Experimental and theoretical XANES study of the effects of Fe-Mg solid solution in the enstatite-ferrosilite series

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Synthetic orthopyroxenes in the join enstatite - ferrosilite ($Mg_2Si_2O_6$-$Fe_2Si_2O_6$) have been studied by XANES with the aim to interpret the variations found in the spectra and evaluate the effects of the Mg-Fe substitution in the orthopyroxene (OPX) structure. The experimental Fe- and Mg-K edge XANES spectra show variations of the peaks intensity as a function of the chemical composition of the samples along the EN-FS join. In the region of the Fe edge, the intensity ratio between peak A and B (IB/IA) varies linearly (R=0.99) with the Mg/Fe substitution. Multiple scattering calculation have been performed both at the Fe and Mg K-edge, to study the geometrical modifications of the M1 and M2 octahedral sites induced by the Mg-Fe substitutions. The spectra, obtained locating Fe (or Mg) in both M1 and M2 and weighing the contributions using the occupancy data for the M1 and M2 sites determined by XRD, allow to discriminate the effects to the total spectrum due to Fe (Mg) located in each sites separately.

Keywords: XANES, Solid solution, Fe and Mg K edges

1. Introduction

Orthopyroxenes (Pbca) are single-chain silicates of ideal composition $Mg_2Si_2O_6$ (enstatite, EN) -$Fe_2Si_2O_6$ (ferrosilite, FS) where Mg and Fe substitute each other in the two octahedral sites M1 and M2, forming a series in solid solution. The two octahedral sites differ in dimension, symmetry and degree of distortion. These differences can be evaluated by considering the data for the pure-iron end-member, ferrosilite (Sasaki et al. 1982), where M1 is smaller than M2 (<Fe-O> 2.135 vs. 2.223) and is much more regular than M2 (M1 has D_{4h} or C_{3h}, M2 has C_{2v}; quadratic elongation = 1.0088 for M1 vs. 1.0700 for M2 (Robinson et al., 1971)). The substitution of Fe with Mg in the structure produces a general decrease of the octahedral bond lengths and a decrease in the distortion of the M2 site. The a_0 and b_0 parameters decrease linearly with En content (a_0=1.843, 1.832, 1.826 nm and b_0=0.908, 0.893, 0.886 nm, respectively, for En0Fs100, En50Fs50 and En80Fs20).

X-ray absorption spectroscopy has been used to investigate these mineralogically-relevant compounds finding that the intensity of the peaks in the edge region could be related to the Mg vs. Fe substitution along the EN-FS join (Mottana et al., 1991; Paris & Tyson 1994) and to a possible quantitative evaluation of the site occupancy. To better evaluate this conclusions, we synthesized a set of samples to cover the entire join EN-FS, from $En_{100}Fs_0$ to EN_0FS_{100} to understand the effects of chemical substitution and site occupancy on the XANES spectra. The advantage of synthetic vs. natural samples is to avoid the presence of trivalent cations, like Al, which can enter the octahedral sites and compete with the other cations. Also the use of a set of samples in a chosen compositional range and with different site occupancies gives a better evaluation of the effects seen in the experimental spectra.

2. Methods

The samples have been synthesized in a pyston-cylinder at high temperature and pressures (1600°C, 20kbar) in compositional steps of 0.20 atoms p.f.u..

XANES spectra were collected at SSRL (Stanford, USA) with the SPEAR storage ring (Stanford, USA) operating at 3 GeV and with ring currents ranging from 60 to 90 mA. Mg K-edge spectra were recorded in total yield mode at the beamline 3-3 where the radiation was monochromatized by two YB_{66} (400) crystals. Experimental resolution at this energy is about 0.4 eV. Fe K-edge spectra were collected in fluorescence mode at the 4-1 beamline using two Si (111) crystals, the experimental resolution being about 1.2 eV. Theoretical spectra have been calculated using the CONTINUUM code, which have been tested extensively and successfully on a number of complex mineral structures and glasses (Wu et al.,1996; 1999; Paris et al., 1995).

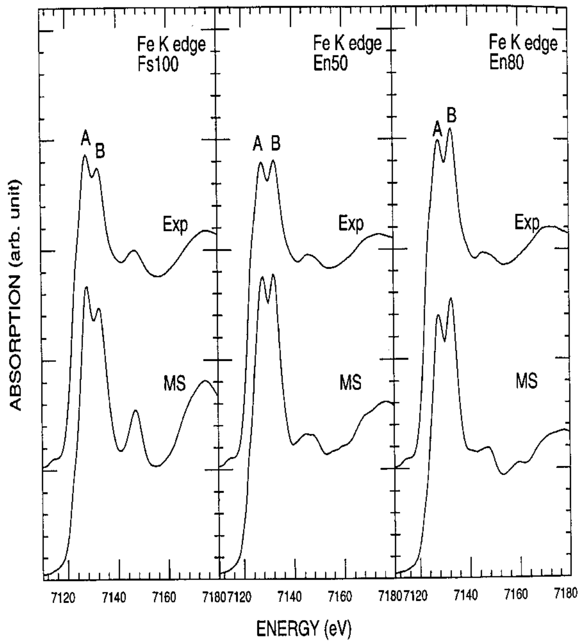

Figure 1
Experimental and theoretical XANES spectra at the Fe K-edge for orthopyroxenes in the join $Fe_2Si_2O_6$-$Mg_2Si_2O_6$ (enstatite-ferrosilite). Fs_{100} is pure ferrosilite ($Fe_2Si_2O_6$, En_0Fs_{100}), En50 is an intermediate composition ($En_{50}Fs_{50}$) and En80 is a Mg rich composition ($En_{80}Fs_{20}$).

3. Fe K-edge XANES spectra

The experimental XANES spectra at the Fe K-edge are shown in Fig. 1, where three different compositions are shown: FS100 (EN_0FS_{100}, pure ferrosilite), EN50 ($En_{50}Fs_{50}$) and En 80 ($En_{80}Fs_{20}$) arranged from left to right as a function of increasing En % (Mg) content. They are characterized by the presence of two peaks (A and B) at the absorption maximum, a peak (C) at ~7150 eV and a broad peak at ~ 7175 eV (D). Several variations occur in the spectra with increasing En content, but in particular:

1) the intensity of peak B increases;
2) peak C splits into two components;
3) peak D broadens and shifts to higher energies

All these changes occur continously along the En-Fs join and experience achieved studying similar or more complex structures

(Wu et al., 1996; Paris et al., 1995; Giuli et al., 2000) allows to interpret these variations. In fact, the changes in the shape of the peaks at higher energy C and D can be mainly assigned to the difference in electronic structure and backscattering effects between Fe and Mg. In fact, peaks C and D are single and less broad in the more Fe-rich spectra and E and F progressively split or grow when the Mg content is high enough (>En30). The variations in the peaks of the edge region (A and B) is also strongly influenced by the first shell of oxygens around the absorber (Fe). The continuous intensity changes of A and B, in the case of orthopyroxene structure, can be related to both the variable chemistry along the EN-FS join but also to the distribution of Fe (and Mg) in the two octahedral sites, as already evidenced on natural orthopyroxenes (Paris et al., 1994). When plotting the intensity ratio I_B/I_A versus En content of the samples we obtain a linear relationship (R=99.2%) demonstrating the direct correlation between the chemistry and this part of the XANES spectrum (Fig. 2). Fig. 2 also reports the correlation between the intensity ratio I_B/I_A and the occupancy for the two individual octahedral sites M1 and M2, as determined by X-ray diffraction Rietveld refinement. The data show that Fe located in M1 and in M2 contributes in a different way to the XANES spectrum, showing a diversion from linearity with opposite slopes as a function of En content of the sample**.**

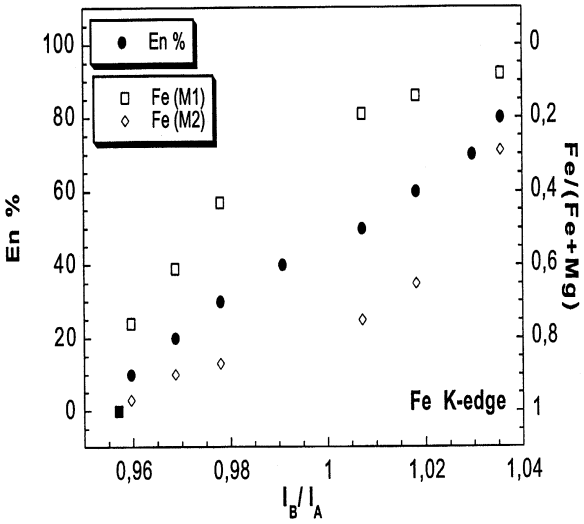

Figure 2
Correlation between Enstatite content (En%) and peaks B and A intensities ratio (I_B/I_A) in the spectra at the Fe edge, showing a linear behaviour.

Figure 1 shows that from the comparison with the theoretical spectra, calculated for the same three compositions all the spectral features in the experimental spectra have been reproduced, both in energy position and intensity. In particular, the intensities of the peaks A and B correspond to those found in the experimental spectra. In fact, the intensity ratio I_B/I_A, as obtained with the calculations, is comparable with the experimentally determined values (FS_{100}0.93-0.96; $EN_{50}FS_{50}$ 1.01-1.01; $EN_{80}FS_{20}$ 1.07-1.04), although the comparison is best for the intermediate compositions. The total theoretical spectra were obtained for all compositions using a cluster of 92 atoms, corresponding to about 6 Å from the absorber and the Hedin-Lundquist potential. More details on the theoretical calculations can be found in the references cited in the text. The absorber, Fe in this case, has been located in the two octahedral sites, M1 and M2, and the individual contributions have been weighted using the occupancy data obtained by X-ray diffraction. Figure 3 shows that in all cases the contributions coming from M1 site differ greatly from those relative to the M2 site, the M1 site being more regular than M2 and different in size and symmetry, but both showing peaks in the position of A and B, as in the experimental spectra. This means that when summing the partial contributions, according to the occupancies obtained by XRD, in the total spectrum the intensities of peaks A and B will be affected both by Fe in M1 and Fe in M2. On the other hand, the different shape of the M1 and M2 partial spectra demonstrate that the identification of the site localization of a diluted element in a structure is straightforward. Even in presence of other interfering elements, the peculiar characteristic of XAS spectroscopy especially when combined with theoretical calculations allows to discriminate between elements with similar atomic number, (contrary to XRD) or distinguish between similar sites.

To better understand the effects of site occcupancy to the spectra we simulated a variable Fe content in M2 by using the $EN_{80}FS_{20}$ theoretical spectrum and calculating the total spectrum by weighting the M2 contribution with amounts of iron from 0 to 100% of the available iron for this composition. This procedure does not take into account the actual occupancy values for this sample (Fe in M1=0.08 and M2 = 0.20) which is artificially modified to understand how the spectrum is affected by site occupancy, leaving the rest of the structure unaltered. The plot in Fig. 4 shows that the peak intensity strongly varies with occupancy, even reversing the intensity of peaks A and B for the compositions of the end-members of the series. This gives a clear indication of the strong effect produced by the site occupancy and reproduces theoretically the results obtained by Paris & Tyson (Paris et al., 1994). The inset in Fig. 4 shows the comparison between the experimental (XRD+XANES) and the theoretical (XANES) data: the agreement is satisfactory and allows to determine the difference in site occupancy (Fe M2/Fetot) as obtained by XRD and by the theoretical XANES (±7%). The results obtained here are important because in the Paris & Tyson's paper the use of only one natural sample disordered at different temperatures, although giving indications of the relation

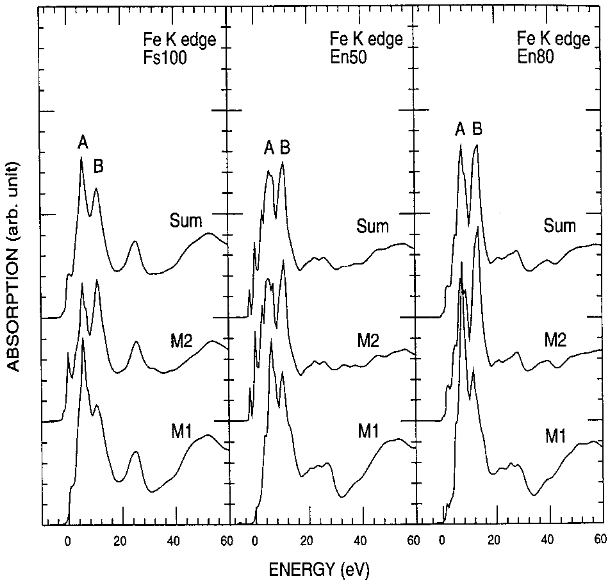

Figure 3
Theoretical spectra at the Fe edge, showing the partial contribution coming from the two octahedral sites, M1 and M2.

between chemistry and XANES peak intensity, could still have arisen doubts on the validity of this correlation. The advances in theoretical studies made it possible to use more detailed versions of the CONTINUUM code, which allowed the utilization of larger cluster and a better reproduction of the experimental spectra.

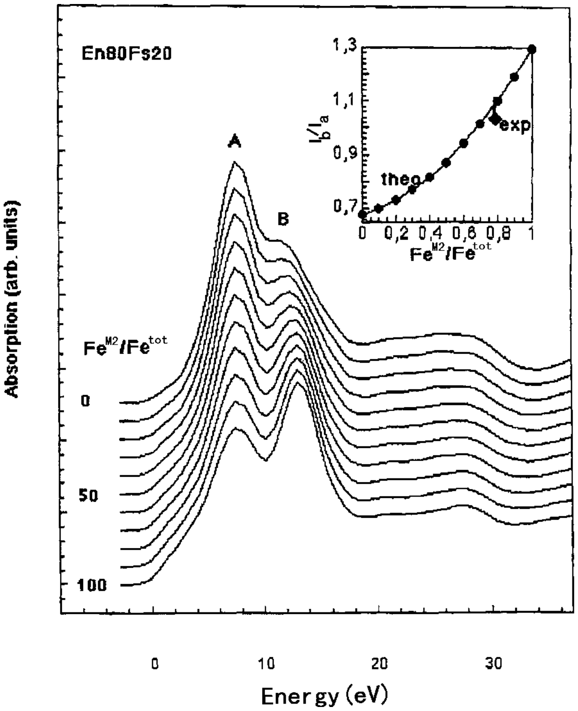

Figure 4
Variation of the spectral features in the theoretical spectrum $En_{80}Fs_{20}$ (at the Fe edge) obtained by changing the value of Fe_{M2}/Fe_{total}. The inset shows how the ratio I_B/I_A for the same composition changes accordingly. The experimental value is shown (diamond).

4. Mg K-edge XANES spectra

The experimental XANES spectra at the Mg K-edge for two OPX compositions ($EN_{20}FS_{80}$ and $EN_{80}FS_{20}$) are shown in Fig.5, arranged from left to right in order of decreasing En content. They are mainly composed of a pre-edge peak (P), three narrow peaks (A, B and C) at the absorption maximum, and a broad peak D. In analogy with the Fe K-edge spectra, also here some variations are evident along the join, in particular the intensities of peak P and peaks A and B increase with Mg content. The same procedure used for the spectra at the Fe K-edge has been used here for the Mg spectra, evaluating how the peaks intensity vary as a function of Mg content of the samples. The intensity ratio I_B/I_A vary with the Mg content but the small number of data and the minor quality of the low-Mg spectra make this correlation not as good as in the iron case.

The same procedure used for the calculations at the Fe edge was used also for calculating the spectra at the Mg K-edge. The partial spectra of the octahedral sites M1 and M2 are again very different one from the other and the total spectrum was obtained by summing the partial contributions weighted for the XRD occupancy data of the samples.

Note that the spectra have not been convoluted to account for the core hole lifetime because at Mg edge its value is comparable with the energy step. In spite of this, the comparison with the experimental spectra is satisfying both in terms of peak positions and intensities.

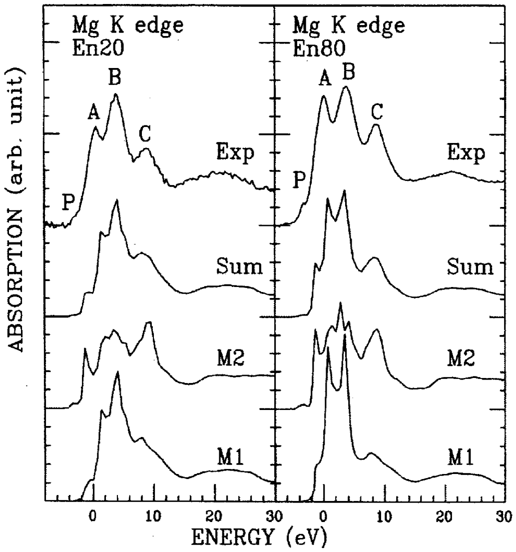

Figure 5
Experimental and theoretical XANES spectra at the Mg K-edge for two orthopyroxenes in the join $Fe_2Si_2O_6$-$Mg_2Si_2O_6$ (enstatite-ferrosilite), $En_{20}Fs_{80}$ and $En_{80}Fs_{20}$.

5. Conclusions

Experimental XANES data for a complete set of synthetic enstatite-ferrosilite orthopyroxene samples are presented in this paper. Variations in the XANES data at both Fe and Mg K-edges are explained using structural data and site occupancies obtained by X-ray diffraction. The experimental data show a clear dependence of the XANES structures on the chemical composition along the EN-FS join where the peak intensity ratio I_B/I_A varies linearly with the total En content, at iron edge. The occupancy XRD data for Fe in the M1 and M2 sites plotted versus the intensity ratio I_B/I_A show a non-linear dependence of the peak intensity on the distribution of iron between the two sites. This indicates different partial contributions of the two sites to the XANES spectrum. Theoretically calculated XANES have been used to evaluate in more detail the single site contributions and iron/magnesium site distribution in the orthopyroxene structure.

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