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The role of aluminium and silicon in the setting chemistry of glass ionomer cements

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Abstract A model of the setting chemistry of glass-ionomer cements (GICs) is proposed based on ^{27}Al and ^{29}Si solid state nuclear magnetic resonance spectroscopy data on three GICs. All the precursor glasses are found to contain three aluminium species viz.: four, five and six-coordinate aluminium environments as well as four-bridging silicate tetrahedra. Upon cement formation, Al^{3+} ions in the glass are leached out from the surface layer of the glass. On entering the cement matrix, these ions adopt six-coordination and crosslink the polymer chains as part of the setting reaction. The remaining four-coordinate aluminium is distributed between two species: one in the inert core of the glass particles; and a second, less concentrated, in the surface layer of the glass particles, modified by the curing reactions. There is some evidence for residual five and six coordinate aluminium species in the final cement in some of the systems. In the case of the silicate tetrahedra, the curing reactions result in a decrease in the number of aluminium atoms in the second coordination sphere, with a subsequent recondensation of silicate network of the glass.

1 Introduction

Glass-ionomer cements (GIC) were first described for use in dentistry by Wilson and Kent [1] in the 1970s. GICs are two components systems consisting of a solid, generally a fluoroaluminosilicate glass, and a liquid, an aqueous solution of polyacrylic acid (PAA) and a small amount of tartaric acid (<2%) [2]. GICs have a series of advantages over other dental materials, in particular their ability to release fluoride, a proven anti-cariogenic component [2–4]. The setting chemistry of these cements has been studied for many years [5, 6]. After mixing both components in the correct proportions, curing reactions occur. Initially, the PAA attacks the surface of glass particles, resulting in the leaching of available cations (e.g. Al^{3+} and Ca^{2+}) [7]. Subsequently, the leached cations cross-link the polymer network within the cement matrix [8]. Models for the setting reaction indicate that aluminium changes its coordination number from four to six during curing [9]. However to date, the detailed nature of the aluminium coordination environment before and after curing remains unclear.

Solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy has previously been used to probe the aluminium and silicon environments in glasses [10–13] and GICs [9, 14, 15]. The ^{27}Al nucleus is quadrupolar with a spin of 5/2 and therefore in addition to the isotropic chemical shift (δ_{iso}), each aluminium environment is also characterised by the quadrupolar interaction between the nuclear electric quadrupolar moment and the electric

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field gradient at the nucleus, described by the quadrupolar coupling constant (C_q) [16]. Characteristic ranges for δ_{iso} and C_q are established for various aluminium coordination environments [17–20]. Using ^{27}Al MAS-NMR, Matsuya et al. [9] investigated aluminium speciation in GICs, but were unable to unambiguously determine the aluminium coordination environments, due to the interference of spinning sidebands in the central transitions of the NMR spectra. However, our recently published ^{27}Al MAS-NMR results [14] at higher spinning rates using the triple quantum (3Q)-MAS technique has given new insights into the aluminium coordination environments in both the cement and precursor glass component of GICs. These results confirmed the existence of three aluminium species in the glass component and four in the cement of a commercial GIC (Fuji II). Additionally, two of the aluminium species present in the inert core of the glass component were also present in the final cement and were unaffected by the curing reactions. The two new signals in the spectrum of the cement were assigned to a four-coordinate aluminium species partially affected by the curing reactions and a six-coordinate aluminium species that cross-links the polymer chains.

Al_2O_3 is a conditional network former. Generally, three types of coordination environment are seen for aluminium in oxide glasses, four-coordinate, five-coordinate and six-coordinate. In both amorphous and crystalline aluminosilicates, vertex sharing between aluminate tetrahedra is thought to be unfavourable due to high instability, and is encompassed in Loewenstein's rule [21] that establishes a limit of 1 for the Si/Al ratio (when both are four-coordinate). Aluminosilicate glass structure is therefore typically characterised by local ordering, with aluminate tetrahedra vertex sharing only with silicate tetrahedra [22]. The silicon coordination environment in these systems is usually described using the Q^n (xAl) terminology, where n indicates the number of bridging oxygen atoms and x the number of aluminium atoms in the second coordination sphere. The silicon speciation can be probed using ^{29}Si MAS-NMR spectroscopy and is aided by the fact that the isotropic resonances (δ_{iso}) shift downfield (higher δ_{iso}) with decreasing n and increasing x and have characteristic shift ranges [23].

In our previous study [14] on a commercial GIC, an upfield (lower δ_{iso}) shift was observed in ^{29}Si resonances after curing, indicating that Al^{3+} ions are leached into the cement matrix, leaving a lower concentration of aluminium in the second coordination sphere of the silicate tetrahedra. Additionally, a re-condensation reaction is believed to occur in order to maintain the observed glass connectivity. In our previous work, only one commercial product was examined. In the present work, we extend our studies to other GIC systems and present a general description of aluminium speciation in GICs before and after curing in order to more clearly establish the critical role of aluminium in GIC setting reactions.

2 Materials and methods

Three different GICs were prepared, either following the instructions of the manufacturers for the commercial formulation *CX-Plus* (*Advanced Healthcare Ltd*, Kent, UK) or mixing the glass component with polyacrylic acid (*Advanced Healthcare Ltd*, Kent, UK), tartaric acid (*Advanced Healthcare Ltd*, Kent, UK) and water in 6:1:0.1:2 weight proportions for the experimental *LG-30* and *XG-153* glasses (*Advanced Healthcare Ltd*, Kent, UK). The formulation of *LG-30* is based on a calcium phosphoaluminosilicate glass ($7.5SiO_2$:$2.5Al_2O_3$:$3.5CaO$:$1.5P_2O_5$), while *XG-153* and *CX-Plus* are lanthanum containing fluoroaluminosilicate glasses, as reported by the manufacturer.

The MAS-NMR spectra were collected on a Bruker MSL 300 P spectrometer at resonance frequencies of 78.2 MHz (^{27}Al) and 59.6 MHz (^{29}Si) and spinning rates of 9.5 kHz (^{27}Al) and 4.5 kHz (^{29}Si). One-pulse radio frequency sequences (Bloch decays) with 0.6 μs or 3.0 μs pulse durations (corresponding to, approximately, 15° or 45° magnetization tip angles) and 5 s or 90 s relaxation delays were used for the observation of ^{27}Al or ^{29}Si spectra, respectively. Aqueous $AlCl_3$ and TMS were used as external references for ^{27}Al and ^{29}Si spectra, respectively. The spectra were modelled using the program *dmfit* [24].

3 Results and discussion

3.1 CX-Plus

The ^{27}Al MAS-NMR experimental and fitted spectra of the *CX-Plus* glass and cement are presented in Fig. 1. Table 1 summarises the NMR parameters and relative concentrations of each aluminium species observed. The results for the glass show the existence of three aluminium species that can be attributed to four, five and six-coordinate aluminium environments based on their characteristic δ_{iso} and C_q values. In the cement, three aluminium species are again observed, two of which have similar NMR parameters at 61.1 ppm (four-coordinate) and 3.1 ppm (six-coordinate) to those observed in the glass. Additionally, a second four-coordinate species at 56.2 ppm is detected in the cement, which corresponds to an aluminium species present in the surface layer of the glass particle, affected by the acid attack. The six-coordinate species in the cement has a slightly lower chemical shift than observed in the parent glass and can be attributed to Al^{3+} cations cross-linking the

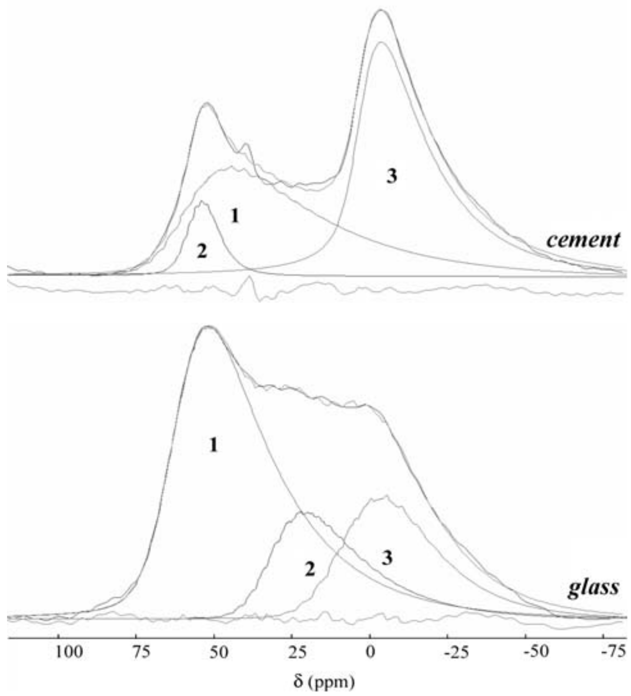

Fig. 1 ^{27}Al MAS NMR experimental and simulated spectra of the glass and cement of the *CX-Plus* material. Peak labels correspond to the assignments given in Table 1

polymer chains in the cement matrix. It is important to note however, that a contribution to this resonance from residual six-coordinate aluminium species in the glass cannot be ruled out. Comparison of the relative concentrations of species between the glass and cement suggest that 17 mol% of the four-coordinate, all the five-coordinate (18 mol%) as well as a part if not all of the six-coordinate aluminium species suffer acid attack in the glass with the corresponding Al^{3+} cations leaching into the cement matrix. Due to the similarity of the NMR parameters for the six-coordinate species in glass and cement it is impossible to establish if all or part of the six-coordinate Al^{3+} ions in the glass are leached out during acid attack. However, considering the relative ionicity of the Al–O contacts surrounding these ions it is predicted that these interactions would be the most susceptible to acid attack and therefore it is reasonable to suppose that a significant proportion of these ions are indeed leached into the cement matrix.

The ^{29}Si MAS NMR spectra of the *CX-Plus* glass and cement are shown in Fig. 2. In this case only a qualitative analysis was performed on cement formation. The spectra show an upfield shift of part of the resonances from the range –90 to –100 ppm assigned to Q^4 (1–4 Al) and/or Q^{0-3} (0 Al) to the range –100 to –115 ppm assigned to Q^4 (0–1 Al) and/or Q^{3-4} (0 Al). This change indicates a general decrease in the number of aluminium atoms in the second coordination sphere and an increase in the connectivity from three to four [23]. The results are consistent with a leaching of Al^{3+} cations from the tetrahedral sites as suggested by the ^{27}Al results. The increase in connectivity detected in the silicon species in the cement suggests re-condensation of the silicate tetrahedra, as observed in previous studies [9, 14].

Table 1 NMR parameters, Al coordination numbers (CN) and relative concentrations of detected species in the glass component and in the final cements of investigated GICs. Peak Labels correspond to those in Figs. 1,3 and 5. Fittings were performed using *dmfit* fitting program [24][a]

Glass component					Cement				
Al CN	Peak	δ_{iso}(ppm)	C_q(MHz)	%[b]	Al CN	Peak	δ_{iso}(ppm)	C_q(MHz)	%[b]
CX-Plus									
4	1	64.9	5.0	64	4	1	61.1	5.2	40
5	2	31.1	4.3	18	4	2	56.2	1.7	7
6	3	6.8	3.6	18	6	3	3.1	3.6	53
LG-30									
4	1	62.6	5.1	71	4	1	62.3	5.1	55
5	2	29.9	4.3	14	4	2	56.2	1.4	2
6	3	11.9	1.6	15	6	3	14.2	1.6	9
					6	4	3.3	3.3	34
XG-153									
4	1	64.8	5.1	67	4	1	63.9	4.5	40
5	2	32.1	4.2	14	4	2	56.3	1.6	5
6	3	6.3	3.8	19	5	3	29.8	4.1	10
					6	4	2.6	3.7	45

[a] Fittings were performed taking into account C_q distributions

[b] Concentration in mol percent

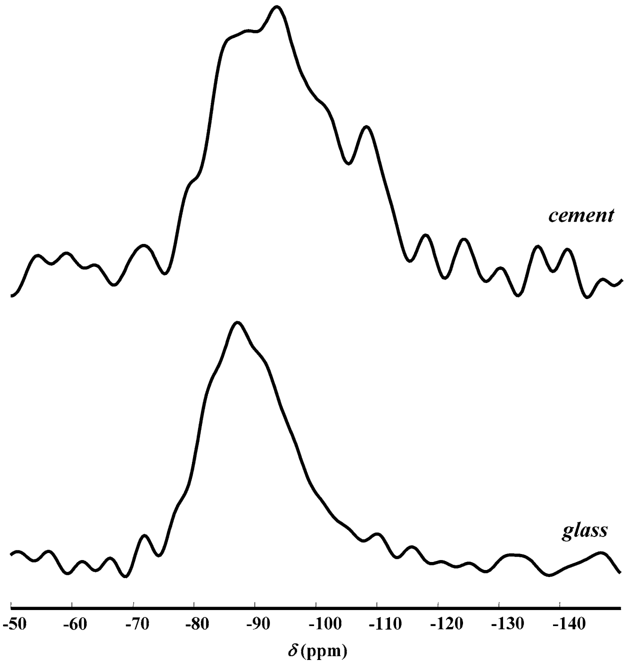

Fig. 2 ^{29}Si MAS NMR spectra of the glass and cement of the *CX-Plus* material

3.2 LG-30

The ^{27}Al MAS NMR spectra of the *LG-30* glass and cement are shown in Fig. 3. As for *CX-Plus*, three aluminium species with four, five and six-coordinate environments are detected in the glass. In the cement, four species are detected, two of which at 62.3 and 14.2 ppm have similar NMR parameters to the four and six-coordinate species in the parent glass and can be attributed to residual four and six-coordinate aluminium species present in the glass particle cores. The resonance from the cement at 56.2 ppm is similar to that seen in the *CX-Plus* cement and, as in that system, can be attributed to a modified four-coordinate aluminium that remains in the reacted surface layer of the glass particles. As in the *CX-Plus* cement, the resonance at 3.3 ppm can be attributed to Al^{3+} cross-linking the polymer chains in the cement matrix. The relative concentrations of species in the cement when compared to those in the precursor glass suggest that Al^{3+} cations in part of the four-coordinate (14 mol%) and six-coordinate (6 mol%) species are leached out of the glass during acid attack as well as all of those in the five-coordinate species (14 mol%).

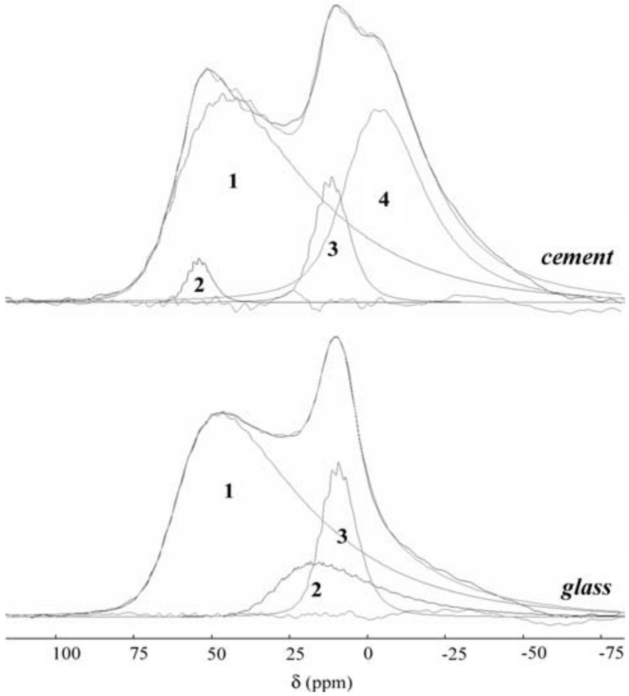

Fig. 3 ^{27}Al MAS NMR experimental and simulated spectra of glass and cement of the *LG-30* material. Peak labels correspond to the assignments given in Table 1

As in the *CX-Plus* system, no five-coordinate aluminium species were detectable in the cement. This is consistent with the presence of this species only in the surface of the glass particle, being leached out as Al^{3+} ions during the acid attack.

The ^{29}Si MAS NMR spectra of the *LG-30* glass and cement are presented in Fig. 4. As in the case of the *CX-Plus* system, the existence of an upfield shift of part of the resonances from the range –80 to –100 ppm (Q^4 (1–4 Al) and/or Q^{0-3} (0 Al)) to the range –100 to –115 ppm (Q^4 (0–1 Al) and/or Q^{3-4} (0 Al)) is consistent with a decrease in

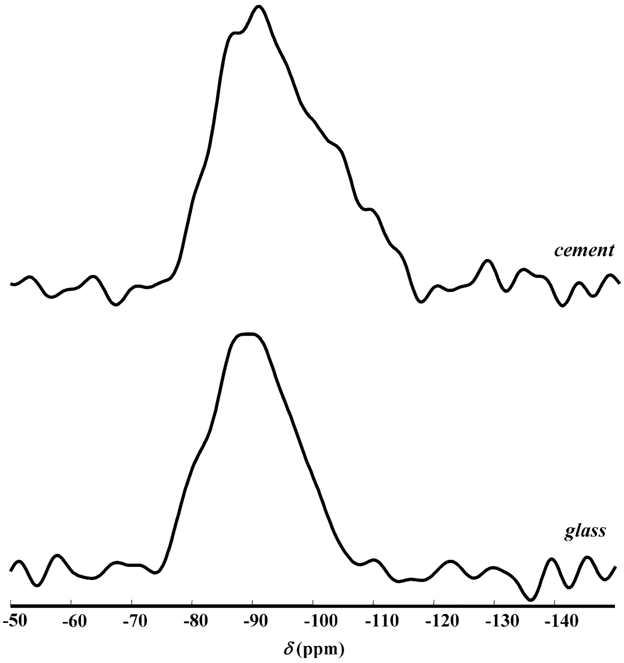

Fig. 4 ^{29}Si MAS NMR spectra of the glass and cement of the *LG-30* material

the number of aluminium atoms in the second coordination sphere and the re-condensation of the silicate species after aluminium leaching.

3.3 XG-153

The ^{27}Al MAS NMR spectra of the *XG-153* glass and cement are presented in Fig. 5. As in the other systems investigated, three species are detected in the precursor glass attributable to four, five and six-coordinate aluminium species. In the spectrum of the associated cement, four-coordinate aluminium resonances at 63.9 and 56.3 ppm are attributed to residual aluminate species in the inert glass core and in the modified surface layer of the glass respectively. Interestingly, unlike the *CX-Plus* and *LG-30* systems some residua1 five-coordinate aluminium species is seen in the cement. As in the *CX-Plus* system, only one six-coordinate species is present in the cement and is due to the partial leaching of Al^{3+} cations from the glass during acid attack. The major contributions to this appear to come from Al^{3+} ions in four and five coordinations in the glass particles (22 and 4 mol%, respectively) and therefore, taking into account the relative concentration of the six-coordinate species in the cement (45 mol%), it is likely to contain a significant contribution (19 mol%) from six-coordinate aluminium species either leached out as Al^{3+} ions from the glass or present as a residual species in the inert glass particle cores and overlapping with this resonance. As discussed above, it is impossible using these techniques to unambiguously establish what proportion of the six-coordinate species in the glass remains unreacted.

The ^{29}Si MAS NMR spectra of the *XG-153* glass and cement are presented in Fig. 6. The presence of a broad shoulder in the cement spectrum (–100 to –110 ppm assigned to Q^4 (0–1 Al) and/or Q^{3-4} (0 Al)), upfield shifted from the silicon glass signal (–75 to –100 ppm assigned to Q^4 (1–4 Al) and/or Q^{0-3} (0 Al)), is consistent with a decrease in the number of four-coordinate aluminium atoms in the second coordination sphere of the silicon and a re-condensation of the affected structures.

3.4 Setting model

A model for the distribution and speciation of aluminium in GICs during setting can now be established. Three aluminium species are present in precursor glass particles, with four, five and six -coordinate environments. During the setting reactions, the glass particles can be described as possessing two distinct regions, a reactive surface layer and an inert core. From previous [14] and present results it is evident that Al^{3+} ions present in the surface layer leach into the cement matrix during acid attack. This leaching phenomenon creates a second six-coordinate environment in

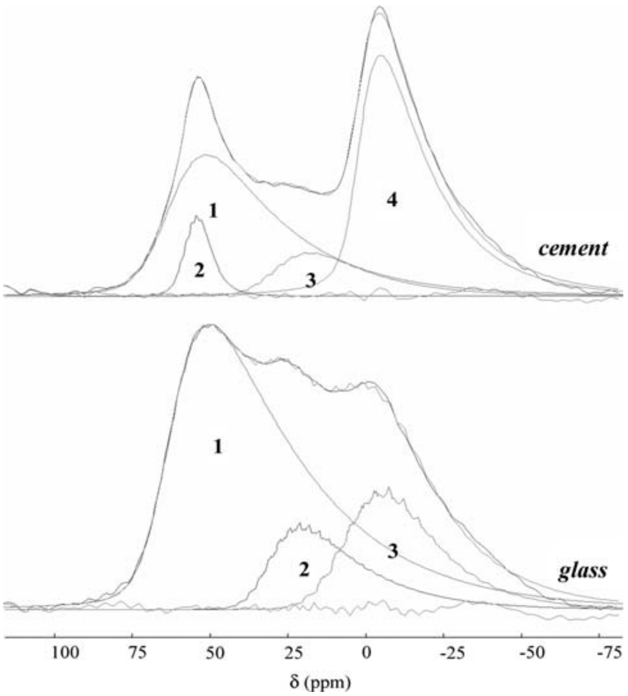

Fig. 5 ^{27}Al MAS NMR experimental and simulated spectra of glass component and cement of the *XG-153* material. Peak labels correspond to the assignments given in Table 1

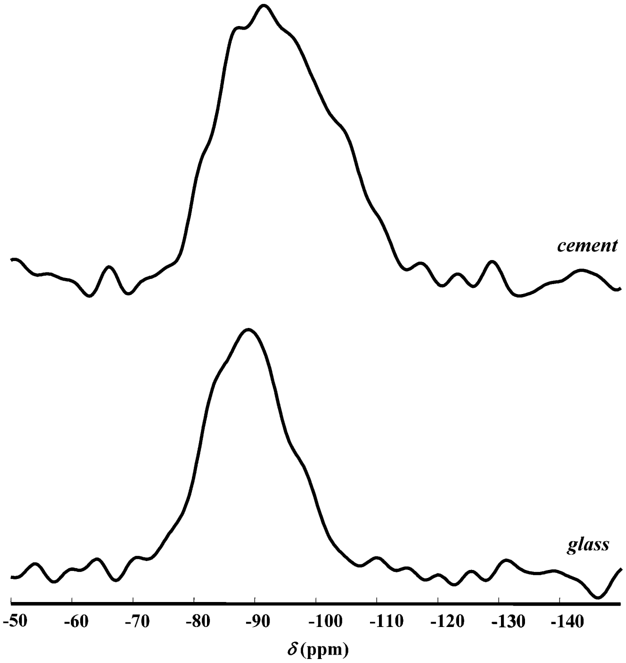

Fig. 6 ^{29}Si MAS NMR spectra of the glass and cement of *XG-153* material

the cement, which can be assigned to Al^{3+} cations cross-linking the polymer chains.

Only a proportion of the Al^{3+} ions in the four-coordinate aluminate species are leached from the glass during acid attack. Additionally, a small amount of a second four-coordinate aluminium species is generated in the surface layer of the glass due to modification of that layer during acid attack. The Al–O bonds in aluminate tetrahedra are considered to be relatively covalent. As such they are more resistant to acid attack, making it more difficult to leach all the tetrahedral aluminium present in the glass. Residual tetrahedral aluminate species are always observed in the spectra of the set cements with those in the surface layer of the glass particle possessing lower C_q values than those in the inert core. Usually, while the δ_{iso} is more sensitive to the Al–O distance, C_q measures the distortion of the aluminate tetrahedra [25]. The observation of a lower C_q value for aluminate tetrahedra in the surface layer suggests a more regular tetrahedral geometry for these moieties. Additionally, ^{29}Si NMR spectra reveal that leaching of Al^{3+} ions from the glass causes a re-condensation of the silicate tetrahedra.

Al^{3+} ions from five-coordinate aluminium species also appear to be leached out from the glass particles during acid attack. Only in one case was a residual five-coordinate aluminium species detected in the final cement. This suggests that generally these species are preferentially located in the reactive surface layer of the glass rather than the inert core. The extent of Al^{3+} leaching from six-coordinate sites in the glass is somewhat less clear, due to similarity of NMR parameters between six-coordinate species in the glass and the cement matrix. Nevertheless, the results would be consistent with a significant proportion of these ions being leached from the glass and entering the cement matrix. Indeed, in the one case (*LG-30*) where a residual six-coordinate aluminium species in the glass was distinguishable from that in the cement matrix, its relative concentration was significantly reduced compared to that in the precursor glass.

4 Conclusions

The data collected on the three GIC systems are consistent with and complement previous results [9, 14] on the setting chemistry of GICs. The results give the type and distribution of aluminium species in the glass precursor and the set cement. They also point to the critical role of aluminium in the setting reaction of GICs as well as giving some insights into that of silicon.

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