

Trimethylsilylation analysis of the silicate structure of fluoro-alumino-silicate glasses and the structural role of fluorine

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Trimethylsilylation (TMS) reactions have been carried out on acid degradable fluoro-alumino-silicate glasses containing a basic oxide. The siloxanes produced by the TMS reactions were analysed in order to gain information about the silicate structure of the glass. The results indicate a non-random arrangement of SiO_4 and AlO_4 tetrahedra in the glasses studied. No fluorinated derivatives of siloxanes were found, indicating that fluorine atoms are not bonded to the silicon atoms of the glass network. It is thought that fluorine atoms are instead bonded to the aluminium atoms present. The bonding of fluorine to aluminium and not to silicon atoms explains the prevention of fluorine loss as silicon tetrafluoride (SiF_4) from melts containing both aluminium and a basic oxide, and in addition explains the reduction in the glass transition temperature behaviour found on incorporating fluorine into alumino-silicate glasses.

The results suggest that the environmental problem of silicon tetrafluoride loss from fluoro-silicate glass melts and its subsequent hydrolysis to hydrofluoric acid and silica can be avoided by including a basic oxide in the composition. © 1999 Kluwer Academic Publishers

1. Introduction

Inorganic silicate glasses are some of the oldest materials known to man, yet are among the least understood materials in terms of their structure and chemical bonding. Even the use of powerful instrumental techniques such as magic angle nuclear magnetic resonance (MAS-NMR), Extended X-ray absorption fine line analysis (EXAFS), infrared and Raman spectroscopy, as well as X-ray and neutron diffraction studies have failed to give conclusive structural information on inorganic glasses. The present paper aims to gain an insight into the silicate structure of fluoro-alumino-silicate glasses using the trimethylsilylation (TMS) technique. In particular the paper will explore the structural role of fluorine and try to relate the structure of these glasses to the glass transition temperature and crystallization behaviour, as well as to commercially important aspects, such as loss of fluorine from the melt during firing. It is assumed in much of the subsequent analysis that the structural units present in the glass at room temperature are closely related to those in the melt at higher temperatures.

Fluoride-containing silicate glasses are used for a variety of purposes [1]: as an opacifying agent in the

production of opal glasses [2, 3], as a dopant in fused silica waveguides to lower the refractive index [4, 5], as a fining agent by means of lowering the viscosity of glass melts [6], in the production of machineable fluoromica based glass-ceramics [7, 8], in Bioglasses™ [9] and bioglass-ceramics [10, 11], since fluoride ions are known to stimulate apatite deposition in bone, and finally in Ionomer glasses used for glass polyalkenoate dental cements [12, 13], where fluorides are added to lower the refractive index of the glass, as well as to enable fluoride ion release from the set cement. Small quantities of fluorides are commonly added to glass-ceramics [2] where they frequently result in amorphous phase separation and subsequent bulk crystal nucleation.

The structural role of fluorine in all these glasses has an important influence on the properties obtained. Fluorine is widely thought to replace bridging oxygens in the glass network by non-bridging fluorines because of the similarity of the radii of oxygen and fluorine [14–16] and consequently it disrupts and weakens the glass network. Dumas [17] has presented strong infrared and Raman spectroscopy evidence for the presence of Si–F

bonds and $[\text{SiO}_3\text{F}]$ tetrahedra in fluorine doped silica glass. However the structural role of fluorine in silicate glasses is far from clear. Rabinovich [18] reviewed this topic of the structural role of fluorine in silicate glasses. He concluded that:

1. in alkali silicate melts, fluoride ions take part in electrical conductivity.

2. volatilization of fluorine as SiF_4 occurs in acid melts, but is significantly reduced with increasing basicity of the melt.

3. there is strong evidence for the formation of $[\text{SiO}_3\text{F}]$ tetrahedra in high silica melts. However, in basic melts free F^- ions or F^- ions bonded to basic ions also exist.

Rabinovich proposed a screening model based on the polarizability of oxygen and fluorine to explain the observed effects in fluoro-silicate glasses. The polarizability of the oxygen anion is three times that of the fluoride ion and this polarizability is important in determining the ability to screen the Si^{4+} ion from other cations. Neither oxygen anions nor fluoride ions can fully screen the central Si^{4+} ion, because only at a radius ratio of 0.225 can spherical anions fully screen the central tetrahedral cation. At low temperatures oxygen is preferable to fluorine for the screening of the central silicon cation.

Not all oxygens surrounding the silicon are equally efficient at screening; negatively charged non-bridging oxygens formed by incorporating a network modifying oxide into the glass will be better at screening the central Si^{4+} cation than bridging oxygens. The network modifying cation present will not be a competitor for the screening ability of the oxygen, since they are generally of lower charge and larger size than the Si^{4+} ion.

At high temperatures Rabinovich envisaged that a fourth screening oxygen could move away from a first central Si^{4+} cation towards a second adjacent silicon and act as a less efficient screen for the central cation. Under these circumstances a fluorine could replace this oxygen to give a $[\text{SiO}_3\text{F}]$ tetrahedra. A second F would not be incorporated so readily onto the central silicon cation because the central silicon cation would not now be shielded so effectively. Consequently the formation of $[\text{SiO}_2\text{F}_2]$, $[\text{SiOF}_3]$ and the volatile SiF_4 would be less likely and these species would only occur at very high temperatures in melts containing large quantities of fluorides. The formation of SiO_3F and other fluorinated silicates would be even less probable in the presence of non-bridging oxygens formed on incorporating a basic network modifying oxide into the fluoro-silicate melt. Thus Rabinovich's Screening-Polarizability model explains the experimental observation that incorporating a basic oxide into fluoro-silicate glasses often suppresses loss of SiF_4 from the melt. Rabinovich assumed the fluoride ions in the presence of a basic oxide to be in the spheres of coordination of the metal modifying cations, and cited the use of fluoride nucleating agents in glass-ceramics and the ease with which metallic fluorides crystallized from silicate melts as evidence for this assumption.

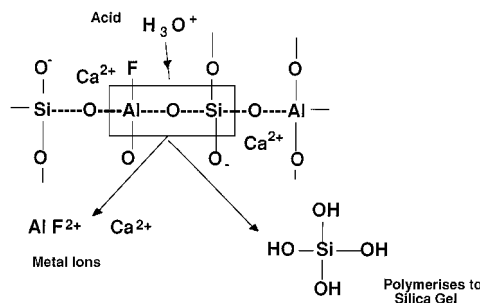


Figure 1 Acid degradation of a fluoro-alumino-silicate glass.

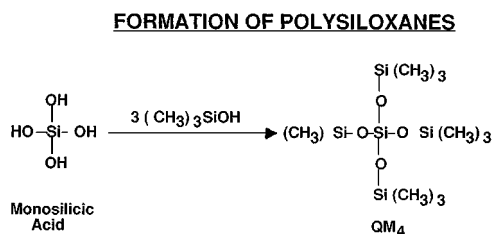


Figure 2 Trimethylsilylation of a $\text{Si}(\text{OH})_4$ to give a QM_4 derivative.

Despite the many advantages the presence of fluorides often confer on glass properties, fluorides often lead to corrosion and environmental problems as a result of the loss from the melt of volatile silicon tetrafluoride (SiF_4). The SiF_4 produced will hydrolyse in the presence of water to hydrofluoric acid and silica. Consequently addition of fluorides to silicate glass melts is often avoided, despite the potential advantages.

The fluoro-alumino-silicate glasses studied here are based on the acid degradable glasses used to produce glass polyalkenoate dental cements [19] and are therefore ideal for analysis by the trimethylsilylation (TMS) technique, since the first step of the analysis involves acid degradation of the glass structure, followed by trimethylsilylation and subsequent analysis of the siloxanes produced. Alumino-silicate glasses are acid degradable because the Al-O-Si bond is weaker than the Si-O-Si bond and is prone to hydrolysis by H_3O^+ . This is shown schematically in Fig. 1.

The TMS technique has been widely used to study the structure of silicate minerals. The technique produces polymers which reflect the silicate ($-\text{Si-O-Si}-$) "backbone" structure of the minerals. A typical reaction sequence is shown in Fig. 2. More recently the trimethylsilylation technique has been used to study inorganic glasses; the polymers produced are similarly believed to reflect the silicate "backbone" structure. The approach pursued here follows the ideas of Holliday and Ray [20] who treated silicate glasses as being inorganic polymers of oxygen crosslinked by silicon atoms.

1.1. Previous trimethylsilylation studies of silicate glasses

Using the Tamas [21] or Dimethylformamide method and lead silicate glasses with the molar ratio ($\text{PbO}:\text{SiO}_2$) between 4:1 and 1:1 Gotz *et al.* [22] found that with the molar ratio $> 2:1$ the glasses contained mainly linear silicates $[\text{SiO}_4]^{4-}$, $[\text{Si}_2\text{O}_7]^{6-}$, $[\text{Si}_3\text{O}_{10}]^{8-}$ and the cyclic tetramer $[\text{Si}_4\text{O}_{12}]^{8-}$. Glasses

with the molar ratio $< 2 : 1$ were composed of mainly polysilicate chains and complex networks. The work concluded that binary lead silicate glasses contain a series of silicate anions of varying sizes and the distribution of anions varies with the silica content. These results on lead silicate glasses were later confirmed by Smart [23].

Gotz *et al.* [24] also studied the effect of heating the lead orthosilicate glasses for varying lengths of time at various temperatures. The concentration of $[\text{SiO}_4]^{4-}$ derivatives initially falls. This is followed by the formation of $[\text{Si}_2\text{O}_7]^{6-}$ derivatives as an intermediate, and finally followed by the formation of the cyclic $[\text{Si}_4\text{O}_{12}]^{8-}$ derivatives from the final crystalline Pb_2SiO_4 formed.

Lead silicate and zinc silicate glasses were studied by Nakamura [25] using a direct or Lentz method [26]. The main products formed were found to be derivatives of $[\text{SiO}_4]^{4-}$, $[\text{Si}_2\text{O}_7]^{6-}$, $[\text{Si}_3\text{O}_{10}]^{8-}$ and small amounts of cyclic $[\text{Si}_3\text{O}_9]^{6-}$ and $[\text{Si}_4\text{O}_{12}]^{8-}$ derivatives. The yields of the various derivatives were found to be dependent on the experimental conditions used.

During a study of the calcium aluminosilicate glasses Atwell *et al.* [27] found that the yield and the structure of the derivatives were affected by the presence of other ions; the yield of soluble polymers was related to the percentage of aluminium oxide present in the glass.

Kolb and Hansen [28] using the Lentz method [29] found the presence of discrete silicate ions ($[\text{SiO}_4]^{4-}$, $[\text{Si}_2\text{O}_7]^{6-}$, $[\text{Si}_3\text{O}_{10}]^{8-}$ and $[\text{Si}_4\text{O}_{13}]^{10-}$) in borosilicate and lithium borosilicate glasses.

Calhoun *et al.* [30] analysed lead-fluoro-silicate glasses using the direct method [26] of trimethylsilylation and found evidence for the presence of silicon-fluorine bonds. The derivatives were found to be $[\text{SiO}_4]^{4-}$, $[\text{Si}_2\text{O}_7]^{6-}$ and $[\text{Si}_3\text{O}_{10}]^{8-}$, together with minor proportions of $[\text{SiFO}_3]^{3-}$, $[\text{Si}_2\text{FO}_6]^{5-}$, $[\text{Si}_3\text{FO}_9]^{7-}$ and $[\text{Si}_4\text{FO}_{12}]^{9-}$.

2. Experimental

2.1. Glass preparation

All the glasses were prepared in the laboratory using standard procedures described previously [31]. The glass compositions studied are given in Table I. The glasses were characterized by X-ray powder diffraction to ensure they were completely amorphous. They were subsequently characterized by differential thermal analysis to determine glass transition temperatures and peak crystallization temperatures, coupled with X-ray powder diffraction to identify the crystal phases formed on heat treating. The fluoride containing glasses were based on the generic composition:

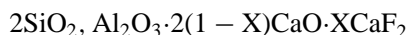


TABLE I Glass compositions studied in molar ratios

Glass	SiO ₂	Al ₂ O ₃	CaO	CaF ₂
G280	2.00	1.00	1.00	1.00
G279	2.00	1.00	1.50	0.50
G276	2.00	1.00	1.67	0.33
G282	2.00	1.00	1.8	0.20

In all these glass compositions there are sufficient calcium ions to ensure a tetrahedral role for the aluminium.

The glass G280 has been extensively studied previously [13, 18, 31] and is a model dental Ionomer glass composition, which can be obtained as a single homogenous glass phase. Furthermore this glass has been shown to undergo minimal fluorine loss during melting. Because of the large amount of data on this glass it was the focus for the trimethylsilylation studies. In addition to the studies on this glass, studies were also performed on selectively heat treated samples of this glass that had partially crystallized to fluorite CaF_2 .

2.2. Trimethylsilylation methods

2.2.1. The Lentz method

The main method of trimethylsilylation used was based on the Lentz method. In this method the powdered glass (10 g) with a particle size less than 45 μm was placed in a round bottom flask. To the glass was added a mixture of water (40 ml), concentrated hydrochloric acid (50 ml), hexamethyldisiloxane (66 ml) and propan-2-ol (100 ml). The mixture was stirred with a magnetic stirrer for a short period, then refluxed for periods of time varying from 1–6 hours in a water bath at 70 °C. The propan-2-ol was used to increase the miscibility of the two phases. The overall reaction is shown in Figs 1 and 2.

A second series of reactions were carried out in which the volume of concentrated hydrochloric acid was 12.5, 25 and 37.5 ml with a constant reflux time of 2 hours.

2.2.2. The dimethylformamide method

In order to investigate the effect of the trimethylsilylation technique, one of the glass samples was analysed using the dimethylformamide method, first used by Tamas *et al.* [32] as a modification of the direct method [28]. This is a less aggressive method of analysis, where the hydrochloric acid is produced in-situ by the breakdown of trimethylchlorosilane. Consequently the acid concentration is much lower and the risk of generating large quantities of $\text{Si}(\text{OH})_4$ species which then undergo condensation polymerization reactions is reduced. The TMS reactions carried out are summarized in Table II.

2.3. Analysis of the products

2.3.1. Gas chromatography

This technique was used to analyse the more volatile components from the polyorganosiloxane mixtures. The GC was fitted with a BPI capillary column. The column temperature was held at 140 °C for one minute, then raised at 10 °C·min⁻¹ to 300 °C, and finally held at this temperature for a further 7 minutes. The siloxanes are eluted in order of increasing molecular weight. This technique is semi-quantitative, since as combustion occurs the flame ionization detector becomes coated with silica which gradually reduces the response factor. Regular calibration reduces this problem but does not overcome it completely.

TABLE II Summary of TMS reactions carried out

Experiment	Silicate source	Reaction conditions
1	G280	6 h Lentz
2	G280	5 h Lentz
3	G280	4 h Lentz
4	G280	3 h Lentz
5	G280	3 h Lentz
6	G280	2 h Lentz
7	G280	2 h Lentz
8	G280	1 h Lentz
9	G280	2 h DMF
10	G280	0.5 h Lentz#
11	G280	1.0 h Lentz#
12	G280	1.5 h Lentz#
13	G280	2.0 h Lentz#
14	G280	2 h Lentz (12.5 ml HCl)
15	G280	2 h Lentz (25.0 ml HCl)
16	G280	2 h Lentz (37.5 ml HCl)
17	G280 (550 °C)	2 h Lentz
18	G280 (580 °C)	2 h Lentz
19	G280 (600 °C)	2 h Lentz
20	G280 (620 °C)	2 h Lentz
21	G280 (720 °C)	2 h Lentz

Only 1.0 g of glass used in these experiments.

2.3.2. Gas chromatography coupled with mass spectrometry (GC-MS)

This technique is a combination of mass spectrometry and gas chromatography. The peaks found by gas chromatography are separated and then identified by mass spectrometry. Previous work [33] has demonstrated that no molecular ions $[M^+]$ are found. The major ion found is $[M-15]^+$, which is believed to be due to the loss of a methyl group from the molecular ion. This technique was used to identify the smaller peaks in the gas chromatogram that did not correspond to simple siloxanes, and in particular those species with the following retention times: 3.1, 5.8 and 7.2 minutes.

2.3.3. Gel permeation chromatography

Gel permeation chromatography was used to characterize and quantify both the low and the high molecular weight polysiloxanes, which could not be quantified by gas chromatography because of their non-volatile nature. A Waters 501 high performance liquid chromatograph was used in gel permeation mode, equipped with a column bank containing 2×10 nm, 2×50 nm and 1×1000 nm microstyrogel columns. Toluene was used as the eluting solvent with a flow rate maintained at $1.5 \text{ cm}^3 \cdot \text{min}^{-1}$.

2.3.4. Nuclear magnetic resonance (NMR) spectroscopy

^{29}Si NMR spectra of the polyorganosiloxanes were run with a Jeol FX270 Multinuclear NMR spectrometer using an INERT pulse sequence technique. The reported chemical shifts of the silicon atoms vary with each different polyorganosiloxane unit; values observed by Harris [34] are shown in Table III. Work performed by Harris and Newman [35], found that ^{29}Si NMR was a useful technique in the identification of trimethylsilyla-

TABLE III Chemical shifts of silicon for different polyorganosiloxanes

Derivative	Unit	Unit causing peak	Chemical shift (ppm)
$\text{SiO}_4[\text{Si}(\text{CH}_3)_3]_4$	QM_4	Q	-104.2
		M	8.6
$\text{Si}_2\text{O}_7[\text{Si}(\text{CH}_3)_3]_6$	Q_2M_6	Q	-106.5
		M	8.9
$\text{Si}_3\text{O}_{10}[\text{Si}(\text{CH}_3)_3]_8$	Q_3M_8	Q	-109.1
		M	9.0
$\text{Si}_4\text{O}_{12}[\text{Si}(\text{CH}_3)_3]_8$	Q_4M_8	Q	-107.8

tion derivatives of silicate minerals, provided the samples were at identical concentration and in the same solvent. The work indicated that the "Q region" of the ^{29}Si spectra gave more useful information than the "M region" because the chemical shifts arising from the Q units were dispersed over a wider range than the M units.

3. Results and discussion

The glass transition temperatures for the range of glasses where fluorite was successively replaced by calcium oxide is given in Table IV. The glass transition temperature is dependent according to Ray [20] on the crosslink density or connectivity of the glass network. The presence of fluorine has a dramatic effect on reducing the glass transition temperature. This effect is consistent with fluorine replacing bridging oxygens between silicons by non-bridging fluorines and disrupting the glass network. A similar effect is obtained when the glass G280 is heat treated and fluorite CaF_2 crystallises out (Table V), however here the ease of crystallization of fluorite, which even occurs readily below the experimentally determined glass transition temperature, supports the contradictory proposal of Rabinovich of fluoride ions being in the sphere of coordination of the

TABLE IV Glass transition temperatures (T_g) as a function of calcium fluoride content for glasses of the series $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2(1-X)\text{CaO} \cdot 2X\text{CaF}_2$

X	T_g
0.10	765 °C
0.17	750 °C
0.25	717 °C
0.50	642 °C
0.9	636 °C

TABLE V Effect of 18 hour heat treatment on the glass transition temperature (T_g) of glass G280 ($X=0.5$) with a particle size $< 45 \mu\text{m}$

Heat treatment	Percent CaF_2	T_g
465 °C	0.00	645 °C
516 °C	trace	642 °C
550 °C	0.40	639 °C
580 °C	8.80	647 °C
600 °C	13.49	650 °C
630 °C	17.00	666 °C

TABLE VI Retention times of polysiloxane standards

Silicate species	Retention time
QM ₄	3.3 min
Q ₂ M ₆	7.9 min
Q ₄ M ₈	13.2 min
Q ₃ M ₈	13.5 min

basic network modifying cation present (in this case calcium). A preliminary attempt was made to investigate the dielectric behaviour of the glass G280, but there was no appreciable conduction and no dielectric losses were observed that could correspond to the hopping of mobile and unbound fluoride ions, so these studies were discontinued. Singer and Tomozoa [36] recently studied fluorine-containing MgO-Al₂O₃-SiO₂ glasses and found no evidence of fluoride ion hopping. The fluorine loss that occurred on melting these glasses was due to the volatilization of magnesium fluoride, rather than silicon tetrafluoride. The results of the analysis of the TMS reactions are shown in Table VII for the gas chromatography data and Table VIII for the gel permeation chromatography. A typical gas chromatogram is shown in Fig. 4. The separation is based on the number of M groups present. Species with the lowest molecular weight are eluted first, followed by species in order of increasing molecular weight. Due to the limited volatility of the higher molecular weight species, it is impossible to detect them by this technique. Samples of the pure polymers were individually analysed and their retention times are given in Table VI. From the gas chromatography results it can be seen that there are peaks present which do not correspond to the retention times given in Table VI. These are at 3.1, 5.8, 7.3, 10.9, 13.3 and 17.9 minutes. The first three of these peaks were subsequently analysed by mass spectrometry. The spectrum for the first unknown peak with the retention time of 3.1 min is shown in Fig. 5. It has the [M-15]⁺ ion at 339 m/e and this suggests the [M]⁺ ion is 354 m/e corresponding to QM₃O_{1/2}IP where IP corresponds to the isopropyl group. The isopropyl derivative is believed to

FORMATION OF ISOPROPYL DERIVATIVE OF POLYSILOXANES

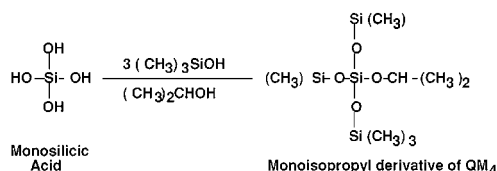


Figure 3 A TMS reaction involving propan-2-ol.

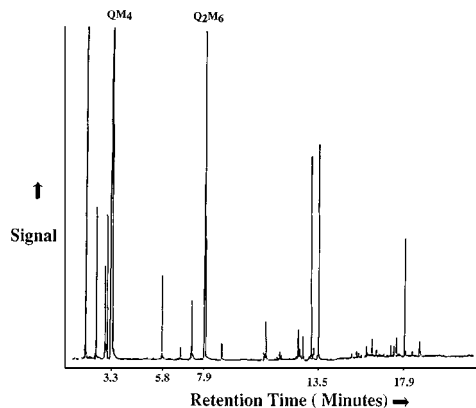


Figure 4 A typical gas chromatograph.

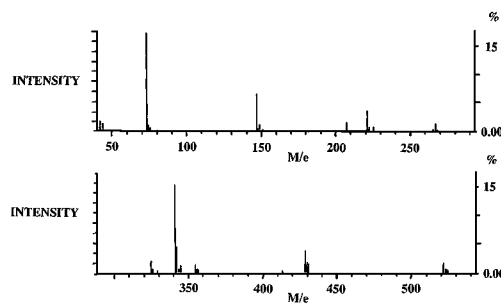


Figure 5 A mass spectrum for the peak with a retention time of 3.1 minutes.

originate from the reaction (Fig. 3) between the silicic acids generated during trimethylsilylation and the isopropyl alcohol added to improve the miscibility of the two phases during the reaction.

TABLE VII Gas chromatography results

Exp	Retention times in minutes									
	3.1	3.3	5.8	7.3	7.9	10.9	13.2	13.3	13.5	17.9
1	—	72.8	—	—	2.5	—	—	—	1.7	6.5
2	—	60.3	—	—	3.6	—	—	—	5.8	2.4
3	1.7	63.9	—	—	7.5	0.4	4.6	—	7.5	0.4
4	—	65.2	1.6	0.6	8.8	—	7.9	—	8.6	1.0
5	—	69.7	—	—	12.1	1.7	4.2	—	3.9	1.8
6	—	50.9	—	1.1	16.3	—	7.7	—	10.4	—
7	—	53.6	1.2	—	12.2	—	8.9	0.2	6.2	—
8	—	69.5	—	—	6.6	2.5	4.5	5.8	13.6	—
9	—	56.7	—	—	14.6	—	6.2	—	8.7	—
14	2.5	78.0	0.9	—	2.2	—	0.6	—	1.2	0.6
15	—	68.8	1.3	0.9	12.4	0.8	3.4	0.2	3.7	2.1
16	1.4	54.7	1.2	0.6	20.6	0.9	8.5	—	7.3	1.2
17	1.6	68.8	2.2	1.0	12.7	1.7	2.7	0.3	3.9	1.4
18	1.6	68.1	2.6	0.7	9.6	1.3	4.5	0.2	5.7	0.6
19	1.4	74.6	1.6	0.4	5.7	0.5	0.6	0.2	0.7	0.4
20	1.4	74.4	5.9	0.8	10.3	1.7	2.6	1.3	3.3	1.3
21	1.5	68.6	2.5	0.9	11.7	1.6	2.5	0.2	3.3	1.4

Note experiments 10–13 were not analysed.

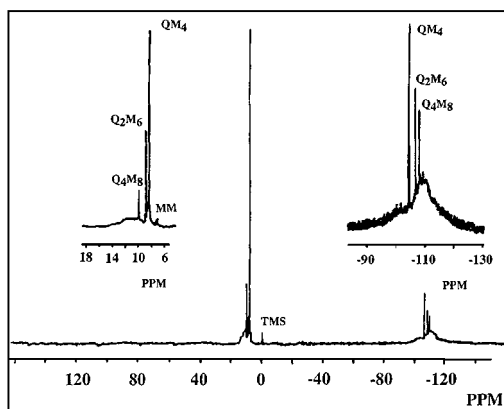
TABLE VIII Gel permeation chromatography results

Analysis	%QM ₄	%Q ₂ M ₆	%Higher species
1	5.5	9.0	85.5
2	6.0	10.0	84.0
3	8.2	26.1	65.7
4	9.0	32.0	59.0
5	10.1	28.3	61.6
6	28.0	7.6	63.4
7	24.3	12.7	63.0
8	32.6	21.0	46.4
9	57.4	8.6	33.7
10	55.6	8.8	34.6
11	50.9	10.2	38.9
12	49.1	11.7	39.6
13	28.9	11.8	59.3
14	40.6	33.1	26.3
15	33.9	33.7	32.4
16	31.2	15.2	53.6
17	11.5	16.4	72.1
18	9.3	17.0	73.7
19	8.0	14.7	77.3
20	8.2	19.0	72.8
21	23.5	9.4	59.3

The second spectrum corresponding to a retention time of 5.8 min showed the $[M-15]^+$ ion at 511 m/e, indicating an $[M]^+$ ion at 526 m/e probably corresponding to $Q_2M_4(O_{1/2}IP)_2$. Finally the last spectrum for a retention time of 7.3 min showed the $[M-15]^+$ ion at 555 m/e for which the M^+ ion would be at 570 m/e, corresponding to the $Q_2M_5O_{1/2}IP$.

The results obtained using GPC were quantitatively confirmed by ^{29}Si NMR (Fig. 6), which clearly showed two distinct areas of resonances. These ^{29}Si resonance areas are from 7 to 14 ppm which is attributed to the $M((CH_3)_3SiO_{1/2})$ groups of the polyorganosiloxane and -104 to -110 ppm which has been attributed to the presence of $Q(SiO_{4/2})$ units. The region from 7 to 14 ppm clearly shows the presence of QM_4 (8.0 ppm), Q_2M_6 (8.5 ppm), Q_3M_8 (9.9 ppm) and a relatively small amount of high molecular weight material (10–14 ppm).

The region from -104 to -110 ppm shows the presence of QM_4 (-104.6 ppm), Q_2M_6 (-106.9 ppm) and Q_3M_8 (-107.3 ppm). The very broad peak from -95 to -125 ppm and centred on approximately -112 ppm

Figure 6 A ^{29}Si nuclear magnetic resonance spectrum.

is due to the silicon from the glass present in the NMR sample tube and the glass contained in the NMR probe.

It can be seen that increased acid concentration results in a larger proportion of the higher molecular weight species. For example in experiments 14, 15 and 16 the acid increases from 12.5 ml to 37.5 ml and the percentage of QM_4 goes from 40.6 to 31.2 whilst the percentage of higher siloxane species go from 26.3 to 53.6. Increased reaction time also results in an increase in the proportion of high molecular weight species. Compare, for example, experiment 8 at 6 hours reaction time with experiment 6 at 2 hours reaction time. The same effect is again observed with experiments 10, 11, 12 and 13 in the GPC data where reaction time is again increased. Thus reactions carried out with the lowest concentration of acid and for the shortest time give the more probable silicate structures of the glasses. Therefore experiment 10 which yielded 55.6 and 8.8 weight percentages of QM_4 and Q_2M_6 respectively is likely to give a slight underestimate of the proportion of isolated SiO_4 tetrahedra in the G280 glass. The DMF technique (experiment 9) gave proportions of QM_4 , Q_2M_6 and higher species in very good agreement with experiment 10 using the Lentz technique. There was no evidence of any fluorinated siloxanes from any of the TMS reactions by GC, in contrast to the fluorinated derivatives found by Calhoun *et al.* [30] and expected on the assumption of there being silicon-fluorine bonds present in the glass. The proportions of QM_4 from both the GPC and GC data are much higher than expected if a totally random structure is assumed consisting of random linking of SiO_4 and AlO_4 tetrahedra with non-bridging oxygens and non-bridging fluorines being associated with the aluminium and silicon atoms in a random fashion. Such an arrangement would give rise to only 12% QM_4 , compared to 57.4% and 55.6% found in experiments 9 and 10 by the more accurate GPC technique. Given that there were no fluorine atoms bonded to silicons, arranging the non-bridging oxygens randomly and allocating the fluorines to bond solely with the aluminium atoms would give rise to only about 6% isolated SiO_4 tetrahedra. The only explanation of the high proportions of QM_4 produced is that the SiO_4 and AlO_4 tetrahedra are not arranged completely randomly. Instead, there is a high frequency of alternating $Al-O-Si$ bonds with the fluorine atoms being associated exclusively with the aluminium atoms and the non-bridging oxygens being associated with the silicon atoms. A completely random arrangement of AlO_4 and SiO_4 tetrahedra would not be expected, because according to Lowenstein's Aluminium Avoidance Principle [37] $Al-O-Al$ bonds are thought to result in electrostatic instability and are consequently unlikely to occur. This proposed structure explains the marked reduction in the glass transition temperature on incorporating fluorine into the glasses shown in Table IV, since fluorine is still acting as a network disrupter. In contrast, if fluorine was bonded to only the calcium atoms present it would not influence the connectivity of the glass network and would not be expected to influence the glass transition temperature behaviour. Further support for fluorine being bonded to the aluminium and not the

silicon comes from some solid state MAS-NMR studies by Kohn *et al.* [38] of similar fluoro-alumino-silicate glass compositions containing a basic oxide in the form of Na₂O rather than CaO.

Comparison of the results of the analysis of the heat treated glasses, heat treated below the glass transition temperature (experiments 17–20 in Table VIII) with the original glass, under identical trimethylsilylation conditions (experiments 6 and 7 in Table VIII) shows a marked reduction in the proportions of QM₄ from > 24% to 8.2%, with a corresponding increase in the proportions of Q₂M₆ and higher species. These results are to be expected as heat treatment results in the crystallization of fluorite, which is a powerful network modifier. Despite the fact that the fluorines only probably bond to the aluminium and therefore should not influence the silicate species present, the calcium ions that crystallize with the fluorines to form fluorite will have a network disrupting role irrespective of the role of fluorines. Removal of the calcium ions from the glass to form fluorite should result in an increase in connectivity of the silicate species and an increase in the proportion of Q₂M₆ and higher silicates at the expense of QM₄. Removal of the fluorines from the aluminium atoms will result in an increase in the connectivity of the glass network and therefore an increase in the glass transition, as found experimentally for the glass heat treated at 635 °C, but it will not directly result in an increase in the connectivity of the silicate network.

The glass heat treated at 720 °C is known to undergo amorphous phase separation into two glass phases prior to bulk crystallization to fluorite, whilst the glasses heat treated below the glass transition temperature are known to undergo crystallization to fluorite by a surface nucleation route. This may explain the very different results obtained in experiment 21 compared to experiments 17 to 20.

4. Conclusions

The trimethylsilylation results and the glass transition temperature and crystallization data support the concept of the fluoro-alumino-silicate glasses studied having a relatively ordered structure, with well defined structural units and a non-random distribution of these structural units. For example there is strong evidence for a repeating sequence of Al–O–Si–O–Al–O–Si–O– in the network as opposed to a completely random distribution of AlO₄ and SiO₄ tetrahedra. Furthermore there is evidence for fluorine being bonded exclusively to the aluminium atoms in the glasses studied and not to the silicon atoms, and there is evidence to suggest that this occurs in the presence of a basic oxide. Thus it appears likely that Rabinovich's hypothesis that fluorine will bond less readily to silicon in the presence of non-bridging oxygens formed as a result of incorporating a basic network modifying oxide is correct, but his assumption that the fluoride ions will instead be in the spheres of coordination of the network modifying cations is incorrect when applied to fluoro-alumino-silicate glasses and may be incorrect when applied to fluorosilicate glasses. The structural role and bonding

of the fluorine has dramatic implications for controlling fluorine emissions from fluoride containing glasses and the indication is that fluorine loss as volatile SiF₄ can be suppressed completely from fluoro-alumino-silicate glasses by appropriate choice of composition and the incorporation of sufficient basic network modifying oxide. In contrast it may well be impossible to prevent loss of SiF₄ from fluoro-silicate glasses. It is also worth noting that in fluoro-alumino-silicate-glasses containing a metallic fluoride such as CaF₂ or NaF loss of SiF₄ will effectively create a basic oxide in the melt and eventually prevent further loss of fluorine as SiF₄. This will almost certainly occur in the existing Ionomer glasses used for dental cements. In contrast, glasses such as the fluorine containing Bioglasses™ will always be susceptible to fluorine loss as SiF₄ since they contain no aluminium. Fluorine loss from these glasses during melting will almost certainly result in marked changes to the glass composition and properties and the final glass composition is likely to depend very critically on the melting temperature and time. This problem has been entirely overlooked in the literature on Bioglasses™.

Many glazes and enamels also contain large amounts of fluorides and are prone to loss of SiF₄. Careful attention to composition and further TMS studies could result in dramatic reductions in hydrofluoric acid emissions and major environmental benefits. It must be remembered, however, that fluorine loss can also occur by direct reaction with water, particularly in gas fired furnaces and also by direct volatilization of metallic fluorides at high temperatures.

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