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# Degradable borate glass polyalkenoate cements

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**Abstract** Glass polyalkenoate cements (GPCs) containing aluminum-free borate glasses having the general composition  $\text{Ag}_2\text{O}-\text{Na}_2\text{O}-\text{CaO}-\text{SrO}-\text{ZnO}-\text{TiO}_2-\text{B}_2\text{O}_3$  were evaluated in this work. An initial screening study of sixteen compositions was used to identify regions of glass formation and cement compositions with promising rheological properties. The results of the screening study were used to develop four model borate glass compositions for further study. A second round of rheological experiments was used to identify a preferred GPC formulation for each model glass composition. The model borate glasses containing higher levels of  $\text{TiO}_2$  (7.5 mol %) tended to have longer working times and shorter setting times. Dissolution behavior of the four model GPC formulations was evaluated by measuring ion release profiles as a function of time. All four GPC formulations showed evidence of incongruent dissolution behavior when considering the relative release profiles of sodium and boron, although the exact dissolution profile of the glass was presumably obscured by the polymeric cement matrix. Compression testing was undertaken to evaluate cement strength over time during immersion in water. The cements containing the borate glass with 7.5 mol %  $\text{TiO}_2$  had the highest initial compressive strength, ranging between 20 and 30 MPa. No beneficial aging effect was observed—instead, the strength of all four model GPC formulations was found to degrade with time.

## 1 Introduction

Glass polyalkenoate cements (GPCs) have been used as dental materials since their development during the late 1960s [1]. Several features make GPCs ideal dental sealants such as good adherence to dentin, good biocompatibility, and proper working and setting times [2–4]. Traditional GPC formulations are typically based on alkali/alkaline earth aluminosilicate glasses containing minor quantities of other elements such as fluorine, lanthanum, etc. to tune various properties of interest. The general strategy in formulating glasses for GPCs is to produce a glass powder that, upon mixing with an aqueous solution containing a polyalkenoate such as poly(acrylic acid) (PAA), will degrade to release cations. The function of the released cations is to crosslink the PAA chains, thereby increasing the viscosity of the composite and ultimately resulting in the formation of a cement.

More recently, the compositional space used to formulate GPCs has expanded to include other elements such as zinc, strontium, and titanium. One motivation for such compositional modifications is the desire to eliminate aluminum. In conventional dental applications, there are minimal toxicity concerns associated with the release of aluminum from GPCs since it is not readily absorbed through the gastrointestinal tract. However, the use of aluminum-containing GPCs outside of the oral environment is problematic because of potential toxicity concerns [5–10]. The elimination of aluminum from GPC formulations has the potential to enable a host of other applications, including medical device coatings [11], vertebroplasty/kyphoplasty [12], and arthroplasty [13].

The objective of this work was to evaluate borate-based glasses as a primary component of GPCs. Prior studies have considered the use of borate glasses for GPCs,

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**Table 1** Initial screening study of glass compositions

Nominal composition (mol %)							Amorphous?	Working time (min)
Ag <sub>2</sub> O	Na <sub>2</sub> O	CaO	SrO	ZnO	TiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>		
10	20	0	20	0	0	50	No	Not tested
10	0	0	20	0	10	60	No	Not tested
0	10	0	20	20	0	50	Yes	∞
0	20	0	20	0	0	60	Yes	6.83 ± 0.18
0	20	20	0	0	0	60	Yes	3.29 ± 0.29
0	20	0	20	0	10	50	Yes	13.57 ± 1.62
5	0	20	15	0	0	60	Yes	6.77 ± 0.41
0	15	20	0	15	0	50	Yes	∞
2.5	17.5	0	0	20	0	60	Yes	3.87 ± 0.31
0	0	16.67	20	0	3.33	60	Yes	3.03 ± 0.20
5	15	10	10	0	0	60	Yes	2.87 ± 0.15
5	5	20	0	20	0	50	Yes	∞
2.5	17.5	10	20	0	0	50	Yes	∞
5	0	20	10	10	0	55	Yes	∞
5	2.5	0	20	10	10	52.5	Yes	∞
5	5	10	20	0	10	50	Yes	3.76 ± 0.39

A value of “∞” for working time indicates a formulation that did not set to form cement

although these glasses also contained a substantial amount of aluminum [14, 15]. On a related point, the use of borax (nominal composition of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O) as an additive to GPC systems has also been considered, although the purpose of this additive was to modify rheological properties of the cement [16]. The borate glass compositions developed in this study possess several key features: (1) they are entirely free of aluminum, (2) they can accommodate substantial loadings of “dissolved” silver in the ionic state, and (3) they may contain substantial amounts of zinc, strontium and/or titanium. The potential for higher loadings of silver in borate glasses is potentially desirable for antibacterial applications [17].

## 2 Materials and methods

### 2.1 Glass preparation

Batches were prepared using reagent grade sodium carbonate, calcium carbonate, strontium carbonate, titanium dioxide, silver nitrate and boric acid as appropriate. The batch was melted at 1,000–1,200 °C in a platinum crucible for 90 min in an electrically heated furnace. The crucible was removed from the furnace after 60 min and gently agitated by swirling to increase homogeneity of the melt. The melt was quenched by pouring onto a flat steel plate. The glass was broken into smaller pieces using a steel crusher, followed by further comminution in a gyro mill.

An initial set of glass compositions listed in Table 1 were used for the purpose of screening glass formation tendencies and cement rheology.

### 2.2 Powder X-ray diffraction

X-ray powder diffraction was used to determine if the water-quenched glass frit was fully amorphous. Powder diffraction patterns were collected using a Siemens D5000 diffractometer with Cu-K $\alpha$  radiation, a 2 $\theta$  scan range of 10° to 70°, a step size of 0.04°, and a count time of 5 s.

### 2.3 Differential thermal analysis

A combined differential thermal analyzer-thermal gravimetric analyzer (TA instruments, USA) was used to measure the glass transition temperature ( $T_g$ ) for each glass. A heating rate of 20 K min<sup>-1</sup> was used with a flowing air atmosphere. An empty platinum pan filled with alumina powder was used as a reference.

### 2.4 Particle size distribution analysis

The particle size distribution of the glass powder was measured by a Coulter Counter Multisizer 4 particle size analyzer (Beckman Coulter, USA). The glass powders were evaluated in the size range of 2.3 to 60.0  $\mu$ m.

## 2.5 Cement preparation

Cements were prepared with a powder to liquid ratio (P:L ratio) of 2:1.5 on a weight basis. The formulations of different GPCs are shown in Table 4. The PAA used in this study (Advanced Healthcare, Product Code E9, Kent, UK) had a  $M_w$  of 80,800 g mol<sup>-1</sup>, a  $M_n$  of 26,100 g mol<sup>-1</sup>, and a polydispersity of 3.1. Prior to use the PAA was processed by freeze drying and subsequently ground and sieved to retain particles <45 µm in size.

## 2.6 Working time and setting time

The working times were measured from the moment that the powder and water were mixed together until the mixture was no longer pliable. The setting times were measured according to the standard ISO 9917 [18]. An empty steel mold was placed on a small piece of aluminum foil. It was then filled with the mixed cement to a level surface. Sixty seconds after mixing, the entire assembly was placed on a metal block in an oven at 37 °C. Ninety seconds after mixing, a Vicat needle indenter (applied mass of 400 g) was lowered onto the surface of the cement. The needle was allowed to stay on the surface of the cement for 5 s, and then the indent was observed. The process was repeated every 1 min until the indenter fail to make a complete circular indent when viewed at 2× magnification. The setting time of three tests was recorded.

## 2.7 Cement compression strength testing

The compressive strength of cements was tested according to ISO 9917 [18]. The molds were filled with freshly mixed cements to excess and were covered with plastic films on both sides. The entire assembly was sandwiched between two plastic plates, clamped, and incubated at 37 °C. The incubation time was controlled at 10 min longer than the setting time of each formulation of cement. Following the incubation, the molds were removed from the clamps. In order to obtain cylindrical cement samples with flat and parallel ends, excessive material was removed by a blade. Once the cement samples were removed from the molds, they were placed into deionized water for different immersion times due to their different solubility. For cement 1 and 4, the immersion times were 10, 20 and 30 min; for cement 2, the immersion times were 15, 30 and 45 min; for cement 3, the immersion times were 20, 40 and 60 min.

## 2.8 Cement dissolution testing

Dissolution behavior of GPC cylinder samples was evaluated in deionized water at 37 °C at a constant surface area

to volume ratio of ~0.1 using a pseudo-dynamic method. In this method, a GPC sample was incubated in deionized water for a time period that varied depending on cement type. At the end of this time period, the GPC sample was retrieved with tweezers and lightly shaken to largely remove adhered water. The sample was then transferred into a fresh aliquot of deionized water for another time interval. This procedure was repeated until the sample could no longer be handled due to physical degradation. The solution from each time interval was processed using a centrifuge filter and retained for characterization. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to measure the concentration of dissolved ions in triplicate sample solutions (Perkin Elmer, USA).

## 3 Results and discussion

An initial screening study was performed using the nominal glass compositions shown in Table 1. The two glass compositions containing the highest levels of Ag<sub>2</sub>O (10 mol %) were found to crystallize immediately upon quenching of the melt and were excluded from further consideration. The formulations containing up to 5 mol % Ag<sub>2</sub>O were found to readily form glasses as determined by powder XRD. This result is notable in that the silver solubility of typical silicate glasses is generally less than 1 mol %. Work by Coughlan et al. [19] suggests that the antibacterial efficacy of degradable glasses used in GPCs may plateau with increasing silver content. However, the glass compositions used in Reference [18] are markedly different than the borate glasses evaluated in this work; a direct translation of this observation of a plateau in efficacy may not be appropriate.

All of the glasses that were found to be amorphous by powder XRD were subsequently evaluated as GPCs according to a fixed P:L ratio of 2:1.5. A majority of those cement formulations prepared from glass compositions containing less than 60 mol % B<sub>2</sub>O<sub>3</sub> did not exhibit an observable change in viscosity, indicating a lack of adequate crosslinking of the PAA matrix. Two cement formulations containing 50 mol % B<sub>2</sub>O<sub>3</sub> exhibited measurable working time; both glass compositions included the highest levels of SrO and TiO<sub>2</sub> considered in this study (20 and 10 mol %, respectively) and contained no ZnO. It should be noted that these observations do not necessarily preclude the use of zinc in this system.

Based on the results of the initial screening experiment and guidelines in the ISO 9917 standard [18], four new model glass compositions shown in Table 2 were formulated for further study. Descriptive parameters for the particle size distributions of these four glass powders are shown in Table 3. No significant differences in the particle

**Table 2** Nominal model glass compositions (mol %)

Glass code	Ag <sub>2</sub> O	Na <sub>2</sub> O	CaO	TiO <sub>2</sub>	SrO	B <sub>2</sub> O <sub>3</sub>
SH1	0	12.5	10	7.5	10	60
SH2	0	15	10	5	10	60
SH3	0	17.5	10	2.5	10	60
SH4	1	11.5	10	7.5	10	60

**Table 3** Particle size distribution of powder prepared from glasses SH1–SH4

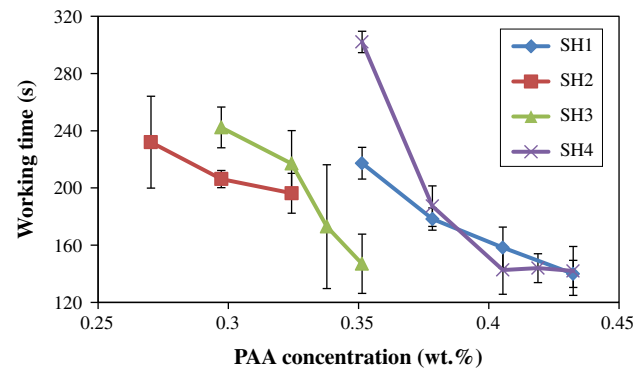
Glass code	d <sub>10</sub> (μm)	d <sub>50</sub> (μm)	d <sub>90</sub> (μm)
SH1	2.6	3.9	7.4
SH2	2.8	4.9	9.1
SH3	2.9	5.4	9.8
SH4	2.8	5.2	9.5
Fuji IX	1.3	4.2	14.4
Ketac Molar	1.2	3.2	8.8

**Table 4** Working time results from screening cement formulations prepared using Glass SH1–SH4

Glass code	Glass (g)	PAA (g)	Water (g)	Mean working time (s)	Standard deviation (s)
SH1	0.5	0.185	0.185	∞	—
	<b>0.5</b>	<b>0.16</b>	<b>0.21</b>	<b>140.0</b>	<b>9.5</b>
	0.5	0.15	0.22	158.3	14.4
	0.5	0.14	0.23	178.3	7.8
	0.5	0.13	0.24	217.3	11.1
SH2	0.5	0.15	0.22	∞	—
	0.5	0.13	0.24	∞	—
	<b>0.5</b>	<b>0.12</b>	<b>0.25</b>	<b>196.3</b>	<b>14.0</b>
	0.5	0.11	0.26	206.3	6.0
	0.5	0.10	0.27	232.0	32.1
SH3	0.5	0.14	0.23	∞	—
	<b>0.5</b>	<b>0.13</b>	<b>0.24</b>	<b>147.0</b>	<b>20.7</b>
	0.5	0.135	0.245	173.0	43.3
	0.5	0.12	0.25	217.0	23.1
	0.5	0.11	0.26	242.3	14.2
SH4	<b>0.5</b>	<b>0.16</b>	<b>0.21</b>	<b>142.0</b>	<b>17.1</b>
	0.5	0.155	0.215	144.0	10.1
	0.5	0.15	0.22	142.7	16.9
	0.5	0.14	0.23	187.3	14.2
	0.5	0.13	0.24	302.0	7.5

Cement formulations selected for further evaluation are formatted with bold text

size distributions were observed, suggesting that particle size is not an explanatory variable for the subsequent differences observed in cement performance. Particle size distribution data are also included for two commercial

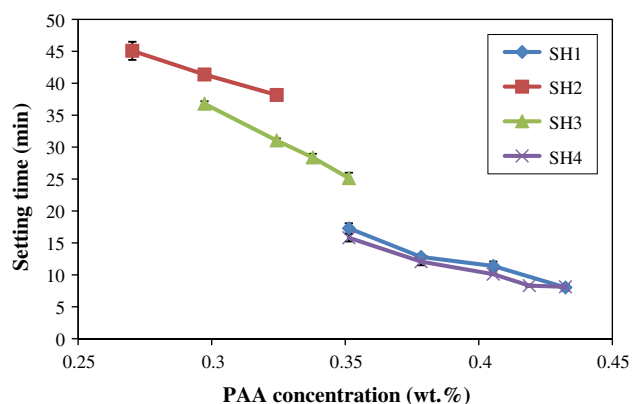
**Fig. 1** Working times of cement formulations prepared from Glasses SH1 to SH4 as a function of PAA concentration (wt % on the basis of the total formulation). Lines are drawn as guides to the eye. Error bars represent  $\pm 1$  standard deviation**Table 5** Setting time results from screening cement formulations prepared using glasses SH1–SH4

Glass code	Glass (g)	PAA (g)	Water (g)	Mean setting time (min)	Standard deviation (min)
SH1	<b>0.5</b>	<b>0.16</b>	<b>0.21</b>	<b>8.03</b>	<b>0.51</b>
	0.5	0.15	0.22	11.39	0.72
	0.5	0.14	0.23	12.81	0.29
	0.5	0.13	0.24	17.29	0.79
SH2	<b>0.5</b>	<b>0.12</b>	<b>0.25</b>	<b>38.17</b>	<b>0.33</b>
	0.5	0.11	0.26	41.37	0.69
	0.5	0.10	0.27	45.08	1.43
	0.5	0.09	0.28	47.76	2.25
	0.5	0.08	0.29	58.61	3.42
SH3	<b>0.5</b>	<b>0.13</b>	<b>0.24</b>	<b>25.14</b>	<b>0.87</b>
	0.5	0.125	0.245	28.38	0.59
	0.5	0.12	0.25	31.04	0.33
	0.5	0.11	0.26	36.79	0.40
SH4	<b>0.5</b>	<b>0.16</b>	<b>0.21</b>	<b>8.13</b>	<b>0.28</b>
	0.5	0.155	0.215	8.31	0.17
	0.5	0.15	0.22	10.11	0.12
	0.5	0.14	0.23	12.07	0.57
	0.5	0.13	0.24	15.81	0.58

Formulations selected for further evaluation are formatted with bold text

glass powders (Fuji IX and Ketac Molar) commonly used in clinical GPCs. The particle size distributions of the laboratory made powders are roughly comparable to the commercial powders.

Table 4 shows the working time results for cements prepared from the four model glass compositions; these same results are also summarized in Fig. 1. The working time was found to decrease with increasing PAA content and decreasing water content for all four model glass compositions. The working time data also exhibited two

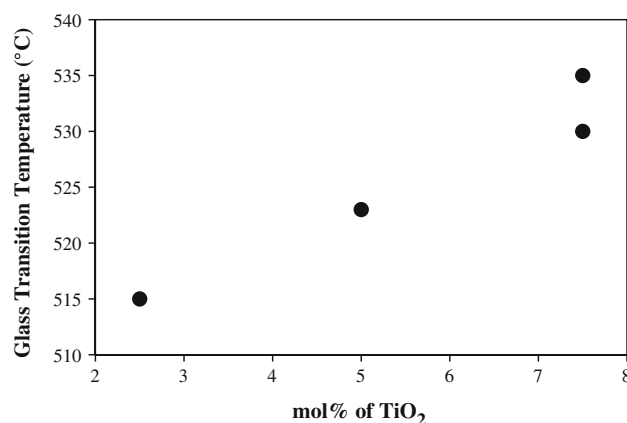


**Fig. 2** Setting time of cements prepared from glasses SH1 to SH4 as a function of PAA concentration (wt % on the basis of the total formulation). Lines are drawn as guides to the eye. Error bars represent  $\pm 1$  standard deviation and are within the symbol when not visible

clusters—i.e., the dependence of working time on PAA concentration was similar for model glasses SH2 and SH3 and again for glasses 1 and 4. A principle difference among the model glass compositions is the  $\text{TiO}_2$  content. Glasses SH1 and SH4 both contain the highest levels of  $\text{TiO}_2$  (7.5 mol %). While the working time data for the two clusters do not significantly overlap along the abscissa of Fig. 1, extrapolation of the plots indicates that cements prepared from glasses SH1 and SH4 at a fixed PAA concentration would have significantly longer working times than cements prepared from glasses SH2 and SH3.

Setting times were also determined for cement formulations that had measurable working times. The setting time results are shown in Table 5 and Fig. 2. Once again, a general trend was observed in which setting time decreased with increasing PAA content and decreasing water content. Glasses SH2 and SH3 exhibited longer setting times relative to glasses SH1 and SH4, although the formulations also contained lower PAA content and higher water content. Nonetheless, extrapolation of the curves suggests that a significant difference in setting time would be observed among the glasses for cements prepared with constant PAA content.

The working time and setting time results are seemingly in conflict. Glasses SH1 and SH4 initially possess longer working times relative to glasses SH2 and SH3, but this ranking is subsequently swapped for setting times. As previously mentioned, glasses SH1 and SH4 contain the highest level of  $\text{TiO}_2$  (7.5 mol %) among the four model glass compositions. It is hypothesized that titanium released from the glass and in the form of oxotitanium species (e.g., the  $(\text{TiO})^{2+}$  cation) may serve a structural role within the PAA matrix of a GPC. This hypothesis is indirectly supported by the wealth of literature demonstrating that carboxylic acid groups are capable of forming



**Fig. 3** Relationship between  $T_g$  and  $\text{TiO}_2$  content of Glasses SH1 to SH4

strong, stable complexes with mono- and multi-nuclear oxotitanium species [20].

In order for titanium-based species to act as a cross-linking agent for PAA chains, it must first be released from the glass. One interpretation of the observed trends in cement rheology is that the more chemically durable glasses SH1 and SH4 are slower to release titanium into the PAA matrix, thereby causing longer working times. However, once sufficient degradation has occurred, glasses SH1 and SH4 may ultimately introduce a higher concentration of titanium into the PAA matrix that reduces the setting time of the cement. This behavior is desirable from a practical standpoint, given that a clinician would presumably prefer a cement formulation with a reasonably long working time that sets quickly after being placed.

The DTA results shown in Fig. 3 demonstrate the positive correlation between  $T_g$  and  $\text{TiO}_2$  concentration in glasses SH1 to SH4, supporting the conclusion that the addition of  $\text{TiO}_2$  to the compositions in this study stabilize the glass network. This stabilizing role is reasonable given that the  $\text{Ti}^{4+}$  cation is generally regarded as an intermediate species within the classical framework for categorizing the tendencies of cations to form oxide glasses [21]—i.e., titanium contributes to the formation of the glass network but is not able to form a glass independent of a primary glass network former such as silicon, boron, etc.

The rheology results shown in Tables 4 and 5 guided the selection of four preferred model cement formulations for further study. The model cement formulation prepared from glass composition SH1 is designated CSH1—glass SH2 was used to prepare model cement CSH2, and so on. Working time and setting time results for the model cement formulations are provided in Tables 6 and 7, respectively. Tukey's Honestly Significant Difference (HSD) test was used to evaluate the rheology results; a  $P$  value of 0.05 was



**Table 6** Working times of four cement formulations

Cement code	Working time (s)
CSH1	140 ± 9.5
CSH2	196 ± 14.0
CSH3	147 ± 20.7
CSH4	142 ± 17.1

**Table 7** Setting times of four cement formulations

Cement code	Setting time (min)
CSH1	8.03 ± 0.51
CSH2	38.17 ± 0.33
CSH3	25.14 ± 0.87
CSH4	8.13 ± 0.28

**Table 8** Tukey HSD analysis of working time data

Working time comparison	<i>P</i> value
CSH1/CSH2	0.0104*
CSH1/CSH3	0.9465
CSH1/CSH4	0.9985
CSH2/CSH3	0.0215*
CSH2/CSH4	0.0128*
CSH3/CSH4	0.9791

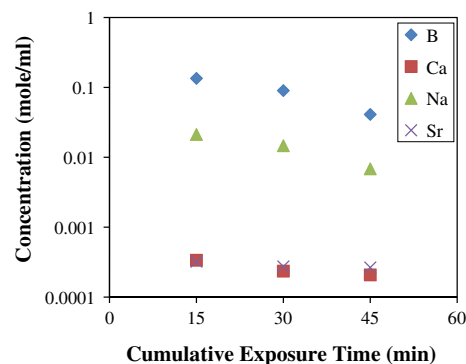
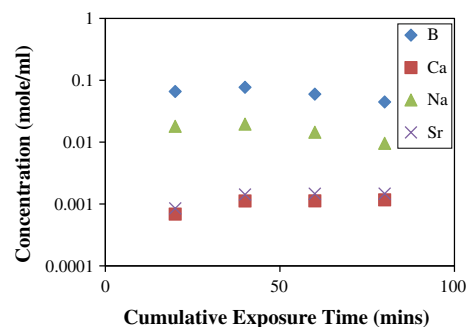
\* Denotes a comparison that is different with greater than 95 % confidence

**Table 9** Tukey HSD analysis of setting time data

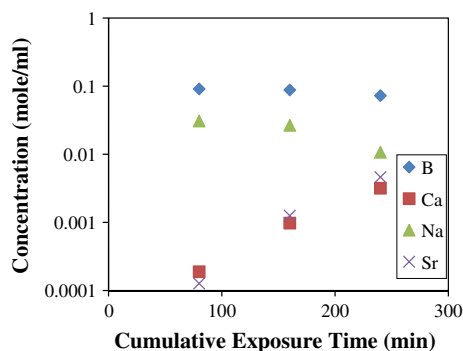
Setting time comparison	<i>P</i> value
CSH1/CSH2	0.0000*
CSH1/CSH3	0.0000
CSH1/CSH4	0.9953
CSH2/CSH3	0.0000*
CSH2/CSH4	0.0000*
CSH3/CSH4	0.0000*

\* Denotes a comparison that is different with greater than 95 % confidence

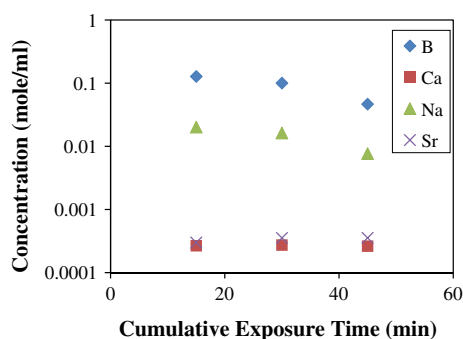
used a threshold for identifying statistically significant differences. The results of Tukey HSD testing on the rheology results are summarized in Tables 8 and 9. A common feature of both results is that the working time and setting time of cements CSH1 and CSH4 were not found to be significantly different. This result is not surprising given that cements CSH1 and CSH4 have identical formulations (ignoring slight differences in glass density and hence differences in the volumetric loading of glass within the cement) and that glasses SH1 and SH4 are compositionally quite similar.

**Fig. 4** Concentration of detectable released ions from Cement CSH1 as a function of cumulative exposure time**Fig. 5** Concentration of detectable released ions from Cement CSH2 as a function of cumulative exposure time

Figures 4, 5, 6 and 7 show the ion release profiles from model cements CSH1–CSH4, respectively, as a function of cumulative exposure time to water. Released titanium was not detectable for any cement over the evaluated time period, supporting the conclusion that titanium is strongly complexed within the PAA matrix. It is also possible that some amount of titanium remains at the surface of the glass particles due to incongruent dissolution. In addition, the release of silver from cement CSH4 was not detected over the time scale of the experiment. The apparent lack of silver release could simply be an issue of instrumental sensitivity, although complexation of silver by PAA cannot be eliminated as a possibility [22]. The release profiles for calcium and strontium were qualitatively similar within each model cement formulation. The concentrations of calcium and strontium released into solution were essentially constant with cumulative exposure time for cements CSH1, CSH2, and CSH4. However, cement CSH3 showed a measurable increase in calcium and strontium release with cumulative exposure time. Cement CSH3 contained glass SH3, the material which had the lowest titanium content (2.5 mol %) of the four model glass compositions used to prepare cements CSH1–CSH4. Assuming that glass SH3 resulted in the least strongly cross-linked PAA matrix, the increased release of calcium and strontium from cement



**Fig. 6** Concentration of detectable released ions from Cement CSH3 as a function of cumulative exposure time

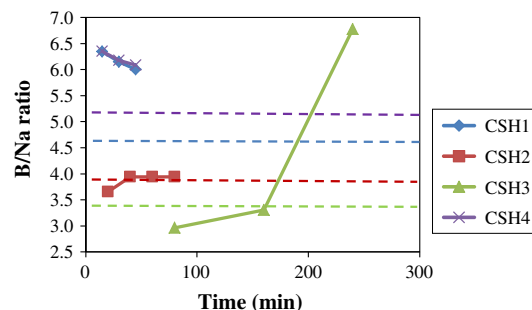


**Fig. 7** Concentration of detectable released ions from Cement CSH4 as a function of cumulative exposure time

CSH3 over time may be an indicator of increased susceptibility to hydrolytic degradation relative to the more strongly cross-linked matrices of cements CSH1, CSH2, and CSH4.

The ion release profiles shown in Figs. 4, 5, 6 and 7 also demonstrate that sodium and boron are released in substantial quantities from all four model cements and, by extension, the constituent glasses. The concentration of sodium in all four model glass compositions is higher than the associated concentrations of calcium and strontium. However, the greatest difference is only 6.5 mol %—i.e., glass SH3 nominally contains 17.5 mol %  $\text{Na}_2\text{O}$  and 10 mol % each of  $\text{CaO}$  and  $\text{SrO}$ . With the exception of cement CSH3, the levels of dissolved sodium are much greater than the associated levels of calcium and strontium, suggesting that calcium and strontium are complexed more strongly by the PAA matrix. The relative levels of sodium, calcium, and strontium released from cement CSH3 converge to a point over time that is more reflective of the starting composition of glass SH3; this again may be due to significant degradation of the PAA matrix.

The ion release profiles for cements CSH1–CSH4 illustrate that the PAA matrix complicates a definitive interpretation of the dissolution behavior of the constituent glass particles. However, a consideration of the results on a



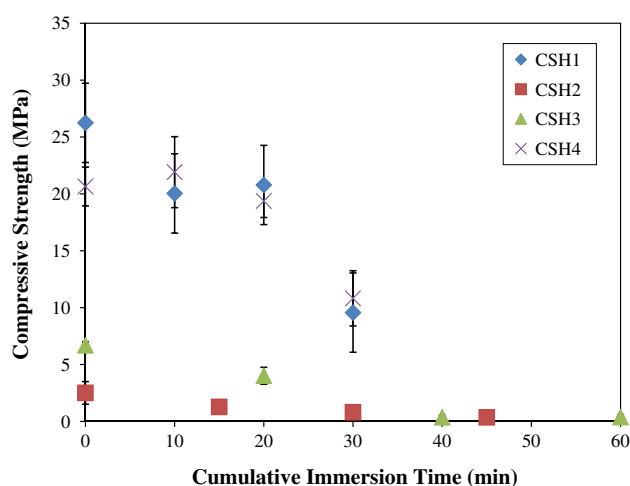
**Fig. 8** B/Na molar ratio dissolved from Cements CSH1 to CSH4 as a function of cumulative exposure time. The horizontal dashed lines represent the nominal starting B/Na molar ratio in the glass powder used to prepare a given cement formulation

relative basis may provide some additional insight. Figure 8 is a compilation of the ion release profiles for cements CSH1–CSH4 that has been constructed using the molar ratio of dissolved boron to sodium (B/Na). The rationale for incorporating boron and sodium into a metric for dissolution behavior is their presumably distinct roles as a network former and a network modifier, respectively, within the glass structure [23]. Congruent dissolution of the entire glass structure is expected to produce a B/Na release profile that is equivalent to the nominal stoichiometric B/Na ratio of the starting glass powder. Incongruent dissolution is generally observed as selective extraction of network modifiers from the glass surface and therefore is expected to produce a B/Na release profile that is below the nominal stoichiometric B/Na ratio.

The horizontal lines included within the figure indicate the starting nominal B/Na ratio of the constituent glass for each cement type. As expected, cements CSH1 and CSH4 produce essentially identical B/Na profiles as a function of cumulative exposure time. The plots for cements CSH1 and CSH4 are negatively sloped and located above the nominal B/Na ratios for the respective glass compositions. The position of the profiles above the stoichiometric B/Na ratio indicates an excess of boron relative to sodium in solution. This might be interpreted on the basis of selective retention of cations by the PAA matrix since prior studies have shown that PAA readily complexes alkali metal cations [24].

The potential importance of selective cation retention within the crosslinked PAA matrix is obscured by the B/Na ratio release profiles generated by cements CSH2 and CSH3, both of which start below the nominal stoichiometric B/Na ratios for the constituent glasses. Furthermore, an extended time point that happened to be collected for cement CSH3 demonstrates that the B/Na release profile crossed over from a state of excess sodium to excess boron. It is unclear at this time why the ion release profiles presented on the basis of B/Na ratios are distinctly different





**Fig. 9** Change in compressive strength of cements CSH1–CSH4 with immersion time. Error bars represent  $\pm 1$  standard deviation and are within the symbol when not visible

between cements CSH1 and CSH4 versus cements CSH2 and CSH3, although there are at least two potentially relevant factors. Firstly, glasses SH2 and SH3 have higher  $\text{Na}_2\text{O}$  and lower  $\text{TiO}_2$  contents relative to glasses SH1 and SH4. Given that the concentrations of the other components ( $\text{CaO}$ ,  $\text{SrO}$ , and  $\text{B}_2\text{O}_3$ ) are all nominally the same among the four glass compositions, it is expected that glasses SH2 and SH3 are less durable and may be prone to readily releasing sodium. Secondly, as shown in the last column of Table 6, the mass ratio of glass to total solids content (defined here as the total mass of glass and PAA powders used to prepare a given cement formulation) also varies among the four model cement formulations. Cements CSH2 and CSH3 contain higher loadings of glass powder relative to cements CSH1 and CSH4. The higher loading of glass powder in cements CSH2 and CSH3 is expected to produce a concomitantly higher level of glass dissolution products within a constant volume of cement.

Figure 9 shows the compressive strength of the four model GPCs versus the immersion time in water. At time zero, cements CSH1 and CSH4 exhibited significantly higher compressive strength than cements CSH2 and CSH3. All four model cements showed a decrease in strength over time when directly immersed in water, with the magnitude of the decrease being significantly larger for cements CSH1 and CSH4. None of the four model cements released detectable levels of titanium from the PAA matrix during the time scale of the experiments. Given the substantial release of the glass network former (i.e., boron) from the cements, it is reasonable to assume that titanium is extracted from the glass powder but is retained within the PAA as a cross-linking cation. The significantly higher compressive strength of cements CSH1 and CSH4 is possibly due to differing concentrations of titanium introduced

into the PAA matrix. However, the initial compressive strengths of even the best performing model cements considered in this study are unfortunately much lower than the 50 MPa minimum compressive strength specified by the ISO 9917 standard for dental cements [18].

## 4 Conclusions

Aluminum-free, borate-based glasses that contain silver (at levels appreciably higher than is typically possible in silicate glasses), sodium, calcium, strontium, zinc, and/or titanium have been evaluated for use in GPCs. Acceptable working and setting times may be achieved through proper selection of glass composition and GPC formulation. It was found that the inclusion of  $\text{TiO}_2$  had a counterintuitive yet potentially beneficial effect with respect to controlling rheological properties—i.e., the model glasses with the highest  $\text{TiO}_2$  content tended to have the longest working times and shortest setting times. Further work should be performed to identify the mechanistic role of titanium. For example, elemental mapping of set GPCs may clarify if titanium is released from the degradable borate glass into the PAA matrix.

While the mechanical properties of the borate-based GPCs considered in this work is not sufficient for structural applications, they may still be of use in applications where minimal load bearing and/or rapid resorption is required. Furthermore, the selected model glass compositions represent a first attempt to explore the possibility of aluminum-free borate-based GPCs. Further work is warranted to determine if improvements in strength, chemical stability, etc. can be obtained through compositional refinements such as increased  $\text{TiO}_2$  content and/or the addition of other relatively high field strength cations.

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