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Short-Range Physicochemical Structure
of Amorphous Aluminosilicates

by

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ABSTRACT

This work was initiated for the purpose of exploring the local structural environment of the alkali and alkaline earth cations in natural silicate melts and glasses. Currently, little is known about the structural environments of Na, K, or Ca in such materials because few types of spectroscopy are sensitive to these elements. However, x-ray photoelectron scattering theory indicates that the spectral fine structure near the absorption edge, denoted XANES (x-ray absorption near edge structure), and the structure within the energy region extending several hundred electron volts from just above the absorption edge, denoted EXAFS (extended x-ray absorption fine structure), is sensitive to the short-range structural environment of the ionized atom. During three experimental sessions at the Stanford Linear Accelerator Synchrotron Radiation Laboratory (SLAC-SSRL), we have been successful in making K-edge XANES and EXAFS measurements for Na, K, and Ca in a variety of model compounds and amorphous aluminosilicates.

In particular, the Ca K-edge spectra of anorthite and diopside composition glasses were found to be similar to their crystalline analogues, suggesting a similarity of local Ca environments in glass and crystal. In contrast, a comparison of the Ca K-XANES spectra for titanite crystal and glass shows a significant difference, possibly reflecting disparity between their respective short-range environments. Sodium K-XANES spectra of all model compounds and glasses show three peaks centered at 1054.5, 1057.8, and 1061.9 eV. In contrast with the Ca K-edge spectra, the Na spectra show no systematic variations in edge energies with changes in Na coordination or Na-O distance. Variations in the intensity of the Na pre-edge feature do occur and may be related to distortion of the Na site.

INTRODUCTION

Since medieval times, when the usefulness of glassy materials was first recognized, and perhaps even since the Bronze Age when glassy slag was inadvertently produced as a by-product in the smelting of copper, amorphous forms of silica have played an increasingly important role in human culture. In recent years, interest in the structure and bonding of the amorphous aluminosilicates has accelerated. Such interest spans the full scope of modern technology from the ceramics industry, with the development of fiber optics and nuclear waste packaging, to the electronics industry, with the advent of amorphous semiconductors. Knowledge of the detailed structural environment of glasses and melts containing alkali and alkaline earth cations and of the role such cations play in the determination of the properties of silicate melts is also of vital interest in geochemistry.

It is generally accepted that amorphous silicate materials exhibit a lack of structural order over extended internuclear distances and are characterized by a three dimensional framework of randomly connected silica tetrahedra. Because properties of geochemical interest such as melt viscosity, nucleation kinetics, and melt-solid element partitioning are all controlled by the breaking and forming of bonds, the focus of this work is on the elucidation of structure within atomic distances corresponding to the first two or three coordination shells.

This Gilbert Fellowship project has been in connection with several ongoing research programs at Stanford University, in particular with the geochemistry program of Professor Gordon Brown, School of Earth Sciences, and with Dr. Glen Waychunas, Center for Materials Research. The team effort is directed toward the development of a predictive theory for the behavior of the amorphous state of silicate materials. The thrust of this effort includes both experimental work at the Stanford Linear Accelerator Center (SLAC) Synchrotron Radiation Laboratory (SSRL) and theoretical work in the area of statistical mechanical simulations; the theoretical work will be reported elsewhere.

The lack of short-range structural information on melts and glasses is perhaps a reflection of the experimental difficulties associated with such measurements. Most x-ray, neutron or electron scattering methods and most spectroscopic techniques (XPS, Optical, ESR, NMR, Mossbauer) are either insensitive to the elements of geochemical interest or provide limited structural information. The main experimental method used for this work, and perhaps the only technique allowing the direct exploration of atomic structure on the 0.1-to-0.2 nanometer scale in non-crystalline materials, is based on the spectral fine structure in the region of x-ray absorption edges as a measure of the chemical environment of a given atomic species. It was recognized over sixty years ago^{1,2/} that x-ray absorption edge fine structure was sensitive to the chemical environment of the x-ray absorber. But because of experimental difficulties with the technique, and also because of conflicts between theoretical treatments of the phenomenon and experimental results, x-ray spectral fine structure has not been widely applied to practical problems. In 1932, Kronig^{3/} proposed a theory for x-ray fine structure observations in the energy range extending above the absorption edge. After considerable discussion of the phenomenon in the literature, the physics of the basic Kronig theory, based on short range order (SRO) of atoms in molecules, is still considered to be correct and also applicable to atoms in a Debye-type atomic network. In the briefest terms, the SRO theory provides that the photoelectron released on ionization serves as a probe of the chemical environment of the ionizing atom by experiencing a single scattering event off of the coordination shells of neighboring atoms.

There are three spectral regions of interest in the vicinity of an absorption edge. The peaks in the energy range just below the absorption edge, often due to bound-state transitions, are useful for understanding the site symmetry (or lack thereof) of the absorbing atom. The spectral region near the absorption edge, denoted XANES (x-ray absorption near edge structure), is sensitive to multiple photoelectron-scattering phenomena. And the energy region extending several hundred electron volts from just above the absorption edge, denoted EXAFS (extended x-ray absorption fine structure), arises from single photoelectron-scattering events.

A formalism that provided a quantitative basis for EXAFS was introduced by Sayers in 1971^{4/}. Sayers recognized that the frequency of the EXAFS wave modulations depends on the distance between the absorbing atom and the neighboring atom. Accordingly, information on distances corresponding to nearest neighbor coordination shells of atoms can be extracted by Fourier analysis of the EXAFS signal. The amplitude of the Fourier peak depends on the number of backscattering centers and on the scattering efficiency of the centers. Thus, the EXAFS region lends itself readily to quantitative interpretation in terms of the number of neighbors and interatomic spacings around a given atom. Because of disorder due to thermal vibrations of the condensed atomic network, EXAFS measures coordination shells at a given average distance from the ionizing atom^{5/}.

Conventional x-ray sources and spectrometers are still experimentally inadequate for EXAFS measurements. The high resolution required for fine structure measurements (1 eV), and the need for collimated beam optics, are handily satisfied by the radiation emitted by an electron storage ring operating in the 2-4 GeV energy range. Through the efforts of Professor Gordon Brown, the Stanford Linear Accelerator Synchrotron Radiation Laboratory has been made available for this study. Although our study is among the first systematic XANES and EXAFS investigations of the alkali and alkaline earth cations in mineral model compounds and in aluminosilicate glasses, others have carried out XANES and EXAFS measurements of Na^{6/}, K^{7,8/} and Ca^{9-13/} in a variety of inorganic and organic compounds.

EXPERIMENTAL

Calcium and potassium K-edge spectra were collected on the SSRL Beam Line I-5 using Si(111) monochromator crystals. The calcium model compounds studies included: CaTiO₃ (perovskite), CaCO₃ (aragonite), Ca₃Al₂Si₃O₁₂ (grossular), CaAl₂Si₂O₈ (anorthite), CaMgSi₂O₆ (diopside), CaTiSiO₅ (titanite), and CaCO₃ (calcite); in all cases Ca is coordinated by oxygens. Several Ca-containing glasses were also studied, including the compositions CaAl₂Si₂O₈, CaMgSi₂O₆, and a granite analogue.

Potassium spectra were collected with samples mounted inside a helium filled path. Model compounds included $\text{KA1}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ (muscovite), KAlSi_2O_6 (leucite), $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$ (nepheline), and KAlSi_3O_8 (microcline); glasses examined included the compositions KAlSi_3O_8 , $\text{K}_{.5}\text{Na}_{.5}\text{AlSi}_3\text{O}_8$ and a granite analogue. Additional work will be needed on the potassium.

Sodium was examined using total electron yield spectroscopy in a series of model compounds and glasses on the III-3 (2-degree) branch line (known as JUMBO). Detailed procedures followed for the experiments on the JUMBO line are outlined in Appendix A. Although the effective electron yield-depth was approximately $100 \text{ \AA}^{14/}$ under the conditions of the experiment, Stohr has shown that total electron yield EXAFS can be used to determine structural features of the bulk as well as of the surface. Measurements were made with beryl (1010) monochromator crystals over the energy range 1045 to 1480 eV; the measured resolution was 0.5 eV (FWHM). Na model compounds included $\text{NaAl}_{11}\text{O}_{17}$ (beta-alumina), $(\text{Na},\text{K})\text{Al}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ (paragonite), $\text{NaAlSi}_2\text{O}_6$ (jadeite), $\text{NaAlSi}_3\text{O}_8$ (albite), $\text{Na}_3\text{KA1}_4\text{Si}_4\text{O}_{16}$ (nepheline), $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ (analcime), and $\text{Na}_{.71}\text{WO}_3$ (a tungstate bronze). All were single crystals which were cleaved or fractured. Glass samples studied included the compositions Na_2SiO_3 , $\text{NaAlSi}_3\text{O}_8$, $\text{NaAlSi}_2\text{O}_6$, NaAlSiO_4 , $\text{Na}_{3.07}\text{Al}_{.05}\text{Si}_{3.16}\text{O}_8$, $\text{Na}_{1.87}\text{Al}_{.53}\text{Si}_{3.13}\text{O}_8$, $\text{Na}_{.83}\text{Al}_{1.05}\text{Si}_3\text{O}_8$, $\text{Na}_{.75}\text{Al}_{1.2}\text{Si}_{2.91}\text{O}_8$, and a granite analogue. Samples were placed in the SSRL VG chamber which was operated in the low 10^{-9} torr range (Appendix A). Analysis of the sodium XANES and EXAFS results have been published by one of our coworkers elsewhere^{16/}.

RESULTS AND DISCUSSION

Calcium K-XANES spectra for seven crystalline model compounds and three silicate glasses are shown in Fig. 1. The number of oxygen atoms coordinating Ca varies between eleven (in perovskite) and six (in calcite), the average Ca-O distance decreases, and the symmetry of the Ca site varies considerably in this series of model compounds.

All of the Ca edges shown in Fig. 1 have three common features centered at 4041.4, 4046.2, and 4051.0 eV; grossular, titanite, and calcite show a fourth feature at higher energies. The pre-edge feature (4041.4) varies in relative intensity and is almost absent in grossular where Ca occupies a triangular dodecahedral (D_2) site with a single Ca-O distance. We assign this peak to a symmetry forbidden 1s-3d transition following the assignment of Bianconi et al.^{11/} for calcium and suggest that its intensity variation is related to site symmetry. Bianconi assigned the second and third peaks in the Ca K-edge spectra of calcite to 1s-4s and 1s-4p transitions. More recent theoretical work on $K^{7,8/}$, $V^{20/}$, $Cr^{21/}$, and $Fe^{17/}$ K-edges for various metal complexes suggests that the main absorption feature is due to a shape resonance. We are not aware of any multiple scattered wave calculations of Ca-oxygen complexes and defer assignment of the second, third, and fourth peaks in our observed Ca K-XANES.

There appears to be only a slight increase in edge crest energy with increase in coordination number and Ca-O distance in the series calcite, titanite, diopside, anorthite, whereas the other three compounds, perovskite, aragonite and grossular, violate these trends. Powers et al.^{9/} observed a general correlation between Ca K-edge energy and Ca-O distance in several compounds and similar correlations have been observed for other elements.

The Ca K-edge spectra of anorthite and diopside composition glasses are similar to their crystalline analogues, suggesting a similarity of local Ca environments in glass and crystal. A comparison of the Ca K-XANES spectra for titanite crystal and glass shows a significant difference. Further details of the Ca environment in these glasses will be revealed when Fourier analysis of their Ca EXAFS spectra is completed.

The varying shape and fine structure of the Ca K-edges in this series suggests that the edge structure is sensitive to variations in coordination number, Ca-O distance, and/or site distortion. Recent multiple scattered wave calculations for metals and transition metal complexes ^{17-19/} indicate that second and third nearest neighbors also affect the general shape of absorption edges, however the effect of second and third nearest neighbors on the absorption edge of Ca has not been evaluated.

Sodium K-XANES spectra of all model compounds and glasses show three peaks centered at 1054.5, 1057.8, and 1061.9 eV. In contrast with the Ca K-edge

spectra, the Na spectra show no systematic variations in edge energies with changes in Na coordination or Na-O distance. Variations in the intensity of the pre-edge feature do occur and may be related to distortion of the Na site. Multiple scattered wave calculations are needed before accurate assignment of the Na K-edge features are possible. Quantitative analysis of the Na EXAFS spectra are discussed elsewhere^{16/}.

SUMMARY

During three experimental sessions at SSRL, we have been successful in making K-edge XANES and EXAFS measurements for Na, K, and Ca in a variety of model compounds and amorphous aluminosilicates. The Ca K-edge spectra of anorthite and diopside composition glasses were found to be similar to their crystalline analogues, suggesting a similarity of local Ca environments in glass and crystal. In contrast, a comparison of the Ca K-XANES spectra for titanite crystal and glass shows a significant difference, possibly reflecting disparity between their respective short-range environments. Sodium K-XANES spectra of all model compounds and glasses show three common peaks that appear to be insensitive to changes in Na coordination or Na-O distance. Variations in the intensity of the Na pre-edge feature do occur and may be related to distortion of the Na site.

Quantitative analysis of an EXAFS profile can identify the number of atoms and their distances surrounding the x-ray absorber. Unfortunately, quantitative interpretation of EXAFS in our experiments, although possible, has been limited by EXAFS signal truncation and poor signal-to-noise ratios in the EXAFS measurements. That notwithstanding, we are preparing (or identifying) computer software for such quantitative interpretation.

A quantitative theory for multiply scattered wave phenomena is still not available for the analysis of XANES spectra. However, we have found that our XANES spectra are remarkably useful as a qualitative fingerprint of the chemical environment of our target atoms, and we expect to have at least a semiquantitative treatment of XANES in the near future.

Appendix A

NOTES ON THE III-3 BRANCH LINE (JUMBO) PROCEDURES

The main components of the experimental set-up on the JUMBO line include (a) an ultra high vacuum system to accommodate beam-entry, samples, and channeltron detector, (b) electronics for analog signal manipulation, and (c) electronics for data collection and storage. Fig. 1A is a block diagram showing the relationships between the various experimental components.

As a matter of efficiency in the use of the beam-line, the sample chamber is usually prepared off-line in advance of the scheduled beam-time. Also, because long time required for chamber pump-down, all samples were mounted and installed in the vacuum chamber at the same time.

I Sample Preparation and Mounting

Inasmuch as total electron yield spectroscopy was used in the JUMBO line experiments, the thickness of the samples was not important. The samples were obtained from a variety of sources, most of which are discussed in detail elsewhere^{16/}.

The mechanical feed-through on the top of the VG chamber permitted about six inches of vertical travel. We attached two 1.5 x 13 cm titanium strips to the stub of the mechanical feed-through and mounted the samples, six or seven per side, on the vertically suspended strips (the mechanical feed-through permitted rotation through 360°). In this work, we mounted 27 samples for consecutive examination without having to break vacuum. The samples, cut to be roughly rectangular and approximately 5 x 10 mm, were secured to the titanium strips with platinum wire which itself was spot-welded to the edge of the strips. In order to delimit the samples under illumination from the synchrotron radiation beam, a spot of phosphor was swabbed onto the metal strip in between each sample.

II Chamber Preparation

Tools and materials: Before work is actually started on the chamber, the chamber should be moved to a preparation area in the vicinity of the beam-line where it will be used. The following tools and materials should be on hand.

1. Clean gloves (for handling gaskets)
2. Gaskets (copper) sufficient for the flanges to be mounted
3. Ethanol (absolute)
4. Dust-free Kimwipes
5. Aluminum foil (to cover open ports and to hold clean gaskets)
6. Wrenches to fit nuts and bolts (open end and box style)
7. Torque wrench for valves
8. Flushing flange (Inlet for dry nitrogen) with pressure relief
9. Source of dry nitrogen (House nitrogen is the best, but pressure greater than 2 psig should not be applied to chamber)
10. Heater tapes sufficient to cover the chamber
11. Variac(s) to control power to the heater tapes

Chamber preparation: The following steps were followed in the preparation of the VG chamber off-line. (a) chamber venting and flushing (usually the chamber is under vacuum when unused), (b) mounting of sample manipulator (loaded with samples), detector(s), and suitable valves and vents, and (c) chamber pump-down and bake. The chamber is vented with a source of clean dry nitrogen throughout all procedures. Clean room procedures are practiced when handling any item that will be exposed to vacuum. Finally, the chamber is pumped-down with a portable pump mounted on a cart and baked off-line.

Pumping system: The pumping system on the portable pump cart consist of four units. These include the rough pump (oilless), dual sorption pumps, a vac-ion pump, and a titanium sublimation pump (TSP). Diffusion pumps are not used because a clean vacuum is required. The pumping system on the chamber itself consists of two units, a large vac-ion pump and a TSP.

Bakeout: The entire system, including the vac-ion pump on the chamber, is baked to approximately 200°C. Aluminum foil is first applied to the chamber and heater tapes then wrapped over the foil. After an additional layer of foil is applied over the heater tapes, a heater blanket is wrapped over the chamber. The power applied to the heater tapes is controlled by a variac. A minimum period of about ten hours is needed to cycle the temperature of the chamber to 200°C and back to room temperature. An extended pumpdown period may be required while the temperature of the chamber is held between 150-200°C.

Pumpdown procedure: The system is pumped down in a three step sequence (the sorption pumps should have been baked for at least two hours to atmosphere before the start of this procedure). (1) The entire system, including the RT-sorption pumps and vac-ion pumps, is roughed to 1 Torr with the mechanical rough pump. (2) At this point, the mechanical pump and the strongest sorption pump are VALVED-OFF. Both sorption pumps are cooled with liquid nitrogen. When the pressure stops decreasing in the system, the weakest sorption pump is valved-off and the strongest sorption pump opened to the system. When the system pressure falls to near 10 millitorr (micron), the TSPs and both vac-ion pumps are valved-off along with the sorption pump. The vac-ion pumps are then energized and allowed to pump on themselves and on the TSPs. Once the vac-ion pumps are properly running (current less than a few milliamp), the TSPs can be "burped" into the vac-ion pumps by operating the pumps for about ten seconds (the pressure within the vac-ion pumps should be carefully watched). The vac-ion pumps can then be opened to the system very slowly so that they will not be shut-down by the surge of gas into the pumps. Once the vac-ion pumps are fully opened, the TSPs can be cycled for a minute or so to assist the vac-ion pumps in pumping the system down to the desired pressure. The TSPs do not have to be water cooled if used intermittently.

III. Installation of Chamber On-Line

There is only one guideline to keep in mind during chamber installation and sample selection: If you can't see the beam on a phosphor when the chamber is more or less lined-up, max-search (the electronically controlled component of the double crystal spectrometer that peaks-up the spectral output) has probably failed and the maximum amount of beam power is not being output from the DC-spectrometer.

IV Line Operation, Electronics, & Software

Procedures for line operation of the spectrometers and electronics are outlined in suitable operation manuals written for each beam-line by the SSRL staff. The data acquisition systems, usually a PDP-11/34 running RT-11 or RSX, are also provided by SSRL for each beam-line. All software for data acquisition is provided with suitable operation manuals.

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SIGNAL PROCESSING CIRCUITRY

