REGULARITIES IN THE INFRARED ABSORPTION SPECTRA OF SILICATE MINERALS

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ABSTRACT

In order to augment the published infrared data on silicate minerals so that any relationship between spectra and structures might be revealed, the infrared absorption spectra of eighteen silicates have been measured from 2 to 15 microns. These spectra were obtained from thin films of powder having particle diameters less than 2 microns. Study of all available silicate spectra shows that the infrared spectrum can be used to characterize the type of silicon-oxygen group. The groups that have been considered are the isolated SiO₄ tetrahedron, Si₂O₅ ring, single chain, double chain, layer, framework, and silica. The region of strongest absorption tends to shift toward shorter wave length as the ratio of silicon to oxygen increases.

INTRODUCTION

Although the absorption of infrared radiation by minerals was first studied a half century ago (1, 2), it was not until recent years that the commercial availability of accurate, automatic-recording infrared spectrometers enabled mineralogists to take advantage of the possibilities afforded by this exceedingly useful tool. The present work concerns the contributions of infrared spectroscopy to the knowledge of the structures of silicate minerals.

The atoms of a solid are constantly vibrating about their equilibrium positions with frequencies of $10^{12}$ to $10^{14}$ cycles per second. Because infrared or heat rays have frequencies in this range, it is possible to determine some of these vibration frequencies by either of two methods. In the absorption method, infrared radiation is passed through a solid; if the frequency of the radiation coincides exactly with a vibration frequency, the solid absorbs some or all of the infrared radiation of this frequency. The reflection method is based on the principle that the reflecting power of a solid increases rapidly in the vicinity of a strong vibration frequency; the reflection maxima show the approximate positions of strong vibration frequencies.

The selective absorption of infrared radiation by silicate minerals has been known since the early 1900's, when Coblentz (1, 2) obtained infrared absorption spectra of cleavage sheets or polished sections of many silicates. The slices he used were about 0.1 mm. thick; they were opaque to infrared radiation having wave lengths longer than 9 microns. Coblentz also examined the reflecting power of polished surfaces of minerals and found that the silicates had reflection maxima in the region of 9 to 12 microns. He made the important observation that "the various silicates have quite different reflection spectra."
In the 1930's Schaefer et al. (3) and Matossi and Krüger (4) published the infrared reflection spectra of some silicate minerals. Matossi and Bronder (5) examined the infrared absorption, in the range 2 to 8 microns, of plates cut from silicate crystals. They assigned the absorption bands observed in this region to combination and overtone frequencies derived from the longer-wave length fundamental vibrations, whose approximate positions were known from reflection spectra. As in the pioneering work of Coblentz, the samples they examined were opaque to wave lengths longer than 9 microns, and the positions of the strong fundamental-vibration frequencies in this region could not be obtained by absorption measurements.

An outstanding advance in experimental technique resulted from the work of Pfund (6) and of Barnes et al. (7), who showed that the infrared absorption spectrum of a solid could be obtained by using a thin film of powder, provided that the powder particles had diameters smaller than the wave length of the infrared radiation. When the particle size was larger than the wave length, the infrared rays were refracted and emerged from the layer in random directions giving an apparent opacity; when the particles were smaller than the wave length, they did not act as refracting centers. The greatest exponent of the powder technique has been Lecomte (8), who used it to obtain the infrared spectra of many inorganic compounds containing polyatomic anions such as PO₄, SO₄, and HCO₃.

The powder technique has only recently been applied to the study of the silicates. Keller and Pickett obtained infrared spectra of some clays (9) and silica minerals (10). A report by Adler et al. (11), under the aegis of the American Petroleum Institute, consists of a collection of infrared studies of clay minerals made at several laboratories. In many of the published powder-film spectra the absorption bands are poorly defined because of large-particle scattering. Hunt et al. (12), who obtained spectra of several silicates, used only particles having diameters less than 5 microns, with the result that their silicate spectra show well-defined absorption bands.

In principle, it is possible to calculate theoretically the vibration frequencies for a solid; however, except for very simple structures, formidable mathematical difficulties are encountered. In such instances it is convenient to adopt an empirical approach that has been useful in the determination of the structures of organic compounds. This approach consists of comparing the infrared spectra of a series of compounds, each containing the same group of atoms. Often such comparisons show that certain groups of atoms have characteristic vibration frequencies giving rise to absorption bands which persist in different compounds.
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Locality</th>
<th>Source</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forsterite</td>
<td>Mg₂SiO₄</td>
<td>Italy</td>
<td>Ward's Natural Science Establishment, Inc., Rochester, New York</td>
<td>Preparation and properties described in reference (13).</td>
</tr>
<tr>
<td>β-Ca₂SiO₄</td>
<td>(Synthetic)</td>
<td></td>
<td>Prepared by K. R. Bonnicksen, Pacific Experiment Station, Bureau of Mines</td>
<td></td>
</tr>
<tr>
<td>Willemitne</td>
<td>Zn₂SiO₄</td>
<td>Franklin, Sussex County, New Jersey</td>
<td>Author's collection</td>
<td>Green, Fluoresces strongly under ultraviolet light.</td>
</tr>
<tr>
<td>Phenacite</td>
<td>Be₂SiO₄</td>
<td>San Miguel di Piracicaba, Minas Gerais, Brazil</td>
<td>Chicago Natural History Museum</td>
<td>Colorless lenticular crystals.</td>
</tr>
<tr>
<td>Zircon</td>
<td>ZrSiO₄</td>
<td>Henderson County, North Carolina</td>
<td>Ward's</td>
<td>Crystals, ca. 1 cm. long.</td>
</tr>
<tr>
<td>Kyanite</td>
<td>Al₂(OH)SiO₄</td>
<td>Clarksville, Georgia</td>
<td>Ward's</td>
<td>Bladed crystals.</td>
</tr>
<tr>
<td>Benitoite</td>
<td>BaTiSi₂O₉</td>
<td>San Benito County, California</td>
<td>Smithsonian Institution, United States National Museum</td>
<td>Fragments of semi-transparent blue crystals. Smithsonian catalog no. 86539.</td>
</tr>
<tr>
<td>Rhodonite</td>
<td>MnSiO₄</td>
<td>Plainfield, Massachusetts</td>
<td>Ward's</td>
<td>Pink, massive. Infrared spectrum shows a carbonate impurity.</td>
</tr>
<tr>
<td>Enstatite</td>
<td>(Mg,Fe)SiO₃</td>
<td>Chester County, Pennsylvania</td>
<td>Chicago Natural History Museum</td>
<td>Bronzite variety.</td>
</tr>
<tr>
<td>Enstatite</td>
<td>(Mg,Fe)SiO₃</td>
<td>North Carolina</td>
<td>Ceramic Division, Champion Spark Plug Company</td>
<td>Bronzite variety. Reference (14).</td>
</tr>
<tr>
<td>Clinoenstatite</td>
<td>MgSiO₄</td>
<td>(Synthetic)</td>
<td>Ceramic Division, Champion Spark Plug Company</td>
<td>Reference (14).</td>
</tr>
<tr>
<td>Mineral</td>
<td>Formula</td>
<td>Locality</td>
<td>Source</td>
<td>Remarks</td>
</tr>
<tr>
<td>------------</td>
<td>--------------------------------------</td>
<td>---------------------------------</td>
<td>-----------------------------------------------</td>
<td>-------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Aegirite</td>
<td>NaFe(SiO₃)₂</td>
<td>Langesundfjord, Norway</td>
<td>Chicago Natural History Museum</td>
<td>Black, prismatic, vertically striated crystals. X-ray diffraction pattern agrees with values in A.S.T.M. index.</td>
</tr>
<tr>
<td>Jadeite</td>
<td>NaAl(SiO₃)₂</td>
<td>Tibet</td>
<td>Chicago Natural History Museum</td>
<td>Green. X-ray diffraction pattern agrees with values in A.S.T.M. index.</td>
</tr>
<tr>
<td>Spodumene</td>
<td>LiAl(SiO₃)₂</td>
<td>near Keystone, South Dakota</td>
<td>Ward's</td>
<td>White, cleavable.</td>
</tr>
<tr>
<td>Anthophyllite</td>
<td>(Mg,Fe)₂Si₃O₁₀(OH)₂</td>
<td>Bakersville, Mitchell County, North Carolina</td>
<td>Ward's</td>
<td>Asbestos-like variety.</td>
</tr>
<tr>
<td>Hornblende</td>
<td>(Mg,Fe)₂Si₃O₁₀(OH)₂</td>
<td>Arendal, Norway</td>
<td>Chicago Natural History Museum</td>
<td>X-ray diffraction pattern agrees with values in A.S.T.M. index.</td>
</tr>
<tr>
<td>Attapulgite</td>
<td>Mg₃Si₅O₁₈(8H₂O)</td>
<td>Gadsden County, Florida</td>
<td>American Petroleum Institute Project No. 49</td>
<td>Collected and identified by American Petroleum Institute Project No. 49, Clay Mineral Standards. Sample no. H-43.</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>(Mg,H₂)₂Si₅O₁₈(H₂O)₄</td>
<td>near Pinos Altos, New Mexico</td>
<td>Ward's</td>
<td>White, amorphous. X-ray diffraction pattern shows lines due to sepiolite, calcite, and α-quartz.</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>KAlSi₅O₈</td>
<td>Fort Bayard, New Mexico</td>
<td>Ward's</td>
<td>Large white crystals.</td>
</tr>
</tbody>
</table>
The purposes of the present work are to present the infrared absorption spectra of eighteen silicate minerals, to compare these spectra with those which have appeared in the literature, and to point out certain similarities in the spectra of minerals having the same type of silicon-oxygen group.

**EXPERIMENTAL**

The minerals used in this study are described in Table 1. They were selected because their absorption spectra were needed to complement published infrared data on silicates.

The infrared absorption spectra were obtained using thin films of powder having particle diameters less than 2 microns. To isolate particles of this size, about 2 g. of the silicate, ground to pass a 300-mesh screen, was shaken with 100 ml. of C.P. isopropyl alcohol in a glass-stoppered, 100-ml. graduated cylinder. The suspension was then allowed to stand 16 hours or longer. At the end of this time an upper layer of the suspension was drawn off to include only particles finer than 2 microns, the depth of this layer being calculated from Stokes' law. A serviceable form (15) of Stokes' law for this calculation is:

\[ S = \frac{D^2 g (\rho_1 - \rho_2) (T \times 60)}{18 \eta \times 10^4} \]

where
- \( S \) = distance in cm. fallen by particle in \( T \) minutes,
- \( D \) = diameter of particle in microns,
- \( g \) = acceleration of gravity (980 cm./sec.²),
- \( \rho_1 \) = density of the particle (g./ml.),
- \( \rho_2 \) = density of the liquid (g./ml.),
- \( \eta \) = absolute viscosity of the liquid (poises).

Isopropyl alcohol rather than water was chosen as a sedimenting liquid because of the work of Webb (15), who showed that during the sedimentation of silica-alumina cracking catalysts flocculation occurs in water but not in isopropyl alcohol.

The isopropyl alcohol suspension withdrawn was evaporated to 15 ml. and centrifuged. Most of the supernatant alcohol was drawn off, the powder and remaining alcohol were stirred, and a few drops of the resulting slurry were transferred with a 1-ml. hypodermic syringe to a weighed sodium chloride plate. When the alcohol evaporated, a thin film of powder was left on the plate, which was again weighed. The weight of the film divided by the area of the plate was recorded on the spectrum in mg./cm.²

The spectra were obtained on a Beckman IR2 infrared spectrometer equipped with a sodium chloride prism. The wave-length scale was
calibrated against known absorption maxima of liquid toluene and of atmospheric water vapor and carbon dioxide. The slits were automatically adjusted by means of a slit drive. The $I_0$, or reference, curve was obtained by recording the radiant power transmitted by a sodium chloride plate having the same dimensions as the plate used to support the sample. The $I$, or sample, curve was obtained by recording the radiant power transmitted by the powder-coated plate.* The repeatability of a recorded curve obtained using the slit drive was about $\pm 0.3\%$ of the recorder chart width. Wave lengths were accurate to $\pm 0.02$ micron. A typical recording is shown in Fig. 1. Percent-transmission curves were obtained from these recordings by measuring the ratio $I/I_0$ in a point-by-point manner. Measurements of percent transmission ($I/I_0 \times 100$) were then transcribed to a chart having a linear wave-length scale.

![Fig. 1. Automatically recorded infrared curves of anthophyllite. $I_0$ curve shows radiant power transmitted by a sodium chloride plate. Values on lower curves give sample thicknesses in mg./cm.$^2$.](image)

The spectra of the eighteen minerals studied are shown in Figs. 2–5, and the positions of the absorption bands are listed in Table 2. Each spectrum has a transmission maximum at or near 8 microns and transmission minima, or absorption bands, in the range of 8 to 15 microns. Scattering by refraction is responsible for the percent-transmission decrease at the lower end of the wave-length scale. Many of the spectra show a weak band at 6.1 microns due to a small amount of entrained water. The 6.1-micron bands are stronger in the spectra of attapulgite and sepiolite, two silicates which contain water of crystallization. The early researches of Coblentz (1) showed that both water of crystallization and liquid water absorb strongly at 6.1 microns.

* In order to obtain reproducible intensities, it is important to compare the $I_0$ and the $I$ sodium chloride plates for equal infrared transmission before each sample preparation. Plates with non-parallel faces cause a prismatic deviation of the infrared beam with a subsequent decrease in the amount of energy reaching the thermocouple. The natural cleavage planes of sodium chloride, lightly polished with jeweler's rouge, make good parallel surfaces.
Fig. 2. Infrared absorption spectra of forsterite, $\beta$-Ca$_2$SiO$_4$, willemite, phenacite, and zircon.
Fig. 3. Infrared absorption spectra of kyanite, benitoite, rhodonite, and aegirite.
Fig. 4. Infrared absorption spectra of enstatite, clinoenstatite, jadeite, and spodumene.
INFRARED ABSORPTION SPECTRA OF SILICATE MINERALS

Fig. 5. Infrared absorption spectra of anthophyllite, hornblende, attapulgite, sepiolite, and orthoclase.
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Wave Length in Microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forsterite</td>
<td>10.00 11.17</td>
</tr>
<tr>
<td></td>
<td>10.45 11.89</td>
</tr>
<tr>
<td>( \beta-Ca_2SiO_4 )</td>
<td>9.7 10.04 11.4</td>
</tr>
<tr>
<td></td>
<td>10.7 11.5 11.78</td>
</tr>
<tr>
<td>Willemite</td>
<td>10.25 11.10</td>
</tr>
<tr>
<td></td>
<td>10.74 11.52</td>
</tr>
<tr>
<td>Phenacite</td>
<td>9.3 10.25 11.10 12.3 13.45 14.40</td>
</tr>
<tr>
<td></td>
<td>10.66 12.90 13.62 13.94</td>
</tr>
<tr>
<td>Phenacite</td>
<td>10.95 13.94</td>
</tr>
<tr>
<td>Zircon</td>
<td>9.7 11.05</td>
</tr>
<tr>
<td>Kyanite</td>
<td>9.5 10.3 11.10 13.62 14.65</td>
</tr>
<tr>
<td></td>
<td>9.92 10.58 11.33</td>
</tr>
<tr>
<td>Benitoite</td>
<td>9.66 10.75</td>
</tr>
<tr>
<td></td>
<td>9.74 11.5 13.13</td>
</tr>
<tr>
<td>Rhodonite</td>
<td>8.95 9.18 10.28 11.17 13.88</td>
</tr>
<tr>
<td></td>
<td>9.47 10.51 10.85</td>
</tr>
<tr>
<td>Enstatite</td>
<td>8.86 9.35 10.28 11.09 13.18 14.44</td>
</tr>
<tr>
<td></td>
<td>9.90 10.62 11.55</td>
</tr>
<tr>
<td>Clinoenstatite</td>
<td>8.35 9.07 10.08 11.12 12.50 13.57 14.63</td>
</tr>
<tr>
<td></td>
<td>8.68 9.29 10.62 11.65 13.80</td>
</tr>
<tr>
<td></td>
<td>9.88</td>
</tr>
<tr>
<td>Aegirite</td>
<td>9.00 10.35 11.62</td>
</tr>
<tr>
<td></td>
<td>9.55 13.62</td>
</tr>
<tr>
<td></td>
<td>9.84</td>
</tr>
<tr>
<td>Jadeite</td>
<td>8.85 9.35 10.70 11.65 13.40</td>
</tr>
<tr>
<td></td>
<td>9.97</td>
</tr>
<tr>
<td>Spodumene</td>
<td>8.65 9.16 10.80 11.60</td>
</tr>
<tr>
<td></td>
<td>9.70</td>
</tr>
<tr>
<td>Anthophyllite</td>
<td>8.86 9.02 10.21 11.11 12.80 13.00 14.03</td>
</tr>
<tr>
<td></td>
<td>9.11 10.97 13.25 14.90</td>
</tr>
<tr>
<td></td>
<td>9.46 13.64</td>
</tr>
<tr>
<td></td>
<td>9.79b</td>
</tr>
<tr>
<td>Hornblende</td>
<td>8.84 9.01 10.14 13.25 14.52</td>
</tr>
<tr>
<td></td>
<td>9.43 10.49</td>
</tr>
<tr>
<td></td>
<td>9.43 10.87</td>
</tr>
<tr>
<td>Attaclgite</td>
<td>8.39 9.68 10.12</td>
</tr>
<tr>
<td></td>
<td>8.87 10.95</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>8.38 9.64 10.13</td>
</tr>
<tr>
<td></td>
<td>8.92 10.93</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>8.85 9.66 12.90 13.75</td>
</tr>
</tbody>
</table>

* Possibly has a shoulder at 10.87 microns.

* Band center uncertain, because talc, a possible contaminant, has its strongest band at 9.8 microns.
The spectrum of rhodonite, in Fig. 3, shows absorption bands due to a carbonate at 5.58, 7.0, and 11.51 microns. The positions of these bands strongly suggest that the carbonate is rhodochrosite, MnCO₃, reported to have absorption maxima at 5.58, 7.0, and 11.50 microns (12). As a confirmatory test for carbonate, an infrared spectrum was obtained of rhodonite which had been treated with hydrochloric acid. In the spectrum of acid-treated rhodonite the carbonate bands are weaker and the silicate bands are stronger.

Both the infrared spectrum, shown in Fig. 5, and an x-ray powder photograph reveal the presence of α-quartz and calcite in the sepiolite sample used for this study. Seven infrared bands can be accounted for by α-quartz (8.6, 9.2, 12.53, 12.83 microns) and calcite (6.95, 11.40, 14.03 microns).

An absorption spectrum of hornblende published by Hunt et al. (12) has bands at 9.8 and 14.95 microns and is unlike the spectrum shown in Fig. 5 for the hornblende sample used in the present study and authenticated by x-ray diffraction.

**DISCUSSION OF RESULTS**

The silicon-oxygen groups to be considered in this report are arranged according to the x-ray-determined structural classification of W. L. Bragg:

I. Isolated SiO₄ tetrahedron  
II. Si₆O₁₈ ring  
III. Single chain  
IV. Double chain  
V. Layer  
VI. Framework  
VII. Silica

In order to ascertain whether infrared absorption can be used to characterize the various types of silicon-oxygen groups which occur in minerals, the experimental results are summarized and correlated with published infrared data by means of the bar charts shown in Figs. 6-12. In these charts, strong infrared bands are depicted by tall bars and weak bands by short bars. Some published spectra were not included because the identity of the silicate was in doubt or because the bands were poorly defined. If the absorption spectrum of a silicate was not available but its reflection spectrum was known, the reflection spectrum (labelled R) was used in the bar charts. The reflection maxima serve to indicate the approximate wave lengths at which absorption bands are expected to occur. Since the reflection method gives only the strong vibration frequencies, the reflection spectrum will usually show less detail than the absorption spectrum.
Fig. 6. Infrared absorption maxima of silicates containing the isolated SiO$_4$ tetrahedron.

"R" indicates the reflection spectrum. Spectra from the literature are identified by reference numbers.
Fig. 7. Infrared absorption maxima of benitoite and other silicates that may contain the SiO₆ ring.

Fig. 8. Infrared absorption maxima of single-chain silicates.

Fig. 9. Infrared absorption maxima of double-chain silicates.
Isolated SiO₄ Tetrahedron

Infrared data on orthosilicates are collected in Fig. 6. All of these orthosilicates have two, three, or four strong bands in the range of 10 to 12 microns. Since these compounds embrace a variety of positive ions and crystal structures, it is reasonable to assign these bands to vibrations of the independent SiO₄ group, which all orthosilicates have in common.

![Infrared absorption maxima of layer silicates.](image)

The absorption spectra of olivine and forsterite are very nearly identical. Synthetic β-Ca₂SiO₄ has a spectrum similar to the spectra of olivine and forsterite. A weak band at 11.9 microns in the olivine and forsterite spectra corresponds to a sharp, much stronger band at 11.78 microns in the β-Ca₂SiO₄ spectrum.

The spectra of the garnet minerals (almandite to andradite) were obtained by Adler (11), who found that the absorption bands of the garnets shift to longer wave lengths as the lattice constant increases.

Phenacite, Be₂SiO₄, and willemite, Zn₂SiO₄, the two major silicates
of the phenacite group, have strikingly similar absorption bands at 10.25, 10.7, and 11.1 microns, despite a sevenfold difference in the atomic weights of the cations. Phenacite has strong absorption bands between

![Diagram of Infrared Absorption Spectra](image)

Fig. 11. Infrared absorption maxima of framework silicates.

![Diagram of Infrared Absorption Spectra](image)

Fig. 12. Infrared absorption maxima of silica minerals.

12 and 15 microns—a region where most of the other orthosilicates do not absorb. It is reasonable to attribute these bands, and possibly the 9.3-micron band, to Be-O vibrations. By the same reasoning, the kyanite 13.6- and 14.6-micron bands are thought to be due to Al-O vibrations.
The spectrum of zircon shows less structure than the spectra of the other orthosilicates. There is some arbitrariness in selecting 9.7 microns as the center of the shorter wave-length band.

The reflection maxima of topaz, Al₂SiO₄F₂, and chondrodite, 2Mg₂SiO₄·Mg(F,OH)₂, fall in the region of the spectrum where the other orthosilicates have their characteristic absorption maxima.

**Si₅O₈ Ring**

Spectra of benitoite, rhodonite, wollastonite, and pectolite are compared in Fig. 7. Benitoite, in which the silicate ion is known to consist of three tetrahedra linked corner to corner in a ring to form Si₅O₈ (16), has strong bands at 9.66, 10.75, and 13.13 microns. The band at 13.13 microns occurs in a region where most silicates do not have strong absorption bands.

Structure determinations of rhodonite, MnSiO₃, and wollastonite, CaSiO₃, are not available; however, these silicates are thought to contain Si₅O₈ rings. Benitoite’s single bands at 9.66 and 10.75 microns appear as triplets in rhodonite and wollastonite. If rhodonite and wollastonite have Si₅O₈ rings, it is surprising that they lack the strong band in the 13-micron region shown by benitoite. Although these data neither confirm nor disprove the presence of Si₅O₈ rings in rhodonite and wollastonite, the marked similarity of the spectra of these two minerals leaves no doubt that rhodonite and wollastonite contain the same type of silicate ion.

Pectolite, NaH₂Ca₂(SiO₃)₃, which is reported (17) to be isomorphous with wollastonite and possibly to have an analogous structure, has strong reflection maxima at 9.4 and 10.8 microns. These maxima correspond to the centers of the wollastonite trifurcated absorption regions. To confirm the structural similarity of pectolite with wollastonite, an absorption spectrum of pectolite is needed.

**Single Chain**

Infrared spectra of six pyroxenes are compared in Fig. 8. With the exception of aegirite, all of these single-chain silicates have three strong bands between 9 and 12 microns.

The spectra of the MgSiO₃ polymorphs, enstatite and clinoenstatite, have the same over-all appearance but show small differences in the wave lengths of two of the strong absorption bands and numerous differences in the weak absorption bands.

Augite, CaMg(SiO₃)₂, has three strong absorption bands like those of enstatite and clinoenstatite, but its spectrum shows fewer weak bands.

The resemblance of the 11.6-micron bands of aegirite, jadeite, and
spodumene suggests that in all three minerals these bands are due to the
same kind of vibration. Jadeite, NaAl(SiO₃)₂, and spodumene, LiAl(SiO₃)₂, have very similar absorption spectra. In this pair, the
substitution of Na⁺ for Li⁺ causes a bathochromic shift of four absorption
bands.

Double Chain

The double-chain silicates, whose spectra are depicted in Fig. 9,
have two strong absorption bands near 10 microns, two or more weak
bands between 8.4 and 9.5 microns, and another weak band near 10.9
microns. The four amphiboles have a band near 13 microns.

Attapulgite, a clay with a double-chain structure (18), has a spectrum
which lacks the 13-micron band of the amphiboles. The examination of
a 1.4 mg./cm.² layer (Fig. 5) confirmed the absence of a 13-micron band
but did reveal bands at 12.53 and 12.83 microns characteristic of α-
quartz, an impurity which was not detected from an x-ray powder
photograph of this sample.

The five absorption bands of sepiolite coincide in positions (within a
few hundredths of a micron) and relative intensities with the bands
of attapulgite. The infrared spectrum of sepiolite supports the double-
chain silicate structure proposed for sepiolite by Longchambon (19).

Layer

Absorption data on minerals containing silicon-oxygen sheets are
collected in Fig. 10. Despite the complexity of these minerals, they all
have one or two strong absorption bands between 9.4 and 10.4 microns.
It is reasonable to assign this strong absorption to a vibration character-
istic of a silicon-oxygen layer, the only grouping of atoms which all of
these minerals have in common.

Another interesting regularity is that the substitution of magnesium
for aluminum reduces the number of absorption bands and causes the
strong silicon-oxygen band to undergo a bathochromic shift. These
effects are illustrated by going from pyrophyllite, Al₂Si₄O₁₀(OH)₂, to
talc, Mg₃Si₄O₁₀(OH)₂; and from muscovite, KAl₂AlSi₃O₁₀(OH)₂, to
biotite, K₂Mg₃Al₂Si₄O₁₀(OH)₂. In the series (20) of related clays: mont-
morillonite, nontronite, and hectorite, these effects are apparent in
going from the spectra of montmorillonite and nontronite to the spec-
trum of hectorite, the aluminum-free magnesium end-member of the
series.

Serpentine, originally described as a double-chain structure, has
been classed by Warren (21) with the layer structures. The dissimilarity
of the spectrum of serpentine and the spectra of the double-chain silicates
supports this change.
A comparison of infrared data on framework structures, given in Fig. 11, shows that the silicon-oxygen framework, like the layer, tends to absorb strongly near 10 microns. All of the absorption spectra and some of the reflection spectra show weak bands in the region of 13 to 15 microns.

The difference between the infrared absorption spectra of two crystal forms of KAlSi₃O₈, orthoclase and microcline, shows again that the infrared spectrum of a mineral depends not only upon chemical constitution but also upon the way in which the atoms are arranged in the crystal structure.

Nephelite, once classed with the orthosilicates, now is known to have a tridymite-like framework (17). The similarity of the nephelite spectrum to the spectra in Fig. 11, along with the absence in nephelite of a second strong band near 11 microns (cf. Fig. 6), is consistent with a framework structure.

Silica

Infrared absorption maxima of α-quartz, α-cristobalite, opal, and fused silica are shown in Fig. 12. These silica minerals have in common a
strong 9.2-micron absorption band and weaker bands between 8.2 and 8.6 microns and between 12.5 and 12.8 microns.

**Conclusion**

A chart showing the wave-length ranges of the strong infrared absorption bands of silicon-oxygen groups is given in Fig. 13, where the region in which strong bands occur is shown by a horizontal line to the left of each group. The silicon-oxygen groups here are arranged according to an increasing ratio of silicon to oxygen. As the Si:O ratio progresses from 0.25 in the isolated SiO₄ tetrahedron to 0.50 in silica, the region of strong absorption shifts to shorter wave lengths, and the wave-length ranges tend to narrow.

One of the best features of the infrared spectrum is that absorption or lack of absorption at certain wave lengths often can be correlated with the type of silicon-oxygen group in the mineral. Small displacements of the vibration frequencies characteristic of a silicon-oxygen group must arise mainly from the fact that these vibrations are not completely independent of the rest of the crystal. It is to be hoped that such frequency shifts ultimately can be interpreted to give information about the structure adjacent to the silicon-oxygen group.

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**References**


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