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Theoretical Analysis of X–Ray–Absorption Near–Edge Structure at the Mg K edge in forsterite, Mg_2SiO_4–*Pbnm*, Under Extreme Conditions

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Abstract

We calculated the Mg K edge X-ray absorption spectra of forsterite both for the $M1$ and $M2$ sites and for the overall edge by using the one-electron multiple-scattering theory. The validity of the theoretical model is well illustrated by comparison of calculations with experimental data at the Mg K edge of MgO (periclase). Based on these results, XAS experiments at the Mg K edge of forsterite are suggested, in as much as calculations performed up to 1020°C and 149 kbar indicate variation of fine structures in the multiple scattering region. We show for the first time that the information, which can be obtained by using this spectroscopy have implications on the structure of the Earth's upper mantle.

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1. Introduction

The structure and electronic properties of forsterite, Mg_2SiO_4-$Pbnm$, are of considerable interest both in geophysics and in crystal-chemistry. Forsterite is the Mg end-member and the structural prototype of the olivine solid-solution series, $\alpha - Mg_{2-x}Fe_xSiO_4$, one of the members of which (with $x \approx 0.1$) is the predominant phase throughout the Earth's upper mantle. Furthermore, forsterite is the precursor of two other polymorphic phases (wadsleyite, $\beta - (Mg, Fe)_2SiO_4$-$Imma$, with modified spinel structure: *Horiuchi and Sawamoto,* [1981]; and ringwoodite, $\gamma - (Mg, Fe)_2SiO_4$-$Fd3m$, with spinel structure: *Sasaki, Prewitt, Sato and Ito,* [1982]) which are believed to be stable deeper in the mantle across the 400 and 650 km seismic discontinuities (e.g. *Ringwood and Irifune,* [1988]; *Akaogi, Ito and Navrotsky,* [1989]; *Katsura and Ito,* [1989]; *Fei, Mao and Mysen,* [1991]; *Jeanloz,* [1991]).

It is well known that X-ray absorption near-edge structure (XANES) spectroscopy provides direct information on the structural arrangement around a selected atomic site. For olivines, theoretical analysis of XANES has not been carried out so far. We want to fill this gap by presenting a set of one-electron·multiple scattering calculations of XANES spectra of the Mg K edge in pure forsterite at ambient and under extreme P, T conditions. We will then turn to a similar study for olivines of greater geophysical significance, where Fe substitutes for Mg in the $M1$ and/or $M2$ site. As for the relevant measurements, they must be deferred to a later time: the Mg K edge can hardly be recorded with the set-ups presently available at synchrotron radiation sources. Furthermore X-ray absorption spectroscopy (XAS) measurements at high temperature and pressure can now be performed only at much higher energy than the Mg K edge.

2. Theoretical methods

The crystal structure of forsterite is long-since known, both on natural material [*Bragg and Brown,* 1926; *Birle, Gibbs, Moore and Smith,* 1968; *Fujino et al.,* 1981], and on synthetic

material of essentially pure composition [*Smyth and Hazen,* 1973]. Furthermore, *Smyth and Hazen* [1973], *Hazen* [1976] and *Takéuchi, Yamanaka, Haga and Hirano* [1984] carried out refinements of the forsterite crystal structure as a function of temperature up to 1020°C. Moreover *Hazen* [1976], *Hazen and Finger* [1980] and *Kudoh and Takéuchi* [1985] determined it as a function of pressure up to 149 kbar. The atomic coordinates given by these authors were the starting data we used to perform our calculations. Table 1 summarizes the different unit cells, average first shell Mg-O bond distances and P and T conditions used for calculations.

Our simulation of the XANES spectra is based on the one-electron multiple-scattering (MS) theory of *Lee and Pendry* [1975], and takes advantage of the refinements to the theory as well as to the computational methods progressively introduced by *Natoli et al.* [1980], *Durham et al.* [1982], *Natoli and Benfatto* [1986] and *Durham* [1988]. We use *Mattheiss* [1964] prescription to construct the cluster density and we obtain the Coulomb part of the potential by superposition of neutral atomic charge densities using *Clementi and Roetti* [1974] tables.

In order to simulate the charge relaxation around the core hole in the photoabsorber of atomic number Z (12 in the case of Mg), we use the well screened $Z+1$ approximation (final state rule) of *Lee and Beni* [1977]. This consists in taking the orbitals of the $Z+1$ atom and constructing the charge density by using the excited electronic configuration of the photoabsorber with the core electron promoted to a valence orbital. In metallic and (nearly) covalent systems, this method is known to provide quite reasonable approximation to the relaxed charge distributions. This is obtained by self-consistent calculations, at least within the muffin-tin (MT) model and for the purposes of calculating absorption spectra in the MS scheme. For more details, the reader is referred to the multichannel MS theory description of *Natoli et al.* [1990].

For the exchange-correlation part of the potential we use the energy- and position-dependent complex Hedin- Lundquist (H-L) self-energy $\Sigma(\vec{r}, E)$, as indicated by *Tyson, Hodgson, Natoli and Benfatto* [1992]. The imaginary part of H-L gives the amplitude at-

tenuation of the excited photoelectron due to inelastic losses, and takes automatically into account the photoelectron mean free path in the final state of the absorber. The calculated spectra are further convoluted with a Lorentzian shaped function with a full width Γ_h to account for the core hole lifetime, as given by *Krause and Oliver* [1979]. For the sake of the argument presented here, substantially similar results are obtained with a calculation using a X-α type of exchange followed by a Lorentzian convolution to account for inelastic losses of the photoelectron in the final state and the core hole width [*Penn,* 1987]. We have choosen the muffin-tin radii according to the criterion of *Norman* [1974], and allowed a 10% of overlap between contiguous spheres to simulate the atomic bond.

3. Results

The theoretical model has been tested to reproduce the available experimental data at the Mg K edge of MgO (periclase) [*Wong,* 1993] which has $Fm3m$ symmetry. Comparison of different cluster calculations for periclase in normal condition is illustrated in Fig.1. Good agreement is obtained for a cluster of 93 atoms around Mg. However, even better agreement with the experimental XANES spectrum of periclase is obtained when we calculate a cluster comprising more then 100 atoms, i.e. extending to 7 Å distance from the Mg absorber taken as origin.

The structure of forsterite comprises three independent sites: T, with coordination number (C.N.) 4 occupied by Si; $M1$, with C.N. 6 occupied by Mg, and $M2$, again occupied by Mg with C.N. 6. The two metallic sites differ in mean size (2.094 Å vs. 2.129 Å at room temperature, RT), but are substantially equivalent in shape. The actual point symmetry is $\bar{1}$ for $M1$ and m for $M2$ but the quadratic elongations (Q.E.: *Robinson, Gibbs and Ribbe,* [1971]) are nearly the same (1.0269 and 1.0260, respectively).

As a first step, we calculated the XANES spectra for each individual site via atomic clusters having increasing number of atoms till convergence. The convergent clusters include over 50 atoms within 5.03 Å from the Mg atom taken as the center and have the *Pbnm*

symmetry of forsterite as a whole. Larger clusters containing up to 89 atoms do not show any significant differences in the MS region as shown by (d) curves in Fig.2. Our first-shell spectra for the $M1$ and $M2$ sites, as reported by curves (a) in Fig.2, are almost identical to the spectrum calculated for periclase (see Fig. 1). With increasing size of both clusters built around the $M1$ and $M2$ sites, definite differences arise between the calculated spectra of the two clusters which depend both on the average lenghts of their bonds, and on their individual point symmetries. Such differences are not to be seen at the edge itself (where calculation certainly gives abrupt swings due to the muffin-tin effect problem) as in the MS region (in this system located between 10 and 40 eV). The convergent $M1$ cluster spectrum has ripples that are more sharply defined than the $M2$ cluster spectrum, besides being shifted to higher energies ($\approx$ 3 eV).

Actually, an experimental Mg K edge XANES spectrum of forsterite would consist in the superimposed contributions of all the Mg atoms present in the structure, i.e. of both clusters. Consequently, we performed a weighted combination of the calculated Mg-$M1$ and Mg-$M2$ cluster spectra in the 1:1 proportion, as in the forsterite stoichiometry. The final results are shown in Fig.2, right panel; the curve (d) is the spectrum that shall be compared with the experimental Mg K edge XANES spectrum of forsterite at room temperature, when it will become available.

We then calculated the spectra to be expected for forsterite when submitted to extreme conditions, namely at high temperature (1020°C, from the in situ crystal structure determinations of *Hazen* [1976]), and at high pressure (at 50 kbar from the structure determinations of *Hazen* [1976], and at 149 kbar from the data of *Kudoh and Takéuchi* [1985]). It appears that a temperature increase of ~1000°C reflects onto the spectrum only in the MS region i.e. 40 eV above the edge (Fig. 3). There is a shift with respect to RT forsterite of $\approx$ 3 eV, that could be easily detected with standard experimental resolution at this energy. Moreover, it is important to underline that the changes in the spectra depend mainly on the contribution of the $M2$ site, because the $M1$ cluster spectrum calculated at 1020°C is almost identical to the RT spectrum (Fig. 3).

As for the effect of pressure, it is just as significant on the calculated spectra as is the temperature effect, but on the opposite direction: the ripples in the MS region are shifted by $\approx$ 3 eV while the whole spectrum becomes better defined and sharper than it is at room conditions (Fig. 4). However changes of the MS structures are now due also to minor contributions coming from $M1$ site as well. This behaviour is consistent with *Natoli*'s energy shift - bond distance rule [*Bianconi et al.*, 1983]. The validity of the rule is verified by our calculations both at HP (= contraction) and HT (= expansion), and holds as long as the variation of the bond lenght does not modify the atomic potential. Indeed we show that the constrained site $M1$ is unaffected while the unconstrained site $M2$ is affected on a local scale by the variation of P and T conditions. Therefore XANES is a local probe that should be used to check HT-HP structural modifications, in connection with X-ray diffraction studies which reveal the average structural changes on a much longer scale.

4. Conclusions

The main results of our study are:

1. Calculations performed using the present set of computer programs based on the one-electron multiple-scattering theory result into computed XANES spectra that reproduce quite well the experimental ones, when these are available as it is the case of MgO-$Fm3m$ (periclase).
2. The calculated Mg K edge XANES spectrum of forsterite is the averaged sum of two contributions: one from the $M1$ site and the other from the $M2$ site.
3. Calculated spectra corresponding to high temperature conditions indicate that shifts up to $\approx$ 3 eV towards low energy occur. They would easily be detected in the experimental spectra if or when it will be possible to perform in situ measurements at the Mg K edge.
4. Calculated spectra at high pressure conditions indicate similar significant shifts, but in the opposite energy direction ($\approx$ +3 eV).

Consequently, variations in structural properties at high P and T such as those occurring

in forsterite can be studied by this method; conversely, pure forsterite appears to be a promising phase to be studied in situ at HP and HT. However, this indication needs to be verified by investigating the changes intervening in the spectra when Fe is partly substituted for Mg since this stoichiometry is closer to the composition of the olivine constituent of the upper mantle. Actually, Fe K edge can be measured at synchrotron radiation sources under extreme conditions whereas XAS experiments at Mg K edge are extremely difficult to perform. Furthermore, given the high-field strength character of Fe, the XANES spectra may undergo changes that would make in situ XAS measurements at high pressure and temperature a promising project to better understanding the crystal-chemistry of olivines and the geophysical characters of the mantle of the Earth.

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TABLES

Table 1. Crystal structure parameters and bond distances of Mg_2SiO_4 – $Pbnm$

Sample	1[a]	2[b]	3[b]	4[c]
a($\AA$)	4.7535	4.7977	4.7125	4.6519
b($\AA$)	10.1943	10.3520	9.9710	9.7701
c($\AA$)	5.9807	6.0588	5.9556	5.7441
T(°C)	23	1020	23	23
P(kbar)	0.001	0.001	50	149
$\langle M1\text{-O}\rangle$	2.0938	2.1188	2.0595	2.0521
$\langle M2\text{-O}\rangle$	2.1314	2.2003	2.1094	2.0504
Q.E.($M1$)	1.0001	1.0005	1.0002	1.0005
Q.E.($M2$)	1.0011	1.0018	1.0038	1.0010

[a]Fujino et al., 1981.

[b]Hazen, 1976.

[c]Kudoh and Takéuchi, 1985.

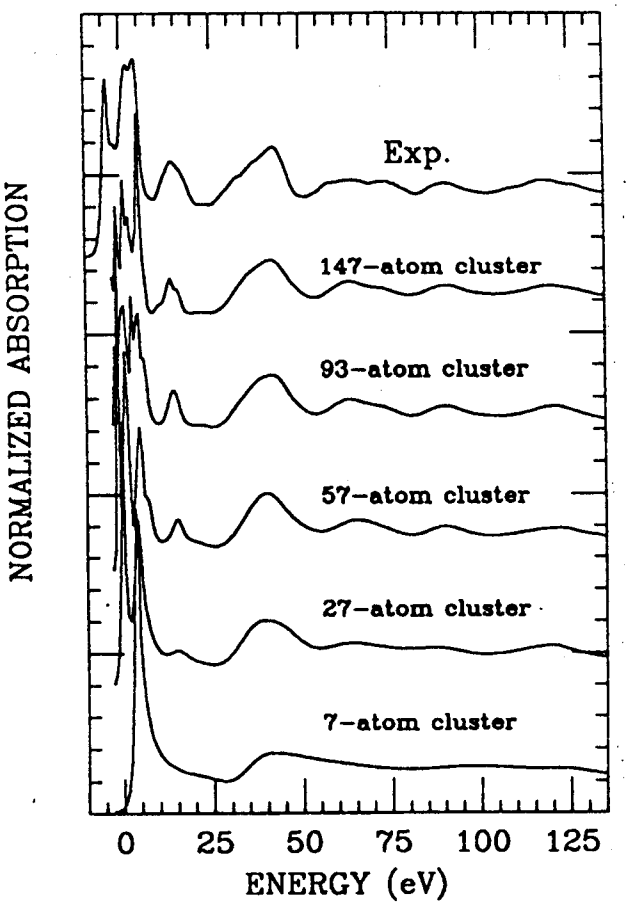

Fig. 1. Mg K edge in MgO (periclase). The top curve is the experimental curve [*Wong,* 1993]. From bottom to top follow the calculated clusters with 7, 27, 57, 93 and 147 atoms, respectively, around the photoabsorber. Good agreement is obtained for both last two clusters.

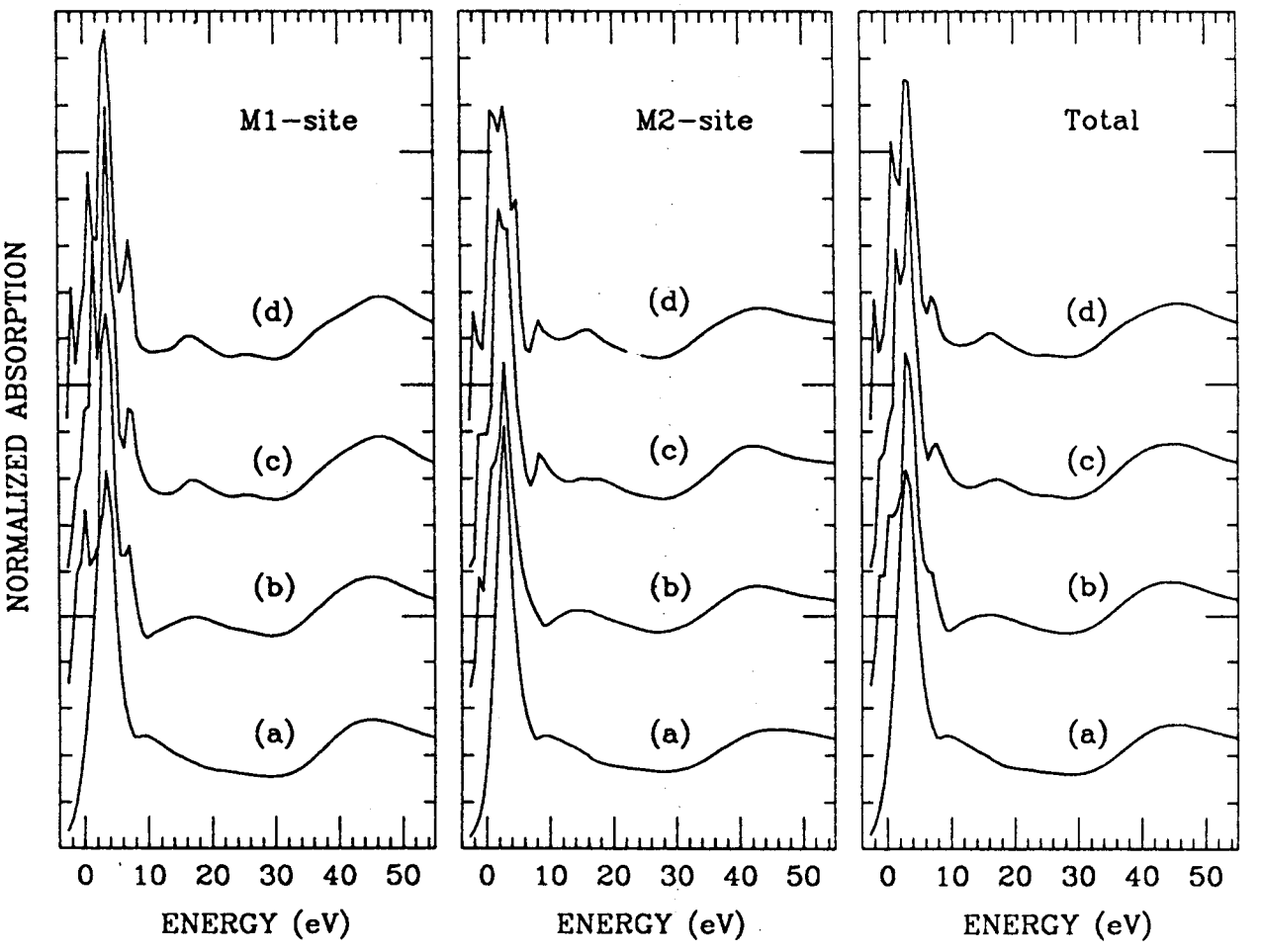

Fig. 2. Mg K edge XANES calculation for forsterite at ambient conditions for the $M1$-site cluster (left panel), the $M2$-site cluster (central panel) and the sum of the two contributions (right panel) (see text for details). Curves (a), (b), (c), (d) refer to cluster calculations with increasing number of atoms: 14, 31, 55, 89, respectively, around the central photoabsorbing Mg.

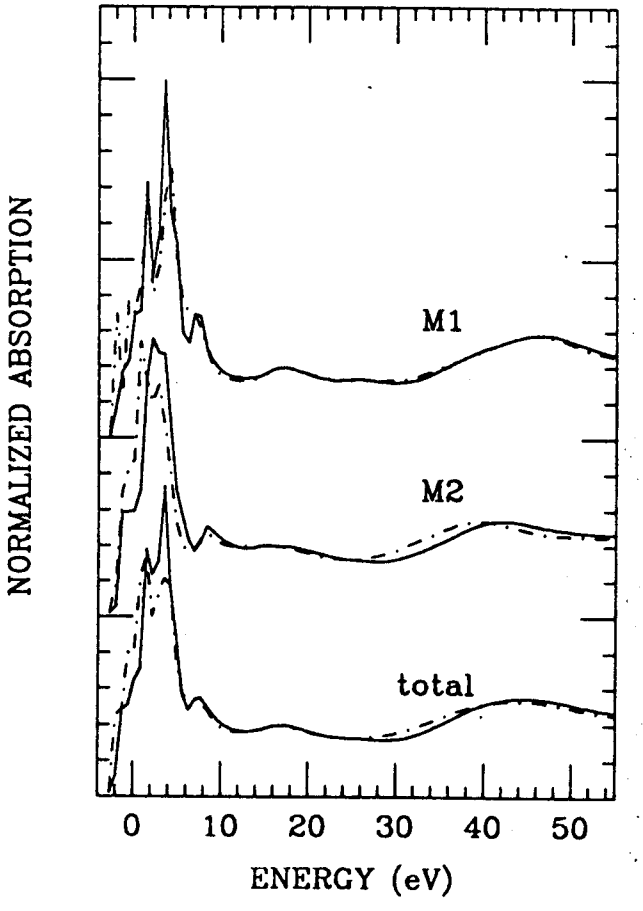

Fig. 3. Comparison of calculated Mg K edge XANES for the forsterite structure at 1020°C (dot dash line) and the forsterite structure at RT (solid line). Upper curves are the $M1$ site contribution calculations as in the text, the middle ones refer to the $M2$ contribution. The bottom curves represent the sum of the above contributions. The dependence on T of the total contribution to the cross section is mainly due to the $M2$ site contribution.

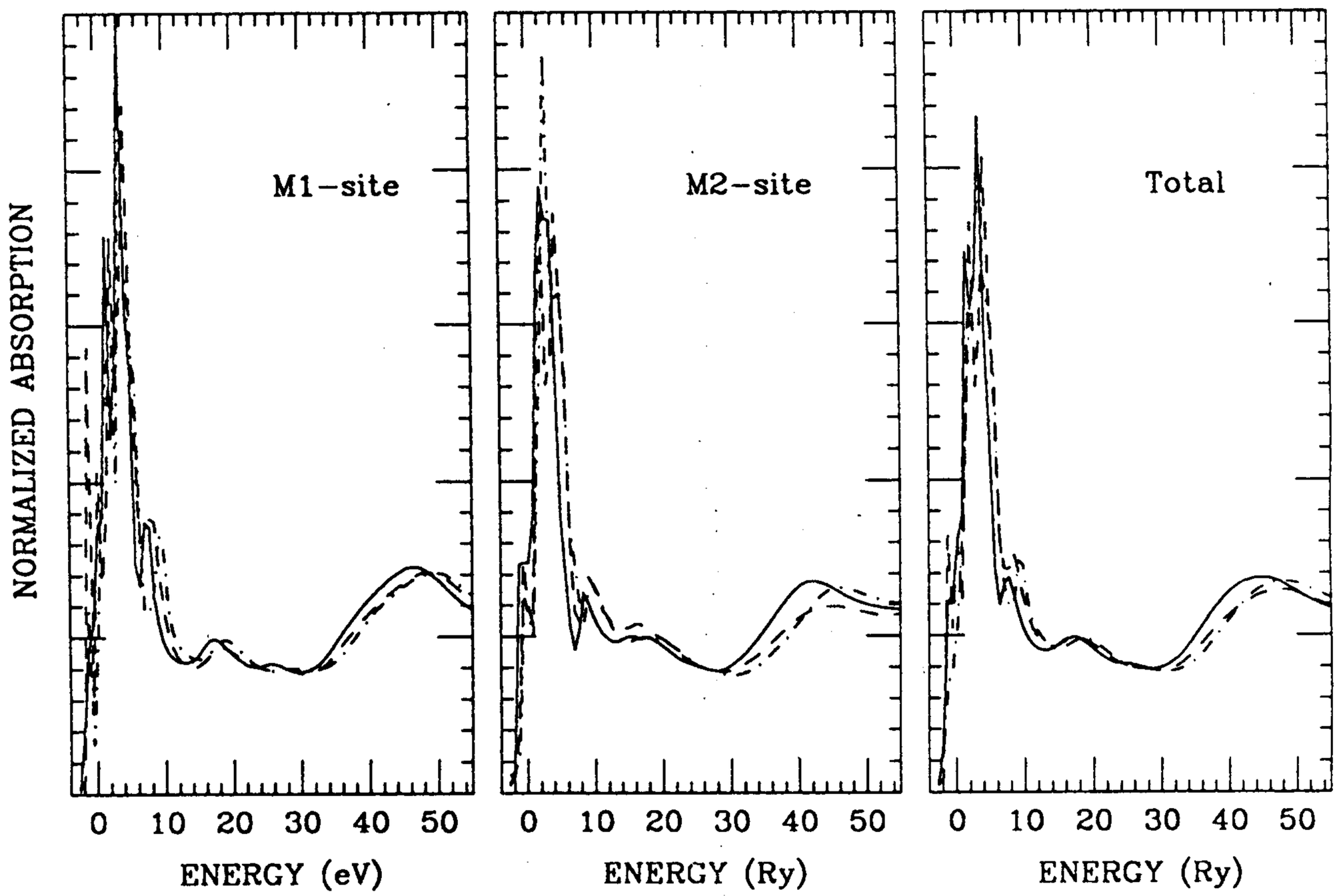

Fig. 4. Comparison among Mg K edge XANES calculations for forsterite at ambient conditions (solid line), 50 kbar (dash) and 149 kbar (dot dash). The dependence on P of the total contribution to the cross section (right panel) is evident in the sum. Again it is mainly due to the $M2$ site contribution (central panel), but some differences are also coming from the $M1$ site contribution (left panel).