

## 2p X-ray Absorption of Titanium in Minerals

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**Abstract.** Ti 2p X-ray absorption spectra for a series of minerals have been measured. Crystal field multiplet calculations can explain the spectral shape. The asymmetry of the  $e_g$  peak is shown to be related to distortions of the  $Ti^{IV}$  octahedron. It is found, theoretically as well as experimentally, that the absorption spectra are more sensitive to tetragonal distortions than to trigonal distortions. A number of silicate minerals and metamict minerals containing titanium are measured and  $Ti^{III}$  has not been observed in any of these minerals. A comparison is made to the 1s X-ray absorption, and the potential of both for the study of minerals is discussed.

### Introduction

The use of X-ray absorption spectroscopy (XAS) in mineralogy has until now largely been limited to the metal  $K$  edges, but there is a real need to investigate the potential of the  $L_{2,3}$  edges. We choose an example from Ti mineralogy where the main questions are the valency of titanium and the geometry of its surroundings. Questions to be answered concern the possibility of tetrahedral site occupation, the existence of  $Ti^{III}$  and the site preference among the possible octahedral sites.  $Ti$  1s (near edge) X-ray absorption spectra can give information on these matters, but it is mostly qualitative in nature (Waychunas 1987). In this study we measured the Ti 2p X-ray absorption edges, which can add extra information because of a more detailed theoretical understanding combined with considerably sharper structures due to better monochromator resolution and smaller intrinsic broadening.

In oxide minerals titanium has a strong tendency to be tetravalent and to be coordinated by 6 oxygens in an octahedral, or distorted octahedral site (Hartman 1969). This situation occurs in binary and ternary oxide minerals, like anatase, rutile, brookite (all  $TiO_2$ ) and

ilmenite ( $FeTiO_3$ ), where  $Ti^{IV}$  occupies more or less distorted octahedral sites. In extreme cases titanium is forced to an alternative situation and it may become 5-coordinated as in the mineral fresnoite,  $Ba_2TiO[Si_2O_7]$  (Moore and Louisnathan 1967), it may become tetrahedrally coordinated as in the compound  $Ba_2TiO_4$  (Günter and Jameson 1984) or it can occur as  $Ti^{III}$ . For clarity we state that with the  $Ti^{IV}$ -notation we mean a formal valency of 4, like in  $SrTiO_3$ . The oxygen 2p-band, that is the band formed from the bonding combinations of oxygen 2p states and metal states (plus non-bonding oxygen 2p states), is completely filled for all transition metal oxides. Therefore the formal valency is directly related to the total occupancy of the transition metal 3d-band. As for  $LaTiO_3$  the formal valency of titanium is 3, its titanium 3d-band will effectively contain one electron, whose character will be mainly titanium 3d but partly oxygen 2p. In some minerals titanium occurs only as a minor constituent. If for a titanium impurity the antibonding Ti 3d-oxygen 2p states (the '3d-band') are empty titanium is tetravalent, but if locally one extra electron is present, filling an antibonding state, this can be denoted as  $Ti^{III}$ .

The presence of  $Ti^{III}$  can be determined with optical spectroscopy, because of the strong transitions within the 3d-band. However in almost all natural minerals titanium is accompanied by iron. The partly filled iron 3d-band dominates the optical spectrum which complicates the detection of features related to  $Ti^{III}$ . Also the quantitative determination of the percentage of  $Ti^{III}$  from wet chemical analysis is questioned (Whipple 1979). If titanium occurs as a minor constituent in for example pyroxenes or amphiboles, it is often tacitly assumed that titanium will fill the remaining tetrahedral sites if the amount of silicon (and aluminium) is insufficient. However this assumption is debated (Waychunas 1987) and it is as yet not resolved because of the difficulty to attain conclusive information on this problem.

In this paper we will address the questions regarding the site-preference, site-geometry and valency from the viewpoint of the electronic structure, by making use of

the titanium  $2p$  X-ray absorption edges. The advent of synchrotron radiation sources and high-resolution soft X-ray monochromators created a novel experimental set-up for detailed X-ray absorption studies, ideally suited for the study of the electronic structure. The use of X-ray absorption in mineralogy has until now largely been limited to the hard X-ray metal  $K$  edges (Waychunas 1987). Analysis of the X-ray Absorption Near Edge Structure (XANES) revealed correlations between the positions of the multiple scattering peaks and the mean oxygen-titanium distance. Also correlations were found between the ( $1s \rightarrow 3d$ ) prepeak intensity and the octahedral site distortions and it was found that  $Ti^{III}$  has a main edge shift of approximately 2 eV with respect to tetravalent titanium (Waychunas 1987; Durmeyer et al. 1990a). Analysis of the Extended X-ray Absorption Fine Structure (EXAFS) spectrum can reveal the nearest neighbour distances (Waychunas 1980), being particularly useful for non-crystalline specimens.

However, the soft X-ray metal  $2p$  or  $L_{2,3}$  edges and the equivalent electron energy loss (EELS) spectra (Leapman et al. 1982; Otten and Busek 1987; Brydson et al. 1989), deserve attention too: The progress in soft X-ray monochromators have made it possible to measure the titanium  $2p$  X-ray absorption edges at about 450 eV with a resolution better than 0.1 eV half width half maximum (hwhm) (Petersen 1986; Chen and Sette 1990), far better than the resolution obtainable at the titanium  $K$  ( $1s$ ) edge. The  $2p$  spectra of  $3d$ -metal compounds are completely dominated by the strong  $2p \rightarrow 3d$  dipole transitions and the spectra present fine details as shown in Fig. 1 (Abbate et al. 1991). In the  $1s$  X-ray absorption spectra the  $3d$ -states are only visible as small pre-peaks and the main edge relates to the  $4p$ -band (see

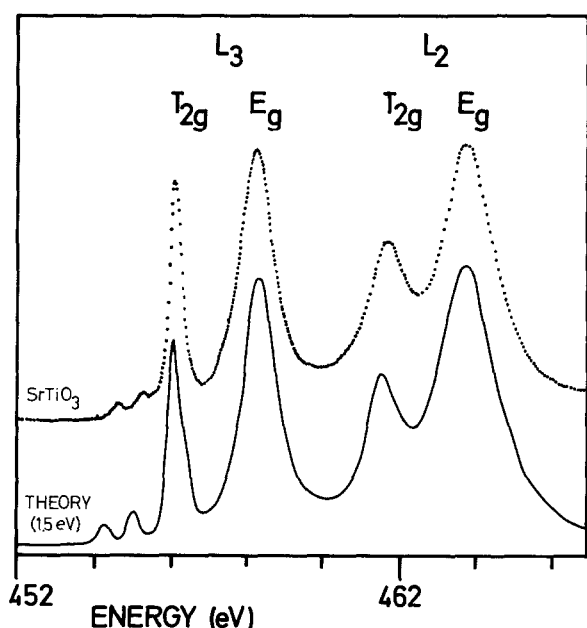


Fig. 1.  $2p$  X-ray absorption spectrum of  $SrTiO_3$  taken with the SX700(II) monochromator, compared with the theoretical atomic multiplet calculation (bottom) and the cubic crystal field calculation with a strength (10 Dq) of 1.5 eV

discussion). The possibility to measure structures with a sharpness up to 0.1 eV creates a powerful tool to study the electronic structure of solids in more detail. With the results of these high resolution data the theoretical methods to establish the electronic structure in minerals can be made more accurate, creating a more complete picture of the chemical bonding. Before presenting the experiments we will shortly discuss the theoretical background for the analysis of the titanium  $2p$  X-ray absorption spectra.

## Theory

The X-ray absorption spectral function is described according to Fermi's Golden rule:

$$\sigma(E_{hv}) \sim \sum_i |\langle \phi_i | X | \phi_f \rangle|^2 \cdot \delta(E_i + E_{hv} - E_f)$$

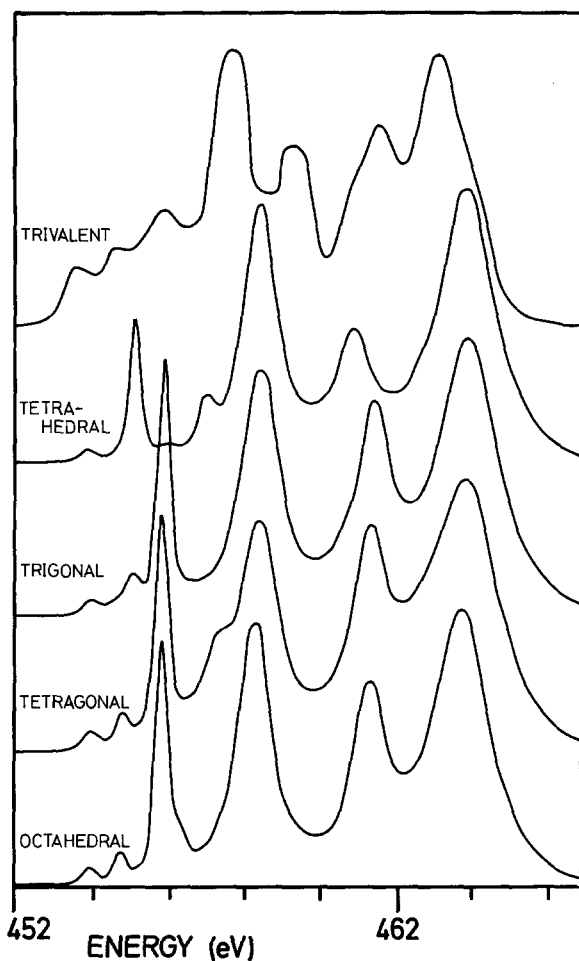
$E_i$ ,  $E_{hv}$  and  $E_f$  are respectively the energy of the initial state, the X-ray and the final state.  $X$  is the operator describing the interaction of X-rays with matter for which the dipole approximation is used (de Groot 1991). To calculate the spectral function it is thus necessary to find the initial and final state energies and wave functions. A central criterion for treatment of this problem for a specific X-ray absorption edge is the influence of the core hole on the final state wave functions (Weijs et al. 1990). For the metal  $K$  edge the  $1s$  core hole does not usually dominate the spectral shape, although its attractive potential can distort the spectra. Therefore the theoretical models to determine the spectral shape are based on finding the projected density of states by an electronic structure calculation. Alternatively a multiple scattering calculation can be performed; both methods are proven to give equivalent results, provided they are applied without further approximations (Natoli and Benfatto 1986). For example the multiple scattering results for the  $1s$  spectra of rutile and anatase show that one still has to improve upon these approximations (Brydson et al. 1989).

In contrast to the  $1s$  edges the titanium  $2p$  edges are dominated by the coupling of the  $3d$  electron with the  $2p$  core hole. This problem has until now only been solved by a crystal field multiplet model; the atomic multiplet spectrum is calculated (Cowan 1981) and the wavefunctions are projected to cubic symmetry. The cubic crystal field strength is fitted to experiment (de Groot et al. 1990a). As an example to explain the general spectral features we show in Figure 1 the titanium  $2p$  X-ray absorption spectrum of  $SrTiO_3$  (Abbate et al. 1991). The experimental spectrum is compared with the crystal field multiplet spectrum for the  $Ti^{IV} 3d^0 \rightarrow 2p^5 3d^1$  transition, with a cubic crystal field strength of 1.5 eV. With this approach all six peaks can be explained in a uniform way: The first two small peaks are related to a transition which is forbidden in LS-coupling, but which becomes allowed because of the multipole  $2p-3d$  interactions. The third and fourth peaks can be related to respectively the  $t_{2g}$  and the  $e_g$  symmetries of the  $L_3$  edge. They are repeated for the fifth and sixth peak for the  $L_2$  edge. The splitting between the third and fourth peak relates closely to the cubic crystal field strength<sup>1</sup>. All details of the  $L_2$  edge are blurred, because the intrinsic broadening is considerably larger than for the  $L_3$  edge, due to an extra Auger decay channel.

$SrTiO_3$  is cubic. For compounds in which the titanium octahedron is distorted, like e.g. for rutile, it is necessary to project the cubic symmetry further to the  $D_{2h}$  point group symmetry of the titanium atom. Distortions from cubic symmetry will give rise to modifications in the spectrum. Calculations in which the symmetry was lowered to tetragonal and trigonal symmetry revealed that the  $e_g$  part<sup>2</sup> of the spectrum is more strongly modified by these

<sup>1</sup> However the splitting is not generally equal to the cubic crystal field, see (de Groot et al. 1990a)

<sup>2</sup> Strictly speaking the description  $e_g$  is not longer appropriate for lower symmetries



**Fig. 2.** Crystal field multiplet calculations for, from top to bottom: octahedral symmetry ( $O_h$ ), tetragonal symmetry ( $D_{4h}$ ), trigonal symmetry ( $D_{3d}$ ) and tetrahedral symmetry ( $T_d$ ) for  $Ti^{IV}$  ( $3d^0 \rightarrow 2p^5 3d^1$ ). The bottom calculation is for  $Ti^{III}$  ( $3d^1 \rightarrow 2p^5 3d^2$ ) in octahedral symmetry ( $O_h$ ). All spectra are calculated with a cubic crystal field strength ( $10Dq$ ) of 2.1 eV (tetrahedral symmetry,  $-2.1$  eV). The parameters describing the tetragonal and trigonal distortions are in the order of 0.5–1 eV

distortions. Figure 2 illustrates this with some representative examples. It can be seen that a tetragonal distortion has a considerably larger effect on the spectrum than a trigonal distortion. The calculation for a tetrahedral surrounding is very distinctive from the octahedral one, which in fact should clearly identify titanium in tetrahedral surroundings. The calculation for  $Ti^{III} - 3d^1$  shows more structure, because of the increased number of final states of the  $2p^5 3d^2$ -multiplet (de Groot et al. 1990b).

## Experimental

The X-ray absorption spectra were measured with the SX700(I) monochromator (Petersen 1986) at the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY). The monochromator resolution was about 0.5 eV (hwhm) at the titanium  $2p$  edge at 450 eV. The energy calibration of the monochromator was determined by comparing the titanium  $2p$  and oxygen  $1s$  spectra of rutile to spectra published previously (de Groot et al. 1989). The spectra were recorded in total electron yield mode (see discussion). They were corrected for intensity loss of the beam during measurement.

The measured minerals are listed in Table 1. The measured material was either mineral fragments taken from museum samples described elsewhere or mineral grains embedded in their host rock. The beam-size on the sample is in the order of a few square millimeters. The samples were mounted to a sample plate and transferred to the Ultra High Vacuum (UHV) system; the pressure during measurements was in the  $10^{-10}$  range. They were not positioned in any specific configuration with respect to the synchrotron beam. (No angular dependence was detected for the single crystalline minerals). With the exception of the metamict minerals, all samples were scraped with a ruby file (in UHV) to ensure surface cleanliness. The single-phase condition of the minerals was checked by X-ray diffraction. Additionally the minerals from the Cape Verde Islands (Ti-Augite, Kaersutite and Melanite-Schörlomite) were checked by electron microprobe analysis.

## Results and Interpretation

Figure 3 shows the titanium  $2p$  X-ray absorption spectra of  $FeTiO_3$  (ilmenite) and of  $TiO_2$  in three different crys-

**Table 1.** Minerals: Origin and simplified chemical formula

Material	Source	Simplified formula	Ref.
Anatase	Blue Piz, Switzerland	$TiO_2$	Palache (1944) <sup>a</sup>
Rutile	Saint Yrieux, Limoges, France	$TiO_2$	Palache (1944) <sup>b</sup>
Brookite	Crystal fragment (location unknown)	$TiO_2$	Palache (1944) <sup>a</sup>
Ilmenite	Blåfjell, Norway	$FeTiO_3$	Newhouse (1936)
Titanite	Renfrew, Canada	$CaTiSiO_5$	Palache (1944) <sup>b</sup>
Ti-Augite	Santiago Island, Cape Verde	$(Ca, Na)(Mg, Fe, Al, Ti)(Si, Al)_2O_6$	Silva (1977)
Kaersutite	Fogo Island, Cape Verde	$Ca_2Na(Mg, Fe)_4Ti(Al, Si)_8O_{22}(OH)_2$	Silva (priv. comm.)
Melanite-Schörlomite	North Santiago Isl, Cape Verde	$Ca_3(Fe, Ti)_2(Si, Ti)_3O_{12}$	Silva and Ubaldo (1985)

<sup>a</sup> Samples from the international collection of the late Mineralogical and Geological Museum, Lisbon University (Machado-Costa 1937)

<sup>b</sup> Samples from the mineralogical collection of the Bensaude Museum, IST, Technical University of Lisbon

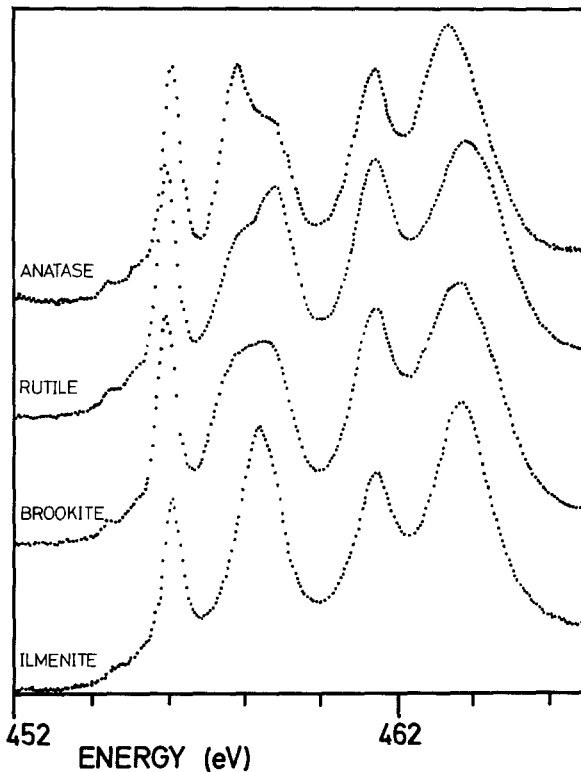


Fig. 3.  $2p$  X-ray absorption spectra of the minerals Rutile, Anatase, Brookite and Ilmenite

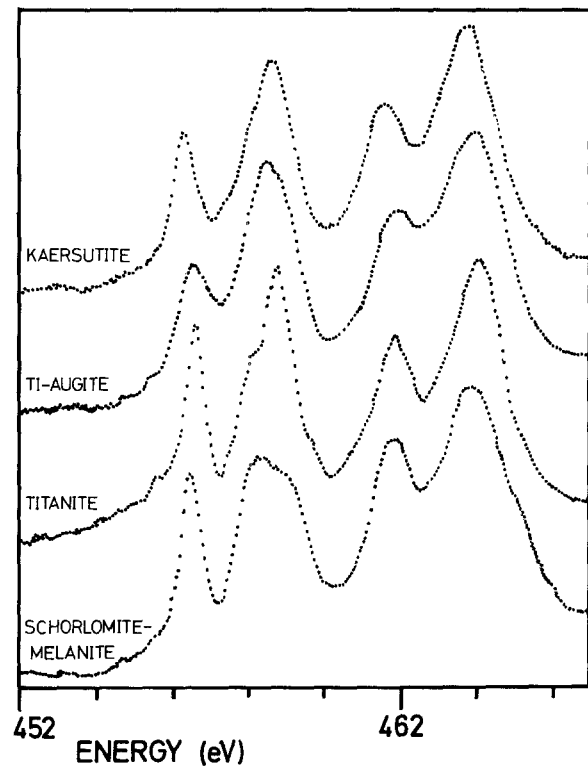


Fig. 4.  $2p$  X-ray absorption spectra of the minerals Titanite, Ti-Augite, Kaersutite and Melanite-Schörlomite

Table 2. Minerals: metal-oxygen bond lengths and site symmetry of the titanium atoms

Sample	Symmetry	Metal-oxygen bond length (Å)	Mean	References
Anatase	$D_{2d}$ ( $\bar{4}2m$ )	1.937 (4) 1.983 (2)	<u>1.952</u>	Horn et al. (1972)
Rutile	$D_{2h}$ ( $mmm$ )	1.946 (4) 1.984 (2)	<u>1.959</u>	Cromer and Herrington (1955)
Brookite	$C_1$ (1)	1.87 1.92 1.94 1.99 2.00 2.04	<u>1.96</u>	
Ilmenite	$C_3$ (3)	1.874 (3) 2.088 (3)	<u>1.981</u>	Wechsler and Prewitt (1984)
Titanite	$C_1$ (1)	1.76 1.97 1.98 2.00 2.01 2.02	<u>1.96</u>	Speer and Gibbs (1976)

tal structures. The spectra of minerals with only minor titanium content are corrected by subtracting a linear background correction. In rutile and anatase the main distortion of the octahedron is the elongation of one axis to form a tetragonal surrounding. There are additional distortions (on the angles) to lower the symmetry as indicated in Table 2. Because of this distortion the  $e_g$  peak is split in agreement with the calculations in Fig. 2 which indeed found the  $e_g$ -peak splitting to be most sensitive to tetragonal symmetry-lowering. Ilmenite does not show any significant splitting of the  $e_g$  peak, which reflects the predicted insensitivity of the spectral shape to trigonal distortions. In Fig. 3 the two prepeaks are barely visible because the resolution ( $\sim 0.5$  eV) is not as good as that of the  $SrTiO_3$  spectrum in Fig. 1.

Figure 4 shows the spectra of four silicate minerals containing titanium. In silicate minerals oxygen is bound to a great variety of cations, with the consequence of another type of behaviour as compared to the binary oxides.

● Kaersutite contains three possible octahedral sites for titanium, labelled M1, M2 and M3 in the usual site nomenclature for amphibole minerals. A number of neutron scattering structural refinement studies have been performed on several amphiboles (Kitamura et al. 1975; Kitamura and Tokonami 1971; Hawthorne and Grundy 1973; Robinson et al. 1973). The results are not uniform and titanium is assigned to different sites in different studies. The observed spectrum for kaersutite consists

of four structureless peaks, from which it is difficult to extract any clear information. From the absence of asymmetry in the  $e_g$  peak it can be concluded that the titanium sites are not tetragonally distorted.

- Ti-augite shows a unique feature in its broad  $t_{2g}$  peak and this suggests that titanium does occupy different sites. A partial occupation of higher coordination sites (M2) or of tetrahedral sites is consistent with a broadening of the  $t_{2g}$  peak because the  $t_{2g}$ -peaks of these different sites will be displaced from each other. The broadening cannot be related to the site-distortion of a single site due to the insensitivity of the  $t_{2g}$ -peak to distortions.

- Titanite is a well studied mineral; its most interesting feature is the existence of an extremely short titanium-oxygen distance of 1.76 Å. The titanium is furthermore surrounded by 5 more or less equidistant oxygens (see Table 2). The Ti 2p X-ray absorption spectrum of titanite is rather sharp. The  $e_g$  peak clearly has a shoulder on the low energy side, which can be related to the energy-difference between the  $d_x^2-y^2$  and the  $d_z^2$  orbitals due to the interaction with the neighbouring oxygen.

- The schörlomite-melanite garnet should contain titanium in octahedra of trigonal site-symmetry  $C_{3i}$  (Novak and Gibbs 1971). The spectrum shows a broad  $e_g$  peak, which might be interpreted as a mixed contribution from octahedral  $Ti^{III}$  and (tetragonally distorted)  $Ti^{IV}$ . More detailed studies of the garnets have to be undertaken before a definite answer can be given.

In summary we conclude that before the 2p X-ray absorption spectra of titanium can unambiguously be relat-

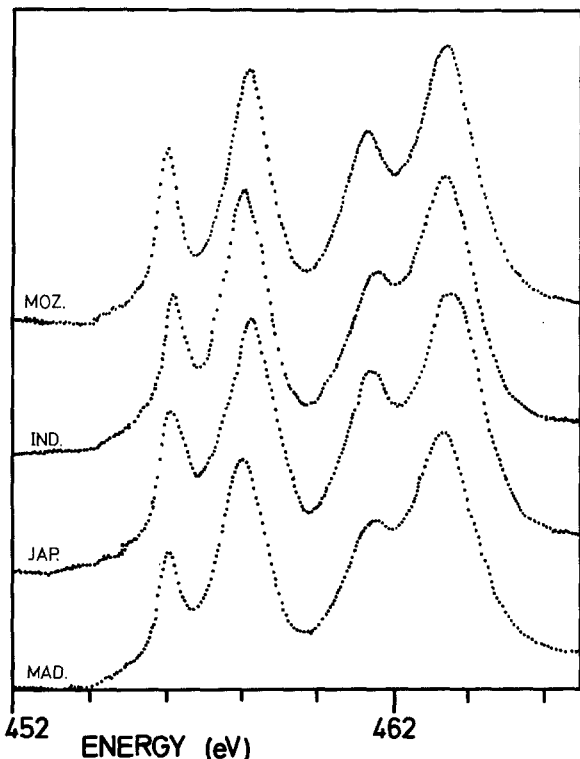


Fig. 5. 2p X-ray absorption spectra of perrierites from (top to bottom) Bingre in Mozambique (MOZ.), Bangalore in India (IND.), Kobe in Japan (JAP.) and Ifasina in Madagascar (MAD.)

Table 3. Approximate contents of the perrierites. For a full account of the contents see Lima de Faria 1964

Constituent	Bingre Mozambique wt. %	Bangalore India wt. %	Kobe Japan wt. %	Ifasina Madagascar wt. %
$TiO_2$	16	17	16	16
$ThO_2$	0	2	2	1
$RE_2O_3^a$	27	20	26	21
$CeO_2$	19	19	19	22
$Fe_2O_3^b$	9	9	9	11
$CaO^c$	4	8	4	2
$Nb_2O_5$	1	0	1	1
$SiO_2$	24	25	23	26

<sup>a</sup> RE includes the Rare Earths (La, Pr, Nd, Sm, Gd, Dy, Er, Yb) and Yttrium

<sup>b</sup> Including minor contents of  $MnO_2$

<sup>c</sup> Including minor contents of  $PbO$  and  $SrO$

ed to a specific phenomenon the study of a larger spare of minerals is necessary. Nevertheless the spectra can add important information as to limit the range of possibilities. In combination with other available techniques a more definitive answer regarding site distortions and mixed occupancy will have to be formulated.

Figure 5 contains the Ti 2p X-ray absorption spectra of perrierite,  $(Ca, Ce, Th)_4(Fe^{II}Mg)_2(Ti, Fe^{III})_3Si_4O_{22}$ , from four different localities, from top to bottom Bingre in Mozambique (MOZ.), Bangalore in India (IND.), Kobe in Japan (JAP.) and Ifasina in Madagascar (MAD.). In Table 3 their chemical composition is summarized (Lima de Faria 1964). The spectra are rather similar and consist of four peaks. The  $e_g$  peak is unstructured which indicates that the Ti-octahedra are not strongly distorted, in accordance with what would be expected from a metamict mineral. There is some variation in the sharpness of the  $t_{2g}$  peak; perrierite from Mozambique has a considerable sharper  $t_{2g}$  peak and this is therefore expected to contain a more uniform distribution of titanium sites. The metamict samples could not be scraped thus their surface cleanliness can not be assured and because electron-yield detection mode was used the differences in spectral shape can be partly due to titanium near the surface. Further study with fluorescence yield detection is necessary to reach unambiguous results.

## Discussion

### Electronic Structure and Site Geometry

Conclusions regarding the site geometry and the valency can be drawn from comparison to calculations. However the possibility of a combination of trivalent titanium, site distortions and multiple site occupation generates a complicated problem. For silicate minerals, in general with only minor titanium contents, no definitive results can be obtained from Ti 2p X-ray absorption alone. In future studies the variations of the Ti 2p X-ray ab-

sorption spectra within a mineral-group or for example garnets will be checked. The spectra contain enough features sensitive to small variations in site symmetry and given the detailed theoretical simulations these variations can be related to the effects discussed.

Even more important will be to relate the Ti 2*p* X-ray absorption spectrum to other X-ray absorption edges of the same compound. The Ti 1*s* edge (see below), the oxygen 1*s* edge and for most compounds also the Fe 1*s* and 2*p* edges contain additional information and a combination of all these spectra will create a more complete picture of the electronic structure. In this respect especially the oxygen 1*s* edge can prove to be important. The oxygen 1*s* X-ray absorption spectra reflect closely the energy distribution of unoccupied oxygen *p*-states (Grioni et al. 1989; de Groot et al. 1989). For 3*d* transition metal ions the first empty states will have a combined metal 3*d*-oxygen 2*p* character and these states will appear clearly before the antibonding oxygen-silicon states. Therefore the states at the oxygen 1*s* edge will contain information about the bonding to the metal 3*d* states. Preliminary results for kaersutite indicate that the 3*d*-part of the oxygen 1*s* spectrum is dominated by oxygen 2*p*-iron 3*d* states.

#### Comparison of Ti 2*p* and Ti 1*s* X-ray Absorption

Comparing the Ti 1*s* (Waychunas 1987) with the Ti 2*p* X-ray absorption spectra one can conclude that both edges are sensitive to the site symmetry. The 2*p* edge is dominated by the 2*p* → 3*d* transitions, whereas the 1*s* edge is dominated by 1*s* → *p* transition with the 3*d*-band region appearing as small pre-peaks only. Therefore the theoretical approaches are quite different: The crystal-field multiplet model accounts well for the 2*p*-edge and the 1*s* edge can be explained accurately by a band structure (or multiple scattering) calculation, with the exception of the 3*d*-part of the spectrum. The 3*d*-part of both the oxygen and the titanium K edge is affected by correlation effects which are not accounted for by single-particle calculations like multiple scattering.

Due to its relatively straightforward calculational method it is possible to relate the crystal-field multiplet results closely to the site geometry as discussed before. These results can add to the information obtained from the K edges such as neighbour distances, etc (Waychunas 1987). The sharpness of the spectral features, due to intrinsic as well as experimental broadening effects is considerably smaller for the 2*p* edges than for the 1*s* edges. The sharpest features seen for oxides are the first peak of the 2*p* edge of *Ti* in *SrTiO*<sub>3</sub>, given in Fig. 1, with a half-width half-maximum of 0.2 eV; for the 1*s*-edges the first pre-peak of *Ti* in *TiO*<sub>2</sub> has a half-width half-maximum of about 0.6 eV (Durmeyer et al. 1990a; Al Shamma and Fuggle 1990). An important advantage of the 1*s* edges is the possibility to measure accurate EXAFS spectra. For the 2*p* edges this is virtually impossible because of overlapping *L*<sub>3</sub> and *L*<sub>2</sub> spectra and the presence of the oxygen 1*s* edge at approximately 530 eV.

The conclusions of both the 1*s* edges and the 2*p* edges with respect to the valency determination are similar. *Ti*<sup>III</sup> gives a completely different 2*p* spectrum and for the 1*s* edge the main edge is shifted by ~2 eV, making the identification of trivalent titanium in principle straightforward. However the existence of small amounts of *Ti*<sup>III</sup> are difficult to detect in both methods if the spectrum is dominated by the signal from *Ti*<sup>IV</sup>. These difficulties can be overcome if one measures standards of similar structure. For the 2*p* edge this has been shown for the *La*<sub>*x*</sub>*Sr*<sub>1-*x*</sub>*TiO*<sub>3</sub> system (Abbate et al. 1991).

The average Ti–O distance will be related to the cubic crystal field parameter (Sette et al. 1989). This will be reflected in the *t*<sub>2*g*</sub>–*e*<sub>g</sub> splitting, and intensity ratio, of the 2*p* spectrum (de Groot et al. 1990a) and can be checked in the spectra. Rutile and anatase have considerably larger splittings and *t*<sub>2*g*</sub> intensities. As it is difficult to find a simple quantitative measure from the spectra, because of the splitting of the *e*<sub>g</sub> peak and the variations in the broadenings, we did not try to determine a quantitative measure. In relation to this trend we note that in Fig. 3. of Waychunas' paper a clear reciprocal relation exists between *Ti*–*O* distance and the splitting between the first and second peak (Waychunas 1987). For clarity we notice that in rutile (and anatase) three prepeaks are found and as has been nicely demonstrated by Uozumi et al. (1991) the first peak relates to quadrupole transitions to *t*<sub>2*g*</sub> states, the second peak to quadrupole transitions to *e*<sub>g</sub> states superimposed with dipole transitions to (*p*-character of) the *t*<sub>2*g*</sub> states. Finally the third peak relates to dipole transitions to (*p*-character of)*e*<sub>g</sub> states. Thus the cubic crystal field splitting is reflected in both the distance between first and second peak as well as between second and third peak (after deconvolution).

#### Experimental Aspects

Until now 2*p* X-ray absorption studies have been performed mostly on ordered solids. For these materials the crystal structures are generally known and the main objective is to elucidate the electronic structure of the 3*d*-states by comparison to the crystal field multiplet calculations. Mostly the oxygen 1*s* edge is measured additionally and compared to electronic structure calculations. In mineralogy the situation is different. As the materials are in general much more complex and no detailed electronic structure calculations can be performed, the analysis of the spectra must be done by comparison to known standards. Furthermore there are variations from one sample to the other and sometimes also within a sample and the determination of these variations is an important goal in mineralogy.

An important experimental aspect is the probing depth of X-ray absorption. In the total electron yield mode the probing depth is, in case of oxides, in the order of 50 Ångstroms (Abbate et al. 1992). Though this will be in general deep enough to ensure a bulk-measurement, it will be advantageous to measure minerals with fluorescence yield (Cramer et al. 1988), which has a probing depth in the order of 1000 Ångstroms.

## Concluding Remarks

We have shown that the  $2p$  X-ray absorption spectra can be explained by crystal field multiplet calculations. The asymmetry of the  $e_g$  peak is shown to be related to distortions of the  $Ti^{IV}$  octahedron. It is found theoretically that the absorption spectrum is more sensitive to tetragonal distortions than to trigonal distortions. This is confirmed experimentally and the spectra of anatase and rutile show a clear asymmetry whereas ilmenite has a symmetric  $e_g$  peak.

The  $2p$  X-ray absorption edges of silicate minerals are quite distinct from each other, which offers the possibility to use the spectra as a fingerprint. The possible variations in the spectra within a class of minerals remains to be checked.  $Ti^{III}$  alone was not observed in any of the minerals, though minor concentrations will not be detected easily.

We have shown that titanium  $2p$  X-ray absorption spectra are sensitive to details of the local chemical environment and can play an important role in the determination of the electronic structure and the site geometry of titanium in minerals. A combination with other X-ray absorption edges, specifically the titanium  $1s$  and the oxygen  $1s$  edge, will reveal significantly new information regarding the electronic structure and chemical bonding in minerals.

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