BASALT GLASS: AN ANALOGUE FOR THE EVALUATION OF THE LONG-TERM STABILITY OF NUCLEAR WASTE FORM BOROSILICATE GLASSES

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ABSTRACT

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The long-term stability of nuclear waste form borosilicate glasses can be evaluated by understanding the processes that effect the long-term alteration of glass and by comparing laboratory alteration of synthetic basalt and borosilicate glasses with the observed stability of naturally occurring basaltic glasses in diverse geologic environments. This paper presents detailed electron microprobe analyses of naturally altered basaltic glasses (with maximum ages of 10,000 to 20 million years) from low-temperature environments. These results are compared to laboratory data on the corrosion of a synthetic basaltic glass in MCC-1 tests (90°C, a SA/V of 0.1 cm⁻¹ and time periods up to 182 days), MCC-2 tests (190°C, a SA/V of 0.1 cm⁻¹ and time periods up to 210 days) and hydration tests in saturated water vapor (240°C, an estimated SA/V of ~10⁶ cm⁻¹ and time periods up to 63 days). Additionally, laboratory induced hydration alteration of synthetic basalt and borosilicate glasses is compared. These preliminary experiments provide evidence that the alteration processes observed for natural basalt glasses are relevant to understanding the alteration of nuclear waste glass, as both appear to react via similar processes.

INTRODUCTION

One important aspect of the evaluation of nuclear waste form behavior is the extrapolation of short-term laboratory experiments (usually less than one year) to long periods of geologic time (greater than 10,000 years). The extrapolation requires accurate experimental measurements of the kinetics of corrosion and the identification of all reaction processes. In addition, it must be possible to verify the validity of the long-term extrapolations.

To accomplish these goals, we simulate in the laboratory, using synthetic basalt glass, those reactions observed to occur in nature. The experimental method so developed will then be used to alter both basalt and nuclear waste glasses, and the results will be of use in demonstrating an understanding of the reaction processes and in providing a means for modeling the alteration reactions.

We are utilizing basalt glasses (SiO₂ = 45 to 50 wt %) and borosilicate nuclear waste glasses (SiO₂ = 40 to 50 wt %). It has been suggested that these glasses are similar in their dissolution mechanisms, as the SiO₂ content of glass has an important effect on glass/water reactions [1,2,3]. We present textural and compositional data on the natural alteration products of basalt glasses. These results are compared to those for a synthetic basalt glass and SRL 131 defense waste borosilicate glass subjected to MCC and hydration tests.

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EXPERIMENTAL

Natural alteration products of basalt glasses from British Columbia, Hawaii, the State of Washington and the deep ocean were characterized by detailed electron microprobe analyses. Sample numbers are given in Figures 1 and 2 and specific locality information can be obtained from the author (RCE). The samples from British Columbia, Hawaii, and Washington were altered by fresh water (glacial melt, rain, or ground waters), whereas the ocean dredge samples were altered while in contact with sea water. All alteration took place at low temperatures, 2°C to ambient. Although the time periods for alteration is difficult to determine, most of the samples range in maximum age from Pleistocene to Miocene (10,000 to 20 million years).

Alteration experiments were conducted on a synthetic basalt glass modeled after the composition of a Hawaiian alkaline basalt. This composition and that of the SRL 131 defense waste borosilicate glass are: oxide wt % (synthetic basalt/SRL 131); SiO₂ (52.6/44.0); TiO₂ (1.8/0.7); Al₂O₃ (10.8/3.5); Fe₂O₃ (13.0/14.3); MnO (0.1/3.1); MgO (12.3/1.6); CaO (4.4/1.4); Na₂O (4.5/13.7); K₂O (0.6/0); B₂O₃ (0/10.9); Li₂O (0/4.2); NiO (0/1.8); ZrO₂ (0/0.4); and La₂O₃ (0/0.4). The synthetic basalt glass was made by mixing powders of reagent grade oxides in a powder

Figure 1. Normalized SiO₂-Al₂O₃-FeO weight percent variation diagram plotting the microprobe analyses of glasses and associated alteration rinds. Range of values for each oxide is: oxide wt % (glass/rind); SiO₂ (45.9-52.2/11.1-55.3); Al₂O₃ (11.4-16.9/3.0-25.8); and all iron as FeO (8.0-16.9/9.5-32.7).

Figure 2. Normalized (Na₂O+K₂O)-CaO-MgO weight percent variation diagram plotting the microprobe analyses of glasses and associated alteration rinds. Range of values for each oxide is: oxide wt % (glass/rind); Na₂O+K₂O (2.02-5.36/0.29-5.32); CaO (7.9-12.5/0.24-4.17); and MgO (3.54-9.4/0.19-9.2).

mill, melting the mixture in a Pt crucible at 1500°C, quenching the melt in water, grinding, remelting the glass to ensure homogeneity, and pouring into a Pt 5% Au mold for sectioning. Composition was determined using quantitative energy dispersive spectroscopy (EDS) with NBS and USNM 111240 basalt glasses as standards. All iron is reported as Fe₂O₃, and Li and B were determined by ICP.

The following laboratory tests were completed: (1) MCC-1, 90°C, a SA/V of 0.1 cm⁻¹ for time periods up to 182 days, (2) MCC-2, 190°C, a SA/V of 0.1 cm⁻¹ for time periods up to 210 days, and (3) hydration tests in saturated water vapor at 240°C, an estimated SA/V of ~10⁶ cm⁻¹ (based on a H₂O film thickness of 100Å) for time periods up to 63 days. Analyses of MCC-1 and MCC-2 leachates for the synthetic basalt glass were done using inductively coupled plasma emission spectroscopy (ICP). Selected data from these experiments are summarized in Table I and Figure 3. Similar data for the SRL 131 defense waste glass have previously been reported [4,5,6].

Table 1. Leach tests of synthetic basalt and SRL 131 glasses with deionized water at 90°C.

Glass Type	Length Days	Final pH	Normalized Elemental Mass Loss, g/m ²								
			Si	Al	Fe	Ti	Mn	Mg	Ca	Na	K
Synthetic Basalt	28	9.0	6.0	1.0	0.03	<0.04	<0.4	1.1	6.3	9.5	8.0
	56	8.8	7.2	3.0	0.11	<0.04	0.9	3.6	6.4	10.2	9.0
	91	8.8	8.3	3.3	0.14	<0.04	1.0	4.8	7.9	12.3	9.5
	182	8.6	10.9	4.8	0.12	<0.04	1.7	7.6	9.2	16.0	15.4
SRL 131	3	9.8	9.2	8.5	<0.05	<1.0	<0.2	<0.7	1.1	13.8	
	7	9.8	12.5	11.0	0.05	<1.0	<0.2	<0.7	<0.6	20.5	
	14	9.8	14.8	11.0	0.17	<1.0	<0.2	<0.7	<0.6	25.5	
	28	9.8	18.6	13.2	0.49	1.6	0.8	<0.7	0.7	33.6	
	91	9.8	27.6	10.9	0.52	1.7	1.2	<0.7	0.6	ND	
	183	9.3	44.2	10.1	0.71	1.8	1.7	1.7	0.9	66.7	
	392	9.7	39.7	15.3	0.63	1.4	1.1	1.1	0.8	69.4	

Initial pH = 5.50, SA/V = 0.1 cm⁻¹, leachate = DIW.
 SRL 131 data from reference [6]. Initial pH = 6.3 for SRL 131.
 ND = Not determined.

Figure 3. Hydration kinetics of laboratory basaltic glass in saturated water vapor at 240°C.

RESULTS AND DISCUSSION

The alteration of basalt glasses in nature proceeds by a hydrolytic dissolution/precipitation mechanism which results in the formation of well-defined surface layers. These alteration rinds are iron-rich aluminosilicate gels (palagonite) which are depleted in alkalis and alkaline earths relative to parent glass. All of the natural basalt glasses exhibit rinds of alteration products which pseudomorphically replace the glass from the outer surface inward. The layer is usually isotropic or weakly anisotropic, yellow to orange (contrasting with brown glass), and often has a laminated appearance with individual layers having submicron to tens of micron thicknesses. Total rind thicknesses range from a few microns to several hundred microns. Glass alteration is accompanied by the precipitation of authigenic cements (e.g., zeolites, clay minerals, calcite, opaline silica, Figure 4).

Relative elemental variation are illustrated in Figures 1 and 2; however, the absolute elemental variations show that with few exceptions, SiO_2 , MgO , and CaO are nearly always depleted in the rind relative to corresponding glass. The amorphous alteration rinds are primarily iron-rich aluminosilicates with Al_2O_3 concentration not changing much from glass to the rind. TiO_2 is retained in the alteration rind during the hydrolysis of the glass. Alteration rinds in the oceanic dredge samples nearly always are significantly enriched in iron relative to their glass progenitors. As compared to subaerially or fresh-water altered samples, the dredge sample alteration rinds have retained alkalis (Na and K) during hydrolysis.

a

b

Figure 4. SEM images in secondary electrons (a) Zeolites in a fresh water altered hyaloclastite from British Columbia (Sample TBI). The prismatic forms are phillipsite. Lower image 5X upper image. The 50 micron scale bar applies to the upper image. (b) Clay mineralization associated with an altered, glassy, pillow basalt rim from the Icelandic Shelf (sample USNM 113432-24).

Results of the MCC-1 tests for the synthetic basalt glass can be compared with previously reported MCC-1 results for SRL 131 defense waste glass [4,5,6]. The former appears to react at a lower rate than SRL 131 glass and has not reached the point where the normalized elemental mass losses, $(NL)_i$, are constant after 182 days. However, for SRL 131 the increase in $(NL)_i$ for most elements has slowed significantly after 182 days. The final pH of the leachate for the synthetic basalt glass is 8.6 compared with 9.3 for SRL 131 glass after 182 days. $(NL)_i$ data for the synthetic basalt show all elements still increasing after 182 days with the exception of Fe and Ti (see Table I). $(NL)_i$ for Na and Si are approximately four times lower in the synthetic basalt than in SRL 131 and Al is two times lower. The value for Ca is ~ 10 times greater in the basalt than in SRL 131 and Mg is ~ 4 times greater. Although the $(NL)_i$ for Fe and Ti is relatively constant in both basalt and SRL 131 over a period of time, $(NL)_i$ for Fe is ~ 6 times lower and Ti is ~ 45 times lower in the basalt compared with SRL 131. Observation of surface alteration indicates that the synthetic basalt glass is covered with a clay type mineralization, typically observed in the leach reaction of waste glasses. No other minerals were observed on the surface.

The MCC-2 tests were done to accelerate the reaction process. The surface alteration from a 28 day MCC-2 test sample analyzed by x-ray diffraction (XRD) indicates the surface layer is composed of the mineral vermiculite [ideally $(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$]. The clay mineralization observed on naturally occurring glasses is very similar to that produced on laboratory altered glasses.

Hydration tests have been shown to accelerate the formation of alteration products without changing the reaction mechanism [6,7,8,9,10]. Thus, this is a good way to demonstrate the similarity between waste glass and natural glass alteration. The hydration process for each glass can be compared by investigating the alteration products and kinetics of the formation of the hydration layer. The alteration process for the synthetic basalt glass is characterized by the initial formation of analcime (ideally $NaAlSi_2O_6 \cdot H_2O$), followed by gyrolite (ideally $Ca_2Si_3O_7(OH)_2 \cdot H_2O$), and montmorillonite (see Figure 5). The surface alteration of defense waste borosilicate glass (Figure 6) is characterized by the initial formation of analcime, followed by gyrolite, calcium silicates, montmorillonite and tobermorite (ideally $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) [7,8]. The correspondence in the alteration products between laboratory-aged synthetic basalt glass and borosilicate waste glass can be seen by comparing Figures 5 and 6.

The kinetics of the hydration layer formation of the synthetic basalt glass are $t^{1/2}$ (see Figure 3) for the period studied (up to 63 days) but about five times slower than that of the relatively sodium-rich defense glass. Hydration rates for naturally occurring glasses have been determined [11,12] and the kinetics of hydration for these glasses are $t^{1/2}$. The kinetics of hydration layer formation of SRL 131 defense glass are initially $t^{1/2}$ during analcime formation. Later, during tobermorite formation, the rate of alteration increases [7,8], although an analogous increase has not yet been observed for the synthetic basalt glass. The similarity of the reaction processes between basaltic and defense glasses is remarkable, considering the significant compositional differences between the glass types.

Figure 5. SEM image in secondary electrons of analcime (blocky aggregates), gyrolite (bladed aggregates) and clay mineralization (mat) covering the surface of a synthetic basalt glass hydrated in saturated water vapor conditions. Scale bar represents 10 μm .

Figure 6. SEM image in secondary electrons of analcime (blocky aggregates), calcium silicate (radiating acicular aggregates) and clay mineralization (mat) covering the surface of SRL 131 borosilicate waste glass hydrated in saturated water vapor conditions. Scale bar represents 10 μm .

CONCLUSIONS

As a result of low-temperature geochemical processes, naturally occurring basaltic glasses from diverse geologic environments and of great age (greater than 10,000 years) form conspicuous alteration rinds. These rinds (palagonites) display diverse compositions depending on the geologic conditions of alteration; but in some cases, they show a striking resemblance to the surface layers formed on experimentally altered borosilicate glasses [2,3]. Similarities are also seen when comparing experimentally altered synthetic basalt glass and SRL 131 defense waste glass.

The similarity of the reaction processes between basaltic and defense glasses is remarkable, considering the significant compositional differences in the glass types. The same alteration products form on both glasses and the reaction kinetics are initially both $t^{1/2}$. The similarity between the hydration aging of basaltic glass and defense glass is sufficiently close to suggest that similar processes control the aging/alteration of both glasses.

Future research will require: (1) the detailed characterization of alteration products on well-documented basalt glasses from known geologic environments and of known age, (2) laboratory experiments designed to simulate these long-term effects, (3) parallel experiments on borosilicate glass waste forms, and (4) the incorporation of these data into release codes for verification of the long-term predicted stability of borosilicate glass waste forms.

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REFERENCES

1. M. J. Plodinec, C. M. Jantzen, and G. G. Wicks, Second Intl. Symp. on Ceramics in Nuclear Waste Management, G. G. Wicks and W. Ross, eds., American Ceramic Society, 491-495 (1984).
2. G. Malow, W. Lutze, and R. C. Ewing, Journal of Non-Crystalline Solids **67**, 305-32 (1984).
3. W. Lutze, G. Malow, R. C. Ewing, M. J. Jercinovic, and K. Keil, Nature (submitted for review).
4. J. E. Mendel, MCC-D2, One-Year Leach Test Data for SRL 131 Glass, Report PNL-3990 (1983).
5. J. K. Bates, D. J. Lam, and M. J. Steindler, "Extended Leach Studies of Actinide-Doped SRL 131 Glass," in Scientific Basis of Nuclear Waste Management VI, D. G. Brookins, ed., North-Holland, 183-190 (1983).
6. M. J. Steindler et al., Report ANL-82-78, pp 6-43 (1982).
7. J. K. Bates, L. J. Jardine, and M. J. Steindler, Science **218**, 51-54 (1982).
8. J. K. Bates, L. J. Jardine, and M. J. Steindler, Report ANL-82-11 (1982).
9. J. K. Bates, M. G. Seitz, and M. J. Steindler, Nuclear and Chemical Waste Management **5**, 63-73 (1984).
10. J. K. Bates, M. J. Steindler, B. Tani, and F. J. Purcell, Chemical Geology (in press).
11. I. Friedman, R. L. Smith, and W. D. Long, Geol. Soc. Amer. Bull. **77**, 323-327 (1966).
12. I. Friedman and W. Long, Science **191**, 347-352 (1976).

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