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INFRARED SPECTRA OF SOME TECTOSILICATES*

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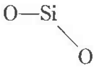
ABSTRACT

In the spectra of the tectosilicates analyzed, the major absorption peaks, which are due to the primarily bond-stretching vibrations of the



linkages, occur within a narrow range of the spectrum from 9.1 to 10.2μ. The spectra may be used in some cases, such as for orthoclase and microcline, to distinguish between similar materials. For others, such as noselite, hauynite, and lapis lazuli, the spectra are too similar for purposes of identification. The specificity of such spectra might be increased by extending the study to include wavelengths longer than 15 microns.

The wavelengths of the major absorption peaks show an irregular, but definite, shift toward longer wavelengths as the aluminum-silicon ratio increases: the introduction of aluminum into the framework increases some of the bond-lengths and decreases bond force constants, resulting in lower frequencies of vibration for the major absorption bands. The infrared spectra could generally be correlated in groups according to similarities in tetrahedral frameworks. However, dissimilar spectra obtained from some tectosilicates with identical frameworks but differing cations, indicated that in some cases the comparatively weak bonds between cation and framework may produce alterations in absorption.

The major absorption peak of most of the tectosilicates showed a high intensity, reflecting the substantial ionic character of the silicon-oxygen bond. As little as a few micrograms of some of the tectosilicates may be detected from their absorptions.

INTRODUCTION

In the literature there have appeared some infrared spectra of various silicates. Hunt, Wisherd, and Bonham (1950), in a survey of some minerals and inorganic compounds, have presented the infrared spectra of some layer silicates and tectosilicates. Launer (1952) has offered the infrared spectra of some silicates of each class, including 4 silica minerals and 9 tectosilicates. Keller, Spotts, and Biggs (1952) also presented several minerals of each silicate class in a similar type of survey. However, no comprehensive survey has been attempted of any of the major classes of silicates.

In this paper, the infrared spectra of 57 tectosilicates are presented, and also some correlations and interpretations of the various absorption bands.

EXPERIMENTAL PROCEDURE

The mineral samples analyzed were obtained from the National Museum, Washington, D. C., from Dr. Frank Schairer, Geophysical Lab-

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oratory, and from Jewell Glass, David Stewart, John Hathaway, and the collection of Esper S. Larsen, Jr., all of the U. S. Geological Survey. Confirmation of identification of the samples from the National Museum was, in each case, made by optical means, and, when necessary, also by *x*-ray and spectrographic analyses. Compositions of the plagioclase feldspars were determined by method of extinction angles, and their compositional error is estimated to be within 5 per cent. *X*-ray analyses were performed by Daphne Ross, optical analyses by Sam Rubinstein and W. W. Virgin, and spectrographic analyses by Katherine Hazel, all of the U. S. Geological Survey.

Each sample was prepared for infrared analysis using the potassium-bromide imbedding-window method:

Two-tenths milligram of the finely divided silicate was mixed with reagent grade KBr which had been ground to pass 300-mesh screen, dried at 110° C. for several days, and thereafter stored over drierite. The silicate was dispersed throughout the KBr by mixing manually in a mullite mortar for about 20 minutes, or alternately by agitation in the bakelite capsule of a mechanical agitator. The mixture of sample and KBr was pressed in a tool-steel die at a pressure of nearly 100,000 psi too form a more-or-less transparent pellet, or window, having a 0.5-inch diameter and a thickness of approximately 0.4 mm. The window was placed in the sample beam of the infrared spectrophotometer.

The infrared spectra were obtained using a Perkin-Elmer Model 21 double beam infrared spectrophotometer, with sodium chloride optics. Instrument settings were: Resolution 927, gain 5, response 1, source amperage 0.3, suppression 2, and speed of recording 1 minute per micron. For wavelengths longer than 7 microns, calibration of the spectrophotometer was made by reference to the polyethylene absorption peaks at 8.662 microns (1154 cm.^{-1}), 9.724 microns (1028 cm.^{-1}), and 11.035 microns (906 cm.^{-1}). The $\Delta(\text{cm}^{-1})$ for these three peaks was -1 cm.^{-1}, $+2$ cm.^{-1}, and -1 cm.^{-1}, and for each peak, the $\Delta\mu$ shown by two successive spectra obtained under the same operating conditions was 0.01μ or less.

OBSERVATIONS OF THE SPECTRA

The spectra were obtained covering the infrared region of the spectrum from 2 to 15 microns. However, the significant absorption peaks of the tectosilicates occurred at wavelengths longer than 8 microns. Therefore only that portion of the spectra between 8 and 15 microns is presented. The spectra are shown in Figs. 1 to 12.

As can be seen from the figures, the absorption spectra of the tectosilicates analyzed showed a general similarity in the region 8 to 15 microns. Most have one major broad absorption peak, the base of which extends over more than a micron. The apex of the peak, for most of them, is situated in the region of the spectrum between 9 and 10.1 microns. Only a few exceptions to this rule (plagioclase feldspars, danalite, helvite) have the peak of their major absorption outside this range, and in no case at a wavelength longer than 10.8 microns. Thus, the peak of absorption of these tectosilicates can generally be correlated within a relatively narrow segment of the spectrum.

This is advantageous for characterizing them as a group. However, it also reduces the usefulness of the spectra for analysis, because the main absorption bands of individual silicates thus commonly overlap; and, therefore, if a spectrum is obtained of a mixture of silicates, there may be difficulty in distinguishing the absorption peaks arising from the individual components. Similarly, for the identification of pure silicate samples, the usefulness of the spectra may also be somewhat limited because of the close similarity of shape that was shown by some of the spectra.

However, others of the spectra are sufficiently distinctive to indicate that the spectra may often be used for purposes of identification or analysis of the pure materials. Thus, for some of the tectosilicates, such as scolecite, mesolite, helvite, eucryptite and marialite, the major absorption bands have a distinctive sequence of two or more discrete absorption peaks whose wavelengths may be used to identify pure samples of these materials. Also, the spectra of others of the tectosilicates, such as quartz, danalite, and sodalite have various sharp secondary peaks at distinctive wavelengths; the occurrence of such peaks outside the range of the major absorption band are helpful for indicating the presence of these latter silicates in a mixture, as well as useful for identifying the pure materials.

From the standpoint of general application to analysis, the specificity of the curves is affected by some materials and unaffected by others. Thus, borates, phosphates, and perchlorates, as well as clay minerals, are examples of types of materials whose spectra exhibit conflicting absorptions, as they all produce strong absorption bands in the 9 to 10 micron range. On the other hand, the tectosilicates can be detected in the presence of such materials as polyvanadates, selenates, bromates, iodates, chromates, and permanganates, all of these inorganic materials having their major absorptions at wavelengths longer than 10 microns, and carbonates, nitrates, and thiocyanates, which have their major absorptions at wavelengths shorter than 8 microns. Of course, a sample producing no strong absorption at 9 to 10.1 microns indicates the absence of most tectosilicates.

Comparisons of the major absorption bands of the curves also indicate the relative ease of detection of these tectosilicates, because in each case two-tenths milligram of the mineral was used in obtaining the spectra. Each curve, however, represented the absorption resulting from only 0.06 mg. of silicate, as approximately only 30% of the face of the potassium bromide window subtended the light beam. At the wavelength where maximum light absorption occurred, the per cent of the incident light beam that was absorbed by the sample ranged from 39% for oligoclase to 86% for quartz. More than half of the silicates absorbed 60% or more of the incident light beam at the wavelength of maximum absorption, and almost all absorbed more than 50%. At the lower limit of detection, experiments indicated that as little as 3.7 micrograms of quartz absorbed about 10% of the incident light beam at the wavelength of maximum absorption. It is evident, therefore, that their infrared spectra may serve to detect almost trace amounts of these silicates, either as pure materials or in mixtures with other substances.

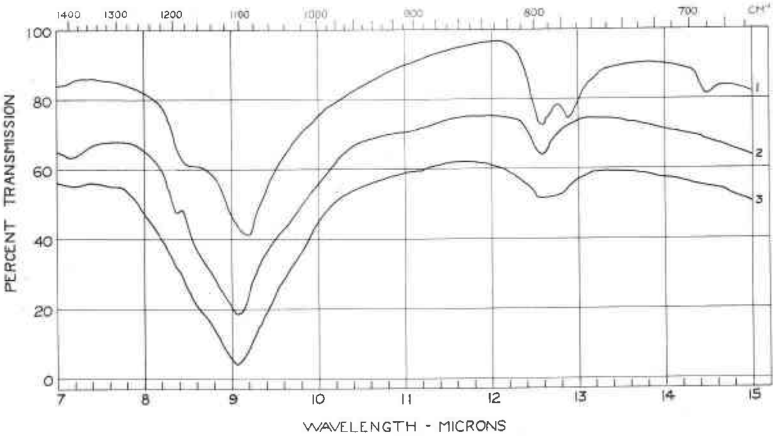


FIG. 1. Spectra of modifications of silica: (1) quartz, (2) α-cristobalite, (3) opal.

Other comments on specific spectra are of interest.

Because much infrared work has been done with the varieties of silica, only quartz, α-cristobalite, and opal of this subgroup were analyzed; the spectra obtained were similar to spectra of these minerals that have appeared in the literature (Plyler, 1929; Keller and Pickett, 1949; Hunt, Wisherd, and Bonham, 1950; Lippincott, Van Valkenburg, Weir, and Bunting, 1958), and generally similar to each other. It may be noted that their major absorption band occurs at shorter wavelengths (9.1 to 9.2 microns) than for any other of the tectosilicates.

The spectra of quartz may be readily distinguished from that of cristobalite by the secondary absorption near 12.6μ; cristobalite had only the one broad peak at near 12.6μ, whereas, in quartz, this absorption occurs as a doublet, at 12.56 and 12.84μ. The absorptions in this region are thought to occur when the silicate structure contains tetrahedra connected together in regular closed rings, as occurs in quartz (Schaefer, Matossi, and Wirtz, 1934; Matossi and Krueger, 1936). The occurrence of the 12.6μ band in the spectra of opal, similar to those of cristobalite and quartz, indicates concurrence with *x*-ray studies that opal contains in its structure, zones with periodic ordered arrangements of the tetrahedra.

The feldspar minerals, like the modifications of silica, have been the subject of various infrared investigations (Thompson and Wadsworth, 1957; Laves and Hafner, 1956). Moreover, the complex relationships of the minerals of this group merit a detailed treatment. The feldspar

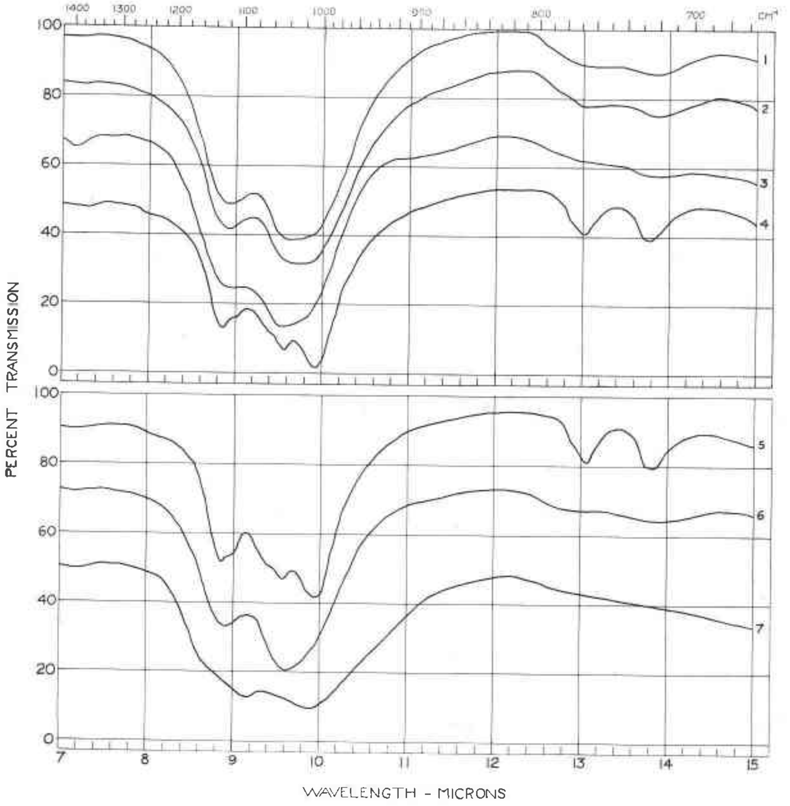


FIG. 2. Spectra of feldspars: (1) orthoclase (Rubidoux Mountains, California), (2) orthoclase (Bearpaw Mountains, Montana), (3) adularia (Miask, Urals, Russia), (4) green microcline and (5) white microcline (Amelia, Virginia), (6) anorthoclase (Essex Co., New Jersey), (7) anemousite, (Skagit River, Washington).

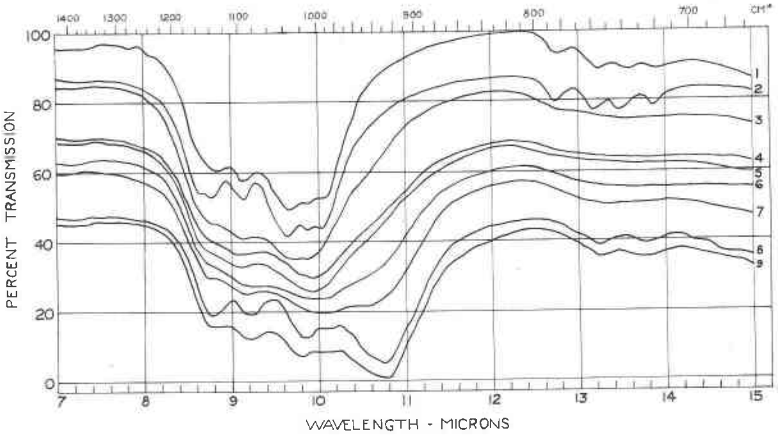


FIG. 3. Spectra of plagioclase feldspars: (1) albite, (2) oligoclase ($Ab_{90}An_{10}$) (Amelia, Va.), (3) oligoclase ($Ab_{75}An_{25}$), (4) andesine ($Ab_{66}An_{35}$) (Izu, Japan),(5), andesine ($Ab_{57}An_{43}$) (Minsen, Korea), (6) labradorite ($Ab_{40}An_{50}$) (Millard Co., Utah), (7) bytownite ($Ab_{30}An_{70}$), (8) bytownite ($Ab_{18}An_{82}$) Europe, (9) anorthite (synthetic).

spectra presented here, including orthoclase, adularia, microcline, anorthoclase, and a series of 10 plagioclases, represent only a brief reconnaissance of this group.

The spectra obtained of orthoclase and microcline conform to the observations of Keller, Spotts, and Biggs (1952), and Hunt, Wisherd, and Bonham (1950). Orthoclase and microcline can be differentiated by their spectra at wavelengths longer than 13 microns, orthoclase having only a diffuse absorption in this region, whereas microcline has two secondary peaks at 13.0 and 13.75μ. The spectra also indicate a differentiation in the main absorption peak—orthoclase having its major peak at 9.6μ, and microcline having twin major peaks at 9.52 and 9.82μ. The samples of adularia and anorthoclase analyzed produced spectra similar to that of orthoclase.

The spectra of the series of plagioclase feldspars produced a progression similar to that shown in Thompson and Wadsworth (1957). At each end of the series, the spectra show numerous well-defined absorption peaks—(the sample of $Ab_{90}An_{10}$ produced a spectra similar to that of $Ab_{97}An_3$, and at the other end of the series, $Ab_{18}An_{82}$ and synthetic anorthite produced similar absorption peaks); in the intermediate spectra, however, the well-defined peaks are replaced by broad, diffuse absorption bands, which do not provide a picture of progressive changes in structure throughout the series. (The spectra of anemousite is closely similar to that of the andesine ($Ab_{57}An_{43}$) region of the series.)

Thompson and Wadsworth extended the wavelength range beyond 15 microns to obtain further information on the intermediate members of the plagioclases; they utilized an absorption peak which undergoes a bathochromic shift from 15.4 to 16.2 microns as the weight per cent anorthite is increased from 0 to 100 per cent, to suggest a definite structural change in the series at a composition of approximately An_{31}–An_{33}. These authors also pointed out that high and low temperature forms of the plagioclase feldspars were not distinguishable by their infrared spectra.

Among the spectra of the feldspars, it is interesting to note that the sharp, well-defined absorption peaks of microcline, albite, and anorthite are indicative of their regular crystalline structures, in which aluminum

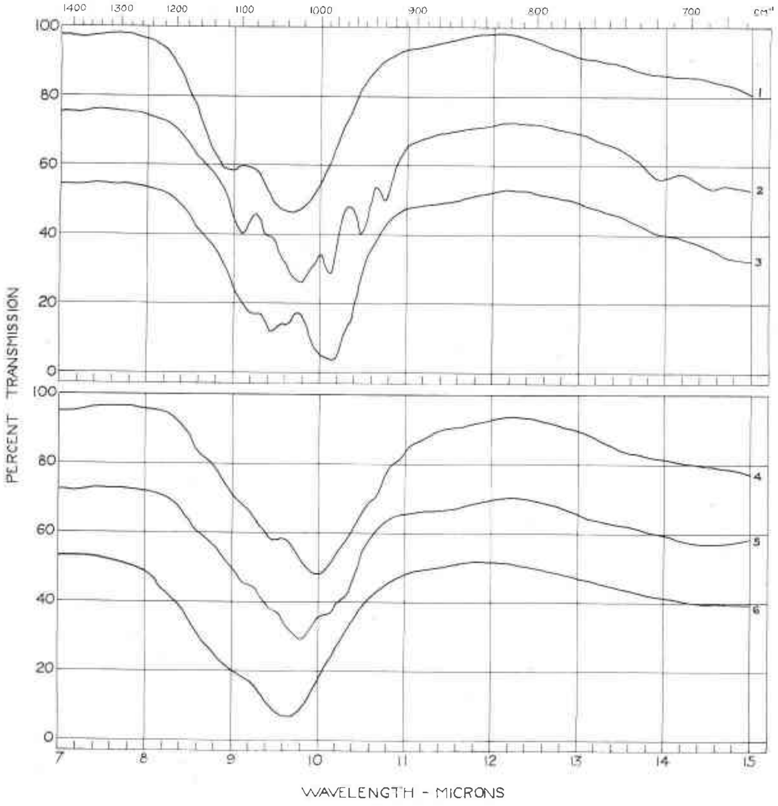


FIG. 4. Spectra of fibrous zeolites: (1) natrolite (Giant's Causeway, Ireland), (2) scolecite (Hyderabad, India), (3) mesolite (Southeast Table Mt., Colorado.), (4) thomsonite (Jefferson Co., Colorado), (5) edingtonite (Bohlet, Sweden), (6) gonnardite (Puy-de-Dome, France).

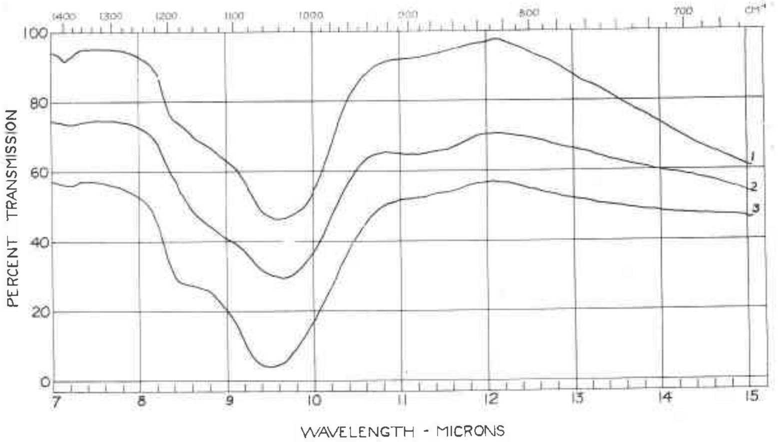


Fig. 5. Spectra of heulandite group: (1) heulandite (Paterson, New Jersey), (2) brewsterite (Argylleshire, Scotland), (3) epistilbite (Bernfiord, Iceland).

and silicon are fully ordered. On the other hand, the broad, diffuse absorption bands and absence of sharp peaks, which characterizes the spectra of orthoclase and the intermediate plagioclases, is a reflection of the irregular structures of these minerals, in which varying degrees of disorder of aluminum and silicon are present.

Among the lamellar zeolites, the minerals of the heulandite subgroup, heulandite, brewsterite, and epistilbite, which are considered to form an isomorphous series, produced spectra which are very similar to each other. Their spectra are also practically identical to the lamellar zeolites

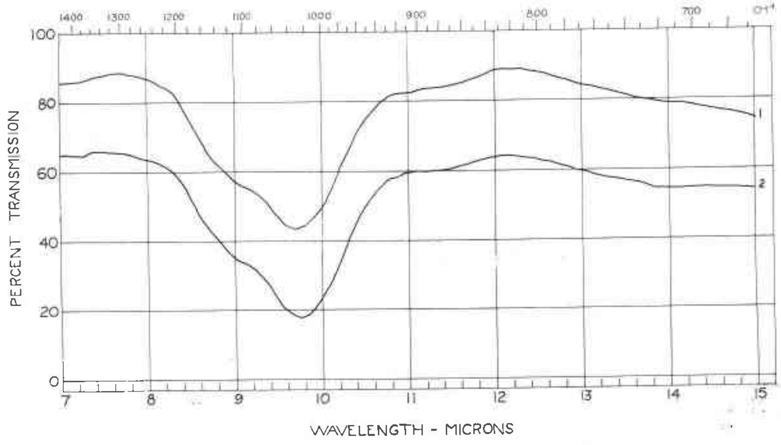


Fig. 6. Spectra of chabazite group: (1) chabazite, (2) levynite (Skye, Scotland).

of the phillipsite group, phillipsite, wellsite, stilbite, harmotome, stellerite, erionite, and gismondite, suggesting that the absorptions are due to similar vibrational modes in all of these zeolites. By contrast, the fibrous zeolites natrolite, scolecite, and mesolite, which are constructed of frameworks similar to each other, have spectra that are distinctively different.

The spectra of helvite and danalite contrast strongly with the spectra of the other minerals in the sodalite group, as well as with the other tectosilicates analyzed, having their major absorption peaks at wavelengths longer than 10.5 microns. Helvite and danalite are also noteworthy among the tectosilicates analyzed, in that all of the substitutions within the tetrahedra take place with beryllium rather than with aluminum; in either mineral the Be:Si ratio is 1:1.

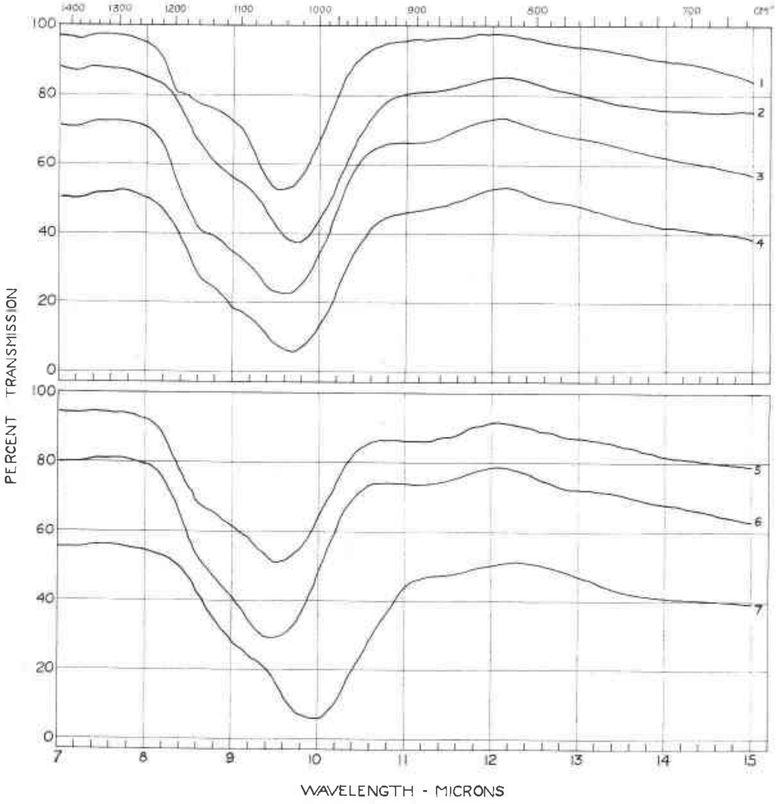


FIG. 7. Spectra of phillipsite group: (1) phillipsite (Antrim, Ireland), (2) wellsite (Clay Co., N. Carolina), (3) stilbite (Faroe Islands), (4) harmotome (Westchester Co., New York), (5) stellerite (Gishu mine, Korea), (6) erionite (Montana), (7) gismondite (Capo di Bove, Italy).

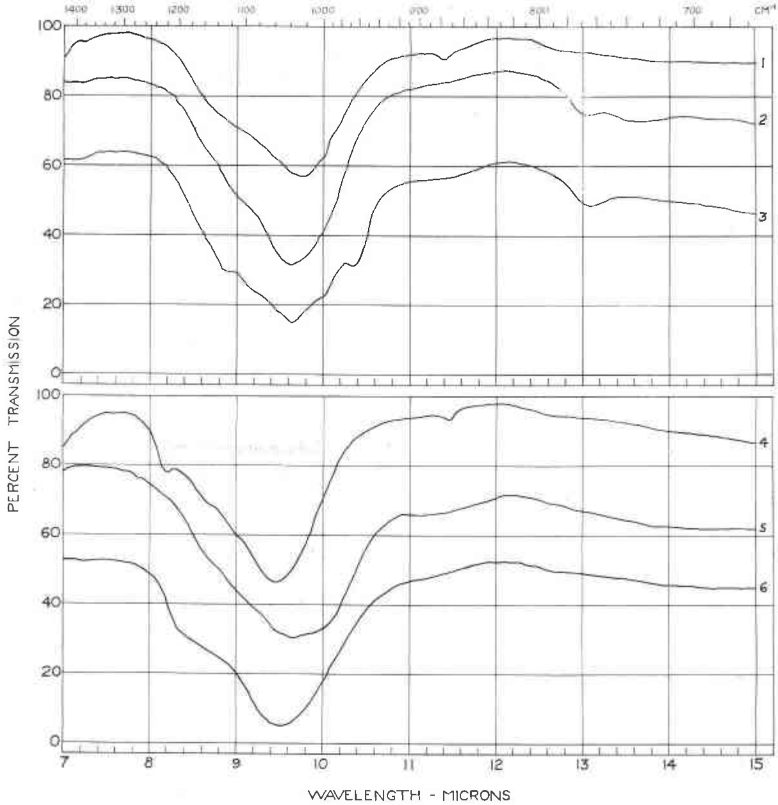
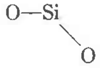


FIG. 8. Spectra of miscellaneous zeolites: (1) faujasite (Hesse, Darmstadt, Germany), (2) analcite (Giant Causeway, Ireland), (3) laumontite (Transylvanian, Hungary), (4) ferrierite (British Columbia, Canada), (5) laubanite (Steinbruch, Silesia), (6) dachiardite (Speranza, Elba).

CRYSTAL VIBRATIONS

The absorption bands of complicated molecules like the tectosilicates, unlike that of some simpler molecules, cannot be assigned by appropriate calculations to specific vibrational modes of the molecule. However, by means of empirical comparisons of spectra, general statements may be made linking absorption bands with the types of vibrations that produced them. Thus, Colthup (1950) has designated the region of absorption of the valence stretching vibration for the Si-O bond as between 9.1 and 10.8 microns, and Wright and Hunter (1947) have used the absorption of polydimethylsiloxanes to assign Si-O absorptions to the 9.1 to 10.0 micron region. As the silicon- (or aluminum-, or beryllium-)

oxygen tetrahedral bond is common to all the silicates, it is inferred that the strong absorption bands shown by most tectosilicates in the wavelength region 9 to 10 microns are due to predominantly bond-stretching vibrations of the



tetrahedral linkage. (As intensity of absorption depends on an effective vibrating charge, the very high level of absorption of these bands is consistent with the highly ionic character of the Si—O bond, reported by Pauling (1930), to be approximately 50% ionic. By contrast a lower intensity of absorption is shown by a more covalent bond, such as the C—O bond, which has only 22% ionic character.)

Compared to the bands in the 9 to 10 micron region, the absorption

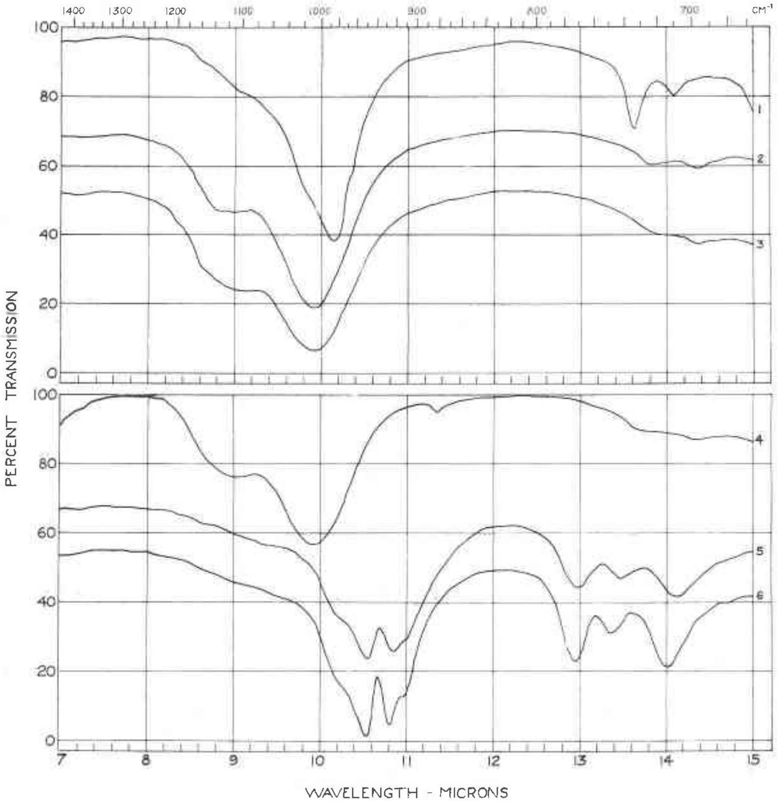


FIG. 9. Spectra of sodalite group: (1) sodalite (Ontario, Canada), (2) noselite (Saache See, Prussia), (3) hauyanite (Deer Lodge, Montana), (4) lapis lazuli (Persia), (5) helvite (Iron Mt., New Mexico), (6) danalite (Rockport, Massachusetts).

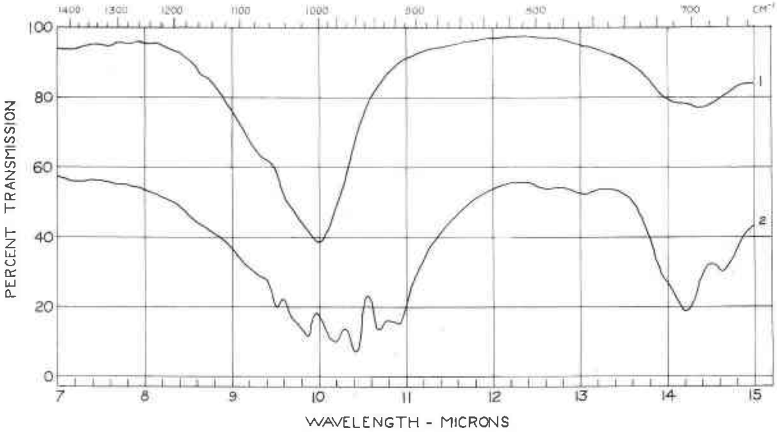


FIG. 10. Spectra of nepheline group: (1) nephelite (Ontario, Canada), (2) eucryptite.

bands that occur at longer wavelengths (including those beyond 15 microns) arise from vibrations in which bond-bending is relatively more important; such absorption bands should be more characteristic of skeletal structure than the primarily bond-stretching vibrations that occur in the 9 to 10 micron region. In the spectra of quartz and cristobalite, for example, the minor absorption bands at 12.5 to 12.8 microns have been termed characteristic of the "ring" structure to be found in quartz in which the silicate tetrahedra are joined together to form rings (Schaeffer, Matossi, and Wirtz, 1934). Probably an extension of the spectra to the wavelength region 15 to 30 microns would reveal greater contrasts and more specific differentiation between spectra that appear generally similar in the 8 to 15 micron region.

EFFECT OF ANION AND CATION

The tectosilicates which are constructed of similar frameworks are most likely to have spectra similar in shape to each other. This is shown by the matching spectra of such groups as orthoclase and adularia, stellerite and stilbite, analcite and pollucite, heulandite, brewsterite and epistilbite, chabazite and levynite, helvite and danalite, or noselite and lapis lazuli. In each case, the members of these groups have similar frameworks of linked tetrahedra, while they have different cations, or differing proportions of the same cation (or, as in the case of noselite and lapis lazuli, different substituted anionic groups). This is similar to what is found in the spectra of simple inorganic compounds, such as metal carbonates, sulfates, and nitrates, in which the shape of the spectra are determined principally by the vibrations of the anion, with only slight effect resulting from the substitution of cation for another.

In the tectosilicate frameworks, the silicon-oxygen and aluminum-oxygen bond distances are in the region of 1.6–1.7 Å. On the other hand, the distance between an oxygen atom and a sodium or calcium cation is comparatively greater; at least 2.5 Å, and sometimes as much as 3.0 Å or more. The distances from H_2O molecules to oxygen atoms are comparable to the distances between oxygen and cations. Moreover, as the co-ordination number of silicon or aluminum is 4, while that of a cation such as sodium may be 6 or 8, from Pauling's electrostatic valence rule, the electrostatic bond strengths of the Si—O or the Al—O bonds may be as much as 6 to 8 times the strength of the bonds between oxygen and a sodium cation. Thus, the restoring forces between oxygen and silicon (or aluminum) in the framework are much stronger than those between oxygen and a sodium or calcium cation. From this general picture, it is to

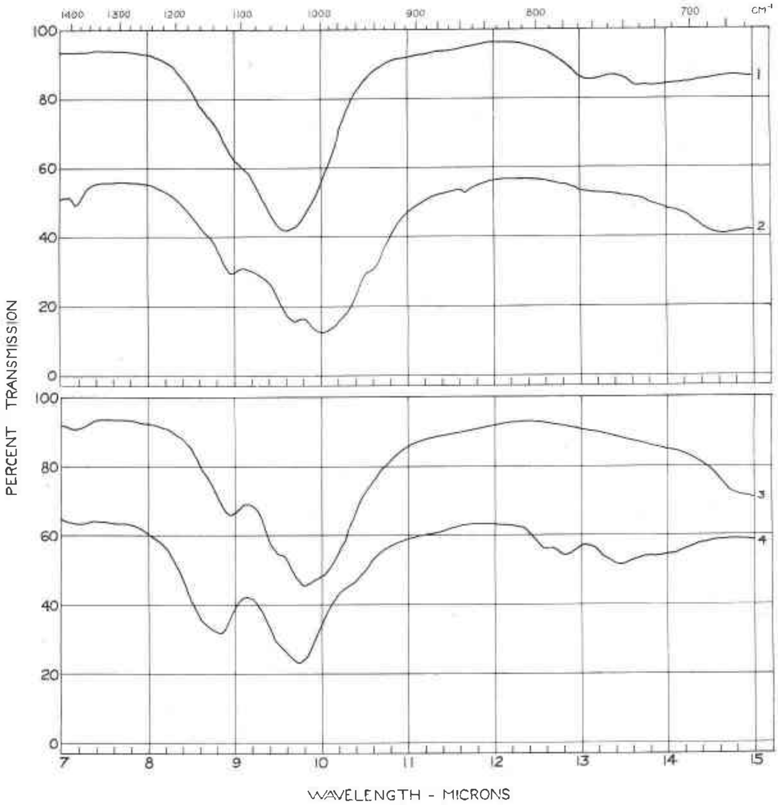


FIG. 11. Spectra of (1) pollucite (Buckfield, Maine), (2) cancrinite (Litchfield, Maine), (3) davyne (Iowa), (4) Milarite (Grisons, Switzerland).

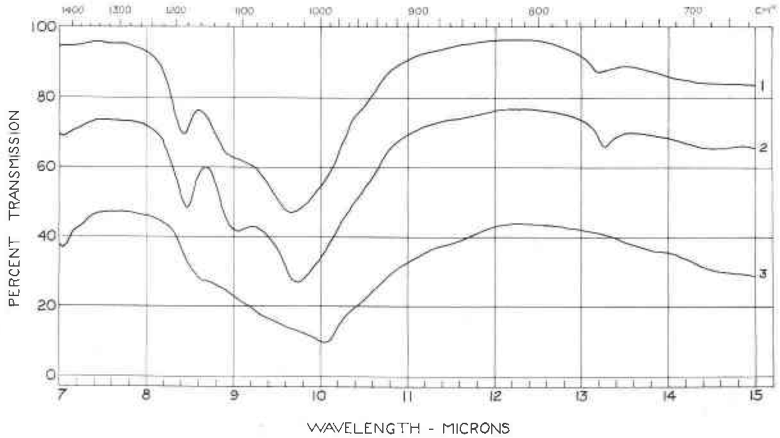


FIG. 12. Spectra of scapolite: (1) marialite ($Ma_{100}Me_0$ to $Ma_{80}Me_{20}$) (French Creek, Pennsylvania), (2) wernerite ($Ma_{80}Me_{20}$ to $Ma_{20}Me_{80}$) (St. Lawrence Co., New York), (3) meionite ($Ma_{20}Me_{80}$ to Ma_0Me_{100}) (Monte Somma, Vesuvius, Italy).

be expected, therefore, that valence stretching vibrations of the strong Al—O and Si—O bonds in the framework should be affected only slightly by changes in the much weaker oxygen-cation bonds, such as by the substitution of one cation for another.

Some of the tectosilicates, notably the fibrous zeolites natrolite, mesolite, and scolecite, showed widely-contrasting spectra, in spite of their being isostructural. However, the frameworks of these fibrous silicates also show other characteristics that differ from those of the more robust, 3-dimensional frameworks of such zeolites as chabazite, analcite, harmotome, or levynite. Thus, the alumino-silicate framework is essentially the same for all alkali-exchanged forms of chabazite from lithium to cesium (Beattie, 1953), and the framework of analcite remains the same when Na^+ is replaced by K^+, NH_4^+, Tl^{+++}, or Rb^+, whereas the fibrous zeolites show a tendency toward lattice changes after outgassing or ion-exchange. Moreover, natrolite, scolecite, and mesolite give off their water at different temperatures, their differential thermal curves are all distinctive and they undergo thermal decomposition at different temperatures (mesolite and scolecite at comparatively low temperatures, 490° and 560° C., while natrolite retains its structure until 940° C. [Peng, 1955]). The decomposition temperatures may be regarded as a measure of bond strengths. In the light of these differences in the characteristics of natrolite, mesolite, and scolecite, their markedly contrasting infrared spectra may serve as additional evidence in support of the hypothesis that these minerals do not constitute an isomorphous series, but rather are independent species.

EFFECT OF ALUMINUM SUBSTITUTION

The spectra show a correlation between the wavelength of the main absorption peak, and the degree of aluminum substitution into the crystal. Thus, the spectra of quartz, with no aluminum substitution, has its major peak at 9.18 microns, while the spectra of noselite, sodalite, hauynite, and others, in which the (aluminum):(aluminum+silicon) ratio approaches the limiting value of 0.5, the major peaks occur near 10.0 microns. Those with intermediate ratios have their major peaks located at intermediate wavelengths. In Fig. 13 is shown the relationship between the wavelengths of the peaks of the major absorption bands and the corresponding (Al):(Al+Si) ratio in the tectosilicate frameworks. The abscissae in Fig. 13 are represented by the published range of (Al):(Al+Si) ratios for each mineral, calculated from chemical analyses appearing in the literature (principally in Dana's System of Mineralogy). Some of the spectra, such as those of the plagioclase feldspars, helvite, or milarite, could not be correlated in this way, as they have series of peaks over a broad absorption band, rather than a sharp, major peak. Others,

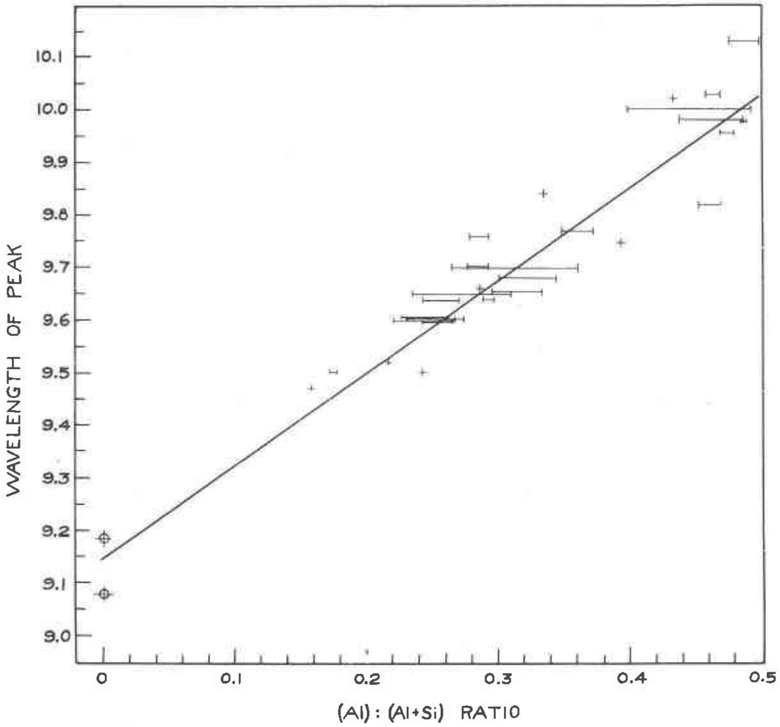


FIG. 13. Relationship of wavelength of absorption peak and published range of (Al):(Al+Si) values of tectosilicates.

such as lapis lazuli and wernerite, were also excluded, as their (Al):(Al+Si) ratios, which may vary appreciably, demand a more specific determination to be useful. The data from 32 of the tectosilicates, are included in the curve.

As the frequency of the valence-stretching vibrations varies inversely with the atomic masses, it might be presumed that the substitution of aluminum, which has a smaller mass than silicon, would result in a higher frequency. However, the vibrational frequency is affected also by the bond force-constant, which varies directly with the electronegativity product of the vibrating nuclei, and inversely with the internuclear distance. As the electronegativity of aluminum is less than that of silicon, and as the internuclear distance of the aluminum-oxygen bond is greater than that of the silicon-oxygen bond, the substitution of aluminum for silicon results in a decreased force constant. Accordingly, the stretching vibrational frequency, which varies directly with the force constant, is also decreased, and therefore the absorption peak is shifted, as is seen in Fig. 13, toward the longer wavelengths.

An idea of the wavelength shift to be expected from the effects of these various factors can be arrived at by calculation of the valence stretching frequency of the metal-oxygen bond, using the expression for an harmonic oscillator, $v=1307\sqrt{k/u}$, where v is vibrations per centimeter, k is force-constant, dynes per centimeter ($\times 10^{-5}$), and u is the reduced mass of the vibrating nuclei of the bond. Force constant values for Al—O and Si—O bonds were obtained from Gordy's (1946) empirical formula for the force constants of tetrahedral AB_4 molecules,

$$k = 3.29\left(\frac{x_A x_B}{d^2}\right)^{3/4} - 0.40,$$

where x_A and x_B are electronegativities of the atoms, and d is internuclear distance, Angstroms. (Although such calculations are not a precise treatment of the stretching vibrations in the framework, as they neglect the effects on a particular vibrating pair caused by bonds from neighboring nuclei, they can be used as an indication of the direction and approximate extent of shift caused by the atom substitution.) Thus, for the case of maximum wavelength shift, when one-half the silicon atoms in the framework have been replaced by aluminum, the calculations indicate a bathochromic shift of 0.5 micron. This is comparable to the actual shift of 0.6 to 0.8 micron shown by those tectosilicates with the one-to-one aluminum-silicon ratio—from the 9.20 microns for quartz, to 10.0 for thomsonite, 10.3 for nephelite, 9.82 for davyne, 10.12 for sodalite, 9.96 for noselite, and 9.97 for hauynite.

The bathochromic shifts shown by beryllium-substituted danalite and helvite are substantially greater than those shown by any of the aluminum-substituted frameworks. The framework structures of both danalite and helvite are similar to the framework of sodalite; and, similar to the Al:Si ratio in sodalite, the Be:Si ratio in danalite and helvite is 1:1. The unique shape of their spectra, however, compared to those of the other members of the sodalite group, suggests that, unlike the substitution of aluminum, the substitution of the small beryllium atom may produce substantial changes in the vibrational modes of the tetrahedrons in the framework.

It is interesting to note the wavelength shift resulting from aluminum substitution in an isomorphous series, as is seen in the spectra of the scapolite group. The changes in Al:Si ratio are reflected in the wavelengths of the absorption peaks. In the sample of marialite analyzed, the peak is at 9.64 microns, and in the sample of meionite, representing a higher Al:Si ratio, the absorption band has shifted toward longer wavelengths, with the peak at 10.02 microns. The sample of wernerite analyzed had a spectra closely similar to that of the marialite, although the peak wavelength has shifted somewhat—from 9.64 to 9.74 microns. The spectra of scapolites should provide a convenient method of characterizing their compositions, since their positions in the isomorphous series ought to bear a direct correlation with the positions of their absorption peaks. Analysis of a series of scapolites for which the Al:Si ratio had been closely determined would provide the curve of the relationship of peak wavelength and aluminum content, from which the Al composition of an unknown could be determined.

Conclusions

Interesting group correlations were made of the infrared spectra of the tectosilicates analyzed, and in many of the spectra features of individual interest occurred. Generally, as little as a few milligrams of the tectosilicates could be detected from their major absorption peaks. The occurrence of the major absorption bands within a relatively narrow wavelength interval of the spectrum was advantageous in characterizing the spectra as a group; however, the accompanying lack of specificity of the spectra has the result of limiting the quantitative or qualitative detection of the tectosilicates in mixtures. Thus, only a few of the spectra, such as those of quartz, danalite, helvite, sodalite, and marialite have discrete substantial absorption peaks outside the wavelength range of the major absorption bands. Perhaps the extension of the spectra from the 15 micron region to the 28 or 30 micron region would prove of particular value, as it is possible that the region of longer wavelengths, where the lower-energy, bond-bending absorption bands occur, might reveal greater contrast among the spectra.

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