



LABORATORI NAZIONALI DI FRASCATI
SIS-Pubblicazioni

LNF-98/037(P)
4 Novembre 1998

**Evidence for Al/Si tetrahedral network in aluminosilicate glasses
from Al K-edge x-ray absorption spectroscopy**

Ziyu Wu^{1,3}, C. Romano^{2,5}, A. Marcelli³, A. Mottana^{2,3}, G. Cibin³,
G. Della Ventura^{2,3}, G. Giuli⁴, P. Courtial⁵ and D.B. Dingwell⁵

¹⁾ *Laboratoire Pierre Süe, CEA-CNRS CE Saclay, F-91191 Gif-sur Yvette Cedex, France*

²⁾ *Università di Roma Tre, Dipartimento di Scienze Geologiche, I-00146 Roma, Italy*

³⁾ *INFN - Laboratori Nazionali di Frascati, I-00044 Frascati, Italy*

⁴⁾ *Università di Firenze, Dottorato di Ricerca in Scienze Mineralogiche,
I-50121 Firenze, Italy*

⁵⁾ *Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany*

Abstract

The structure of aluminosilicate melts/glasses plays a key role in the Earth Sciences for the understanding of rock-forming igneous processes, as well as in the Materials Sciences for their technical applications. In particular, the alkaline earth aluminosilicate glasses are an extremely important group of materials, with a wide range of commercial application, as well as serving as analogue for natural basaltic melts. However, definition of their structure and properties is still controversial, and in particular the role and effect of Al has long been a subject of debate. [1–8] Here we report a series of experimental x-ray absorption near-edge structure (XANES) spectra at the Al K edge on a series of synthetic glasses of peralkaline composition in the CaO- Al₂O₃-SiO₂ system, together with a general theoretical framework for data analysis based on an *ab initio* full multiple scattering (MS) theory. We propose an Al/Si tetrahedral network model for aluminosilicate glasses based on distorted polyhedra, with varying both the T-O (T = Al or Si) bond lengths and the T-O-T angles, and with different Al/Si composition. This model achieves a significant agreement between experiments and simulations. In these glasses, experimental data and theoretical results concur to support a model in which Al is network-former with a comparatively well ordered local medium-range order (up to 5 Å).

PACS:78.70.Dm, 91.35.-x, 91.60.-x, 61.43.Fs

Submitted to Science, 28 October 1998, Frascati, Italy

The assumption of prevailing disorder in glasses [9] has recently met with a number of direct and indirect challenges [10–21]. All of this has arisen from the increasing interest in local structure determination (5-10 Å) beyond the pair distribution function, stimulated by the growth of XANES studies both from a theoretical and an experimental point of view. The low-energy side of an absorption spectrum is very sensitive to the geometrical arrangement of the environment surrounding the selected atom, due to the multiple scattering processes of the photoelectron emitted by the x-ray-absorbing atom. Unlike neutron diffraction (ND) or extended X-ray-absorption fine-structure (EXAFS) spectroscopy which may give only the pair-correlation function of the system, in MS processes the photoelectron interacts with many other atoms and thereby simultaneously probes their presence and their geometrical arrangement around the photoabsorber; in other words, the photoelectron probes an n-particle distribution function. This sensitivity makes XANES a unique probe in many systems, especially glass and melt [10,16,20,22–25]. Since the years ’80 many investigations [26–29] have provided powerful algorithms to numerically simulate experimental XANES data. However, only recently a better understanding of atomic potentials in the Al systems have been made to let comparison with experimental spectra become quantitative.[30]

Table 1: The compositions (in mol percent) of the samples used.

Samples	SiO ₂	Al ₂ O ₃	CaO
65.09	64.85	9.09	26.06
53.12	52.96	11.86	35.18
44.12	44.45	12.47	43.08
36.16	36.06	16.04	47.90
22.19	21.92	19.37	58.71
09.23	9.19	22.80	68.01

The samples of a join in the CaO-Al₂O₃-SiO₂ system were prepared by quenching high temperature melts obtained at 1 atm rapidly to the glassy state. TEM (transmission electron microscopy) investigations confirmed that they were completely free of crystals (Romano et al., in prep.). The compositions of the samples along the join SiO₂-Ca₃Al₂O₆ are tabulated in Table I.

The experimental data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) at beamline 3-3 equipped with a monochromator using YB₆₆ (440) crystals. XANES spectra have been simulated via the full multiple-scattering (MS) theory [31–34]. We use the Mattheiss prescription [35] to construct the cluster density. The Coulomb part of the potential is obtained by superposition of neutral atomic charge densities either taken from the Clementi-Roetti tables [36] or simply generated by the atomic relativistic Hartree-Fock-

Slater code of Desclaux [37]. For the exchange-correlation part of the potential we have used the complex optical Hedin-Lundqvist (H- L) potential[38–40]. In order to simulate the charge relaxation around the core hole in the photoabsorber of atomic number Z (Al = 13) we use the well tested screened $Z + 1$ approximation (final state rule)[38] which 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. The consequent solution of the effective Schrödinger equation for final state is solved numerically.

The unpolarized photoabsorption cross section for photons with energy ω , in Rydberg units of energy and lengths, is proportional to the imaginary part of the scattering path operator [41]

$$\sigma(\omega) = 8\pi^2 \alpha \omega \frac{k_0}{\pi} \sum_{m_0, L, L'} \Im(M_L^{L_0} \tau_{LL'}^{\circ\circ} M_{L'}^{L_0}) \quad (1)$$

with amplitude for the creation of the electron at central atom

$$M_{L'}^{L_0} = \langle \underline{R}_{L'}^{\circ}(Y_{L'}(\hat{r})) | \hat{\epsilon} \cdot \vec{r} | \phi_{L_0}^c(\vec{r}) \rangle \quad (2)$$

and amplitude of multiple scattering propagation matrix, which describes the interactions of photoelectron with neighbouring atoms,

$$\tau_{LL'}^{00} = [(T_a^{-1} + G)^{-1}]_{LL'}^{00} = \sum_0^{\infty} [(-T_a G)^n T_a]_{LL'}^{00} \quad (3)$$

where $\hat{\epsilon}$ is the photon polarisation vector, α is the fine structure constant, $\underline{R}_{L'}^i(r_i)$ is radial part of normalised scattering wave function for the photoelectron, $\phi_{L_0}^c(\vec{r})$ is the core electron wave function with angular momentum $L_0 \equiv (l_0, m_0)$; T_a and G are the amplitude of atomic scattering and propagation, respectively.

Al K-edge absorption spectra of the samples are shown in Fig. 1(a). The spectra are characterised by a main feature composed of two peaks A and B with variable intensities at about 1567 and 1570 eV. The energy positions of the A and B peaks do not shift significantly as the composition changes, whereas their relative intensities exhibit a distinct variation, with the first peak decreasing and the second one increasing as the silica content decreases (see Table I). Fig. 1(b) reports *ab initio* MS theoretical computations of the same Al K-edge spectra. They are based on our proposed model cluster composed of an $\text{AlO}_4/\text{SiO}_4$ tetrahedral network as shown in Fig. 2, with possible variation of T-O bond lengths and T-O-T angles, and with different Al/Si ratios. All parameters of the six clusters, which best reproduce the experimental spectra, are listed in Table II. They are the final results of about 1000 simulations.

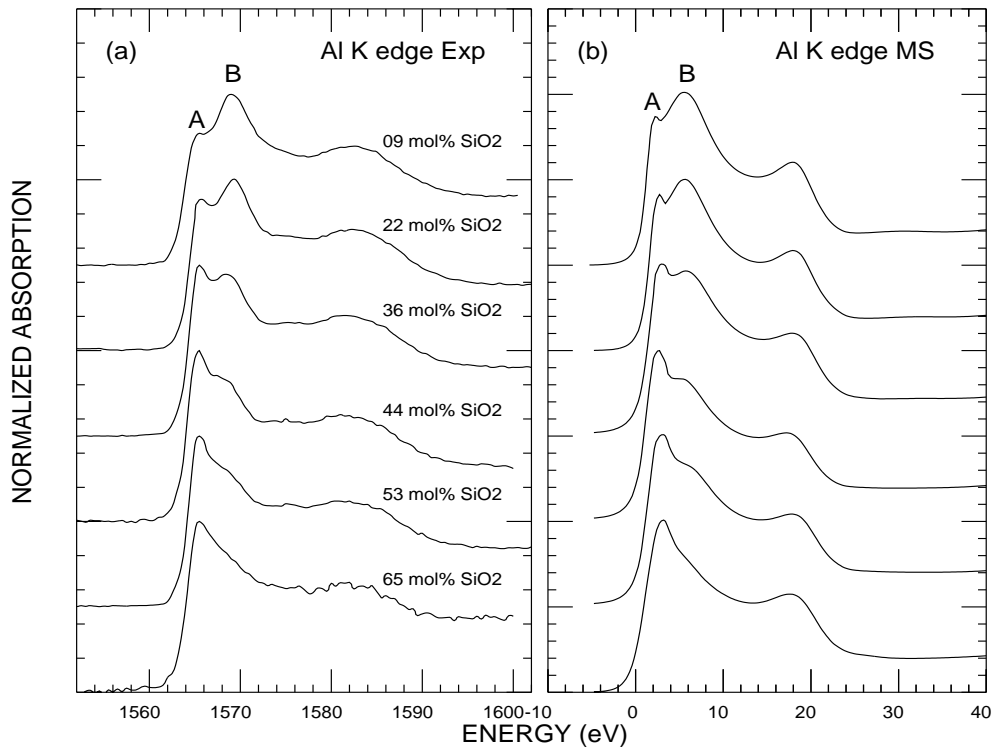


Figure 1: (a) Experimental (Exp) and (b) multiple-scattering (MS) calculated Al K-edge XANES spectra of the six samples along the join $\text{SiO}_2\text{-Ca}_3\text{Al}_2\text{O}_6$.

An almost perfect agreement is obtained when the Al/Si ratio increases (in order to match the composition of the corresponding glass), the T-O bond length increases and the T-O-T angle decreases (as reported in Table II).

Table 2: The mean T-O bond length (in Å), TOT angles (in degree) and Si/Al ratios used to reproduce experimental data in cluster models.

Samples	d(T-O)	TOT	ratio (Si/Al)
65.09	1.624	144	4.0
53.12	1.652	138	3.0
44.12	1.678	138	3.0
36.16	1.690	136	2.0
22.19	1.746	134	1.0
09.23	1.768	132	0.0

This trend is in agreement with the molecular dynamics simulations of Geisinger [42] and

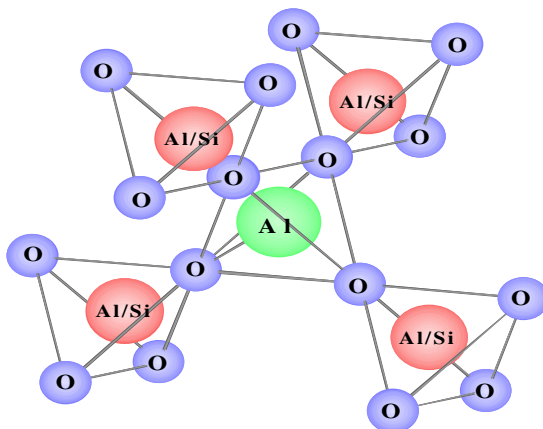


Figure 2: The proposed medium-range atomic environment around Al up to 5 Å in aluminosilicate glasses $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$.

Scamehorn and Angel[43]. Going back to the XANES data, the increase in the intensity of the B peak and of the width of the white line can be attributed to MS contributions from outer-shell Al tetrahedral orbitals. The successful reproduction of the experimental spectra (especially for the two main peaks with their relative intensities), determined by contributions of the outer-shell atomic configuration, indicates that Al has not only a well-ordered first-neighbour tetrahedral coordination polyhedron as a simple network-former, but it is also linked through its corners to other Al or Si tetrahedra (i.e., the four oxygens of the central tetrahedron are bridging the central Al with other tetrahedral cations).

Additional evidence for the corner-linked polyhedral medium-range structure can be derived from other calculations shown in Fig. 3. The first one (curve a) concerns the simple 5-atom cluster, i.e., the central tetrahedron: the calculated spectrum does not fit the experimental data. The three ones following upwards (curves b to d), concern a 9-atom cluster that contains the central tetrahedron surrounded by four Al/Si atoms with decreasing T-O-T angles (150° , 137° and 123° , respectively): none of these clusters improves the result of the first model. Curve e refers to the structural model in Al-rich composition (the top line in Fig. 1(b)) where one outer Al network unit is not considered, i.e., it consists of a central network-forming AlO_4 connected with three Al network units only, and with one corner oxygen left alone as non-bridging oxygen. Also this calculation does not fit the experimental result. The last model (curve f) is based on a central tetrahedron with two Al network units only and two non-bridging oxygens with one Ca around them: the result again does not match the experimental data.

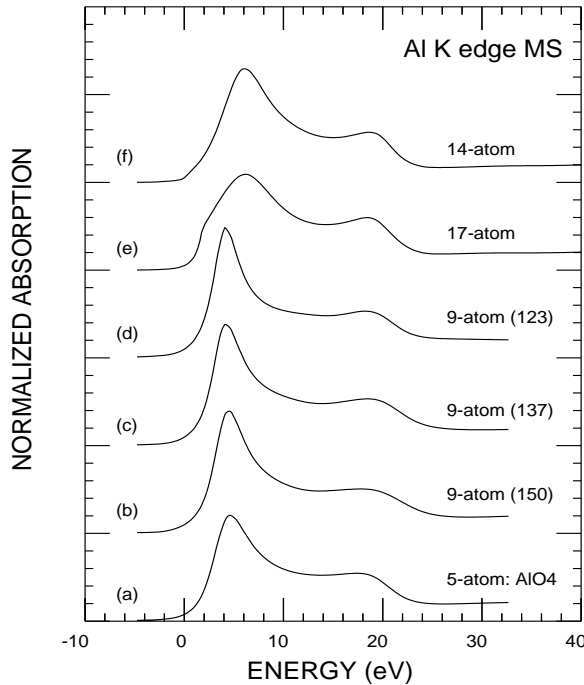


Figure 3: Simplified MS calculations at Al K edge using different cluster models: (a) central Al tetrahedron (5 atoms); (b-d) 9-atoms cluster (Al + 4O + 4 Al/Si) as a function of T-O-T angle (150° , 137° and 123° , respectively); (e) 17-atom cluster derived from the one used for the top curve in Fig. 1(b) by suppressing one Al network units (Al + 4O + 3 AlO₃); (f) 14-atom cluster obtained from that used for the top curve in Fig. 1(b) by suppressing two Al network units and add one Ca around the two non-bridging oxygens.

In conclusion, we present for the first time a series of experimental XANES spectra and MS theoretical simulations that probe the many-body correlation distribution at the Al K-edge in the CaO-Al₂O₃-SiO₂ system in the glassy state, and determine the short- and medium-range structures. All evidence from this direct spectroscopic probe of structure supports the conclusion that Al (in the system here investigated) occurs as network-former with a well-defined first coordination shell consisting of 4 oxygens. However, according to our model, in the medium-range, the tetrahedra are regularly linked through all their four corners to other tetrahedral Al/Si units (even in the Al-rich composition: in other words, Al enters fully polymerized Q4 sites[4,44,45]). The unique information extracted from XANES, when combined with MS calculations, strengthens the current evidence for the ordered structure of aluminosilicate glasses and can be used for the first time to develop quantitative models to better describe bulk properties of glasses and melts such as viscosity, density and compressibility[46–48]. The derived basic network cluster model may be

used in future to develop a more general model of the medium-range structural order of aluminosilicate glasses as well as of other amorphous systems.

1 Acknowledgements

We acknowledge MURST (Italy) for the grant that permitted our experimental work both at Frascati and Stanford. Here Stanford University on behalf of DOE is operating SSRL. The EC "TMR - Large Scale Facilities" programme (Contract No. ERBFMGECT980111 to D.C. Rubie) is also acknowledged for the work performed at the Bayerisches Geoinstitut, Bayreuth. A Vigoni/DAAD project contributed to the exchange scientists. Helpful discussions with F. Seifert and B. Poe are appreciated.

References

- [1] Daniel, I., McMillan, P. F., Gillet, P. & Poe, B. T. *Chemical Geology* **128**, 5-15 (1996).
- [2] Dutt, D. A., Higby, P. L. & Griscom, D. L. *J. Non-cryst Solids* **130**, 41-51 (1991).
- [3] Huang, C. & Behrman, E. C. *J. Non-Cryst Solids* **128**, 310-320 (1991).
- [4] Merzbacher, C. I., Sheriff, B. L., Hartman, J. S. & White, W. B. *J. Non-Cryst Solids* **124**, 194-206 (1990).
- [5] Poe, B. T., McMillan, P., Cote, B., Massiot, D. & Coutures, J. P. *J. Am. Ceram. Soc.* **77**, 1832-1838 (1994).
- [6] Sato, R. K., McMillan, P., Dennison, P. & Dupree, R. *Phys. Chem. Glasses* **32**, 149-155 (1991).
- [7] Engelhardt, G., Nofz, M., Forkel, K., Wihsmann, F. G., Magi, M., Samoson, A. & Lippmaa, E. *Phys. Chem. Glasses* **26**, 157-165 (1985).
- [8] Kirkpatrick, R. J., Oestrike, R., Weiss, C. Jr., Smith, K. A. & Olfeld, E. *Am. Mineral.* **71**, 705-711 (1986).
- [9] Zachariasen, W. H. *J. Am. Chem. Soc.* **54**, 3941-3851 (1932); *J. Chem. Phys.* **3**, 162-163 (1933).
- [10] Greaves, G. N., Fontaine, A., Lagarde, P. & Gurman, S. J. *Nature* **293**, 611-616 (1981).

- [11] Geere, R. G., Gaskell, P. H., Greaves, G. N., Greengrass, J. & Binsted, N. in *EXAFS and Near Edge Structure Springer Series in Chemical Physics* **27**, 256- 260 (1983).
- [12] Binsted, N., Greaves, G. N. & Henderson, C. M. B. *Contr. Miner. Petrol* **89**, 103 (1985).
- [13] Brown, G. E., Waychunas, G. A., Ponader C. W., Jackson, W. E. & McKeown, D. A. *J. Phys. Paris* **47**, Colloque C8, 665-668 (1986).
- [14] Stebbins, J. F. *Nature* **330**, 465-467 (1987).
- [15] Eckersley, M. C., Gaskell, P. H., Barnes, A. C. & Chieux, P. *Nature* **335**, 525-527 (1988).
- [16] Waychunas, G. A., Brown, G. E., Ponader C. W. & Jackson, W. E. *Nature* **332**, 251-253 (1988).
- [17] Gaskell, P. H., Eckersley, M. C., Barnes, A. C. & Chieux, P. *Nature* **350**, 675-677 (1991).
- [18] McKeown, D. A., Waychunas, G. A. & Brown, G. E. *J. Non- Crystal Solids* **74**, 349-371 (1985).
- [19] Elliott, S. R. *Nature* **354**, 445-452 (1991).
- [20] Jackson, W. E. et al. *Science* **262**, 229-233 (1993).
- [21] Farnan, I. et al. *Nature* **358**, 31-35 (1992).
- [22] Filipponi, A., Di Cicco, A., Benfatto, M. & Natoli, C. R. *Europhys. Lett.* **13**, 319 (1990); Filipponi, A., Evangelisti, F., Benfatto, M., Mobilio, S. & Natoli, C. R. *Phys. Rev. B* **40**, 9636 (1989).
- [23] Kizler, P. *Phys. Rev. Lett.* **67**, 3555-3558 (1991).
- [24] Di Cicco, A., Minicucci, M. & Filipponi, A. *Phys. Rev. Lett.* **78**, 460-463 (1997).
- [25] Brown, G. E., Farges, F. & Calas, G. *X-ray Scattering and X-ray Spectroscopy Studies of Silicate Melts in Structure, Dynamics and Properties of Silicate Melts*, eds: J.F. Stebbins, P.F. McMillan & D.B. Dingwell, *Rev. Mineral.* **32** p 317-410 (1995). Mineral. Soc. Am., Washington, DC.
- [26] Durham, P. J., Pendry, J. B. & Hodges, C. H. *Solid State Commun.* **38**, 159 (1981); Durham, P. J., Pendry, J. B. & Hodges, C. H. *Comput. Phys. Commun.* **25**, 193 (1982).

- [27] Vvedensky, D. D., Saldin, D. K. & Pendry, J. B. *Comput. Phys. Commun.* **40**, 421 (1986).
- [28] Natoli, C. R. & Benfatto, M. *J. Physique* **47**, C8: 11-23 (1986).
- [29] Rehr, J. J., Zabinsky, Z. I. & Albers, R. C. *Phys. Rev. Lett.* **69**, 3397-4000 (1992).
- [30] Mottana, A., Murata, T., Marcelli, A., Della Ventura, G., Cibin, G., Wu, Z. Y., & Tessadri, R. *J. Applied Crystal.* **31** (in press).
- [31] Lee, P. A. & Pendry, J. B. *Phys. Rev.* **B 11**, 2795 (1975).
- [32] Durham, P. J. in *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, XANES*, edited by Prins, R. & Koningsberger, D. (Wiley, New York, 1988).
- [33] Natoli, C. R., Misemer, D. K., Doniach, S. & Kutzler, F. W. *Phys. Rev.* **A 22**, 1104 (1980); Natoli, C. R., Benfatto, M., Brouder, C., Ruiz Lopez, M. Z. & Foulis, D. L. *Phys. Rev.* **B 42**, 1944 (1990).
- [34] Wu, Z. Y., Benfatto, M. & Natoli, C. R. *Phys. Rev.* **B 45**, 531 (1992); Wu, Z. Y., Ouvrard, G., Lemaux, S., Moreau, P., Gressier, P., Lemoigno, F. & Rouxel, J. *Phys. Rev. Lett.* **77**, 2101 (1996).
- [35] Mattheiss, L. *Phys. Rev.* **A 134**, 970-975 (1964).
- [36] Clementi, E. & Roetti, C. *Atomic Data and Nuclear Data Tables*, **Vol. 14**, 177-478 (1974).
- [37] Desclaux, J. *Comp. Phys. Commun.* **9**, 31 (1975); *J. Phys.* **B 4**, 631 (1971).
- [38] Lee, P. A. & Benni, G. *Phys. Rev.* **B 15**, 2862 (1977).
- [39] Chou, H., Rehr, J. J., Stern, E. A. & Davidson, E. R. *Phys. Rev.* **B 35**, 2604 (1987).
- [40] Tyson, T. A., Hodgson, K. O., Natoli, C. R. & Benfatto, M. *Phys. Rev.* **B 46**, 5997 (1992).
- [41] Gunnella, R., Natoli, C. R. & Wu, Z. Y. (unpublished).
- [42] Geisinger, K. L., Gibbs, G. V. & Navrotsky, A. *Phys. Chem. Mineral* **11**, 266-283 (1985).
- [43] Scamehorn, C. A. & Angell, C. A. *Geochim. Cosmochim. Acta* **55**, 721-730 (1991).

- [44] Mysen, B. O. (1988) "Structure and properties of silicate melts" Development in Geochemistry, Advisor Editor: W.S. Fyfe Carnegie Institution of Washington, Geophysical Laboratory, Washington D.C., U.S.A. Elsevier.
- [45] Oestrike, R., Yang, W. H., Kirkpatrick, R. J., Hervig, R., Navrotsky A. & Montez, B. *Geochim. Cosmochim. Acta* **51**, 2199- 2210 (1987).
- [46] Courtial, P. & Dingwell, D. B. *Geochim. Cosmochim. Acta* **59**, 3685-3695 (1995).
- [47] Hess, K. U. Dingwell, D. B. & Webb, S. *Eur. J. Mineral.* **8**, 371-381 (1996).
- [48] Webb, S. & Courtial, P. *Geochim. Cosmochim. Acta* **60**, 75-86 (1996).