Silicate, borosilicate, and borate bioactive glass scaffolds with controllable degradation rate for bone tissue engineering applications. I. Preparation and in vitro degradation

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Abstract: Bioactive glass scaffolds with a microstructure similar to that of dry human trabecular bone but with three different compositions were evaluated for potential applications in bone repair. The preparation of the scaffolds and the effect of the glass composition on the degradation and conversion of the scaffolds to a hydroxyapatite (HA)-type material in a simulated body fluid (SBF) are reported here (Part I). The in vitro response of osteogenic cells to the scaffolds and the in vivo evaluation of the scaffolds in a rat subcutaneous implantation model are described in Part II. Scaffolds (porosity = 78–82%; pore size = 100–500 μm) were prepared using a polymer foam replication technique. The glasses consisted of a silicate (13-93) composition, a borosilicate composition (designated 13-93B1), and a borate composition (13-93B3), in which one-third or all of the SiO2 content of 13-93 was replaced by B2O3, respectively. The conversion rate of the scaffolds to HA in the SBF increased markedly with the B2O3 content of the glass. Concurrently, the pH of the SBF also increased with the B2O3 content of the scaffolds. The compressive strengths of the as-prepared scaffolds (5–11 MPa) were in the upper range of values reported for trabecular bone, but they decreased markedly with immersion time in the SBF and with increasing B2O3 content of the glass. The results show that scaffolds with a wide range of bioactivity and degradation rate can be achieved by replacing varying amounts of SiO2 in silicate bioactive glass with B2O3. © 2010 Wiley Periodicals, Inc. J Biomed Mater Res Part A: 95A: 164–171, 2010.

Key Words: scaffold, bioactive glass, hydroxyapatite, bone repair

INTRODUCTION
Bioactive glasses are attractive materials for filling bone defects because of their widely recognized ability to support the growth of bone cells1,2 and to bond strongly with hard and soft tissue.3,4 Upon implantation, bioactive glasses convert to an amorphous calcium phosphate or hydroxyapatite (HA) material, which is responsible for their strong bonding with surrounding tissue. Bioactive glasses are also reported to release ions that activate expression of osteogenic genes5,6 and to stimulate angiogenesis.7,8 Since reported by Hench et al. in 1971,3 the silicate bioactive glass designated 45S5, with the composition (weight %): 45 SiO2, 24.5 Na2O, 24.5% CaO, and 6 P2O5, has been used in most biomedical research and applications. More recently, another silicate bioactive glass designated 13-93,9 with the composition (weight %): 53 SiO2, 6 Na2O, 12 K2O, 5 MgO, 20 CaO, and 4 P2O5, has been receiving interest for potential biomedical applications.10 Both 45S5 and 13-93 glass are approved for in vivo use by the U.S. Food and Drug Administration. However, both 45S5 and 13-93 glass may have potential limitations as scaffold materials for bone repair and regeneration. Because of the tendency of the glass to crystallize before appreciable viscous flow, it is difficult to thermally bond (sinter) 45S5 particles into a porous three-dimensional (3D) network with adequate strength for repairing bone defects. Furthermore, both 45S5 and 13-93 glass convert slowly and incompletely to HA when placed in the body fluid.

Borate-based bioactive glasses have been developed recently for potential biomedical applications.11 Because of their low chemical durability, some borate glasses can convert faster and more completely to HA when immersed in an aqueous phosphate solution, such as a simulated body fluid (SBF). Huang et al.12 studied the effect of partially or fully replacing the SiO2 content of 4SS5 glass with B2O3 on the kinetics and mechanism of converting particles (150–300 μm) of the glass to HA. A similar study was performed subsequently by Yao et al.13 for 13-93 glass. These studies with glass particles showed that the conversion rate of the glass increased markedly with the B2O3 content.

Porous 3D scaffolds of B2O3-containing glasses with specific compositions have been prepared recently, and their conversion to HA in an aqueous phosphate solution in vitro has been evaluated.14–17 However, the effect of the B2O3 content of the glass on the degradation of the scaffolds has not been investigated systematically. Furthermore, the effect

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of the B₂O₃ content on important requirements of the scaffolds for bone repair, such as the ability to support the proliferation and function of osteogenic cells in vitro and the ability to support tissue infiltration in vivo, has not been evaluated.

The objective of this work was to evaluate the degradation, in vitro bioactivity, mechanical response, and biological properties of bioactive glass scaffolds with varying B₂O₃ content for potential applications in bone repair and regeneration. Three groups of scaffolds with the same microstructure but with glass compositions of varying B₂O₃ content were evaluated. In this study, the preparation of the scaffolds and the effect of the glass composition on the degradation, in vitro bioactivity, and mechanical response of the scaffolds were investigated. The in vitro response of osteogenic cells to the three groups of scaffolds and the in vivo evaluation of the scaffolds in a rat subcutaneous implantation model are described in a companion manuscript (Part II).

MATERIALS AND METHODS
Preparation of porous glass scaffolds
Porous scaffolds with a "trabecular" microstructure, similar to the microstructure of dry human trabecular bone, but with three different glass compositions, were used in this work. The three groups of scaffolds consisted of silicate 13-93 glass, a borosilicate glass (designated 13-93B1) obtained from 13-93 glass by replacing one-third of the molar SiO₂ content with B₂O₃, and a borate glass (13-93B3) obtained by completely replacing the SiO₂ molar content of 13-93 glass with B₂O₃. The compositions of these three glasses are given in Table I.

The glasses were prepared by melting reagent-grade CaCO₃, Na₂CO₃, MgCO₃, K₂CO₃, SiO₂, H₃BO₃, and CaHPO₄·2H₂O (Fisher Scientific, St. Louis, MO) in a Pt crucible in air for 2 h at 1100°C for the 13-93B3 composition, 1250°C for 13-93B1, and 1350°C for 13-93 and quenching between cold stainless steel plates. Particles of size smaller than 150 μm were obtained by crushing and grinding the glass using a hardened steel mortar and pestle and sieving through stainless steel sieves. These particles were further comminuted to produce sizes smaller than 5 μm for use in preparing the scaffolds. In this step, 13-93 and 13-93B1 particles were ground for 2 h in an attrition mill (Model 01-HD, Union Process, Akron, OH), using high-purity Y₂O₃-stabilized ZrO₂ as the milling media and water as the solvent. Because of their markedly higher reactivity with water, the 13-93B3 particles were comminuted by ball milling for 48 h in ethanol using Al₂O₃ milling media.

Porous scaffolds were prepared using a polymer foam replication technique, as described in detail elsewhere. Briefly, a slurry containing 35 vol % glass particles was prepared by dispersing the particles in water using poly(methylvinyl ether) (EasySperse; ISP, Wayne, NJ) as dispersant for 13-93 and 13-93B1. In the case of 13-93B3, ethanol and ethyl cellulose were used as solvent and dispersant, respectively. A polymer foam with a pore architecture similar to that of dry human trabecular bone was immersed in the slurry to coat the walls of the foam with the slurry. The coated foam was dried and subjected to a controlled heat treatment to decompose the foam and sinter the glass particles into dense network. The samples were heated in air for 1 h at 700°C for the 13-93 composition, 630°C for 13-93B1, and 570°C for 13-93B3. These sintering temperatures were used because they were found to produce a dense network without crystallizing the glass.

TABLE I. Nominal Compositions (mol %) of Silicate 13-93, Borosilicate 13-93B1, and Borate 13-93B3 Bioactive Glasses Used in This Work

<table>
<thead>
<tr>
<th>Glass</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>MgO</th>
<th>CaO</th>
<th>SiO₂</th>
<th>B₂O₃</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>13-93</td>
<td>6.0</td>
<td>7.9</td>
<td>7.7</td>
<td>22.1</td>
<td>54.6</td>
<td>0</td>
<td>1.7</td>
</tr>
<tr>
<td>13-93B1</td>
<td>6.0</td>
<td>7.9</td>
<td>7.7</td>
<td>22.1</td>
<td>36.4</td>
<td>18.2</td>
<td>1.7</td>
</tr>
<tr>
<td>13-93B3</td>
<td>6.0</td>
<td>7.9</td>
<td>7.7</td>
<td>22.1</td>
<td>0</td>
<td>54.6</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The porosity of the as-prepared glass scaffolds was measured using the Archimedes method. Scanning electron microscopy, SEM (Hitachi S-4700, Hitachi, Tokyo, Japan) was used to observe the microstructure of the scaffolds. The samples were sputter coated with Au/Pd and examined at an accelerating voltage of 10 kV and a working distance of 12 mm.

Degradation and in vitro bioactivity of the scaffolds
The degradation of the three groups of scaffolds and their conversion to HA were evaluated as a function of immersion time of the scaffolds in a SBF with a starting pH = 7.2 at 37°C, as described in detail elsewhere. The degradation and conversion process is accompanied by a weight loss, and this weight loss versus time was used to monitor the conversion kinetics. A ratio of 1 g of scaffold to 100 mL of SBF was used in all of the conversion experiments. After removal from the SBF at selected times, the scaffolds were dried at 90°C and weighed. The weight loss is defined as 

\[ \Delta W_t = \frac{W_0 - W_t}{W_0} \]

where \( W_0 \) is the initial mass of the scaffolds and \( W_t \) is the mass at time \( t \). The solution was cooled to room temperature, and its pH was measured using a pH meter. The microstructure of the converted scaffolds was observed in the SEM using the aforementioned conditions.

Mechanical response
The compressive strength of the scaffolds (6 mm in diameter \( \times 12 \) mm), as-prepared or after immersion in the SBF for selected times, was measured using an Instron testing machine (Model 4881; Instron, Norwood, MA) at a cross-head speed of 0.5 mm min⁻¹. For the scaffolds immersed in the SBF, the compressive strength of the wet scaffolds was measured, without drying the scaffolds. Five samples were measured for each time point, and the mean strength and standard deviation were determined.

Analysis of conversion kinetics
For the scaffolds immersed in the SBF, the weight loss data obtained in the experiments described earlier were
converted to fractional weight loss ($\alpha$) by dividing the measured weight loss by the maximum weight loss measured for each sample. The fractional weight loss data were fitted by two kinetic models, a geometrical model and diffusion model. In these models, it is assumed that the reaction at the interface is rate controlling, and that the interface moves inward at a uniform rate. In the geometrical model, nucleation at the reaction interface is assumed to be fast, so the reaction rate depends on the geometry only. For a spherical geometry, the contracting volume model (CVM) predicts that

$$1 - (1 - \alpha)^{1/3} = k_1 t,$$

(1)

where $k_1$ is a constant and $t$ is the time. If diffusion to the reaction interface is rate controlling, and assuming a 3D model, the 3D diffusion model predicts that

$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = k_2 t,$$

(2)

where $k_2$ is a constant. The data for $\alpha$ versus $t$ for the three groups of scaffolds were fitted using Eqs. (1) and (2) to test

FIGURE 1. SEM images of (a) silicate 13-93, (b) borosilicate 13-93B1, and (c) borate 13-93B3 glass scaffolds prepared by a polymer foam replication method. A SEM image of a dry human trabecular bone is shown in (d) for comparison.

FIGURE 2. (a) Weight loss of scaffold, and (b) and pH of a simulated body fluid (SBF) as a function of immersion time of silicate 13-93 (B0), borosilicate 13-93B1, and borate13-93B3 bioactive glass scaffolds in the SBF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
the ability of these models to describe the conversion kinetics of the scaffolds. The constants $k_1$ and $k_2$ in the equations were adjusted to give the best fit to the data.

**RESULTS**

**Microstructure of trabecular glass scaffolds**

SEM images of the fractured cross sections of the scaffolds showed that the three groups of scaffolds (13-93, 13-93B1, and 13-93B3) had a similar microstructure [Fig. 1(a–c)], which was almost identical to that of dry human trabecular bone [Fig. 1(d)]. The scaffolds consisted of a dense glass network and interconnected cellular pores. The three groups of scaffolds had approximately the same porosity, within the range 78–82% and pores of size 100–500 μm.

**Degradation of the scaffolds and conversion to hydroxyapatite**

Figure 2(a) shows the weight loss of the 13-93, 13-93B1, and 13-93B3 scaffolds as a function of immersion time in a SBF, which was used to monitor the conversion kinetics of the scaffolds to HA. In all three cases, the weight loss increased rapidly during the first 50 h of immersion, slowed between 50 and 200 h, and reached a nearly constant, limiting value above ~200 h. At any time, the weight loss increased with the B$_2$O$_3$ content of the scaffold. The limiting weight loss was 8% ± 1% for 13-93, 30% ± 3% for 13-93B1, and 67% ± 2% for 13-93B3 (Table II). Figure 2(b) shows that the change in pH of the SBF, resulting from the reactions accompanying the conversion of the glasses to HA, followed the same trend as the weight loss data. The increase in conversion rate of the scaffolds with B$_2$O$_3$ content is accompanied by an increase in the pH of the SBF.

SEM images of the three groups of scaffolds immersed in the SBF for 14 days showed that the surfaces of the scaffolds consisted of a porous structure of nanometer-sized particles (Fig. 3). The morphology of the particles changed from needle-like for the 13-93 scaffold to nearly spherical shape for 13-93B3 scaffolds. The morphologies of the particles were typical of HA deposited by precipitation from solution. Both X-ray diffraction and Fourier transform infrared spectroscopy (not shown) confirmed the presence of HA.

**Comparison of conversion kinetics with model predictions**

Figure 4 shows data for the fractional weight loss, $\alpha$, of the 13-93, 13-93B1, and 13-93B3 scaffolds versus time, $t$, fitted by the CVM and the 3D diffusion model. The data for the initial 50 h for all three groups of scaffolds were well fitted by the CVM [Fig. 4(a)]. At longer times, the CVM overestimated the conversion rate. The 3D diffusion model provided a good fit to the data for the 13-93B3 scaffold throughout the entire period.
conversion process [Fig. 4(b)]. However, the 3D diffusion model provided a good fit to the data for the 13-93B1 scaffolds only after \( t \approx 100 \) h and for the 13-93 scaffolds only after \( t \approx 200 \) h, but overestimated the conversion rate for these two groups of scaffolds at shorter times. These results indicate that the complete conversion of the borate 13-93B3 glass scaffold was controlled by a diffusion mechanism. On the other hand, the conversion of the silicate 13-93 and borosilicate 13-93B1 scaffolds was controlled initially by dissolution of the glass and by a diffusion mechanism at later times.

The values of \( k_1 \) and \( k_2 \) in Eqs. (1) and (2) used for the curve fitting are given in Table III. The \( k_1 \) value for the CVM ranged from \( 2.5 \times 10^{-3} \) for the 13-93 scaffold to \( 10 \times 10^{-3} \) for the 13-93B3 scaffold, indicating that the conversion rate of the borate 13-93B3 glass scaffolds was approximately four times faster than that of the silicate 13-93 glass scaffolds during the initial 100 h of immersion in the SBF. For the 3D diffusion model, the \( k_2 \) value ranged from \( 6 \times 10^{-4} \) for 13-93 scaffold to \( 18 \times 10^{-4} \) for the 13-93B3 scaffold. According to these models, the conversion rate of the borate 13-93B3 glass scaffolds was three to four times faster than that of the silicate 13-93 scaffolds.

### Mechanical response of scaffolds

The compressive strength of the as-prepared scaffolds decreased with increasing \( \text{B}_2\text{O}_3 \) content of the glass, from 11 ± 1 MPa for silicate 13-93, to 7.0 ± 0.5 MPa for borosilicate 13-93B1, to 5.0 ± 0.5 MPa for borate 13-93B3. When immersed in the SBF, the three groups of scaffolds showed a marked decrease in strength with time (Fig. 5). The strength decreased more rapidly during the first 50–100 h of immersion, which corresponded to the time range for the fastest conversion rate to HA (see Fig. 4). At longer times, the strength decreased less rapidly and reached a nearly steady value after \( t \approx 200 \) h of immersion. The 13-93B3 scaffold, which had completely converted to HA by this time, was particularly weak.

### DISCUSSION

The ability to prepare bioactive glass scaffolds with a similar, anatomically relevant microstructure (Fig. 1) provided a basis for evaluating the effect of the glass composition on

### Table III. Measured Weight Loss (\( \Delta W_{\text{meas}} \)) and Calculated Weight Loss (\( \Delta W_{\text{theo}} \)) for Silicate 13-93, Borosilicate 13-93B1, and Borate 13-93B3 Bioactive Glass Scaffolds, and the Parameters \( k_1 \) and \( k_2 \) in Eqs. (1) and (2) Used for Fitting the Measured Weight Loss Data

<table>
<thead>
<tr>
<th>Scaffold</th>
<th>( \Delta W_{\text{meas}} ) (%)</th>
<th>( \Delta W_{\text{theo}} ) (%)</th>
<th>( k_1 ) ((10^{-3} \text{ h}^{-1}))</th>
<th>( k_2 ) ((10^{-4} \text{ h}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>13-93</td>
<td>8 ± 1</td>
<td>64.1</td>
<td>2.5</td>
<td>6.0</td>
</tr>
<tr>
<td>13-93B1</td>
<td>30 ± 3</td>
<td>65.1</td>
<td>4.0</td>
<td>13.0</td>
</tr>
<tr>
<td>13-93B3</td>
<td>67 ± 2</td>
<td>67.0</td>
<td>10.0</td>
<td>18.0</td>
</tr>
</tbody>
</table>
the degradation rate of these scaffolds and their conversion to HA in a SBF. In a subsequent study, the effect of the scaffold degradation rate on the ability to support in vitro cell proliferation and function, as well as in vivo tissue infiltration, was evaluated.

The weight loss data in Figure 2 indicate that the replacement of SiO2 with B2O3 in the 13-93 glass scaffolds to give the borosilicate 13-93B1 and borate 13-93B3 compositions resulted in an increase in the degradation rate of the scaffolds. The marked difference in the degradation rate of the three groups of scaffolds is due to the difference in the glass network structure caused by replacing SiO2 with B2O3. The addition of B2O3 to silicate glass results in the breakup of the 3D Si–O network and the formation of [BO3] triangles or chains of [BO3]3 tetrahedra.23 In contrast to Si, B has a threefold coordination number, which prevents the complete formation of a 3D network, resulting in a lower chemical durability of borate-based glass.

If it is assumed that ions such as Na+, K+, (B2O3)3−, and (SiO3)3− dissolve in the solution and that all the Ca in the glass reacts with the phosphate ions in the SBF to form HA, Ca10[-PO4]6(OH)2, then the theoretical weight loss of the fully converted glass scaffolds, \( \Delta W_{\text{theo}} \), is 67%. However, two additional factors should be taken into account. First, magnesium phosphate, \( \text{Mg}_3(\text{PO}_4)_2 \), has a low solubility product \( (K_{\text{sp}} = 1.0 \times 10^{-25}) \).22 and Mg2+ is isostructural with Ca2+. Therefore, the Mg2+ ions could precipitate on the glass surface as a separate \( \text{Mg}_3(\text{PO}_4)_2 \) phase or be incorporated into the HA-type material as a solid solution. Previous work on the conversion of silicate 13-93 glass showed the formation of a HA-type phase, with no evidence for the formation of a separate \( \text{Mg}_3(\text{PO}_4)_2 \) phase.23 It is therefore likely that the Mg2+ ions are incorporated into an Mg-substituted HA phase. Because MgO from the glass is retained in the product, the weight loss should be smaller than the value (67%) based on the formation of (stoichiometric) HA. Second, because of the presence of dissolved CO2, conversion of bioactive glass in an aqueous phosphate solution in air often leads to the formation of a carbonate-substituted HA, in which some \( \text{CO}_3^{2−} \) ions substitute for \( \text{PO}_4^{3−} \) ions.12 The concentration of \( \text{CO}_3^{2−} \) in the HA was not determined in these experiments. However, when compared with the formation of (stoichiometric) HA, the formation of a carbonate-substituted HA is expected to produce a larger weight loss because the molecular weight of \( \text{CO}_3^{2−} \) ions is smaller than that of \( \text{PO}_4^{3−} \). In the present analysis, these two factors will be neglected, and the theoretical weight loss given above (67%) will be taken as an approximation.

Figure 2 shows that the measured limiting weight loss \( \Delta W_{\text{meas}} = 68.0\% \) for the 13-93B3 glass scaffold is almost identical to \( \Delta W_{\text{theo}} \), which indicates complete conversion of this scaffold to HA. The smaller \( \Delta W_{\text{meas}} \) values for the 13-93B1 and 13-93 scaffolds (Table I) indicate only partial conversion of these scaffolds, with the silicate 13-93 scaffold having the smallest conversion rate. The weight loss data indicate that by replacing a selected amount of SiO2 in a silicate bioactive glass with B2O3, the conversion rate of the scaffold can be varied over a wide range.

The weight loss data were further compared with the predictions of models in an attempt to evaluate the mechanism of converting the glass scaffolds to HA. Although several models are available, depending on the assumed rate-controlling mechanism, the CVM and the 3D diffusion model were selected because they describe processes relevant to the conversion of a bioactive glass to HA. The CVM assumes that diffusion of ions is fast, so the reaction at the interface is rate controlling. In this case, the thickness of the converted layer increases linearly with time. On the other hand, in the 3D diffusion model, diffusion of ions to the interface is rate controlling, so the thickness of the converted layer increases with the square root of time. A spherical geometry is assumed in the model equations used in this study, Eqs. (1) and (2).

The 3D diffusion model provided a good fit to the conversion kinetics of the borate 13-93B3 glass scaffold throughout the degradation process [Fig. 4(b)], indicating that the conversion process was controlled by diffusion of ions to the reaction interface. On the other hand, the CVM model provided a good fit to the conversion kinetics of the borosilicate 13-93B1 and silicate 13-93 scaffolds initially, whereas the 3D diffusion model provided a good fit to the data at later times. This indicates that the conversion of the 13-93B1 and 13-93 scaffolds was controlled initially by dissolution of the glass, but by diffusion of ions to the reaction interface at later times.

The degradation and conversion of the bioactive glass scaffolds to HA in a SBF occurs by dissolution of components such as Na2O, K2O, B2O3, and SiO2 into the solution to form Na+, K+, \( \text{BO}_3^{3−} \), and \( \text{SiO}_3^{4−} \) ions, coupled with the reaction of \( \text{Ca}^{2+} \) ions from the glass with \( \text{PO}_4^{3−} \) from the solution to form a HA layer on the glass.12 In the conversion of silicate bioactive glasses, a thin SiO2-rich layer (1–2 μm) first forms on the surface of the glass, which separates the unconverted glass from the precipitated HA, whereas no SiO2-rich layer is present in the conversion of borate bioactive glasses.12 Because of the low durability and rapid dissolution of borate 13-93B3 glass, apparently the diffusion of \( \text{Ca}^{2+} \) and \( \text{PO}_4^{3−} \) ions to the interface is the rate-limiting step. The borosilicate 13-93B1 and silicate 13-93 glasses are more durable than 13-93B3, so initially, when the diffusion distances are small, the dissolution of the glass apparently controls the conversion rate. However, at longer times (larger diffusion distances), apparently the diffusion of ions to the reaction interface is rate controlling.

The CVM and 3D diffusion model have also been used to fit the conversion kinetics of silicate 45S5 and borate-based glass particles (150–300 μm) to HA.24 The rate-controlling mechanisms determined for the conversion of these particles are similar to those found in this work, which indicates that the geometry of the glass sample has little effect on the conversion mechanism.

During the conversion reaction, the increase in pH of the SBF with immersion time of the scaffolds [Fig. 2(b)] showed trends similar to those described earlier for the weight loss data. The increase in the weight loss with immersion time or with the \( \text{B}_2\text{O}_3 \) content of the glass scaffold is...
accompanied by an increase in the pH of the SBF. This indicates that the same reactions are responsible for the conversion to HA and the pH increase. The increase in the pH resulted from the dissolution of the glass modifiers (Na\(^+\) and K\(^+\)), coupled with the difference in the acidity of the borate and phosphate ions. As boric acid is a weaker acid than phosphoric acid, release of BO\(_3^–\) ions from the glass, coupled with the consumption of PO\(_3^–\) ions from the solution and the release of the (basic) alkali ions resulted in an increase of pH of the solution.

The strengths of the as-prepared scaffolds (Fig. 5) are comparable to higher range of values for human trabecular bone (2–12 MPa). The strength is also at least one order of magnitude higher than the value reported for biodegradable polymer scaffolds or polymer–ceramic composites prepared by the thermally induced phase separation method or by the gas foaming method.\(^{25–27}\) The strength of the scaffolds prepared in this investigation is also significantly higher than that for 4555 glass–ceramic constructs (0.3–0.4 MPa; porosity = 89–92%) prepared by a polymer foam replication technique\(^{29}\) similar to that used in this work.

The conversion of the glass to HA in the SBF resulted in a significant decrease in the strength of the scaffolds (Fig. 5). As the basic load-bearing units of the porous scaffolds were the glass struts of the trabecular microstructure, the decrease in strength might be explained in terms of the reduction in the thickness of the unconverted glass struts as a function of immersion time in the SBF (Fig. 6). With the conversion of the glass to HA, a porous layer was formed on the surface of the scaffold. This porous layer showed no obvious strength compared with the dense glass network. Therefore, as this layer becomes thicker, the strength of the scaffold decreases. The degradation rate of the scaffolds, \(D_t\), was defined as the percentage of the glass that has been converted to HA. Figure 6 shows that \(D_t\) is related to the strut thickness by the equation

\[
D_t = 1 - S_t/S_o = 1 - \frac{\pi (h_t/2)^2}{\pi (h_o/2)^2} = 1 - \frac{h_t^2}{h_o^2},
\]

where \(S_o\) and \(S_t\) are the cross-sectional areas of the glass strut before and after immersion for time \(t\), \(h_o\) is the initial strut thickness, and \(h_t\) is the strut thickness of the unconverted glass after an immersion time \(t\). The value of \(D_t\) was obtained by dividing the weight loss at time \(t\) by the theoretical weight loss, that is, \(D_t = \Delta W_t/\Delta W_{theo}\). Therefore, the change in the strut thickness is given by

\[
\frac{h_t}{h_o} = \left(1 - \frac{\Delta W_t}{\Delta W_{theo}}\right)^{1/2}.
\]

The compressive strength of the porous glass scaffolds depended exponentially on the thickness of the glass struts.\(^{29}\) Therefore, the compressive strength change of the glass scaffolds after immersion in SBF was correlated with the weight loss of the scaffolds by the equation:

\[
\sigma_t = \sigma_o \left(1 - \frac{\Delta W_t}{\Delta W_{theo}}\right)^n,
\]

where \(\sigma_o\) and \(\sigma_t\) are the compressive strengths of glass scaffolds before and after immersion in SBF for time \(t\) and \(n\) is the fitting parameter. As \(\Delta W_t\) and \(\Delta W_{theo}\) were given by Figure 2(a) and Table III, \(n\) was found to be 20, 5, and 1 for the 13-93, 13-93B1, and 13-93B3 scaffolds, respectively. The theoretical compressive strengths are in good agreement with the experimental values (Fig. 5). The smaller the value of \(n\) indicates the greater impact of degradation on the decrease of compressive strength after immersion.

CONCLUSIONS

Bioactive glass scaffolds with controllable degradation and bioactivity were produced by replacing varying amounts of SiO\(_2\) in silicate 13-93 glass with B\(_2\)O\(_3\). The conversion rate of the scaffolds to HA increased markedly with increasing B\(_2\)O\(_3\) content of the glass. Scaffolds of a borate glass (designated 13-93B3), obtained by replacing all the SiO\(_2\) in 13-93 with B\(_2\)O\(_3\), converted completely to HA at a rate that was three to four times faster than silicate 13-93 scaffolds. The conversion of borate 13-93B3 scaffolds was apparently controlled by diffusion of ions to the reaction interface. Scaffolds of silicate 13-93 and borosilicate 13-93B1 glass (obtained by replacing one-third of the SiO\(_2\) content in 13-93 with B\(_2\)O\(_3\)) converted only partially to HA. The conversion of 13-93 and 13-93B1 scaffolds was apparently controlled initially by dissolution of the glass and later by diffusion of ions to the reaction interface. Concurrently, with the increase in conversion rate, the pH of the SBF increased with the B\(_2\)O\(_3\) content of the glass, from 7.5 for silicate 13-93 glass to 8.5 for borate 13-93B3 glass. The compressive strength of the as-prepared scaffolds, in the range 5–11 MPa, decreased with the B\(_2\)O\(_3\) content of the glass. The strength also decreased markedly with immersion time of the scaffolds in the SBF, which can be explained in terms of the degradation and conversion of the scaffolds to HA. Because of the rapid decrease in strength with immersion time in the SBF, these scaffolds with a trabecular microstructure (porosity = 75–85%; pore size = 100–500 \(\mu\)m)
may be suitable only for repairing contained defects in bones.

REFERENCES


