Dissolution behavior of ternary alkali-alkaline earth-borate glasses in water

Kathryn L. Goetschius, Michaela A. Beuerlein, Christian M. Bischoff, Richard K. Brow*

Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65409, USA

ABSTRACT

The compositional dependence of the dissolution rates of ternary alkali-alkaline earth borate glasses in water were characterized. These glasses dissolve congruently and the dissolution kinetics were linear, following the contracting volume model for spherical particles. The dissolution rates were dependent on the glass structure, with slower rates associated with glasses with greater fractions of four-coordinated borate sites in their network structures, as determined by nuclear magnetic resonance spectroscopy. For glasses with a fixed alkaline earth identity, the dissolution rates increased in the order Li < Na < K. For glasses with a constant alkali identity, the dissolution rates increased in the order Ca < Sr ≈ Mg. The effects of composition on dissolution rates are discussed in terms of the reactions between water and different borate and metal-oxide sites in the glass structure.

1. Introduction

Borate glasses in general are more reactive in aqueous environments than silicate glasses. Their fast reactivity can be an advantage in many biomedical applications where tailored ion release rates are desired [1].

The processes by which glasses react in an aqueous solution include hydrolysis, hydration, and ion exchange [2]. Hydrolysis is the process where water reacts with the bridging oxygens that link two glass-forming polyhedra to form two hydroxyl bonds and so break down the glass network. Hydration is a similar process that affects the bonds between modifying metal cations and oxygens associated with the glass-forming polyhedra to form hydrated metal ions that can be released to the solution. Ion exchange is a process by which the modifying metal ions in a glass structure are replaced by protons (or hydronium ions) as a result of the hydration reactions, leading to the selective leaching of mobile metal ions from the glass into the solution. Ion exchange reactions dominate the initial dissolution processes of alkali-containing silicate glasses in acidic and neutral conditions, and are a transport-limited process, whereas the network hydrolysis processes often exhibit linear reaction-controlled kinetics. These different reactions are coupled and all can contribute to the overall dissolution rates of a glass [2].

One difference between silicate and borate glasses is how the addition of modifying oxides affects the network structure. When modifying oxides are added to SiO_2, the additional oxygens are incorporated into the silicate network as non-bridging oxygens (NBO). This will cause the network to dissolve faster because fewer bridging oxygens

must be hydrolyzed to release a silicate anion. On the other hand, the oxygen from a modifying oxide is initially incorporated into a borate glass as a B-tetrahedron, replacing a B-triangle [3], and the greater number of structural cross-links in the modified borate network has been associated with lower aqueous dissolution rates for these glasses [4,5].

The identity of the alkali in binary borate glasses will also affect the dissolution rate of a borate glass. Zhang [6] found that larger, lower field strength alkali ions cause an increase in the dissolution rate and El-Alaily et al. [7] report similar trends for divalent cations.

The aqueous dissolution rate is one of the factors that determine the bioactive response of a glass. Different dissolution rates may be required for different applications; e.g. slower rates for bone repair scaffolds versus materials designed for soft tissue repair [8,9]. For example, replacing Na_2O with CaO in ternary Na-Ca-borate glasses decreases the rates at which they react with phosphate-containing solutions [5]. Knowing how composition, including the presence of different alkali and alkaline earth oxides, affects the dissolution mechanism and kinetics will be useful in the design of new borate glasses for biomedical applications.

2. Experimental procedures

Sixteen glasses in the $xR_2O\text{-}xR'O\text{-}(100\text{-}2x)B_2O_3$ systems (R = Li, Na or K, R′ = Mg, Ca, or Sr and x = 5, 10, 15 or 20 mol%) were batched using reagent grade carbonates and boric acid (H_3BO_3, Li_2CO_3, Na_2CO_3, K_2CO_3, $MgCO_3$, $CaCO_3$, and $SrCO_3$). Batches were melted in air in a

platinum-rhodium crucible at 800–1100 °C, generally for 30 min after complete charging of the batch, based on the composition, and then quenched on steel plates. Samples from each glass were dissolved completely in a weak nitric acid and were analyzed using a Perkin Elmer Optima 2000 inductively couple plasma-optical emission spectrometer (ICP-OES). These analyzed compositions are used throughout this paper.

For the dissolution study, quenched glass samples were crushed and sieved to 75–150 μm powder. Powders were rinsed with ethanol through the 75 μm sieve to remove fines. Sample powders were weighed and 150 mg were placed in a 45 μm mesh nylon bag, also washed with ethanol, and sealed using a butane torch. Bags were placed in a polypropylene container with 50 mL of deionized water and placed in a shaking water bath at 37 °C. Samples were run in triplicate. Ion concentrations for each element were measured using ICP-OES after different times, up to 24 h for the glasses batched with 80 or 90 mol% B_2O_3, and up to 168 h for the glasses batched with 60 or 70 mol% B_2O_3. After each dissolution time increment, the bags were removed from the water and dried in a 60 °C drying oven overnight before re-measuring the mass. The final pH of each solution was measured at room temperature using an Accumet pH electrode.

A Bruker Avance II Spectrometer with a 14.1 Tesla/600 MHz field was used to collect ^{11}B MAS NMR spectra from each glass at a frequency of 192.54 MHz and a spinning rate of 12 kHz. The applied pulse length was 0.8 μs and a 2 s recycle delay with a 20° tipping angle was used to enable quantification of different boron species. Chemical shifts were referenced to boric acid with borax as a secondary reference. The ratio of the areas of peaks assigned to trigonal and tetrahedral borate units, after accounting for contributions from spinning sidebands, were used to determine the fraction of tetrahedral ($B\varnothing_4^-$) units in the network structure of each glass.

3. Results

3.1. Glass compositions

The analyzed compositions of each glass are given in Table 1. Specific glasses are designated by their nominal compositions; e.g., 10Li10Mg80B designates the glass with the nominal molar composition $10Li_2O$-$10MgO$-$80B_2O_3$. In general, the analyzed compositions are in good agreement with the intended batched compositions, varying by < 5% (relative) from the respective targeted oxide contents. Infrared and Raman analyses of these cast glasses (not shown) revealed no evidence for significant amounts of residual water or carbonates.

Table 1
Analyzed compositions (mol%), densities, fractions of tetrahedral borate units, and dissolution rates (B-release) of the glasses with their designated molar compositions.

| Glass designation	R_2O (mol%)	R'O (mol %)	B_2O_3 (mol %)	$fB\varnothing 4^-$ (NMR)	k(B ICP) (hr^{-1})
5Na5Ca90B	5.4	5.0	89.6	0.13	0.320
10Li10Mg80B	10.1	9.1	80.7	–	0.091
10Li10Ca80B	10.7	10.3	78.8	0.30	0.043
10Li10Sr80B	10.4	9.0	80.6	–	0.097
10Na10Mg80B	10.4	9.1	80.5	0.26	0.127
10Na10Ca80B	9.8	10.3	79.9	0.29	0.063
10Na10Sr80B	10.0	9.8	80.2	0.27	0.082
10K10Mg80B	9.4	8.7	81.9	0.24	0.217
10K10Ca80B	9.3	9.9	80.8	0.29	0.104
10K10Sr80B	9.6	9.3	81.1	0.29	0.138
15Li15Ca70B	16.1	16.2	67.7	0.47	0.008
20Li20Ca60B	20.6	20.1	59.2	0.54	0.006
15Na15Ca70B	16.4	16.6	67.0	0.44	0.017
20Na20Ca60B	19.0	19.8	61.2	0.45	0.020
15K15Ca70B	13.8	14.9	71.4	0.43	0.013
20K20Ca60B	18.2	19.7	62.1	0.42	0.030
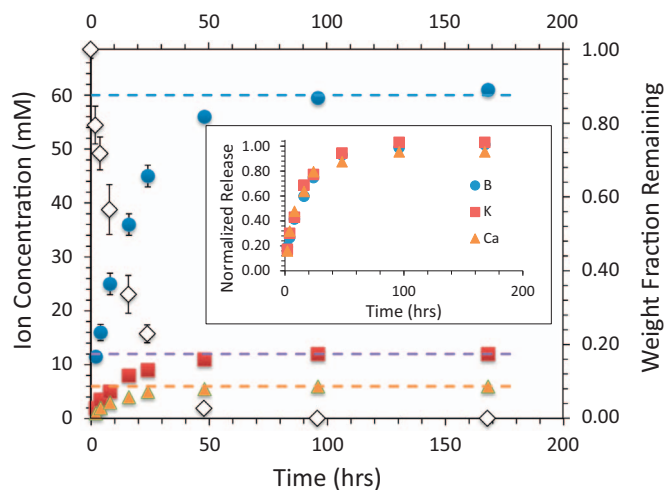
Fig. 1. Ion release (closed symbols) and mass loss (open symbols) dissolution data for the $15K_2O$-$15CaO$-$70B_2O_3$ glass in water at 37 °C. Error bars represent standard deviations larger than the symbols from tests run in triplicate. The horizontal dashed lines indicate the respective ion concentrations assuming complete dissolution of the sample. The inset shows the normalized ion release data, where the ion concentrations in solution are divided by the respective analyzed concentrations in the as-made glass.

3.2. Glass reaction in water

The ion release and weight loss data for the $15K_2O$-$15CaO$-$70B_2O_3$ glass are shown in Fig. 1. The horizontal dotted lines in Fig. 1 are the respective concentrations of each element assuming complete dissolution of the sample. The inset shows the normalized ion release data, where the ion concentrations in solution are divided by the respective ion concentrations in the original glass. These data are representative of the dissolution behavior of the other glasses studied.

For the $15K_2O$-$15CaO$-$70B_2O_3$ glass shown in Fig. 1, dissolution is complete after approximately 48 h in water. The normalized ion release data shown in the inset overlap for each time period, an indication that the glasses are dissolving congruently throughout the experiment.

The ion release and the weight loss data collected in this study were fit using the contracting volume model (CVM) for reacting spheres [10]:

$$kt = 1 - (1 - \alpha)^{\frac{1}{3}} \tag{1}$$

where k is the reaction rate constant, t is reaction time, and α is the fraction of sample dissolved, determined either by the fraction of an ion released to solution or the fraction of the total weight of sample dissolved.

The ion release and weight loss data for the $15K_2O$-$15CaO$-$70B_2O_3$ glass in Fig. 1 were each fit using the CVM and these data are replotted in Fig. 2 using Eq. (1). The slopes of these plots are the respective reaction rate constants (k) for each data set; these reaction rate constants are indicated on the plot and are equivalent within the uncertainty of the measurements, consistent with congruent dissolution of these glasses.

Fig. 3a shows CVM analyses of the weight loss data for three glasses from the xK_2O-$xCaO$-$(100-2x)B_2O_3$ series. The lowest dissolution rate occurs at x = 0.15. Fig. 3b shows the weight loss data for three glasses in the $10Na_2O$-$10R'O$-$80B_2O_3$ series, where the dissolution rate constant increases in the order Ca < Sr < Mg.

The dissolution rate constants determined from the boron release measurements (k (B ICP)) agree very well with those calculated from the weight loss measurements (k (Δw)), as shown for the $10R_2O$-$10R'O$-$80B_2O_3$ series of glasses in Fig. 4. Since the reaction rate constants were similar regardless of the measurement method, the boron release data are used for the reaction kinetics study that follows.

Table 1 summarizes the CVM reaction rate constants from the B ion release data for the dissolution of every glass in 37 °C water. The