American Mineralogist, Volume 62, pages 136–141, 1977

A comparison of silicon–oxygen bonding in quartz and magnesian olivine from X-ray spectra and molecular orbital calculations

J. A. TOSSELL

Department of Chemistry
University of Maryland
College Park, Maryland 20742

Abstract

X-ray photoelectron (XPS) and X-ray emission spectra (XES) show the valence region of magnesian olivine to be narrower than that of SiO_2. The observed narrowing of the upper valence region results from a destabilization of the $5a_1$ and $4t_2$ bonding orbitals of the SiO_4^{-4} unit in olivine indicative of weaker Si–O bonding. Molecular orbital calculations suggest that this destabilization is not a result of the change in the Si–O distance, but must be attributed to differences in the identity of the second-nearest-neighbor cations in quartz and olivine. The separation of the photoelectron peaks arising from the $3t_2$ (O2*s* nonbonding) orbital and the $5a_1$ (Si3*s*–O2*p* bonding) orbitals of the SiO_4^{-4} unit is used in a XPS-based theory of ionicity to calculate ionic characters of 58 and 63 percent for the Si–O bond in quartz and olivine, respectively.

Introduction

The idea that the silicon to oxygen bond is different in neso- and tektosilicates is not new. Ramberg (1952) developed a model to explain element partitioning between silicate minerals based on the idea that Si–O bond covalency increased with degree of polymerization. White and Gibbs (1967) have since related the decrease in energy of the main Si$K\beta$ X-ray emission in tektosilicates to stronger silicon–oxygen covalent bonding. However, in the past, such concepts were necessarily somewhat qualitative, since no reliable theoretical or experimental techniques existed for the quantitative assessment of covalency.

Recently quantum-mechanical calculations have been performed on the tetrahedral oxyanion SiO_4^{-4}, using the SCF-Xα scattered wave MO method, and these calculations have been used to assign and interpret the X-ray emission, X-ray photoelectron, and UV spectra of quartz. (Tossell *et al.*, 1973; Tossell, 1975a). However, one might expect the SiO_4^{-4} calculation to be a more accurate representation of the isolated SiO_4^{-4} tetrahedra found in nesosilicates. Quartz was chosen as the basis for comparison of calculation and experiment primarily because of the large amount of experimental data available for it. Relatively little experimental spectral data could be found for the nesosilicates. Fairly good agreement was obtained between the SiO_2 (quartz) data and the SCF-Xα calculation. There did, however, seem to be a somewhat greater discrepancy between calculation and experiment in the SiO_4^{-4} case than had been found in the case of SCF-XαMO calculations on similar oxyanions (Johnson and Smith, 1970; Tossell, 1975a).

Spectral studies from diverse sources which have since been examined have indicated measurable, and in some cases substantial, spectral differences between quartz and the nesosilicates (White and Gibbs, 1967; Kuroda and Iguchi, 1971; Nefedov *et al.*, 1972). These spectral differences are in such a direction as to give improved agreement with the silicate SCF-Xα calculation. Systematic analysis of the X-ray spectra of the third-row oxyanions also suggests that the spectral energies of the SiO_4^{-4} group in SiO_2 are anomalous; *i.e.*, they are inconsistent with the trends observed in the ionic salts of ClO_4^-, SO_4^{-2} and PO_4^{-3}. These three observations, *i.e.* (1) agreement between the SiO_4^{-4} calculation and the quartz experimental data that was poorer than that obtained for the oxyanions ClO_4^- and SO_4^{-2}, (2) observed X-ray spectral differences between quartz and the nesosilicates, and (3) the anomalous position of the quartz experimental energies within the third row oxyanion series, encouraged a new effort to correlate the SiO_4^{-4} calculations with nesosilicate experimental data.

The basic orbital structure of SiO_4^{-4}

The highest occupied molecular orbital in the SiO_4^{-4} cluster is of symmetry type and number $1t_1$. It is an oxygen $2p$ non-bonding orbital with an experimental ionization potential around 7 eV. At about 2 eV higher ionization potential are the $5t_2$ and $1e$ orbitals which are essentially nonbonding, but do possess some silicon p and d character. Next lower in energy are the main bonding orbitals of the system, the $4t_2$ and the $5a_1$. In quartz these orbitals lie, respectively, 5 and 8 eV below the $1t_1$. Finally, the lowest energy orbitals are the oxygen $2s$ orbitals, $3t_2$ and $4a_1$ which are essentially nonbonding. The orbital sets $1e$, $5t_2$, and $3t_2$, $4a_1$ do possess both oxygen and some Si character and make some contribution to the bond strength, but the major part of the Si–O bond strength derives from the $5a_1$ and $4t_2$ bonding orbitals. Therefore we might expect changes in Si–O bond energies to be manifested by changes in the energies of the $5a_1$ and $4t_2$ orbitals.

Agreement between SCF-Xα calculation and experimental spectra for third-row tetrahedral oxyanions.

Absolute ionization potentials cannot be accurately determined from SCF-Xα cluster calculations, since the assumed stabilization of the cluster by a uniformly positively charged sphere is a crude approximation to the effect of the other atoms of the lattice. This problem is not particularly critical, since absolute experimental IP's are also difficult to obtain because of charging and relaxation effects. Therefore we shall simply set the experimental and calculated IP's to be equal for the highest occupied orbital, the $1t_1$, and concentrate our attention upon calculated and experimental relative IP's. In Table 1 we compare calculated and experimental relative IP's for ClO_4^-, SO_4^{-2}, and SiO_4^{-4}. All the calculations listed employed very similar schemes for choosing the parameters required as input to the SCF-Xα calculation, and all the experimental energies are obtained from X-ray photoelectron spectroscopy, (XPS). Note that for each ion the calculated energies of the $5t_2$, $1e$ and $4a_1$, $3t_2$ orbital sets are too high and that the errors are of similar magnitude for all three oxyanions. For ClO_4^- these errors have since been reduced substantially by a slight modification of the calculational method (Norman, 1974). For the $5a_1$ and $4t_2$ orbitals, on the other hand, agreement of calculation and experiment is quite good for all the oxyanions *except* SiO_4^{-4}, for which the experimental data used for comparison is the XPS of amorphous SiO_2. This discrepancy is particularly apparent in the case of the $4t_2$ orbital. There seems to be no significant difference between the technique used in the SiO_4^{-4} calculation and that used for the other oxyanions; thus within the model of an isolated TO_4^{-n} cluster no theoretical reason is apparent for the poorer $5a_1$ and $4t_2$ energies in SiO_4^{-4}. Consideration of transition state rather than ground state orbital energies does not remove the discrepancy. (Tossell, 1976).

TABLE 1. Comparison of experimental and calculated relative orbital energies (in eV) for ClO_4^-, SO_4^{-2}, and SiO_4^{-4}

	ClO_4^-		SO_4^{-2}		SiO_4^{-4}	
	exp.[a]	calc.[b]	exp.[a]	calc.[b]	exp. (SiO_2)[c]	calc.[d]
$1t_1$	0	0	0	0	0	0
$5t_2$, $1e$	-2.7	-1.0	-1.9	-1.2	-1.9	-1.2
$4t_2$	-7.1	-6.8	-5.6	-5.4	-4.8	-3.2
$5a_1$	-10.2	-11.3	-8.5	-8.5	-7.8	-7.4
$3t_2$	-20.7	-17.1	-19.5	-16.8	-18.4	-14.5
$4a_1$	-28.1	-23.4	-23.2	-20.8	-20.8	-17.4

(a) *Prins and Novakov (1971)*

(b) *Johnson and Smith (1970)*

(c) *XPS of amorphous SiO_2, Distefano and Eastman (1971)*

(d) *Tossell (1975a)*

Spectra differences between quartz and nesosilicates

Kuroda and Iguchi (1971) have studied the Si*L* X-ray emission spectrum (XES) of quartz and several olivines. Their quartz spectrum is very similar to that of Ershov *et al.* (1966) which has been previously interpeted (Tossell *et al.*, 1973; Tossell, 1975c). The lowest energy peak (*D*) arises from the $4a_1$ O2*s* nonbonding orbital, and the two intense peaks (*C*,*A*) at higher energy from the $5a_1$ bonding orbital and the $5t_2$, 1*e* O2*p* nonbonding orbital set. A weak feature (*B*) intermediate between the two intense peaks is assigned to the $4t_2$ orbital. The spectra of Kuroda and Iguchi, reproduced in Figure 1, show measurable differences between quartz and magnesium-rich olivine (unfortunately the exact composition of the olivine is not given). The peaks *D* derived from the $4a_1$ orbital and the peaks *A* from $5t_2$, l*e* are at relative constant energy in the two spectra, but the $5a_1$ peak (*C*) occurs at ~0.7 eV higher energy in olivine. To obtain relative energies with respect to the $1t_1$ orbitals, assumed at constant energy because of their nonbonding nature, these energies should be corrected for the difference between the energy of the Si2*p* orbital (the core orbital involved in Si*L* XES) in quartz and its energy in olivine. Nefedov *et al.* (1972) have found the Si2*p* binding energy to be higher in quartz than in olivine by about 0.7 eV. Combining the XPS and XES data we thus find the $4a_1$, $5a_1$, and ($5t_2$, 1*e*) energies to be higher in olivine than in quartz by about 0.6, 1.4, and 0.8 eV, respectively. The width of the upper valence region in silicon oxides is determined by the $5a_1$ orbital energy. Thus, olivine with a less stable $5a_1$ orbital will have a narrower upper valence region than SiO_2.

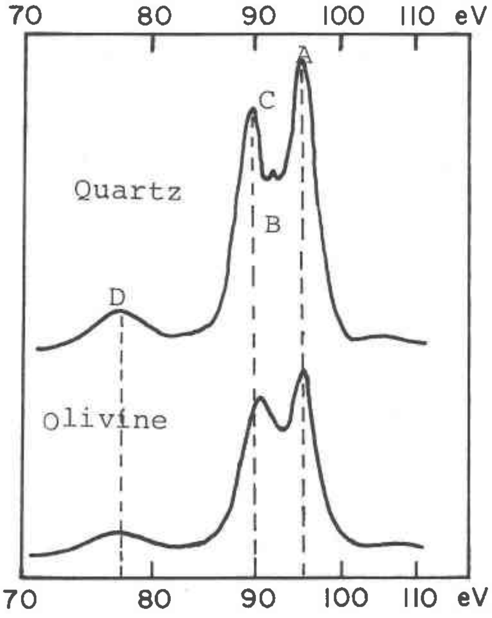

FIG. 1. Si*L* XES quartz and (cleavable) olivine (from Kuroda and Iguchi (1971)

The weak $4t_2$ feature is not resolvable in the olivine spectrum, so to determine its position we must study the Si*Kβ* XES. The main peak in this spectrum arises from the $4t_2$ orbital, and its energy has been accurately determined for a number of silicates. White and Gibbs (1967) find the main Si*Kβ* peak to be 1.1 eV higher in energy in olivine than in quartz. To determine the relative $4t_2$ orbital energies, we must also assess the relative Si1*s* energies in these two minerals. Si1*s* binding energies are very high and thus not readily measurable with most spectrometers, but since both the Si1*s* and the Si2*p* are deep core levels we expect their binding energies to shift in much the same way. We therefore set the difference of Si1*s* binding energies equal to the value of 0.7 eV measured for the Si2*p* shift. Using this value, the $4t_2$ orbital in olivines lies 1.8 eV higher in energy than that in quartz. In Table 2 the estimated olivine orbital energies relative to the $1t_1$ orbital are compared with those obtained from the SiO_2 XPS and from the SCF-X*α* calculations. It is apparent that the SCF-X*α* energies agree more closely with the olivine experimental energies than with those from SiO_2.

This result holds in spite of the fact that the Si–O distance [*R*(Si–O) av = 1.634Å in Mg_2SiO_4; Birle *et al.*, 1968] is larger in olivine than the value of 1.609Å found for quartz and used in the original SCF-X*α* calculation. The orbital energies resulting from an SiO_4^{-4} SCF-X*α* calculation with *R*(Si–O) = 1.634Å are also given in Table 2. Differences in orbital energies as a result of the Si–O distance variation are obviously very small. Therefore the SCF-X*α* calculations suggest that the difference in electronic structure of the SiO_4^{-4} oxyanion in quartz and olivine should not be attributed to the direct effect of variation in average Si–O distance.

Approximate LCAO MO calculations using previously described methods (Tossell, 1973) also indicate that average $4t_2$ and $5a_1$ orbital energies for an SiO_4^{-4} oxyanion with bond distance and angles as observed in olivine differ by less than 0.2 eV from those for a perfect tetrahedral cluster with the same average Si–O distance. Thus, distortion does not appear to have a strong effect on the orbital energies in the context of the isolated tetrahedron calculations. The large differences observed must then arise from

TABLE 2. Comparison of experimental quartz and olivine relative orbital energies with SCF-Xα results for R(Si–O) = 1.609 and 1.634Å

	$4a_1$	$3t_2$	$5a_1$	$4t_2$	$1e,5t_2$	$1t_1$
SiO_2 XPS[a]	-20.8	-18.4	-7.8	-4.8	-1.9	0
Olivine XPS & XES[b]	-20.2	-	-6.4	-3.0	-1.1	0
Difference (SiO_2 vs. olivine)	-0.6	0	-1.4	-1.8	-0.8	0
SCF-Xα calc.[c] R(Si-O) = 1.609Å	-17.4	-14.5	-7.4	-3.2	-1.2	0
SCF-Xα calc.[d] R(Si-O) = 1.634Å	-17.2	-14.4	-7.3	-3.1	-1.2	0
Difference (1.609 vs. 1.634Å)	-0.2	-0.1	-0.1	-0.1	0.0	0

(a) *DiStefano and Eastman (1971)*

(b) *Kuroda and Iguchi (1971), White and Gibbs (1967), Nefedov et al. (1972), orbital energies from XES with correction for shift of core levels measured by XPS*

(c) *Tossell (1975a)*

(d) *present work*

the identity of the cations next-nearest-neighbor to Si. or similarly, from the extent of silicate polymerization. This conclusion is identical to that previously reached on the basis of approximate SCF-MO calculations (Tossell, 1973). Observed changes in Si$K\beta$ spectral intensities have been interpreted on a similar basis (Wiech *et al.*, 1976). The rate of change of the $4t_2$ orbital energy as a function of distance calculated using the SCF-Xα method is also in good agreement with the previous estimate obtained from approximate LCAO MO calculations (Tossell, 1973).

Anomalous spectral energies in quartz compared to those for ionic salts of ClO_4^-, SO_4^{-2}, PO_4^{-3} and SiO_4^{-4}

The above analysis of the spectral differences between olivine and quartz is supported by comparison of the quartz XPS data with XPS studies (Prins, 1974) of the lithium salts of third-row oxyanions in which the TO_4^{n-} are isolated from one another. Figure 2 shows relative quartz XPS energies, along with Prins' XPS energies for the ionic salts. It is clear that energy trends within the series of ionic salts are internally consistent and that the quartz XPS energies are anomalously low (*i.e.* the orbitals of SiO_2 are more stable than those of Li_4SiO_4). The estimated lowering of the quartz orbitals from the data in Figure 2 are 0.8, 0.9, and 1.3 eV for the (1e, $5t_2$), $4t_2$, and $5a_1$ orbitals respectively, in acceptable agreement with the previous estimates from XES and core XPS spectra. The Li_4SiO_4 *vs.* SiO_2 comparison further supports the contention that degree of polymerization strongly affects valence orbital energies.

Spectral ionicities of the Si–O bond in quartz and olivine

Recently Kowalczyk *et al.* (1974) have developed a method for estimating ionicity from XPS valence band spectra for AB compounds. They measure the energies of two orbitals, one of B2s nonbonding type and the other of A2s–B bonding type. The appropriate orbitals in the Si–O system are the $3t_2$ (O2s nonbonding) and the $5a_1$ (Si3s–O2p bonding). The experimental energy difference is expressed as the sum of a covalent term, dependent only upon nearest-neighbor distance, and an ionic term. The covalent term is given by the simple expression $\Delta E_s^c = 8.0-2.2d$, where the energy is in eV and d, the nearest neighbor distance, is in Å. The ionic term is then the difference; $\Delta E_s^i = \Delta E_s^{XPS} - \Delta E_s^c$, and the fractional ionicity is defined as $F_i^{XPS}(AB) = \Delta E_s^i/\Delta E_s^{XPS}$. This ionicity calculation is similar to that performed earlier by Phillips (1970) (who used dielectric constant data) and by Grobman *et al.* (1973). Although a strict correspondence with the Phillips model can be made only for AB compounds, we expect that relative Si–O bond ionicities in SiO_2 and Mg_2SiO_4 should be meaningful and semiquantitatively comparable to those for AB compounds. Assuming the $3t_2$ orbital energies to be

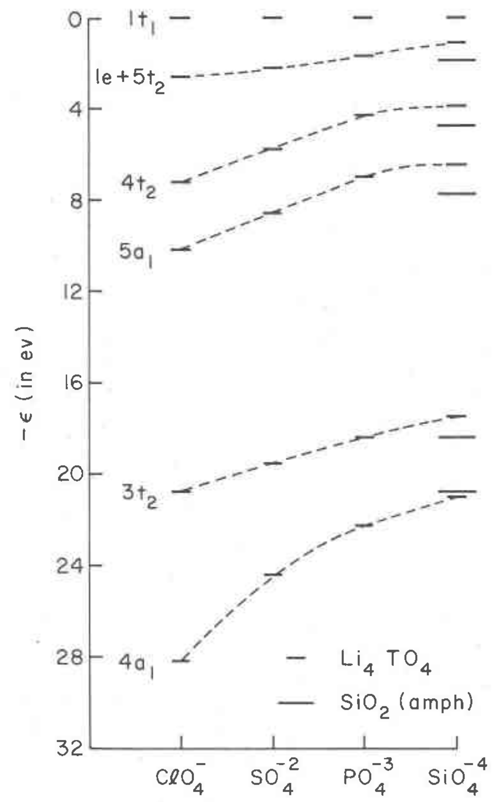

FIG. 2. XPS energies for valence orbitals of third-row tetrahedral oxyanions (data from Prins, 1974 and Distefano and Eastman, 1971)

equal in SiO_2 and Mg_2SiO_4 (consistent with the near equality of $4a_1$ energies) and using $5a_1$ energies from Table 2, we calculate ionicities of 58 and 63 percent for the Si–O bond in SiO_2 and Mg_2SiO_4, respectively. Both values are well below the value of 67 percent determined as the transition value between four- and six-coordination for many compounds (Kowalczyk *et al.*, 1974).

Differences in electron distribution between olivine and quartz

The effect of polymerization upon the energies of the Si–O bonding orbitals is evident from the X-ray data. A determination of the effects of polymerization upon the electron density distribution is more difficult. Approximate LCAO MO calculations indicate that the Si atom becomes more positive as polymerization increases (Tossell, 1973). The calculated trend is in agreement with trends in Si2*p* binding energies (Nefedov *et al.*, 1972) and with atomic charges estimated from Si*K* XES (Urusov, 1970). Approximate LCAO calculations indicate that much of the reduction in electron density on Si takes place within the set of O2*s* nonbonding orbitals, changes in electron distribution with the bonding orbital set being rather small. On the other hand, a lowering in energy of a bonding orbital certainly implies more covalency corresponding to more charge in the bonding region. To clarify this situation we require more accurate calculations on polymeric systems and direct analysis of electron density distributions, *e.g.* from X-ray minus neutron diffraction maps, as opposed to Mulliken charge analyses which are highly basis set dependent.

The influence of Si–O bond strength upon the stability of olivine

Das Gupta (1952) suggested a method for estimating heats of formation from K XES energies. This method has been discussed by Tossell (1975b) and a generalized alternative suggested. The new method gave acceptable results for the heats of atomization of SiO_2, Al_2O_3, and MgO. Briefly, the method sums the measured ionization potentials for the electrons of the free atoms and the solid compound, and corrects the molecular sum for charging and polarization effects by reducing each IP by a constant energy, chosen to give best fit with experiment. The difference in IP sum between the 12 valence electrons in SiO_2 and the 12 valence electrons in the hypothetical SiO_2 molecule within Mg_2SiO_4 is about 180 kcal/mole, with the olivine "SiO_2" being less stable. However, Mg_2SiO_4 has a heat of formation of −15.2 kcal/mole with respect to SiO_2 + 2MgO. Therefore the weakening of the Si–O bond in Mg_2SiO_4 must be compensated by a strengthening of the Mg–O bonds or by a change in the absolute ionization potentials of the entire orbital set. Iguchi (1974) has also found somewhat different Si*L* spectral widths, and consequently different orbital energy separations in Mg, Fe, and Ni olivines. The Ni olivines have the most stable $5a_1$ orbital. The effect of different cations on the energies of Si–O bonding orbitals may influence the stability of cations within the olivine lattice.

Conclusion

Experimental X-ray photoelectron and emission spectra show differences in Si–O bonding orbital energies between quartz and olivine which are consistent with the results of molecular orbital calculations for the third-row tetrahedral oxyanions. These differences appear to be a result not of differences in Si–O distances, but rather of differences in second-nearest-neighbor identity. The orbital energy differences are substantial, indicating that Si–O bonds in olivine are considerably weaker than those in quartz. Conversely, the stability of Mg_2SiO_4, relative to $2MgO + SiO_2$ requires the Mg–O bonds to be stronger in olivine than in MgO.

Acknowledgments

The computer time for this project was supported in part through the facilities of the Computer Science Center of the University of Maryland. The author gratefully acknowledges support from the General Research Board of the University of Maryland and from the Research Corporation.

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Manuscript received, December 30, 1975; accepted for publication, July 13, 1976.