

Structural environment of Al dissolved in $2\text{PbO}\cdot\text{B}_2\text{O}_3$ glasses used for solution calorimetry: An ^{27}Al NMR study

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ABSTRACT

^{27}Al NMR spectroscopy of glassy $2\text{PbO}\cdot\text{B}_2\text{O}_3$ calorimetric fluxes containing from 1.0 to 23.8 mol% Al [from dissolved $\alpha\text{-Al}_2\text{O}_3$ or $\text{NaAlSi}_3\text{O}_8$ (albite) glass] shows that about 92% of the Al is in fourfold coordination to oxygen [Al(4)] with the remainder mostly in sixfold coordination to oxygen [Al(6)] and that the chemical shifts and Al(4)/Al(6) ratios do not change measurably in this composition range. Some spectra appear to contain a small (<2%) peak at about 30 ppm, which may be due to fivefold coordinated Al [Al(5)] (Risbud et al., 1987) or Al(4) with four B next-nearest neighbors (Dupree et al., 1985). The enthalpy of solution of Al_2O_3 in $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at 700°C is independent of composition in the range 0.5 to ~ 6 mol% Al, with possible changes at higher concentrations (which may be related to slow rates of dissolution). The NMR results provide a structural basis for the observed Henry's law behavior of the enthalpies of solution.

The presence of Al in several different coordinations in these glasses is consistent with ^{27}Al NMR data for other B-containing glasses and may represent coupling of the B(3)-B(4) and Al(4)-Al(6) equilibria.

INTRODUCTION

High-temperature solution calorimetry in molten $2\text{PbO}\cdot\text{B}_2\text{O}_3$ is a well-established method to determine enthalpies of formation of refractory materials, including many of geologic importance (Charlu et al., 1975; Navrotsky, 1977; Carpenter et al., 1983; Akaogi et al., 1984). The interpretation of enthalpy of solution data is greatly simplified if the heats of solution depend neither on solute concentration nor on the presence of small amounts of other dissolved solutes (i.e., that Henry's law is obeyed). Repeated calorimetric experiments have verified this assumption for oxide concentrations of less than ~ 1 wt% (Charlu et al., 1975; Navrotsky et al., 1986; Navrotsky, unpub. data). This paper presents the results of an ^{27}Al solid-state NMR study demonstrating that the structural environment of Al in $2\text{PbO}\cdot\text{B}_2\text{O}_3$ fluxes does not change significantly for Al concentrations between 1.0 and 23.8 mol% Al, supporting the Henry's law behavior observed in calorimetry.

EXPERIMENTAL METHODS

Sample preparation

The $2\text{PbO}\cdot\text{B}_2\text{O}_3$ starting material used in this study was from a master batch (~ 50 kg) of calorimetric flux previously prepared

from reagent-grade PbO and H_3BO_3 . This batch has been analyzed repeatedly for Pb by X-ray fluorescence spectroscopy to verify composition and homogeneity. For the experiments described here, batches of approximately 15 g of the flux were fused at $\sim 740^\circ\text{C}$ in a Pt crucible, air-cooled to a glass in the crucible, and weighed. Dried $\alpha\text{-Al}_2\text{O}_3$ (corundum) or $\text{NaAlSi}_3\text{O}_8$ (albite glass) were weighed and added to the glassy flux in the Pt crucible. Table 1 lists the compositions used. The flux plus solute mixtures were then melted at $\sim 740^\circ\text{C}$ for 1 to 2 h (less time for lower concentrations of solute). During this time the solution was agitated vigorously and repeatedly with a Pt stirrer to ensure homogeneity. The solution was then air-quenched by pouring into a graphite bowl. The product was a transparent yellow glass. The glass samples were examined in immersion oils with a petrographic microscope to verify the absence of any crystals.

Spectroscopic methods

All spectra were obtained with a "home-built" 11.7-T spectrometer using the methods described by Kirkpatrick et al. (1985a) and Turner et al. (1986). A pulse width equal to one-sixth of the 90° pulse for the standard solution was used to ensure that signal intensity is not substantially dependent on quadrupole coupling constant (Fenzke et al., 1984). The standard solutions used were 1M AlCl_3 for ^{27}Al and $\text{BF}_3\cdot\text{Et}_2\text{O}$ (boron trifluoride etherate) for ^{11}B . Peak positions (chemical shifts at maximum intensity) are reported as the parts per million (ppm) difference in frequency

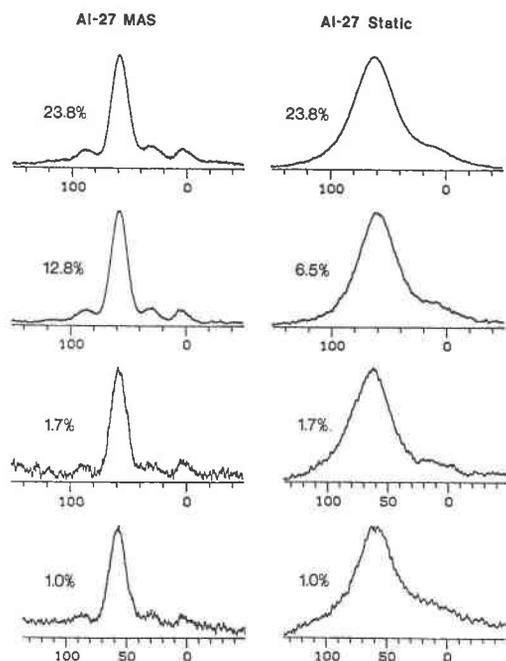


Fig. 1. ²⁷Al NMR spectra of Al-containing 2PbO·B₂O₃ glasses obtained at a field strength 11.7 T. Left-hand column shows MASS spectra obtained at a spinning speed of about 4 kHz, and right-hand column shows static spectra. The number next to each spectrum is the mol% Al in that sample. All chemical shifts are in ppm from 1M AlCl₃ solution. See text for spectrometer conditions.

between the standard solution and the sample. The recycle times used, 1 s for ²⁷Al and 5 s for ¹¹B, were more than sufficient to avoid signal saturation. Because of the low Al concentration, between 600 and 48 000 free induction decays (FID) were collected to produce the ²⁷Al spectra. The larger number of FIDs were used for the lower Al concentrations to ensure an adequate signal-to-noise ratio. Exponential multiplication resulting in an artificial line broadening of 65 Hz (~0.5 ppm) was employed to improve the signal to noise of all ²⁷Al spectra.

The magic-angle sample spinning (MASS) spectra were collected with two sample probes. One probe has a low Al-background signal, but has a maximum spin rate of about 4 kHz. This rate places spinning sidebands from Al(4) at ~90 and 30 ppm, obscuring any resonance that may be present near 30 ppm. Spin-

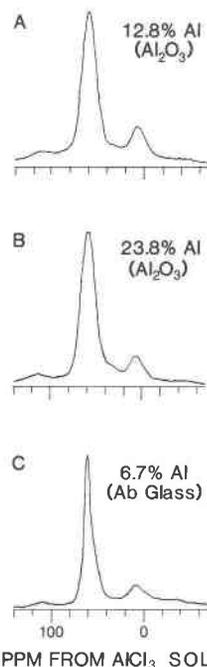


Fig. 2. ²⁷Al MASS NMR spectra obtained at 11.7 T and spinning speeds of between 7.0 and 7.5 kHz. In these spectra the spinning sidebands from the Al(4) peak are at about 115 and 0 ppm, and a small peak at about 30 ppm is seen in spectra A and B (prepared using α-Al₂O₃ solute) but not in spectrum C (prepared using Ab glass solute). This peak may be due to either Al(5) or to Al(4) with four B next-nearest neighbors. Fast-spinning spectra from samples with less than 6 mol% Al have a relatively larger background signal that obscures the region near 30 ppm.

ning more slowly produces four overlapping spinning sidebands between the tetrahedral and octahedral peaks [two from Al(4) and two from Al(6)], once again obscuring any resonance near 30 ppm. Therefore a second, faster-spinning probe was also used to obtain ²⁷Al MASS spectra. The second probe can attain spinning speeds of 7–8 kHz, which puts spinning sidebands from Al(4) at about 110 and 0 ppm. Unfortunately, this probe has a large Al(6) background signal centered near 0 ppm. Therefore, ²⁷Al MASS spectra were obtained using both sample probes. The static ²⁷Al spectra and the ¹¹B MASS spectra were collected with the slower-spinning probe.

TABLE 1. Sample compositions and ²⁷Al MASS NMR data

Solute	Solute (g)	Flux (g)	Moles Al/ moles solution	Al(4) MASS peak maximum (ppm)	Al(6) MASS peak maximum (ppm)	% Intensity of Al(6) peak
α-Al ₂ O ₃	0.015 28	15.0259	0.0102	55.8 ± 1.5	4.0 ± 2.0	6.0 ± 2.0
α-Al ₂ O ₃	0.025 38	15.0027	0.0170	57.7	4.0	10.0
α-Al ₂ O ₃	0.050 49	15.0399	0.0334	56.2	4.0	6.5
α-Al ₂ O ₃	0.100 68	15.0503	0.0655	57.3	2.0	6.5
α-Al ₂ O ₃	0.203 96	15.0476	0.1284	58.1	2.0	7.0
α-Al ₂ O ₃	0.400 83	15.0333	0.2378	57.5	4.0	8.0
Ab glass	0.110 16	15.0490	0.0142	56.0	1.0	6.5
Ab glass	0.225 42	15.0529	0.0286	55.6	4.0	8.0
Ab glass	0.550 56	15.0894	0.0670	55.4	1.0	4.5

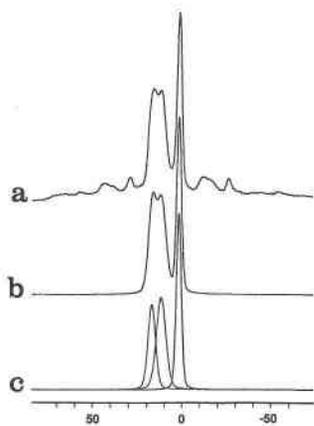


Fig. 3. ¹¹B MASS NMR spectrum and its deconvolution for 2PbO·B₂O₃ base glass. (a) ¹¹B MASS spectrum obtained at 11.7 T. The B(3) doublet has maxima at 15.5 and 11.6 ppm, and the B(4) singlet has a maximum at 1.4 ppm. (b) Simulated composite peak obtained using the curve-fit program NMRCAP; spinning side bands not modeled. (c) Component peaks for the simulated spectra. The two overlapping peaks at the left are in reality a single quadrupolar split peak, but this does not affect the modeled B(3)/B(4) ratio.

RESULTS AND DISCUSSION

The ²⁷Al ~4-kHz MASS spectra (Fig. 1) clearly show peaks for Al(4) at about 50 ppm and Al(6) at about 3 ppm (chemical shifts summarized in Table 1). The peaks at about 90 and 30 ppm are spinning sidebands from the Al(4) peak. The static spectra (Fig. 1) also show an Al(4) peak at about 60 ppm and an Al(6) shoulder at about 0 ppm, although the peaks are not as well resolved owing to orientation-dependent broadening effects (Kirkpatrick et al., 1985b). The peaks near 0 ppm in the static spectra confirm that the peaks near 0 ppm in the MASS spectra are not spinning sidebands, but represent signal from Al(6) sites.

The MASS spectra obtained at about 7 kHz (Fig. 2) are less useful because of Al(6) background in the probe, but do show the presence of a very small peak at about 30 ppm for the more-concentrated samples made with Al₂O₃. This peak is not present for the most Al-rich sample made with albite glass solute. We cannot determine whether this peak is present for samples having lower concentrations of Al because of the probe background signal. In these faster-spinning-speed spectra, the peaks at about 110 ppm and -50 ppm are spinning sidebands. The relative intensity of the peak for Al(6) appears to increase with decreasing Al content of the sample, owing to the increasing relative contribution from the broad Al(6) probe background.

The significance of the small peak at about 30 ppm is not clear. Dupree et al. (1985) have assigned it to Al(4) with four B next-nearest neighbors. Risbud et al. (1987), however, have observed it in spectra of SiO₂-Al₂O₃ glasses and have assigned it to pentahedrally coordinated Al

[Al(5)]. There are few model compounds with ²⁷Al chemical shifts in this range, and discrimination between these two possible assignments is not currently possible. The absence of the peak at about 30 ppm for the most-concentrated sample made with albite glass solute may indicate that the presence of Si or Na in the glass changes the structural environment giving rise to this peak. Since the total intensity of this peak is low ($\leq 2\%$) and its assignment so poorly understood, further interpretation is unwarranted.

With the exception of the small peak at ~30 ppm, the ²⁷Al spectra of all the samples are essentially identical. The Al(4) and Al(6) chemical shifts are essentially identical within experimental error. What small variation there is (56.5 ± 1.5 ppm and about 2 ± 2 ppm) is not systematic with Al content and is likely due primarily to poor signal-to-noise ratio for some spectra, small phasing errors, and to overlap of the Al(6) peak and the second spinning sideband from the Al(4) peaks. Similarly, the area of the Al(6) peak relative to that for Al(4) is essentially constant at $8 \pm 2\%$ (as determined by computer simulation using the Nicolet program NMRCAP and the 4-kHz MASS spectra). Because these spectra were obtained under short-pulse-width conditions, this peak area probably represents the relative abundance of Al(6) in the sample (Fenzke et al., 1984; Kirkpatrick et al., 1986). The presence of a very broad peak due to sites with very large quadrupole coupling constant (≥ 15 MHz) cannot be ruled out but seems unlikely. The quantitation method of Kirkpatrick et al. (1986) cannot be used for these samples because of the multiple peaks.

These spectroscopic results are fully consistent with calorimetric experiments, which show that reproducible and constant enthalpies of solution are obtained up to a maximum of 50 to 100 mg of solute per 15 g of 2PbO·B₂O₃ flux (corresponding to 3 to 6 mol% Al for α -Al₂O₃ solute) (Navrotsky, 1977, and unpub. results). At higher concentrations, somewhat erratic results are obtained. These may represent a real concentration dependence of the enthalpy of solution or may be due to the observed decrease in the rate of dissolution, causing incomplete reaction during a calorimetric experiment. The constancy of chemical environment over a wide concentration range inferred from the NMR experiments provides a structural basis for the observed Henry's law behavior of the heats of solution.

We have also obtained a ¹¹B spectrum of the 2PbO·B₂O₃ calorimetric glass (Fig. 3). Signal for both trigonally coordinated B [B(3)] between 7 and 20 ppm (split and broadened owing to second-order quadrupolar effects) and tetrahedrally coordinated B [B(4)] at 1.4 ppm are readily distinguished (Turner et al., 1986). Simulation of this spectrum yields a B(4)/[B(3) + B(4)] value of $0.38 (\pm 0.03)$, in excellent agreement with the results obtained by Kim et al. (1976) using wide-line ¹¹B NMR methods.

The ²⁷Al spectra presented here provide further evidence that Al commonly exists in more than one coordination in glasses containing both Al and B (Schiller et al., 1982; Dupree et al., 1985; Oestrike et al., 1986; Hah-

nert and Hallas, 1986). In contrast, aluminosilicate glasses containing no B do not have detectable amounts of nontetrahedral Al if the ratio of Al/(M⁺ + 0.5M²⁺) is less than unity (i.e., peralkaline and framework compositions; Riebling, 1966; Taylor and Brown, 1979; Mysen et al., 1981; McMillan and Piriou, 1983; Oestrike and Kirkpatrick, in prep.). This difference suggests that the stabilization of nontetrahedral Al may be due to coupling between the B(3)-B(4) equilibria and the Al(4)-Al(6)-Al(5) equilibria, because borate and borosilicate glasses usually contain both B(3) and B(4) (Bray, 1985, and reference therein).

Although the ²⁷Al NMR data presented here appear to confirm the lack of change in the structural environment of Al suggested by the calorimetric results, one note of caution is that NMR spectra were obtained for glasses, whereas the solution calorimetric data were obtained for melts of the same composition. At present there is no fully effective way of assessing possible changes in the Al environment during the glass transition. Several studies suggest, however, that major structural changes in the nearest-neighbor configurations do not occur between the molten and glassy states (Riebling, 1966, 1967; Waseda and Toguri, 1977; Seifert et al., 1981; Domine and Piriou, 1983; Hochella and Brown, 1984, and references therein), and we believe that it is unlikely that there are significant changes in local coordination during quenching.

ACKNOWLEDGMENTS

This work was supported by NSF Grants EAR 8513916 (A.N.) and EAR 8408421 (R.J.K.). We wish to thank J. Stebbins and M. F. Hochella, Jr., for reviews that have improved this paper and Brian Phillips for the deconvolutions of the ²⁷Al mass spectra.

REFERENCES

- Akaogi, M., Ross, N.L., McMillan, P., and Navrotsky, A. (1984) The Mg₂SiO₄ polymorphs (olivine, modified spinel and spinel)—Thermodynamic properties from oxide melt solution calorimetry, phase relations, and models of lattice vibrations. *American Mineralogist*, 69, 499–512.
- Bray, P.J. (1985) Structural models of borate glasses. *Journal of Non-Crystalline Solids*, 75, 29–36.
- Carpenter, M.A., Putnis, A., Navrotsky, A., and McConnell, J.D.C. (1983) Enthalpy effects associated with Al/Si ordering in anhydrous Mg-cordierite. *Geochimica et Cosmochimica Acta*, 47, 899–906.
- Charlu, T.V., Newton, R.C., and Kleppa, O.J. (1975) Enthalpy of formation at 975°K of compounds in the system MgO-Al₂O₃-SiO₂ from high temperature solution calorimetry. *Geochimica et Cosmochimica Acta*, 39, 1487–1497.
- Domine, F., and Piriou, B. (1983) Study of sodium silicate melt and glass by infrared reflectance spectroscopy. *Journal of Non-Crystalline Solids*, 55, 125–130.
- Dupree, R., Holland, D., and Williams, D.S. (1985) An examination by magic-angle spinning NMR of the changes in the environment of ²⁷Al during the devitrification of an aluminoborate glass. *Physics and Chemistry of Glasses*, 26, 50–52.
- Fenzke, D., Freude, D., Frohlich, T., and Haase, J. (1984) NMR intensity measurements of half-integer quadrupole nuclei. *Chemical Physics Letters*, 111, 171–175.
- Hahnert, M., and Hallas, E. (1986) Zur aluminum koordinaton in aluminoborate-glasern. *Zeitschrift für Chemie*, 26, 144–145.
- Hochella, M.F., Jr., and Brown, G.E., Jr. (1984) Structure and viscosity of rhyolitic composition melts. *Geochimica et Cosmochimica Acta*, 48, 2631–2640.
- Kim, K.S., Bray, P.J., and Merrin, S. (1976) Nuclear magnetic resonance studies of the glasses in the system PbO-B₂O₃-SiO₂. *Journal of Chemical Physics*, 64, 4459–4465.
- Kirkpatrick, R.J., Kinsey, R.A., Smith, K.A., Henderson, D.M., and Oldfield, E. (1985a) High-resolution solid-state sodium-23, aluminum-27, and silicon-29 nuclear magnetic resonance spectroscopic reconnaissance of alkali and plagioclase feldspars. *American Mineralogist*, 70, 106–123.
- Kirkpatrick, R.J., Smith, K.A., Schramm, S., Turner, G., and Yang, W.H. (1985b) Solid-state nuclear magnetic resonance spectroscopy of minerals. *Annual Review of Earth and Planetary Science*, 13, 29–47.
- Kirkpatrick, R.J., Oestrike, R., Weiss, C.A., Jr., Smith, K.A., and Oldfield, E. (1986) High-resolution ²⁷Al and ²⁹Si NMR spectroscopy of glasses and crystals along the join CaMgSi₂O₆-CaAl₂SiO₆. *American Mineralogist*, 71, 705–711.
- McMillan, P., and Piriou, B. (1983) Raman spectroscopic studies of silicate and related glass structure—A review. *Bulletin de Minéralogie*, 106, 57–75.
- Mysen, B.O., Virgo, D., and Kushiro, I. (1981) The structural role of aluminum in silicate melts—A Raman spectroscopic study at 1 atmosphere. *American Mineralogist*, 66, 678–701.
- Navrotsky, A. (1977) Recent progress in high temperature calorimetry. *Physics and Chemistry of Minerals*, 2, 89–104.
- Navrotsky, A., Wechsler, B.A., Geisinger, K., and Seifert, F. (1986) Thermochemistry of MgAl₂O₄-Al₂O₃ defect spinels. *American Ceramic Society Journal*, 69, 418–422.
- Oestrike, R., Yang, W.H., Montez, B., Turner, G.L., and Navrotsky, A. (1986) Applications of high resolution NMR to aluminosilicate glass structure. *International Mineralogical Association Abstracts with Program*, 188–189.
- Riebling, E.F. (1966) Structure of sodium aluminosilicate melts containing at least 50% SiO₂ at 1500°C. *Journal of Chemical Physics*, 44, 2857–2865.
- (1967) Structural relationships between the liquid and glass states for binary and ternary oxide systems: A density study. *Revue Internationale de hautes Temperatures et des Refractaires*, 4, 65–76.
- Risbud, J., Kirkpatrick, R.J., Tagliavere, A.P., and Montez, B. (1987) Solid-state NMR evidence of 4-, 5-, and 6-fold aluminum sites in roller-quenched SiO₂-Al₂O₃ glasses. *American Ceramic Society Journal*, 70, C10-C12.
- Schiller, W., Muller, D., and Scheler, G. (1982) ²⁷Al-NMR-Untersuchungen zur reaktion von alkali-aluminoborosilicat-glasern mit korund beim sintern. *Zeitschrift für Chemie*, 22, 44–45.
- Seifert, F.A., Mysen, B.O., and Virgo, D. (1981) Structural similarity of glasses and melts relevant to petrological processes. *Geochimica et Cosmochimica Acta*, 45, 1879–1884.
- Taylor, M., and Brown, G.E., Jr. (1979) Structure of mineral glasses—I. The feldspar glasses NaAlSi₃O₈, KAlSi₃O₈, CaAl₂Si₂O₈. *Geochimica et Cosmochimica Acta*, 43, 61–75.
- Turner, G.L., Smith, K.A., Kirkpatrick, R.J., and Oldfield, E. (1986) Boron-11 nuclear magnetic resonance spectroscopic study of borate and borosilicate minerals, and a borosilicate glass. *Journal of Magnetic Resonance*, 67, 544–550.
- Waseda, Y., and Toguri, J.M. (1977) The structure of molten binary silicate systems CaO-SiO₂ and MgO-SiO₂. *Metallurgical Transactions B*, 8B, 563–568.

MANUSCRIPT RECEIVED APRIL 23, 1986

MANUSCRIPT ACCEPTED MARCH 23, 1987