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Cover: *Bulk glassy TeO_2 made at Coe College; taken from Figure 28, this issue pages 153–167.*

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A 44 Year Search:

How do the fundamental physical properties of borate glass reveal its underlying atomic structure: an adventure with undergraduates

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In this career review article, I have gone over several key accomplishments that span nearly half a century. The review is divided between my work done at Brown University, as a graduate student (1973–1979), and work done with hundreds of undergraduate physics students at Coe College, as well as with dozens of collaborators around the world (1979–2017). Several important aspects of the work are discussed, including how it was possible to work productively with undergraduates over a large number of years. Spectroscopic and physical property results led to comprehensive models that relate glass structure to property. Data from this research have been made available to researchers through publishing in the literature of the field, as well as in other places such as the SciGlass database. Also, this paper includes selected student outcomes, and a comprehensive list of collaborators and funding sources.

A.1 Graduate school at Brown University with Phil Bray

In fall 1973, I entered graduate school at Brown University in Providence, Rhode Island. By the end of that first year of graduate study in physics, I began my journey into glass science. I joined Phil Bray's research group that made much use of nuclear magnetic resonance (NMR) to study the atomic structure of glass.

Use it they did! From the first report of ^{11}B NMR in borates,[1] the group was the pioneer in NMR in glass, and was at a world class level until the 1990s. I was present during the group's heyday, at the time that ^{10}B, ^{17}O and ^{29}Si NMR was first being done, and when well known models for alkali borosilicate glasses were being developed. I need not repeat the details of those accomplishments, since Phil himself wrote a series of review papers,[2,3] prior to his death in 2004. My own work focused on the following areas:

1. ^{7}Li motional narrowing NMR experiments on mixed alkali glasses.
2. ^{11}B NMR on a wide range of compositions in the lithium borate system.
3. Doing third-order perturbation calculations of the integer spin quadrupole perturbation of the Zeeman NMR interaction (only the 1→0 and 0→−1 transitions). This was then used to determine the spin 3 powder patterns resulting from a large number of ^{10}B enriched borate short range structures oriented randomly in a glass or a polycrystalline powder.
4. ^{10}B NMR on lithium borate glasses enriched in ^{10}B, fitting the data using the theory from step three, and developing models for the intermediate range order in these glasses.
5. Making lithium oxide enriched in ^{17}O, and verifying the presence of ^{17}O.
6. Using the lithium oxide enriched in ^{17}O to produce polycrystalline lithium metaborate and lithium orthoborate.
7. Performing ^{7}Li, ^{11}B, and ^{17}O NMR on the resulting compounds of steps five and six. The spectra were deconvoluted to find the quadrupole parameters of these nuclei.
8. Doing a Townes–Daily[4] calculation with the results of step six to determine the charge densities on the boron, bridging oxygens, and the nonbridging oxygens.

This resulted in six journal papers:
"B^{10} NMR Studies of Lithium Borate Glasses,"[5]
"Preparation of O^{17}-Labelled Glass and Glass Precursers,"[6]
"B^{10} NMR Studies of the Structure of Borate Glasses,"[7]
"Correction and Addendum to "Nuclear Magnetic Resonance Studies of the Glasses in The System Na_2O–B_2O_3–SiO_2,"[8]
"A Re-examination of the Fraction of 4-Coordinated Boron Atoms in the Lithium Borate Glass System,"[9]
"NMR Powder Patterns for Integer Spin Nuclei in

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Original version presented at IX Int. Conf. on Borate Glasses, Crystals and Melts, Oxford, UK, 23–26 July 2017
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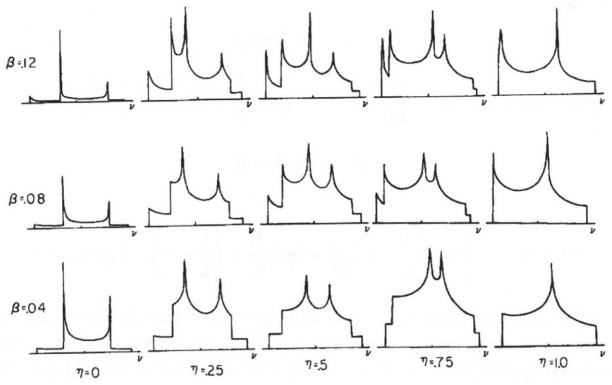


Figure 1. Calculated ^{10}B NMR powder patterns for the 1→0 and 0→−1 transitions.[10] $\beta=\nu_Q/\nu_0$, where $\nu_Q=3Q_{cc}/(2I)(2I-1)$ and ν_0 is the Larmor frequency. η is the quadrupole asymmetry parameter, a measure of axial symmetry. Reproduced with permission from Elsevier

the Presence of Asymmetric Quadrupole Effects."[10]

Some highlights of this work are described below in sections A.1.1, A.2.2 and A.1.3.

A.1.1 Calculation of spin-3 quadrupolar-broadened powder patterns

The calculated spin-3 quadrupolar-broadened powder patterns are shown in Figure 1.

The patterns were determined for the two central transitions, 1→0 and 0→−1, since, out of the possible six transitions, they were the only two that could be observed back then.[10]

A.1.2 Determination of N_4, the fraction of four-coordinated borons in lithium borate glasses

The fraction, N_4, of four-coordinated borons in lithium borate glasses was determined using signal averaging and numerical integration compared with single standard-driven measurements done earlier by O'Keefe & Bray,[11] see Figures 2 and 3.

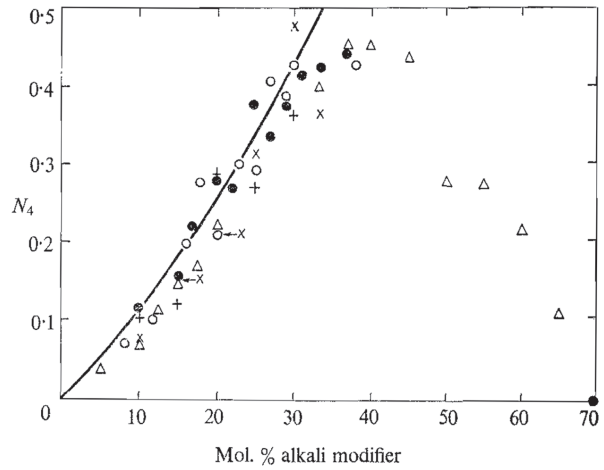


Figure 2. The fraction of four-coordinated borons as a function of the molar percentage of alkali oxide in alkali borate glasses, from O'Keefe & Bray[11]

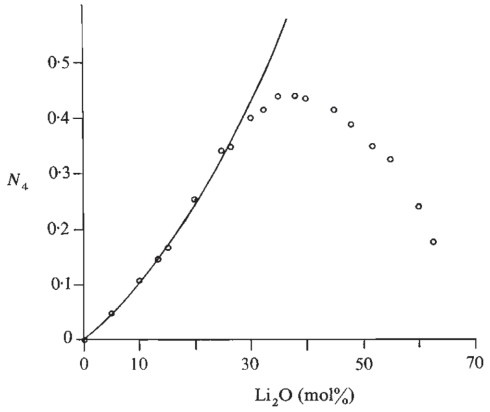


Figure 3. The fraction of four-coordinated borons in lithium borate glasses as a function of the lithium oxide molar percentage, from Jellison, Feller & Bray[9]

A.1.3 ^{10}B NMR spectra with computer fitting for lithium borate glasses enriched in ^{10}B

The ^{10}B NMR responses from a wide variety of lithium borate glass compositions may be seen in Figure 4. The fits in Figure 4 resulted in the model for the intermediate range order within lithium borate glasses depicted in Figure 5.[5,12] This model is consistent with several others offered up over the years. For example, while a direct connection to Youngman & Zwanziger's work[12] is difficult, it is certainly consistent with their findings of boron oxide groups in rings.

A.2 Off to Coe College

In July 1979, I defended my thesis and made my way from Brown University to Coe College in Cedar Rapids, Iowa. Coe College is one of about 30 liberal arts colleges in Iowa; these are schools that have just undergraduate students. At the time I carefully considered where I wanted to work, and settled on a college where teaching came first.

Shortly thereafter, I began to work on research with Coe College undergraduates, and as time went by doing research with students became a major part of my teaching. Since that time, and with the collaboration of Mario Affatigato, first as a student from 1986 to 1989, and later as a professor since 1995, we have worked with over 300 undergraduates in research. My projects have been numerous, and some highlights are given here with a focus on borates.

These projects have included forming new glasses of unusual compositions using various methods such as roller quenching. The first of these efforts was in the sodium borate system,[13] see Figure 6. The following sections (B, C, D) report, among other things, extended glass forming ranges in many glass forming systems, including virtually all alkali and alkaline earth borates. In addition, we have studied extended glass formation in alkali silicates, lead borates and

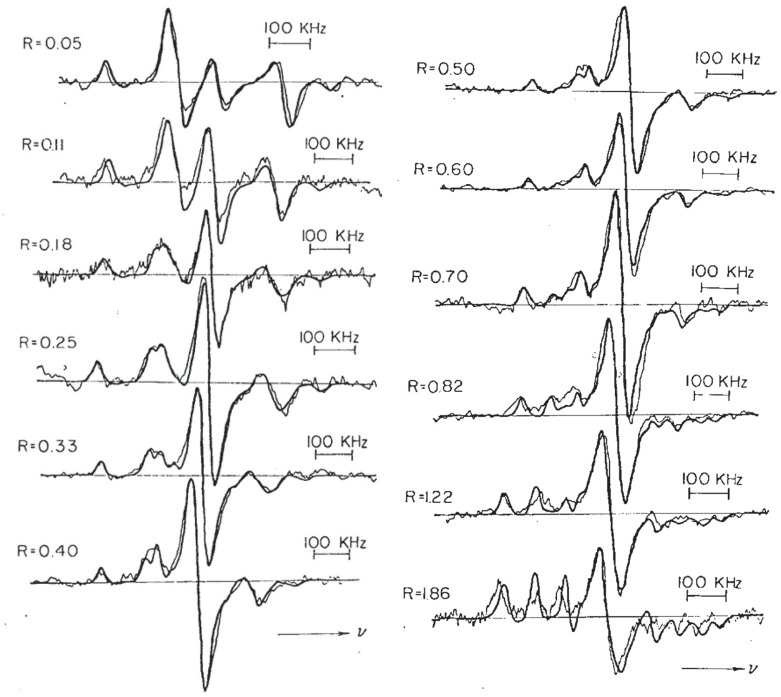
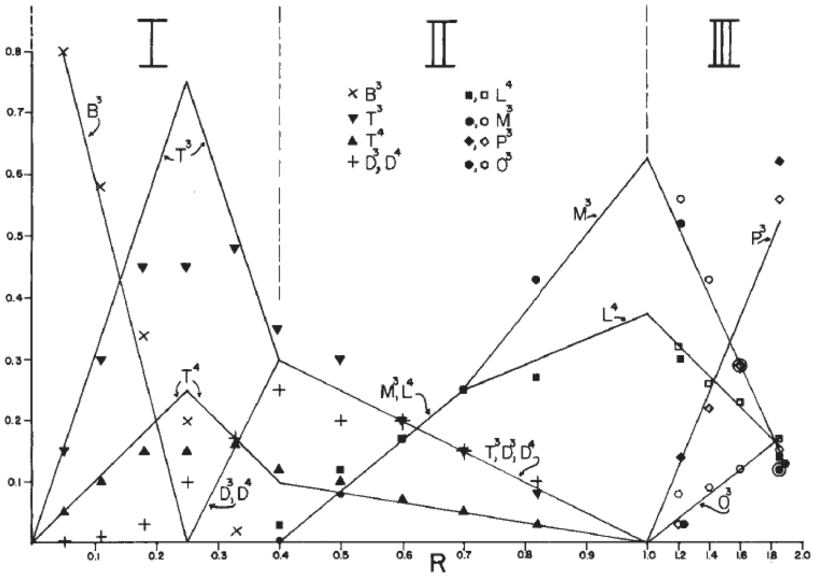


Figure 4. ^{10}B derivative NMR spectra from the two central transitions (1→0 and 0→–1) for lithium borate glasses.[5] R is the molar ratio of lithium oxide to boron oxide. Reproduced with permission from Elsevier

Figure 5. Model for superstructual group fractions in lithium borate glasses.[5] B^3, T^3, T^4, D^3, D^4, L^4, M^3, P^3, O^3 are the fractions of borons in various short and intermediate range structures. B = boroxol rings, T = Tetraborate units, D = diborate rings, L= are loose tetrahedra, M = metaborate groups, P are pyroborate units and O are isolated orthoborate triangles. The superscript 3 or 4 represents the coordination of the boron in each respective unit. Reproduced with permission from Elsevier

Region I $0 \leqslant R < 0.4$	*Region IIa* $0.4 \leqslant R < 0.7$
Allowed units: B^3, T^3, T^4, D^3, D^4	Allowed units: T^3, T^4, D^3, D^4, L^4, M^3
$B^3 = 1 - 4R + 2D^3$	$M^3 = \frac{5}{6}R - \frac{1}{3}$
$D^3 = D^3$	$D^3 = D^3$
$T^3 = 3\,(R - D^3)$	$T^3 = 1 - R - D^3$
$D^4 = D^3$	$D^4 = D^3$
$T^4 = R - D^3$	$T^4 = \frac{1}{3}(1 - R - D^3)$
$N_4 = R$	$L^4 = \frac{1}{2}R - \frac{2}{3}D^3$
	$N_4 = \frac{1}{3} + \frac{1}{6}R$
Region IIb $0.7 \leqslant R < 1.0$	*Region III* $1.0 \leqslant R \leqslant 1.86$
Allowed units: T^3, T^4, D^3, D^4, L^4, M^3	Allowed units: L^4, M^3, P^3, O^3
$M^3 = \frac{5}{4}R - \frac{5}{8}$	$M^3 = \frac{11}{8} - \frac{3}{4}R + O^3$
$D^3 = D^3$	$P^3 = R - 1 - 2O^3$
$T^3 = 1 - R - D^3$	$O^3 = O^3$
$D^4 = D^3$	$L^4 = \frac{5}{8} - \frac{1}{4}R$
$T^4 = \frac{1}{3}(1 - R - D^3)$	$N^4 = \frac{5}{8} - \frac{1}{4}R$
$L^4 = \frac{7}{24} + \frac{1}{12}R - \frac{2}{3}D^3$	
$N_4 = \frac{5}{8} - \frac{1}{4}R$	



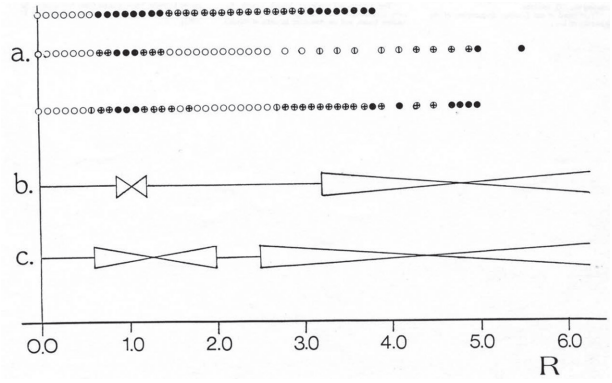


Figure 6. Glass formability of sodium borate glasses: (a) top: air cooling on a brass plate, middle: roller quenching, bottom quenching between brass plates; (b) roller quenching by Ota & Soga;[14] (c) air cooling in platinum crucible. Open circles and horizontal lines represent glass formability at those compositions, R is the molar ratio of sodium oxide to boron oxide. Data taken from Ref. 13. Reproduced with permission from The American Ceramic Society

silicates, bismuth borates, and many more glass forming systems. The next sections discuss density, molar volumes, carbon dioxide retention, and the glass transition temperature of these glasses.

B. Density

The densities of various binary and ternary borate, silicate, germanate, and vanadate glasses have been measured and modelled. Figure 7 depicts the density of the lithium borate system over the widest known composition range.[15] In 1978, the limit of glass formation using plate quenching[13] was found to be R=1·86, compared to R=2·8 in our lithium borate paper[15] describing work done at Coe College in 1986.

Figure 8 shows a model for density invoking fractions of atomic-level structures; namely five in total: B_3, B_4, B_2, B_1, and B_0 where the subscript is the number of bridging oxygens per boron. B_4 is tetrahedral while the other borate units are all trigonal planar.

B.1 Modelling density

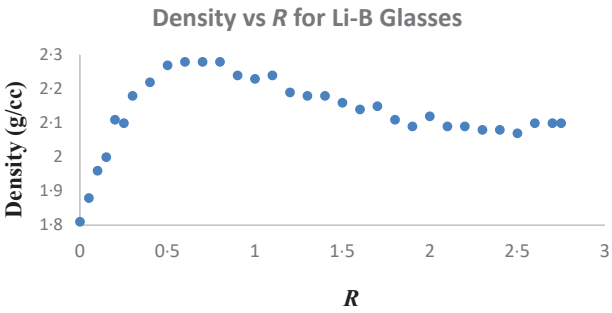


Figure 7. The density of lithium borate glasses[15] as a function of the molar ratio of lithium oxide to boron oxide, R. Reproduced with permission from Elsevier [Colour available online]

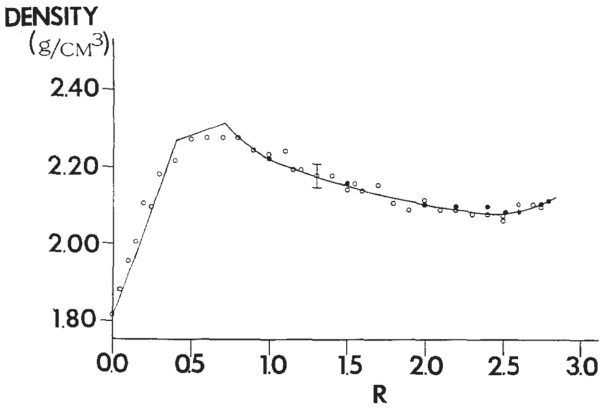


Figure 8. Density model superimposed on density data for the lithium borate glass system.[15] The model volumes are listed in Table 1, whereas the fractions of the structural units were taken from NMR results.[16] Open circles are for samples prepared from lithium carbonate, and filled circles are for glasses prepared from lithium oxide. R is the molar ratio of alkali oxide to boron oxide. R=1 corresponds to 50 mol% lithium oxide. Reproduced with permission from Elsevier

Using NMR-derived fractions of the groups, it was possible to model the density and determine the relative size of the B_i units for many borate systems.[16] The density model may be written as:

$$\rho = \text{Mass}/\sum B_i V_i \quad (1)$$

where B_i represents the fraction of the i-th unit and V_i is its volume. A least squares fit of the model density to the density data yielded the relative volumes, V_i. These are shown in Table 1 and were used to calculate the model overlaid on the density shown in Figure 8.

Note that the lithium system shows some especially easy trends in the resulting volumes. The four trigonal volumes, V_1, V_2, V_3, and V_4 are 1, 1·37, 1·68 and 1·95. This is consonant with the volumes being dominated by the amount of oxygen in each unit (boron and lithium volumes may be approximated to zero). In this case the volumes would scale as 1, 1·33, 1·67, and 2·00. The density trend (see Figure 9) is then controlled by the concentration of tetrahedral boron units, for which the relative volume is only 0·84.

We have also made density measurements on the other alkali systems, where the volume of the modi-

Table 1. Relative B_i unit volumes compared to B_1 for the short range structures found in lithium borate glasses. Ø represents a bridging oxygen, while O is a nonbridging oxygen

Unit	*Unit formula*	*Symmetry*	*Relative volume compared to B_1*
B_3	$BØ_3$	planar trigonal	1·00
B_4	$BØ_4$–Li^+	tetrahedral	0·84
B_2	$B(Ø_2O)$–Li^+	planar trigonal	1·37
B_1	$B(ØO_2)$–$2Li^+$	planar trigonal	1·68
B_0	$B(O_3)$–$3Li^+$	planar trigonal	1·95

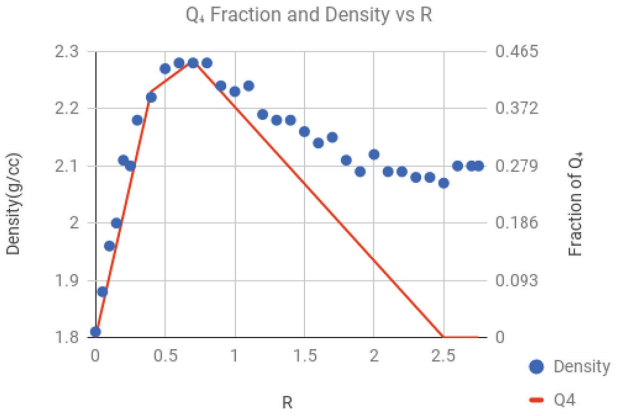


Figure 9. Comparison of the fraction of four-coordinated borons, B_4, with the density of lithium borate glasses [Colour available online]

fier eventually becomes completely dominant, and the packing is then controlled by the modifying ion, such that at high loading the packing approaches that of random spheres, 63·6%. This occurs in the potassium, rubidium, and caesium borate systems.

C. Discovery of bulk invert glass formation in the alkali borate system

Together with other groups, we noticed early on that carbon dioxide was retained in all alkali containing glasses of high modifier content (borates, silicates, germanates, etc.) In Figure 10 we show the carbon dioxide retention in a series of sodium borate glasses.[13] The carbonate retention can easily be seen in the weight of the sample after heating and from the Leco

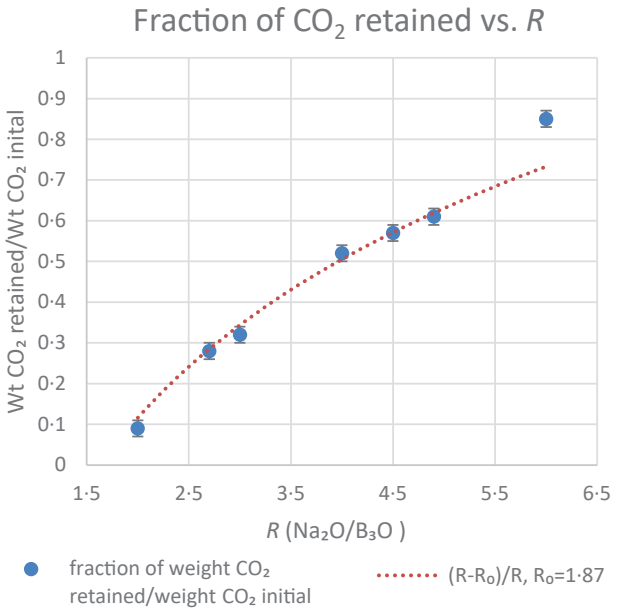


Figure 10. Carbon dioxide retention in sodium borate glasses. The red dotted line is from a model, Equation (2), in which the fraction of CO_2 retention is given by $(R-R_0)/R$ with R_0=1·87 or 65 mol% sodium oxide [Colour available online]

combustion method, performed by the Coors spectrographic laboratory located in Golden, Colorado. The model shown in this figure states that above a certain threshold composition, R_0, all remaining CO_2 is retained by the sample:

$$\text{Fraction of } CO_2 \text{ retained} = (R-R_0)/R \qquad (2)$$

The carbon dioxide retention, at a given composition, was least in the lithium system, and most in the caesium-containing glasses. It was so massive in rubidium and caesium borates that crystallisation into the alkali carbonate occurred for these systems above the metaborate composition. In an attempt to study non-carbonated glasses we changed the starting materials from alkali carbonates to alkali oxides. All alkali oxides are available commercially except potassium oxide.

When we made the glasses, we were surprised to see bulk glass yields of 100% at compositions up to 75 mol% Na_2O, Rb_2O and Cs_2O, and glass formation in the lithium system (starting with Li_2O) using roller quenching.[17] This led to spectroscopic and physical property determination in these systems. Figure 11 exhibits the Raman spectra from rubidium borate glasses; spectra from caesium borates have a similar

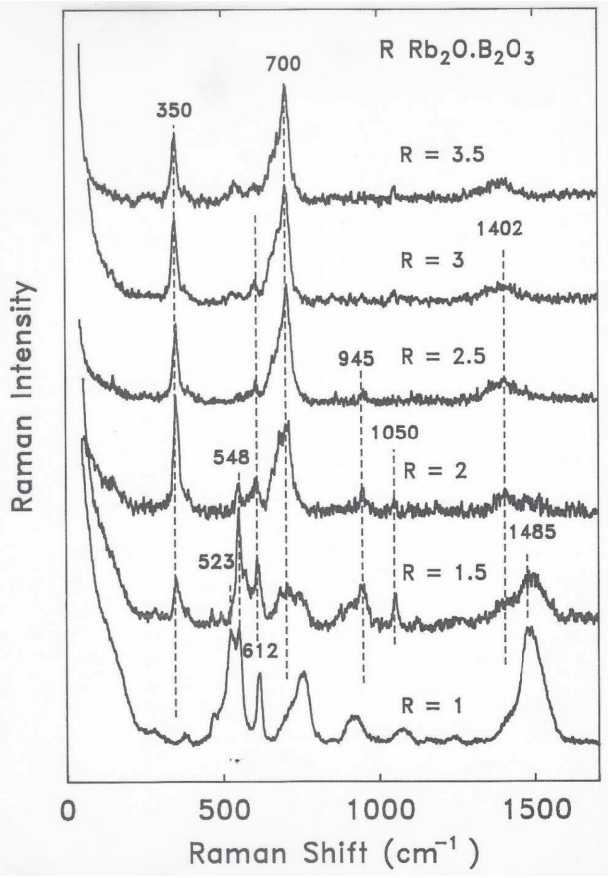


Figure 11. Raman spectra from a series of invert rubidium borate glasses. R is the molar ratio of alkali oxide to boron oxide.[18] R=1 corresponds to the metaborate composition, and R=3 refers to the orthoborate composition. Reproduced with permission from The Association of Greek Chemists

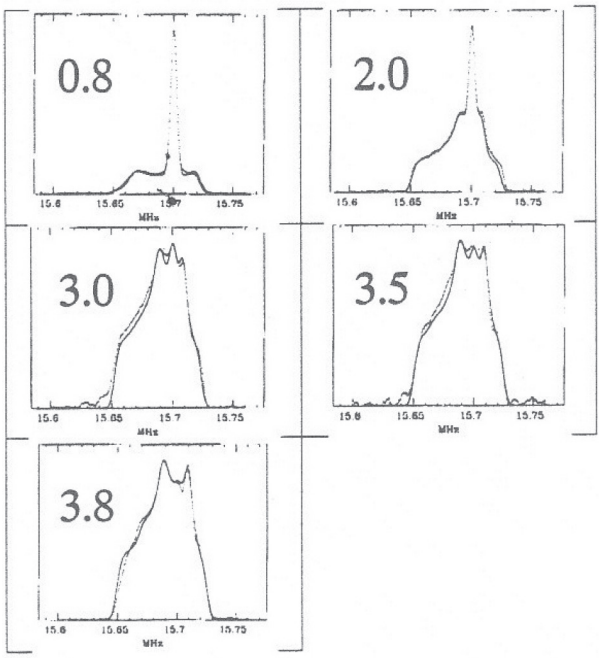


Figure 12. ^{11}B NMR spectra measured by the non-adiabatic superfast passage technique for a series of rubidium borate glasses.[18] The R value is given for each spectrum, with R being the molar ratio of rubidium oxide to boron oxide. The fits allowed the fraction of four coordinated borons to be determined, as given in Table 2. They were found to be negligible in comparison to their exclusive presence in the Raman spectra of Figure 11. Reproduced with permission from The Association of Greek Chemists

Table 2. Fraction of four coordinated borons in a series of rubidium borate glasses[18]

R	*Rubidium oxide (mol%)*	*B_4 fraction*
0·8	44	0·44
2·0	67	0·14
3·0	75	0·00
3·5	78	0·02
3·8	79	0·01

appearance.

The Raman spectra were interpreted by Stratos Kamitsos for both rubidium borate and caesium borate invert glasses. The spectral features near 350 cm^{-1} and 700 cm^{-1} indicate a new borate short range structure; namely a tetrahedral boron with two nonbridging oxygens and two bridging oxygens. These are named B_4* here, and have the unit formula $B(Ø_2O_2)–2M^+$.

However, the NMR spectra shown in Figure 12 are overwhelmingly consistent with three coordinated borons of the sort seen in pyroborates, B_1, (due to both their high coupling constant and their high asymmetry parameter). This has created a nearly 30 year discussion with my good friend Stratos Kamitsos. It has greatly deepened our mutual respect. Each of us has additional evidence supporting our respective positions, and I will leave further discussion for another paper.

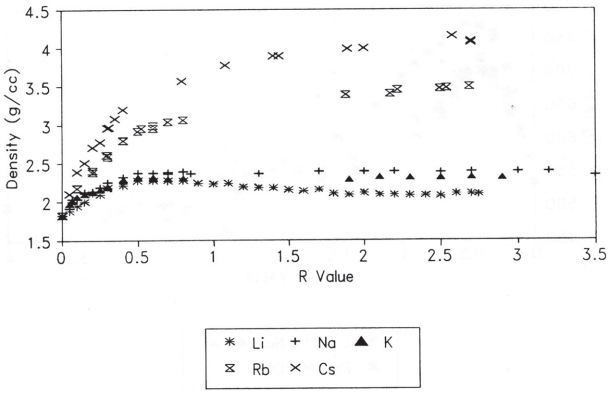


Figure 13. Densities of alkali borate glasses cross a wide range of alkali oxide concentrations.[18] Reproduced with permission from The Association of Greek Chemists

The densities of the resulting new glasses (with potassium glasses made from potassium carbonate using roller quenching) are shown in Figure 13.

We finally completed the alkali borates made from non-carbonate starting materials with the use of Masao Kodama's "Solution Method." In this method, solutions of boric acid and alkali hydroxide are mixed are room temperature, and allowed to react for about a day.[19] The reaction produces a precipitate that is then heated to produce the glass without carbon dioxide retention. This method was able to reproduce the bulk glass formation previously achieved using the alkali oxides, and potassium borates were added to our carbonate-free glass families. I note that Kodama invented this method to make low alkali content borate glasses that were ultra-homogeneous for velocity of sound measurements.

Other scientific highlights of the 1990s include using ^{29}Si NMR to probe alkali borosilicate glasses, from which models could be tested. This work was done with Steve Martin of Iowa State University. Also, we observed glass formation in carbonate-free glasses in the alkali silicates up to the pyrosilicate (R=2, or $67M_2O.33SiO_2$) glass compositions.

By the end of the 1990s and early 2000s, we had observed glass formation in binary alkali borate, silicate, and germanate families, as well as the alkaline earth borates. We had also studied many ternary systems, including alkali borosilicates, alkaline earth borosilicates, alkali borogermanates, and alkali borovanadates.

D. Molar volumes and the glass transition temperature

Examples of work on binary borates may be found in Figure 14, which shows the molar volumes of alkali and alkaline earth borates measured over an extensive compositional regime.[20] As an example of work on ternary glasses, Figure 15 presents glass

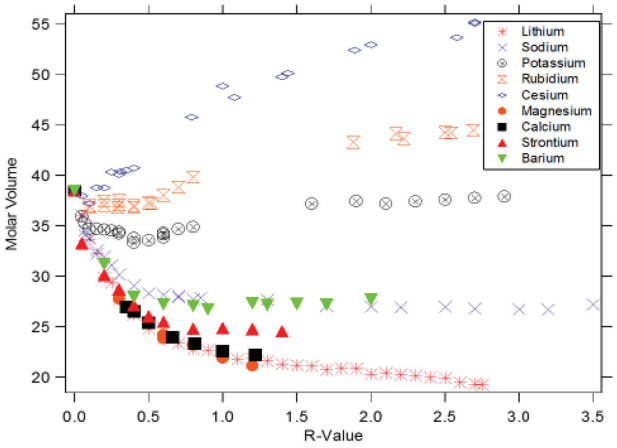


Figure 14. The molar volumes of alkali and alkaline earth borates as a function of R. R is the molar ratio of alkali oxide to boron oxide. R=1 corresponds to the metaborate composition, and R=3 refers to the orthoborate composition [Colour available online]

transition temperature, T_g, data for a wide range of lithium borosilicates.[21] It is noteworthy that T_g follows the binary lithium borate system diluted by the addition of silicate.

The maximum T_g value is just below 800 K for each system. The value of R at which this maximum occurs is most strongly related to the number of boron–oxygen bridges per boron, as can be seen in Table 3.

Table 3. A comparison of the values of R at which the glass transition temperature, T_g, and the number of bridging oxygens/boron are maximised for the lithium borosilicate glass system.[21] R is the molar ratio of lithium oxide to boron oxide, and K is the molar ratio of silica to boron oxide

K	*Value of R which maximises T_g*	*Value of R which maximises B–O bridges/B*
0·0	0·5	0·4
0·5	0·6	0·5
1·0	0·6	0·6
2·0	1·0	0·8
3·0	1·5	0·9

Evidence for a form of proportional sharing is provided in the post maxima slopes, $S(K)$, of the T_g versus R curve as a function of K. Proportional sharing would indicate that $S(K)$ is given in terms of the slope of the binary system, $S(0)$, by

$$S(K)=S(0)/(1+K) \quad (3)$$

The comparison to experiment is found in Table 4 and is quite close.

Table 4. Slopes of the straight line region past the maxima in T_g, S(K), as a function of K for lithium borosilicate glasses[21]

K	*$S_{exp}(K)$ (°C/unit R)*	*S(K)=S(0)/(1+K) (°C/unit R)*
0·0	−173±4	−173
0·5	−113±2	−115
1·0	−80±4	−87
2·0	−57±2	−58
3·0	−43±1	−43
4·0	−31±2	−35

This proportional sharing was found in our NMR study with Steve Martin[22] to commence past a certain value of R that is a function of K, $R_0(K)$, as given in Table 5.

Table 5. The initiation composition, $R_0(K)$, at which proportional sharing begins in the lithium borosilicate glass system[22]

K	*$R_0(K)$*
0·5	0·016
1·0	0
2·0	0
4·0	0·14
4·0	0

The values for $R_0(K)$ for lithium borosilicate glasses are nearly zero, unlike the case for the other alkali borosilicate systems.

Past the linear region the T_g slopes reach a plateau. This is due to the zeroing out of the fraction of four-coordinated borons as the end of the ternary glass formation occurs at R=3+2K. Past this composition carbonate retention is present and this is no longer a ternary glass.

The T_g model is able to explain the T_g experimental results in terms of the underlying atomic structure and a form of proportional sharing of the alkali oxide between the borate and silicate subnetworks. This works quite well in the lithium borosilicate system.

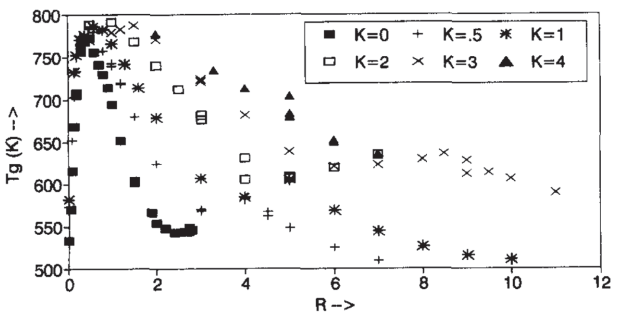


Figure 15. The glass transition temperatures, T_g, of lithium borosilicate glasses.[21] R is the molar ratio of lithium oxide to boron oxide, and K is the molar ratio of silica to boron oxide. Reproduced with permission from Elsevier

E. Neutron scattering

Numerous neutron scattering experiments first were performed with Adrian Wright and later with Alex Hannon. An especially interesting case is summarised in Figure 16. Here inelastic neutron scattering experiments yielded the density of states of vitreous boron oxide, crystalline caesium triborate ($Cs_2O.3B_2O_3$ or R=1/3≈0·33), and crystalline caesium enneaborate[23] ($Cs_2O.3B_2O_3$ or R=1/9≈0·11). In boron oxide the sharp peak at 100 meV (or 808 cm^{-1}) is from the breathing mode of the boroxol rings. In polycrystalline caesium triborate, composed wholly of triborate rings (Figure 17 presents the triborate ring structure; the boroxol

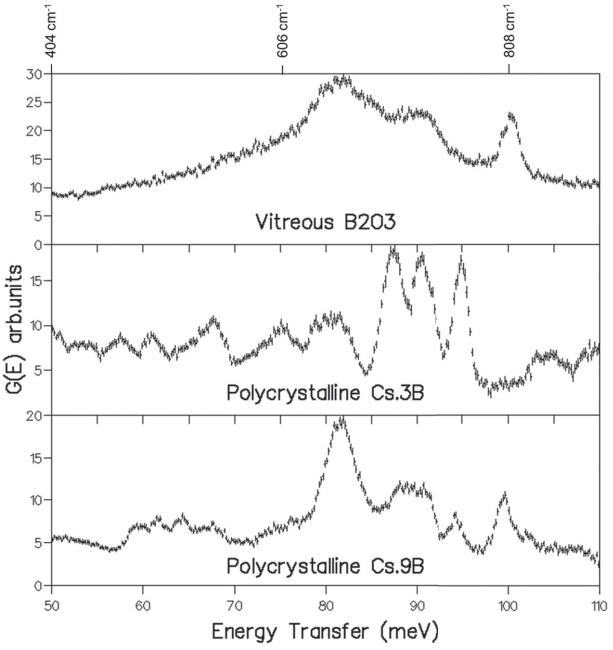


Figure 16. Inelastic neutron scattering measurements of the vibrational density of states, G(E), for vitreous boron oxide, crystalline caesium triborate (Cs.3B, R=1/3), and crystalline caesium enneaborate (Cs.9B, R=1/9).[23] The horizontal axis is the energy transfer measured in meV, whilst some corresponding energy values in wavenumbers are given along the top of the figure

ring is similar except all borons are trigonal), the breathing mode of the ring is located at about 95 meV, see Figure 16. However, in polycrystalline caesium enneaborate the structure is composed of an admixture of triborate rings (1/3) and boroxol rings (2/3). Examination of the bottom part of Figure 16 shows this clearly in terms of the two ring vibrations and the relative abundances. Comparison of the boron oxide spectrum to the spectra from the two crystals indicates boroxol rings in boron oxide with an abundance near 2/3.

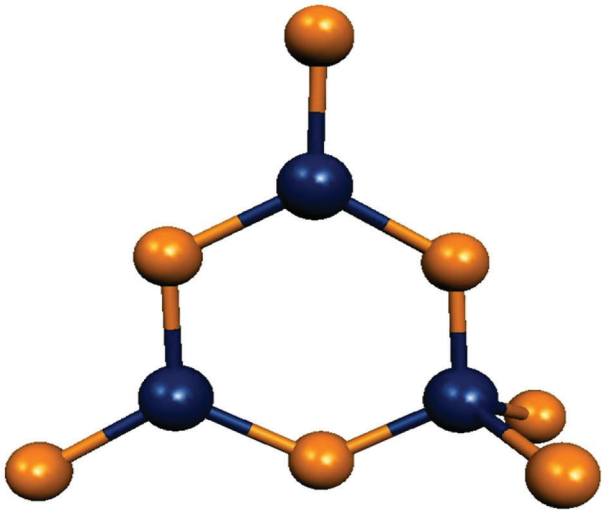


Figure 17. The triborate ring [Colour available online]

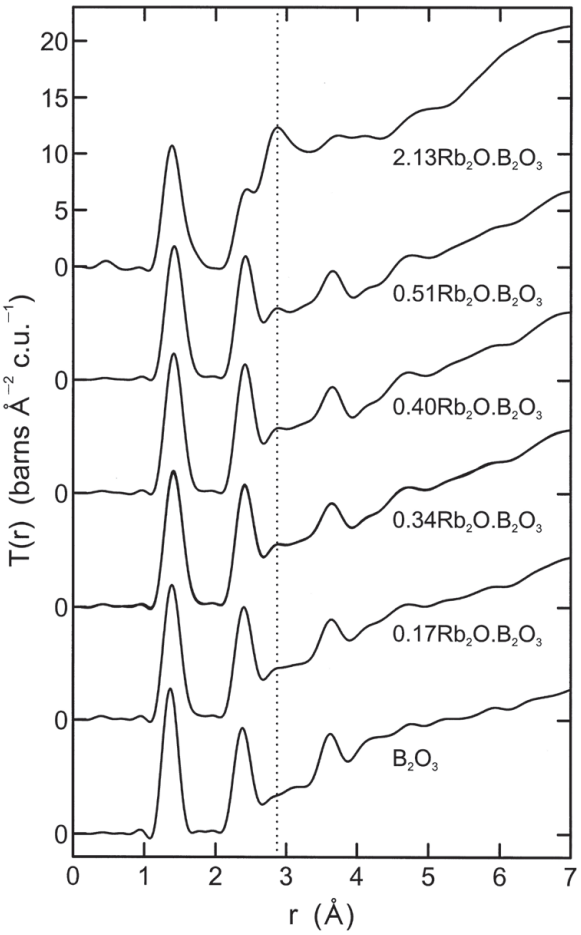


Figure 18. Neutron diffraction measurements of the total neutron correlation function for rubidium borate glasses across a wide compositional range[24]

Adrian and I have performed a large number of neutron diffraction experiments on borates, and a representative set of results from rubidium borates[24] is given in Figure 18. The first peak in the neutron correlation function, due to B–O bonds, spans the range 1·37 to 1·48 Å and arises from both three and four coordinated borons. The second peak is due to the shortest O–O distance, whereas the feature near 2·9 Å is due to Rb–O bonds. Near 3·6 Å is an intra-ring separation. The figure shows that the invert glass $2{\cdot}13Rb_2O.B_2O_3$ has a very different structure than the other samples. The total correlation function of the invert glass is dominated by Rb–O bonds, whereas the ring structure is nearly gone, due to the trigonal metaborate ring having yielded to form more trigonal isolated units, such as the pyroborate group, B_4. More recently, I have been involved in a number of neutron diffraction projects, several of which are borate-related.

F. New and improved ^{11}B NMR

F.1 NMR with Scott Kroeker

Using higher field ^{11}B MAS NMR, it has become possible to see and quantify different kinds of tetra-

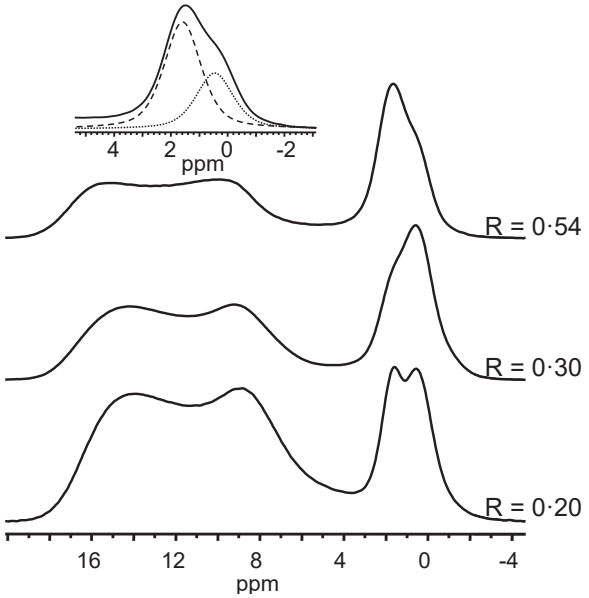


Figure 19. ^{11}B MAS NMR spectra of $RCs_2O.B_2O_3$, measured at 14·1 T[25]

hedral borate groups. The significance of this result is that Scott Kroeker and our group saw the effects of intermediate range order on the tetrahedral borons of caesium borate glasses, where a low and a high field response was observed and deconvoluted, see Figures 19 and 20. The high field response near 1·6 ppm has been hypothesised to be from tetrahedral borons in diborate groups, and the low field response near 0·4 ppm may be from the triborate four-coordinated borons.[25] This may serve as a window into the intermediate range order.

F.2 NMR with Diane Holland

Beginning in the middle of the first decade of the 2000s, I returned to ^{10}B NMR, this time doing much

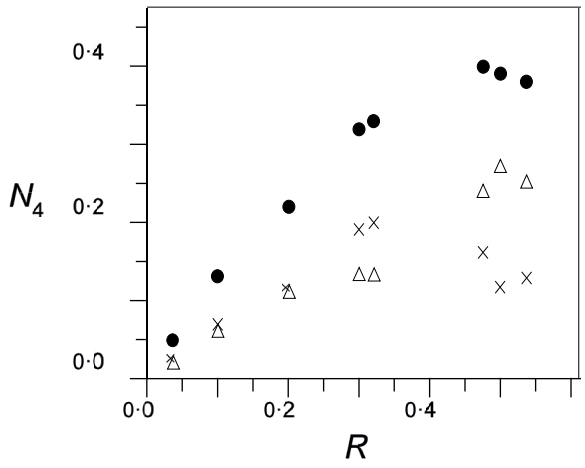


Figure 20. Deconvolution of the two tetrahedral boron sites in caesium borate glasses.[25] Triangles come from the low frequency (0·4 ppm) feature, whereas crosses are from the high frequency peak (1·6 ppm)

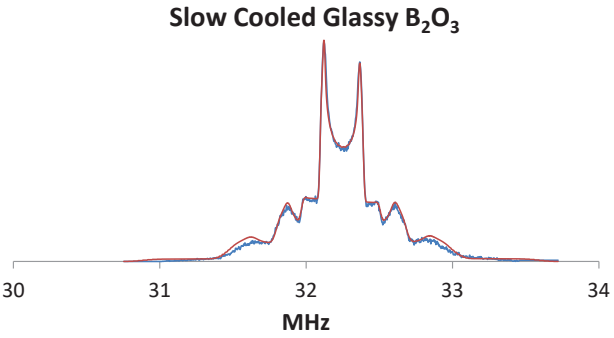


Figure 21. Experimental (blue) and simulated (red) ^{10}B NMR from boron oxide glass cooled over a five-day period [Colour available online]

collaborative work with Diane Holland. The University of Warwick has a marvellous NMR facility, including a field-stepping addition to one of their superconducting magnets. This allows very wide scans to be performed, and it became possible to see all six NMR transitions from spin-3 ^{10}B. Furthermore, the large quadrupole interaction allows for high resolution acquisition of the quadrupole parameters. We have been able to measure these parameters for trigonal and tetrahedral borons in various intermediate range structures. Figure 21 depicts the simulated and experimental ^{10}B NMR response from boron oxide cooled over a five-day period ("slow cooled").[26] ^{10}B studies remain in progress, and due to the exquisite resolution of ^{10}B it has become possible to see the effects of the intermediate range on both the trigonal and the tetrahedral borons.[27] In many respects I have come full circle with my studies of ^{10}B NMR; initially we could see only two of the transitions, and the experiments took a long time. The Warwick experiments took up to two weeks each to perform; now in an hour or so and using newer methods, such as (CPMG), we can obtain truly exquisite spectra that contain all six transitions.

G. Other and newer work on borates

G.1. Glass transition widths

In the last few years we have remained vitally active in our study of borates. We discovered an anomaly in the widths of the glass transition in low alkali content borates. The lithium system displays glass transitions that are triply wide compared to caesium borates, see Figures 22 and 23 for DSC (differential scanning calorimetry) results and both simulated and experimental width results.[28,29] Furthermore, we have been able to replicate the results using MD (molecular dynamics) simulations.

G.2 Elastic moduli work with Masao Kodama

Elastic properties of alkali borate glasses may directly be related to structure. One way to investigate this

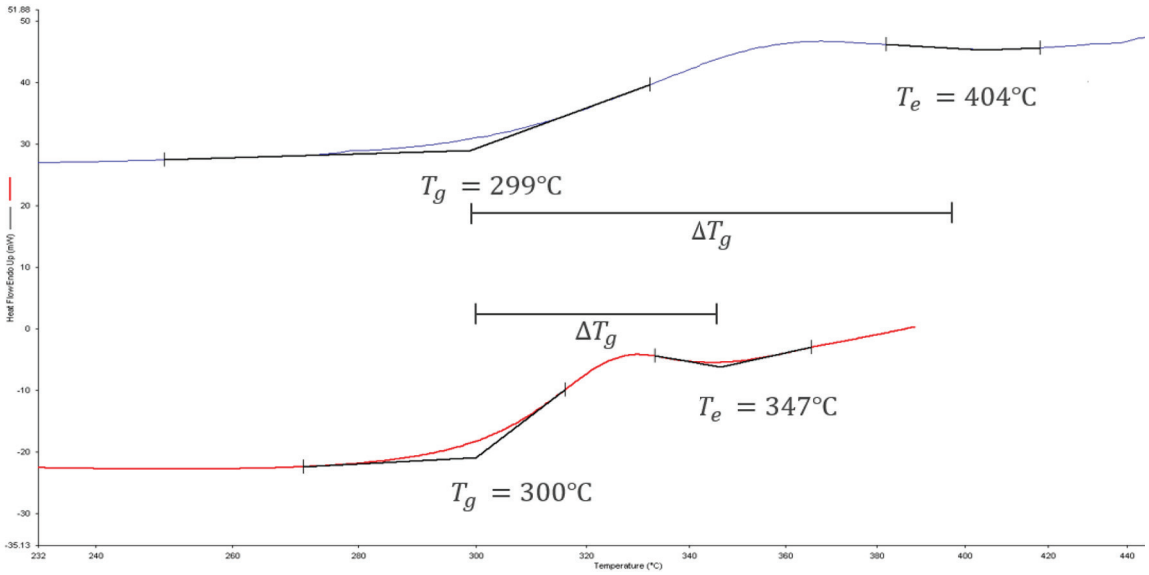


Figure 22. Superimposed DSC traces from R=0·05 (5 mol% alkali oxide) lithium borate glass (top) and caesium borate glass (bottom). This comparison shows that the glass transitions for the two samples begin at similar temperatures, but end at widely disparate temperatures [Colour available online]

is to plot the stiffness against the molar volume measured on the same samples. Figure 24 shows this relationship for caesium borate glasses.[30] The paper, given at the Borate IV conference, shows the effects of the ring-structures on the intermediate range order in the evolution of the elastic properties when plotted against the molar volume. Each region of elastic moduli behaviour as a function of molar volume is correlated to a different ring-structure. Similar behaviour is found in the other alkali borate glass families.

G.3 Packing in glass

We now believe that packing is the best measure of structure related to density. The packing fraction of the glasses was determined by using Shannon radii to calculate the molar ionic volume, and then dividing by the molar volume of the glass. Figure 25 displays the packing found in binary borate glasses.[31] A few observations are as follows:

1. The light alkali borates, such as lithium and magnesium, display packing that is controlled by the fraction of four-coordinated borons, and they have similar packing values to each other.
2. The largest ions, K, Rb, and Cs all follow the same packing curve, which approaches the value for a random packing of monodisperse hard spheres,

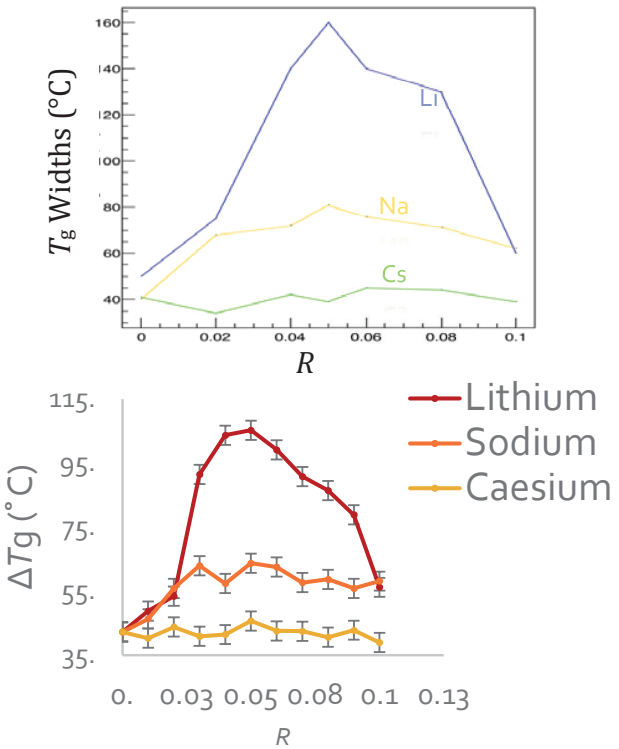


Figure 23. (Top) Simulated and (bottom) glass transition widths for alkali borate glasses. R is the molar ratio of alkali oxide to boron oxide [Colour available online]

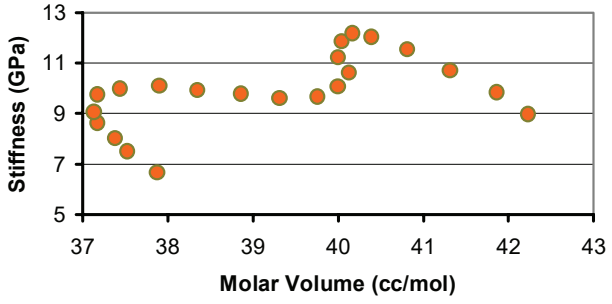


Figure 24. Stiffness versus molar volume for a series of caesium borate glasses prepared by Masao Kodama[30] [Colour available online]

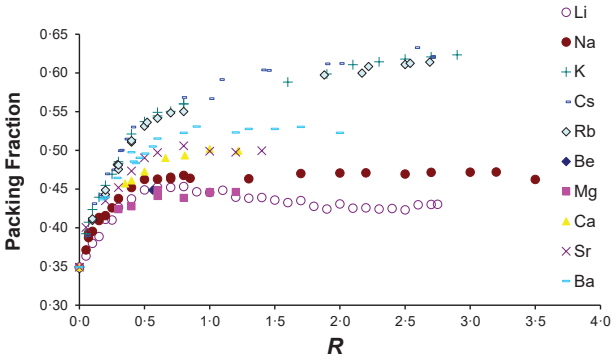


Figure 25. Packing fractions of alkali and alkaline earth borate glasses[31] [Colour available online]

0·636.

3. Other systems exhibit intermediate packing. Examples of these systems include sodium, strontium, and barium borate glasses.

H. Other glass forming systems

While our Coe College researchers have examined other borate systems, including many ternary systems, we have also studies several non-borate families. These include binary and ternary germanates, silicates, tellurites, and vanadates. Rapid cooling has allowed us to extend glass formation in many of these systems. I present here some of the more interesting results from these systems to round out my career investigations and results.

H.1 Invert lithium silicate glasses

We studied lithium and lead silicate glasses to very high modifier levels. Figure 26 displays the Q unit distribution found in lithium silicate glasses.[32] A modified version of the binary lever-rule model seems to be at play here.

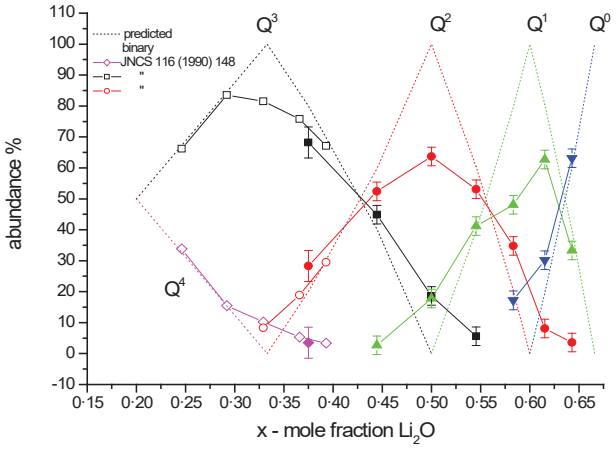


Figure 26. ^{29}Si NMR derived fractions of the Q units in lithium silicate glasses; Q^n indicates a SiO_4 tetrahedron with n bridging oxygens. Note the wide range of compositions studied [Colour available online]

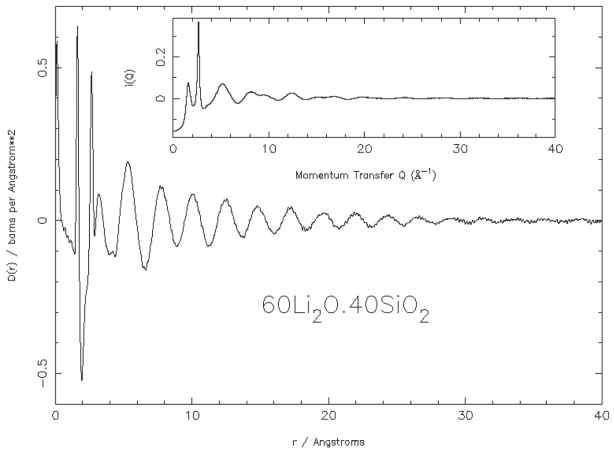


Figure 27. The differential neutron correlation function from neutron diffraction for a lithium silicate glass as a function of interatomic distance, r, in Angstroms[33]

Another interesting set of results for the lithium silicate glass system has been obtained by neutron diffraction,[33] an example of which is shown in Figure 27 for $60Li_2O.40SiO_2$ glass. This exhibits a most unusual and still unpublished result that there is a repeating distance of about 2·37 Å, which extends out to a very long distance ~40 Å.

H.2 TeO_2 glass

A recent project has involved the formation of tellurium dioxide glass by a number of methods. Roller quenching[34] and laser levitation has produced small quantities of the amorphous phase. Recently, Tagiara & Kamitsos have reported the formation of bulk TeO_2 glass by rapidly dipping a platinum crucible into and out of an ice-water mixture.[35] We have been able to duplicate this method and create ^{17}O enriched TeO_2 glass for a ^{125}Te and ^{17}O NMR study of the amorphous phase. The NMR results are shown in Figure 28.[36]

I. Current projects

Other current projects include:

4. Continued studies of the T_g width anomaly, now focusing on mixed alkali borates
5. Raman and neutron diffraction studies of carbon dioxide retention on glasses, with a present focus on sodium silicate glasses. This work is being done in collaboration with Dr Alex Hannon of the ISIS neutron source at the Rutherford Appleton Laboratory in the UK.
6. Continued B NMR work on caesium borate glasses using the new and improved CPMG NMR method. This work is in collaboration with Dr Nathan Barrow of Johnson Matthey (Reading, UK).
7. MD simulations of borate glass work.
8. Glass stability against crystallisation with Professor Edgar Zanotto. Present work is centred

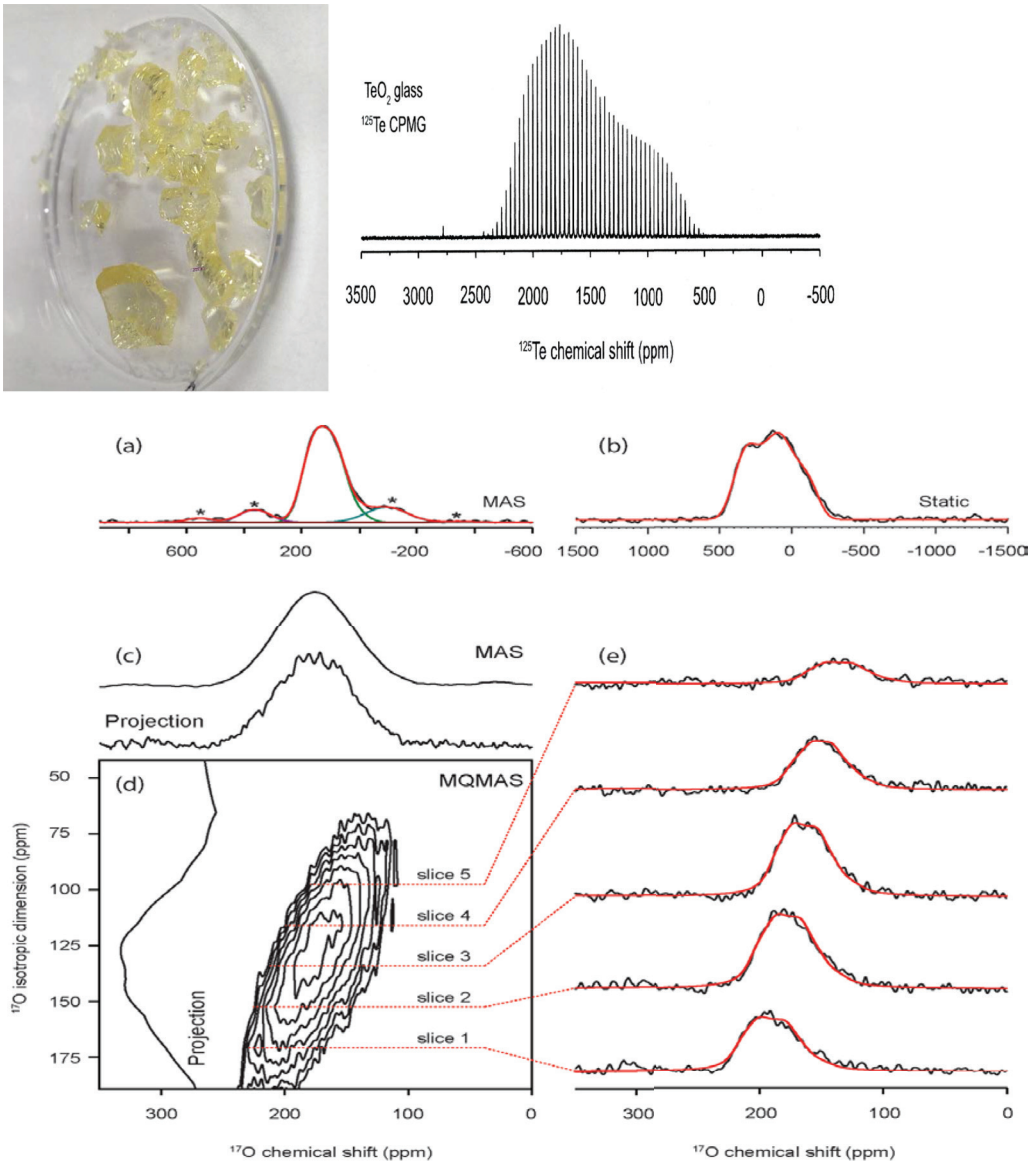


Figure 28. A montage of research on amorphous TeO_2. Top: Bulk glassy TeO_2 made at Coe, and ^{125}Te NMR on a-TeO_2. Bottom: The first ^{17}O NMR results on TeO_2 (measurements were made on our samples by the J. Zwanziger group[36]) [Colour available online]

on the sodium borate system at invert compositions made with and without carbonate starting materials.

9. The continued education of new glass scientists at Coe College. Figure 29 shows Katie Bozer, a high school student who worked on the production and study of tellurium dioxide glass. With Professor Mario Affatigato we now train over 20 research students per year. Several have subsequently continued to work in the field of glass science.

J. A few concluding comments and acknowledgements

Science is wonderfully collaborative by its very nature. Certainly, I have been the beneficiary of many good ideas and much help from others.

It was my good luck to work with Professor Phil Bray of Brown University as my PhD supervisor. He was insightful, clever, always a colleague, and I learned a lot from him. I learned much from my fellow members of the NMR group at Brown including Gary Petersen, Jay Jellison, Larry Panek, Frank Bucholtz, Isaac Harris, Art Geissberger, Steve Greenbaum, Yun Hun Yun, Warren Dell, and S. N. Subbarao.

I have been most fortunate to work with colleague and friend Professor Mario Affatigato, and together we have mentored well over 300 students in research on glass, most of whom were Coe College undergraduates. They are all very much appreciated. Of these students the following have gone on to earn a PhD or equivalent (* indicates the degree is in the

Figure 29. Katie Bozer, high school student from Iowa City West High School, prepares a sample of glassy TeO_2 [Colour available online]

field of materials science, or that they did work in glass science for their degree):

Dr Mario Affatigato*	Dr Faisal Alamgir*
Dr Joy Banerjee*	Dr Heidi (Feller) Berger
Dr John Berkowitz	Dr Ajay Bhatnagar*
Dr Sarah Blair*	Dr Rachel Boekenhauer*
Dr Tom Britton	Dr Matt Burch*
Dr Sara Campbell*	Dr Bee Choo Liang Chong*
Dr Warren Clarida	Dr Prabesh Dulal*
Dr Trent Edwards*	Dr David Feil
Dr Maranda Franke	Dr Benjamin Franta
Dr Janice Frueh	Dr Henry Bola George
Dr Vijaya Gosula	Dr Eric Hemesath*
Dr. Kyle Hershey*	Dr T.,J. Kiczenski*
Dr Victor Khristenko	Dr Chris Larson*
Dr Deserae Lieppley	Dr Grant Lodden*
Dr Kong Loh	Dr Nathan Lower*
Dr Christopher Ma*	Dr Amy Marquardt*
Dr Benjamin Meyer*	Dr Tyler Munhollan*
Dr Tyler Mullenbach*	Dr Craig Nie*
Dr Ryan Nieuwandaal*	Dr Sumit Nijhawan*
Dr Greg Ongie	Dr Hitendra Patel*
Dr A. Michael Peters*	Dr Dale Stentz
Dr Brad Tischendorf*	Dr Adam Vitale*
Dr Bryan Vitale*	Dr Deborah Watson*
Dr Carissa Wiederholt	Dr Richard Williams
Dr Dustin Winslow*	

Many others have secured master's degrees in physics and materials science. Mario Affatigato and I also worked with students and teachers by means of the Research Experiences for Undergraduates and Research Experiences for Teachers schemes, respectively.

Domestic undergraduate and graduate students visited me from Iowa State University (Professor Steve Martin's group), Missouri Institute of Science and Technology (Professor Dick Brow's group), Cornell University (Professor Baker's group), and William Jewell College (Professor Blane Baker's Group). Other colleges have sent students and faculty to visit Professor Mario Affatigato.

I also hosted several international scientific visitors including the following graduate students who earned their doctorates from the University of Warwick (UK), in part due to their work at Coe College:

Dr Emma Barney	Dr Robin Orman
Dr Martin Mee	Dr Nathan Barrow
Dr Natapol "Meng" Laorodphan	Dr Andy Grigg
Dr Oliver Alderman	

Numerous colleagues collaborated with me over the course of this research and all are thanked. Many Coe College students also visited their laboratories. These colleagues include:
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The Rutherford Appleton Laboratory (UK) is thanked for their generous material and expert help in performing a myriad of neutron scattering experiments. Dr Alex Hannon and Prof. Adrian Wright are thanked for their kind help. The Institute of Advanced Study at the University of Warwick (UK) is thanked for sabbatical assistance that led to both NMR measurements and the performance of the play *Copenhagen*.

Nuclear magnetic resonance and nuclear quadrupole resonance experiments have taken place at Brown University (with Prof. Phil Bray), Iowa State University (with Prof. Steve Martin), University of Manitoba (with Prof. Scott Kroeker), Dalhousie University and Indiana University (with Prof. Josef Zwanziger), University of Warwick (with Prof. Diane Holland, Dr Tom Kemp, Prof. Ray Dupree, and Professor Mark Smith), IFSC São Carlos, Brazil (with Prof. Hellmut Eckert), Corning, Inc (with Dr Randall Youngman), and Hunter College of the City University of New York (with Prof. Steve Greenbaum and Dr Phil Stalworth).

Electron spin resonance experiments have taken place at William Jewell College (with Prof. Blane Baker).

Vibrational spectroscopy has taken place at NHRF, Athens, Greece (with Stratos Kamitsos and Dr George Chryssikos), Iowa State University (with Prof. Steve Martin), University of Nottingham (with Dr Emma Barney), University of Tsukuba, Japan (with Profs Seiji Kojima and Maso Kodama).

Viscosity and thermal measurements were done at UF São Carlos-SP, Brazil with Prof. Edgar Zanotto and Sojo University (Japan) (with Prof. Masao Kodama).

The Iowa College Foundation, the Research Corporation, the McElroy Foundation of Eastern Iowa, The State of Texas, Motorola, Corning, Inc., The American Institute of Physics, The American Physical Society, the Jeff Busse Family, Coe College, John Salzer, Coe College 1980, distinguished astronomer and my first student here, Coe College and its physics alumni are all thanked for supporting this research.

I thank Coe College for much support of this work. Many administrators and colleagues have been very helpful. A special thank you is due to James Phifer, former President and Vice President of Academic Affairs and Dean of the Faculty. Professors Joseph Kasper and Stan Watkins are thanked for help in launching the research at Coe College. B. D. Silliman is thanked for endowing the chair I hold.

Finally, and principally, I thank my family. They have shared my life, my trials, tribulations, and triumphs. They have endured my time away from them as I travelled around the globe to do my work and I very much appreciate their sacrifices. These include Barbara Feller, my wife of 46 years, my daughters Heidi Berger and Ray Feller, my sons-in-law Howard Berger and Michael McCloskey, and my grandchildren Max Berger, Leonardo McCloskey Feller, Isaac Berger and Ramona McCloskey Feller.

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