

INFRARED INVESTIGATION OF THE OLIVINE GROUP MINERALS

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ABSTRACT

Natural and synthetic minerals of the olivine group were investigated using infrared absorption techniques. Group members studied include those formed by substitutions involving the following cation pairs: Mg-Fe, Fe-Mn, Mg-Ca, Ca-Mn, Mg-Mn, Mg-Ni, and Mn-Ni. Infrared absorption spectra were obtained in the frequency range 4000 cm^{-1} to 400 cm^{-1} .

Seven absorption bands were noted in the spectra of all of the samples. Configurations of the spectra were similar, but minor variations distinguished each solid solution system. Within any one substitution system the frequency of each absorption band varied systematically with the ratio of the substituent cations. These variations are due to differences in the mass and ionic radii of the substituent cations as a function of the ionic character of the bond. Other factors such as electronegativity and polarizability also affect the bond character.

The frequency of each absorption band varied linearly with composition within any one substitution system. When this relationship was plotted, determinative curves were obtained which could be utilized to determine the composition of samples for which analytical data were not available. The precision of the determination was within 5 mol %. Accuracy of the determinations decreased rapidly when a solid solution series was contaminated with a third substituent cation.

The approximate positions of the bands were calculated by assuming they were caused by vibrations within the SiO_4 tetrahedra. The symmetry properties of the olivine unit cell reveal the distortion of the tetrahedral symmetry of the SiO_4 to a point group symmetry of C_s . Analysis of the group character tables reveals that the observed absorption bands are explained by this symmetry distortion.

INTRODUCTION

The purpose of this investigation was to correlate the compositions of the olivine group minerals with systematic variations in their infrared absorption spectra and to assign the observed absorption bands to vibrations within the olivine structure. Thirty-seven olivine samples were investigated, including twenty-two natural and fifteen synthetic specimens.

A suite of samples representative of the entire forsterite-fayalite series was obtained from Dr. H. S. Yoder. These samples had been the subject of a previous study and analytical and x-ray diffraction data were available (Yoder and Sahama, 1957). Other natural olivines were identified

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using x-ray diffraction, x-ray fluorescence, and optical techniques.

The sample compositions were related empirically to variations in the infrared absorption spectra. Each substituent cation pair was treated separately and shifts in the frequencies of the absorption bands were correlated with the ratio of the substituting cations and with the physical and chemical properties of the cations.

Due to availability of samples, only the forsterite-fayalite series was studied in detail. Other natural systems investigated include the forsterite-monticellite series, the monticellite-glaucocroite series, the glaucocroite-tephroite series, and the fayalite-tephroite series. These systems involve various substitutions of magnesium, iron, calcium and manganese in the olivine structure. Synthetic solid solution series studied were the Mg-Mn olivines, the Mg-Ni olivines, and the Mn-Ni olivines.

The configuration of the infrared spectra is similar and characteristic of olivine group minerals. In general, seven major absorption bands are noted in the frequency range 4000 cm^{-1} to 400 cm^{-1} . The frequency of the absorption maxima for each band is tabulated.

When the absorbance data for members of the forsterite-fayalite series were plotted versus composition, in molecular per cent forsterite, a linear relationship was obtained. This may be used in estimating the composition of samples for which analytical data are not available.

The shifts in the absorption maxima with compositional variations were empirically related to the properties of the substituent cations. The theoretical vibration frequencies were calculated by assuming the structure to be isolated SiO_4 tetrahedra. By taking into account the distortion of the tetrahedra in the crystal lattice, it was possible using group theory, to assign the observed absorption bands to specific molecular vibrations.

CRYSTAL STRUCTURE

The olivine group minerals have the general formula M_2SiO_4 , where M is a divalent cation such as Ca, Mg, Fe, Mn or a mixture of such cations.

The olivine structure may be described as tetrahedral SiO_4 groups bonded together by divalent cations. An alternative description is that of an array of hexagonal close-packed oxygen atoms with silicon in tetrahedral holes and divalent cations in octahedral holes. The structure is characterized by an orthorhombic symmetry, a tetramolecular unit cell and a chrysoberyl type (Al_2BeO_4) structure. The space group is V_h^{16} which provides for the close-packed oxygens (Bragg, 1926).

The close-packing of the oxygen atoms is however, only an approximation. The oxygen lattice is distorted slightly by the cations. The amount of distortion depends upon the size, mass, electronegativity,

and polarizability of the substituting cation. The dimensions of the unit cell are changed accordingly (Wyckoff, 1960, p. 5).

EXPERIMENTAL PROCEDURES

One of the major problems in a study of this type is the accumulation of a sufficient number of samples to be representative of a mineral series. Separation from the rock of the individual mineral species and the determination of their chemical composition is sometimes difficult. Fortunately, some of the samples obtained were individual minerals which had been chemically analyzed, and the data published by Yoder and Sahama (1957, p. 475). Other specimens required separation of the desired mineral.

Standard separation methods were used. These included magnetic, heavy liquid, and hand-picking techniques. The presence of impurities, if any, was revealed in the petrographic microscope or in the initial infrared absorption spectrogram. Only cleaned samples were used for the subsequent infrared analyses.

Infrared. The preparation of the infrared sample discs followed techniques described by Tuddenham and Lyon (1960, p. 1632). The sample concentration was 0.25% in KBr and the thickness of the two discs were 1.4 mm and 0.5 mm. A reference disc of potassium bromide was made each day that sample discs were prepared. By using this disc in the reference beam of the infrared spectrophotometer, effects of hydration were minimized.

An infrared spectrogram was made for each mineral using a Perkin-Elmer Model 421 grating spectrophotometer in the frequency range from 4000 cm^{-1} to 535 cm^{-1} . The spectrum was also examined in the frequency range 666 cm^{-1} to 400 cm^{-1} using potassium bromide optics in a Perkin-Elmer model 21 prism spectrophotometer.

Synthesis. A number of olivine-type minerals were synthesized using one of two methods. The first method involved melting of the sample material in an arc spectrograph. Oxides of the various metals were thoroughly mixed in a mechanical mortar to give the proper stoichiometric proportions and these mixtures were then loaded into preformed graphite electrodes, and arced for 20 seconds. This was sufficient time to remove volatile impurities, and to allow complete melting of the sample. A small bead was formed in the electrode cup which in almost every case was found to be essentially an olivine-type mineral. It should be noted that the rate of volatilization is different for the different elements and the exact composition of the bead was not known. However, for an arcing time of 20 seconds it was assumed that the bead obtained had the com-

position of the stoichiometric mixture. A number of attempts to synthesize Ni_2SiO_4 in this manner were unsuccessful. Ringwood (1956) noted the same difficulty using fusion techniques. A Ni_2SiO_4 olivine was prepared using a procedure as outlined by Ringwood (1956). Analytical grade NiO, a colloidal form of SiO_2 , and approximately 2% CaF_2 were thoroughly mixed in a mechanical mortar. This material was pressed into small discs using a metal die and sintered at 1400°C . for two hours. X-ray and infrared analyses showed the sample to be approximately

TABLE 1. SOURCE OF ANALYZED OLIVINES¹

Fo Mol %	Original Sample No.	Source
5.5	F	Sahama (Sahama and Torgeson, 1949)
32.3	USNM11913	G. Switzer (Penfield and Forbes, 1896)
39.7	FEAE 121	K. Hytonen (Yoder and Sahama, 1957)
53.9	E	Sahama (Sahama and Torgeson, 1949)
55.6	D	Sahama (Sahama and Torgeson, 1949)
61.3	FEAE 62	Sahama (Yoder and Sahama, 1957)
80.6	FEAE 139	K. Hytonen (Yoder and Sahama, 1957)
87.8	C	Sahama (Sahama and Torgeson, 1949)
94.7	150	Sahama (1953)

¹ Data after Yoder and Sahama (1957).

75% Ni_2SiO_4 with some unreacted NiO. The excess SiO_2 present was converted to cristobalite.

RESULTS AND DISCUSSION

Forsterite-Fayalite Series. A suite of chemically analyzed minerals in the forsterite-fayalite series was obtained from Dr. H. S. Yoder. These samples and the original source are listed in Table 1. The analyses, along with x-ray diffraction data were published by Yoder and Sahama (1957). The chemical analyses are reported in Table 2.

The infrared absorption maxima for this suite of chemically analyzed olivines are listed in Table 3.

The precision of the frequency determination was calculated from data

TABLE 2. OLIVINE CHEMICAL ANALYSES¹

Fo Mole %	Theoretical 0.0%	5.5 ²	32.3	39.7	53.9 ³	61.3	80.6 ⁴	87.8	94.7	Theoretical 100%
SiO ₂	29.48	29.96	33.77	34.08	35.31	36.25	38.53	40.24	41.07	42.69
TiO ₂		0.00	n.d.	0.04	0.00	0.00	0.04	0.00	0.05	
Al ₂ O ₃		0.00	n.d.	0.00	0.00	0.14	0.74	0.01	0.56	
Fe ₂ O ₃		0.00	n.d.	0.27	1.70	0.64	0.67	0.68	0.65	
FeO	70.52	63.31	47.26	47.30	36.91	32.60	16.60	10.92	3.78	
MnO		4.40	4.54	0.65	0.53	0.26	0.27	0.28	0.23	
MgO		2.23	13.88	17.83	25.55	30.04	43.15	48.08	54.06	57.31
CaO		0.10	n.d.	0.00	0.00	0.12	0.00	0.00	0.00	
H ₂ O ⁺		0.00		0.05	0.00	0.00	0.00	0.00	0.00	
			0.48							
H ₂ O ⁻		0.00		0.00	0.00	0.00	0.00	0.04	0.00	
	100.00	100.00	99.93	100.22	100.00	100.05	100.00	100.32	100.45	100.00

¹ Data from Yoder and Sahama (1957).

² Corrected for an estimated 1% magnetite.

³ Corrected for estimated 0.75% ilmenite and magnetite.

⁴ Corrected for 1.6% analyzed clinopyroxene.

for sample Fo 94.7. Seven spectrograms were run on the same sample disc with the disc being rotated between runs. The scan speed was as slow as possible and the wavenumber was read directly for the instrument. The deviation was ± 1 cm⁻¹. The wavenumbers tabulated for all absorption maxima were obtained in this manner. The routine spectra from which the tracings are taken, were run at a scan time of 32 minutes.

Figures 1 and 2 show diagrammatically some spectrogram tracings of minerals in this series. The general configuration of the olivine spectrum is maintained. However, there is a decrease in the frequency of each band with the increase of iron in the forsterite molecule. This frequency

TABLE 3. INFRARED ABSORPTION DATA FOR ANALYZED OLIVINES

Fo Mol %	Wavenumber of Absorption Bands in cm ⁻¹						
	1	2	3	4	5	6	7
5.5	950	916	874	826	557	507	477
32.3	970	930	878	830	577	521	484
39.7	963	925	878	830	576	517	486
53.9	970	933	880	832	584	521	487
55.6	970	932	880	832	585	520	490
61.3	974	936	881	833	587	527	490
80.6	980	945	883	835	600	532	497
87.8	983	950	884	836	602	538	503
94.7	986	953	885	837	606	542	504

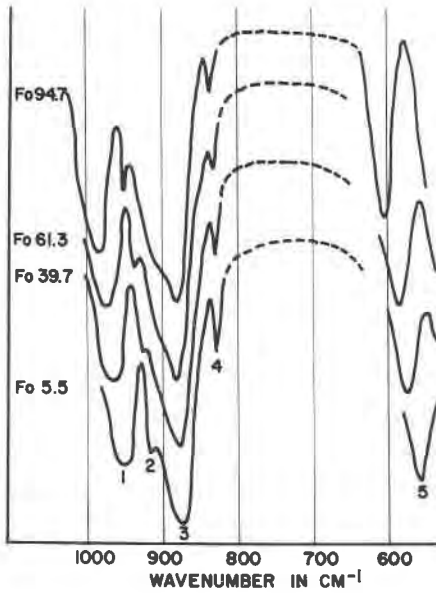


FIG. 1. Spectrogram tracings in the forsterite-fayalite series in the region 1000-535 cm^{-1} .

decrease is a linear function of composition for each absorption band. The shift for each band is however, not the same linear function. Figure 3 illustrates the linear nature of the frequency decrease with composition for absorption bands 1 and 5. Each of the other bands show a similar relationship.

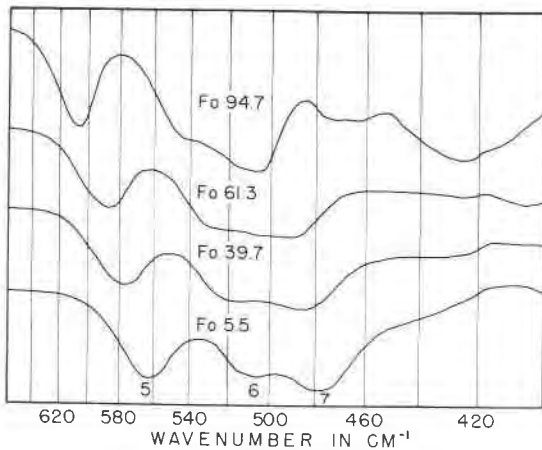


FIG. 2. Spectrogram tracings in the forsterite-fayalite series in the region 660-400 cm^{-1} .

The sample determined as 32.3 mol per cent forsterite by chemical analysis yielded anomalous results as seen in Fig. 3. The same anomalous values were noted for each of the other absorption bands. The discrepancy in the frequencies of the absorption bands suggests that the composition of this sample is between 40 and 50 mol per cent forsterite. In

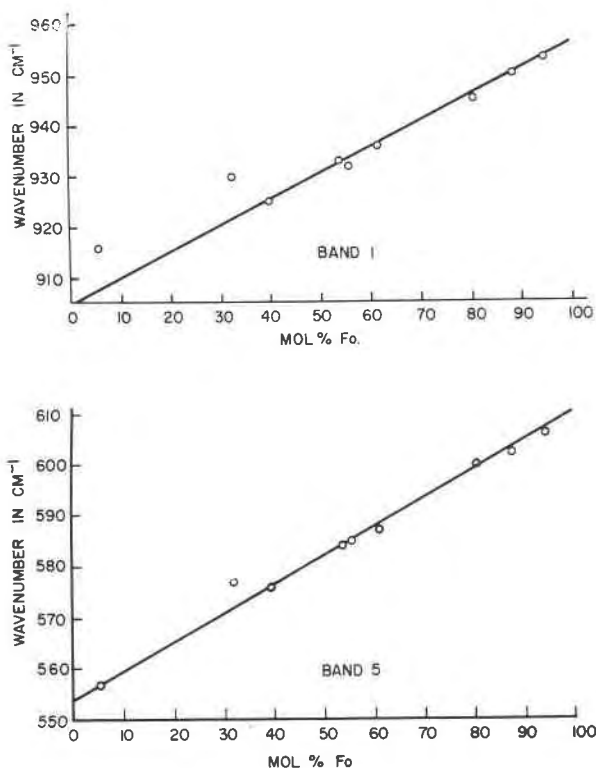


FIG. 3. Forsterite-fayalite composition *vs.* wavenumber for absorption bands 1 and 5.

the *x*-ray diffraction study of this sample, Yoder and Sahama (1957, p. 484) obtained a composition of approximately 44 mol per cent forsterite but rejected the determination due to the relatively high manganese content of this sample. Manganese also shifts the positions of the infrared absorption maxima and may account for the anomalous results.

Lehmann *et al.* (1961) noted that there was a linear relationship between the fayalite content of the olivine and the frequency of absorptive oscillations. They felt that this relationship could be used for analytical purposes.

Slaydon and Ehlmann (1961) also examined the forsterite-fayalite series and used bands 2 and 5 for calculating compositions of minerals in this series. In comparing the data compiled in the present study with that of Slaydon and Ehlmann, some discrepancies were noted. Their regression equations could not be fitted exactly. A general fit was possible for band 2, but it was not possible to fit their equation for band 5. This could be due to differences in the resolution at this frequency between the instruments used.

Seven samples in the forsterite-fayalite series were compared as further evidence of the determination of composition using the frequencies of the absorption bands. The composition of each sample was determined

TABLE 4. COMPOSITION OF SAMPLES IN THE FORSTERITE-FAYALITE SERIES FROM INFRARED ABSORPTION DATA

Sample	Location	Mol % Fo				Max. Deviation
		1	2	4	5	
Forsterite	Cecchina, Italy	88	89	88	89	±0.5
Forsterite	Bolton, Mass.	93	95	88	91	±3.5
Peridot	Unknown	97	93	88	88	±4.5
Olivine	Monroe, N. Y.	37	36	30	33	±3.5
Olivine	Monroe, N. Y.	35	37	30	33	±3.5
Fayalite	Unknown	0	16	6	6	±8.0
Fayalite	Rockport, Mass.	10	13	0	3	±6.5

using the absorption maxima for bands 1, 2, 4 and 5. The data are listed in Table 4.

The correlation of compositions determined from each band was reasonably good except for the two fayalite samples. For these, the deviation from the mean was a maximum for band 2. This indicated the presence of another cation such as manganese which caused anomalous values in the analyzed samples. X-ray fluorescence analyses showed 4.1 and 3.7 weight per cent manganese respectively for the unknown locality fayalite and the one from Rockport, Massachusetts. This may account for the wide variation in composition as determined from the absorption frequencies. Lacking exact chemical data, this method affords a rapid estimation of the composition of an olivine mineral in the forsterite-fayalite series.

As yet, the factors responsible for the frequency decrease of the absorption bands with an increase in iron have not been discussed. In this case the frequency of each band decreases as the radius and mass of the

cation linking the SiO_4 tetrahedra increase. These two properties are probably the principal factors but certainly not the only ones. Factors such as electronegativity, polarizability, per cent ionic bonding, and the relative perturbation and distortion of the lattice by the substituent cation also influence the vibration frequencies.

Other Olivine Group Minerals. Other olivine minerals studied were monticellite, glaucochroite, tephroite and knebelite. The infrared absorption data for these minerals are listed in Table 5.

The substitution of Mn^{2+} for Fe^{2+} in the fayalite-tephroite solid solution yielded results very similar to those found in the forsterite-fayalite series. Figure 4 illustrates the change in the infrared spectrum with the

TABLE 5. INFRARED ABSORPTION DATA FOR OTHER OLIVINE GROUP MINERALS

Species	Wavenumber in cm^{-1}					
	1		2	3	4	5
Monticellite	971		942	880	827	587
Glaucochroite	956	938	915	865	816	560
Tephroite	943		908	855	813	554
Knebelite	953	940	913	870	823	560

substitution of Mn^{2+} for Fe^{2+} . There is a general decrease in the frequencies of the absorption bands with the increase in Mn^{2+} . This was again found to be a linear function of the composition as shown for band 4 in Fig. 5. The two samples fayalite and tephroite were assumed to be pure end members. The knebelite absorption frequency for the band was plotted as 79 mol per cent fayalite as determined from the x-ray fluorescence data. This point was within the limit of precision of the wavenumber determination and the accuracy of determination of the composition.

Spectrogram tracings for olivine minerals in which divalent calcium and manganese are substituted for magnesium are illustrated in Fig. 6. This shows a decrease in frequency of the absorption bands with the substitution of calcium for one of the magnesium ions in monticellite. A further decrease in the frequencies of the absorption bands results with the substitution of manganese for the other magnesium ion in glaucochroite. In tephroite, the calcium ion is replaced with another manganese ion and again the frequencies of the absorption bands decrease. As in the forsterite-fayalite series, the decrease in frequency of the absorption

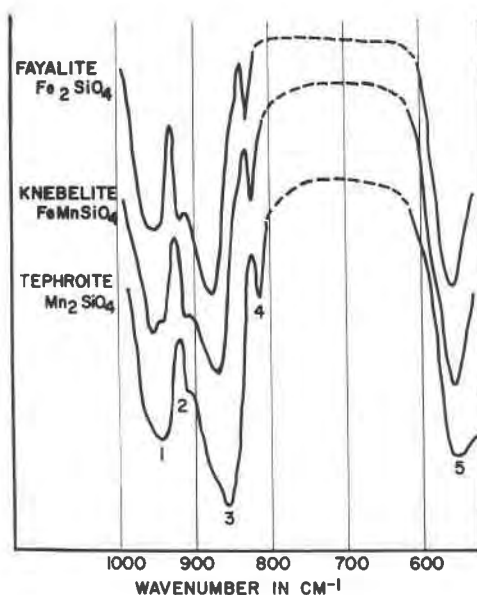


FIG. 4. Spectrogram tracings in the fayalite-tephroite series in the region 1000-535 cm^{-1} .

bands may be related to either an increase in the mass or ionic radius of the substituent cation.

One anomalous feature in the spectra of both knebelite and glaucroite is worth discussion. This is the development of an additional absorption maximum in band 1. In the spectra of fayalite and tephroite by Tarte (1963, p. 28) a doublet is also observed although no such doublet was noted in our spectra of these two minerals. The reason for development of this doublet has not been established. However, in the isostructural monticellite, there are two crystallographically independent

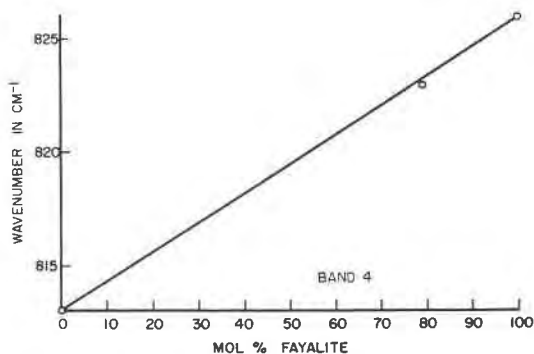


FIG. 5. Fayalite-tephroite composition *vs.* wavenumber for absorption band 4.

cation sites— M_I corresponding to the magnesium position and M_{II} corresponding to the calcium position. Ghose (1962, p. 392) postulated the ordering of magnesium and iron in the olivines and predicted that Fe^{2+} would be preferred in the M_{II} site, whereas Mg would be preferred in the M_I site. Yoder *et al.* (1957) detected no ordering of the magnesium and iron cations in the olivine lattice. There was no evidence from our infrared spectra, of ordering of magnesium, iron or calcium in preferred

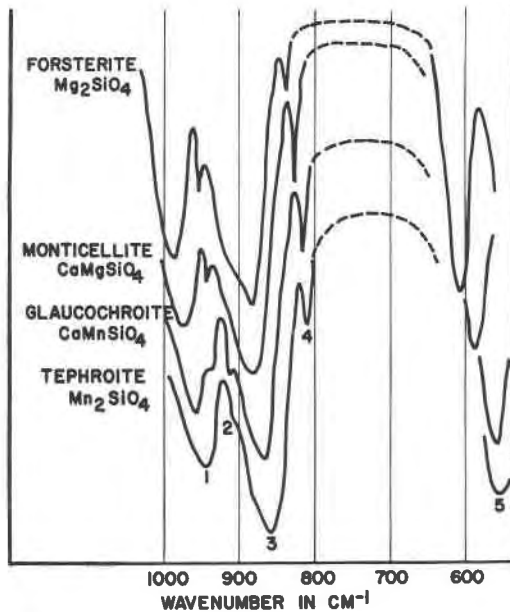


FIG. 6. Spectrogram tracings of other olivine group minerals in the region 1000-535 cm^{-1} .

cation positions. The infrared spectra exhibited the same configuration with only changes in the frequencies of the absorption bands.

Only in solid solutions involving Mn^{2+} with Ca or Fe^{2+} , was an additional absorption band noted. In the synthetic series Mg_2SiO_4 - Mn_2SiO_4 as seen in Fig. 7, there was no doublet formed in band 1.

One possible explanation of the doublet is that ordinarily Mn^{2+} would preferentially order in the M_{II} cation position with Mg in the M_I position. However when Fe^{2+} or Ca is in the lattice with Mn^{2+} the Mn^{2+} is forced into an M_I position with the Fe^{2+} or Ca in the larger M_{II} position. This type of ordering could result in the formation of the additional absorption band.

Synthetic Olivines. The olivine group minerals made synthetically were members of the Mg_2SiO_4 - Mn_2SiO_4 series, the Mg_2SiO_4 - Ni_2SiO_4 series, and the Mn_2SiO_4 - Ni_2SiO_4 series. These yielded infrared absorption spectra which were identical to the natural olivines. The absorption band frequencies were within a few wavenumbers of those of the natural minerals having similar compositions. The configurations and intensities of the absorption bands were also comparable. Table 6 lists the infrared absorption maxima for the synthetic olivine minerals.

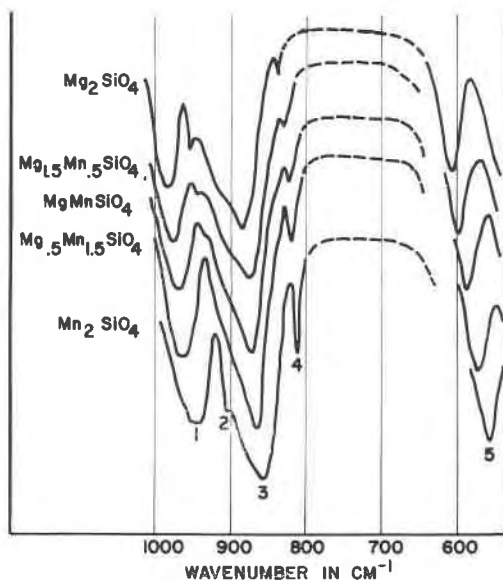


FIG. 7. Spectrogram tracings in the synthetic Mg_2SiO_4 - Mn_2SiO_4 series.

Five members of the Mg_2SiO_4 - Mn_2SiO_4 series were synthesized. This has been called a solid solution series by Poldervaart (1950). Tracings of the infrared spectra for samples in this series are presented in Fig. 7. There is a decrease in frequency of each of the absorption bands with the addition of manganese. The disappearance of band 2 in the intermediate members and its reappearance in Mn_2SiO_4 should be noted. The frequency decrease is again a linear function of composition as shown for band 4 in Figure 8.

Five members of the Mg_2SiO_4 - Ni_2SiO_4 series were prepared. Tracings of the infrared spectra for samples of this series are shown in Fig. 9. There was a general decrease in the frequencies of the absorption bands with the substitution of nickel for magnesium. The frequency decrease

TABLE 6. INFRARED DATA FOR SYNTHETIC OLIVINE GROUP MINERALS

Species	Wavenumber of Absorption Band in cm^{-1}				
	1	2	3	4	5
Mg_2SiO_4	984	954	885	837	608
$(\text{Mg}_{1.5}\text{Mn}_{0.5})\text{SiO}_4$	977	945	878	831	598
$(\text{Mg}_{1.0}\text{Mn}_{1.0})\text{SiO}_4$	970	—	872	825	587
$(\text{Mg}_{0.5}\text{Mn}_{1.5})\text{SiO}_4$	964	—	867	819	574
Mn_2SiO_4	944	906	860	812	556
Mn_2SiO_4	946	906	860	814	559
$(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{SiO}_4$	948	905	860	814	560
$(\text{Mn}_{1.0}\text{Ni}_{1.0})\text{SiO}_4$	957	—	865	817	560
$(\text{Mn}_{0.5}\text{Ni}_{1.5})\text{SiO}_4$	964	—	868	818	565
Ni_2SiO_4	972	916	868	823	575
Mg_2SiO_4	982	954	885	836	607
$(\text{Mg}_{1.5}\text{Ni}_{0.5})\text{SiO}_4$	980	953	884	835	605
$(\text{Mg}_{1.0}\text{Ni}_{1.0})\text{SiO}_4$	972	—	878	835	590
$(\text{Mg}_{0.5}\text{Ni}_{1.5})\text{SiO}_4$	964	—	874	826	572
Ni_2SiO_4	972	916	868	823	575

in this series was not a linear function of composition. The non-linearity of the absorption band shifts suggests that this is not a simple solid solution series. Ringwood (1956) showed this to be the case using melting relationships.

With the substitution of nickel for manganese in the synthetic Mn_2SiO_4 - Ni_2SiO_4 series, there was a slight increase in the frequency of the absorption bands. The frequency increase for each of the bands was again not a linear function of composition and suggested that this was not a simple solid solution series.

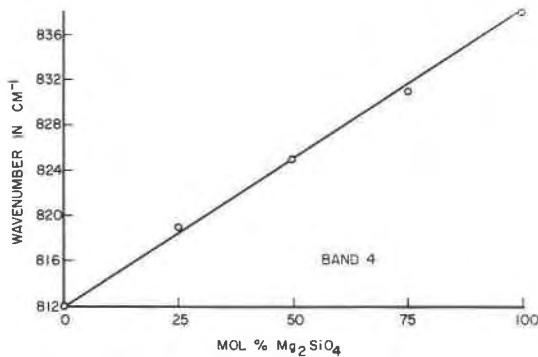


FIG. 8. Composition *vs.* wavenumber for band 4 in the synthetic series Mg_2SiO_4 - Mn_2SiO_4 .

THEORETICAL DISCUSSION

The theoretical treatment of mechanisms producing changes in the frequencies of the absorption bands requires relating, if possible, the absorption bands to particular vibrations in the olivine lattice.

One method is to treat the molecular vibrations using the classical equations for a simple harmonic oscillator. This is at best an approximation and in addition necessitates relating in advance each absorption band to a particular vibration of the molecule. It would be incorrect to

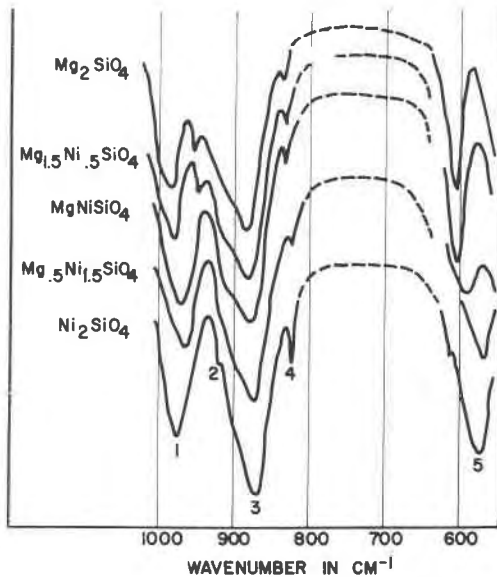


FIG. 9. Spectrogram tracings in the synthetic Mg_2SiO_4 - Ni_2SiO_4 series.

use the reduced mass for Mg and O if the absorption band considered was due primarily to Si-O stretching.

A better understanding of the relation between the structure of the molecule and the resulting infrared spectrum requires a detailed examination of the symmetry of the olivine molecule.

Isolated SiO_4 Tetrahedra. As a first approximation, the olivine lattice may be considered as composed of independent tetrahedra. Their positions in the olivine lattice or possible interactions may be excluded. In this case the SiO_4 molecules may be related to the XY_4 molecule discussed by Herzberg (1945) which has a point group symmetry T_d . The symmetry modes for the tetrahedral XY_4 molecule are represented schematically in Fig. 10.

It is necessary to determine which of these species are active in the infrared. This is accomplished by examining how the species transform in terms of the components of the dipole moment. It may be seen from the symmetry modes or from the character tables given by Herzberg (1945) that there is no dipole change in the species A_1 and E and that the F_2 species do have a dipole moment change. A_1 and E are therefore inactive in the infrared since there is no mechanism for an energy interchange

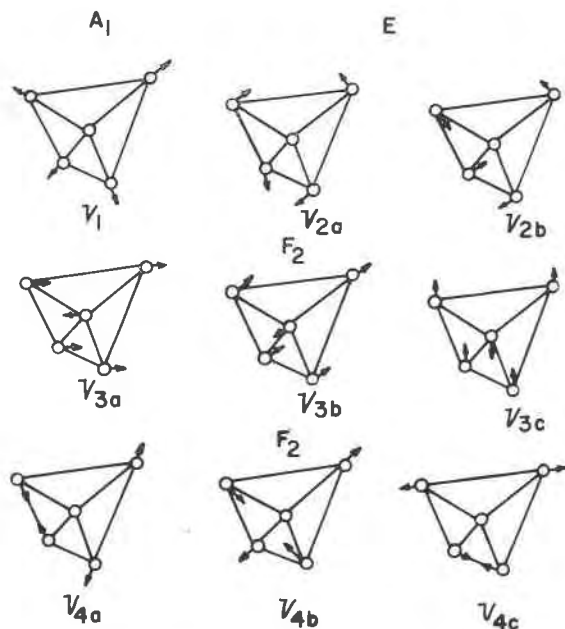


FIG. 10. Symmetry modes for an isolated XY_4 molecule.

from the infrared sample beam to the molecule. The F_2 species are active since they do undergo a dipole change.

It is possible to calculate the theoretical frequency of each vibration in the species and to compare these frequencies with the observed spectra. Assuming that valence forces exist between the Si and O nuclei Saksena (1961) calculated these theoretical frequencies using approximate force constants. He obtained the following frequencies $\nu_1 = 729 \text{ cm}^{-1}$, $\nu_2 = 473 \text{ cm}^{-1}$, $\nu_3 = 1031 \text{ cm}^{-1}$, and $\nu_4 = 493 \text{ cm}^{-1}$.

The correlation of the theoretical vibration frequencies for the isolated SiO_4 tetrahedron with the observed spectra is useful in the general assignment of the absorption bands. The triply degenerate vibration ν_3 , at approximately 1000 cm^{-1} , could account for absorption bands 1, 2 and

3, as seen in Fig. 1, if it could be shown that ν_3 is split into three distinct non-degenerate vibrations.

The frequency of absorption band 4 compares closely with the calculated frequency of ν_1 . However, ν_1 in the isolated tetrahedron is inactive in the infrared, and should not be observed. The frequency of bands 5, 6 and 7 are in the frequency range of that calculated for either ν_2 or ν_4 . However, ν_2 is also inactive in the infrared for an isolated tetrahedron. The ν_4 frequency could account for these bands if it were also split into three non-degenerate vibrations.

The assignment of the observed absorption bands is not complete using the model of an isolated tetrahedron. This model does not account for the splitting up of ν_2 , ν_3 and ν_4 into non-degenerate vibrations and the activation of ν_1 and ν_2 in the infrared which is required for an adequate assignment of the absorption bands.

SiO₄ Tetrahedra in the Olivine Lattice. In olivine, the SiO₄ tetrahedra are not isolated but are actually in a crystal lattice and therefore influenced by the potential field of that lattice. The effect of this potential field on the SiO₄ tetrahedra has already been empirically evidenced by changes in frequency of the absorption bands due to different substituent cations. It is therefore necessary to examine the symmetry of the olivine unit cell and to determine, if possible, the nature of this potential field and its effect on the vibrations of the SiO₄ tetrahedra. Thus, the forsterite structure can be thought of as consisting of SiO₄ tetrahedra distorted in a potential field of Mg nuclei.

The space group of the olivine minerals has been established as V_{11}^{16} by Bragg and Brown (1926). According to Halford (1946, p. 14) the possible symmetries in this space group are $2 C_i(4)$ and $C_s(4)$. This means that there are two distinct sets of lattice sites with C_i symmetry with four equivalent sites in each set. There is only one set of sites with a C_s symmetry and four equivalent positions per set. For Mg₂SiO₄ it is possible to distinguish each of these sets. The Mg ions have a center of symmetry corresponding to C_i . In addition, Wyckoff (1930, p. 64) lists the two general positions of the Mg ions corresponding to two distinct sets of sites with 4 Mg ions in each set. The SiO₄ group with no center of symmetry is then assigned to the C_s point symmetry.

Since the SiO₄ vibrations are believed to account for the observed absorption bands, it is now necessary only to analyze the C_s symmetry in terms of the group characters. This may be done by considering the symmetry distortion of the SiO₄ tetrahedra from T_d to C_s due to the influence of the surrounding potential field. The character table for the

point group T_d resolved to a C_s symmetry yields the following results (Herzberg, 1945, p. 237).

$$\begin{aligned} A_1 &\rightarrow A' \\ E &\rightarrow A' + A'' \\ F_2 &\rightarrow A' + A' + A'' \end{aligned}$$

Since there are two F_2 species, the total number of vibrational species are 6 A' and 3 A'' and all 9 become active in the infrared.

The infrared absorption spectra of the olivine minerals may now be interpreted in terms of these nine infrared active vibrations. The F_2 species ν_3 , split into three distinct non-degenerate vibrations, accounts for bands 1, 2 and 3. A similar assignment was made by Saksena (1961) and more recently by Tarte (1963). The A_1 species is now an A' species and is active in the infrared. Absorption band 4 is attributed to this ν_1 vibrational mode. The other F_2 species ν_4 is also split into three non-degenerate vibrations and accounts for bands 5, 6 and 7. The minor bands observed beyond approximately 450 cm^{-1} as seen in Fig. 2, may be assigned in part to the A' and A'' species, ν_{2a} and ν_{2b} , and in part to vibrations of the cation octahedra.

CONCLUSIONS

This study has shown that the olivine group minerals are characterized by their infrared absorption spectra. The configuration of the absorption bands was the same for all members of the olivine group. Each of the absorption bands shifted in frequency upon substitution of various cations into the lattice and the total frequency shift was different for each band. The frequency decrease of the absorption bands was linear for the forsterite-fayalite solid solution series. Linear shifts were also noted for other solid solution series such as the fayalite-tephroite series, and the synthetic $\text{Mg}_2\text{SiO}_4\text{-Mn}_2\text{SiO}_4$ series. Synthetic series containing Ni were assumed not to be simple solid solutions since the change in frequency of the absorption bands was not a linear function of composition.

The frequencies of the absorption bands decreased as the mass and ionic radii of the cations increased. The effects were algebraic functions, but their quantitative characteristics were not determined due to the influence of other factors such as electronegativity, polarizability, etc.

The observed spectra were correlated with the theoretical vibration frequencies of the olivine molecule. This correlation was inadequate when the SiO_4 tetrahedra were considered as isolated. This approximation, however, facilitated the calculation of the general positions of the SiO_4 vibrations.

The observed absorption bands can be assigned to particular molecular

vibrations by including the influence of the potential field surrounding the SiO_4 tetrahedra. These tetrahedra are distorted in the olivine crystal lattice from a T_d to a C_s symmetry which results in splitting of degenerate vibrations. Other vibrational modes are made active in the infrared by this symmetry distortion. Further refinements of frequency calculations in the complex symmetry field would allow the calculation of exact force constants from the observed spectra and facilitate an understanding of the effect of substituent cations on the intermolecular forces.

ACKNOWLEDGMENTS

We wish to thank those individuals and institutions who so gladly furnished mineral samples. Thanks are due to Dr. H. S. Yoder, Dr. Th. G. Sahama, Dr. A. Pabst, Dr. M. L. Jensen, and Drs. Holland and Sampson.

The assistance of personnel at the Kennecott Research Center is acknowledged. Discussions with Dr. W. M. Tuddenham were especially helpful. Thanks are due to Mr. E. R. Bingham for his help with the x-ray fluorescence analyses.

One of the authors, D. A. Duke, wishes to thank the University of Utah Research Committee which granted financial assistance during the course of this study. He especially wishes to thank the members of his research committee.

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Manuscript received, February 25, 1964; accepted for publication, June 29, 1964.