>65}$ suggests that putting an equal number of Al and Si atoms in the T_1 ring dampens the mode, so that the intensity of the band in this region arises only out of the rings with an Al/Si ratio of $\frac{1}{4}$. The slope of this part of the curve as before is due to constantly changing factors in intra ring geometry and in the environment immediately around the ring.

Band *R* shows a distinct flexure at Me_{75} . Since the standard deviation of points at compositions $\text{Me}_{>75}$ (calculated on the basis of the least squares function for compositions $\text{Me}_{<75}$) lies outside twice the standard

deviation for that function, it is believed that this flexure is real. A scanning of bands *P* and *M* also suggest a similar flexure at Me_{75} , but statistically cannot be justified. Evans, Shaw, and Haughton (1969) propose that anion substitution of CO_3^{2-} for Cl^{-1} is completed at Me_{75} . Structurally, this implies that there should be, at this composition, a change in rate of change of bond angle between the T_1 and T_2 rings with change of composition. We infer, then, that Band *R* is associated with the $T_2\text{-O-}T_2$ bond.

Looking at the asymmetric ν_3 bands, band *D* appears to be due to the convergence of bands D_1 and D_2 . D_1 and D_2 show breaks in slope similar to, but antithetic to, those of bands *M* and *P*. Band *E* is very complex; its behavior at compositions greater than Me_{75} is not understood. Probably the effect is one of several overlapping bands rather than splitting of the band. The form of Band *E*, however, is strikingly similar to that of Band *P*, so we suggest that it too is a $T_2\text{-O-}T_2$ structural unit vibration. In the same way, Band *G* might be assigned to a $T_1\text{-O-}T_1$ vibration, however, the exact form of the fundamental Matossi modes is not known and they might add intensities to give the intermediate maximum that is observed.

At the present time, there does not appear to be any way to assign the asymmetric ν_4 modes.

THE QUESTION OF THERMAL HISTORY

Although infrared absorption is a very sensitive technique to discerning ordering in crystals, the data in Figure 2 do not give any suggestion, at least in the range $\text{Me}_{20}\text{-Me}_{75}$, that order-disorder plays a role *independent* of composition in the scapolites. A possible exception to this is the scapolite described by Papike (1966) that was found by M. Bown to show weak reflections that violate body-centered symmetry in single crystal photographs. Unfortunately, this sample was not studied. If any of the samples studied had a thermal history significantly different from that of samples of neighboring compositions, for example the cluster of samples near Me_{33} , one would expect a greater deviation in wavenumber from the curves than actually is observed.

Since the character of the curves in Figure 2 is considerably changed for compositions greater than 75 percent meionite, the possibility should be considered that perhaps part of this might be due to ordering effects. Several overexposed *c*-axis rotation photographs were made of sample 1928b (Me_{87}), but no diffraction spots were found that indicated anything other than a simple body-centered cell. It is more reasonable to suggest that, in the absence of crystal structural information on the calcic scapolites, the decrease in intensity of certain bands may allow

the unmasking of other low intensity bands to give rise to an apparent splitting. It should be noted that no splitting of bands is seen in the 600–770 cm^{-1} range where bands are well resolved. The reason for the decrease in intensity must be merely speculative, but slight changes of structure are known to cause major changes of intensities of bands.

Heitanen (1967) on the basis of field observation has shown an empirical relationship between the grade of metamorphism and the composition of scapolite. If this relationship is dominantly controlled by temperature, then one can immediately see that the state of ordering of most scapolites would not be independent of their compositions and that both would be dependent upon the conditions of formation. Hence, thermal history probably will not show up in the scapolites as it does in the infrared spectra of feldspars (Laves and Hafner, 1956). It should be noted that the scapolites studied in this work come from a wide range of occurrences and environments of formation.

CONCLUSIONS

The scapolite infrared absorption spectrum may be almost entirely qualitatively explained in terms of three sets of vibrational modes based upon highly simplified models that are consistent with present day concepts of the scapolite stoichiometry and structure.

The first set of modes arises from the carbonate ion which, being placed in a low symmetry site, behaves like an XZY_2 molecule.

The second set of modes is invariant with chemical composition. These modes arise out of the vibrations of discrete $T(O/2)_4$ tetrahedral units. They have been observed primarily so far in the framework structures but have also been observed in cordierite. They have been observed for both Si and Al occupied sites and are generally split, probably for symmetry reasons. It is proposed that these modes be called Matossi modes to distinguish them from the variable modes that arise out of the averaged tetrahedral site population (herein called structural modes).

The third set of modes, the structural modes, vary in wavenumber with composition. Their behavior may be tentatively explained by assuming that each of three sets of very small structural units independently give rise to a set of vibrations whose positions are a function of the Al/Si ratio in the tetrahedral sites associated with the unit. The precise nature of these structural units is undefined, but one seems to involve only $T_1\text{-O-}T_1$ bonds, the second $T_2\text{-O-}T_2$ bonds, and third $T_1\text{-O-}T_2$ bonds.

The effects of tetrahedral site population changes are readily discerned in the scapolite spectra. They allow the following conclusions with respect to the Al/Si distribution in scapolite. (1) The Al/Si dis-

tribution between the T_1 and T_2 sites are proposed by Papike and others (1965 and 1966) on the basis of two crystal structure determinations is supported in the present study over a range of Me_{20} - Me_{75} . Until a full X-ray structural determination is made on a $>Me_{75}$ scapolite, full interpretation of the infrared silicate structural modes is not possible for the calcic scapolites. (2) Within a given site, the distribution (over the whole structure) of Al and Si is random, with the proviso that wherever possible, the nearest cation neighbors of Al-Al are not permitted in accordance with the Loewenstein rule (Loewenstein, 1954). (If this random distribution did not obtain, one would expect a splitting of ν_3 bands as observed by Laves and Hafner, 1955, in feldspars).

The suggested assignments for each band are listed on the left side of Figure 3 beside their respective band.

As a general conclusion, the approach towards the interpretation of the spectra of scapolite used in this study suggests that an empirical approach to the interpretation of the infrared spectra of alumina-silicates using a very simple model of small structural units giving rise to discrete sets of vibrational modes should be readily proven valid or not by a similar study of another mineral group such as the plagioclase feldspars. They, of course, have the added variable of structural state.

ACKNOWLEDGEMENTS

This work was carried out during the course of a sabbatical year granted by the University of Montana to the writer who gratefully thanks Professor W. A. Deer for the hospitality of the Department of Mineralogy and Petrology, University of Cambridge, where the work was done during the year 1969-1970. Further thanks are extended to Dr. J. D. C. McConnell for the use of laboratory facilities, to Dr. S. O. Agrell, Dr. M. Bown, and Professor D. M. Shaw for generously supplying samples, as well as John M. Scoon for the chemical analysis.

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Received December 22, 1977; accepted March 25, 1971.