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Alteration of Natural Glass in Radioactive Waste Repository Host Rocks: A Conceptual Review

by

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Abstract

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The storage of high level radioactive wastes in host rocks containing natural glass has potential chemical advantages, especially if the initial waste temperatures are as high as 250°C. However, it is not certain how natural glasses will decompose when exposed to an aqueous phase in a repository environment.

The hydration and devitrification of both rhyolitic and natural basaltic natural glasses are reviewed in the context of hypothetical thermodynamic phase relations, infrared spectroscopic data and laboratory studies of synthetic glasses exposed to steam. The findings are compared with field observations and laboratory studies of hydrating and devitrifying natural glasses. The peculiarities of the dependence of hydration and devitrification behavior on compositional variation is noted.

There is substantial circumstantial evidence to support the belief that rhyolitic glasses differ from basaltic glasses in their thermodynamic stability and their lattice structure, and that this is manifested by a tendency of the former to hydrate rather than devitrify when exposed to water. Further research remains to be done to confirm the differences in glass structure, and to determine both physically and chemically dependent properties of natural glasses as a function of composition.
Introduction

For various scientific and technical reasons, the deep burial of high level radioactive wastes in geologic repositories is now accepted as the most reasonable means for isolating these hazardous materials from the biosphere. Several countries are studying the design, construction and integrity of radioactive waste repositories in order to resolve the uncertainties attending this disposal option, to select sites, and to reassure the public that underground repositories will function properly.

Current U.S. practice is to design for maximum temperatures in the host rock to range from about 160°C in salt to 260°C in basalt, (Raines et al., 1981). These maxima would be attained close to the container-host rock interface and occur between 35 and 60 years after burial of the waste, (Wang et al., 1979). The temperature of the waste would still be 50 to 100°C above the ambient temperature of the host rock, some 1,000 years after burial, and the region affected by elevated temperature would extend up to 500 m from the waste containers. A substantial volume of rock could alter therefore hydrothermally. A repository designed to operate at temperatures to 250°C would be both more compact and potentially cheaper per unit of disposed waste than one designed to operate at lower temperatures. It would also possess the advantage that the higher temperatures would increase the reactivity of the host rock in the near field, and enhance the capacity of the rock to sorb and coprecipitate radionuclides.

Rocks containing either acid or mafic glass possess potential advantages over other rocks as hosts for radioactive waste. Because glasses are much less stable than most minerals, they will react with dissolving radioactive waste under hydrothermal conditions to produce secondary minerals, that would entrap harmful radioelements.
The alteration products of natural silicic glasses are normally zeolites, such as clinoptilolite or heulandite, and smectites, both of which possess the potential to sorb radioelements such as cesium, or strontium. When basaltic glass alters, it releases ferrous iron, which induces a low environmental oxidation state as a result of disproportionation reactions in which ferric ions enter into secondary nontronite, magnetite or hematite. The lowered oxidation state ensures that the actinides, such as uranium, neptunium, plutonium and americium are maintained in the +4 or +3 oxidation states, which are the least soluble. Technicium also is strongly sorbed when reduced to the +4 state. The lower oxidation state also favors the formation of pyrite, which can reduce selenium and precipitate it as a selenide.

At higher temperatures, basalt alteration is also favorable for the formation of secondary sphene, which will accept tin-126 (and actinides?), and for the formation of epidote, which is isomorphous with allanite, a well known potential host for actinides (U.S. D.O.E., 1980).

In the Western United States use could be made of glassy rocks at two potential repository sites, both of which are currently under active consideration. One is at the Hanford site in Richland, in the Pasco Basin of Washington, where the underlying rocks are composed of massive flood basalt flows. These flood basalts still contain a vitreous mesostasis where the glass varies from a few weight percent to as much as 20 weight percent. The cumulative thickness of the flows is nearly 5,000 feet and they are overlain by up to 700 ft. of surficial sediments. The other repository site is at the Nevada Test Site in Nevada. Here, widespread acid ash flows and welded tuffs have accumulated as a result of several immense caldera eruptions during the past 26 million years. Although most of the welded tuffs have devitrified, probably immediately following their deposition, many horizons are present where vitroclastic tuffs and vitrophyres still
remain substantially unaltered.

The basalts of the Pasco Basin are for the most part below the water table and are therefore saturated, whereas in Nevada, because of the nature of the terrain, the low rainfall, and the high evapotranspiration rates, the water table is often many hundreds of feet below the surface. The present candidate repository location at the Nevada Test Site therefore happens to be in the unsaturated zone above the water table.

In this paper I would like to discuss some aspects arising from the selection of rocks containing natural glass as hosts for a nuclear waste repository, particularly if the initial repository temperatures are as high as 250°C. In particular, I would like to address some of the contrasting alteration mechanisms between acid rhyolitic glasses and glasses of basaltic or mafic composition. There is substantial circumstantial evidence to suggest that their mode of alteration is very different and that this must be accounted for in the prediction of repository behavior in either basalt or acid tuff.

To investigate this issue requires a knowledge of glass alteration from experiment and theory, supplemented by field observations of natural glass altering under conditions similar to those expected in a repository. This approach must be taken in order to extrapolate observations of short term laboratory experiments, to natural processes taking place over periods of thousands of years; i.e. time spans comparable with that necessary to isolate radioactive waste from the biosphere.

Thermodynamics of Glasses in Relation to
Hydration and Devitrification

Silicate glass is primarily a polymerized network of covalently bonded \([\text{SiO}_4]^{4-}\) tetrahedra, linked by their oxygen apices. Other cations can substitute
for Si$^{4+}$ such as Al$^{3+}$ and B$^{3+}$, and sometimes Fe$^{3+}$. The charge deficiency is made up by interstitial cations. The continuity of the network is disrupted by the presence of so called "network modifiers" such as the alkali metals, the alkali earths ions, and some transition group metal ions such as Fe$^{2+}$. Some cations such as Zn$^{2+}$, or Pb$^{2+}$ may occupy either the tetrahedral network or the interstitial sites.

Silicate glasses can be synthesized over a very large range of chemical compositions. However, the range of natural glass is restricted to SiO$_2$ contents ranging from 40 to 80 wt%, and with varying amounts of other network builders, principally Al$_2$O$_3$, and network modifiers such as Na$_2$O, K$_2$O, CaO, MgO, and FeO. Together, these constituents usually make up over 95 wt% of the total composition.

Glasses are conceived to be supercooled liquids in which rotational and translational degrees of freedom among the constituent molecules have been quenched, leaving only vibrational modes. This picture is an over simplification as noted in several studies of the thermodynamic properties of glass, (e.g. Goldstein, 1975; Richet and Bottinga, 1983) but it suffices for this discussion.

The transition from supercooled liquid to glass is characterized by a substantial change in heat capacity, which closely approaches the change between the liquid and the solid crystalline equivalent. It may be viewed as a second order thermodynamic transition. Even though interpretation of the glass transition as a thermodynamically reversible phenomenon is controversial, it will be here so treated as a matter of interpretive convenience. The measured glass transition temperature may vary by as much as 100°C for a given silicate glass composition, due in part to the prior cooling history of the glass. A reversible transition is not observable because of the sluggishness of the reaction at the transition temperature, (Gibbs and DiMarzio, 1958). Hence true metastable thermodynamic
equilibrium is never attained, and measured thermodynamic and transport properties of a given glass are often dependent on its previous history. Yet an extensive literature reveals that glasses have relatively consistent physical properties, suggesting that a qualitative if not quantitative thermodynamic treatment is possible.

When exposed to water, glasses have a tendency to alter by a variety of temperature, composition, and system dependent mechanisms. Wu (1980) categorised glasses into four types depending on their behavior when exposed to steam at elevated temperature, viz, those that: (a), hydrate; (b), do not hydrate; (c), dissolve in the aqueous phase, and (d), devitrify or crystallize. Because all glasses could eventually crystallize to a more stable phase assemblage, the last category is a manifestation of more rapid crystallization kinetics.

To place these mechanisms into context and relate them to natural glass alteration, I will discuss some of the hypothetical phase relations that might be involved. Figures 1 - 4 are temperature composition diagrams portraying an arbitrary pseudo-binary system involving a stoichiometric anhydrous silicate as one end member, and water as the other end member. The temperature range extends from about \(-50^\circ\) C to beyond the melting point of the stoichiometric crystalline silicate. The pressure is arbitrarily set between 1 bar and 400 bars, a range expected to include most waste repository conditions. The typical waste repository environment will encompass a temperature domain around the boiling point of water, the upper limit being determined by the design specifications of the repository.

Features common to all diagrams are a pseudo-binary immiscibility loop between vapor (steam) and liquid (silicate melt) phases, culminating in a critical phase, a solidus curve with respect to the stable essentially stoichiometric solid and the liquid (i.e. melt/water) phase, and a subsolidus pseudo-binary solvus
leading to the formation of coexisting supercooled water rich and water poor melts (or glasses). Evidence for the existence of the binary solvus is speculative and is based on the assumption that glasses have a finite and definable saturation limit with respect to hydration, and a finite equilibration solubility. Superimposed on the supercooled liquid field is the glass transition. Apart from the pseudo-binary miscibility loop, all stable phase transitions are drawn with light lines, whereas metastable transitions are drawn with heavy lines.

In Figure 1, it is assumed that the glass will hydrate to a significant extent. Hydrated glass may be produced either by quenching of a hydrous melt, along path, a'-b, or by hydration in contact with either a vaporous or a liquid aqueous phase along path a-b. Rhyolitic or rhyodacitic glasses most probably follow path a-b during hydration in closed systems, as will be discussed further on.

Figure 2 represents Wu's 2nd case in which an anhydrous glass exposed to a steam atmosphere will hydrate to an inconsequential extent before saturation, as indicated by path a-b. However, a "superhydrated" unstable glass could in principle be produced in the system by quenching a hydrated melt along path c-d. This case may be representative of very high silica glasses such as tektites or vitreous silica.

Silicate glasses containing high concentrations of alkali metals are represented in Figures 3 and 4. In these cases, the glass will actually liquify or dissolve in the presence of an aqueous phase. Figure 3 represents the situation of liquifaction in the presence of steam, as indicated along path a-d. The glass will first hydrate along a-b, then transition to a supercooled liquid, along b-c, finally becoming a stable liquid at c and eventually saturating at d with respect to the aqueous (steam) phase. Figure 4 shows the corresponding case in which the glass is dissolved by an aqueous liquid, along path a-b-c. These last two cases have not been observed to occur naturally, although they represent variations of the
third case listed by Wu.

There remains the question as to how Wu's fourth category can be fitted into this scheme. Furthermore, field and laboratory observations to be discussed below, suggest that basaltic glass would also fall into the same category. Here we must speculate that, with falling temperature, a hypothetical stoichiometric silicate mimicking a basaltic melt in composition would, on cooling, recrystallize to form a stable hydrated phase in the pseudo-binary cross section. We must further assume that metastable equilibrium hydration in the glass would be transient, because hydration would so lower the activation energy of devitrification, that devitrification would immediately follow. As it turns out, this is true to a certain extent, but other thermodynamic and structural factors also play a role as will be discussed further on.

Correlation of Extent of Hydration with Glass Composition

In the discussion which follows, a distinction is attempted between saturation hydration of a glass, and the rate of hydration. Unfortunately, in some glasses, hydration induces rapid devitrification, so the saturation hydration cannot be determined. In others, the rate of hydration may be so slow that saturation hydration cannot be achieved, either in the laboratory, or through prolonged exposure in the field. These differing properties often lead to ambiguities in interpretation, sometimes compounded by lack of a critical distinction being made in the literature.

Scholtze (1959a,b,c, and 1966) has measured changes in the infrared absorption spectra due to silanol groups on of a large range of weakly hydrated silica glasses, to study the effect of substituting various metal oxides for silica. Scholtze found that metal oxide substitution could be correlated with the fraction, r, of non hydrogen-bonded silanol groups, which is in turn, correlated
inversely with the polarisability of the oxygen ions in the lattice and the basicity of the glass.

As will be noted from Figure 5 (redrawn from Scholze, 1959b), network modifiers such as the alkali metals, potassium and sodium, have a powerful effect in decreasing $r$, whereas network builders such as aluminum have the opposite effect. Wu (1980) correlated $r$ with the four response modes of glass when exposed to steam. Those glasses with $r$ approaching unity did not hydrate, or at least were not observed to hydrate in the laboratory; those with intermediate $r$ values i.e. $\approx 0.3$ to $0.7$ hydrated, but otherwise showed no other alteration, whereas those with low $r$ factors, either dissolved completely as a liquid phase or devitrified, i.e. crystallised. Those with high alkali metal contents dissolved, whereas those with alkali earths contents devitrified.

Unfortunately, variation of $r$ is not linear with composition, so it is not possible to predict the hydration behavior of the natural glasses from Scholtze's data. However, it is reasonable to assume that rhyolitic glass, with its higher silica and alkali metal content will have a higher $r$ factor than basaltic glass with its lower silica content and significant enrichment in CaO and MgO. The former would therefore tend to hydrate, catalysed by the alkali metal cations, as suggested by Wu (1980), whereas the latter would tend to devitrify. This contrasting behavior is consistent with field and laboratory observations.

Field evidence also shows that rhyolitic and basaltic glasses behave quite differently regarding hydration and devitrification. Natural rhyodacitic and rhyolitic glasses containing between $65$ and $80$ wt\% silica, will hydrate under earth surface conditions, apparently without destruction of the SiO$_4$/AlO$_4$ tetrahedral framework, and with only partial or even no loss of interstitial alkali cations, (Scheidegger and Kulm, 1975; Scheidegger et al., 1978; Jezek and Noble, 1979; Federman 1984; Forsman, 1984). According to Federman, (1984), rhyodacitic and
rhyolitic glasses in abyssal tephra deposits from the Eastern Mediterranean, initially containing 0.3 to 1.0 wt% H₂O+, hydrate to between 4 and 5 wt% H₂O after 10⁵ to 10⁷ years. Scheidegger et al. (1978) and Ninkovich (1979) have made similar observations in their studies of ash layers in the Northwestern Pacific and Indian Oceans respectively. Such hydrated glasses may persist in nature for very long periods. Forsman, (1984) describes several ash beds from North Dakota containing "unaltered glass" ranging in age from Upper Cretaceous to Paleocene. The ash beds have been saturated with water during much of their history and are believed to be "superhydrated", as gas bubbles in the glass shards are now filled with water. It is probable that the glass was preserved partly because the aqueous phase also saturated metastably with respect to the glass structure, and that devitrification through dissolution and precipitation of secondary minerals was inhibited by the relatively low ambient temperatures.

Basaltic glasses containing 45 to 55 wt% SiO₂ in abyssal tephra also appear to persist in an essentially undevitrified state, at least up to 3.8 million years, (Scheidegger, 1973). In contrast to more silica rich glasses, they do not appear to hydrate, or perhaps hydrate at a much slower rate. Scheidegger (1973), found that basaltic glasses ranging in SiO₂ content from 47 to 51 wt% from the Cobb Seamount on the Juan de Fuca Ridge in the Pacific Ocean contained between 0.10 to 0.38 wt% H₂O+, essentially similar to glass from fresh basalt pillows, which, according to Moore, (1970), contain between 0.06 to 0.42% H₂O+. However, naturally occurring basaltic glasses containing up to 1.84% H₂O have been analysed, (Delaney and Karsten, 1981).

An even older basaltic glass of olivine tholeiite composition has been described by Muffler et al. (1969) in a late Triassic (180 my) "aquagene tuff" from southeastern Alaska. Although the tuff fragments display 30μm alteration rims, the bulk of the glass shows no apparent alteration. The H₂O+ content of
the "unaltered" glass is 1.58 wt%, somewhat higher than that reported for the Cobb Seamount tephra, although the SiO$_2$ content is similar, i.e. 48 wt%.

While it is evident from field observations that the saturation hydration level of rhyolitic glasses is of the order of 5 wt% H$_2$O+ at 0 to 25°C, the saturation hydration of basaltic glasses within the same temperature range is unknown. Stolper (1982) claims that water solubility in magmas is insensitive to composition. It is not clear whether the saturation concentration of water in glass is also insensitive to composition, and that basaltic glasses, given sufficient time would hydrate to the same water concentration as obsidians. In synthetic systems, which cover a wider range of compositions, it is known that vitreous silica hydrates less than alkali silicate glasses under comparable conditions, (Wu, 1980; Della Mea et al., 1984). This suggests that the saturation hydration in natural glasses could well be sensitive to composition. However, it is presently not possible to estimate whether a basaltic glass can hydrate to a significant extent.

**Kinetics of Hydration and Devitrification**

The rate of natural glass hydration has been determined both experimentally and from field observations. Although the hydration mechanism for basaltic glasses has not been unequivocally determined, as will be discussed further below, hydration in obsidians and perlites appear to be a diffusion controlled process following a parabolic rate law, (Friedman and Smith, 1960; Marshall, 1961; Friedman et al., 1966; Lofgren, 1968; Friedman and Long, 1976; Michels et al., 1983). This process is sufficiently uniform and slow at earth surface temperatures, that it has found application as a dating method for obsidian artifacts, (Friedman and Smith, 1960; Meighan et al., 1968; Michels et al. 1983), and for recent, i.e. up to 200,000 year old rhyolitic or obsidian flows, (Friedman, 1968; Pierce et al., 1976).
Rhyolitic glasses undergo significant density and optical changes when they hydrate (Lofgren, 1968). This leads to localized stress concentrations at the interface between the hydrated and unhydrated glass, which is sufficient in some cases to cause fracturing, or at least show optical strain (Lofgren, 1968). Evidence that hydration induces fracturing has also been observed by Morgenstein and Riley (1975) in basaltic glasses. The fracturing permits access of water to the glass interior and facilitates transport of chemical components in and out of the glass, thus accelerating both hydration and devitrification.

According to Friedman and Long (1976), increasing SiO₂ and H₂O content in obsidian increases the diffusion rate of water, whereas increasing CaO, and MgO, decreases the rate of diffusion. Al₂O₃, FeO, Na₂O, and K₂O contents appear to have little effect on the rate, at least over the narrow range of compositions studied by the investigators. The effect of minor changes in CaO and MgO content is substantial, with the hydration rate declining from 5 \( \mu \text{m}^2/\text{10}^3 \text{yr} \) to 0.2 \( \mu \text{m}^2/\text{10}^3 \text{yr} \) at 10 °C over a narrow SiO₂ compositional range between 72.2 and 76.9 wt% SiO₂. Extrapolation of hydration rates to basaltic glass composition is unfortunately not possible because of the scatter in Friedman and Long’s data, the empirical correlation used, and the length of the extrapolation required. Their data strongly suggest, however, that basaltic glass hydration rates would be at least two and possibly three orders of magnitude slower than for a typical obsidian. This is consistent with the field observations of Scheidegger, (1973) that basaltic glasses several million years old have not hydrated. It might also be construed that the Triassic basaltic glass described by Muffler et al. (1969) has taken 180 million years to hydrate to no more than 1.6 wt% H₂O+.

In synthetic silica-metal oxide glass systems, the evidence of Yoko et al., (1983) and Moriya and Nogami, (1980) indicates that substitution of up to 10 wt% Al₂O₃, MgO or CaO for SiO₂ in a 20 wt% NaO₂ SiO₂ glass decreases the
hydration rate by as much as 500 times. However, the hydration process does not uniformly follow parabolic kinetics, suggesting that a simple diffusive hydration of the glass structure is no longer the principal alteration mechanism.

Another interesting observation, which may be germane, is provided by LaMarche et al. (1984), who attempted to hydrate a silica rich (80 wt% SiO₂) tektite glass containing 2.48 wt% MgO and 1.91 wt% CaO at 90°C. No surface hydration layer could be produced, consistent with field observations of weathered tektites. This could be interpreted either as evidence that the kinetics of hydration is slowed by the presence of MgO and CaO, or that the very high silica content prevents significant hydration, i.e. the tektite glass falls into non hydratable glass category of Wu (1980a).

In rhyolitic glasses, hydration facilitates the diffusion of some metal cations in and out of the glass. White and Yee (1986) find that the diffusion coefficients of rubidium, cesium, and strontium are markedly greater when exposed to the aqueous phase below 100°C than would be expected based on extrapolation of high temperature diffusion coefficients to the same temperature region. Field evidence, e.g. Jezek and Noble (1978) also report on the exchange of potassium for sodium in perlites. Thus the chemical composition of an exposed natural rhyolitic glass can change with time and therefore affect the mineral composition on devitrification.

While the evidence that basaltic glass will hydrate is equivocal at best, in contrast to rhyolitic glass, there is plenty of evidence that basaltic glass will devitrify to form secondary smectites and zeolites. In nature, basaltic glass originates in three ways;

1. Through the quenching of basaltic lavas in submarine environment. In this situation basaltic pillows are encased in a glassy rind known as sideromelane;
2. As air fall tephra.

3. As hyaloclastites. Hyaloclastites are most notably formed in Iceland, where the rapid injection of basaltic lava into ice or water leads to quenching and fragmentation.

The process by which basaltic glass alters to secondary minerals is known as palagonitization. It is most frequently studied under circumstances in which the glass is exposed to seawater under essentially "open system" conditions. Palagonitization is not a simple process in which water diffuses into the glass lattice, but instead may involve initial hydration of a thin rind less than 50 \( \mu \text{m} \), thick. The thin rind induces high stresses in the adjacent unaltered glass, and leads to the formation of array of microcracks penetrating the glass ahead of the "hydration" zone, (Morgenstein and Riley, 1975). Rapid devitrification of the "hydrated" rind then produces a palagonite layer, which may be poorly coherent, spall and leave more fresh glass exposed for hydration.

Repeated cycles lead to the formation of a cumulative alteration layer that in some cases possesses characteristics reminiscent of Liesegang banding. It is quite likely that a Liesegang alteration mechanism occurs in which counter diffusion of two or more components is involved (Fisher and Lasaga, 1981). Certainly the mineralogical and chemical evidence of the palagonitization of sideromelane in seawater indicates extensive exchange of elements between the glass and seawater (Staudigal and Hart, 1983).

Basalt glass alteration implies that the process of glass hydration will make devitrification possible i.e. the activation energy barrier inhibiting devitrification will be removed, or at least decreased significantly. Unfortunately, the initial hydration process, has not been confirmed. It is not clear whether devitrification proceeds simultaneously with hydration or whether hydration precedes devitrification as is the case in rhyolitic glasses, or indeed whether hydration
occurs at all as suggested by the recent work of Crovisier et al. (1986).

Average alteration rates in basaltic glasses are difficult to establish, but several studies, including that by Morgenstein and Riley (1975) on basaltic glass artifacts from Hawaii, in which alteration rates are correlated with C-14 dating, that by Burnett and Morgenstein (1976) on submarine palagonites dated by means of the uranium decay series, and those correlating the age of exposure with the accumulation of manganese oxide layers (Bender et al., 1966, Moore, 1966; Hekinian and Hoffert, 1975, and Burnett and Morgenstein, 1976) indicate that the net rate of alteration is linear and not parabolic. The palagonite layer, does not therefore act as a rate-controlling diffusive barrier.

Experimental studies on basaltic glasses e.g. by Furnes (1975) and Crovisier et al. (1983) do not contradict available field evidence regarding the alteration mechanism, whereas the most recent experimental findings by Crovisier et al. (1986) supports the view that a linear alteration process is involved, at least at earth surface temperatures, in which there is no evidence of the formation of an initial hydration layer.

Rhyolitic glasses devitrify through nucleation, spinodal decomposition or through dissolution in and precipitation from the aqueous phase. The relative importance of the last process is strongly dependent on the environmental conditions. Field evidence in altering acid vitroclastic tuffs and basalts clearly shows, through the presence of secondary clays and zeolites in pores, fractures and vesicles, that is important in the 25–400 °C range, and probably dominates alternative devitrification mechanisms in many situations. An extensive literature exists describing the surface dissolution kinetics of glasses, but its review is beyond the scope of this paper.

High temperature nucleation above, or around the glass transition temperature leads to the formation of a characteristic spheroidal texture in which
cristobalite or quartz in association with feldspar forms radial aggregates. In anhydrous glasses, this process is slowed so substantially below 600 °C that it cannot be considered of relevance to a waste repository environment. However, initial hydration of the glass permits devitrification to proceed at a greatly accelerated rate. Lofgren (1968) notes that hydrated glasses are characterized by the formation of "globulites". These minute spherical bodies have not been characterized so far, so it is impossible to assess whether they represent the initial stages of nucleation and devitrification in the hydrated glass. Nothing has been reported in the literature regarding the spinodal decomposition of hydrated glasses.

According to Friedman and Long (1984), hydration of rhyolitic glass will substantially decrease the activation energy of devitrification, thereby permitting measurable devitrification to proceed at much lower temperatures. These authors calculate that a hydrated rhyolitic glass will devitrify at 200 °C at about the same rate that an anhydrous glass will at 600 °C, (c.f. also Marshall, 1961). The relative rates of devitrification of natural glass in the host rock of a waste repository may therefore be strongly dependent on its hydration rate and saturation level. A rhyolitic glass will hydrate more rapidly than it will devitrify, whereas one could speculate that basaltic glass will devitrify as fast as it hydrates, so that the hydration rate becomes the rate limiting step in devitrification. Lofgren (1968) has tentatively established that rhyolitic glasses devitrify about four orders of magnitude slower than the hydration process. In contrast, nothing is known quantitatively about the relationship of hydration to devitrification in basaltic glass.
Evidence for Structural Differences between Rhyolitic and Basaltic Glasses

Field and laboratory studies, show that fundamental differences exist between basaltic and rhyolitic glasses in their manner of alteration in the presence of an aqueous phase. What this is due to cannot be conclusively resolved at this time, but there is both thermodynamic and spectroscopic evidence indicating that the differences may be attributed to a structural dissimilarity between the two glasses.

Navrotsky and her coworkers (e.g. McMillan et al., 1982; Navrotsky et al., 1982; Roy and Navrotsky, 1984; Navrotsky et al., 1985 a,b) have investigated the heats of solution in molten lead borate of glasses in the system SiO₂-M₁/₅Al₂O₃ where M = Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Pb. They find that the glass stability tends to increase with substitution of M₁/₅Al₂O₃ for SiO₂, apparently reaching a maximum when X₉5Al₂O₃ = 0.5, i.e. the heat of solution, ΔHₖ₉sol, reaches a maximum value. They also found that, for a given value of X₉5Al₂O₃, ΔHₖ₉sol decreases progressively in the sequence Cs ~ Rb ~ K, Na, Li, Ba, Pb ~ Sr, Ca, Mg. These observations may be interpreted to indicate that the alkali metals interact very weakly with the alumino-silicate framework structure whereas the alkali earths, particularly Ca and Mg interact much more strongly and tend to destabilize the structure. Navrotsky et al. (1982, 1985a) have derived the enthalpy of mixing binary composition plots from the heat of solution data. These show that compensated SiO₂-M₁/₅Al₂O₃ melt joins show a much smaller tendency towards liquid immiscibility than do the corresponding SiO₂-M₁/₅O₉/₂ systems. However, this tendency increases progressively in the same sequence Cs, .... Ca, Mg noted above, with the potential for separation into respectively a very silica rich phase and a silica poor phase.
The significance of these findings in relation to rhyolitic and basaltic glasses is evident and consistent with independent lines of evidence. Clearly, the rhyolitic glass, whose aluminosilicate structure is charge compensated with the alkali metals, will be more stable and less likely to break down than a basaltic glass containing substantial amounts of alkali earths. The weaker structure of the latter would also have a tendency to react more rapidly and devitrify, thereby not giving it the opportunity to hydrate as with the former. The tendency towards immiscibility in the charge compensated alkali earth aluminosilicate melt systems also suggests that significant structural differences may exist between the two glasses, for which there appears to be independent supporting evidence.

X-ray scattering studies of albitic (NaAlSi₃O₈) and anorthitic (CaAl₂Si₂O₈) glasses by Taylor and Brown (1978a,b) and Taylor et al. (1980) show substantially different radial distribution functions for the two glasses. The investigators conclude that albite glass possesses a structure somewhat similar to a disordered cristobalite, being composed of linking six-membered tetrahedral rings. This structure is quite open and could allow the diffusive penetration of water or permit ion exchange of potassium for sodium. In contrast, anorthitic glass is perceived to contain 4-membered tetrahedral rings similar to the feldspar structure. The smaller ring size could inhibit diffusion of water and/or cations through the lattice. It is possible that the higher concentration of magnesium, calcium, and ferrous iron in basaltic glass as compared to rhyolitic glass, coupled with the lower silica content, could lead to structural differences analogous to those believed to occur between albite and anorthite glasses. Detailed studies to verify such structural differences remain to be conducted on a broader range of glass compositions.

Further circumstantial evidence that significant structural differences may exist in natural glasses of different chemical compositions is the existence of an
immiscibility phenomenon in the corresponding liquid state (Philpotts, 1976), and
the evidence of spinodal decomposition in glasses. In the former case, Philpotts
and his colleagues have made a thorough study of the formation of immiscible
melts in basalts (Philpotts, 1977, 1978; Philpotts and Doyle, 1982). Although
there is some question whether melt immiscibility occurs above or below the
solidus, i.e. whether or not the melt was supercooled at the time, e.g. see Biggar,
(1979); Freestone (1979), Philpotts and Doyle (1980), the fact remains that
unmixing occurs, and that there is evidence of a discontinuity in the melt struc­
ture, which may also be reflected in a corresponding structural discontinuity
between basaltic and rhyolitic glasses.

Evidence for spinodal decomposition in natural glasses in the composition
range of interest is much more tenuous. However, Manankov (1979) has exam­
ined glasses of basic composition after annealing then at 500-750°C, and found
that they decomposed spinodally into calcium rich and calcium poor phases. He
associated this phenomenon with observations in igneous rocks where coherent
breakdown of natural pyroxenes leads to phases respectively enriched and im­po­
verished in calcium, e.g. albite (= plagioclase?) and pigeonite respectively. Simi­
larly, Barron (1981), in modelling spinodal decomposition in synthetic silicate sys­
tems, concludes that a subsolidus diopside-quartz melt immiscibility occurs
100-150°C below the diopside liquidus in both diopside-nepheline-quartz and
diopside-leucite-quartz systems. Again, we may note the potential immiscible
separation of Ca(-Mg) rich and Ca(-Mg) poor silicate liquids.

Implication of Glass Composition and Structure on the Radioactive
Waste Burial in Rocks Containing Igneous Glass

Hydrothermal alteration in a waste repository under present design concepts
considered by the United States Department of Energy will range from ambient
temperature to as high as 250 °C. Most field observations, and experimental studies of natural glass alteration are at near earth surface temperatures. No studies have been made on basaltic glass hydrothermal alteration at significantly elevated temperatures. In fact, almost nothing is known of the relative kinetics of hydration and devitrification with increasing temperature in such glasses. We must speculate that increasing temperature will accelerate these processes in basaltic glasses.

The composition of the glass mesostasis in basaltic rocks can be quite variable, depending on the history of the magma, and its mode of cooling. In large flood basalt flows, cooling is slow, and the residual magmatic liquid can become highly enriched in silica. Although the silica content of the glass mesostasis may be as low as 65% wt% SiO$_2$, some basalt flows in Iceland contain mesostasis glass with SiO$_2$ concentrations of as high as 80 wt% (Kacandes et al., 1986). This is precisely the range of silica concentrations over which melt miscibility may occur (Philpotts and Doyle, 1982). Thus the mode of hydrothermal alteration of glass in basaltic flows may vary depending on its composition:

We may summarize the available evidence for glass alteration mechanisms in a repository environment in schematic diagrams as illustrated in Figures 6 and 7 for rhyolitic and basaltic glasses respectively. These diagrams are subject to modification as various issues and uncertainties are resolved.

**Conclusions and Recommendations.**

From the foregoing discussions, we can draw the following conclusions.

1. Experimental and infrared spectroscopic evidence shows that the extent to which silicate glasses hydrate appears to be dependent on their composition.

2. Laboratory evidence on synthetic silicate glasses suggests that those rich in MgO and CaO are likely to devitrify rather than hydrate.
3. Rhyolitic and rhyodacitic glasses can hydrate without apparent devitrification or breakdown of the glass structure.

4. Experimental evidence indicates that the hydration of rhyolitic glasses follows a parabolic role law, i.e. a diffusion controlled process is involved.

5. Rhyolitic and rhyodacitic glasses, when exposed to the aqueous phase under closed system conditions, at earth surface temperatures will hydrate to 5-6 wt% $H_2O$. In contrast, glasses of basaltic composition will either hydrate exceedingly slowly, or devitrify immediately upon hydration,

6. Circumstantial evidence suggests that increasing concentrations of $MgO$ and $CaO$ in alumino-silicate glass will substantially decrease the rate of hydration.

7. Basaltic glass, under open system aqueous conditions, will devitrify to form a weakly coherent rind of secondary clay minerals. The alteration front advances according to an effective zero order rate law, although a diffusion controlled process may be implicated in part due to the apparent formation or a Liesegang band texture. Evidence for glass hydration before devitrification is equivocal.

8. Hydration of a rhyolitic glass will greatly accelerate devitrification.

9. The reason for the different alteration mechanisms between rhyolitic and basaltic glasses may be due to differences in the structure of the glass as well as their polarisability.

10. Thermodynamic evidence suggests that the presence of alkali metal ions, eg $Na^+$ and $K^+$ in the interstices of charge compensated aluminosilicate glass structures tends to stabilize the tetrahedral framework, whereas the converse applies to alkali earth ions, e.g. $Mg^{++}$ and $Ca^{++}$. This suggests that alkali metal aluminosilicates would be more likely to hydrate than alkali earth
aluminosilicates. Also, the latter would be more prone to devitrify than the former.

11. Thermodynamic evidence also indicates that alkali earth aluminosilicate melts have a tendency to display immiscibility phenomena in the silica rich region of binary SiO₂ - M₁ₓAl₂O₃ systems.

12. X-ray diffraction studies show that albite glass has a different structure from anorthite glass. This structural distinction may extend to similar differences between rhyolitic and basaltic glass structures.

13. Both petrographic observations and experimental phase equilibrium studies support the existence of an immiscible two liquid region at or below the solidus in differentiating basaltic magmas. This suggests the existence of structural differences between magmas of different silicic compositions, which might reasonably be expected to extend to structures of the corresponding glasses.

To provide convincing evidence of some of the tentative conclusions reached above will require further experiments.

An interesting approach would be to synthesize a range of glass compositions between rhyolite and basalt in composition, and then proceed with a complete characterization of their physical and transport properties, e.g. specific volume, heat capacity, compressibility, expansivity, electrical conductivity, refractive index. X-ray radial distribution functions and infrared spectra might also be measured with advantage. The goal for such characterization studies would be to establish whether a discontinuity exists in the properties of the glasses, and which reflects a structural difference, and at what composition this structural change occurs. Controlled experimental studies should then be made on selected glasses over a range of temperatures between 25 and 250 °C to measure the rates of hydration, the saturation hydration, and the surface reaction rates with respect
to the aqueous phase.

With the results of such experiments in hand, it should then be possible to conduct modelling studies of the rate of alteration of the host rock glass in the immediate vicinity of the waste repository.

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Figure Captions

Figure 1. Hypothetical pseudobinary temperature-composition diagram to illustrate the metastable field of hydrated silicate glass in equilibrium with the aqueous phase.

Figure 2. Hypothetical pseudobinary temperature-composition diagram to illustrate the metastable field of a non hydrated glass in equilibrium with the aqueous phase.

Figure 3. Hypothetical pseudo-binary temperature-composition diagram to illustrate the hydration and liquifaction of an alkali silicate glass by steam.

Figure 4. Hypothetical pseudo-binary temperature-composition diagram to illustrate the hydration and dissolution of an alkali silicate glass by a liquid aqueous phase.

Figure 5. Correlation of non hydrogen-banded silanol groups in a 80 mole % SiO₂, 20 mole % Na₂O glass as a fraction of the mole percentage substitution of metal oxides for silica (after Scholze, 1959b).

Figure 6. Schematic diagram to show the decomposition paths of rhyolitic glass when exposed to the aqueous phase.

Figure 7. Schematic diagram to show the decomposition paths of basaltic glass when exposed to the aqueous phase.
Composition

Silicate

H₂O

Temperature

M.P.

L₁

L₁ - V

V

C - L₁

C

C - V

L₁ - L₂

G₁ - G₂

C - L₂

B.P.

XCG 871-6726
Supercooled Liquid

Temperature

Composition

Silicate

H$_2$O

C

L

M.P.

C - L

G$_1$

G$_2$

G$_1$ - G$_2$

T$_G$

Hydrated Glass

L - V

B.P.

XCG 871-6728
BASALTIC GLASS (Sideromelane)

Fracturing due to palagonitization (or hydration?)

MICROFRACTURED HYDRATED GLASS (?) wt% of H₂O)

+ H₂O (diffusive hydration)

MICROFRACTURED GLASS

+ H₂O, Mg, Fe
- Na, Ca, Al, Si

Diffusion, devitrification

Liesegang banding

PALAGONITE (10-20 wt% of H₂O)

Diffusion, devitrification

SECONDARY MINERALS
Zeolites, smectites

Dissolution, precipitation

MOST STABLE MINERAL ASSEMBLAGE
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