Local structures around Mn, Co and Ni atoms in glasses of the systems $\text{CaMgSi}_2\text{O}_6$ - $\text{CaMnSi}_2\text{O}_6$, $\text{CaMgSi}_2\text{O}_6$ - $\text{CaCoSi}_2\text{O}_6$ and $\text{CaMgSi}_2\text{O}_6$ - $\text{CaNiSi}_2\text{O}_6$ determined by the XAFS spectroscopy

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Abstract

Local structures around transition-metal atoms in silicate glasses of the systems $\text{CaMgSi}_2\text{O}_6$ (Di)- $\text{CaMnSi}_2\text{O}_6$ (CaMnPx), $\text{Di-CaCoSi}_2\text{O}_6$ (CaCoPx) and $\text{Di-CaNiSi}_2\text{O}_6$ (CaNiPx) were investigated with the XAFS (X-ray Absorption Fine Structure) spectroscopy, by making use of SR (Synchrotron Radiation). The obtained distances suggest that the preference to the octahedral coordinations is in the decreasing order Ni^{2+} , Co^{2+} and Mn^{2+} . This order can be explained in view of the difference between the crystal-field stabilization energies for octahedral and tetrahedral coordinations in the high-spin states. ELNES (Energy-Loss Near Edge Structure) spectra were also measured around the Mn $L_{2,3}$ edges to determine the oxidation states of Mn ions in glasses of the system Di-CaMnPx . Chemical shifts of the $L_{2,3}$ edge threshold-energy and the ratios of L_3/L_2 threshold peaks in all the examined glasses were similar to those in MnO but unlike those in MnO_2 . The observed tendency of chemical shifts in the XANES spectra of Mn K-edges was identical with that in ELNES. The shifts of Co K- and Ni K-edges in the XANES spectra of all the examined glasses were similar to those of Co-olivine and NiO, respectively. These facts suggest that Mn, Co and Ni ions in the glasses are in divalent states.

Introduction

The present authors have already reported the local structures around transition-metal atoms in glasses of the systems $\text{CaMgSi}_2\text{O}_6$ (Di)- $\text{CaTiAl}_2\text{O}_6$ (CaTiPx), Di-CaFeAlSiO_6 (CaFePx) and Di-CaCrAlSiO_6 (CaCrPx) obtained by the XAFS (X-ray Absorption Fine Structure) spectroscopy and X-ray diffraction method (Marumo *et al.*, 1989, 1990; Tabira and Marumo, 1992). The distances between transition-metal and oxygen atoms in the first coordination shells are clearly shorter than those expected for octahedrally coordinated Ti^{4+} and Fe^{3+} ions in the first two systems. On the contrary, Cr^{3+} ions showed the strong preference to octahedral coordination, giving longer Cr-O distances.

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Di-CaMnSi₂O₆ (CaMnP_x), Di-CaCoSi₂O₆ (CaCoP_x) and Di-CaNiSi₂O₆ (CaNiP_x) systems are supposed to have solid solutions as the primary phases in wide composition ranges. The local structures around Mn, Co and Ni atoms were investigated by the XAFS spectroscopy to add knowledges on the correlation expected to exist between the coordination environments of the first-row transition-metals and the liquidus phase relations in the rock-forming silicate systems.

One of the most important parameters of a local structure revealed by the XAFS spectroscopy is a distance from the relevant central atom to the nearest neighbors. This parameter has a large correlation with oxidation states as well as average coordination number of those atoms. Thus, it is necessary to determine both the oxidation states of transition-metal ions and the bond distances to the surrounding atoms in order to study coordination numbers of the transition-metal ions in glasses quenched from high-temperature liquids by the XAFS spectroscopy.

Chemical shifts of the L_{2,3}-edge threshold-energy and the ratios of L₃/L₂ threshold peaks observed by the EELS (Electron Energy-Loss Spectroscopy) technique can be used to determine valence states of transition-metal ions (Otten *et al.*, 1985; Paterson and Krivanek, 1990; Leapman *et al.*, 1982). Similar chemical shifts in the K-edge threshold-energy can be observed in XANES spectra, where 1s electrons are excited. Quite distinctive L_{2,3}-edges observed in ELNES (Energy-Loss Near Edge Structure) spectra of the first-row transition-metal atoms, which have been known as *white lines* since they were first observed in X-ray absorption spectra as white lines caused by high absorption rate at the ionization threshold, correspond to absorptions by the transitions of inner-shell electrons of the states 2p^{3/2} and 2p^{1/2} to unoccupied 3d orbitals, respectively (Leapman *et al.*, 1982). In the case of these atoms, the dipole transition to the narrow unoccupied 3d orbitals makes the L_{2,3} edges sharp doublets, separated in energy ranging from *ca.* 6 eV in Ti to *ca.* 20 eV in Cu.

Experimental

Sample preparation

The glasses were prepared from mixtures of reagent-grade CaCO₃, MgO, SiO₂ and the relevant transition-metal oxides, *i.e.* MnO, Co₃O₄ and NiO. The mixtures were melted in a Pt crucible at 1500°C for 2h, dropped into ice-water, and then pulverized in a mortar. The glass powders were annealed for 24h to crystallize. These poly-crystalline powders were melted for 2h at temperatures above the melting points by about 20°C, and dropped into ice-water to get glasses. All these procedures were performed in atmosphere. Homogeneity of the obtained glasses was checked under a polarizing microscope and a transmission electron microscope (JEM-2000EX) equipped with an energy-dispersive X-ray detector and analyzer (TN-2000). The glasses were mixed with polyethylene powders after pulverized, and shaped into pellets with suitable thickness for XAFS measurements.

XAFS spectra

The XAFS spectra near the K absorption edges of the respective transition-metal atoms were measured on the glasses with a XAFS spectrometer (BL7-C) at the Photon Factory in the Institute for High Energy Physics, Tsukuba, Japan, by making use of SR (Synchrotron Radiation). All the experiments were carried out in the transmission mode at room temperature, using a Si(111) double-crystal monochromator. The beam size irradiated on a specimen was $1.0 \times 6.5 \text{ mm}^2$. Intensities of incident and transmitted beams were measured with ion chambers at 326 energy points ranging from 6.098 to 7.338 keV for Mn K, from 7.270 to 8.510 keV for Co K and from 7.892 to 9.132 keV for Ni K spectra, respectively. An apparent absorption coefficient was calculated from $\ln(I_0/I)$, depicted in Fig. 1(a), (b) and (c). Each spectrum was divided into four blocks with different energy ranges, *i.e.* from -440 to -50 eV (1.2 eV), from $+100$ to $+400 \text{ eV}$ (2.5 eV) and from $+400$ to $+800 \text{ eV}$ (8 eV) with reference to the relevant K-edge threshold energy. The values in parentheses are the energy steps in the respective ranges in the measurements. The diffraction angle of the monochromator was calibrated by scanning a characteristic peak observed on the slope of Cu K-edge threshold from a copper foil.

The XANES spectra (Fig. 2(a), (b) and (c)) were measured on the same spectrometer (BL-7C) with much finer energy steps (0.16 eV), with scanning width 90 eV from 6510 eV for Mn K, from 7680 eV for Co K- and from 8510 eV for Ni K-edges, respectively.

(a)

(b)

(c)

FIG. 1. The observed XAFS spectra on glasses of (a) Di-CaMnPx, (b) Di-CaCoPx and (c) Di-CaNiPx systems. CaMnPx10 *etc.* represents the composition of 90 wt% Di-10 wt% CaMnPx, *etc.*.

(a)

(b)

FIG. 2. The observed XANES spectra on glasses of (a) Di-CaMnPx, (b) Di-CaCoPx and (c) Di-CaNiPx systems. Small pre-edge peaks are existed in all spectra as indicated by arrows except for MnO, Co-olivine and NiO, where the transition-metal ions are rather regularly and octahedrally coordinated by oxygen ions.

XAFS spectra of reagent-grade MnO, NiO and synthetic olivine with the composition of $\text{Co}_{0.4}\text{Mg}_{1.6}\text{SiO}_4$ (hereafter referred as Co-olivine) were measured as reference materials for octahedrally coordinated transition-metal ions in divalent states. Because different oxidation states may be possible for Mn and Co ions in the glasses examined, spectra of reagent-grade $\alpha\text{-Mn}_2\text{O}_3$, MnO_2 and Co_3O_4 were also measured for octahedrally coordinated cations in tri- or tetra-valent states.

The XAFS components $\chi(k)$'s were extracted from the spectra, after subtracting backgrounds and normalizing the values by the usual method (Tohji *et al.*, 1984). The functions k^3 -weighted $\chi(k)$'s were Fourier-transformed in the ranges from $k = 30\sim 115\text{ nm}^{-1}$ for Mn K-, $30\sim 120\text{ nm}^{-1}$ for Co K- and Ni K-edges spectra, where k is the wave number of the ejected photoelectron, to obtain the radial distribution functions $|F(r)|$'s. Results are shown in Fig. 3(a), (b) and (c). In this calculation, no corrections for absorption-edge energy (ΔE_0) referred as inner potential and the phase shift were performed, so that the peak positions on the obtained $|F(r)|$'s appeared at distances slightly shorter than the actual ionic separations. Detailed procedure was mentioned elsewhere (Tada *et al.*, 1982).

FIG. 3. The radial distribution functions $|F(r)|$'s of the glasses in the (a) Di-CaMnPx, (b) Di-CaCoPx and (c) Di-CaNiPx systems.

ELNES spectra

ELNES spectra for Mn $L_{2,3}$ edges were measured on the glasses in the system Di-CaMnPx, using the Gatan model 666 parallel-detected energy-loss spectrometer and Noran TN-5500 multi-channel analyzer mounted on a transmission electron microscope JEM-2010. The incident energy of electron from a LaB₆ filament was 200 keV and its energy spread

estimated from the full-width of the zero-loss (no-loss) peak at the half height was *ca.* 2.1 eV. All the spectra were recorded in the TEM-diffraction mode and the collection semi-angle was set to *ca.* 20 mrad. The integration of the counts was carried out for 20 seconds and the number of read-outs from the photodiode arrays was 3, that is, each spectrum was measured for 60 seconds in effect. Energy range measured was 470 to 776.9 eV, in which O K-edge as well as Mn L_{2,3}-edge were contained, with the energy dispersion of 0.3 eV per channel. Reagent-grade MnO and MnO₂ were used as reference materials for Mn²⁺ and Mn⁴⁺ ions, respectively. The specimens used in this experiment were prepared by crushing the respective glasses or the reference materials finely in ethanol in a mortar, and supported on a holey carbon thin film on a copper grid. Loss energy was calibrated by determining the energy difference between the zero-loss peak and each spectrum, using a voltage scan module (Gatan model 607-2600). Energy drifts were checked with changes of the positions of the zero-loss peaks before and after acquisition of the respective spectra (less than 0.6 eV). Obtained EELS spectra of reference materials were shown in Fig. 4, where no background was subtracted.

Backgrounds were fitted by the least-squares method to an exponential form of $A \cdot E^{-r}$ as a function of the absolute loss-energy E , where A and r are adjustable parameters, and subtracted from each spectrum after making corrections for the dark current and channel-to-channel gain for 1024 photodiode arrays. The background-subtracted ELNES spectra are given in Fig. 5. In all of the spectra, no plural scatterings were deconvoluted because of the very thin thicknesses of the specimens.

FIG. 4. EELS spectra of MnO and MnO₂. O K- as well as Mn L_{2,3}-edge is observed. We can notice the distinctive doublets of Mn L_{2,3} peaks.

FIG. 5. Background-subtracted ELNES spectra of Mn $L_{2,3}$ edges. Chemical shifts and the intensity ratios of the doublet in the glasses are like those in MnO but unlike those in MnO_2 .

Results and discussion

In order to analyze the local structures around the respective transition-metal ions (M), the first peaks on the $|F(r)|$'s which are due to the nearest neighbor M-O pairs were inversely transformed and analyzed by the curve-fitting method, based on the theoretical equation of single scattering. The energy shift caused by the inner potential and the mean free path of ejected photoelectrons were refined as least-squares parameters for each reference material, using the theoretical values of phase shifts and backscattering amplitude tabulated by McKale *et al.* (1988). The obtained distances between the transition-metal and the nearest neighbor oxygen ions are about 0.208, 0.200 and 0.201 nm in the glasses of the systems Di-CaMnP_x, Di-CaCoP_x and Di-CaNiP_x, respectively. These distances are plotted against chemical compositions in Fig. 6, where the plots for the systems Di-CaTiP_x, Di-CaCrP_x and Di-CaFeP_x (Marumo *et al.*, 1989, 1990) are also contained for comparison. Except for the Di-CaTiP_x system, the distances are independent of the composition within the experimental errors.

The obtained distances in all the glasses are clearly shorter than the sums of ionic radii (Shannon, 1976) for octahedral coordinations. Especially in the system Di-CaMnP_x, the obtained distances are surprisingly short and might suggest four-fold coordinations of Mn ions

in divalent states or sixfold coordinations in higher oxidation states. However, the possibility of the latter case was denied with the results of ELNES spectra shown in Fig. 5, *i.e.* the chemical shifts in $L_{2,3}$ -edge threshold energy and the ratios of L_3/L_2 threshold peaks in all the glasses examined were similar to those in MnO but unlike those in MnO_2 . The observed tendency of chemical shifts in XANES spectra of Mn K-edge were identical with that in ELNES spectra. The shifts of Co K- and Ni K-edges in XANES spectra of the examined glasses were similar to those of Co-olivine and NiO, respectively. These facts suggest that the Mn, Co and Ni ions are in divalent states in the glasses.

The presence of small pre-edge peaks in XANES spectra of all the glasses and some of the reference materials (indicated by the arrows in Fig. 2(a), (b) and (c)) might imply irregularities in coordination polyhedra of the transition-metal ions as pointed out by Waychunas *et al.* (1983) and Waychunas (1987) for Fe and Ti compounds giving pre-edge peaks in the K-edge XANES spectra.

M-O distances for octahedral coordinations in crystals are: $Mn^{2+}-O^{2-} = 0.222$ nm in MnO ($a = 0.44448$ nm), $Co^{2+}-O^{2-} = 0.210$ nm (averaged value) and 0.211 nm (average value in the M1 site) in $CaCoSi_2O_6$ with diopside-type structure (Ghose *et al.*, 1987) and the synthetic Co-olivine (Miyake, *et al.*, 1987), respectively, and $Ni^{2+}-O^{2-} = 0.208$ nm, 0.208 nm (averaged value in the M1 site) and 0.207 nm (averaged value) in NiO ($a = 0.41684$ nm), Ni_2SiO_4 with

FIG. 6. The obtained distances between the transition-metal and the nearest neighbor oxygen ions, plotted against chemical compositions of the glasses. The upper three systems are based on the results after Marumo *et al.* (1989, 1990). The dotted lines indicate the M-O distances for octahedral coordinations in crystals MnO, $CaCoSi_2O_6$ (Ghose *et al.*, 1987) and NiO (the upper) and those for tetrahedral coordinations estimated from the sums of the effective ionic radii (Shannon, 1976).

olivine-type structure (Rajamani *et al.*, 1975) and $\text{CaNiSi}_2\text{O}_6$ with diopside-type structure (Ghose *et al.*, 1987), respectively.

On the other hand, those for tetrahedral coordinations which are estimated from the sums of the effective ionic radii (Shannon, 1976), where oxygen ions are assumed to be the same in size as those for octahedral coordinations in the crystals mentioned above, are: $\text{Mn}^{2+}\text{-O}^{2-} = 0.205$ nm, $\text{Co}^{2+}\text{-O}^{2-} = 0.193$ nm and $\text{Ni}^{2+}\text{-O}^{2-} = 0.194$ nm. These distances are indicated as dotted lines in Fig. 6. If we compare the distances with those obtained by the XAFS spectroscopy, we notice that the preference to the octahedral coordinations is in the decreasing order Ni^{2+} , Co^{2+} and Mn^{2+} . This fact is understood qualitatively from the crystal-field stabilization energy (CFSE) of these transition-metal ions, *i.e.* the tendency of preference to

TABLE 1. Electron configurations and crystal-field stabilization energy (CFSE) of transition-metal ions in octahedral coordinations in the high-spin states.

Number of 3d electrons	Ions	Electron configurations		Unpaired electrons	CFSE
		t_{2g}	e_g		
0	$\text{Ca}^{2+}, \text{Sc}^{3+}, \text{Ti}^{4+}$			0	0
1	Ti^{3+}	$\uparrow$		1	$\frac{2}{5}\Delta_o$
2	$\text{Ti}^{2+}, \text{V}^{3+}$	$\uparrow\uparrow$		2	$\frac{4}{5}\Delta_o$
3	$\text{V}^{2+}, \text{Cr}^{3+}, \text{Mn}^{4+}$	$\uparrow\uparrow\uparrow$		3	$\frac{6}{5}\Delta_o$
4	$\text{Cr}^{2+}, \text{Mn}^{3+}$	$\uparrow\uparrow\uparrow$	$\uparrow$	4	$\frac{4}{5}\Delta_o$
5	$\text{Mn}^{2+}, \text{Fe}^{3+}$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow$	5	0
6	$\text{Fe}^{2+}, \text{Co}^{3+}, \text{Ni}^{4+}$	$\uparrow\downarrow\uparrow\uparrow$	$\uparrow\uparrow$	4	$\frac{2}{5}\Delta_o$
7	$\text{Co}^{2+}, \text{Ni}^{3+}$	$\uparrow\downarrow\uparrow\uparrow$	$\uparrow\uparrow$	3	$\frac{3}{5}\Delta_o$
8	Ni^{2+}	$\uparrow\downarrow\uparrow\uparrow$	$\uparrow\uparrow$	2	$\frac{4}{5}\Delta_o$
9	Cu^{2+}	$\uparrow\downarrow\uparrow\uparrow$	$\uparrow\downarrow\uparrow$	1	$\frac{1}{5}\Delta_o$
10	$\text{Zn}^{2+}, \text{Ga}^{3+}, \text{Ge}^{4+}$	$\uparrow\downarrow\uparrow\uparrow$	$\uparrow\downarrow\uparrow\downarrow$	0	0

TABLE 2. Electron configurations and crystal-field stabilization energy (CFSE) of transition-metal ions in tetrahedral coordinations in the high-spin states.

Number of 3d electrons	Ions	Electron configurations		Unpaired electrons	CFSE
		e	t_2		
0	$\text{Ca}^{2+}, \text{Sc}^{3+}, \text{Ti}^{4+}$			0	0
1	Ti^{3+}	$\uparrow$		1	$\frac{3}{5}\Delta_t$
2	$\text{Ti}^{2+}, \text{V}^{3+}$	$\uparrow\uparrow$		2	$\frac{6}{5}\Delta_t$
3	$\text{V}^{2+}, \text{Cr}^{3+}, \text{Mn}^{4+}$	$\uparrow\uparrow$	$\uparrow$	3	$\frac{4}{5}\Delta_t$
4	$\text{Cr}^{2+}, \text{Mn}^{3+}$	$\uparrow\uparrow$	$\uparrow\uparrow$	4	$\frac{2}{5}\Delta_t$
5	$\text{Mn}^{2+}, \text{Fe}^{3+}$	$\uparrow\uparrow$	$\uparrow\uparrow\uparrow$	5	0
6	$\text{Fe}^{2+}, \text{Co}^{3+}, \text{Ni}^{4+}$	$\uparrow\downarrow\uparrow$	$\uparrow\uparrow\uparrow$	4	$\frac{3}{5}\Delta_t$
7	$\text{Co}^{2+}, \text{Ni}^{3+}$	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\uparrow\uparrow$	3	$\frac{1}{5}\Delta_t$
8	Ni^{2+}	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow\uparrow$	2	$\frac{4}{5}\Delta_t$
9	Cu^{2+}	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow\uparrow$	1	$\frac{1}{5}\Delta_t$
10	$\text{Zn}^{2+}, \text{Ga}^{3+}, \text{Ge}^{4+}$	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	0	0

the octahedral coordinations is in the order of the magnitude of the difference between CFSE for octahedral and tetrahedral coordinations in the high-spin states. Tables 1 and 2 show the electron configurations and CFSE of the transition-metal ions in the high-spin states in the octahedral and tetrahedral coordinations, respectively. Ni^{2+} in the high-spin states shows large CFSE in the octahedral coordination. On the other hand, Mn^{2+} has zero CFSE in both coordinations in the high-spin states. It is concluded that for transition-metal ions in the same oxidation states, coordination environments seem to be largely dependent on the CFSE, even in quenched silicate glasses from high temperature.

Acknowledgment—The authors would like to thank Prof. Kojima (Yamanashi Univ.) for giving synthetic Co-olivine powders.

References

- GHOSE, S., WAN, CH'ENG and OKAMURA, F.P. (1987) Crystal Structures of $\text{CaNiSi}_2\text{O}_6$ and $\text{CaCoSi}_2\text{O}_6$ and Some Crystal-Chemical Relations in C2/c Clinopyroxenes. *Am. Mineral.*, **72**, 375-381.
- LEAPMAN, R.D., GRUNES, L.A. and FEJES, P.L. (1982) Study of the $L_{2,3}$ edges in the 3d Transition Metals and Their Oxides by Electron-Energy-Loss Spectroscopy with Comparisons to Theory. *Phys. Review*, **B, 26**, 614-635.
- MARUMO, F., TABIRA, Y., MABUCHI, T. and MORIKAWA, H. (1989) Correlation of Local Structures around Transition-Metal Elements in Silicate Melts to Phase Relation. *J. Jpn. Assoc. Min. Pet. Econ. Geol. Special Issue No. 4*, 87-93.
- MARUMO, F., TABIRA, Y., MABUCHI, T. and MORIKAWA, H. (1990) Coordinations of Transition-Metals in Amorphous Silicate. *Dynamic Processes of Material Transport and Transformation in Earth's Interior*, 53-65, edited by F. Marumo, Terra Scientific Publishing Company, Tokyo.
- McKALE, A.G., VEAL, B.W., PAULIKAS, A.P., CHAN, S.K. and KNAPP, G.S. (1988) Improved *ab Initio* Calculations of Amplitude and Phase Functions for Extended X-ray Absorption Fine Structure Spectroscopy. *J. Am. Chem. Soc.*, **110**, 3763-3768.
- MIYAKE, M., NAKAMURA, H., KOJIMA, H. and MARUMO, F. (1987) Cation Ordering in Co-Mg Olivine Solid Solution Series. *Am. Mineral.*, **72**, 594-598.
- OTTEN, M.T., MINER, B., RASK, J.H. and BUSECK, P.R. (1985) The Determination of Ti, Mn and Fe Oxidation States in Minerals by Electron-Energy Loss Spectroscopy. *Ultramicroscopy*, **18**, 285-290.
- PATERSON, J.N. and KRIVANEK, O.L. (1990) ELNES of 3d Transition-Metal Oxides II. Variation with Oxidation State and Crystal Structure. *Ultramicroscopy*, **32**, 319-325.
- RAJAMANI, V., BROWN, G.E. and PREWITT, C.T. (1975) Cation Ordering in Ni-Mg Olivine. *Am. Mineral.*, **60**, 292-299.
- SHANNON, R.D. (1976) Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Cryst.*, **A32**, 751-767.
- TABIRA, Y. and MARUMO, F. (1992) Local Structures around Fe and Cr Atoms in Glasses of the Systems $\text{CaMgSi}_2\text{O}_6$ - CaFeAlSiO_6 and $\text{CaMgSi}_2\text{O}_6$ - CaCrAlSiO_6 Determined by X-ray Diffraction Method. *Mineral. J.*, **16**, 21-27.
- TADA, M., MARUMO, F., OYANAGI, H. and HOSOYA, S. (1982) Structural Investigation of an $\text{Na}_2\text{O} \cdot 4\text{GaO}_2$ Glass with EXAFS Measurements. *Yogyo-Kyokai Shi*, **90**, 247-253 (in Japanese).
- TOHJI, K., UDAGAWA, Y., TANABE, S. and UENO, A. (1984) Catalyst Preparation Procedure Probed by EXAFS Spectroscopy. 1. Nickel on Silica. *J. Amer. Chem. Soc.*, **106**, 612-617.
- WAYCHUNAS, G.A. (1987) Synchrotron Radiation XANES Spectroscopy of Ti in Minerals: Effects of Ti

Bonding Distances, Ti Valence, and Site Geometry on Absorption Edge Structure. *Am. Mineral.*, **72**, 89-101.

WAYCHUNAS, G.A., APTED, M.J. and BROWN, G.E. (1983) X-ray K-Edge Absorption Spectra of Fe Minerals and Model Compounds: Near-Edge Structure. *Phys. Chem. Minerals*, **10**, 1-9.

Received March 15, 1993; accepted May 10, 1993