

A NATURAL BASALTIC GLASS ANALOGUE FOR THE LONG-TERM
EXTRAPOLATION OF NUCLEAR WASTE GLASS AGING

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ABSTRACT

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Increased confidence is provided to the extrapolation of long-term waste form behavior by comparing the alteration of experimentally aged natural basaltic glass to the condition of the same glass as it has been geologically aged. The similarity between the laboratory and geologic alterations indicates that important aging variables have been identified and incorporated into the laboratory experiments. This provides credibility to the long-term predictions made for waste form borosilicate glasses using similar experimental procedures. In addition, these experiments have demonstrated that the aging processes for natural basaltic glass are relevant to the alteration of nuclear waste glasses, as both appear to react via similar processes.

The alteration of a synthetic basaltic glass was measured in MCC-1 tests done at 90°C, a SA/V of 0.1 cm⁻¹ and time periods up to 182 days. Tests were also done using (1) MCC-2 procedures at 190°C, a SA/V of 0.1 cm⁻¹ and time periods up to 91 days and (2) hydration tests in saturated water vapor at 240°C, a SA/V of ~10⁶ cm⁻¹, and time periods up to 63 days. These results are compared to alteration observed in natural basaltic glasses of great age.

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 back-reactions. In addition, it must be possible to verify the long-term validity of the extrapolated reactions. It has been suggested that basaltic glasses (SiO₂ = 45 to 50 wt %) and borosilicate waste glasses (SiO₂ = 40 to 50 wt %) are similar in their dissolution rates and mechanisms, as the SiO₂ content of glass has been shown to have an important effect on glass/water reactions [1,2,3]. In this paper, we present a physical and chemical description of the alteration products of naturally reacted basaltic glasses as a function of their age and geologic environment. These results are then compared to basaltic glass aged by laboratory hydration and leaching experiments. Additionally, the corrosion behavior of basaltic glasses and waste form borosilicate glasses is compared. The results can be used to model the long-term extrapolation of radionuclide release [3].

EXPERIMENTAL

The initial field effort has been to obtain detailed information on natural basaltic glasses that can be used as nuclear waste analogues in accelerated testing. Samples collected include nonreacted glass and glass that has been altered under various conditions (e.g., by steam, hydrothermal, and lower temperature environments).

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The thrust of experimentation has been 1) to simulate in the laboratory those reactions observed to have occurred in nature and 2) compare the behavior of nuclear waste glass and natural glass by subjecting unreacted nuclear waste glass to the same laboratory (i.e., accelerated) conditions as unreacted simulated natural glass.

Accelerated testing was done using a Hawaiian basaltic glass and SRL 131 defense waste borosilicate glass. The composition of each is given in Table I. The natural Hawaiian sample was chosen because of its relatively young age and documented history. Preliminary testing on the Hawaiian glass with 2.5 wt % Na₂O under strenuous conditions (7 days @ 240°C) indicated that little alteration occurred. Therefore, a glass with a higher Na₂O content (4.5 wt %) was used which can still be considered representative of a natural Hawaiian basalt. Aging of SRL 131 borosilicate waste glass by water vapor saturation has been reported previously [4,5].

Hydrothermal dissolution tests in deionized distilled water were used in the laboratory to accelerate alteration of the synthetic basaltic glass. The alteration of the synthetic basaltic glass was measured in MCC-1 tests at 90°C and MCC-2 tests at 190°C, a SA/V of 0.1 cm⁻¹, and time periods up to 182 days. Hydration tests were also completed in saturated water vapor at 240°C, a SA/V of ~10⁶ cm⁻¹, and time periods up to 63 days. Hydration tests have been shown as a way of accelerating alteration product formation without changing the reaction mechanism [4,5,6], thus this is a good way to demonstrate the similarity between waste glass and natural glass alteration.

The identification of alteration products and chemical characterization of the reaction layer were done using a combination of instrumental techniques which include electron microprobe analysis, scanning electron microscopy, energy dispersive x-ray analysis, and x-ray diffraction.

Table I. Composition (wt %) of Synthetic Basaltic Glass and Savannah River Laboratory Waste Glass

	Basaltic Glass	SRL 131
SiO ₂	52.6	44.0
TiO ₂	1.8	0.7
Al ₂ O ₃	10.8	3.5
Fe ₂ O ₃	13.0	14.3
MnO	0.1	3.1
MgO	12.3	1.6
CaO	4.4	1.4
Na ₂ O	4.5	13.7
K ₂ O	0.6	-
B ₂ O ₃	-	10.9
Li ₂ O	-	4.2
NiO	-	1.8
ZrO ₃	-	0.4
La ₂ O ₃	-	0.4
Total	100.1	100.0

Analysis by EDS.

RESULTS AND DISCUSSION

The alteration of basaltic glasses in nature proceeds by a hydrolytic dissolution/precipitation mechanism which results in the formation of well defined surface layers. These alteration rinds generally are iron-rich aluminosilicate gels (palagonite) which are depleted in alkalis and alkaline earths relative to parent glass. The precise composition depends on properties of the aqueous solution (e.g., proportions of dissolved cations, pH, etc.).

All the natural samples 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.

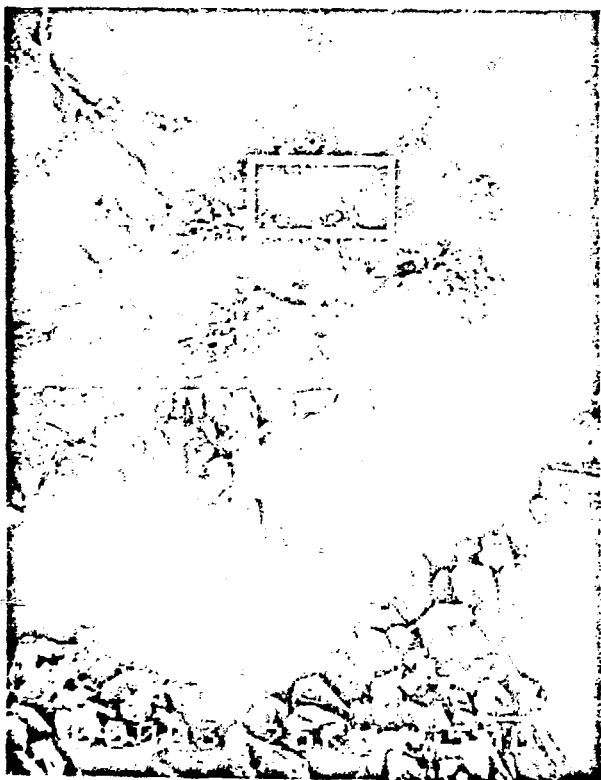
Glass alteration is often accompanied by the precipitation of authigenic cements (e.g., zeolites, clay minerals, calcite, opaline silica) as shown in Figure 1, a consequence of the interdependence between solution composition and progressive hydrolysis. Commonly there is a partial replacement of this apparently amorphous layer by smectite clay or chlorite. The glass next to the alteration rind is typically dissolution pitted. Authigenic cements in the British Columbia hyaloclastites include calcite, chabazite, phillipsite, analcime, iron-rich smectites, and some iron oxy-hydroxides.

Electron microprobe analyses of natural glasses and corresponding pseudomorphic alteration layers were done for the major elements. Figures 2 and 3 illustrate general features and trends of seven elements for glasses from different environments. With few exceptions, SiO_2 , HgO , 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 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.

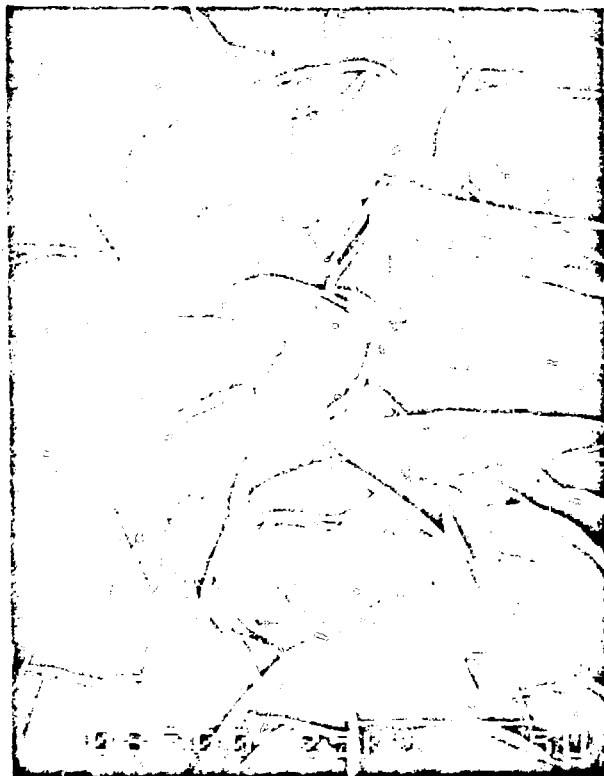
The type and extent of synthetic basaltic glass hydration was studied by analyzing the alteration products and kinetics of alteration layer formation as a result of reaction in a saturated water vapor environment. The alteration process can be characterized for the basaltic glass by initial formation of analcime, followed by the formation of gyrolite, montmorillonite, vermiculite, and tobermorite (see Figure 4). The layer is depleted in Na and slightly depleted in Al relative to the parent glass. Hg is enriched in the layer relative to the bulk glass. Ti is relatively unaffected.

Natural glass alteration was also studied via leach testing. Because of the extended time required to reach solution saturation, the MCC-type tests did not achieve as great a degree of aging as the hydration tests but alteration of the glass to the clay mineral vermiculite is observed. These tests provide an indication that processes that alter basaltic glass in the natural environment have, to date, been partly reproduced in the laboratory.

The relationship between natural glass and nuclear waste glass alteration can be investigated by comparing the hydration process for each glass. The surface alteration of defense waste borosilicate glass can be characterized by initial formation of analcime, followed by the formation of gyrolite, calcium silicates, montmorillonite and tobermorite [4,5]. The behavior of elements in the hydration layer of the defense waste glass is very similar to that of the natural basaltic glass. The correspondence in the alteration products between laboratory-aged natural glass and borosilicate waste glass can be seen in Figures 4 and 5.



a



b

Figure 1. (a) Scanning electron images of zeolites in a fresh water altered hyaloclastite from British Columbia (Sample TBI). The prismatic forms are phillipsite. Magnification 170X (upper) and 850X (lower). The 50 micron scale bar applies to the upper image. (b) Scanning electron image of clay mineralization associated with an altered, glass pillow basalt rim from the Icelandic Shelf (sample USNM 113432-24). Magnification: 5,200X.

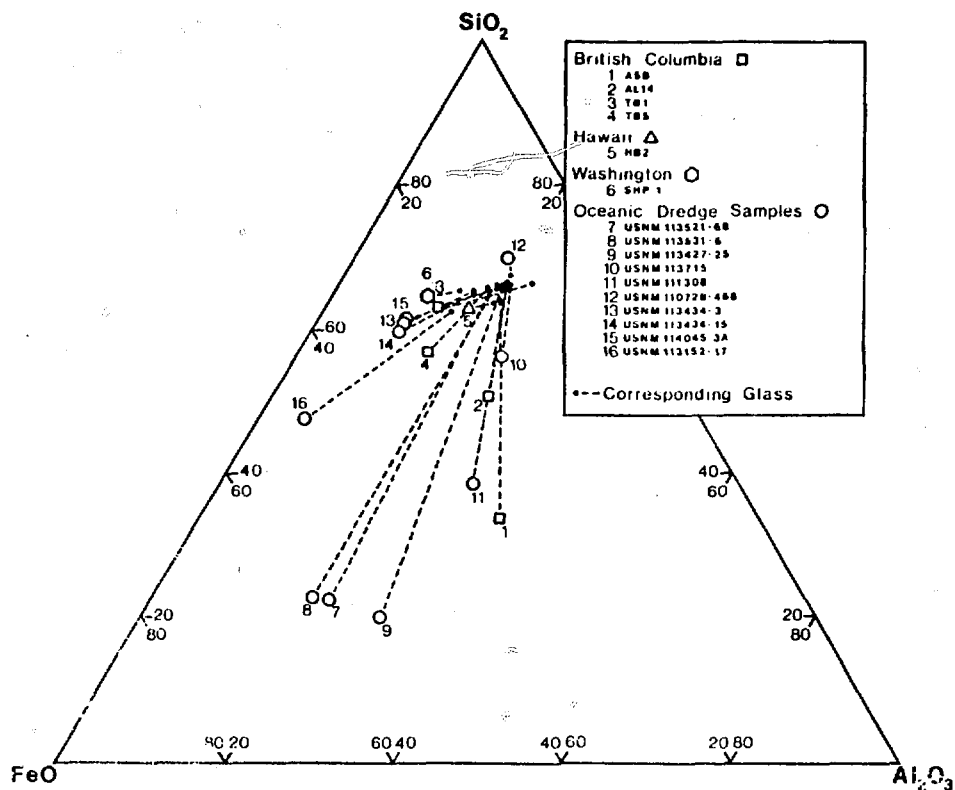


Figure 2. SiO₂-Al₂O₃-FeO Weight Percent Variation Diagram Plotting the Microprobe Analyses of Alteration Rinds and Associated Glasses.

The kinetics of hydration layer formation of SRL 131 defense glass are initially $t^{1/2}$ during analcime formation and then accelerated during tobermorite formation [1]. The kinetics of hydration layer formation of basaltic glass are $t^{1/2}$ (see Fig. 6) for the period studied (up to 63 days) but about five times slower than that of the relatively sodium-rich defense glass. No break was noted in the kinetics of hydration of basaltic glass as observed for defense borosilicate glass.

The similarity of the reaction processes between basaltic and defense glasses are remarkable, considering the significant compositional differences in the glass types. These compositional differences account for the differences in the reaction rates (less Na in basaltic glass decreases the rate) and in the fact that no tobermorite acceleration of the reaction process has yet been observed (different Ca concentration in the glass and in the reaction layer).

CONCLUSIONS

The initial effort in this program has provided a well-documented collection of basaltic glasses with their respective palagonites formed in diverse geologic environments and over a wide range of geologic ages. As a result of geochemical alteration, all of the glasses form a conspicuous alteration rind. These rinds (palagonites) display diverse chemistries

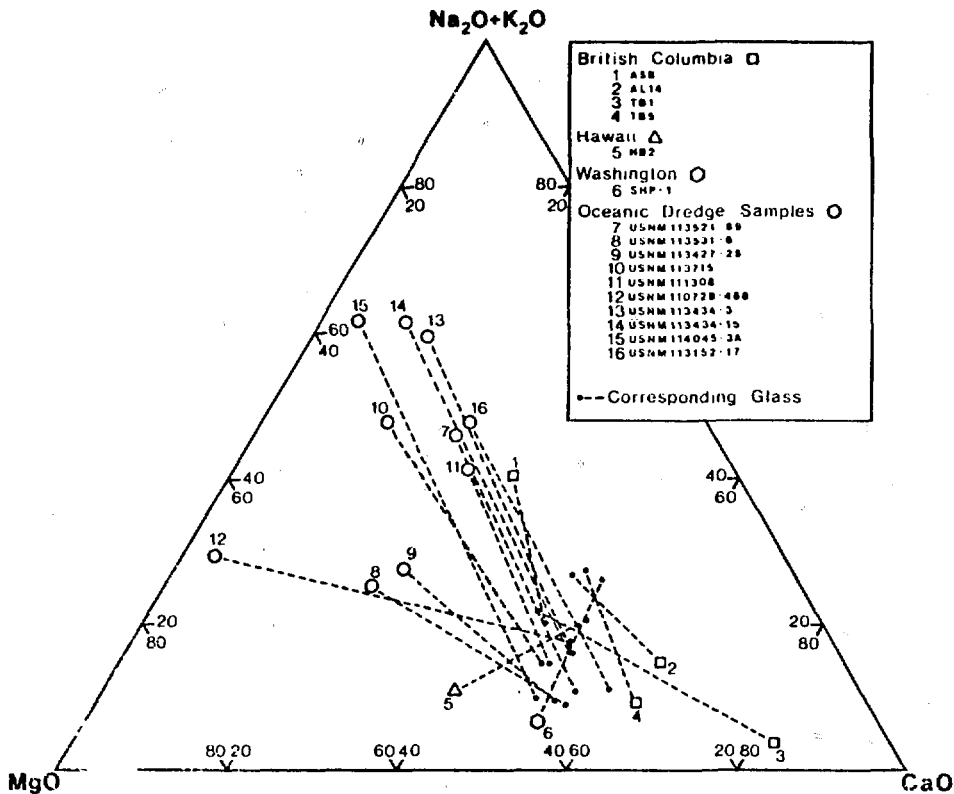


Figure 3. (Na₂O+K₂O)-CaO-MgO Weight Percent Variation Diagram Plotting the Microprobe Analyses of Alteration Rinds and Associated Glasses.

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. These physical and chemical similarities provide additional support for the idea that basaltic glasses are good analogues for the long-term alteration of borosilicate glasses may be used to verify release codes used to evaluate the long-term stability of borosilicate glass waste forms.

The similarity of the reaction processes between basaltic and defense glasses are 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 basalt glass and defense glass is close enough to suggest that similar processes control the aging/alteration of both glasses.

Future studies will require: (1) the detailed characterization of alteration products on well-documented basaltic 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.



Figure 4. Scanning electron images of analcime, gyrolites and clay mineralization surface covering of a synthetic basaltic glass hydrated in saturated water vapor conditions. Micron marker represents 10 μm . Magnification: 450X.

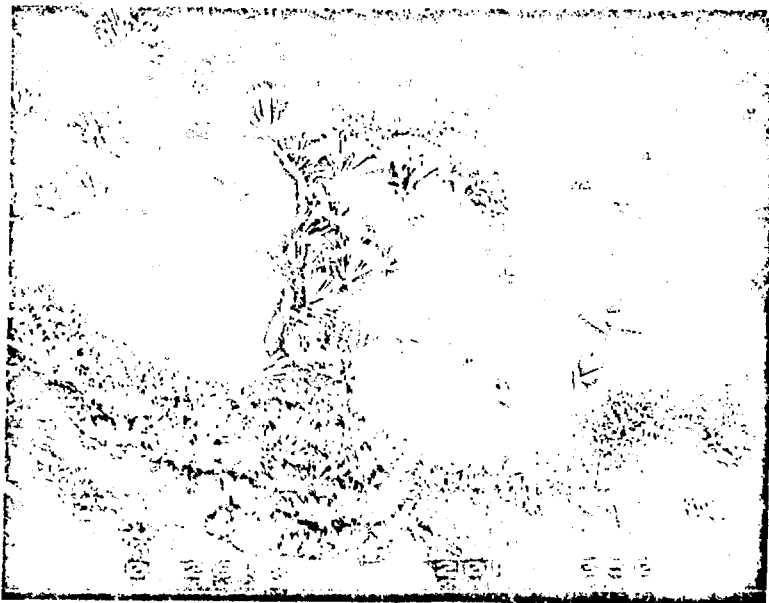


Figure 5. Scanning electron images of analcimes, calcium silicates and clay mineralization surface covering of SRL 131 borosilicate waste glass hydrated in saturated water vapor conditions. Micron marker represents 10 μm . Magnification: 260X.

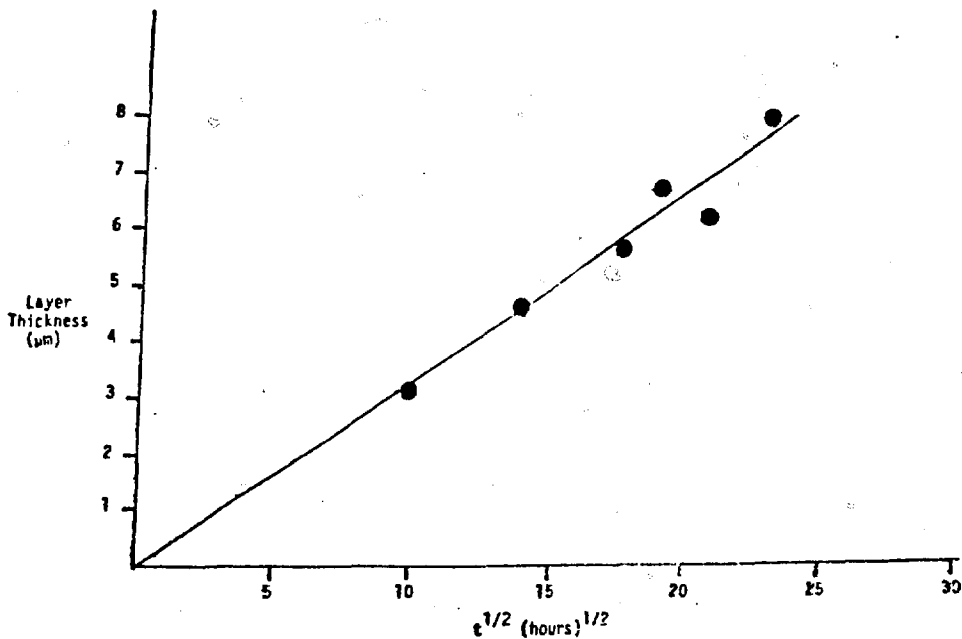


Figure 6. Hydration Kinetics of Laboratory Basaltic Glass

REFERENCES

1. M. J. Plodinec, C. M. Jantzen, and G. G. Wicks, "Thermodynamic Approach to Prediction of the Stability of Proposed Radwaste Glasses," 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, "Alteration Effects and Leach Rates of Basaltic Glasses: Implications for the Long-Term Stability of Nuclear Waste Form Borosilicate Glasses," *Journal of Non-Crystalline Solids* (in press).
3. W. Lutze, G. Malow, R. C. Ewing, M. J. Jercinovic, and K. Keil, "Long-Term Alteration Effects of Basaltic Glasses: Implications for Modeling the Long-Term Stability of Nuclear Waste Form Borosilicate Glasses," *Nature* (submitted for review).
4. J. K. Bates, L. J. Jardine, and M. J. Steindler, "Hydration Aging of Nuclear Waste Glass," *Science* **218**, 51-54 (1982).
5. J. K. Bates, M. G. Seitz, and M. J. Steindler, "The Relevance of Vapor Phase Hydration Aging to Nuclear Waste Isolation," *Nuclear and Chemical Waste Management* (in press).
6. J. K. Bates, M. J. Steindler, B. Tani, and F. J. Purcell, "The Hydration Alteration of a Commercial Nuclear Waste Glass," *Chemical Geology* (in press).