

High-resolution silicon $K\beta$ X-ray spectra and crystal structure

J. PURTON AND D. S. URCH

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

Abstract

High-resolution X-ray emission spectra (XES) are presented for minerals with a variety of structures. The participation of the Si $3p$ orbitals in bonding is influenced by the local structure around the silicon atom. In orthosilicates the distortion of the SiO_4^{4-} -tetrahedron influences both peak-width and the intensity of the high-energy shoulder of the Si- $K\beta$ spectrum. In minerals containing Si-O-Si bonds there is mixing of the Si $3s$ and $3p$ orbitals giving rise to a peak on the low-energy side of the main Si- $K\beta$ peak. When combined with X-ray photoelectron spectra (XPS), a complete molecular orbital picture of bonding can be established.

KEYWORDS: X-ray emission spectroscopy, silicon $K\beta$ X-ray, silicates, electronic structure, chemical bond.

Introduction

AFTER core ionization of an atom has occurred, it may relax by either of two competing processes; by the emission of an Auger electron or a quantum of X-radiation. The latter process, which forms the basis of X-ray emission spectroscopy, involves the transition of an electron from an orbital of low ionization energy (which may be a valence shell orbital) to a vacancy on a core orbital (Fig. 1). In this paper the orbitals are assumed to be 'frozen' during ionization and relaxation, so that the energy of the emitted radiation is equal to the difference in energy of the two orbitals, in the ground state.

For light elements the relaxation process is governed by the dipole selection rule ($\Delta l = \pm 1$) allowing only $p \rightarrow s$ and s or $d \rightarrow p$ transitions. $K\beta$ spectra are generated by the transitions of electrons from $3p$ to $1s$ orbitals and in this paper Si- $K\beta$ spectra are used to provide information on the role of the $3p$ electrons in bonding in various mineral structures.

Experimental

The majority of samples analysed were kindly donated by the Earth Sciences Department at Queen Mary College and Dr N. West of the Health and Safety Executive; other minerals were purchased from R. Tayler Minerals. The source of each mineral, together its nominal chemical

composition is given in Table 1. Before being placed in the spectrometer, the minerals were crushed to a fine powder and pressed into a disc with Specure polyethylene powder as a matrix.

The Si- $K\beta$ spectra were recorded on a Philips PW1410 flat crystal spectrometer, the resolution of which is largely controlled by two Soller slit collimators. The 'fine' primary collimator, which gives a minimum peak width of $\pm 0.07^\circ 2\theta$, was used throughout this work. An additional collimator (Haycock and Urch, 1982), with blades perpendicular to those of the primary collimator, was inserted in the X-ray path to control vertical divergence which causes peak distortion at high 2θ angles. The minimum peak-width (FWHM) observed for Si- $K\beta$ was 1.7 eV. A Philips side window scandium anode X-ray tube operated at 40 mA, 50 kV was used for excitation. The X-rays emitted from the sample were dispersed by an ADP (200) crystal ($2d$, 0.750 nm) and were detected in a gas-flow (90% Ar + 10% CH_4) proportional counter fitted with a $1\ \mu\text{m}$ aluminized mylar window. The whole spectrometer was evacuated to a pressure of about 0.2 torr. Pulses from the proportional counter were amplified by Harwell 2000 series electronics and fed, via an interface, to a Commodore 8096 microcomputer. The computer allowed a repetitive step-scanning technique to be used to improve the signal to noise ratio of the spectra. Measurements were taken at 0.03° intervals throughout the range 127 – 132.5°

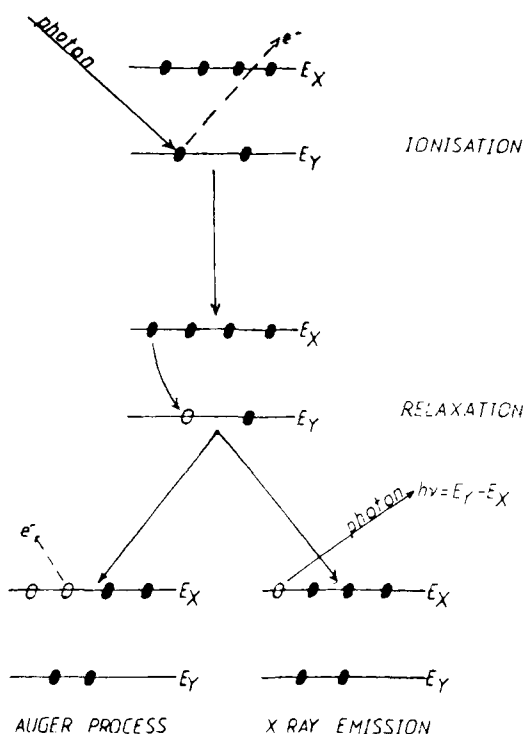


Fig. 1. Schematic diagram of the ionization, X-ray emission and Auger processes.

2 θ . Second-order Ca- $K\alpha$ and third-order Cr- $K\alpha$ peaks were used for calibration.

Results

The Si- $K\beta$ spectra of minerals with a wide variety of structures, such as orthosilicates, diorthosilicates, chain silicates, sheet silicates, and framework silicates have been recorded. Representative spectra from these groups are displayed in Figs. 2–8 and the energies of the Si- $K\beta$ and $K\beta'$ peaks are listed in Table 1. Where direct comparison is possible, these spectra are similar to those of Dodd and Glenn (1969). For convenience the structure of each spectrum can be divided into four parts:

1. a low-energy satellite ($K\beta'$) at 1818–1819 eV;
2. a feature of variable intensity on the low-energy side of the main peak, 1829–1830 eV;
3. the main Si- $K\beta$ peak at 1832–1833 eV; and
4. a high-energy shoulder, also of variable intensity, at about 1834–1834 eV.

Of all the mineral spectra recorded, that of larnite had the narrowest peak and the least number of components.

In spectra of minerals containing calcium, a peak due to second-order Ca- $K\alpha$ is present to the high-energy side of Si- $K\beta$. Unfortunately it was not possible to completely resolve it from Si- $K\beta$ by pulse-height analysis, so that in minerals containing appreciable amounts of calcium, the silicon $K\beta$ spectrum had a high and varying background.

Discussion

The spectrum of larnite (Fig. 2a), being the simplest, provides the basis for the interpretation of the spectra of the other minerals. It is similar to the P and S- $K\beta$ spectra from phosphate and sulphate anions. These anions, like the SiO_4^{4-} in larnite, are tetrahedral in shape and have point group symmetry T_d . Group theory then allows the valence atomic orbitals to be classified under different irreducible representations as shown in Table 2.

The silicon 3p makes σ bonds with the oxygen 2p' and 2s t_2 orbitals to generate $4t_2$ and $3t_2$ orbitals respectively. As oxygen 2s orbitals are much more tightly bound than either oxygen 2p or silicon 3p orbitals, which have similar energies, the silicon 3p component in $4t_2$ is greater than in $3t_2$. This results in a much more intense peak from the $4t_2 \rightarrow \text{Si } 1s$ transition (i.e. $K\beta$) than from the $3t_2 \rightarrow \text{Si } 1s$ transition (i.e. $K\beta'$)—Urch (1970). The high-energy shoulder is due to silicon 3p character in the $5t_2$ molecular orbital as a result of interaction between silicon 3p orbitals and the oxygen 2p'' ('lone pair') orbitals. This peak is weaker due to the less efficient overlap of these π orbitals. This simple model is in agreement with the molecular orbital calculations of Nefedov and Fomichev (1968), Tossell *et al.* (1973), and Tossell (1975).

Although the orthosilicates, zircon and forsterite, have different crystal structures their Si- $K\beta$ spectra (Fig. 2b and c) are very similar to one another and both are broader, by about 1.3 eV, than that of larnite. In both cases the overall Si- $K\beta$ peak shows a distinct asymmetry on the high energy side, but it would also appear (from the less steep gradient, 1831–1832.5 eV) that the main peak itself is broader in zircon and forsterite than in larnite. This increased breadth may be due to a weak peak at about 1829.5 eV (as observed by Nefedov and Fomichev, 1968, for Be_2SiO_4) or to distortions of the silicate anion related to changes in crystal structure. However, it must be admitted that the resolution of the present work is not really sufficient to differentiate between these two possibilities. [Changes in the polarizing power of the cations alone probably would not cause peak broadening as this was not observed by Taniguchi, 1984, for S- $K\beta$ and Cl- $K\beta$ in a series of sulphates

Table 1. Si $K\beta$ X-ray data

Mineral	$K\beta$ Energy (FWHM)	$K\beta'$ Energy	Source
ORTHOSILICATES			
larnite $\beta\text{-Ca}_2\text{SiO}_4$	1833.1 (2.3)	1819.2	RTM
olivine $(\text{Mg,Fe})_2\text{SiO}_4$	1832.9 (3.6)	1818.9	HSE
zircon ZrSiO_4	1832.8 (3.5)	1819.0	HSE
DIORTHOSILICATE			
lawsonite $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$	1833.0 (4.1)	1819.4	RTM
CHAIN SILICATES			
enstatite MgSiO_3	1832.6 (4.4)	1818.7	QMC
diopside $\text{CaMg}(\text{SiO}_3)_2$	1832.7 (4.6)	1818.9	RTM
wollastonite CaSiO_3	1833.0 (5.3)	1819.0	QMC
anthophyllite $(\text{Mg,Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	1832.4 (3.5)	1818.6	HSE
tremolite $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	1832.4 (4.0)	1818.8	QMC
SHEET SILICATES			
biotite $\text{K}(\text{Mg,Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$	1832.4 (3.0)	1818.6	QMC
taic $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$	1832.3 (3.3)	1818.6	QMC
kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	1832.3 (3.7)	1818.4	HSE
FRAMEWORK SILICATES			
orthoclase $\text{K}(\text{AlSi}_3\text{O}_8)$	1832.3 (3.7)	1818.5	QMC
albite $\text{Na}(\text{AlSi}_3\text{O}_8)$	1832.4 (4.1)	1818.6	QMC
anorthite $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$	1832.4 (3.8)	1818.5	HSE
nepheline $\text{KNa}_3(\text{AlSiO}_4)_4$	1832.4 (2.6)	1818.6	QMC
quartz SiO_2	1832.0 (2.9)	1818.6	QMC

HSE: Health and Safety Executive

QMC: Queen Mary College, Dept. of Earth Sciences

RTM: Richard Taylor Minerals

and perchlorates nor by the present authors—unpublished work—for Si- $K\beta$ from MSiF_6 ($M = \text{Na}_2, \text{K}_2$ or Ba).

It has been found that the O-Si-O is reduced when the edge opposite this angle is shared with a cation (M) polyhedron (Tossell and Gibbs, 1976, 1977; Robinson *et al.*, 1971), thus straightening Si-O- M angles. This distortion of the tetrahedral environment of the silicon atom will remove the degeneracy associated with t_2 molecular orbitals and thus cause X-ray peaks involving such orbitals (e.g. Si- $K\beta$) to be broadened. Such distortions will also affect the freedom with which the oxygen 'lone pair' ($2p''$) orbitals can interact with the silicon $3p$ orbitals and so affect the Si $3p$ contribution to $5t_2$. These changes will be reflected in the intensity of the Si- $K\beta$ peak at 1834–1835 eV.

By contrast with the orthosilicates the Si- $K\beta$ spectra of lawsonite, pyroxenes, amphiboles and sheet silicates (Figs. 3–6) have a pronounced feature on the low-energy side of the main $k\beta$ peak, at about 1829.5 eV. Myers and Andermann (1972), in their study of phosphate spectra, noted the presence of a similar low-energy peak which they ascribed to a reduction in local symmetry about phosphorus associated with the formation of P-OH (as well as P-O⁻) bonds. A similar reduction in symmetry is found in the series of compounds studied here, lawsonite (C_{3v}), pyroxenes (C_{2v}), amphiboles and sheet silicates (C_{3v}), where the local point group symmetry about silicon is given in brackets. The triple degeneracy of the t_2 irreducible representation is broken, to $a_1 + e$ for C_{3v} or to $a_1 + b_1 + b_2$ for C_{2v} . Such relaxation of symmetry will not only lead to main

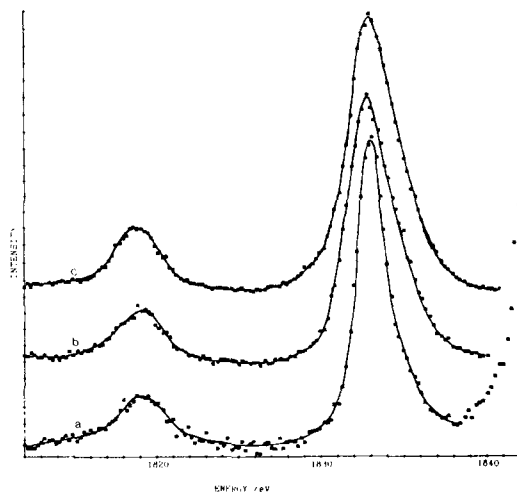


FIG. 2. Si- $K\beta$ spectra of (a) larnite, (b) zircon, and (c) forsterite.

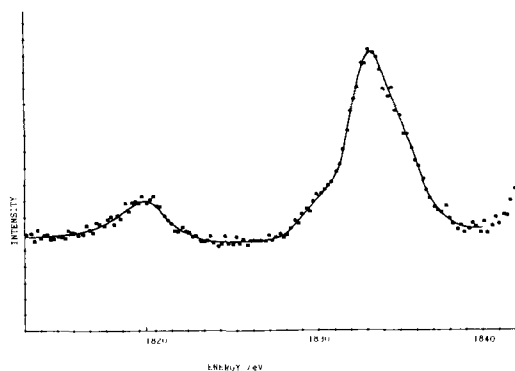


FIG. 3. Si- $K\beta$ spectrum of lawsonite.

peak broadening as discussed above but it will also permit Si $3s$ (always a_1), Si $3p$ mixing so that Si $3p$ character may be found in molecular orbitals that have predominant silicon $3s$ character, as their silicon component. The extent of this mixing can be measured by the intensity of the low-energy component of the Si- $K\beta$ spectrum, and can be seen, for lawsonite, bronzite and diopside, to be sensitive to distortions caused by changes in the Si-O-Si bond angle and in the cation of the lattice. Confirmation that the peak at 1829.5 eV in the Si- $K\beta$ spectrum is indeed due to silicon $3s$, $3p$ mixing is presented in Fig. 9 where the silicon $L_{2,3}$ spectrum (Si $3s$, $3d \rightarrow$ Si $1s$) has been aligned on a common energy scale with $K\beta$. The

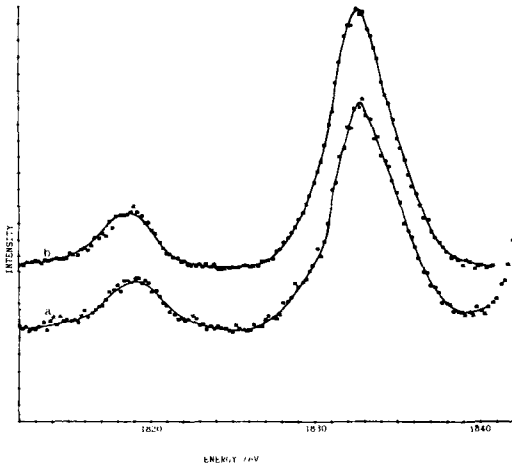
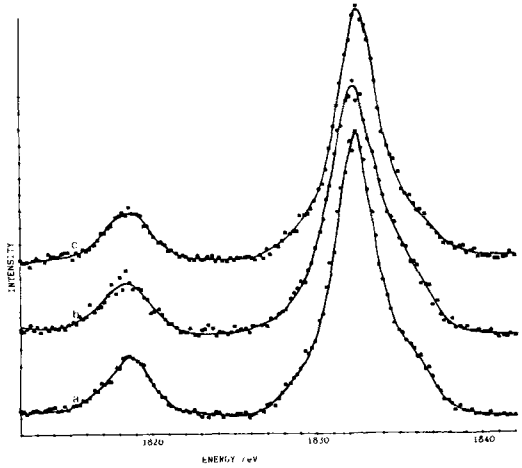
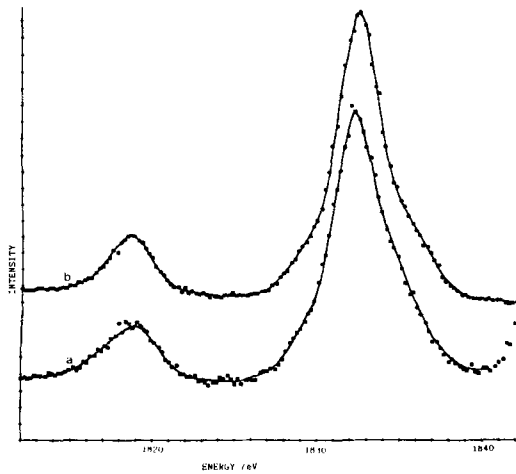
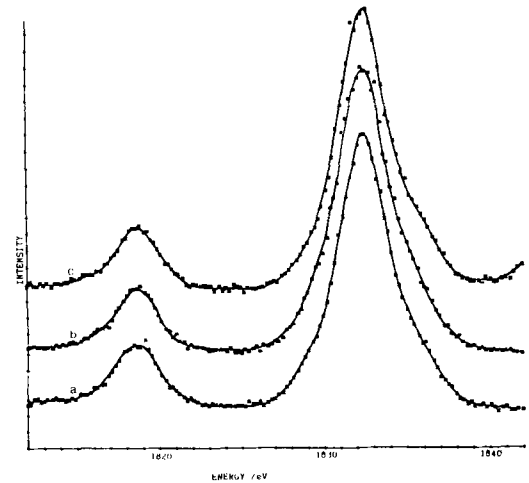
energy difference between the two spectra is the energy of the Si- $K\alpha$ X-ray (1739.6 eV). The Si- $K\beta$ peak at 1829.5 eV coincides with the peak at 90.0 eV, indicative of a common orbital as the origin for both peaks—a molecular orbital with both Si $3s$ and Si $3p$ character.

The Si- $K\beta$ spectra from silica and a range of feldspars are shown in Figs. 7 and 8. As might be expected they are all very similar to each other, the local symmetry about the silicon atom being very nearly tetrahedral in all cases. Some slight departure from ideal symmetry may be inferred from the slight broadening on the low-energy side of the main peak, but this can only correspond to a very weak peak and it does not vary significantly in intensity for different feldspars. Thus it can be concluded that the substitution of some silicon atoms by aluminium does not distort the environment of those silicons that remain even when the Si:Al ratio reaches 1:1 in anorthite. As Al $3p$ orbitals are less tightly bound than Si $3p$ orbitals the presence of aluminium atoms in the silica lattice will cause the band of molecular orbitals associated with Si-O σ bonds to become broader in going from silica to a feldspar. This broadening is reflected in the increased width of Si- $K\beta$ in the feldspars (2.8 eV silica, 3.5 eV feldspar).

It is also interesting to note that in the feldspar spectra, as for silica, there is significant X-ray emission at about 1836 eV, reflecting Si $3p$ character in orbitals that would be called $5t_2$ in an isolated tetrahedron. But, of course, in these minerals the tetrahedra are by no means isolated and at least one of the 'lone-pairs' from each oxygen atom is engaged in σ bond formation to another silicon or aluminium atom. Bonding to bridging oxygen atoms will involve two of the three $2p$ orbitals but, unless the bond angle is 90° , to differing extents. Two different molecular orbitals can be anticipated, one with greater Si $3p$ -O $2p$ overlap, which would be more tightly bound and have a higher Si:O ratio and a second with less efficient Si $3p$ -O $2p$ overlap and which will consequently be less tightly bound and in which the Si:O ratio would be less. This distribution of Si $3p$ character will give rise to two peaks in the Si- $K\beta$ spectrum, a main peak and a less intense peak at a slightly higher X-ray energy, as is observed. The overlap efficiencies which differentiate the two orbitals will be a direct function of the Si-O-Si (or Al) bond angle, being equal when this angle is 90° and reducing to zero for the 'less efficient' when the angle is 180° . Changes in the relative intensities of the main peak and the high-energy satellite can therefore be associated with changes in the bond angle at oxygen.

TABLE 2

Si (central atom)	four O (ligand atoms)		
3s (one orbital)	a_1	2s (four orbitals)	$a_1 + t_2$
3p (three orbitals)	t_2	2p' (four orbitals, one from each oxygen, orientated towards Si)	$a_1 + t_2$
3d (five orbitals)	$e + t_2$	2p'' (eight orbitals, two from each oxygen, perpendicular to Si-O bonds)	$e + t_1 + t_2$

FIG. 4. Si- $K\beta$ spectra of (a) diopside, and (b) bronzite.FIG. 6. Si- $K\beta$ spectra of (a) talc, (b) kaolinite, and (c) biotite.FIG. 5. Si- $K\beta$ spectra of (a) tremolite, and (b) anthophyllite.FIG. 7. Si- $K\beta$ spectra of (a) orthoclase, (b) albite, and (c) anorthite.

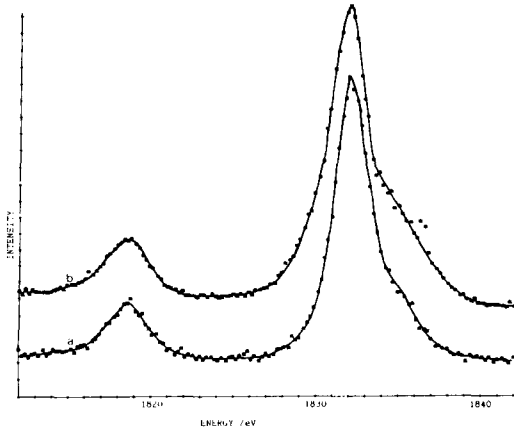


FIG. 8. Si- $K\beta$ spectra of (a) nepheline, and (b) quartz.

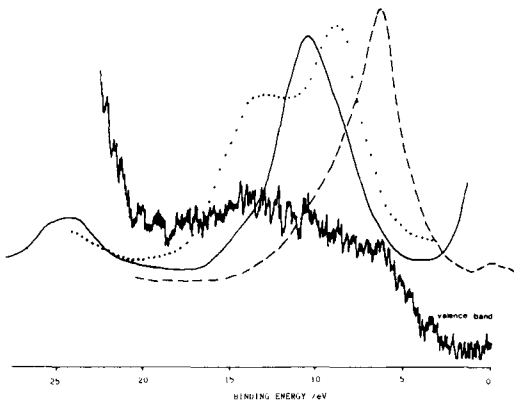


FIG. 9. Si- $K\beta$ (solid line), Si- L (dotted line) and O- $K\alpha$ (dashed line) of diopside aligned using XPS binding energies of Si $2p$ and O $1s$. The XPS valence band spectrum is also shown. The binding energies are only relative since the XPS data have not been corrected for sample charging. Si- L spectrum is from Brytov *et al.* (1976).

Conclusions

The structure of a mineral is determined by the balance of attractive and repulsive forces within the lattice. The bonding of any individual atom within such a lattice is very complex, and physical

distortions can cause subtle changes in electronic structure. These changes can be observed directly by means of X-ray emission spectroscopy. The results presented above, for Si- $K\alpha$, show how changes in the local symmetry of the silicon atom, related to changes in silicate type, affect the electronic structures of different minerals.

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