INVESTIGATING ALTERATION OF PRE-VIKING HILLFORT GLASSES FROM THE BROBORG HILLFORT SITE, SWEDEN

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Introduction
Radioactive waste, produced as a result of nuclear fission for power generation and weapons production, must be immobilized to limit radionuclide release into the biosphere over periods of many thousands of years. Several countries, including the United States, have chosen to vitrify nuclear waste materials prior to disposal. The solubility of ions in liquid, including if the liquid is super-cooled to a glass phase, is greater than in a corresponding crystalline solid; thus, radioactive ions are incorporated into a broad distribution of available sites in the glass structure, and the product is highly durable [1]. However, a glass phase is not thermodynamically stable and will, in principle, undergo some degree of alteration with time. Low level vitrified wastes will be disposed of in near surface sites, such as the Integrated Disposal Facility at the Hanford Nuclear Reservation, WA. Near-field solution chemistry, water diffusion, ion exchange, precipitation of mineral alteration phases, and microbial colonization could influence long-term glass performance, but not all of these parameters are currently captured in the modeling and performance assessments for low level nuclear waste glass disposal sites. Thus, robust models based on a mechanistic understanding of the processes responsible for glass degradation and radionuclide release in near surface environments are needed. These models will give confidence to performance assessments for nuclear waste disposal sites by predicting the durability of vitrified nuclear wastes over the course of thousands of years.

Alteration rates of nuclear waste glasses have been predominantly determined by short-term (a few days to a few months) laboratory alteration tests. These tests provide information on initial rate(s) of corrosion, occurring at a fast rate but only over a short period of time. Per one model of glass alteration, the first step in alteration (Stage I) is initiated by hydrolysis of the silicate network, followed by rapid dissolution and ion exchange between the glass and its altering medium. The rate of glass dissolution then decreases by several orders of magnitude as the gel-like alteration layer, formed in Stage I, is stabilized (Stage II). This results in a leveling out of the dissolution rate and a pseudo equilibrium between formation and dissolution of the alteration layer. Occasionally, given the correct chemical conditions, glass alteration rates have been observed to increase by orders of magnitude (Stage III), concomitant with the precipitation and growth of crystalline secondary phases (zeolites, magnesium silicates, iron silicates, etc.). Short-term experiments are incompletely informative with regard to predicting how a glass will alter in
the long-term (Stage II and III). Experts in the field [2, 3, 4] maintain that studying analogues which: (i) are representative of long time scales; (ii) have similar chemical characteristics to the waste glass; and (iii) have been altered under comparable conditions to those expected for nuclear waste disposal, can indeed be used to address this issue [5]. For a good analogue, the altering environment over time and the original chemistry of the unaltered glass, must be known sufficiently well [4, 5]. These analogues can be used to validate glass alteration models, currently based on short-term (≤ ≈ 10 yrs) tests with real or simulated nuclear waste glass, by comparing the alteration processes and products observed to those predicted by the models.

Methods

The anthropogenic glass from vitrified hillforts, specifically from the Broborg hillfort, are viable analogues for nuclear waste glass [6, 7]. Broborg is a ~1500 year old hillfort located near Uppsala, Sweden. Broborg hillfort glasses have a wide range of chemistries, including dark (basalt-like) glass and clear (silica-rich) glass [8]. Vitrification of the walls at Broborg has been ascribed to melting of rock rich in amphibole [7, 9]. Information on the excavation of the Broborg glass sample analyzed in this study, along with a description of the sample chemistry, can be found in [8, 10-12]. The sample is of historical significance, and special handling and sampling procedures were implemented so that only small portions of glass were extracted in a manner that was not detrimental to structural integrity of the object. The sample was analyzed using: (i) X-ray computed tomography (XCT) to assess internal microstructure and define key regions of interest for sectioning; (ii) dry cutting with a band saw or circular saw to preserve alteration layers; (iii) subsequent analysis by micro X-ray diffraction (µ-XRD) and micro X-ray fluorescence (µ-XRF) for glass crystal structure and composition; and (iv) focused ion beam-scanning electron microscopy (FIB-SEM), followed by scanning transmission electron microscopy with energy dispersive spectroscopy (STEM-EDS) to analyze alteration layers.

Results and Discussion

The sample selected for investigation is composed of the local granitic gneiss and partly melted amphibolite. µ-XRD of exposed clear and dark glass regions suggest that they are predominantly amorphous, with a very minor crystalline component. From µ-XRF, Na, K, Al and Si represent the major elemental constituents of the clear glass, whereas the dark glass is enriched in Fe and Ca. SEM images show evidence of significant microbial activity on the glass surface. Preliminary investigations suggest that this microbial community is composed of bacteria, vitricolous lichen, fungal hyphae with associated mineral precipitates, and testate amoebae. To investigate alteration of clear and dark glass, in the presence and absence of microbial colonization, FIB cross-sections were analyzed by STEM-EDS. A FIB section was extracted from an area with a range of melting and solidification textures, including relict granitic solids and dendritic crystallization, and the clear glass melt area showed very little alteration. In contrast, a FIB-section taken from a bead-like area of clear glass, with evidence for microbial colonization on the surface, showed semi-circular alteration patterns, depleted in Na and K, on a micron-scale. Research has shown that colonizing microbes can alter the pH, resulting in localized glass dissolution. The formation of semi-circular alteration patterns on a micron scale has been observed as a result of microbial colonization and local dissolution in volcanic glass [13]. The dark glass region, near the clear glass, had areas with and without significant amounts of organic material on the surface. SEM images of the dark glass surface without organic material showed some pitting. The FIB section showed regions depleted and enriched in Fe and Ca, suggesting phase separation, but no semi-circular alteration patterns were evident.
Koestler et al. defined the role of the surrounding environment on glass alteration in terms of three agents; physical, chemical and biological. Under natural conditions, these agents can occur independently or in combination to produce the alteration patterns observed [14]. Physical, chemical and biological factors are also expected to influence nuclear waste glass alteration [15]. For the Broborg glasses, the impact of each factor on glass alteration can be estimated based on knowledge of sample age, variations in climate, water activity and land use. SEM suggests that microorganisms interact with the glass surfaces, and may play a significant role in glass alteration, as they do in chemical weathering of the Earth’s upper crust [16]. The microorganisms that are present provide information on the chemistry of the surrounding soil (water activity, nutrient concentrations, temperature and pH) and on cyclic weather patterns (freeze-thaw, wet-dry, and hot-cold conditions). A detailed study of the climate and environment around the Broborg site over the last ~1500 years is under way to understand this relationship. This will be combined with analysis of fresh glass and soil samples obtained from Broborg, to confirm preliminary findings and to test microbial alteration theories. Experiments are also being conducted to replicate the glassy phases for corrosion studies to validate current alteration test methods and models.

The glasses from Broborg fulfill several important prerequisites for good analogues for nuclear waste glass: a similar chemical compositional space, similar mechanisms of corrosion, and alteration in similar, known environmental conditions.

References