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ABSTRACT

We have examined the weathered surfaces of 720 year old Hawaiian basalt glasses that were recovered from a subaerial environment with high-resolution transmission electron microscopy (TEM) and energy filtered imaging and electron energy loss spectroscopy (EELS) techniques. Whereas the alteration products (palagonite) were physically detached from the underlying glass in most samples, a gel-like amorphous layer was observed adjacent to the glass in a few samples. To our knowledge, this is the first time a gel layer has been observed on weathered basalt. This is significant because analogous gel layers have been observed on nuclear waste glasses reacted in laboratory tests, and this demonstrates an important similarity in the mechanisms of the weathering of basalt and the corrosion of waste glasses.

INTRODUCTION

Because of the similarity in composition, basalt glasses have been utilized as a natural analogue for nuclear waste glasses to predict long-term performance in a geologic repository.[1] Basalt and other naturally occurring glasses serve as natural analogues for both thermodynamic and kinetic aspects of waste glass corrosion. The alteration phases formed during the corrosion of basalt under natural conditions can be compared to the phases formed during reaction of samples of the same basalt in laboratory tests designed to accelerate corrosion. This comparison provides confidence that the test method accelerates corrosion to the same end-state that occurs naturally, and an indication of the degree of acceleration provided by specific test conditions. The test method can then be used with confidence to accelerate the corrosion of nuclear waste glasses to a similar degree.

Another use of basalt as a natural analogue is through comparison of the corrosion products that are formed during reaction of nuclear waste glasses in laboratory tests with those formed by the weathering of basaltic glasses in nature. These comparisons provide insight into the effects of glass composition on the phases that form as the glass corrodes and whether radionuclides become incorporated into common mineral phases. Detailed analysis of the altered surface can also be used to gain information regarding the reaction path and the rate-controlling process.

In this work, we have characterized the glass/palagonite interface of subaerially altered Hawaiian basalt glass by using a combination of high-resolution transmission electron microscopy (TEM) with associated energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). In our previous investigation of the natural alteration of Hawaiian basalt glasses, we identified the palagonite layer to contain mainly iron oxide hydroxide (goethite), aluminum hydroxide hydrate (scarbroite), and an amorphous phase that was rich in Fe and Al. The purpose of the present study was to examine the microstructure and chemical nature of the palagonite/glass interface to compare the alteration processes that dominated in a 700-year-old Hawaiian basalt glass with those that dominate the corrosion of waste glasses to characterize the reaction pathway of glass corrosion.

EXPERIMENTAL

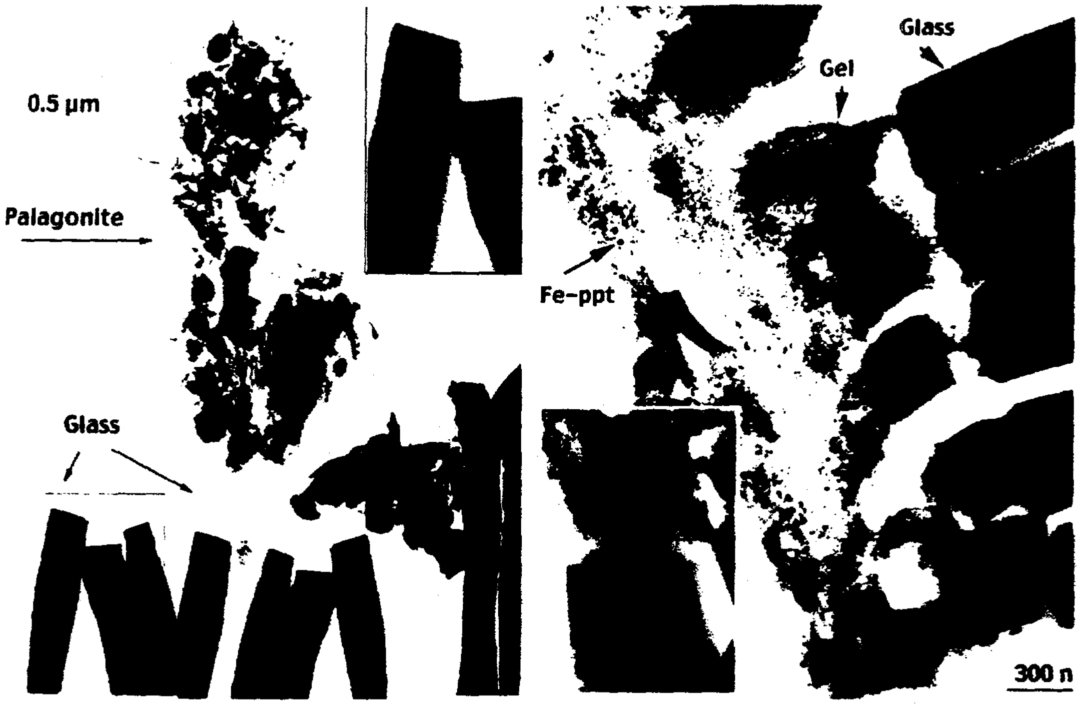
The samples of volcanic basaltic glass were provided by curators of Bishop museum from material collected from an archaeological site at Oahu, Hawaii. The site is located about 85 cm below the ground level and provided a wet and cool environment. Although its exposure history is not known, the basalt had likely been altered through contact with meteoric water and the humid atmosphere. The age of the sample had been determined to be about 720 ± 80 years by radiocarbon dating of the occupation layer of charcoal. The palagonite layer formed on the surface had a yellowish color. The palagonite was removed from one sample and the underlying glass was chemically dissolved and analyzed with inductively coupled plasma atomic emission spectroscopy (ICP). The analyzed composition of the glass is given in Table 1 on an oxide basis.

Samples were prepared for TEM analysis of the palagonite/glass interface by fixing small chips of the basalt that had been carefully removed onto an epoxy resin block. The chip was carefully oriented so that samples for analysis of the palagonite/glass interface could be prepared. After a small amount of resin was placed on the surface of the specimens, they were placed in a vacuum to facilitate penetration of the resin into the surface layer and elimination of air bubbles. After the resin had cured, TEM samples were cut with a Reichert-Jung Microtome to a thickness of about 50 nm. Samples were examined with a JEOL 2000FX unit operating at 200 kV. The microscope is equipped with an ultra-thin window energy dispersive X-ray spectrometer (EDS) and a Gatan Filtering Imaging (GIF) system. The dispersion of the spectrometer was set to 0.5 eV/channel and calibrated using the ls/π transitions on the K edges of carbon at $\Delta E = 285$ eV and oxygen at $\Delta E = 532$ eV. The energy resolution was estimated to be about 1.9 eV based on the measured full width at half maximum of the zero-loss peak. Chemical analysis by EDS was performed with a electron beam focused to about 15 nm; this corresponds roughly with the spatial resolution of the EDS analysis. Unreacted glass beneath the interface was used as a standard for the quantitative determination of major components in the alteration products by means of the well-established Cliff-Lorimer method.[7]

RESULTS AND DISCUSSION

Figure 1 shows two types of interfaces that were observed in this investigation. The glass had chattered in all TEM samples during microtome sample preparation parallel to the knife edge. The alteration phases did not chatter because they are less brittle than the glass and because they were impregnated with the epoxy. The interface in Fig. 1a is that typically observe with TEM. The alteration layer was usually seen to be detached from the glass surface. The presence of epoxy between the layer and the glass indicates the layer had separated from the glass prior to microtomy, which suggests that the layer was only loosely fixed to the glass. The high-magnification image of the glass surface shows no evidence of alteration (see inset in Fig. 1a). Characterization of the edge of the glass nearest the palagonite with EDS line profiling indicated a slight depletion of alkali metals at the outer 0.1 μm. No variation in silicon or aluminum was observed. Similar palagonite/glass interfaces have been observed in basalt glasses reacted in sea water,[2] glacial water,[5] and samples recovered from Deep Sea Drilling Project (DSDP).[8]

The majority of the palagonite consisted of hemispherical masses that were identified as goethite [FeO(OH)] by selected area electron diffraction (SAED) and EDS. The details of identification of the phases that were present in palagonite will be published elsewhere.[6] The formation of a layer comprised predominantly of goethite is consistent with the very low solubilities of Fe, Ti, and Mn. Other major elements of basalt (e.g., Na and Ca) are more soluble and remain in solution. Other crystalline precipitates that were identified generally had a layered or fibrous texture characteristic of smectite-type clays.[6]



(a) (b)

Fig. 1. Transmission electron micrograph of (a) typically observed glass/palagonite interface and (b) interface with gel layer.

Figure 1b is a TEM image of the glass/palagonite interface on another sample recovered from same location. This sample exhibits a very different microstructure than the sample shown in Fig. 1a. In the sample in Fig. 1b, a layer as thick as 0.5 μm in some areas was observed to remain fixed at the outer surface of the glass. The image of this layer had a uniform amorphous contrast and the layer is referred to as a gel layer. The gel layer remained attached to the underlying glass (see inset in Fig. 1b). Electron diffraction confirmed that the gel layer was mostly amorphous, although small crystalline domains reminiscent of clays were seen within the layer. Many small dark spots were observed to be distributed throughout the layer. These spots were typically about 10 nm in size, and were determined to be iron-rich by EDS analysis. The results of EDS analyses of the glass and the gel layer are summarized in Table 1. The gel layer was significantly depleted in Na, Ca, and Mg, and Si, and enriched in Fe, Ti, and Al relative to the glass. That the sum of oxides for the gel layer is appreciably less than 100% is probably due to the presence of water, which cannot be quantified with EDS.

Although many basalt/palagonite interfaces have been examined for samples recovered from various environments,[2,5,8] this is the first time, to the best of our knowledge, that a gel layer has been observed on a naturally altered basalt glass. On the other hand, gel layers have been frequently observed in laboratory reacted nuclear waste glasses, usually seen at early stages of reaction progress.[9] At more advanced stages of reaction, the gel layers formed on nuclear waste glasses transform into a clay. Elements in the gel that are not totally incorporated into the clay may form other phases.[2,5,8] Once the gel transforms into clay, subsequent glass dissolution does not form new clay. Instead, components released as the glass dissolves form clay. The observation of the gel layer in Hawaiian basalt glass provides important evidence for the similar corrosion paths of basalt and nuclear waste glasses. The reason that gel layers have not been observed previously is probably because the corrosion of most samples recovered from natural environments have progressed to the point where the gel has transformed to other phases.

Table 1. Results of Analysis of Glass and Gel Layer

Oxide	ICP Glass, wt%	EDS Glass, wt%	EDS Gel, wt%	Oxide	ICP Glass, wt%	EDS Glass, wt%	EDS Gel, wt%
Al_2O_3	14.4	15.3	17.0	MnO	0.13	0.13	0.17
CaO	9.68	10.4	0.18	Na_2O	2.81	3.70	0.00
Fe_2O_3	12.0	9.39	54.8	SiO_2	51.5	51.8	13.8
K_2O	0.50	0.69	0.17	TiO_2	2.05	1.61	2.07
MgO	6.69	6.90	0.00	others	0.24	0.08	11.8

To further investigate the nature of the gel layer, EELS spectra were generated with GIF for the Si-K edges of both the gel layer and the glass. The results were then used to calculate the momentum transfer-weighted scattering factor, $k^2\chi(k)$, and the radial distribution function (RDF), both of which provide information on local environments of Si in the glass or in the gel layer. Figure 2 shows the EELS spectra of background-subtracted Si-K edges acquired from the glass and the gel layer. Both curves feature similar energy-loss near-edge structure for Si atoms in the layer and in glass. There is no indication of extra pre-edges or substantial peak shifts, which suggests that the valence states of Si atoms are similar in the glass and gel layer. Figure 2b and 2c shows the $k^2\chi(k)$s and RDFs of

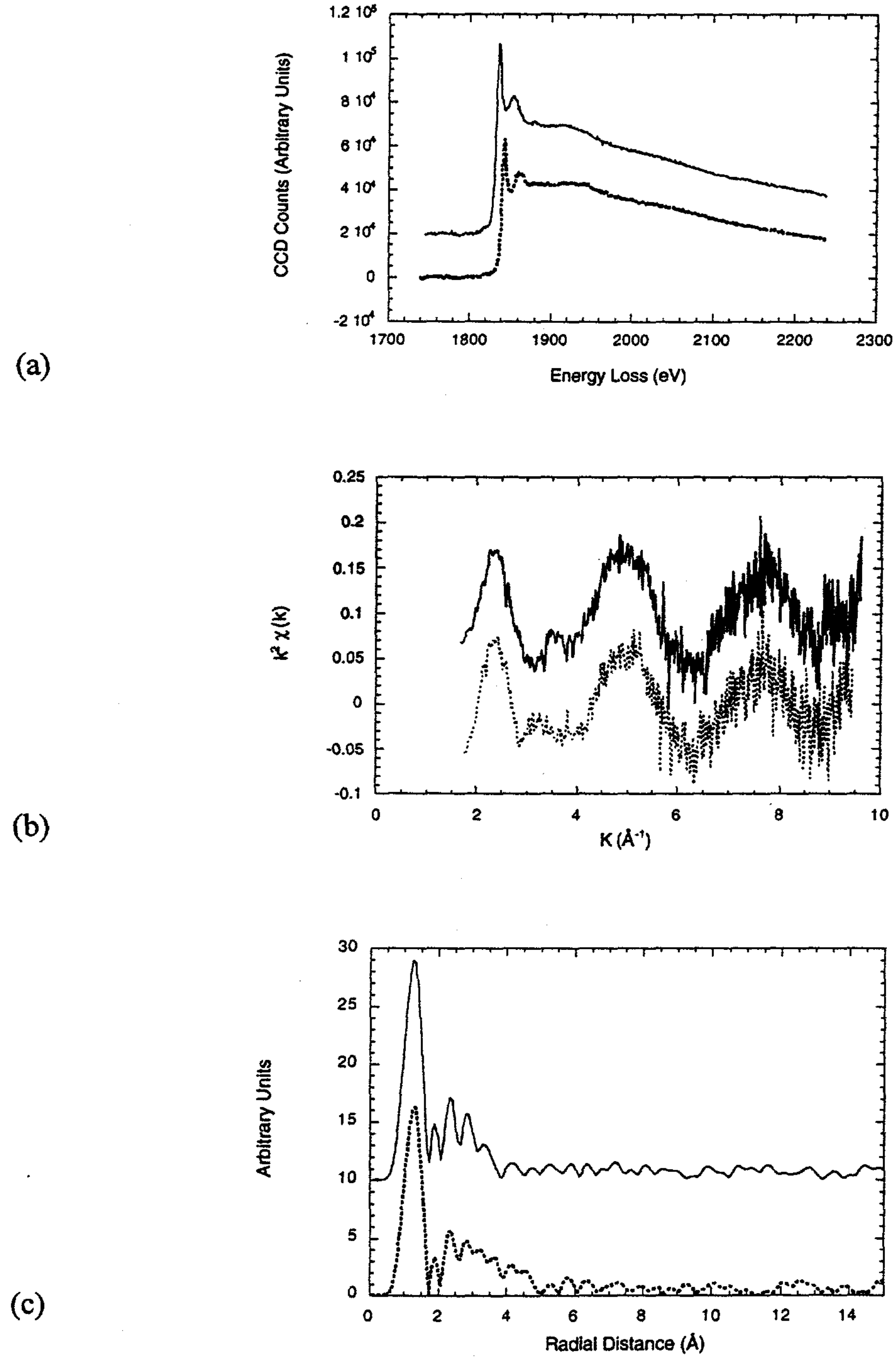


Fig. 2. (a) Si-K ionization edges, (b) EXELFS, and (c) RDF from the Si-K edges in gel layer (upper spectra, solid lines) and in glass (lower spectra, dotted lines).

Si-K edges in the glass and in the layer, respectively. Both of these functions provide information regarding the local order around the Si atoms. Again, the spectra have very similar features; in particular, both first peaks of RDFs, which represent the Si-O bond lengths, are located at nearly identical positions (1.62Å). These results reflect that both the glass and the layer have comparable Si-O structural arrangements, indicating that the gel layer preserves the Si-O network of the precursor glass and has not yet transformed into a clay.

CONCLUSIONS

We have analyzed the interface between palagonite and glass in 700-year-old subaerially altered Hawaiian basalt glasses with high-resolution TEM, EDS, and GIF. Different AEM samples prepared from basalt recovered from the same vicinity displayed two significantly different interfacial microstructures. In the most commonly seen type of interface, the glass and palagonite were physically separated, the glass surface was smooth and unaltered, and the palagonite was crystallized primarily as goethite. The other type of interface showed a gel layer between the glass and the crystalline phases. The gel layer was depleted of Na, Ca, and Mg relative to the glass and had a Si environment similar to that in the glass. To our knowledge, this is the first time that a gel layer has been observed on a naturally reacted basalt glass. This observation provides an important link in the corrosion mechanism of basalt in natural environments and nuclear waste glasses in laboratory tests.

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