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MINERALOGICAL,TEXTURAL AND COMPOSITIONAL DATA ON THE ALTERATION OF BASALTIC GLASS FROM KILAUEA, HAWAII TO 300°C: INSIGHTS TO THE CORROSION OF A BOROSILICATE GLASS WASTE-FORM

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ABSTRACT

Mineralogical, textural and compositional data accompanying greenschist facies metamorphism (to 300°C) of basalts of the East Rift Zone (ERZ), Kilauea, Hawaii may be evaluated relative to published and experimental results for the surface corrosion of borosilicate glass. The ERZ alteration sequence is dominated by intermittent palagonite, interlayered smectite-chlorite, chlorite, and actinolite-epidote-anhydrite. Alteration is best developed in fractures and vesicles where surface reaction layers root on the glass matrix forming rinds in excess of 100 microns thick. Fractures control fluid circulation and the alteration sequence. Proximal to the glass surface, palagonite, Fe-Ti oxides and clays replace fresh glass as the surface reaction layer migrates inwards; away from the surface, amphibole, anhydrite, quartz and calcite crystallize from hydrothermal fluids in contact with the glass. The texture and composition of basaltic glass surfaces are similar to those of a SRL-165 glass leached statically for sixty days at 150°C. While the ERZ reservoir is a complex open system, conservative comparisons between the alteration of ERZ and synthetic borosilicate glass are warranted.

INTRODUCTION

The alteration of porphyritic basalt by hot brines (to 300°C) in the ERZ provides mineralogical, textural and compositional data on alteration processes potentially of relevance in assessing models of borosilicate glass corrosion. Data on the identity and composition of these secondary phases is necessary to validate mechanisms controlling glass reactions and verify models of long-term glass dissolution. Because glass is a metastable solid, with time, it transforms in a hydrous environment to crystalline and thermodynamically stable phases. These secondary phases control the solution concentration of elements; unfortunately, poor crystallinity, minute grain size and finely laminated secondary texture combine to complicate identification and characterization [1]. Geologic systems provide a window to investigate the alteration of an analogous glass in the presence of circulating hot water; water-glass surface reactions and resultant secondary phases evolve conspicuously in the natural system. A 1962m deep geothermal well (HGP-A) penetrates a sequence of ERZ basalt, tephra, flows and intrusions which have been altered by fluids of low salinity (5-25 mg/ml). Progressing down-hole, the alteration sequence is dominated by intermittent palagonite (0-675m), smectite (675-1350m), chlorite (1350-1890m) and actinolite-epidote-anhydrite (1840m-total depth) (see [2,3]). Alteration of HGP-A glass is the result of hydrothermal alteration involving both meteoric and saline waters as well as contact metamorphism associated with the intrusion of subvolcanic basaltic intrusions [2]. Hydrothermal alteration affecting glass surfaces may be discriminated from matrix metamorphism; texturally, alteration is best developed in fractures and vesicles where surface alteration and amorphous gel layers mantle the glass matrix forming rinds in excess of 100 microns thick.

GEOLOGIC SETTING, SAMPLES AND METHODOLOGY

Basalts from the ERZ cluster near 51 weight % SiO_2 with FeO_{total} ranging between 10 and 11 wt% with olivine and intermittent clinopyroxene and plagioclase phenocrysts [4]; all Kilauean basalts are tholeiitic and quartz normative. High permeability of both subaerial and submarine extrusives (5×10^4 darcies) allows for very high recharge rates and circulation of hydrothermal fluids that moderate temperatures at depth; bottom hole temperatures are near 300°C. ERZ fluids are low salinity (5-25 mg/ml) meteoric waters which are recharged from the surface into the fractured dike rocks of the ERZ. Within the ERZ there is a range of groundwater chemistry indicative of several different sources: 1) cold meteoric waters, 2) sea waters, 3) hydrothermal fluids of meteoric origin and 4) hydrothermally modified seawater (see [5,6]).

In 1976 the HGP-A well was drilled in the ERZ; drill-core and cuttings form the sampling base for this investigation. Core samples were provided as thin sections from the ten intervals over which core was taken; cuttings came as drilling chips representative of 14 depth intervals. Samples were characterized by optical microscopy, scanning electron microscopy (with backscattered and secondary electron imaging), X-ray diffraction (XRD) and electron microprobe analysis (EPMA). Clays were separated for XRD as a <2.0 micron size fraction by centrifuge and were exchanged with 1N $MgCl_2$. Diffraction patterns were obtained before and after glycol solvation. A primary consideration in the microbeam analysis of glass and clays is the migration of alkalis [7]. For these reasons, sodium by EPMA was always analyzed first, count times were reduced and the spot was enlarged to raster 25 to 100 $micron^2$.

ALTERATION TEXTURES

At shallow depths (466m), much of the original basaltic glass is still intact and recognizable. Some incipient clay mineralization is developed on rock surfaces, but a vitric matrix prevails. Smectite grows from the matrix at intermediate depths (1376m) in characteristic honeycomb habit identical to that produced by leaching experiments of synthetic and natural glass at temperatures near 100°C [8,9,10]. Chlorite replaces smectite in subsequent intervals as the principal alteration phase in both groundmass and vesicles; HGP-A chlorites are similar to the clay described by Byers et al. [11] from the alteration of an altered, glassy pillow basalt from the Icelandic Shelf. Near total depth (1960m), actinolite is conspicuous particularly as vesicle-fill.

Palagonite and Fe-Ti oxides grow coincident to glass surfaces. At 917m vesicles and fractures are filled by clays. Interlayered smectite-chlorite crystallizes along vesicle and fracture surfaces; with increasing alteration, chlorite replaces smectite-chlorite away from the surface. Notable is a uniform, almost circular, distribution of opaques associated with the vesicle fill. With increasing depth, actinolite, oxides and anhydrite crystallize in the presence of quartz and calcite and replace chlorite as vesicle fill; as well, the glass matrix becomes increasingly recrystallized. Commencing at 1000m to near total depth ilmenite crystallizes with a reticulated pattern. The textures described here are similar to the alteration sequence for altered tholeiitic basalts from the Peru Trench [12].

Proximal to the glass surface, palagonite, Fe-Ti oxides and clays replace fresh glass as the matrix reacts; away from the glass surface, amphibole, anhydrite, quartz and calcite precipitate from hydrothermal fluids. Reacted surfaces within the glass typically reveal a front developed along the glass surface on which secondary minerals have crystallized. Backscattered electron imaging suggests the surface reaction layer variably migrates from into the fresh glass; aided by fractures, pieces of the glass matrix may get incorporated in the alteration rind as exfoliated "islands" or spalled fragments. Secondary minerals crystallize in regular bands coincident to reacted glass surfaces (figure 1); imaging indicates the banding is composed of horizons of contrasting mean atomic number. Closest to the glass surface is a band of low mean atomic number which is followed by layers of higher number. EDS analyses indicate the Si/Al ratios decrease from 6 closest to the reacted glass surface to approximately 3 farthest from surface. Fe, Ca, Ti show little variance over the same interval; similarly, there is little variation between alternate bands.

As expected, the trend in Si/Al parallels increasing clay content away from the reacted glass surface. Staudigel and Hart [13] describe the alteration of basaltic glass similarly occurring along an interface riddled with microchannels separating fresh glass and palagonite. Palagonite is often concentrically banded with horizons rich in opaques accentuating the banding. Glass alteration incorporates two basic processes [13]: the decomposition of primary vitric phases and the addition of secondary phases which precipitate on the reacting glass surface. The alteration process provides a chemical flux of constituent elements released during alteration which are largely redeposited in vesicles and veins as smectites, carbonates and zeolites. The textural data suggests a similar model for HGP-A basalts.

ALTERATION MINERALOGY

X-ray studies of clay separates indicates that shallow (1077m) clay is an interlayered smectite-chlorite; after glycolation, the first order (001) reflection suggests the interlayer is composed of randomly oriented smectite with 10-20% chlorite [14]. With increasing depth (1850m), interlayered smectite-chlorite consists of 10% chlorite in the presence of discrete chlorite. Regularly interlayered smectite/chlorite with a 1:1 interstratification of 14 angstrom chlorite and 14 angstrom smectite is characterized by a 28.0-30.0 angstrom peak when air dried and a 30.5-31.5 angstrom peak when glycolated for the superlattice. From 1850m to total depth, chlorite and interlayered smectite-chlorite persist together with strong peaks for talc and amphibole. Feldspar peaks are ubiquitous throughout the sequence. XRD for whole rock samples indicates iron sulfides (pyrite, pyrrhotite) first appear at shallow depths (145m) and persist to total depth. Oxides (ilmenite, magnetite) crystallize at intermediate depths (450m to 1530m).

The contribution of Ca from basalt and SO_4 from dilute seawater allows anhydrite to precipitate in vesicles at depths of 1966m. Anhydrite will precipitate from seawater at 150°C *in the presence of basalt [15]; accordingly, down-hole fluids were sufficiently* oxidizing and concentrated in SO_4.

ALTERATION CHEMISTRY

Glass and Palagonite

HGP-A glass compositions show considerable range relative to slightly altered glass from shallow well depth (15m) and submarine dredges of the ERZ [4]. To obtain a measure of the relative enrichment and depletion in the altered glass and palagonite relative to the original glass, the index proposed by Staudigel and Hart [13] was adapted for this purpose. Ti was chosen as a measure of the maturity of alteration/palagonization - Ti being passively accumulated by the removal of other cations. An "unaltered" glass composition was determined by averaging compositions for shallow (15m) HGP-A samples and published analyses [4] for the submarine basalts of the ERZ. Ti^* is a measure of the extent of the alteration and increases with alteration maturity (see caption for figure 2). Using the average "unaltered" glass composition as a denominator, the relative enrichment and depletion of particular cations are a function of the maturity of alteration/palagonization. The results for FeO, K_2O, MgO and CaO are plotted in figure 2. Ordinate values >1.0 indicate enrichment, values <1.0 indicate depletion; scatter in the data for altered glass is manifest in some values for Ti^* less than zero. Data for HGP-A glasses and palagonites indicate enrichments in FeO and K_2O and depletions in CaO and MgO with increasing alteration maturity. These results are in concert with the observations of Staudigel and Hart [13], Scheidegger and Stakes [12] and Arai et al. [10]. With the exception of K introduced by dilute seawater, glass and palagonite compositions seemingly

Figure 1: Backscattered electron image of glass rind developed on a vesicle surface. EDS analyses indicate the Si/Al ratios for each layer decrease from 6 closest to the glass surface to 3 furthest from the surface. Fe, Ca and Ti show little variance over the same interval. Note regular banding of the layers. Bright phase on the bottom of the image is a clinopyroxene phenocryst. Depth 614m. 1300x magnification with 10 micron scale bar.

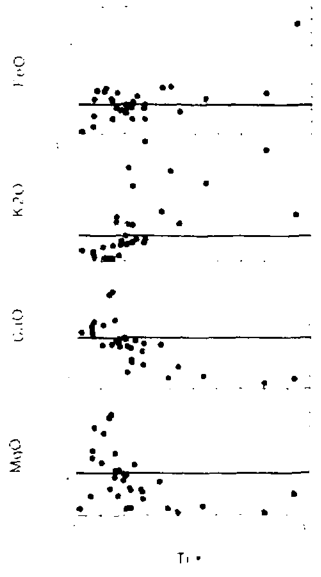

Figure 2: Oxide gain or loss between an average for shallow (15m) HGP-A and dredge samples (AVG SHALLOW) of ERZ basalts [4] and palagonite and altered glass (DEEP) from HGP-A down-hole. Heavy line = 1.0; ordinate values > 1.0 indicate enrichment, values < 1.0 indicate depletion.

Ti* = [Ti[illegible]-Ti[illegible]]/Ti[illegible]

MgO* = MgO[illegible] MgO[illegible]

follow the general trend for ion mobility determined for fresh-water alteration of glass at low temperature of Byers et al. [16] (in order of decreasing mobility):

$$Na > K > Mg > Ca > Al > Si > Fe > Ti.$$

Smectite $(\frac{1}{2}Ca,Na)_{0.7}(Al,Mg,Fe)_4[(Si,Al)_8O_{20}](OH)_4 \cdot nH_2O$

Smectite analyses recalculated on the basis of 22 oxygens are intermediate between di- and tri-octahedral compositions. Generally, di-octahedral-like smectite occurs at shallower depths with an increase in the tri-octahedral-like species with increasing depth. The di-octahedral species resembles montmorillonite while the tri-octahedral species are saponite or Fe saponite. A di- and tri-octahedral smectite admixture is reported from altered submarine tholeiites collected from the Peru Trench [12]. Similarly, Fe saponite is the primary alteration phase of basalt reacted in a Dickson bomb with seawater at 150°C at 500 bars for 150 days [15].

Chlorites $(Mg,Al,Fe)_{12}[(Si,Al)_8O_{20}](OH)_{16}$

Chlorites generally increase in Mg and decrease in Fe and Al with depth and compare with ophiolitic and DSDP chlorites reported by Bettison and Schiffman [17]. Chlorites from 1850m are anomalous, having lower Fe content than ophiolitic chlorites but higher Mg content than chlorites from total depth. Bettison and Schiffman [17] indicate that the compositional transition from mixed layer chlorite/smectite to true chlorite occurs within the range 6.25 to 5.95 Si cations per 28 oxygens; in concert with results from XRD, the HGP-A chlorites are more appropriately mixed layer chlorite/smectites than true chlorites. At intermediate and extreme depth, the clays become truly chloritic by this definition. Bailey [18] notes Mg and Fe/(Fe+Mg) for chlorite are poorly correlated with alteration temperature and are more sensitive to the bulk composition of the host rock; HGP-A chlorites may be similarly affected. The range in Ca may be an effect of the Ca component introduced by mixed layer clays [17].

Actinolite $Ca_2(Mg,Fe^{+2})_5[Si_8O_{22}](OH,F)_2$

Using the criteria of Leake [19], HGP-A amphiboles are transitional between actinolitic hornblende and, at total depth, true actinolite. Si/Al ratios for amphiboles increase with depth. Laird [20] reports that for amphiboles produced by low P metamorphism of basalts, TiO_2 and FeO/MgO increase with temperature; experimental work further suggests that Al, Ti, Na and Fe/Mg in greenschist facies amphiboles all increase with increasing temperature. HGP-A amphiboles are depleted in Al with depth; Fe/Mg fluctuates down-hole. As such, the function relating composition with temperature is complex. The presence of actinolite is indicative of environments with higher P_{H_2O} relative to P_{CO_2} and consistent with that envisaged for the deep HGP-A reservoir [21].

APPLICATION TO DISSOLUTION OF A BOROSILICATE WASTE-FORM

The alteration morphologies documented in HGP-A are similar to those described for the static leaching of borosilicate glasses. Stabilization of a 100-200 micron thick surface alteration layer by dehydration and critical point drying [22] of a SRL-165 glass leached statically for sixty days in a pH 8.2 HCO_3 buffer solution at 150°C (see [23]) revealed structure and composition comparable to that of the natural glass. A symmetrical fit of the glass surface with the alteration rind emphasizes the migration of a reaction layer into the fresh glass; the alteration rind mantles the glass surface without isolating the surface layer from further reaction. Backscattered electron imaging suggests that the surface reaction layer may have grown into the glass preferentially along fractures; similar to textures described for HGP-A basalts, pieces of the glass matrix become incorporated in the alteration rind as exfoliated "islands" or spalled fragments. A heterogeneous stratigraphy is manifest in the alteration layer; oxide phases are disseminated throughout the interior of the rind and to a lesser extent along the glass surface. Clays encompass the perimeter of the alteration layer. The alteration layer is physically separated from the glass surface and neither attenuates nor armors the glass surface from further reaction with circulating fluids. These textures are similar to those documented [1] for a simulated waste glass leached at 90°C in deionized water; Bates [24] suggests the alteration layer consists of a relatively insoluble core, enriched in Fe and depleted in alkalis, which separates from the glass matrix allowing smectite to crystallize. An amorphous gel layer of low atomic number is clearly recognized at the surface of the glass. EDS analysis indicates the Si/Al ratio decreases from approximately 10 in the glass interior to 1.9 in the gel layer; Ca, Mn, Fe are relatively depleted in the gel layer.

Basaltic glasses have been proposed by many as reasonable geologic analogs of vitric waste-forms for their nearly identical Si content and stability, alteration mineralogies and alteration mechanisms [11,16,25,26,27,28]. Kilauean basaltic and SRL-165 glass compositions are compared in Table I:

Table I: Major element compositions of SRL-165 glass and mean of ten analyses of Kilauean submarine basaltic glass [4]. Total Fe reported as FeO; n.d. = not determined; -- = absent.

GLASS	SiO_2	TiO_2	Al_2O_3	FeO^T	MgO	CaO	Na_2O	K_2O	P_2O_5	B_2O_3	Li_2O
SRL-165	52.86	0.13	4.08	10.56	0.70	1.62	10.85	n.d.	0.29	6.76	4.17
BASALT	51.32	2.76	13.85	10.57	6.37	10.89	2.34	0.48	0.29	--	--

The alteration of basaltic glass occurs by dissolution of the vitric matrix and release of constituent cations into nearby circulating reservoir fluids. Secondary minerals precipitate from the fluids and crystallize as a mantle on the glass surface. The precipitating phases fix many of the cations released by the dissolution process. While specifics of the alteration process vary relative to time, temperature, pH and fluid/matrix composition, investigations of natural (HGP-A; [13]) and synthetic glasses [1,23] validate the general mechanism.

While the alteration of HGP-A basalts are illustrative of corrosion mechanisms affecting glass surfaces, there are several differences which detract from HGP-A as a well constrained analog: 1) bottom-hole temperatures are higher (300°C) than generally expected after repository closure; 2) the basalt contains a crystalline phenocryst component lacking in the waste-form; 3) waste-form glasses contain >5 wt% B_2O_3 as well as actinides absent in basalt; 4) the basalt has been altered by vapors and low salinity brines which contrast with dilute bicarbonate groundwaters expected near the proposed repository; 5) basaltic systems reflect hydrothermal alteration that is overprinted by contact metamorphism accompanying basaltic intrusion; 6) the Kilauean basalts are much older and have been altered for considerably longer periods, at high temperatures, relative to a repository glass; and 7) basalt is variably fractured and vesiculated while the waste-form will be ideally isotropic; thus permeability is more variable in a natural system. These factors may similarly complicate interpretations from other proposed basaltic analogs. While alteration morphologies documented from HGP-A are similar to those recognized from simple and static leaching tests in the laboratory [9,29], the HGP-A reservoir, for the reasons discussed above, is a considerably more complex open system.

Knauss et al. [30] in experiments of the dissolution of a simple five component analog glass found the highest dissolution rates at 50°C and 70°C for Na, Ca and B; rates for Si and Al in slightly acidic to nearly neutral fluids (pH 4-8) are one to two orders of magnitude less. Comparable pH for HGP-A fluids is 5.7-6.2 [31]. Data from HGP-A indicates the major elements exclusive of Si and Al are redistributed by a dissolution front that migrates inwards from the surface into the glass matrix. Si and Al constitute an amorphous alteration (gel?) layer; Si/Al ratios increase along a transect from surface of the layer inwards to the unaltered matrix with little corresponding change in Ca, Fe, Mg and Ti. A more aluminous gel edge may afford cross-links in the polymerized layer because of valency differences - as the surrounding fluid is saturated in Si and Al, clays may crystallize on this substrate. Fractures can facilitate the expansion of the amorphous (gel?) layer within the glass matrix; often pieces of the glass will exfoliate and spall off to be incorporated in the trailing layers with precipitated secondary phases.

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