CORRELATION BETWEEN CHEMICAL SHIFTS OF X-RAY PHOTOELECTRON SPECTRA AND Si-O BOND LENGTHS IN $M_2^{2+}SiO_4$ OLIVINES

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The mean Si-O bond length in $M_2^{2+}SiO_4$ olivine decreases with an increase of the binding energy of O(1s) electrons.

Since Bragg and Brown (1926) determined the basic structure of olivine, structural refinements of $M_2^{2+}SiO_4$ olivines of different compositions have been carried out by many workers. However, they could not find any rule between the Si-O bond lengths and the sizes, the electronegativities and the electronic structures of the M^{2+} cations. The mean Si-O bond lengths in six olivines are listed in Table 1 with the electronegativities of M^{2+} cations. A scatter diagram of the mean Si-O bond length versus the electronegativity is presented in Figure 1. The plots are scattered and the correlations are obscure.

Table 1. The Si-O bond lengths (Å), the electronegativities of M^{2+} cations, and the binding energies of oxygen (1s) electrons in $M_2^{2+}SiO_4$ olivines

	mean of Si-O	χ^*	BE of O(1s) (eV)	Reference	
				X-ray	ESCA
Ca_2SiO_4	1.646	1.0	530.4	1	4
Ni_2SiO_4	1.641	1.8	530.7	2	4
Mn_2SiO_4	1.639	1.4	530.7	3	4
Co_2SiO_4	1.637	1.7	-	2	-
Mg_2SiO_4	1.636	1.2	530.9	3	4
Fe_2SiO_4	1.636	1.7	531.4	3	5

*Gordy and Thomas(1956) 1)Brown and Gibbs(in prep.)
2)Brown(1970) 3)Fujino et al.(in press) 4)Kaneke
and Suginochara(1977) 5)Huntress and Wilson(1972)

Fig. 1. The mean Si-O bond lengths plotted against the electronegativities of M^{2+} cations for six $M_2^{2+}SiO_4$ olivines.

Electron spectroscopy for chemical analysis (ESCA) is a technique for the study of the electronic structure of atoms and molecules. The position of an atomic line in an ESCA spectrum is determined by the binding energy of the ejected electron. Binding energies of inner shell electrons have been shown to exhibit significant small shifts depending on the charge distribution in the atom (Siegbahn *et al.*, 1967). In olivine structure the silicate tetrahedra are completely isolated and there are three non-equivalent oxygens (Bragg and Brown, 1926). So, in an ESCA spectrum of olivine

there must be three independent O(1s) peaks. However, as the result of small shifts it is difficult to obtain such a spectrum and one broad O(1s) peak can be observed (Huntress and Wilson, 1972).

The mean binding energies of O(1s) electrons in $M_2^{2+}\text{SiO}_4$ olivines have been reported by Huntress and Wilson (1972) and Kaneko and Sugihara (1977). The values of the binding energies are listed in Table 1. These values were recalculated with reference to quartz O(1s) (532.4 eV)

Fig. 2. The mean Si-O bond lengths plotted against the binding energies of oxygen (1s) electrons in $M_2^{2+}\text{SiO}_4$ olivines.

peak. The variation of the mean Si-O bond lengths with the average binding energies of O(1s) electrons in $M_2^{2+}\text{SiO}_4$ olivines is shown in Figure 2. The mean Si-O bond length decreases with an increase of the binding energy of O(1s) electrons.

The binding energies of Si(2s) and O(1s) electrons in a number of silicate compounds have been reported and correlated with their respective calculated charges by applying an iterative Pauling method by Clarke and Rizkalla (1976). They concluded that the binding energies of Si(2s) and O(1s) electrons increase with increasing the calculated charges. The five $M_2^{2+}\text{SiO}_4$ olivines are isostructural and the calculated charges of the oxygens are equal to each

other. Therefore, the observed shifts of the binding energies of O(1s) electrons are dependent on the substitutions of the M^{2+} cations. Assuming that the binding energies of O(1s) electrons increase with increasing the charges, the mean Si-O bond length in $M_2^{2+}\text{SiO}_4$ olivine decreases with increasing the charges of oxygens.

The Si-O bond length in $M_3^{2+}\text{Al}_2\text{Si}_3\text{O}_{12}$ garnet is strongly correlated with the electronegativity and the electronic structure of non-tetrahedral cations (Ohashi, 1980; Ohashi, Fujita and Osawa, 1981). The silicate tetrahedra are completely isolated as in olivine structure and there is only one non-equivalent oxygen (Menzer, 1926). So, it is expected that one sharp O(1s) peak can be observed. To confirm the correlation between the Si-O bond length in an isolated silicate tetrahedron and the charge of oxygen, the measurements of ESCA spectra of $M_3^{2+}\text{Al}_2\text{Si}_3\text{O}_{12}$ garnets are very desirable.

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$M_2^{2+}SiO_4$ カンラン石における光電子スペクトルの化学シフトと Si-O 結合距離との間の相互関係

大 橋 晴 夫

$M_2^{2+}SiO_4$ カンラン石における Si-O 結合距離の平均値は、O(1s) 結合エネルギーが増加するとともに短くなる。