

Cation field effects on orthosilicate glass vibrations

QUENTIN WILLIAMS

Institute of Tectonics, Board of Earth Sciences, University of California, Santa Cruz, California 95064, U.S.A.

THOMAS F. COONEY

Hawaii Institute of Geophysics, University of Hawaii at Manoa, Honolulu, Hawaii 96822, U.S.A.

ABSTRACT

The infrared spectra of a range of binary orthosilicate glasses containing Fe, Ca, Mg, and Mn are presented. In particular, the frequencies of the ν_3 asymmetric stretching vibration (between 900 and 980 cm^{-1}) and the ν_4 bending vibration (between 508 and 555 cm^{-1}) of the SiO_4 tetrahedron are examined as a function of divalent cation content. Both bands decrease in frequency with greater mass and radius of the divalent cation at rates larger than those observed within the crystalline counterparts of these glasses. Calculations of force constants using a valence force-field model yield values compatible with previous investigations of phases containing isolated silica tetrahedra.

INTRODUCTION

The bonding properties of the SiO_4 tetrahedron are of critical importance in determining both the structural and thermodynamic characteristics of silicate melts, crystals, and glasses. The vibrational behavior of this species in a range of chemical environments is thus of significant interest, as the observed vibrational properties of the silica tetrahedron are dependent on the valence, radius, mass, and coordination of the cations acting to charge balance the tetrahedron. This study focuses on the effect of a range of divalent cations on the vibrations of SiO_4 units within orthosilicate composition glasses. We present new infrared spectra of olivine glasses on the Fe-Ca, Fe-Mg, Fe-Mn, Ca-Mg, and Ca-Mn joins, complementing previous infrared data on the Fe end-member (Kusabiraki and Shiraishi, 1981), Raman and infrared data on glasses on the Mg-Mn join (Williams et al., 1989), Raman data on glasses of monticellite (CaMgSiO_4) composition (Piriou and McMillan, 1983) and on the Fe-Mg, Fe-Mn, Ca-Mg, and Ca-Mn joins (Cooney and Sharma, 1990).

There have been numerous studies of the vibrations of the SiO_4 unit in crystalline environments, from which correlations between the observed vibrational bands and masses of neighboring cations and distortions of the SiO_4 group from ideal tetrahedral symmetry have been derived (Tarte, 1965; Burns and Huggins, 1972; Lazarev, 1972). Within amorphous materials, however, the study of the dependence of the vibrational modes of the isolated SiO_4 tetrahedron on local environment has been limited: although several studies have resolved vibrations resulting from this species, there has been little effort spent in characterizing the changes in energy of these modes that result from changes in neighboring cations. This is in marked contrast to more polymerized silicate anions in which one or more of the O atoms bridges between tetrahedra, the behavior of which has been extensively

examined (Furukawa et al., 1981; Mysen et al., 1982; McMillan, 1984). Probing nonpolymerized glasses spectroscopically has at least two advantages: First, as there is no long-range symmetry, the average vibrational properties of tetrahedra in the range of local environments present within the glass may be examined. Second, data on a range of class compositions may be used to infer the effect of different charge-balancing cations on the bonding forces of the SiO_4 unit.

EXPERIMENTAL

All glasses were synthesized by splat-quenching olivine liquid between Al blocks in an Ar atmosphere, using a technique described elsewhere (Williams et al., 1989; Sur and Cooney, 1989; Cooney et al., in preparation). Glasses containing more than 50% Ca as the divalent cation proved impossible to synthesize using this technique, as even at these rapid quench rates crystallization of these compositions occurred. Electron microprobe results document that the cation compositions of all glasses are within 2 mol% of the intended initial content, and no phase separation was observed at the optical microscopic level in any of the samples. Additionally, wet chemical and Mössbauer analyses of the fayalite glass sample document that any trivalent Fe present within this glass is present at a concentration below that detectable by these methods, although electron spin resonance techniques do detect a small concentration of Fe^{3+} (see Sur and Cooney, 1989). Trivalent Fe is thus present at levels significantly less than 1% of the Fe_{tot} , confirming that these samples were synthesized in an environment with limited oxidation capacity (Cooney, 1988; Williams et al., 1989).

All infrared spectra were taken using a DA3.02 Bomem Fourier transform infrared spectrometer with 4- cm^{-1} resolution between 400 and 4000 cm^{-1} . Approximately 90 μg of each glass were ground under acetone to an average

particle size of 2–3 μm . This powder was then mixed with about 9 mg of KBr and pressed into pellets with a diameter of 3 mm. This KBr pellet technique was expected to produce peak locations that closely approximate those of the true transverse optic (TO) frequencies of the glass, as the accuracy of this technique for corresponding crystalline orthosilicates is excellent. The maximum deviation between peak locations determined from single-crystal reflectance studies of orthosilicates and powder infrared measurements is $\sim 20\text{ cm}^{-1}$ in the frequency range above 400 cm^{-1} , and for most modes the two techniques differ by between 0 and 10 cm^{-1} (Paques-Ledent and Tarte, 1973; Oehler and Günthard, 1969; Servoin and Piriou, 1973; Hohler and Funck, 1973; Stidham et al., 1976; Iishi, 1978; Hofmeister, 1987). Moreover, any deviations from the true transverse optic frequency are likely to be systematic among samples prepared in a similar manner. One notable limitation of the powder technique in crystalline studies is that modes of similar frequency but produced by vibrations of different symmetries are indistinguishable. However, in the studies of isotropic glasses described here, this difficulty was alleviated, and we anticipated that our results would accurately approximate the average frequency of vibration of the SiO_4 tetrahedron within these amorphous environments.

RESULTS AND DISCUSSION

Spectral results

Infrared spectra of glasses on the Mg-Fe and Fe-Mn joins are displayed in Figures 1A and 1B; Figure 1C shows spectra of Ca-bearing glasses. All glasses have spectra that are extremely similar to one another and to those of glasses on the Mg-Mn binary (Williams et al., 1989). The spectra are characterized by two strong absorption peaks, one varying in frequency between 900 and 980 cm^{-1} and the other between 510 and 560 cm^{-1} . Undistorted tetrahedra have four optically active vibrational modes corresponding to a symmetric stretch of the O atoms (ν_1), a symmetric bending vibration (ν_2), and an asymmetric stretch and bend (ν_3 and ν_4 , respectively); of these, ν_3 and ν_4 are strongly infrared active. Therefore, the peaks we observe are almost certainly associated with the ν_3 asymmetric stretching and ν_4 bending vibrations of the SiO_4 tetrahedron, with the ν_3 band appearing at higher frequency. Within many of the Mg-bearing glasses, there is a shoulder observed at about 850 cm^{-1} on the low-energy side of the strong ν_3 peak. This feature is likely to be associated with weak infrared activity of the ν_1 symmetric stretching vibration, in accord with its similarity in frequency to that of the ν_1 vibration in the Raman spectrum of these glasses (Cooney and Sharma, 1990). Such infrared activity of ν_1 could be induced by either the SiO_4 group itself or its local environment deviating from ideal tetrahedral symmetry (cf. Williams et al., 1989). Secondary absorption features are present in the spectra of all glasses at between 680 and 720 cm^{-1} , a spectral region in which vibrations attributed to symmetric stretching vibrations

of the Si-O-Si unit occur (Tarte, 1965; Lazarev, 1972). Notably, the lack of significant shifts in the energy of these bands with respect to cation substitution confirms that these weak features are associated with vibrations of silica units. Were these modes due to combination bands (involving divalent cation motion) such as those observed weakly in forsterite in this frequency range (Hofmeister, 1987), these modes would be expected to vary markedly in energy across the compositional range probed in this study. This presence of a small amount of polymerization in orthosilicate glasses appears to be ubiquitous: all such glasses characterized to date show evidence of the presence of some Si-O-Si linkages (Piriou and McMillan, 1983; Williams et al., 1989; Cooney and Sharma, 1990). Nevertheless, Raman spectral data strongly indicate that the dominant silicate units within such glasses are, in fact, tetrahedra without inter- SiO_4 group polymerization (Piriou and McMillan, 1983; McMillan, 1984; Williams et al., 1989). Also, Raman spectra of Fe-bearing olivine glasses indicate that these glasses are more polymerized than Fe-free compositions and that this polymerization is plausibly associated with linkages between SiO_4 tetrahedra and less than sixfold coordinated Fe (Cooney and Sharma, 1990).

The only infrared spectrum reported for a vitreous sample of any of these compositions, that of Fe_2SiO_4 glass by Kusabiraki and Shiraishi (1981), is of similar morphology to ours, with strong ν_3 and ν_4 peaks and a weak intermediate frequency band near 700 cm^{-1} . However, their ν_3 and ν_4 vibrations appear at 933 and 508 cm^{-1} , respectively, as compared to 916 and 524 cm^{-1} in the present study. As no postsynthesis compositional analyses of their fayalite glass sample, quench rates, or accuracies in frequency measurement were reported by Kusabiraki and Shiraishi, it is difficult to evaluate the origin of the discrepancy in frequency between their spectrum and that of Figure 1A.

The Mg-bearing glasses also have an absorption near 400 cm^{-1} , which probably results from vibrations of Mg in octahedral coordination (see Williams et al., 1989). Within the $(\text{Mg}_{1.5}\text{Fe}_{0.5})_2\text{SiO}_4$ composition and to a lesser extent in the Ca-Mg glasses, a band or shoulder is present at about 580 – 590 cm^{-1} . A similar feature also occurs in $(\text{Mg}_{1.5}\text{Mn}_{0.5})_2\text{SiO}_4$ glass (Williams et al., 1989). This spectral region has been associated with Mg in tetrahedral coordination based on spectral studies of akermanite-type structures (Tarte, 1965). Indeed, if this band does represent a vibration of Mg in tetrahedral coordination, then our assignment of this band is analogous to that originally utilized to identify spectroscopically fourfold coordinate Al in soda-aluminosilicate glasses (Kolesova, 1959; Day and Rindone, 1962). Thus, it appears that the presence of larger cations within magnesian glasses may cause some of the Mg to enter fourfold coordination. An alternative interpretation, which we cannot preclude, for the origin of this shoulder at 580 – 590 cm^{-1} is that it is also generated by the ν_4 vibration, as peaks associated with this vibration in crystalline silicate olivines span a spectral

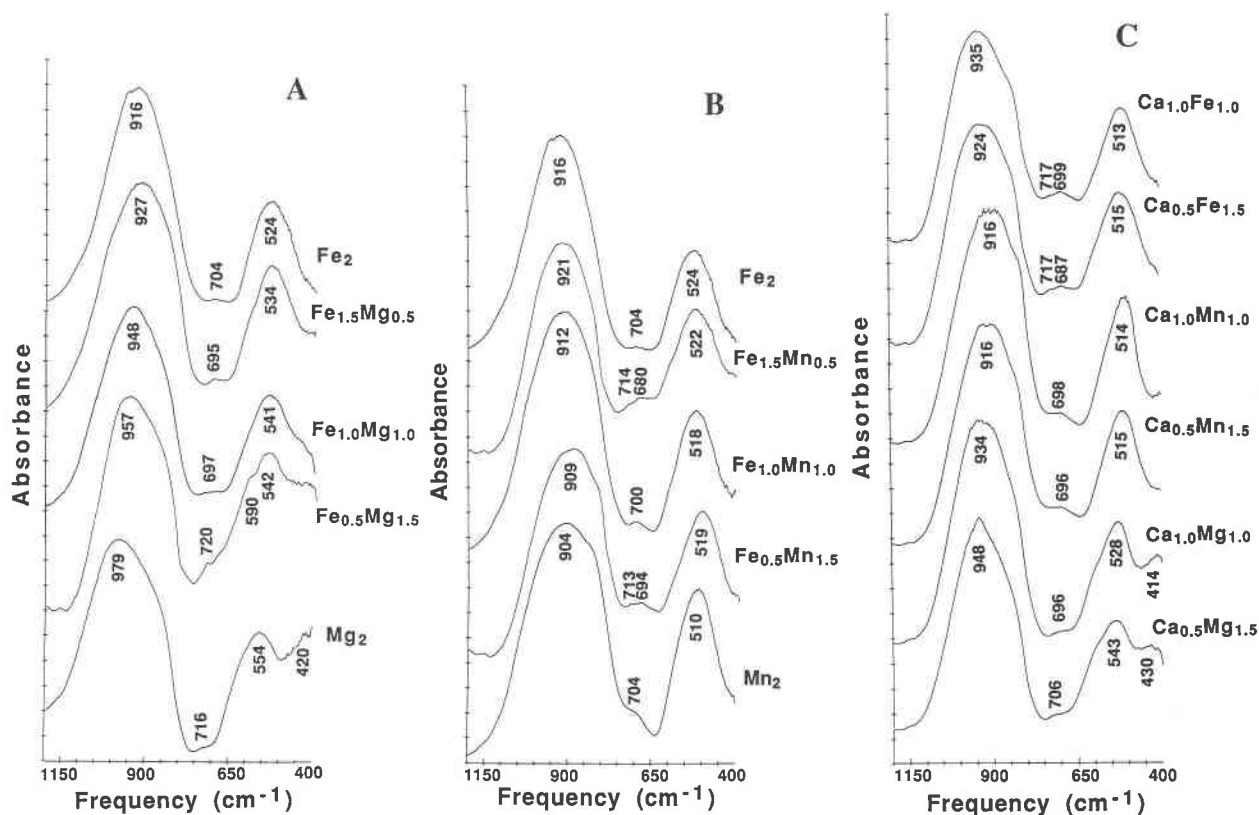


Fig. 1. (A) Infrared absorption spectra of glasses on the Fe-Mg join. Spectrum of the forsterite composition end-member is from Williams et al. (1989). (B) Infrared absorption spectra of glasses on the Fe-Mn join. Spectrum of the tephroite composition end-member is from Williams et al. (1989). (C) Infrared absorption spectra of Ca-bearing olivine composition glasses.

range between about 450 and 600 cm^{-1} (Duke and Stephens, 1964; Paques-Ledent and Tarte, 1973; Iishi, 1978; Hofmeister, 1987). However, if this latter interpretation is correct, we must invoke a compositional effect induced only by Mg among the range of divalent cation compositions examined in this study, as only the presence of Mg induces this possible splitting of the ν_4 vibration. Finally, we note that in several Fe-rich glasses the Si-O-Si symmetric stretching mode is split into two components, at about 680–700 and 710–720 cm^{-1} , with the lower frequency band being consistently higher in amplitude. This splitting of these stretching bands may result because there are two distinct types of Si_2O_6 environments within the glass or, alternatively, because one of these bands may represent the symmetric stretching vibration of more highly polymerized species than those containing two Si atoms.

Compositional variations of orthosilicate glass vibrations

One of the major questions we wish to address is that of the role of different cations in determining the vibrational frequencies of the SiO_4 tetrahedron within these glasses. Such trends between composition and infrared mode frequency have been documented in crystalline ol-

ivines by many authors (Duke and Stephens, 1964; Tarte, 1965; Burns and Huggins, 1972; White, 1975), but as yet no analogous study has been conducted within their amorphous analogues. In Figures 2A and 2B, the ν_3 and ν_4 mode frequencies are shown as a function of $(\mu^*R^3)^{-1/2}$, where μ is the reduced mass of the metal-O system and R is an average ionic radius for each cation in octahedral coordination with O (Shannon, 1976); thus, we assume for this comparison that octahedral coordination of the M^{2+} cations predominates within these glasses. For comparison, we also show in Figure 2A representative distances by which the trends in Figure 2 would be offset if entirely tetrahedral coordination of divalent cations were present within these glasses. [Although transition metal cations with such low coordination numbers have been documented within a range of silicate glasses and melts (Waseda, 1980; Waychunas et al., 1988; Williams et al., 1989; Cooney and Sharma, 1990), their absolute abundance is uncertain within orthosilicate glasses.] This analysis is based upon a semitheoretical model in which a coulombic interaction between the metal cation and O is assumed, and the vibration is assumed to be harmonic (cf. White and Roy, 1964; Batsanov and Derbeneva, 1969). This comparison should hold in that vibrational

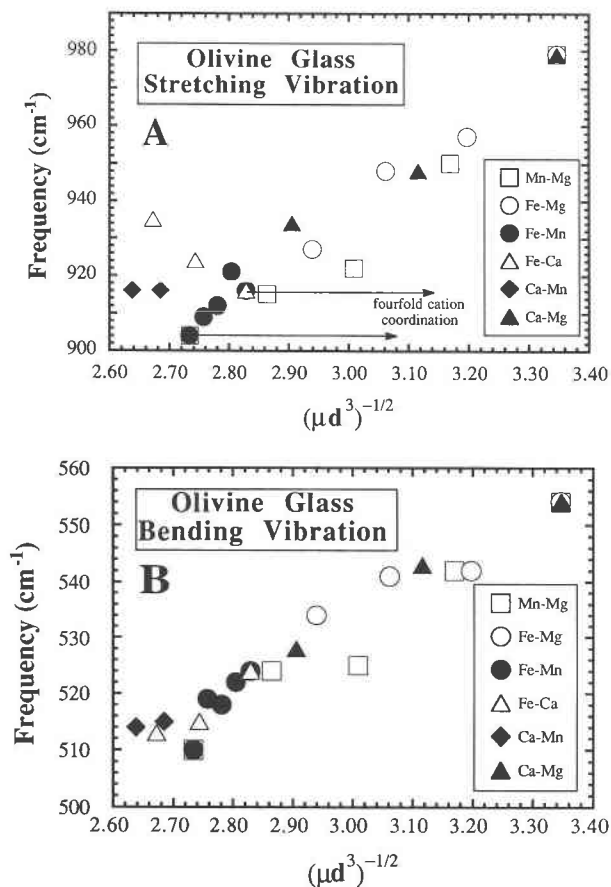


Fig. 2. (A) Frequency of the ν_3 tetrahedral stretching vibration as a function of the divalent cation harmonic stretching force constant. M-O bond lengths are from Shannon (1976) and assume octahedral coordination of the M^{2+} cations. Data on the Mg-Mn join are from Williams et al. (1989). Abscissa units are in $\text{g}^{-1/2} \text{nm}^{-3/2}$. Arrows indicate positions where the fayalite and tephroite composition end-members would lie if entirely tetrahedral coordination of cations were present in these glasses. (B) Frequency of the ν_4 bending vibration as a function of the harmonic stretching force constant of the divalent cations. Points with the appropriate superimposed symbols represent the end-member compositions.

expansion (or compression) of the tetrahedral Si-O bond results in a change in length of the bonds between any neighboring metal cations and the nonbridging O atom. However, the force exerted on the Si-O vibrations by juxtaposed divalent cations should also be dependent both on the number of metal cations coordinating the O and on the Si-O-M bond angle as well as the amount of lower than sixfold coordinated divalent cations in these glasses.

The shift in frequency with the mass-weighted force constant is systematic, with both the ν_3 and ν_4 vibrations decreasing in energy with greater cation radius. The only major deviations from these trends occur in the ν_3 vibrations of the Ca-Mn and Ca-Fe systems; we have no simple explanation for this but note that the numerical range

of mass-weighted force constant spanned by these glasses is narrower by a factor of 4 than the binaries involving Mg. Thus, we speculate that structural effects associated with Ca, such as the possible presence of irregular divalent cation coordination (cf. Waseda, 1980) or of low-coordination transition metal ion environments in calcic glasses, dictate the shift in the ν_3 frequency of the Ca-transition metal joins.

Notably, the energy of the ν_4 vibration is better described by the correlation of frequency with $(\mu^*R^3)^{-1/2}$ than is the ν_3 vibration. The maximum deviation of the ν_4 vibration of any glass from the linear trend of Figure 2B is 10 cm^{-1} , whereas that for the ν_3 vibrations (Fig. 2A) is nearly 25 cm^{-1} . We speculate that the greater success of this relation in describing the frequency of the ν_4 vibration relative to the ν_3 mode is due to the interaction of each mode with its neighboring divalent cations. In an ideal tetrahedron, the motion of O atoms in both the ν_3 and ν_4 vibrations is oblique to the Si-O bonds (Herzberg, 1945). As such, each vibration must produce contraction and expansion of neighboring metal-O bonds, and it is this effect that is reflected in the correlation in Figure 2. Depending on both the coordination number of the O anion and the M-O-Si bond angles, however, each vibration will also generate some bending of M-O bonds. As the formula used to derive Figure 2 strictly applies only in the case of harmonic stretching vibrations, it may be that the poorer correlation exhibited by the ν_3 vibration relative to the ν_4 mode is due to a larger component of bending of the neighboring M-O bonds than in the ν_3 mode.

The vibrational frequencies of the isolated SiO_4^{4-} tetrahedron are unknown, as this group is likely to be unstable when not charge balanced by positively charged groups in either solutions, crystals, or glasses (e.g., Jug and Ozias, 1985; Lazarev, 1988). Within solutions, the frequencies of the asymmetric bending and stretching vibrations of SiO_4 tetrahedra in aqueous solutions are variously estimated at between 520 and 610 cm^{-1} and between 930 and 960 cm^{-1} , respectively (Fortnum and Edwards, 1956; Handke, 1984; Nakamoto, 1986). These values are in a similar range as the frequencies of these vibrations observed in this study for orthosilicate glasses, implying that the silica tetrahedron has similar bonding properties within the two amorphous networks. If we simply extrapolate the trends of Figure 2 to the extreme in which the M-O bond strength is zero $[(\mu^*R^3)^{-1/2} = 0]$, we derive estimates of the ν_4 and ν_3 frequencies of an isolated tetrahedron of approximately 370 and 750 cm^{-1} . The validity of this extrapolation to infinite divalent cation distance depends, however, on the charge distribution within the tetrahedron itself remaining constant during this transformation (cf. Ohwada, 1980). Nevertheless, the marked discrepancy of these frequencies with those measured for the charge-balanced SiO_4 tetrahedron within crystals, liquids, and glasses illustrates the marked effect of the stabilizing environment on the vibrations of this group.

Comparison with crystalline olivines

The trend of decreasing frequency with increasing cation radius has been well documented in the case of crystalline olivines (Toropov et al., 1963; Duke and Stephens, 1964; Tarte, 1965; Burns and Huggins, 1972; White, 1975; Handke, 1984). One of the goals of this study is to compare our spectral data on amorphous olivine compositions with average trends observed in their crystalline analogues. However, a precise derivation of such an average frequency of the ν_3 or ν_4 vibrations within olivine crystals would require (1) averaging to remove the effect of distortions of the SiO_4 group from ideal tetrahedral symmetry within the olivine structure and (2) incorporating the effects of dispersion across the Brillouin zone, as symmetry dependent selection rules will be relaxed within these glassy environments. In the latter case, the magnitude and sign of such dispersive effects are ill constrained, and we treat dispersion as producing an average frequency equivalent to that produced by an average of the experimentally observed zone-center modes. Both the ν_3 and ν_4 modes give rise to six Raman and five infrared bands in single-crystal olivines; therefore, an average of these frequencies requires oriented single-crystal Raman and infrared reflectance data. Unfortunately, among the compositions studied here, this combination of data only exists for forsterite (Servoin and Piriou, 1973; Iishi, 1978; Hofmeister, 1987); although two studies of the single-crystal Raman and infrared spectra of tephroite exist, positions of several of the ν_3 bands of this material remain unconstrained (Hohler and Funck, 1973; Stidham et al., 1976).

Because of this lack of single-crystal data, we utilize a simpler averaging technique based on results from powder infrared data, for which data exist in the literature for compositions within 4 mol% in divalent cation content of 11 of the 18 olivine glass compositions studied to date. From group theoretical constraints, the average frequency of the ν_3 tetrahedral vibration in crystalline olivines is intermediate between the highest and third highest frequency infrared bands resolvable in powder spectra (labeled bands 1 and 3, respectively, by Duke and Stephens, 1964, and Burns and Huggins, 1972). In particular, it should lie at about one-third of their energy separation above the lower frequency band (Servoin and Piriou, 1973; White, 1975). Although an approximation, we note that this technique produces an average ν_3 energy of 918 cm^{-1} for forsterite using the data of Duke and Stephens and 921 cm^{-1} using the relations of Burns and Huggins extrapolated to end-member forsterite. For comparison, an average of the 11 ν_3 infrared and Raman vibrations of Iishi (1978) yields 924 cm^{-1} ; incorporating the more recent infrared assignments of Hofmeister (1987) with the Raman data of Iishi lowers this value to 920 cm^{-1} . Therefore, we regard this approximation as producing a reasonable average of the ν_3 frequency for the olivines in this study. Comparable efforts to remove site-group and factor-group splitting effects from the frequency of the ν_4

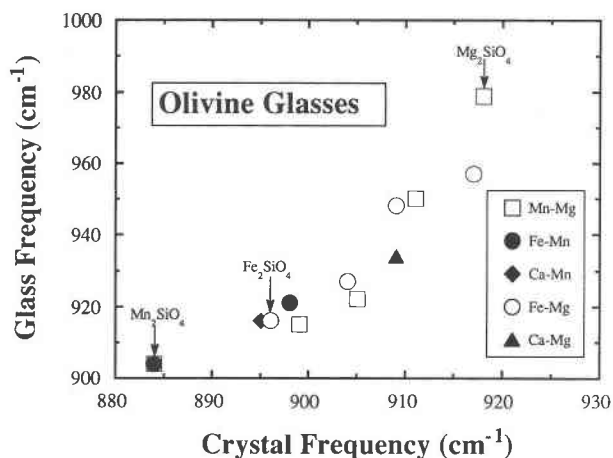


Fig. 3. Comparison of the frequency of the tetrahedral stretching vibration in olivine glasses and crystals. Note the different frequency scales of the axes. Crystalline vibrational frequencies are from Duke and Stephens (1964) and Burns and Huggins (1972) and are for either isochemical compositions or those within 4 mol% of the composition of the corresponding glass. The frequencies have also been averaged to remove effects of site-group splitting within the crystalline olivines (see text).

bending mode are complicated by the presence of overlapping bands, bands involving cation motion, and more limited data in this lower frequency spectral range. However, such bending averages (where feasible) scatter on both the high- and low-frequency sides of those of the isochemical glasses.

Figure 3 shows a comparison of the averaged frequency of the ν_3 vibration of crystalline olivines from Duke and Stephens (1964) and Burns and Huggins (1972) with those of the glasses measured in this study. The frequencies of the glass asymmetric stretching vibration are between 20 and 65 cm^{-1} greater than our estimates of the average crystalline frequencies, with a systematic trend toward greater frequency differences in the case of Mg-rich glasses. There are three possible origins for these trends. First, the larger energy for the glass vibrations may be partially due to the presence of some bridging O atoms within the amorphous network, as manifested by the Si-O-Si stretching vibration at about 700 cm^{-1} in the spectra of Figure 1. Such bridging O atoms would be expected to produce a high-frequency component to this stretching mode (Furukawa et al., 1981; Dowty, 1987). Second, if some four- or fivefold coordinated cations exist within the glass, the frequency of the SiO_4 stretching vibration would be raised because of the presence of these more tightly bound cations. In this regard, the notable increase in separation from the crystalline frequencies of Mg-rich glasses may be correlated with the presence of some tetrahedral Mg, as indicated by the presence of a shoulder at 580 cm^{-1} in the spectra of these glasses. Third, although in silicate olivines the Si-O distances are notably invariant with respect to changes in divalent cation composition (cf. Brown, 1980), this constraint may be relaxed

within the amorphous structures described here. Thus, a compositionally dependent contraction of the Si-O bond, such as that proposed to explain the high frequencies of the ν_1 vibration in many of these glasses relative to that of the isochemical crystals, could produce the observed shift in frequencies between glasses and olivine crystals (Cooney and Sharma, 1990).

Tetrahedral force constants

The force constants of the SiO_4 group, and their shifts with composition, may provide insight into changes in the local bonding environment of the tetrahedron. To calculate these constants, we utilize a modified valence force field with four force constants (Siebert, 1953; Tarte, 1965). This approach treats the vibrations of the SiO_4 group as those of an isolated tetrahedron and assumes that vibrations in the calculated force constants of this unit are not produced by changes in the internal geometry or charge distribution in the group. Notably, this internal mode approximation for the SiO_4 tetrahedron, in which the cations stabilizing the SiO_4 group are ignored in the force constant calculation, is essentially identical to that made by a variety of other authors in calculating force constants for this group from experimental data or in comparing ab initio calculations with those derived from experimental data on aqueous fluids, minerals, or glasses (e.g., Tarte, 1965; Furukawa et al., 1981; Gibbs et al., 1981; Handke, 1984; Hess et al., 1986; Dowty, 1987).

Our rationale for using this type of force field is straightforward: we may solve for the stretching, bending, and bond-bond interaction forces from the observed ν_1 , ν_3 , and ν_4 vibrations without being required to assign frequencies to the ill-constrained ν_2 vibration or to estimate the angle-angle force constant. This approach also represents an approximation to the actual force field within the silica tetrahedron because both bond-angle and higher order interactions are neglected. In order to solve for these three force constants, we utilize the observed frequencies of the ν_3 and ν_4 infrared vibrations and those of the ν_1 vibration for glasses on the Mg-Mn join and CaMgSiO_4 (Williams et al., 1989; Piriou and McMillan, 1983). In two cases, we iterate to find the nearest nondivergent force-constant solution from this force field: these solutions had frequencies that were within 3 cm^{-1} of the experimental observations.

The calculated Si-O stretching force constant varies from about 4.05 to $4.55 \times 10^5 \text{ dyn/cm}$ as Mg content is increased across the Mg-Mn join, whereas that of CaMgSiO_4 is about $4.25 \times 10^5 \text{ dyn/cm}$. These values are consistent with previous estimates based on spectra of the silica anion in aqueous solution (4.30 – $4.4 \times 10^5 \text{ dyn/cm}$, Basile et al., 1973) and are in the range of those derived from both crystalline and amorphous orthosilicates using various force-constant models (3.5 – $5.9 \times 10^5 \text{ dyn/cm}$, Tarte, 1965; Devarajan and Funck, 1975; Iishi, 1978; Furukawa et al., 1981; Handke et al., 1984; Dowty, 1987). Our calculated values of the bending force constant increase slightly from ~ 0.9 to $1.1 \times 10^5 \text{ dyn/cm}$

with greater Mg content, whereas the bond-bond interaction decreases from 1.1 to $0.8 \times 10^5 \text{ dyn/cm}$ across the same compositional range. This negative change in the bond-bond interaction is generated by the increase in frequency of the ν_1 Raman vibration across this system, an effect attributed to a shift in coordination of the divalent cation from dominantly octahedral to partially four- or fivefold in Mn-rich glasses (Williams et al., 1989). Thus, the bond-bond interaction force constant may be particularly sensitive to shifts or local variations in cation coordination in these glasses, with this interaction weakening as divalent cation-O bonds are strengthened.

CONCLUSIONS

Olivine glasses on the Mg-Fe, Mn-Fe, Ca-Mg, Ca-Mn, Mg-Mn, and Ca-Fe binary joins all have markedly similar infrared spectra, characterized by dominant asymmetric stretching and bending peaks. Both bands decrease in frequency systematically as a function of increased mass and radius of divalent cations. However, shifts in the asymmetric stretching band are significantly greater than those for isochemical crystals. Force constants derived from the observed spectra are in good agreement with previous estimates of these parameters for SiO_4 tetrahedra in a range of environments.

ACKNOWLEDGMENTS

Work supported by NASA and the W.M. Keck Foundation at UCSC and NSF at UC Berkeley; we thank R. Hemley, A. Hofmeister, and an anonymous reviewer for helpful comments. Contribution no. 77 of the Institute of Tectonics at UCSC.

REFERENCES CITED

- Basile, L.J., Ferraro, J.R., LaBonville, P., and Wall, M.C. (1973) A study of force fields for tetrahedral molecules and ions. *Coordination Chemistry Reviews*, 11, 21–69.
- Batsanov, S.S., and Derbeneva, S.S. (1969) Effect of valency and coordination of atoms on position and form of infrared absorption bands in inorganic compounds. *Journal of Structural Chemistry*, 10, 510–515.
- Brown, G.E. (1980) Olivine and silicate spinels. In *Mineralogical Society of America Reviews in Mineralogy*, 5, 275–381.
- Burns, R.G., and Huggins, F.E. (1972) Cation determinative curves for Mg-Fe-Mn olivines from vibrational spectra. *American Mineralogist*, 57, 967–985.
- Cooney, T.F. (1988) Spectroscopic and calorimetric studies of olivine glass and crystal and the origin of ultramafic liquid immiscibility. Ph.D. dissertation, Department of Geological Sciences, University of Oregon, Eugene, Oregon.
- Cooney, T.F., and Sharma, S.K. (1990) Structure of glasses in the systems Mg_2SiO_4 - Fe_2SiO_4 , Mn_2SiO_4 - Fe_2SiO_4 , Mg_2SiO_4 - CaMgSiO_4 , and Mn_2SiO_4 - CaMnSiO_4 . *Journal of Non-Crystalline Solids*, 122, 10–32.
- Day, D.E., and Rindone, G.E. (1962) Properties of soda aluminosilicate glasses: I. Refractive index, density, molar refractivity, and infrared absorption spectra. *Journal of the American Ceramic Society*, 45, 489–496.
- Devarajan, V., and Funck, E. (1975) Normal coordinate analysis of the optically active vibrations ($k = 0$) of crystalline magnesium orthosilicate Mg_2SiO_4 (forsterite). *Journal of Chemical Physics*, 62, 3406–3411.
- Dowty, E. (1987) Vibrational interactions of tetrahedra in silicate glasses and crystals: I. Calculations on ideal silicate-aluminate-germanate structural units. *Physics and Chemistry of Minerals*, 14, 80–93.
- Duke, D.A., and Stephens, G.D. (1964) Infrared investigation of the olivine group minerals. *American Mineralogist*, 49, 1388–1406.
- Fortnum, D., and Edwards, J.O. (1956) The Raman spectrum and the

- structure of the aqueous silicate ion. *Journal of Inorganic and Nuclear Chemistry*, 2, 264–265.
- Furukawa, T., Fox, K.E., and White, W.B. (1981) Raman spectroscopic investigation of the structure of silicate glasses. III. Raman intensities and structural units in sodium silicate glasses. *Journal of Chemical Physics*, 75, 3226–3237.
- Gibbs, G.V., Meagher, E.P., Newton, M.D., and Swanson, D.K. (1981) A comparison of experimental and theoretical bond length and angle variations for minerals, inorganic solids, and molecules. *Structure and bonding in crystals*, vol. 1, p. 195–225. Academic Press, New York.
- Handke, M. (1984) Force constants and chemical bond character in (SiO_4) and (GeO_4) anions in orthosilicates and orthogermanates. *Journal of Molecular Structure*, 114, 187–190.
- Handke, M., Kosinski, K., and Tarte, P. (1984) Vibrational spectra and force constants calculations of the isotopic species of CaMgSiO_4 . *Journal of Molecular Structure*, 115, 401–404.
- Herzberg, G. (1945) *Molecular spectra and molecular structure. II. Infrared and Raman spectra of polyatomic molecules*. Van Nostrand, New York.
- Hess, A.C., McMillan, P.F., and O'Keeffe, M. (1986) Force fields for SiF_4 and H_2SiO_4 : Ab initio molecular orbital calculations. *Journal of Physical Chemistry*, 90, 5661–5665.
- Hofmeister, A.M. (1987) Single-crystal absorption and reflection infrared spectroscopy of forsterite and fayalite. *Physics and Chemistry of Minerals*, 14, 499–513.
- Hohler, V., and Funck, E. (1973) Vibrational spectra of crystals with olivine structure I. Silicates. *Zeitschrift für Naturforschung*, 28b, 125–139.
- Iishi, K. (1978) Lattice dynamics of forsterite. *American Mineralogist*, 63, 1198–1208.
- Julg, A., and Ozias, Y. (1985) Stabilization of complex ions by the crystal field: CO_3^{2-} , NO_3^- , O_3^- , $[(\text{OH})_4]^{4-}$, $[(\text{OH})_3\text{F}]^{4-}$, $[(\text{OH})_2\text{F}_2]^{4-}$. *Physics and Chemistry of Minerals*, 12, 307–310.
- Kolesova, V.A. (1959) Study of the structure of alkali aluminosilicate glasses based on their infrared absorption spectra. In E.A. Porai-Koshits, Ed., *Structure of glass*, vol. 2, p. 177–179. Plenum Press, New York.
- Kusabiraki, K., and Shiraishi, Y. (1981) The infrared spectrum of vitreous fayalite. *Journal of Non-Crystalline Solids*, 44, 365–368.
- Lazarev, A.N. (1972) *Vibrational spectra and structure of silicates*. Consultants Bureau, New York.
- (1988) Vibrational spectra, lattice dynamics and chemical constitution of oxides. *Physics and Chemistry of Minerals*, 16, 61–72.
- McMillan, P. (1984) Structural studies of silicate glasses and melts: Applications and limitations of Raman spectroscopy. *American Mineralogist*, 69, 622–644.
- Mysen, B.O., Virgo, D., and Seifert, F.A. (1982) The structure of silicate melts: Implications for chemical and physical properties of natural magma. *Reviews of Geophysics and Space Physics*, 20, 353–383.
- Nakamoto, K. (1986) *Infrared and Raman spectra of inorganic and coordination compounds* (4th edition). Wiley-Interscience, New York.
- Oehler, O., and Günthard, H.H. (1969) Low-temperature infrared spectra between 1200 and 20 cm^{-1} and normal-coordinate analysis of silicates with olivine structure. *Journal of Chemical Physics*, 51, 4719–4728.
- Ohwada, K. (1980) The application of an effective nuclear charge model to the prediction of valence force constants in tetrahedral XY_4 molecules. III. *Journal of Chemical Physics*, 73, 5459–5463.
- Paques-Ledent, M.Th., and Tarte, P. (1973) Vibrational studies of olivine-type compounds I. The IR and Raman spectra of the isotopic species of Mg_2SiO_4 . *Spectrochimica Acta*, 29A, 1007–1016.
- Piriou, B., and McMillan, P. (1983) The high-frequency vibrational spectra of vitreous and crystalline orthosilicates. *American Mineralogist*, 68, 426–443.
- Servoin, J.L., and Piriou, B. (1973) Infrared reflectivity and Raman scattering of Mg_2SiO_4 single crystal. *Physica Status Solidi (b)*, 55, 677–686.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.
- Siebert, H. (1953) Raman spectra and constitution of orthoperiodic acid and metaperiodate ions. *Zeitschrift Anorganische Allgemeine Chemie*, 274, 21–27.
- Stidham, H.D., Bates, J.B., and Finch C.B. (1976) Vibrational spectra of synthetic single crystal tephroite, Mn_2SiO_4 . *Journal of Physical Chemistry*, 80, 1226–1234.
- Sur, S., and Cooney, T.F. (1989) Electron paramagnetic resonance study of iron (III) and manganese (II) in the glassy and crystalline environments of synthetic fayalite and tephroite. *Physics and Chemistry of Minerals*, 16, 693–696.
- Tarte, P. (1965) Étude expérimentale et interprétation du spectre infrarouge des silicates et des germanates. Application à des problèmes structuraux relatifs à l'état solide. *Mémoires Académie Royale Belgique*, 35(4) 1–260a, 1–139b.
- Toropov, N.A., Fedorov, N.F., and Shevyakov, A.M. (1963) Infrared absorption spectra of orthosilicates of some bivalent elements. *Russian Journal of Inorganic Chemistry*, 8, 697–699.
- Waseda, Y. (1980) *The structure of non-crystalline materials*. McGraw-Hill, New York.
- Waychunas, G.A., Brown, G.E., Jr., Ponader, C.W., and Jackson, W.E. (1988) Evidence from X-ray absorption for network-forming Fe^{2+} in molten alkali silicates. *Nature*, 332, 251–253.
- White, W.B. (1975) Structural interpretation of lunar and terrestrial minerals by Raman spectroscopy. In C. Karr, Jr., Ed., *Infrared and Raman spectroscopy of lunar and terrestrial minerals*, p. 325–358. Academic Press, Orlando, Florida.
- White, W.B., and Roy, R. (1964) Infrared spectra-crystal structure correlations: II. Comparison of simple polymorphic minerals. *American Mineralogist*, 49, 1670–1687.
- Williams, Q., McMillan, P., and Cooney, T.F. (1989) Vibrational spectra of olivine composition glasses: The Mg-Mn join. *Physics and Chemistry of Minerals*, 16, 352–359.

MANUSCRIPT RECEIVED FEBRUARY 20, 1990

MANUSCRIPT ACCEPTED SEPTEMBER 9, 1991