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Evidence of a complex species controlling the setting reaction of glass ionomer cements

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ABSTRACT

Objective. To elucidate the mechanism(s) responsible for the profound impact germanium has on the setting reaction of zinc silicate glass ionomer cements (GICs).

Methods. Five <45 μm glass powder compositions (0.48-xSiO_2, xGeO_2, 0.36 ZnO, 0.16 CaO; where x = 0.12, 0.24, 0.36, 0.48 mol. fraction) were synthesized. Glass degradation was assessed under simulated setting conditions using acetic acid from 0.5 to 60 min, monitoring the concentrations of ions released using ICP-OES. Subsequently, GICs were prepared by mixing fresh glass powders with polyacrylic acid (PAA, Mw = 12,500 g/mol, 50 wt% aq. solution) at a 1:0.75 ratio. Cement structure and properties were evaluated using ATR-FTIR and rheology (for 60 min), as well as 24 h biaxial flexural strength.

Results. Reduced Si:Ge ratios yielded faster degrading glasses, yet contrary to expectation, the corresponding ATR-FTIR spectra indicated slower crosslinking within the GIC matrix. Rheology testing found the initial viscosity cement pastes reduced with decreased Si:Ge, and Ge containing cements all set significantly slower than the Si based GIC. Interestingly, biaxial flexural strength remained consistent regardless of setting behavior.

Significance. This counter-intuitive combination of behaviors is attributed to the presence of a chemical complex species specific to Ge-containing glasses that delays, but does not hinder, the formation of the GIC matrix. These findings embody chemical complex species as a mechanism to decouple glass reactivity from cement setting rate, a mechanism with the potential to enhance the utility of GICs in both dental and orthopaedic applications.

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1. Introduction

Glass ionomer cements (GICs) demonstrate an innate relationship between handling characteristics and mechanical behavior. Both of these properties are highly dependent on the reactivity of the glass, and altering one often has a reciprocal effect on the other [1–4]. GICs are the product of mixing a basic glass powder with an aqueous solution of polyalkenoic acid. Initial setting of the cement results from the formation of a polysalt matrix produced as multivalent cations (e.g. Al^{3+}, Ca^{2+}, Zn^{2+} leached from the acid degradable glass) crosslink the polyanion chains of the deprotonated acid [5]. After the initial set (i.e. gelation), GICs continue to harden over time due to continued crosslinking [6] and as hydrated silicate or phosphate networks are formed [7,8]. This setting reaction serves as the origin for the innate relationship between the handling and mechanical properties of GICs. Setting times can be adjusted by controlling the rate and the extent to which the glass degrades, but mechanical integrity is dependent on the number and strength of the metal-carboxylate crosslinks within the matrix [5]. This imbalance is present in both conventional GICs (i.e. those comprising aluminosilicate glasses) used in dentistry [1,9,10], and aluminum-free GICs (e.g. zinc silicates) proposed for various orthopaedic applications [3,11–15]. For conventional cements, this issue has been practically circumvented through the application of fluoride-containing glasses and or the use of (+)-tartaric acid as an additive in GIC systems [8]. However for the aluminum-free compositions, this correlation has yet to be adequately addressed and represents a fundamental obstacle towards their clinical applicability.

The authors have previously reported on the unexpected findings that a full replacement of SiO_2 with GeO_2 in zinc silicate glasses significantly extends the setting time of GICs while maintaining their strength [16]. These slow setting and high strength characteristics have potential implications to the use of GICs in both dental and orthopaedic applications, but are completely counterintuitive given the innate relationship between handling and mechanical performance described above. Current knowledge regarding the impact of germanium (Ge) on the GIC setting reaction is limited, as only discrete data derived from the assessment of handling characteristics (i.e. working and setting times), of cement systems comprising overly complex glasses have been obtained [16–18]. The present study addresses this knowledge gap by examining various stages of the cement setting reaction over time in simplified Ge-modified zinc silicate GIC systems. Specifically, (i) the assessment of glass reactivity by profiling glass degradation rates under simulated setting conditions; (ii) profiling in situ structural changes as the GIC matrix is formed using attenuated total reflectance Fourier transform infrared spectroscopy; (iii) directly measuring the progression of GIC setting using rheology to obtain viscosity profiles; and (iv) monitoring the post-gelation hardening of the GIC matrix by measuring the biaxial flexural strength. The objective of this work is to elucidate the mechanism(s) associated with the delayed setting of GICs containing Ge.

Table 1 – Composition of 5 experimental BD series glasses (mol. fraction) with corresponding glass transition temperatures (T_g).

	Si: Ge Ratio	SiO_2	GeO_2	ZnO	CaO	T_g [°C]
BD1	1:0	0.48	0	0.36	0.16	673
BD2	3:1	0.36	0.12	0.36	0.16	653
BD3	1:1	0.24	0.24	0.36	0.16	631
BD4	1:3	0.12	0.36	0.36	0.16	620
BD5	0:1	0	0.48	0.36	0.16	597

2. Experimental

2.1. Glass synthesis

Five experimental glasses (BD1-5) were synthesized with molar compositions of: $(0.48\text{-}x)$ SiO_2, $xGeO_2$, 0.36 ZnO, 0.16 CaO; where $x = 0.12, 0.24, 0.36, 0.48$. Analytical grade reagents silica, germanium dioxide, zinc oxide and calcium carbonate (Sigma–Aldrich, Canada) were weighed out and blended together for 1 h in a mechanical mixer. Post-mixing, powder compositions were packed into platinum crucibles (Alfa-Aesar, USA) and fired (1500 °C, 1 h) in a high temperature furnace (Carbolite RHF 1600, UK) then subsequently quenched in water at room temperature. The resultant glass frit was dried overnight (120 °C) then ground in a planetary ball mill (Fritsch Pulverisette 7, Germany) and sieved to retrieve a particle size less than 45 μm. All glass powders were subsequently annealed in platinum crucibles in a high temperature furnace at T_g − 30 °C for 3 h and left to furnace cool (T_g provided in Table 1). All prepared glass powders were stored in a desiccator for subsequent analysis.

2.2. Differential scanning calorimetry

The glass transition temperature (T_g) for each glass composition was determined using a differential scanning calorimeter (Netzsch STA 409PC, USA). Approximately 30 mg of glass powder was placed into a platinum closed pan with the reference pan left empty. Samples were heated at 10 °C min^{-1} to 1000 °C. Proteus Thermal Analysis software (Netzsch Instruments, USA) was used for data analysis with T_g taken as the point of inflection.

2.3. X-ray diffraction

Prior to heat treatment, glass powders were analyzed with an x-ray diffractometer (Bruker, D8 Advanced, Canada) equipped with a LynxEye silicon strip detector and Cu Kα radiation generated at 40 kV and 40 mA. Specimens were pressed in round polymethyl methacrylate holder and exposed to x-ray beam incident at 5° with the detector collecting scatters between $5° < 2\theta < 100°$ over 950 s.

2.4. Glass ion release profiles under simulated setting conditions

To simulate the setting process of a GIC, each experimental glass was mixed with acetic acid for 0.5, 1, 2, 5, 10, 15, 30, and 60 minutes and concentration of released ions were