

An extended X-Ray absorption fine structure (EXAFS) study of the calcium site in a model basaltic glass, $\text{Ca}_3\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{24}$

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ABSTRACT. Short-range order in the oxygen co-ordination shell of the Ca ion in a glass of composition $\text{Ca}_3\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{24}$ is investigated by analysis of the extended X-ray absorption fine structure. The estimate of disorder in the short-range oxygen co-ordination is no greater than that for crystalline samples of diopside and bytownite. An estimate of the oxygen environment of calcium in the particular glass is included.

KEYWORDS: EXAFS, basaltic glass, short-range order, diopside, bytownite.

A KNOWLEDGE of the structure of aluminosilicate glasses and, by extrapolation, aluminosilicate melts, is important in the development of an understanding of their physical and thermodynamic properties. The long-range order of crystalline aluminosilicate minerals is lost in glasses and melts, but a number of experimental measurements of various types [X-ray diffraction, Raman spectroscopy (McMillan *et al.*, 1982), and gas chromatography (Götz and Masson, 1970)] indicate the existence of short-range order with the AlO_4 and SiO_4 tetrahedral structural units being retained and cross-linked to a degree determined by composition. X-ray diffraction, in particular, has been successfully applied to the elucidation of local structures in glasses, and information on the nature of the anion network of a number of aluminosilicate glasses and melts has been obtained from the radial distribution functions, acquired by Fourier transformation of the diffraction data (Taylor and Brown, 1979*a, b* and Taylor *et al.*, 1980). The radial distribution functions give one-dimensional structural information and have contributions from interactions between all con-

stituent atoms. Extended X-ray absorption fine structure (EXAFS) similarly gives one-dimensional structural information, but the signal has contributions resulting only from the interaction of the ejected K-shell electron with the local environment of the chosen element. This simplifies the interpretation of such radial information as illustrated by the work of Greaves *et al.* (1981), Greaves and Raoux (1982) and Greaves (1983). The use of EXAFS has become really practicable at adequate resolution through the availability of the high intensity synchrotron X-ray source. In the present work we report measurements of the co-ordination of the calcium ion in an aluminosilicate glass of composition $\text{Ca}_3\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{24}$.

The glass composition, $\text{Di}_2\text{-An-Fo}$ in petrological terms, was one of a suite of compositions prepared by Shepperd (1980) for X-ray diffraction studies, and was chosen to be representative of a natural magma within simple bounds and such that the glasses were effectively 'stable' at room temperature. As an aid to the interpretation of the glass EXAFS, similar data were also recorded for two crystalline minerals of known structure. In the absence of a direct crystalline analogue of the same composition as the glass, bytownite and diopside were chosen as structures that might provide relevant possible models for the calcium environment in the glass (see fig. 1). EXAFS studies of anorthite and diopside have been reported previously in conjunction with EXAFS work on glasses having the same composition as these minerals (Greaves and Raoux, 1982). Details of the specimens used are given in Table I. In the aluminosilicate network of the glass the mean connectivity of the tetrahedral structural unit is approximately

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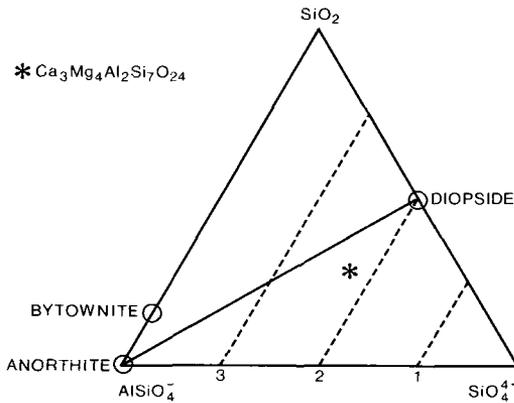


FIG. 1. Ternary diagram illustrating the composition of the anion network of the glass $\text{Ca}_3\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{24}$ with respect to the components SiO_2 , SiO_4^{4-} , and AlSiO_4^- . The broken lines correspond to integral mean connectivities for the tetrahedral anion units.

2.3, on the assumption that all the Al and none of the Mg is tetrahedrally co-ordinated. In diopside the connectivity is two, and in the bytownite it is four.

Minerals and methods. The preparation and characterization of the glass was described by Shepperd (1980). It was formed from a gel of appropriate composition prepared according to the recommendations of Hamilton and Henderson (1968). After melting at 1600°C it was quenched to 600°C , then slowly cooled to room temperature at $10^\circ\text{C}/\text{hour}$ in order to produce large clear specimens (required for another purpose). The sample was checked for homogeneity by spot electron probe analysis and found to correspond to $\text{Ca}_3\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{24}$. The material chosen for study was transparent, showing no evidence of phase separation or devitrification. The glass and characterized pure samples of crystalline bytownite and diopside were powdered and mounted in an aluminium sample holder on a Sellotape window. For X-ray absorption measurements EXAFS spectra were recorded in the transmission mode

at the Daresbury Synchrotron Radiation Source operating at an energy of 1.8 GeV with an average beam current of 90 mA with a Si(220) double crystal monochromator. Measurements were carried out at room temperature in a single scan extending from c. 200 eV below the Ca K-edge to c. 500 eV above it. Data analysis, by the program EXCURVE developed by Binsted, utilized the single-scattering spherical wave method for calculating EXAFS, with phase shifts derived from 'ab-initio' calculations (Lee and Pendry, 1975). A curve fitting procedure was used to match the model EXAFS to the experimental data. The measured EXAFS spectra were Fourier-filtered over the distance range of interest. The Fourier-filtered EXAFS spectra were plotted in k -space (where k is the electron momentum vector) and weighted by a factor of k^3 for the purposes of fitting. An iterative non-linear least-squares minimization procedure allowed the use of a single parameter, the fitting index (FI), as a measure of fit between the model and experimental EXAFS. In testing the suitability of a particular co-ordination model the factors varied were: (a) the distances of co-ordination shells from the central atom; (b) the number and kind of atoms in each shell; (c) thermal and structural disorder (modelled by a Debye-Waller term $\exp(-2\sigma_j^2 k^2)$, where σ_j^2 is the mean square displacement between the emitting and scattering atoms); and (d) E_0 , the shift in energy of the absorption edge. For a particular co-ordination model estimates of shell distances and E_0 were allowed to vary first, then the estimates of the Debye-Waller terms, and then E_0 and the shell distances once more.

Results and discussion. The normalized, background-subtracted, EXAFS spectrum of the Ca site in the glass $\text{Ca}_3\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{24}$ is shown in fig. 2. The Fourier transform of the EXAFS has only one significant peak, corresponding to atoms within 3 \AA of the Ca ion, suggesting that any short-range structural order does not extend beyond the first co-ordination sphere. In contrast the EXAFS of the crystalline samples of bytownite and diopside gave Fourier transforms that showed several peaks corresponding to ordered co-ordination shells extending to more than 6 \AA from the Ca ion.

To provide the best basis of comparison with the glass EXAFS it was desirable to fit only those peaks from the bytownite and diopside that lay at values of less than 3 \AA . Accordingly, these initial co-ordination peaks in the Fourier transforms were back-transformed to provide Fourier filtered EXAFS spectra corresponding to interaction only with the initial co-ordination sphere. The oxygen co-ordination pattern of this initial sphere is known for diopside and bytownite from single-crystal

TABLE I. The mineral standards used

	Oxford University Museum number	Locality	Composition
Diopside	OUM 22526	Hull, Iowa, USA	$\text{CaMgSi}_2\text{O}_6$
Bytownite	OUM 23147	Mooihoek, S. Africa	$\text{Ca}_{0.87}\text{Na}_{0.14}\text{K}_{0.01}\text{Fe}_{0.01}\text{Si}_{2.15}\text{Al}_{1.83}\text{O}_8$

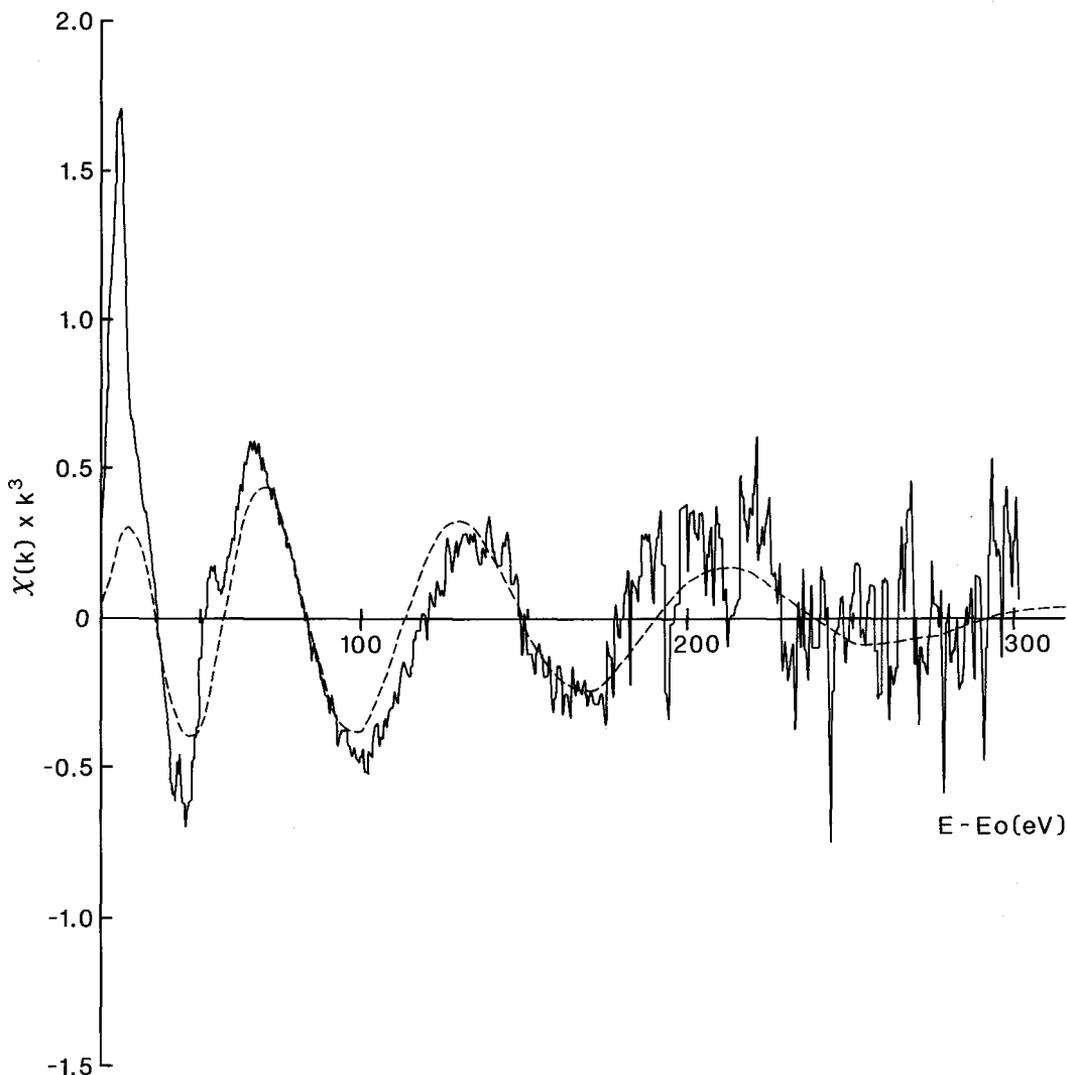


FIG. 2. Ca K-edge EXAFS of $\text{Ca}_3\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{24}$ glass. The continuous line is the experimental spectrum; the broken line is the simulated spectrum of the model D listed in Table IV. A fit index parameter of 8.52 to the experimental EXAFS was obtained.

X-ray diffraction investigations (Clark *et al.*, 1969; Fleet *et al.*, 1966). Diopside has a unique Ca site (Table II); in bytownite there are four distinct but similar Ca sites; a simplified representation of the mean, given in Table III, was used to model the EXAFS. The results of the fitting procedures using the known oxygen co-ordination patterns for diopside and bytownite are listed in Tables II and III respectively. This allowed estimation of appropriate Debye-Waller factors for a Ca ion in an

environment chemically similar to that in the aluminosilicate glass, and acted as a test of the EXAFS model by comparison of the known Ca-O shell distances (R_{crystal}) with the calculated shell distances (R). The EXAFS model distances for the inner shells are shorter than the known values by *c.* 0.1 Å. Sources of error include the estimation of phase shifts by 'ab-initio' calculation, which is probably the major cause, and the assumption of a simple Gaussian pair distribution function. Fourier

filtering may affect the amplitude of the EXAFS, causing errors in Debye-Waller factors or co-ordination number, but does not significantly alter the phase.

TABLE II. *Diopside; fit using known co-ordination pattern*

Number of O atoms	$\sigma_j^2(\text{\AA}^2)$	$R(\text{\AA})$	$R_{\text{crystal}}(\text{\AA})$
4	0.006	2.26	2.36
2	0.006	2.44	2.56
2	0.012	2.71	2.71

TABLE III. *Bytownite; fit using known mean co-ordination pattern*

Number of O atoms	$\sigma_j^2(\text{\AA}^2)$	$R(\text{\AA})$	$R_{\text{crystal}}(\text{\AA})$
1	0.003	2.24	2.33
2	0.013	2.34	2.41
2	0.004	2.42	2.51
1	0.013	2.75	2.72

The co-ordination number, N , of the Ca atom is, in principle, discernible from the area under the first peak in the Fourier transform. N is known for diopside and bytownite and the area of the peak for the glass sample is intermediate between those for the two crystalline samples. However, varying disorder factors between different environments can affect the estimates of N , and there is a large error in the peak area estimate for the glass due to

high background noise, so only an estimate of N in the range 6–9 for the glass is possible.

To match the observed EXAFS of the Ca ion in the glass with a suitable model environment, a series of oxygen co-ordination shell patterns was used in the curve fitting procedure to obtain a minimum value of the fitting index with physically reasonable Debye-Waller factors. An estimate of the co-ordination pattern was obtained by using models involving six and eight one-atom oxygen shells, although such models contain too many parameters for the program to function in an optimum fashion. The results of the fitting procedure applied to various models are summarized in Table IV. The EXAFS signal of the glass does not correspond precisely to the environment of bytownite or diopside, and models involving a single oxygen co-ordination shell around the calcium atom provided poor fits. Using the co-ordination shell pattern suggested by one-atom shell fits over a range of co-ordination numbers, the model Ca–O environments denoted D and E in Table IV emerged as the most likely models, having a low FI and non-zero values of σ_j^2 of a physically reasonable magnitude. However, in view of the systematic differences between R and R_{crystal} in Tables II and III it is necessary to apply corrections to the values of R in Table V to give values of R_{corr} .

Conclusion. The EXAFS of Ca ions in the glass $\text{Ca}_3\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{24}$ suggests that each Ca ion has a well defined short-range oxygen co-ordination. This short-range order does not extend beyond an initial sphere of about 3 Å. The estimate of disorder in the Ca site co-ordination based on the Debye-Waller factors is no greater than in crystalline samples of diopside or bytownite. The best estimate of the oxygen environment of Ca in the glass is probably a ninefold co-ordination similar to that indicated by D in Table IV, although an eightfold

TABLE IV. *Glass; fits assuming various co-ordination shells*

Model	Oxygen shell pattern	FI	σ_j^2 range
Diopside	4:2:2	0.138	0.010–0.018
Bytownite	1:2:2:1	0.066	0.004–0.015
Single Shell	6	0.254	0.018
Single Shell	8	0.476	0.025
Combinations of Shells A	1:3:1:1	0.177	0.000–0.012
Combinations of Shells B	1:3:2:1	0.055	0.000–0.005
Combinations of Shells C	3:3:2	0.105	0.005–0.012
Combinations of Shells D	3:3:2:1	0.034	0.004–0.009
Combinations of Shells E	2:3:2:1	0.039	0.002–0.010

Details of the co-ordination in D and E, which give the two best fits, are given in Table V.

TABLE V. $Ca_3Mg_4Al_2Si_7O_{24}$ glass: details of the best two co-ordinations, D and E, of Table IV

Number of O atoms	$\sigma_i^2(\text{\AA})^2$	$R(\text{\AA})$	$R_{\text{corr}}(\text{\AA})$
Co-ordination D			
3	0.004	2.23	2.33
3	0.003	2.39	2.49
2	0.008	2.51	2.58
1	0.009	2.72	2.72
Co-ordination E			
2	0.002	2.20	2.30
3	0.004	2.36	2.46
2	0.008	2.46	2.56
1	0.010	2.67	2.67

co-ordination similar to E gives almost as good a fit. The estimates of Ca-O distances may reasonably be supposed to have an uncertainty of about $\pm 0.05 \text{ \AA}$.

Greaves *et al.* (1981) similarly found local order around the Na cation in EXAFS studies of sodium disilicate glass and soda-lime-silica glass. The specific co-ordination environment of a cation in a glass will be dependent on chemical composition. Further studies of cation local order in glasses covering a range of compositions should therefore prove valuable in an understanding of the properties of aluminosilicate melts and glasses.

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