Na K-edge XANES spectra of minerals and glasses

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Abstract: Na K-edge X ray absorption near-edge structure (XANES) spectra for minerals and glasses were collected using synchrotron radiation. Na-K XANES is a good structural probe to determine the coordination state of this element in important minerals and glasses. From the XANES spectra on crystalline reference phases with different chemical environment, information can be obtained and compared with the structure of the minerals and glasses. The different classes of studied minerals correspond to distinct Na K-edge spectra which have been examined. The XANES spectra for the crystalline references are used as fingerprint to interpret those obtained on silicate and borate glasses. Experimental spectra for jadeite and carnegieite crystals can be satisfactorily reproduced by theoretical calculations using the Full Multiple Scattering formalism.

Key-words: sodium, minerals, glass, XANES.

1. Introduction

Sodium is one of the eight most common elements in the Earth's Crust and has a major structural role in minerals and glassy materials. The structural coordination of Na is not always well-established since Na is easily subject to diffusion and therefore change in its environment. The first coordination shell is often a continuous distribution of Na-O distances so that a distinct coordination number is somewhat difficult to establish. Moreover, Na-bearing minerals are often hygroscopic which modifies the Na surroundings. X-ray absorption spectroscopy (XAS) is a chemically selective method that can be used to investigate both the local and medium range environment around one specific element in complex materials. The XAS technique has been widely used to study disordered materials where traditional X-ray or neutron diffraction are unable to resolve the structure due to the lack of periodicity (Brown *et al.*, 1995). In the XAS spectra, the X-ray Absorption Near-Edge Structure (XANES) region is of particular interest since this part is highly sensitive to the symmetry and the medium range order around the absorbing atom. However, the interpretation of XANES spectra is difficult because in this region multiple scattering effects take place and *ab initio* theoretical calculations are required. A way of interpreting the XANES spectra for complex or disordered materials is through a comparison with spectra from reference compounds.

Very few studies have been reported on the Na K-edge XANES in crystalline materials where the absorption K-edge lies at low energy (1070 eV). Silicate minerals (albite, jadeite, nepheline) were earlier studied (McKeown *et al.*, 1985) but on a limited energy range and with poor resolution. In contrast, Na-halides and Na-carbonates have been widely investigated (Yamashita *et al.*, 1991; Hudson *et al.*, 1994; Riedler *et al.*, 2001; Teodorescu *et al.*, 2001) since these compounds are good test cases for multiple scattering calculations.

In this paper, we present several results on the Na K-edge for a range of crystalline minerals. This study allows a better understanding of the sensitivity of the XANES spectra to structural differences in the local and medium range environment around Na atoms. The different classes of minerals studied correspond to distinct Na K-edge spectra which have been examined qualitatively and related to different Na environments and different structure types. The XANES spectra for silicate and borate glasses are presented and analyzed by comparison with the crystalline references. Theoretical calculations were carried out and showed good agreement with experimental data for jadeite and carnegieite crystals.

2. Experimental methods

Starting materials: Mineral samples were obtained from the Collection de Minéralogie (University of Paris VI). The

Table 1. Chemical analysis in weight %. Values in parenthesis are for atom.

Sample	SiO$_2$	Al$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O	FeO	MnO	TiO$_2$	B$_2$O$_3$	F	Cl	H$_2$O	CO$_2$	SO$_4$
Cryolite		(12.7)			(33.87)						(53.33)				
Villaumite					(54.7)						(45.2)				
Halite					(42.3)							(57.1)			
Natron					39.86								20.28	37.16	
Jadeite	68.64	19.02			11.54										
Aegyrine	53.63	13.59		5.22	2.22	10.89	6.02	1.65	1.99						
Acmite	52.62	28.03	0.02	3.38	3.80	8.53	3.74	0.10	0.25						
Riebeckite	47.66			1.21	6.23		39.76						2.17		
Arfvedsonite	47.10	2.05	1.60	0.03	7.39	1.85	35.13	0.57	0.42				4.36		
Sodalite	35.01	28.70			23.32								12.86		
Hauyne	33.92	28.26	7.85	0.02	16.32	0.41	0.01	0.01	0.02			6.40			6.46
Labradorite	57.39	25.68	3.91		10.42	5.22									
Albite	68.93	19.91	0.14		11.30	0.12									
Nepheline	37.35	31.95			24.82										
Carnegieite	42.21	35.71			21.74										
Heulandite	58.16	14.00	4.97		1.79	0.67							15.98		
Analcime	45.49	22.13			13.03								8.60		
Ulexite			6.20		15.31					46.34			29.93		
Borax					21.73					46.36			29.65		

samples were characterized by microprobe analysis with a Camebax SX50 or by wet analysis (CRPG-CNRS), powder X-ray diffraction and Raman spectroscopy. We used a carnegieite sample that was synthesized at 1650 K and previously characterized by Richet *et al.* (1990). The chemical compositions of the minerals are reported in Table 1.

Glasses with the composition NaAlSi$_3$O$_8$ (albite), NaAlSi$_2$O$_6$ (jadeite), NaAlSiO$_4$ (nepheline) were synthesized from a mixture of reagent grade SiO$_2$, Al$_2$O$_3$ and Na$_2$CO$_3$ powders. After a decarbonatation step of 25 hours at 900 °C, the mixture was melted in a Pt crucible for one hour at 1550 °C. The liquid was quenched by immersion of the bottom of the crucible in water. This procedure was repeated three times to ensure glass homogeneity. Microprobe analysis indicates no deviation from the nominal composition (Neuville & Mysen, 1996). Three borate glasses of composition xNa$_2$O (1-x)B$_2$O$_3$, with x=10, 20 and 30, were prepared by melting reagent grade sodium carbonate (Na$_2$CO$_3$,) and boric acid (H3BO$_2$). After decarbonatation at 750 °C, the compositions were melted in platinum crucibles at 1100 °C over 4 hours to avoid alkali losses. The glasses were quenched by pouring onto a Cu-metallic plate and were not annealed. Glasses were kept in vaseline oil to prevent glass hydration. All glass compositions were analyzed by wet analysis and no deviation from the nominal composition was observed.

XANES spectra: Na K-edge (1070 eV) absorption spectra were collected at room temperature on the SA32 beamline at the Super-ACO storage ring (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Orsay, France) operating at 800 MeV and 200 mA current. A beryl (10$\underline{1}$0) double-crystal monochromator was used, with a resolution of about 0.5 eV. The samples were ground in air into powder and uniformly spread on graphite tape. The Na K-edge spectra were recorded over the photon energy range 1065-1165 eV, with 0.1 eV step and 1 s integration time using the total yield detection mode by measuring the drain current of the sample. Total electron yield is a technique very sensitive

to the surface of the sample and the sodium environment may be affected in some hygrosocopic glasses (*e.g.*, sodium silicate glasses, D. Cabaret, personal communication). However, no surface modifications are expected for the studied samples and, indeed, comparison with previous results shows a very good agreement, including samples prepared under vacuum conditions (*e.g.*, NaF in Kikas *et al.*, 2001). Spectra were calibrated using the inflection point of the L$_{III}$ absorption edge of Ge (1217 eV) and energy calibration was periodically checked during the measurements. A Victoreen pre-edge was removed for each spectra and the data were normalized.

Theoretical calculations: Theoretical multiple-scattering calculations of the XANES spectra were carried out using the *ab initio* FEFF8 code (Rehr & Albers, 2000). Several parameters of the code were varied to analyze their influence on the theoretical spectra for jadeite and carnegieite crystals.

3. Results

The Na K-edge XANES spectra can be divided into different groups according to the class of the minerals.

Halides and carbonates

Fig. 1 shows Na K-edge spectra for Na-halides, Na-chlorate and Na-carbonates. The spectrum of NaCl (halite) agrees well with previously measured data (Kasrai *et al.*, 1991). The labelling of the peaks is taken from this reference and the peak positions (Table 2) have been obtained through the first derivative. The NaF (villaumite) and NaCl (halite) XANES spectra present sharp features whose origins have been carefully investigated (Kikas *et al.*, 2001; Prado & Flank, 2004), and are due to the high symmetry of the close packed B1 structure type. These spectra represent good test cases to
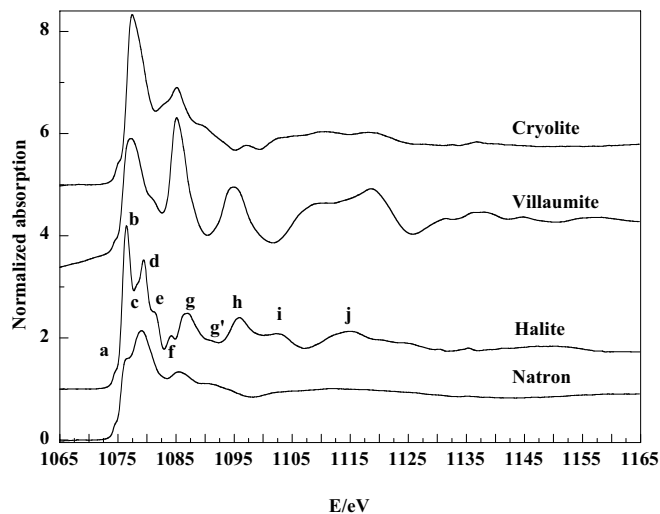
Fig. 1. Na K-edge XANES spectra of various Na-halides and carbonates.

Fig. 2. Na K-edge XANES spectra of various pyroxene minerals.

apply multiple scattering calculations and good agreement is obtained between experimental and calculated data (Gunnella *et al.*, 1990; Hudson *et al.*, 1994; Prado & Flank, 2004). These studies have evidenced the influence of multiple scattering effects and the contribution from scatters above 7 Å from the absorber in the XANES spectra.

The natron ($Na_2CO_3.10H_2O$) XANES spectrum is similar to previously published data (Yamashita *et al.*, 1991). The main peak is at 1079.06 eV with a shoulder at 1076.68 eV. A small pre-peak is also clearly apparent at 1074.42 eV.

This weak pre-edge at about 1074.4 eV (peak *a*) is present on some samples as a bump on the rising slope of the first feature and was ascribed to 1s->3s transition (Teodorescu *et al.*, 2001). This transition is parity forbidden in a free ion and not observed in the XANES spectrum of atomic sodium. The sharp peaks close to the threshold are attributed to core-level excitons, *i.e.*, an excitation of a core-level electron into an unoccupied bound state. The first sharp feature in the absorption spectra, peak *b*, can be associated with a localized transition from the 1s core level to the 3p state of Na^+ (Teodorescu *et al.*, 2001; Murata *et al.*, 1988; Riedler *et al.*, 2001). Although the detailed interpretation of some peaks energetically close to the strong peak *b* is under discussion, there is a consensus that broad peaks above 1090 eV are due to single or multiple photoelectron scattering resonances.

Pyroxene minerals

The Na XANES spectra for jadeite, aegyrine and acmite crystals are shown in Fig. 2. These three samples have a similar composition but jadeite is a pure aluminosilicate while a substitution of Al by Fe exists in aegyrine and acmite. The XANES spectrum of jadeite agrees with previously published results (Mottana *et al.*, 1997). The same peaks are observed at 1077.8, 1082.3, 1088.4 and 1113.8 eV. Three weak oscillations are observed between 1088 and 1113 eV: they are above the background level and should correspond to multiple scattering effects (Mottana *et al.*, 1997). The acmite and aegyrine XANES spectra have peaks at the same po-
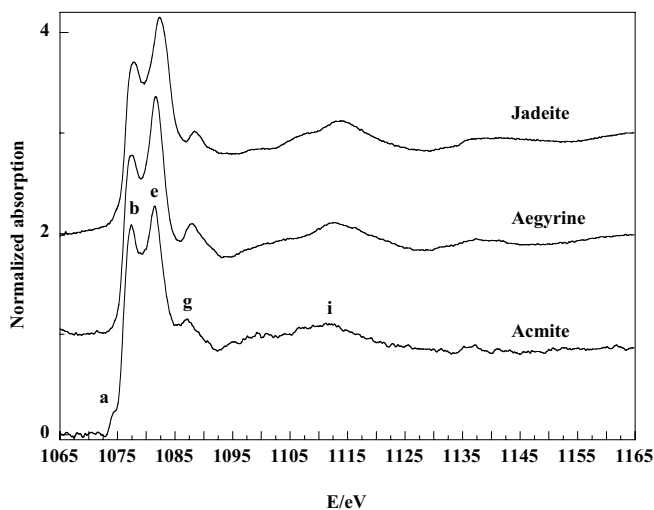
sition as that of the jadeite spectrum but with some variations in their relative intensities and widths, which are likely related to differences in composition (substitution Al/Fe). Peaks *e* and *g* in the aegyrine spectrum are more intense and sharper compared to the jadeite features, while the reverse is observed in the acmite spectrum and finally the position of peak *e* shifts to high energy in jadeite compared to aegyrine.

In jadeite, Na is in an octahedral site with 6 oxygens at a mean Na-O distance of 2.391 Å and two farther oxygen neighbours at 2.803 Å. The chain structure of the $(Si,Al)O_4$ tetrahedra presents similarities with amphibole minerals, which is reflected by the great similarities of the XANES spectra (Fig. 3).

Amphibole minerals

Arfvedsonite (Hawthorne, 1976) and riebeckite (Hawthorne, 1978) are two *C*2/*m* sodo-iron amphiboles that have similar double-chain silicate structures. Due to a lower Na content, the XANES spectrum of riebeckite has a lower signal to noise ratio compared to that of arfvedsonite (Fig. 3). In particular the small bump at 1074.4 eV in the arfvedsonite spectra cannot be resolved for riebeckite. Yet, the two spectra show similar peaks at 1077.5, 1081.6 and 1087.4 eV. Though located at the same position, the contributions *b*, *e* and *g* have different intensities with wider peak widths in the case of arfvedsonite. Two broad features at 1101.5 and 1112 eV are also apparent. Apart from differences in intensities and, especially, a more intense *g* peak, the XANES spectra of amphiboles are similar to those obtained for pyroxene (Fig. 2). In these amphiboles, the FeO content is important compared to the pyroxenes that contain Al_2O_3 and this could be the reason for the differences in the XANES spectra because Fe atoms have a scattering amplitude that is more important than Al atoms.

In riebeckite, Na atoms are mainly present in M4-sites that correspond to six oxygen neighbours with a mean Na-O distance of 2.431 Å (2.469 Å for arfvedsonite) and two further oxygen neighbours at 2.906 Å (2.937 Å for arfvedsoni-

Fig. 3. Na K-edge XANES spectra of various amphibole minerals.
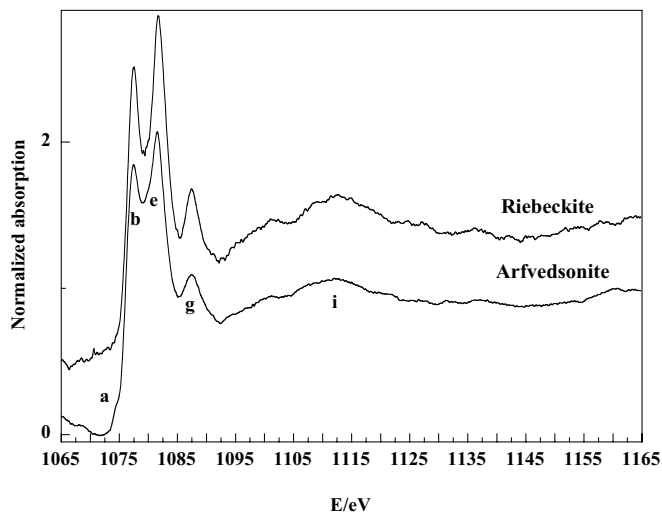

Fig. 4. Na K-edge XANES spectra of various feldspath minerals.

te). This site is similar to that found in jadeite, in line with the similarity between the spectra. Excess Na can also be found in a large cavity (A-site) surrounded by an irregular shell of 12 bridging anions with mean distances of 2.812 Å (2.862 Å for arfvedsonite). This A-site is positionally disordered and the wider features of the XANES spectrum of arfvedsonite may reflect higher amount of Na in A-sites than for riebeckite.

Feldspars and tecto-silicates or similar minerals

Much more diversity is observed in the XANES spectra of feldspar structures and other silicate minerals (Fig. 4). The major features are the b and e peaks at 1076.8-1077.9 eV and 1081.3-1082 eV, which present different relative intensity and broadening for the various feldspars.
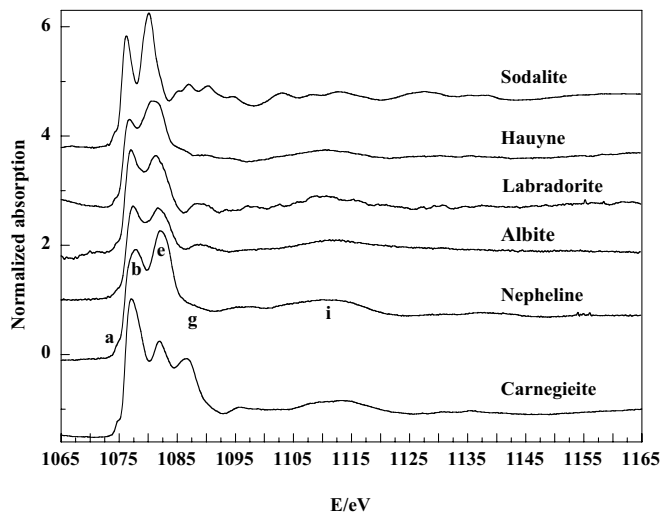
Sodalite is a lattice structure of SiO_4 and AlO_4 tetrahedra with voids occupied by sodium and chlorine ions (Pauling, 1930). Na is in a tetrahedral site surrounded by three O at 2.398 Å and one Cl at 2.701 Å in a trigonal pyramid. This could be the reason peaks b and e appear at about 2 eV below those for the other framework compounds (Table 2). A similar trend is observed for hauyne where Na is surrounded by $(3O+1SO_4)$ neighbours (Löhn & Schulz, 1968). Labradorite contains Na in 6-7-fold coordinated sites and its XANES spectrum has peaks a and b at intermediate energies between sodalite-hauyne and the other framework silicates. These two contributions a and b could thus be regarded as a good indication of the local ordering around Na.

The high symmetry of the sodalite structure (cubic system) can be observed in the well resolved separation between peaks b and e and the number of contributions above 1080 eV. In hauyne (Löhn & Schulz, 1968), the substituted

Table 2. Names, chemical formulae and coordination numbers of sodium containing minerals studied in this work.

Mineral name	Formula	CN and ligand	Reference
Cryolite	Na_3AlF_6	6–8 F	
Villaumite	NaF	6 F	
Halite	NaCl	6 Cl	
Natron	$Na_2CO_3.10H_2O$	6 O of water molecules	Taga (1969)
Jadeite	$NaAlSi_2O_6$	6 O (+ 2 O)	Cameron et al. (1973)
Aegyrine	$NaFeSi_2O_6$	6 O (+ 2 O)	
Acmite	$NaFeSi_2O_6$	6 O (+ 2 O)	Cameron et al. (1973)
Riebeckite	$Na_2(Fe^{2+},Mg)_3(Fe^{3+})_2Si_8O_{18}(OH)_4$	8 O	Hawthorne (1978)
Arfvedsonite	$Na_3(Fe^{2+},Mg)(Fe^{3+},Al)Si_8O_{22}(OH)_2$	8 O	Hawthorne (1976)
Sodalite	$Na_4Si_3Al_3O_{12}Cl$	3 O and 1 Cl	Pauling (1930)
Nepheline	$(Na,K)AlSiO_4$	6 O (+ 2 O)	Henderson & Roux (1977); Gregorkiewitz (1984)
Labradorite	$(Ca,Na)(Si,Al)_4O_8$	6-7 O	Wenk et al. (1980)
Hauyne	$(Na,Ca)_4Si_3Al_3O_{12}(SO_4)$	3 O and 1 SO_4	Löhn & Schulz (1968)
Albite	$NaAlSi_3O_8$	5 O (+ 2 O)	Prewitt et al. (1976)
Carnegieite	$NaAlSiO_4$	4 O (+ 2 O)	Withers & Thompson (1993)
Heulandite	$(Ca,Na_4)Al_2Si_7O_{18}.6H_2O$	3 O and 5 H_2O	Merkle & Slaughter (1968)
Analcime	$NaAlSi_2O_6.H_2O$	4 O and 2 H_2O	Mazzi & Galli (1978)
Ulexite	$NaCaB_5O_6(OH)_6.5H_2O$	6 H_2O	Ghose et al. (1978)
Borax	$Na_2B4O_5(OH)_4.8H_2O$	4 H_2O and 2 OH	Levy & Lisensky (1978)

group SO$_4$ is much larger than Cl, and this distorts the lattice. The close Na environment corresponds to 3 O at 2.632 Å and 1 oxygen from SO$_4$ at 2.340 Å, but the presence of more distant oxygen atoms at 2.942 Å and 2.760 Å indicates a more distorted Na environment in hauyne than in sodalite. This is indeed observed as a broadening of peaks *b* and *e* in the XANES spectra.

The XANES spectra of nepheline and albite show a very good signal to noise ratio compared to previously published data (McKeown *et al.*, 1985). Both XANES spectra exhibit similarities with the spectrum of jadeite. However, the most intense peak in the nepheline spectrum is peak *e* as in the jadeite spectrum while peak *b* is the most intense in albite. The labradorite spectrum, which differs from albite by only few % of CaO in the chemical composition, is very similar to that of albite (*cf.* Table 1). The coordination of Na in albite, nepheline and jadeite is 5-8 oxygen neighbours with a wide range of Na-O distances between 2.35 and 3.15 Å. However, the Na environment in nepheline and in jadeite is more ordered than in albite which explains the more intense and well defined structures *b* and *e*.

The Na XANES spectrum of carnegieite differs from all others minerals, with three intense peaks at 1077.08 (peak *b*), 1081.97 (peak *e*) and 1086.63 eV (peak *g*) and a well defined pre-peak at 1074.65 eV. In this structure, Na is surrounded by 4 oxygens with a mean Na-O distance of 2.426 Å with further 2 oxygens at 2.85-2.95 Å (Withers & Thompson, 1993). The high symmetry of the carnegieite structure (cubic) is likely responsible for the intense features resulting from multiple scattering processes.

Zeolites

XANES spectra for two hydrated zeolites, heulandite and analcime, are presented in Fig. 5. It should be noted that heulandite is the mineral with the lowest Na$_2$O content (1.79 mol %) among the minerals studied. In heulandite, sodium atoms are located in channels formed by the SiO$_4$ and AlO$_4$ tetrahedra (Merkle & Slaughter, 1968). They are in an eight-fold s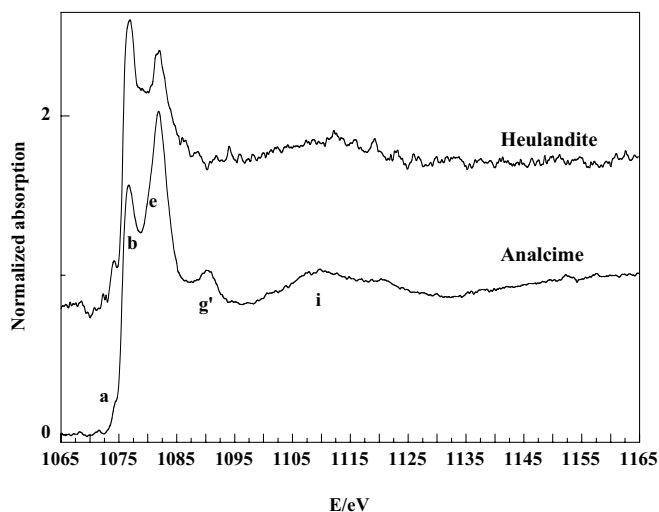ite, bonded to three framework oxygens atoms of aluminium-substituted tetrahedra and surrounded by five water molecules. Moreover, they occupy three different positions in the channels. In analcime (Mazzi & Galli, 1978), sodium atoms are in octahedral positions with four framework oxygens and two water molecules. The spectra of analcime has some similarities with that of amphibole minerals (Fig. 3), which is probably the signature of hydrated silicate, but peak *g* is shifted upwards by more than 3 eV.

Borate

Two borate samples, ulexite (Ghose *et al.*, 1978) and borax (Levy & Lisensky, 1978), have been studied (Fig. 6). The XANES spectra are very similar with a pre-edge peak at 1074.3 eV, two peaks with almost the same intensity at 1077.4 and 1081.6 eV, a small feature at 1091.7 eV and a broad contribution at 1108.7 eV (borax) and 1109.4 eV (ulexite). The similarity between the XANES spectra reflects the similarities between Na local structures in these compounds. In ulexite, Na is octahedrally coordinated by four water molecules and two hydroxyl ions and, in borax, Na ions are coordinated by six bridging water molecules. In both structures, the distorted Na-octahedra share edges to form a chain parallel to *c*. The XANES spectra are different from other oxides samples due to the broad contribution of the 1081.6 eV peak extending to high energies and to a peak near 1092 eV that appears about 5 eV above the peak *g* common to other oxide compounds. These widths of the peaks could reflect the influence of water molecules and of a more disordered environment. Ulexite contains Ca and Na while borax is a pure sodic borate, and these differences could explain why peaks *b* and *e* are less defined in the case of ulexite.

Silicate and borate glasses

In Fig. 7, we present the XANES spectra for some silicate glasses of compositions jadeite, albite and nepheline, which
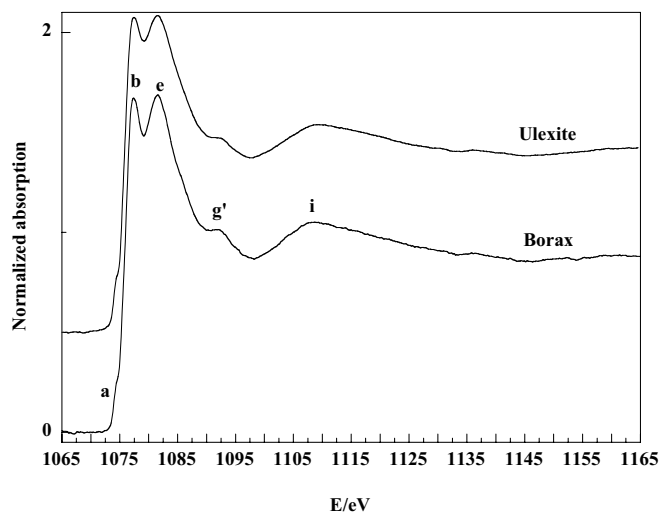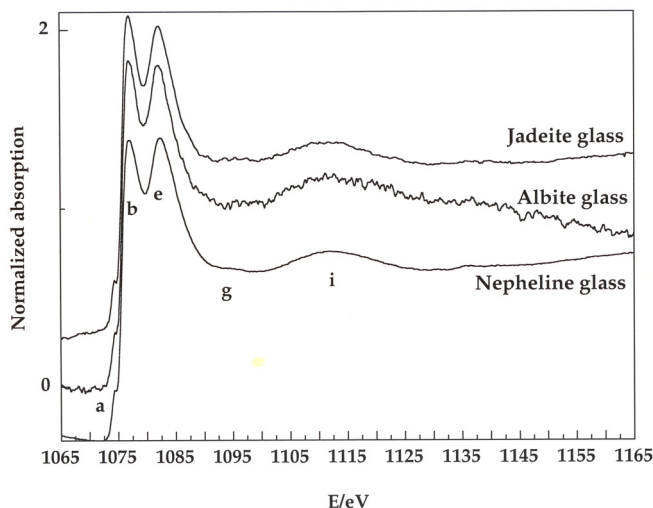

Fig. 5. Na K-edge XANES spectra of various zeolites.

Fig. 6. Na K-edge XANES spectra of various borate minerals.

Fig. 7. Na K-edge XANES spectra of glasses of jadeite, albite and nepheline composition.

Fig. 8. Na K-edge XANES spectra of sodium borate glasses containing 10, 20 and 30 mol% Na_2O (from bottom to top).

can be directly compared with the equivalent crystalline materials. These glasses have been previously studied at the Na K-edge (McKeown *et al.*, 1985) but the resolution and signal to noise ratio were of poor quality at that time. In this study, an EXAFS analysis indicates 5-6 oxygen neighbours around Na but an exact determination of the coordination is difficult since Na sites are statically disordered and irregular. Based on the partial molar entropies, Richet *et al.* suggest an increase in the Na coordination when Al polymerized the network (Richet *et al.*, 1993) but this is not evidence in EXAFS results (McKeown *et al.*, 1985) which may be due to the difficulty to determine the asymmetric distribution of Na-O distances using EXAFS (Cormier & Neuville, 2004).

XANES spectra are very similar for the different glasses (Fig. 7) with a double peak at 1077 and 1082.2 eV followed by a smooth resonance around 1111 eV. A pre-peak at 1074.5 eV and a weak structure 1095.5 eV can also be dis-
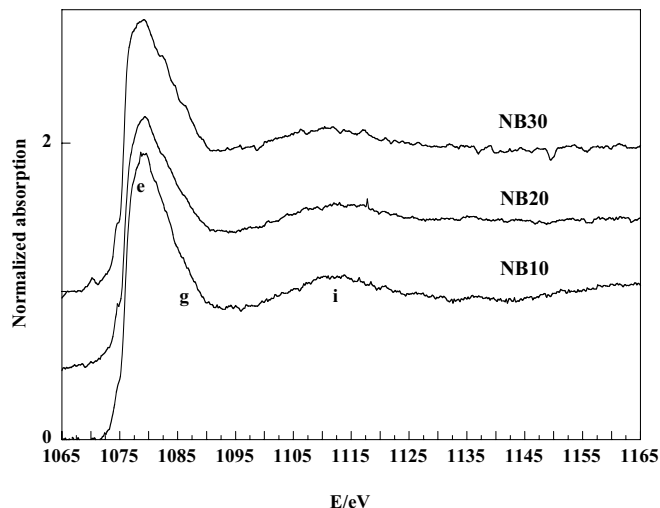
cerned. The overall similarity of the spectra for these three aluminosilicate glasses indicates that the close environments of sodium are similar in all three samples. Compared with their crystalline counterparts, nepheline and jadeite glasses present a structure *e* that is less intense that in crystalline samples while the intensities of structures *b* and *e* for the albite glass and crystal are of similar ratio. Beyond these two first peaks, the glasses present a less defined structure in agreement with increased disorder of the sodium environment. Based on the intensities of peaks *b* and *e*, the Na K-edge spectra of the glasses provide an indication that the sodium environment in glasses is more similar to that in crystalline albite crystals than in crystalline nepheline or jadeite.

Fig. 8 shows the Na K-edge spectra for binary sodium borate glasses with 10, 20 and 30 mol% Na_2O, in order to investigate the influence on the XANES spectra of the Na concentration in the glass and on its increasing role as a network modifier of the borate network. We can observe that the

Table 3. Energy positions of the main peaks in the XANES spectra determined by first derivative of the experimental data.

Mineral	a	b	c	d	e	f	g	g'	h	i	j
Cryolite	1074.97	1077.45				1083.00	1085.15	1090.10	1097.13		
Villaumite	1074.42	1077.24			1081.24		1085.12		1094.92	1110.17	1118.59
Halite	1074.42	1076.48	1078.38	1079.42	1081.11	1084.21	1086.98	1090.86	1095.90	1102.24	1114.98
Natrite	1074.42	1076.68		1079.06			1085.47				
Jadeite		1077.83			1082.32		1088.37				1113.83
Aegyrine		1077.50			1081.66		1087.98				1112.76
Acmite	1074.10	1077.40			1081.50		1087.12				
Riebeckite		1077.48			1081.74		1087.42				
Arfvedsonite	1074.36	1077.49			1081.55		1087.43				
Sodalite	1074.20	1076.26			1080.12	1085.27	1087.02	1090.31	1094.58	1103.06	
Nepheline	1074.43	1077.89			1082.05						
Labradorite	1074.39	1076.97			1081.33						
Hauyne	1074.20	1076.79			1080.65						
Albite		1077.40			1081.67		1088.76				
Carnegieite	1074.65	1077.08			1081.97		1086.63		1095.76		
Heulandite		1076.88			1082.00						
Analcime	1074.20	1076.70			1081.88			1090.27			
Ulexite	1074.30	1077.45			1081.56			1091.70		1109.43	
Borax	1074.31	1077.34			1081.59			1091.60		1108.70	

spectra are very different from that of the other glasses and from borate reference minerals since only one peak at 1079 eV dominates, with a small prepeak at 1074.5 eV and a broad feature at 1111 eV. The position of the main peak is intermediate between that of peaks *b* and *e* observed in reference spectra and could thus result from a merging of these two peaks. Compared to silicate glasses, this suggests that the environment of sodium in borate glasses is more distorted or that several different sites are present. We do not observe any significant chemical modifications of the XANES spectra, which indicates that the average Na surrounding remains the same for the three glasses. It was also observed on silicate glasses that an increase of the Na content does not modify the XANES spectra.

Theoretical calculations

We have tried to simulate some of characteristic near edge spectra by means of the Full Multiple Scattering (FMS) theory using the Feff8 code (Rehr & Albers, 2000). The use of the FMS, which is included in Feff8, as compared to the path decomposition, definitely improves the modelling of the low energy part (about the first ten eV) of the spectra above the leading edge. In all calculations shown below the input parameters of the code have been kept to their default values. The exchange potential is of the Hedin-Lundqvist type, the radius of the cluster for self-consistent calculation of the potential has been set to 4.8 Å and the radius for the full multiple scattering is 8 Å. The modelling has been done for two silicate crystalline references: jadeite (Cameron *et al.*, 1973) and cubic carnegieite (Whiters & Thompson, 1993). These crystals correspond to XANES spectra characterized by several well-defined structural oscillations and contain Na surrounded only by O atoms.

The theoretical spectra are compared with the experimental ones in Fig. 9a and c. A reasonable agreement is achieved in the reproduction of the structural features though some discrepancies exist in particular in the position of the peaks. In a recent attempt to model the near edge structure of sodium halides, Prado & Flank (2004) have demonstrated in the case of sodium halides that the use of the 'Z+1 atom approximation' significantly improves the agreement with experiment. Using this approach, Mg is used as the central absorbing atom in FEFF calculations and the spectra are then rescaled at the Na K-edge to compare easily with the experimental data. The theoretical XANES spectrum is thus able to reproduce the very low energy part of the experimental spectrum. This has been done in Fig. 9b and d, where an improvement in the relative intensities of the peaks *b* and *e* can be seen, especially for carnegieite. This approach can then be used to interpret the chemical dependence of the XANES spectra for crystals and, when atomic simulations are available, for glasses.

4. Conclusions

Na K-edge XANES spectra were obtained for a number of minerals with different structures, different type of Na neighbours and different Na coordination numbers. The spectra reported in this study indicate important similarities in the XANES features for minerals belonging to the same class of minerals. The Na XANES spectra consist generally of two features whose relative intensities vary. The position of these two contributions could also be regarded as a good indication of the number of oxygen around Na. Important modifications of the XANES spectra can be observed for glasses with different network formers (Si or B), which indicate that this technique could be used to get information on the glass structure for multicomponent systems. The coordination state is a hard task to determine from the XANES spectra. However, the difference in the Na XANES spectra, particularly the intensities of peaks *b* and *e*, shows the possibility to better understand the structural environment around Na in disordered materials using a 'fingerprint' technique. Full Multiple Scattering calculations can also be used to simulate theoretical spectra which could provide more information on the Na environment in both crystals and glasses.
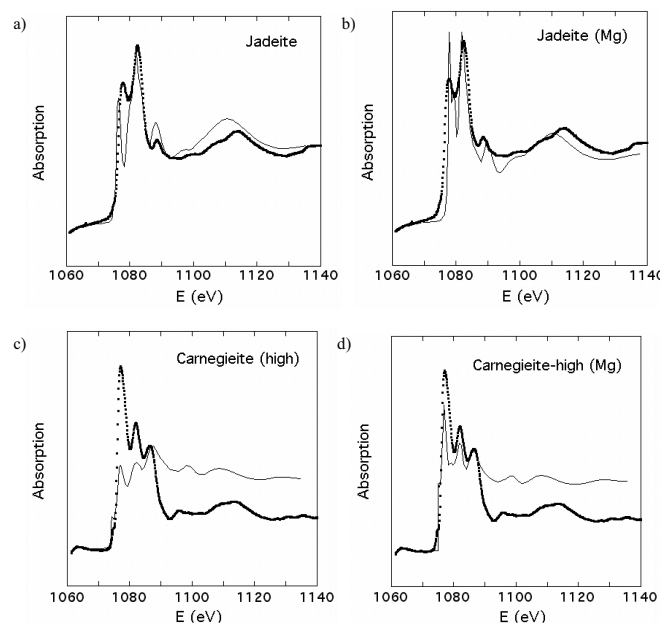
Fig. 9. Comparison of the experimental and theoretical spectra for jadeite (a, b) and cubic carnegieite (c, d). The experimental data are in dots while the theory ones are the solid line.

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