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Kinetics and mechanisms of converting bioactive borate glasses to hydroxyapatite in aqueous phosphate solution

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Abstract Borate bioactive glasses are receiving increasing attention as scaffold materials for bone repair and regeneration. In this study, the kinetics and mechanisms of converting three groups of sodium–calcium–borate glasses with varying CaO:B_2O_3 ratio to hydroxyapatite (HA) in 0.25 M K_2HPO_4 solution were investigated at 10–70 °C. Glass disks with the composition $2Na_2O\cdot(2-x)CaO\cdot(6+x)B_2O_3$ ($x = 0$, 0.5, and 1.0) were immersed for up to 8 days in the potassium phosphate solution. The conversion kinetics to HA were monitored by measuring the weight loss of the glass, while X-ray diffraction, scanning electron microscopy, and Fourier transform infrared spectroscopy were used to study structural and compositional changes. All three groups of glasses formed HA on their surfaces, showing that the glasses were bioactive. At 10–37 °C, the conversion kinetics was well fitted by the contracting sphere model. Also, the contracting sphere model has a good fit for the early stage of conversion at 70 °C, whereas a three-dimensional (3D) diffusion model provided a good fit to the data of the later stage. The results of this study provide kinetic and structural data for the design of borate bioactive glasses for potential applications in bone tissue engineering.

Introduction

Bioactive glasses are attractive materials for repairing bone defects because of their widely recognized ability to support the growth of bone cells [1, 2], and to bond strongly with hard and soft tissue [3, 4]. Upon implantation, bioactive glasses react with the body fluids to form an amorphous calcium phosphate or hydroxyapatite (HA)-type material, which is responsible for their strong bonding with surrounding tissue. Since the discovery of silicate 45S5 glass by Hench et al. [4], bioactive glasses based on the 45S5 composition have been used in several biomedical applications, such as scaffolds for bone tissue engineering, endosseous ridge maintenance implants, orthopedic repair, and artificial vertebrae [5–8]. However, the tendency of 45S5 glass to crystallize prior to appreciable viscous flow makes it difficult to thermally bond (heat treatment) 45S5 particles into a porous three-dimensional (3D) network with adequate strength for repairing bone defects. Furthermore, silicate bioactive glasses such as 45S5 and 13-93 commonly convert slowly and incompletely to HA when reacted with an aqueous phosphate solution, such as the body fluids.

Borate-based bioactive glasses have been developed recently for biomedical applications [9–12]. Owing to their low chemical durability, some borate glasses can convert faster and more completely to HA in an aqueous phosphate solution, when compared to silicate 45S5 glass. Some borate-based bioactive glasses have shown the ability to support cell proliferation and function in vitro [13, 14], as well as tissue

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infiltration in vivo [15, 16]. The release of controlled amounts of boron during degradation of these borate-based bioactive glasses can have beneficial effects on bone repair, since small concentrations of boron have been reported to be beneficial for bone metabolism and for favorably influencing the compositional and functional properties of bone [17]. Furthermore, boron can also quickly dissolve into the body fluid, and be excreted through urine [18].

Huang et al. [11, 19] studied the effect of partially or fully replacing the SiO_2 content of 45S5 glass with B_2O_3 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. [20] for 13-93 glass particles. These studies showed that the conversion rate of the 45S5 and 13-93 glass particles to HA increased markedly with the B_2O_3 content. Particles of a sodium–calcium–borate glass (125–180 μm) with the composition $2Na_2O\cdot 2CaO\cdot 6B_2O_3$ were shown to convert to HA within 3 days [10]. An analysis of the kinetic data obtained by Huang et al. [19, 21] for 45S5-based glass particles with varying amounts of SiO_2 replaced with B_2O_3 showed that the conversion of the borate glass particles could be well described by a 3D diffusion model [22]. However, the conversion of the silicate and borosilicate particles was well fitted by a contracting sphere model in the initial stage of conversion and by a 3D diffusion model in the later stages.

The objective of this study was to investigate the kinetics and mechanisms of converting sodium–calcium–borate glasses with varying $CaO:B_2O_3$ ratio to HA in an aqueous phosphate solution at practical temperatures (10–70 °C). The conversion kinetics was studied by measuring the weight loss of the glass samples, while the data were fitted by models to provide information on the conversion mechanisms. Structural and compositional changes, which resulted from the conversion of the glass to HA, were characterized using X-ray diffraction, scanning electron microscopy, and Fourier transform infrared spectroscopy.

Experimental procedure

Preparation of glasses

Three groups of borate bioactive glasses, with the composition $2Na_2O\cdot(2-x)CaO\cdot(6+x)B_2O_3$, where $x = 0$, 0.5, and 1.0, were investigated. On the basis of the molar concentrations of Na_2O, CaO, and B_2O_3, these glasses were designated 2–2–6, 2–1.5–6.5, and 2–1–7. The compositions of these three glasses, on a molar and weight basis, are given in Table 1. The glasses were prepared by mixing reagent-grade H_3BO_3, Na_2CO_3, and $CaCO_3$, melting the mixture in a platinum crucible for 30 min at 1200 °C, and casting the molten glass into preheated rectangular steel molds, to produce samples of size 14 × 12 × 6 mm. The glass samples were annealed for 4 h at 500 °C to reduce residual stress, ground with 2000 mesh sand paper, and cleaned ultrasonically in ethanol.

The conversion of the glasses to HA was studied by immersing the glass samples for up to 8 days in 0.25 M K_2HPO_4 solution with a starting pH value of 9.0 ± 0.1 at temperatures in the range 10–70 °C. Reaction in an aqueous phosphate solution to form an HA-type material has been shown to be an effective method for assessing the in vitro bioactivity of a glass [21, 23]. Although far higher than the concentration of the body fluid, a phosphate concentration of 0.25 M was used in this study to accelerate the conversion process in order to compare glass compositions with different bioactive potentials. The ratio of the surface area of the starting glass sample to the volume of the phosphate solution was kept nearly constant ($\sim 0.07\ \mathrm{cm}^{-1}$; equivalent to 1 g of glass in 100 mL solution) for all the conversion experiments. At selected time intervals, glass samples were removed from the solution, and dried overnight at 60 °C. During the drying process, the reaction layer was easily separated from the surface of the samples, and the unconverted glass core was ultrasonically washed and dried overnight at 60 °C. The mass of the glass before and after reaction, as well as the mass of the reaction products, was measured. The weight loss was used to evaluate the conversion kinetics of the glass samples [24]. It was defined as $\Delta W = [(W_0 - W)/W_0)]$, where W_0 is the initial mass of the glass sample, and W is the mass of the unconverted glass core at time t. The mass of the HA-type material was determined as $M = (W_1 - W - W_2)$, where W_1 is the total mass of the container with the glass and reaction layer, and W_2 is the mass of the container only. The mass was measured to an accuracy of ±0.0001 g. For each glass composition, five samples were used for each reaction time, and at each experimental time point, a new sample was

Table 1 Compositions of three groups of sodium–calcium–borate glasses (in mol% and wt%) used in this study

Glass	Na_2O (mol%)	CaO (mol%)	B_2O_3 (mol%)	Na_2O (wt%)	CaO (wt%)	B_2O_3 (wt%)
2–2–6 ($x = 0$)	20	20	60	18.96	17.15	63.89
2–1.5–6.5($x = 0.5$)	20	15	65	18.76	12.73	68.51
2–1–7($x = 1.0$)	20	10	70	18.57	8.40	73.03

The molar composition can be written as $2Na_2O\cdot(2-x)CaO\cdot(6+x)B_2O_3$, where $x = 0$, 0.5, and 1.0

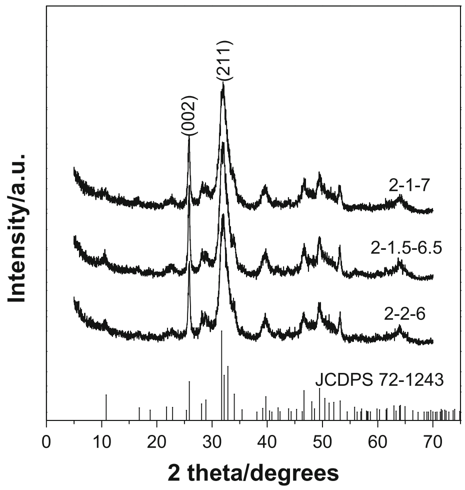

Fig. 1 XRD patterns of the products formed by reacting three groups of sodium–calcium–borate glasses (designated 2–1–7; 2–1.5–6.5; 2–2–6) for 3 days in 0.25 M K_2HPO_4 solution at 70 °C. For comparison, the pattern of a reference hydroxyapatite (JCPDS 72-1243) is shown

used. The average value ± the standard deviation were determined.

The crystalline phases present in the reaction layer of the glass samples were determined using X-ray diffraction (XRD; Rigaku D/max2550VB3+/PC; USA) in a step-scan mode (0.05° per step) in the 2θ range 5–70° (Cu Kα radiation; $\lambda = 0.15406$ nm). Scanning electron microscopy (SEM; Hitachi S2360N; Japan) was used to investigate the surface morphology of the reaction products. Functional groups in the reaction layer were analyzed using Fourier transform infrared (FTIR) spectroscopy (Bruker EQUINOXSS/HYPERION 2000; Germany) on disks prepared from a mixture of 2 mg of the product with 150 mg of high-purity grade KBr. The spectra were corrected by subtracting the KBr spectrum.

Results

Structure and composition of conversion product

Figure 1 shows XRD patterns of the conversion products formed on the three groups of glass disks after immersion for 3 days in 0.25 M K_2HPO_4 at 70 °C. The peaks corresponded to those a reference hydroxyapatite, HA (JCPDS 72-1243), indicating the formation of a HA-type conversion product for all three groups of glasses. The broadness and low intensity of the major peaks (002 and 211 reflections) indicated that the HA product was weakly crystallized or that the crystallite size was in the nanometer range, or a combination of both.

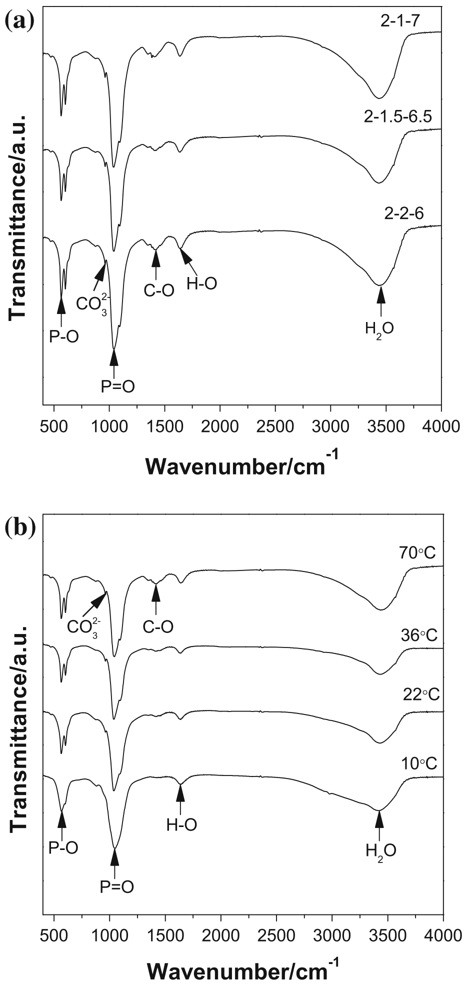

Fig. 2 FTIR spectra of the products formed by **a** reacting three groups of sodium–calcium–borate glasses (2–1–7; 2–1.5–6.5; 2–2–6) for 3 days in 0.25 M K_2HPO_4 solution at 70 °C, and **b** reacting 2–2–6 glass for 3 days in 0.25 M K_2HPO_4 solution at the temperatures shown

The FTIR spectra of the conversion products (Fig. 2a) formed after immersion of the glass samples for 3 days in 0.25 M K_2HPO_4 at 70 °C show resonances at 560 and 1040 cm^{-1}, and three shoulders at 605, 962, and 1100 cm^{-1}, which corresponded to P–O bonds in the $(PO_4)^{3-}$ group of HA [25]. The resonances at 1415 and 866 cm^{-1}, corresponding to those of the CO_3^{2-} group, indicated that the product was a carbonate-substituted HA. At lower conversion temperatures (10–37 °C), the resonances corresponding to the P–O bond at wave numbers of 605, 962, and 1100 cm^{-1} merged with neighboring resonances or vanished (Fig. 2b). In general, the FTIR observations were consistent with those of the XRD analyses, which showed the formation of an HA-type product on the surfaces of all three groups of glasses.

Figure 3a–c shows SEM images of the surface of the HA layer formed on the three groups of glasses after immersion for 3 days in the K_2HPO_4 solution at 70 °C. For all three groups, the HA product consisted of an interconnected

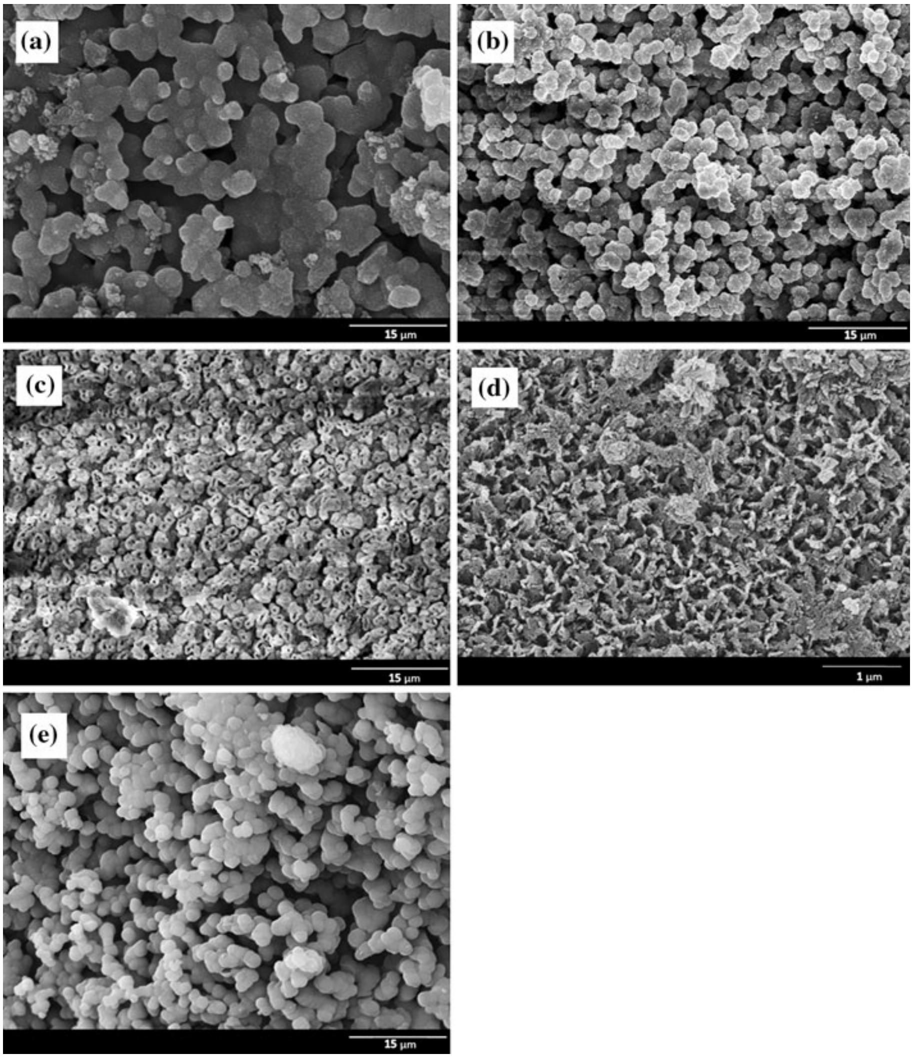

Fig. 3 SEM images of the surface of the hydroxyapatite (HA) product formed by reacting **a** the 2–1–7 glass, **b** the 2–1.5–6.5, and **c** the 2–2–6 glass for 3 days in 0.25 M K_2HPO_4 solution at 70 °C; **d** a higher magnification SEM image of the product shown in (**a**); **e** SEM image of the HA product formed by reacting the 2–2–6 glass for 3 days in 0.25 M K_2HPO_4 solution at 37 °C

network of nearly spherical particles. The average size of these HA particles decreased with increasing CaO content (or with decreasing B_2O_3 content) of the starting glass. The average HA particle size decreased from ~ 6 µm for the product formed from the 2–1–7 glass (10 mol% CaO; 70 mol% B_2O_3) to ~2 µm for the product formed from the 2–2–6 glass (20 mol% CaO; 60 mol% B_2O_3). The HA product formed on the 2–2–6 glass (Fig. 3c) appeared to consist of hollow particles, but the reason for the formation of this interesting particle morphology is not clear.

Higher magnification SEM images showed that the HA particles consisted of agglomerates of nanosize HA crystals. For example, a comparison of the SEM image shown in Fig. 3a with a higher magnification image of the same product (Fig. 3d) showed that the HA product formed from the 2–1–7 glass consisted of crystals of size 30–70 nm. These results indicated that the composition of the starting glass influenced the morphology of the HA product formed in the conversion reaction. The difference in HA particle size among these three groups of borate glasses might be related to the effect of the CaO content of the starting glass on the nucleation of HA. The nucleation sites at the reaction interface are determined by the concentrations Ca^{2+} ions resulting from dissolution of the glass and the $PO_4{}^{3-}$ ions from the phosphate solution [21]. Presumably a higher amount of calcium in the starting glass resulted in a larger number of nucleation sites at the interface, leading to the formation of HA with smaller size. For the same group of glass (e.g., 2–2–6) converted at different temperatures, Fig. 3c and e show that the HA formed at a higher temperature (70 °C) had a larger particle size than the HA formed at a lower temperature (37 °C). Presumably, the higher temperature resulted in faster growth of the HA particles.

Kinetics of glass conversion to hydroxyapatite (HA)

Figure 4 shows data for the amount of HA formed, normalized to the theoretical amount of HA formed by complete conversion of the glass, as a function of reaction time of the 2–2–6 glass in the K_2HPO_4 solution at temperatures

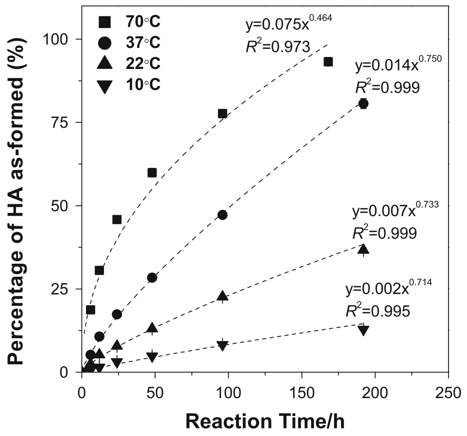

Fig. 4 Fraction of HA formed, normalized to the theoretical amount of HA formed in the conversion reaction, as a function of reaction time, for samples of 2–2–6 glass converted in 0.25 M K_2HPO_4 solution at the temperatures shown

in the range 10–70 °C. The theoretical amount of HA (30.7% for this 2–2–6 glass) was determined by assuming that all the CaO of the glass is converted to HA. For any reaction time, the amount of HA formed increased with increasing temperature. At 70 °C, the amount of HA formed after reaction in the phosphate solution for 8 days was 93% of the theoretical value, which indicated almost complete conversion of the glass disk to HA.

The conversion data for the 2–2–6 glass (Fig. 4) could be well fitted by a power-law equation of the form

$$y = At^n \tag{1}$$

where y is the fractional amount of HA formed at a reaction time t, A is a temperature-dependent parameter, and n is an exponent that gives the time dependence of the conversion. At temperatures of 10, 22, and 37 °C, n had values of 0.71, 0.73, and 0.75, respectively. This narrow range of n values indicated a similar conversion mechanism at these three temperatures. On the other hand, the marked difference in the n value (0.46) at 70 °C presumably indicated a change of conversion mechanism at this higher temperature. Using a similar curve-fitting procedure, the n values for the conversion of the 2–1–7 and 2–1.5–7.5 glasses were approximately the same as those for the 2–2–6 glass (Table 2), indicating that the composition of the three groups of borate glasses had little effect on the mechanism of conversion to HA.

Figure 5 shows the weight loss of the glass samples, ΔW, normalized to the starting weight of the glass, after different immersion times, t, in the 0.25 M K_2HPO_4 solution at 10, 22, 37, and 70 °C. At any temperature, ΔW showed little dependence on the glass composition, while at any reaction time, ΔW increased with the reaction temperature. All three groups of glasses were completely converted to HA within 8 days at 70 °C.

Table 2 Values of n obtained from Fig. 4 by fitting the conversion data for the three groups of borate glasses (2–1–7; 2–1.5–6.5; 2–2–6) with the power-law equation $y = At^n$

Glass	n value			
	10 °C	22 °C	37 °C	70 °C
2–2–6	0.71	0.73	0.75	0.46
2–1.5–6.5	0.71	0.76	0.75	0.46
2–1–7	0.72	0.72	0.76	0.46

Discussion

While the composition of the three groups of borate glasses influenced the morphology of the HA formed by conversion of the glasses in 0.25 M K_2HPO_4 solution (Fig. 3), the glass composition had little effect on the kinetics and mechanism of conversion to HA (Fig. 5; Table 2). For borate glasses, such as the sodium–calcium–borate glasses used in this study, previous studies supported a conversion process in which the sodium and borate ions dissolve into the solution, while the calcium ions from the glass react with phosphate ions from the solution to precipitate HA [9–11]. Formation of HA starts at the surface of the glass and moves inward. The conversion process could, therefore, be controlled by diffusion of the calcium and phosphate ions to the reaction interface, or by the reaction at the interface. The reaction at the interface involves dissolution of the glass into the solution or deposition of HA at the interface.

In order to provide information on the rate-controlling mechanism of converting these borate glasses to HA, the isothermal weight loss data were used as a measure of the conversion kinetics, and they were compared with the predictions of theoretical models [26]. When diffusion is rate-controlling, for a spherical geometry, the fraction of material reacted, α, is related to time, t, by the Jander equation [26]:

$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = Kt \tag{2}$$

where K is a temperature-dependent parameter. If the nucleation step controls the reaction at the interface, a possible model for describing the process is the Avrami–Erofe'ev equation [26]:

$$[-\ln(1 - \alpha)]^{1/n} = Kt \tag{3}$$

where $n = 2$, 3, or 4. On the other hand, if nucleation is fast, the conversion reaction could be controlled by the dissolution of the glass and, in this case, the reaction front moves uniformly inward. The conversion depends only on the geometry of the reacting system, and for a spherical geometry ('contracting sphere' model), the conversion kinetics are given by [26]

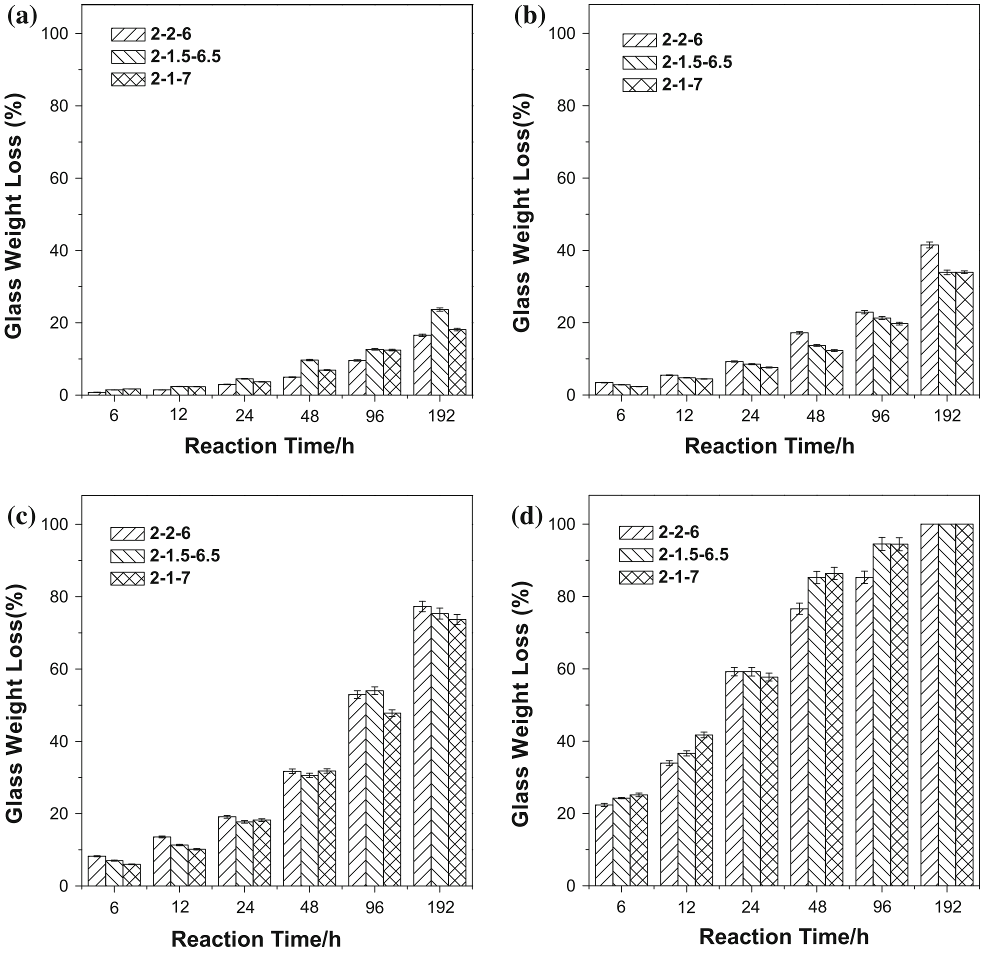

Fig. 5 Weight loss of the three groups of sodium–calcium–borate glasses (2–1–7; 2–1.5–6.5; 2–2–6) after conversion for various times in 0.25 M K_2HPO_4 solution at **a** 10 °C, **b** 22 °C, **c** 37 °C, and **d** 70 °C

$$\left[1 - (1 - \alpha)^{1/3}\right] = Kt \tag{4}$$

According to Eqs. 2–4, a plot of the left-hand side of the equation versus t should result in a straight line of slope K.

In order to provide information on the mechanism of converting the three groups of borate glasses to HA, the weight loss data (Fig. 5) were fitted using Eqs. 2–4. The value of α was taken as the weight loss of the glass normalized to the starting weight of the glass sample. Figure 6 shows the results for the 2–2–6 glass sample at the four temperatures used. The best fit to the data at temperatures of 10, 22, 37 °C was obtained using the contracting sphere model (Eq. 4). Interestingly, the values of α below 70% for 70 °C were also in accordance with the contracting sphere model. However, the 3D diffusion model (Eq. 2) gave a better fit for the value above 70%. This could be well explained by the formation of HA to such a thickness that the movement of various ions was controlled by diffusion through this HA layer. Similar results were obtained for the 2–1–7 and 2–1.5–6.5 glasses, and they are omitted for brevity.

Since the data for all three groups of glasses indicated the same mechanism operating at temperatures of 10, 22, and 37 °C, and the contracting sphere model also fits well for the early stage of conversion at 70 °C, the activation energy of the conversion reaction was determined by these data points. The temperature-dependent parameter in Eqs. 2–4 is given by an Arrhenius relation:

$$K = K_0 \exp(-Q/RT) \tag{5}$$

where K_0 is a constant, Q is the activation energy for the process, R is the gas constant, and T is the absolute temperature. According to Eq. 5, a plot of ln K versus $1/T$ gives a slope equal to $-Q/R$. Using the K values determined from Fig. 6, a plot of ln K versus $1/T$ for the 2–2–6 glass gave activation energy of 36 ± 5 kJ/mol (Fig. 7). A similar analysis gave activation energies of 32 ± 8 kJ/mol for the 2–1–7 glass and 36 ± 4 kJ/mol for the 2–1.5–6.5 glass

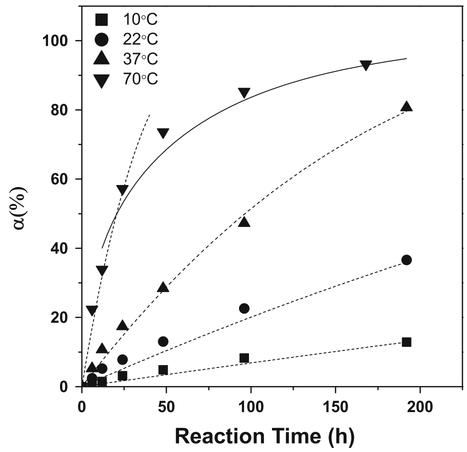

Fig. 6 Weight loss (α) vs. reaction time for the 2–2–6 glass sample at the temperatures shown with models of the contracting sphere model (*dashed lines*) and 3D diffusion model (*solid lines*). The contracting sphere models fit well for the data of 10, 22, 36 °C and the early stage of 70 °C, whereas 3D diffusion model has a better fit for the later stage of conversion at 70 °C

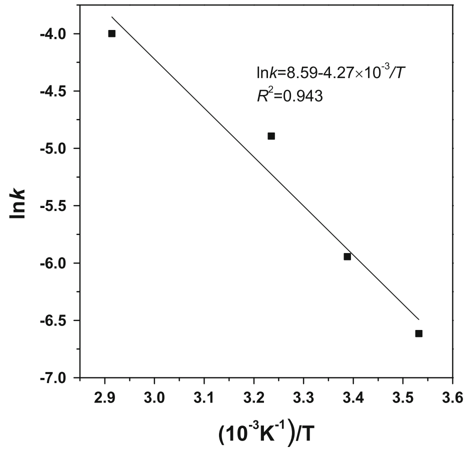

Fig. 7 Arrhenius plot of ln *K* vs. 1/*T* for the conversion of 2–2–6 glass in 0.25 M K_2HPO_4 solution at 10–70 °C. The activation energy for the conversion process was determined from the slope of the plot

Table 3 Activation energies for the conversion of the three groups of borate glasses (2–1–7; 2–1.5–6.5; 2–2–6) at 10–37 °C in 0.25 M K_2HPO_4 solution (pH 9.0)

Glass	Activation energy (kJ/mol)
2–2–6	36 ± 5
2–1.5–6.5	36 ± 4
2–1–7	32 ± 8

(Table 3). Within the limits of experimental error, the activation energies show no significant dependence on the glass composition, indicating the same conversion mechanism for the three groups of glasses at 10–70 °C. These results are consistent with the kinetic analysis of the amount of HA formed in the conversion reaction (Fig. 4), which showed *n* values that were almost independent of the glass composition for the conversion experiments performed at 10–70 °C.

Conclusion

Three groups of sodium–calcium–borate glasses, designated 2–1–7, 2–1.5–6.5, and 2–2–6, with varying $CaO:B_2O_3$ molar ratios in the range 1/7 to 1/3, reacted in 0.25 M K_2HPO_4 solution at pH 9.0 to form a hydroxyapatite (HA)-type material, show that these three glasses were bioactive. The $CaO:B_2O_3$ molar ratio influenced the morphology of the HA particles formed in the conversion reaction, but had little effect on the kinetics of conversion to HA. The average size of these HA particles decreased with increasing CaO content (or with decreasing B_2O_3 content) of the starting glass. The contracting sphere model had a good fit for the conversion at 10, 22, 37 °C, and the early stage of 70 °C, indicating that the dissolution of the glass into the solution was the rate-controlling mechanism. However, at the later stage of 70 °C, the conversion kinetics was well fitted by a three-dimensional diffusion model, indicating that diffusion of the calcium or phosphate ions to the reaction interface was rate-controlling. The activation energy for the conversion reaction at 10–70 °C was in the range 32–36 kJ/mol for the three groups of glasses.

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