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PHYSICS AND CHEMISTRY OF THE TRANSITION OF GLASS TO AUTHIGENIC MINERALS

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The Nevada Agency for Nuclear Projects/Nuclear Waste Project Office was created by the Nevada Legislature to oversee federal high-level nuclear waste activities in the state. Since 1985, it has dealt largely with the U.S. Department of Energy's siting of a high-level nuclear waste repository at Yucca Mountain in southern Nevada. As part of its oversight role, NWPO has contracted for studies of various technical questions at Yucca Mountain.

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PHYSICS AND CHEMISTRY OF THE TRANSITION OF GLASS TO AUTHIGENIC MINERALS

by Maurice E. Morgenstein

FOREWORD

The purpose of this paper is to provide a basic review of the topic of volcanic-glass hydration and the diagenetic formation of authigenic minerals from the hydrated-glass products. The Yucca Mountain Draft Environmental Assessment (DOE/RW-0012) of December 1984 indicates that:

1. Most of the available glass in the proximity of the repository horizon has been already hydrated and authigenic minerals which could form have already done so.
2. Zeolites could form from as yet unreacted glass during transport of water exiting from the repository.
3. The zeolites and other authigenic minerals provide sorptive barriers to radionuclide migration.

Very little informative information has been supplied by the support literature to the Draft Environmental Assessment. Consequently, conclusions 1 and 2 appear somewhat contradictory and unsupported. This document surveys the available literature and concludes that the topic appears more complex than as it is treated in the DEA (DOE/RW-0012).

It is concluded that an insufficient quantity of raw data exists. This paucity of information does not allow the determination of which authigenic minerals (if any) may form from the alteration of volcanic glass in Yucca Mountain; and consequently, radionuclide retardation leading from this reaction process is undeterminable.

INTRODUCTION

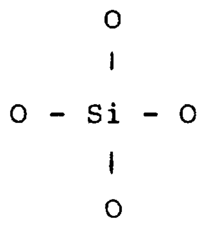
In 1932, W.H. Zachariasan[1] proposed the random network theory of glass structure. In essence, the structure is one which is void in symmetry and periodicity in comparison with the crystalline state. In 1947, K.H. Sun[2] advanced the theory that glasses are formed with bonding strengths between oxygen and a cation in the following minimum value: formers > 80; intermediates 80-60; modifiers < 60 (Kcal per Avogadro bond). The greater the number of non-bridging oxygens, the weaker is the structure of the glass. One of several ways the non-bridging oxygen ratio of the glass can be increased is by introducing water where OH^- ions combine in the structure[12].

In the 19th century, Von Waltershausen[3] introduced the term palagonite to describe altered glasses associated with pyroclastics in eastern Sicily and Iceland. Palagonite is the hydrated glass component formed from sideromelane (basaltic glass). Marshall[4] (1961) suggested that water molecules contained in glass are capable of breaking the Si-O-Si and Al-O-Al cross-bonds by adding hydroxyl groups to an Si or Al atom. In 1966, Freidman, Smith, and Long[5] suggested that perlite (hydrated glass from obsidian) can form during diagenesis at measurable rates and applied Fisk's Law to describe the depth of [HOH] penetration as a function of environmental temperature at given glass compositions. In 1969, Morgenstein[6] described the alteration process of palagonitization from sideromelane and developed a linear reaction-autocatalytic - which conformed to observed products during halmyrolysis. Much work with respect to glass hydration has been done since, especially in the field of chronology, yet little is known with respect to the chemistry and physics of these reactions.

Our concern at this juncture is to develop a chemical and structural model of glass hydration which will explain the formation of authigenic and syngenetic zeolites, clays, and oxides. The purpose of the model is to provide a testing platform for these reactions which will eventually lead towards the capability of using these reactions in environmental reconstruction, as well as in the assessment of diagentic-mineral formation for providing sorptive barriers to radionuclide migration.

STRUCTURE OF GLASS

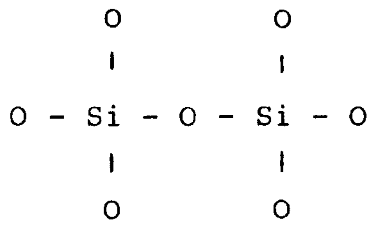
In accordance with Zachariasan[1] (1932), the structure of glass is based upon the tetrahedral network former such as silica in four-fold coordination:



$$\begin{array}{ccccc} & & O & & \\ & & | & & \\ O & - & Si & - & O \\ & & | & & \\ & & O & & \end{array}$$

Four-fold coordinated silica tetrahedra.

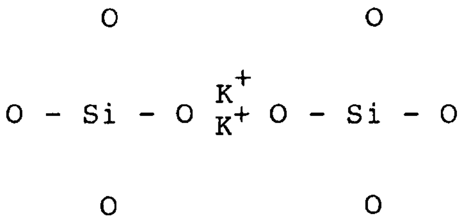
These tetrahedra are cross-bonded to other network formers by bridging oxygens in a unit which has an unbalanced negative charge:



$$\begin{array}{ccccccccc} & & O & & & & O & & \\ & & | & & & & | & & \\ O & - & Si & - & O & - & Si & - & O \\ & & | & & & & | & & \\ & & O & & & & O & & \end{array}$$

Unbalanced negative-charge bonded tetrahedra.

The oxygens which are not acting as bridging oxygens are designated nonbridging oxygens. In addition to the silica tetrahedra, AlO^{-}_{4} acts as a network former. Networks of tetrahedra are further bonded by network modifiers such as: AlO_6, Na^+, K^+, Ca^{++}, and Mg^{++}. These network modifiers are coordinated with six oxygen ions:



$$O - \underset{O}{\overset{O}{Si}} - O \; \overset{K^+}{K^+} \; O - \underset{O}{\overset{O}{Si}} - O$$

K_2O added as a network modifier.

During hydration diffusion (autocatalytic) [HOH] enters the glass structure and forms either bridging or nonbridging silanol groups:

$$\equiv Si - O - Si \equiv + HOH = 2[\equiv Si - OH]$$

The mechanism of autocatalytic diffusion requires examination since it is this process which is responsible for the transition of glass through its hydrated glass product to authigenic minerals.

GLASS REACTIONS SYSTEM - AUTOCATALYTIC DIFFUSION

Little, if any, attention has been paid to the variations in glass composition and its hydrated-glass products other than the distinction made between perlites and palagonites and their corresponding parents, obsidian and sideromelane. These distinctions have been made with respect to average chemical composition and gross morphology. Exacting boundaries have not been provided in definitions.

There are intermediate-glass compositions such as trachylite which hydrate to undefined hydrated glass which is commonly designated in the obsidian-perlite system by students of rhyolite, and in the sideromelane-palagonite system by students of basalt. Apparently no resolution of this problem is forthcoming, and consequently, we define here only the end members of the reaction series as follows:

ULTRA MAFIC - BASALTIC COMPOSITION GRANITIC COMPOSITION

Sideromelane..............................Obsidian

Palagonite................................Perlite

SiO_2 40% fresh 75% fresh

(-)-------⊥---⊥-----------┘(+)

FeO+ > 15% 0.5 fresh
Fe_2O_3

└--------┘---------------------------------┘-----------┘

Total MgO, CaO

Na_2O, K_2O fresh Fresh

25% 10%

---------⊥-------------⊥-------------⊥---------⊥---------┘

The weight percentages shown in the above scales can be used in a relative manner and are not fixed as to actual glass-type composition. In general, sideromelanes are typified by having significantly higher alkalis, iron and manganese than obsidian, and a lower incidence of silica bonding. On this basis, the hydration reactions in the mafic glass should be more rapid and base-controlled autocatalytic than in the obsidians (see below). Actual observation of rates of hydration conform to this pattern[4,5,6]. Both types in the alkalic and calc-alkalic suites may show abnormally higher hydration rates than normal basalts. The fact that Ericson and Berger[8] (1976) find a strong relationship between Si/O ratios and hydration rates in obsidian is not surprising as they are looking essentially at the concentration of silica tetrahedra and the quantity of bridging bonds. The greater the silica bonding (as has been indicated by Marshall[4], 1961), the slower the rate of hydration.

Norton[9] (1953) has stated that inert gases diffuse through glass without reacting with the glass network. If water were to behave in this same manner, glass composition would probably be relatively unimportant with respect to transport rates.

Charles[10] (1958), among others, recognizes that the water-diffusion mechanism is autocatalytic, suggesting that the actual transport process is a function of diffusional characteristics[4,5] and variable reaction, characteristics which are dependent upon glass composition and characteristics of a diffusing species.

If autocatalytic mechanisms in part control the reaction rates, the effects of such would be more marked with increasing concentrations of network modifiers. Network formers (tetrahedra) are apparently disrupted during diffusional attachment to bridging oxygens (e.g., the formation of silanol groups). The rock-compositional characteristics indicate that alkalic, calc-alkalic, and basaltic suites would contain glasses composed of more network modifiers (e.g., alkalis ions) than their (obsidian) granitic counterparts. This assumes that the alkali concentrations controlling the hydration reactions, as variable reactants, are sourced from the glass and not from the aqueous phase. Both aklali sources are probably important, and thus the previous argument requires modification. That is, although autocatalytic reactions appear more significant in the mafic-rock suites, they do play an important role in the obsidians, especially where the alkali concentrations are prevalent in the reacting-aqueous phase.

Scholze[11] (1966), using infrared absorption, reported that free and bonded OH groups are dependent on the boundary conditions of the bonded oxygens. The free OH groups (infrared spectrum of 2.73 - 2.95) apparently are overwhelmingly numerous in vitreous silica[11]. Modification by alkalis changes the reaction-role of the oxygens and causes the OH groups to be bound instead of free[11]. The bonded OH groups, characterized by the 3.35 - 3.85 and 4.25 spacing, are created by alkali modification[11]. Both free and bonded OH groups, therefore, occur in alkali-modified vitreous silica. By increasing the amount and/or the basicity (Na to K) of the alkali, the quantity of bonded OH is increased[11]. With this increase of alkali content of the glass, the diffusion rate increases and the viscosity decreases[12]. Diffusion is inversely proportional to viscosity[12].

The mechanism of diffusion is stated as the transport of one H^+ ion to a neighboring non-bridging oxygen (singly-bonded). The balance of charges can take place during the counter diffusion of alkali ions as well as the co-diffusion of OH groups[12].

Ericson et al.[12] (1971) report that during the first stages of chemical attack of a glass surface containing alkalis there is a base-exchange process where H^+ ions replace Na^+ ions (this attack is influenced by the alkali content of the glass surface). Alkali ions will migrate to the glass surface and can be removed from the glass in water at high temperatures. The silica network may be disrupted by OH^- ions released in the water by dissolved Na^+ ions. Charles[10] (1958) found that the activation energy of the alkali-water reaction on the surface of the glass correlated to the activation energy for the migration of sodium ions to the glass/corrosion layer interface. If the silica network in the alkali-leached glass is broken down by hydroxyl groups formed in the water by dissolved sodium ions, then the growth rate of the leached layers under diffusion conditions will equal its rate of disruption (at equilibrium). Thus, once equilibrium is reached, the depth of attack becomes proportional to time, because other sodium ions diffuse within a layer whose concentration gradient remains constant with time[12]. The model, here proposed by Charles[10] (1958), is that of base exchange of water and alkalis and the diffusion of alkalis is the rate-limiting factor of the double-diffusion system of water and alkalis. This model is supported by numerous chemical analyses of the glass to hydrated-glass reactions indicating increases of water of hydration and decreases of certain alkalis. In the marine system, during halmyrolysis, Morgenstein [13,6] has shown the significant loss of Ca^{++} accompanied by water enrichment. In addition, Na^+ and Mg^{++} were removed during hydration, but there was a very significant increase in K^+ coming from the seawater. Apparently, cation exhange towards more basicity is indicated. This causes a significant increase in OH bonding and apparent linear-diffusion rates. Zeolitization of the palagonite is prominent in the harmotome-phillipsite series conforming to a relatively rapid OH reaction. If base exchange is accomplished in the marine system, then rather than alkali removal with hydration the alkali partake in both transport directions; that is, the system is actually a triple diffusion where: HOH + $K^+ \longrightarrow$ diffuses into the glass and Na^+, Ca^{++}, $Mg^{++} \longrightarrow$ are released by the glass to the aqueous state. The rate of potassium uptake is proportional to the rate of Na^{++}, Ca^{++}, and Mg^{++} removal at equilibrium and this is the hydration-rate limiting factor (without considering the transport path channels, e.g., the physical attributes of the system).

In the terrestrial environment for sideromelane to palagonite transition, the behavior of K^+ and Ca^{++} are reversed with a general Na^+ and Mg^{++} loss in the hydrated product (palagonite). Thus, the rate of terrigenous hydration, given similar temperature to the halmyrolysis reaction, will differ as a consequence of alkalinity; however, the observed rate-controlling factors remain. Nevertheless, the resultant authigenic-mineral assemblage favors the heulandite-clinoptilolite, laumontite minerals over the phillipsite series observed in the marine environment. Of particular importance is the relative chemical composition of the zeolites observed in each of these two environments in comparison to the hydration reactions proposed. Phillipsite is a potassium-calcium zeolite in a solid-solution relationship with harmotome which is a barium zeolite. Base-exchange between the two end members of the series is prominent. The low-temperature (non-albitized) clinoptilolites, laumontites, and heulandites are for the most part calcic zeolites with base-exchange capacity to handle Na^+, K^+, and Mg^{++}. The mobility of alkalis in each environment, marine and terrestrial, during glass autocatalytic hydration, apparently is reflected in the final authigenic-zeolite package formed. To further exemplify this apparent relationship, harmotome-phillipsite have eight structural formers of Al-Si tetrahedra, and heulandite-clinoptilolite have nine and twelve respectively, correlating to a difference in availability of formers in the parent glass.

STRUCTURE OF AUTHIGENIC CLAYS AND ZEOLITES

Clays are phyllosilicates with Si:O ratios of 2:5 in a structural unit called a siloxene sheet which is composed of an SiO_4 tetrahedron. Three of the four oxygens in each SiO tetrahedron are shared with neighboring tetrahedra. Two kinds of sheet structure occur: tetrahedral and octahedral.

The most important clay mineral based upon occurrence with volcanics is montmorillonite. A cross-sectional diagrammatic view of the siloxene-sheet complex is given for the 2:1 layered clay.

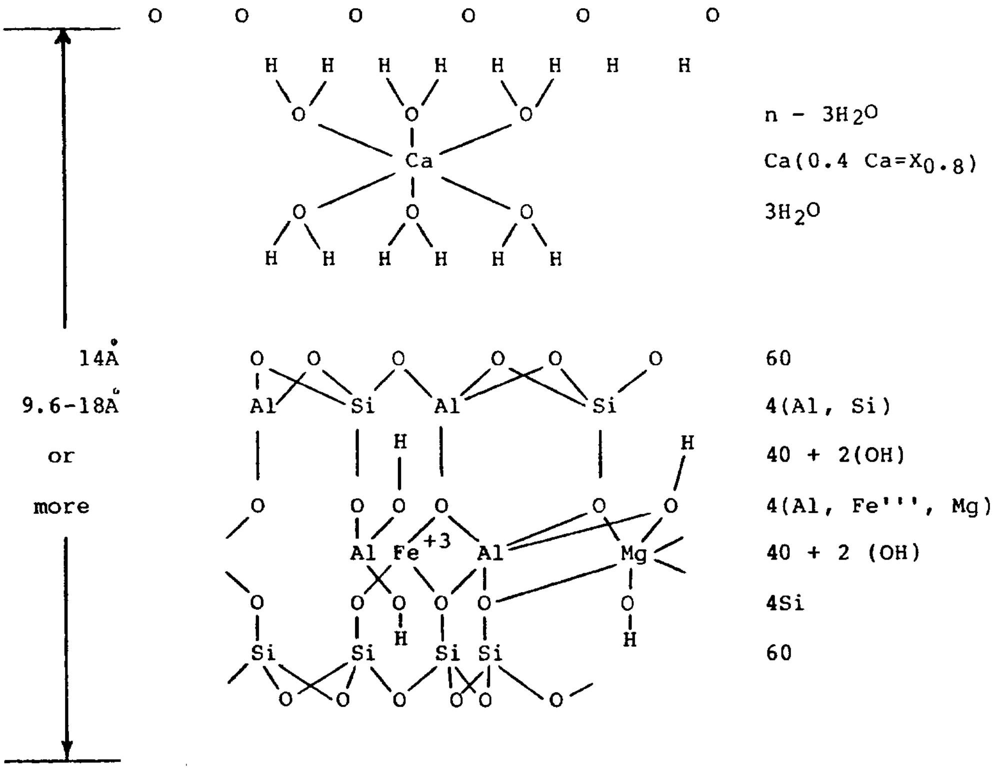


Figure 1. Cross-sectional diagram of montmorillonite.

The standard formula for montmorillonite is:

$$X_{0.8}(Al_{0.3}Si_{7.7})\ (Al_{2.6}Fe^{3+}_{0.9}Mg_{0.5})\ O_{20}(OH)_4\ ''\ nH_2O$$

Isomorphous substitution occurs yielding variations of mineralogy in the smectite group such as where Mg^{2+} and Fe^{2+} substitute for Al^{3+} and where Al^{3+} substitute for Si^{4+}. The resulting net-negative charge is partially balanced by interlayer-hydrated cations that bond adjacent siloxene sheets. Montmorillonite shows a symmetrical arrangement of two tetrahedral sheets about a central octahedral sheet. In the octahedral sheet the six ions surrounding the central cation include both O and OH ions.

Zeolites are tectosilicates in which the oxygen ions in each SiO_4 tetrahedron are shared with neighboring tetrahedra. The Si:O ratio of the structure is 1:2. Zeolites are built as chains composed of four rings of SiO_4 and AlO_4 tetrahedra, somewhat similar to feldspar structure. These chains are bound by interstitial cations: Na^+, K^+, CA^{++}, Ba^{++}, and Mg^{++} which form an open structure with wide channel-ways in which water and other molecules move, and in which ions in solution may be exchanged for ions in structure through cation exchange (base exchange).

The zeolites under consideration and clinoptilolite, heulandite, mordenite, and analcime. Base exchange in the zeolites is controlled by alkali concentrations in the liquid passing through the material. Sodium zeolites in a calcium environment will exchange $2Na^+$ for Ca^{++}. The reaction is reversible when the calcium zeolite is brought into contact with a high concentration of sodium in solution. Consequently, the nature of the alkali in the zeolite structure often is an indicator of the chemical composition of the liquid it has been in contact with (assuming equilibrium).

The standard formulae used here are:

Heulandite	$Ca[Al_2Si_7O_{18}]$ " $6H_2O$
Clinoptilolite	$X_2[Al_2Si_{10}O_{24}]$ " $8H_2O$ $Y[Al_2Si_{10}O_{24}]$ " $8H_2O$ where: X = Na, K Y = Ca, Mg
Mordenite	(NaORK) $[AlSi_5O_{12}]$ " $3H_2O$
Analcime	$NaAlSi_2O_6$ " H_2O

AUTHIGENIC MINERAL STABILITY IN THE PRESENCE OF:

H^+, HCO_3^+, $[OH]^-$

Authigenic minerals form from hydrated glass such as perlites and palagonites as opposed to unhydrated obsidians and sideromelanes. Thus, a measure of water has been introduced to the glass structure, either during syngenesis or diagenesis, prior to authigenic mineralization. The chemistry of the aqueous phase reacting with the glass structure in part controls which minerals will form, and their respective chemistry. Consequently, we must explore the controlling parameters in the aqueous phase.

Within the reacting water, as the PCO_2 concentration is elevated, the aqueous phase is driven towards higher H^+ and (HCO_3^-) concentrations favoring the formation of clays. In addition, calcium is driven into solution and combines with HCO_3^- to form $CaCO_3$ - calcite and aragonite - to zones of neutralization. The presence of $CaCO_3$ in the reaction glass proximity can neutralize H^+ as the previous reaction is reversible:

$$CaCO_3 + H^+ \rightleftarrows Ca^{2+} + HCO_3^-$$

As the alkali concentration increases, or the basicity of alkalis increases, the amount of bonded [OH] is increased and the diffusion rate of water into the glass is also increased. In addition, the reaction is driven towards zeolite formation. In theory, the sensitivity of mineral formation, be it clays or zeolites as a function of pH, arises because hydrogen competes with base cations for positions in the alumino-silicate framework. Consequently, the law of mass action suggests that a phyllosilicate will form rather than a zeolite under low pH. High pH is an important control on the stability of zeolite minerals. If too high, the activity of HOH is lowered, which hinders zeolite formation. In addition, sufficient carbonate ions may be produced to cause calcite to form as the stable authigenic calcium-rich mineral rather than a zeolite. Zen[7] (1961) showed that when the fugacity of carbon dioxide is high, authigenic calcite forms rather than a calcic zeolite.

The rates of authigenic mineral formation from hydrated glass are not well known, however, the formational rates of clays and zeolites are not the same. As high hydroxal concentrations favor zeolitization they also favor increased [HOH] diffusion rates. Consequently, zeolites are formed more rapidly than clay minerals, given the appropriate pH conditions. Zeolites require a [HOH]-saturated environment to form, whereas clay-mineral formation is probably enhanced by periodic dehydration. With dehydration, the reacting constituents are brought into close proximity to each other, enhancing siloxene-sheet interactions.

RATES OF GLASS HYDRATION AS A FUNCTION OF TEMPERATURE

It has been shown by various students of hydration that the rates of reaction are dependent upon environmental temperature[4,5 6,29]. Friedman, Smith, and Long[5] (1966) have shown for obsidian to perlite that a 1°C temperature change will produce approximately 10% change in the hydration rate. Morgenstein[6] (1969) and Morgenstein and Rosendahl[13] (1976) indicate that the palagonite-banding widths are a function of reaction-rate; the larger the band, the larger the rate to the point where during syngenesis only one very large band is formed (e.g., generally the complete palagonitization of the sideromelane).

Since the rate of hydration is partially dependent upon glass chemistry (quantity of network-former bonds and concentrations of alkalis), actual temperature-dependent reaction-rates must be calculated from each glass composition. It is also obvious that the composition of the aqueous phase with respect to pH and alkalis concentration is an important controlling factor.

Thus, although temperature effects on the reaction-rates are important, temperature alone is not all-controlling. Given similarities in reactant chemistry (one glass to another and one aqueous phase to another) variations in temperature will produce variations in reaction-rates.

AUTHIGENIC MINERALOGY AS A FUNCTION OF TEMPERATURE

Both zeolites and clay minerals are sensitive to temperature change. Perry and Hower[14,15] (1970, 1972) have documented the effects of temperature on the smectities/illite clays as a transition from predominantly swelling smectite, to an interstratified illite/smectite and finally to a nonexpanding illite-rich material. The percent of expandability in smectite/illite decreases to 60% at 60°C, 40% at 80°C, and 20% at 100°C in argillaceous sediments subject to low-temperature metamorphism[14]. Iijima[16] (1980) and Iijima and Ohwa[17] (1980) have documented the metamorphic zeolite series as a function of temperature; and Iijima[18] (1975) has shown that pore-water alkali concentration, such as with sodium, affect the temperature of the reaction of clinoptilolite to analcime to albite in the following reaction:

$$\text{clinoptilolite} + \text{silica} + \text{HOH} \longrightarrow \text{analcime} + \text{quartz} + [\text{HOH}]$$
$$\text{analcime} + \text{quartz} + \text{HOH} \longrightarrow \text{albite} + \text{quartz} + [\text{HOH}]$$

Much is known, therefore, about the behavior of the smectites and zeolites with respect to low-temperature metamorphism. A general trend of temperature-effects on mineral structure and stability is observed, whereby the expandable and open structures are formed in ambient to slightly-above ambient conditions. As temperature rises, the structures become tighter with less water of hydration, lower base-exchange capacities, and volumetrically-smaller unit structures. Alkalis concentration in the aqueous phase during mineral transition appears to affect the transition temperature[18]. However, the effects of the degree of alkalinity and degree of basicity have not been fully investigated. It appears that the sodium zeolite-albitization reactions are similar in phase relationship to a calcium wairakite-anorthite system. The availability of the alkali component must in part determine the reaction system and the degree of basicity that may affect the phase change temperature of the reaction as well as its rate. These are, however, conjectural arguments which must await actual data.

REACTIONS AND STRUCTURE OF THE AUTHIGENIC OXIDES

In addition to smectite and zeolite formation during the devitrification process, various oxides and hydroxides of iron, manganese, and silica are formed.

The silicates are composed of linked SiO_4 tetrahedra in which all the oxygen ions in each SiO_4 tetrahedra are shared with neighboring tetrahedra. Consequently, the Si:O ratio of these tectosilicates is 1:2. The minerals of interest are alpha and beta quartz, high and low tridymite and cristobalite, and opal (hydrated SiO_2 alpha quartz). There are, therefore, six polymorphs which have characteristic external morphology, cell dimensions, and lattice energy. Stability is determined by energy, i.e., higher temperature forms have more expanded structures with greater lattice energy. Thus, alpha quartz has the lowest symmetry and the most compact-lattice structure. Tridymite has a higher symmetry and a more open structure, and finally, cristobalite has the highest symmetry and the most expanded lattice. These polymorphs can be transformed into each other by disrupting the Si-O bonds and rearranging the tetrahedra.

At higher temperatures, volcanic glass devitrification proceeds in the direction of the formation of tridymite and cristobalite; at moderate temperatures, tridymite and quartz and opal; and at ambient temperatures these oxides are generally not produced.

High quartz crystallizes as a stable form at 573°, high tridymite at 870°, and high cristobalite at 1470°. Opal is an amorphous form of alpha quartz which is generally deposited during hydrothermal action.

The iron and manganese oxides and hydroxides are a complex group of minerals which are interrelated structurally and serve as environmental indicators. The minerals of concern are: geothite (Fe_2O_3 " H_2O), lepidochrocite (Fe_2O " H_2O), maghemite (Fe_2O_3), hematite (Fe_2O_3), ramsdellite (MnO_2), birnessite (7°A manganite), todorokite (Mn, Mg, Ca, Ba, K, Na) (Mn_5O_{12} " $3H_2O$), among others. These minerals form at diagenetic temperatures and are generally recognized in spatial association with hydrating volcanics.

Iron within the volcanic glass has essentially three choices for stable sites: 1) in the aqueous phase; 2) in the smectite structure such as nontronite; and 3) in the oxide-hydroxide ferromanganiferrous-oxyhydroxide structures. Iron is generally mobilized preferentially to manganese (as is indicated by ionic potential). Manganese generally follows iron and is precipitated in the Mn^{4+} state spacially associated with iron. In the palagonite-sideromelane system, iron is first recognized as the hydrated form within the palagonite structure and as a coating on the altering volcanics. Manganese oxyhydroxide precipitation occurs on the outer ferrogenous coating surface. Much of the ability to optically identify palagonite from its sideromelane parent is in the recognition of the iron oxyhydroxides within the hydrated-glass structure. Although the concentration of iron is much greater in the sideromelanes than the obsidian glasses, there are relatively significant observations of iron precipitation in the obsidians as well. Apparently, $[OH]^-$ groups react with the iron very early in the hydration process. Presumably the iron is attached within the glass as network modifiers and under moderate to high pH values the $[OH]^-$ combines with the iron to form hydroxides. The iron is mobilized somewhat similar to potassium in the marine environment. The alkalis (K and Ca) are, however, significantly more mobile.

Of particular concern is the optical birefringence of hydrated glass. The birefringence has been characterized as strain birefringence by most of the students of the obsidian-perlite system. The fact that ferrugenous-hydroxide formation is observed within the hydrating glass structure suggests that:

1. Mineralization of the perlites and palagonites occurs not only in the aqueous media, on volcanoclastic and volcanic surfaces, but also within the reorganizing hydrate-glass structure.
2. Birefringence, therefore, may be a function of structural reorganization independent of stress production. Very little supportive evidence exists suggesting that the birefringence is actually strain-related.

If this is in fact the case, then the nature of authigenic mineralization must be viewed as a structural reorganization of freed monomer building blocks that are capable of recombination into phyllosilicate and zeolite structures. Further, the alkalis bonding in the zeolites structure would then be accomplished by the most geochemically-active ions, and these would also be adsorbed by the smectite structure. In other words, the site-locality of authigenic mineralization limits the availability of ions to the newly-formed structure. The energy requirement to release a large complex monomer is less than the energy requirement to disengage many bonds to form small tetrahedra. Although this argument is supported by observed spacial precipitation of authigenic minerals, other conclusions could be drawn from the observed data. Nevertheless, the argument is consistent with the observations and is energy-efficient with respect to the proposed reactions. Consequently, it provides a format for further investigations.

CHEMICAL AND CHEMO-PHYSICAL REACTIONS DURING GLASS TRANSITION TO HYDRATED GLASS AND AUTHIGENIC MINERALS WITH EXPERIMENTAL-WATER CHEMISTRY

Much data exists concerning the chemical composition of glasses and to a lesser extent their hydrated-glass phases. Chemical data exist for clays and zeolites with associated fresh and altered glasses, although these data are not generally from the same samples (e.g., truly matched sets). *In situ* pore-water chemistry with associated glass and mineral chemistry as matched sets are rarely found in the literature. Those data presented here report an average behavior of the elements during weathering reactions.

In the reactions of sideromelane to palagonite for terrigenous regions, iron appears to be the most active going into mineral sinks, and sodium appears to be the most active going into solution (remaining with the fresh glass structure and increasing in concentration in that structure). In the marine environment, during halmyrolysis, potassium and calcium are the most active with potassium increasing in the palagonite and calcium increasing in the sideromelane. Iron appears to follow potassium with relative icreases observed in the palagonite.

The follwing two tables report several matched analyses for sideromelane to palagonite as oxide-to-oxide ratios derived from the percentage of change in composition during weathering.

TABLE 1. Terrestrial Reactions of Sideromelane to Palagonite

Palagonia, Sicily*			Iceland**		
Fe_2O_3	9.50	sink	MnO	99.00+	sink
CaO	1.49		Fe_2O_3	7.61	sink
SiO_2	1.57		K_2O	1.33	sink
MgO	1.74		SiO_2	1.31	
Al_2O_3	1.77		Al_2O_3	1.46	
K_2O	1.85		MgO	1.50	
Na_2O	3.71		CaO	1.85	
			FeO	4.55	
			Na_2O	12.12	

* Hoppe[26] (1941) recalculated to matched analyses and resolved as ratio of reaction (matched-oxide ratio normalized to 100% of oxide in parent and product).

** Peacock[27] (1926) recalculated to matched analyses and resolved as ratio of reaction (matched-oxide ratio normalized to 100% of oxide in parent and product).

Sink equates to an increase of that oxide in palagonite over sideromelane.

TABLE 2. Marine Weathering of Sideromelane (Halmyrolysis)

Oxide	% Change Average Reaction*	Ratio of % Change**		
K_2O	+79.0	K	9.28	
FeO	+2.1 sink in palagonite	Fe	1.76	
TiO_2	-13.7	O	1.60	sink in palagonite
Al_2O_3	-23.0	Al	1.05	
Na_2O	-41.4	Ti	1.18	
MgO	-41.8	Na	1.37	
SiO_2	-42.4	Mg	1.77	
CaO	-53.9	Si	1.82	
		Mn	1.82	
		Ca	7.95	

* Average % change in composition of basalts due to weathering and palagonitization. K. Muehlengachs and R.N. Clayton[28] (1972).

** V22-227, Mid-Atlantic Ridge, Matched Analyses of Sideromelane to Palagonite, electron microprobe analyses, resolved as ratio of reaction, Morgenstein and Rosendahl[13] (1976), Table 8.3. (Matched oxide ratio normalized to 100% of oxide in parent and product).

The chemical and physical attributes of the sideromelane-to-palagonite transition have been discussed by Morgenstein[6,13,-19,20] in which micro-channel fractures were shown to be transporters of the aqueous phases during halmyrolysis. The genesis of these channels was explained as chemical-attack channels which extended themselves in response to stress generation caused by an increase in volume due to hydration. Palagonite banding was shown to be a function of microchannel growth, the development of a solid-solution border and the accompanying crystallization of ferruginmeous oxyhydroxides. The source of the attack-channel configuration (microfracture) was thought to be the point of bonding collapse due to the entrance of water and alkalis and the removal of alkali. Propagation of that structure was reported as stress-related. If these observations and conclusions are accurate, th n little evidence exists for strain birefringence within these glasses.

One modification of the above concept is required for channel propagation. As channel extension is a function of stress due to hydration, the hydration reaction does not necessarily determine the locus of chemical-autocatalytic diffusion, rather fracturing based upon stress production is the controlling parameter. The chemical reaction, (e.g., bonding collapse) is the initial determining facet for the location of the channel itself. The rate of stress production is related to the rate of chemical transport within the channel, which controls the widening of the channel, the rate inter-growth of the channel with another, and the volume of material added to the glass, which is ultimately responsible for stress production.

The significance of these morphological attributes is that the zone of hydration-alkali activity is not solely surficial, but extends to a depth in the glass structure which is dependent upon the rate and nature of the reaction(s). Consequently, the exchange of calcium with potassium requires a significant exchange between the aqueous state and the glass, a significant local change in pH, and reasonably high reaction rate.

Nasedkin[21] suggested that the hydration of obsidian and the formation of perlite were a result of the water migration along channels which did not exceed 200°A. His conclusions were based upon the observed reversibility of induced hydration experiments and electron photomicrographs of perlite. The similarity between Nasedkin[21] data (and conclusions) and Morgenstein[6,13,19,20], with respect to channel morphology and aqueous-phase reactions with the glass, suggests that the similar controlling reactions occur in sideromelane and obsidian.

The chemical analyses of obsidian-to-perlite and perlite-to-authigenic minerals suggest that these (above) conclusions are warranted (as attested to by the following chemical data).

Volcanic glass dissolution rates for Yucca Mountain, Nevada, glass as reported by Kerrish[22] (1983) have been given as a function of pH. The following table reports glass-dissolution rates normalized to SiO[22], matched-oxide analyses for fresh glass to zeolite and smectites[23,24], and ionic potentials for the reacting ions.

TABLE 3. Glass-Dissolution Rates

					Matched oxide ratio analysis normalized to 100% of oxide in parent and product.					
Oxide	Rate Proportional to Composition^{B66}	pH 7* Dissolution Rate^{B66}	pH 5*	Z/r	Glass	3037' Clay	561' Glass	to Zeolite	3492' Glass	to Zeolite
CaO	0.0176	0.0064	0.1758	2.00		9.04		14.17		8.61
FeO	0.020	0.020	0.020	2.67		2.52				
Al_2O_3	0.220	0.226	0.020	5.45		1.88		1.03		
TiO_2				6.67		1.21				
SiO_2	1.000	1.000	1.000	10.00	1.31		1.07			
Na_2O	0.0657	0.101	0.1437	1.05	3.95		19.37		1.80	
K_2O	0.170	0.094	0.0170	0.74	11.90		3.54		11.21	

* Ionic dissolution rates, not for the oxides.
** Z/r = ionic potential.

The following conclusions can be drawn from these data:

1. Calcium behaves inversely proportional to potassium. Calcium sinks in the clays and zeolites. Potassium is preferentially removed from the glass structure and does not sink preferentially in smectites or zeolites, but presumably is released to solution of found in illite-sericite structures.
2. Sodium follows potassium, is less active except at the surface of the tuffs where it appears more active than potasium with respect to the zeolites (more sodic zeolites at depth, and exhibit greater sodium evolution to aqueous solution at the surface).
3. Iron follows calcium, is less mobile, and preferentially sinks in the clay structure and not in the zeolites. Data on iron oxyhydroxides are not offered here and one might presume that this is the major sink.
4. Ionic potential depicts and predicts reaction behavior in the tuffs.
5. Normalized dissolution rates as reported by Kerrick[22] best fit the observed matched-oxide chemistry at pH 7 and above, indicating a slightly basic environment which presumably favors zeolite over clay production.

Well-water (J-13)[25] chemistry and reacted-tuff wafers with well-water chemistry[25] correlate fairly well with observed glass-to-clay and zeolite-matched reactions as can be observed in the following tables. Iron data does not conform to predicted water behavior on the basis of clays and zeolites. This might be anticipated since no oxide and hydroxide minerals have been used in these calculations. In addition, there appears to be an increase in dissolved iron over sinked iron in mineral structure. This may be a function of rates of reaction at elevated temperatures (152°C) and/or sites for precipitation (there is an apparent difference between whole-rock dissolution and glass dissolution).

TABLE 4. Well J-13 Water and Reacted Tuff Chemistries

Oxide	mg/l J-13 water** Standard	mg/l J-13 water 152 1°C Reacted*	Behavior of clay and zeolite from core stratigraphy	
Cao	14.0	0.56	9.0	14.17
FeO	0.04	0.60	2.52 to mineral sink	
Al_2O_3	0.03	0.009	1.88	1.03
TiO_2		0.000	1.21	
SiO_2	31.0	27.1	1.31	1.07
Na_2O	51.0	89.0	3.95 to solution	19.37
K_2O	4.9	4.9	11.9	3.54
	Oxide	Element	Clay	Zeolite

* J-13 groundwater after contact with tuff at 152+°C for three weeks and filtered with nuclepore, polycarbonate membrane 0.05 m.

** J-13 is at pH of 7.1.

TABLE 5. Well J-13 Water and Reacted Tuff Chemistries

Oxide	J-13 water Standard	G1-2476 Bullfrog II Devitrified Welded Tuff		G1-1436 Calico Hills Zeolitized Non-welded Tuff		G1-1292 Topopah Spring Vitrophyre	
Cao	14.0	9.5	0.657	0.176	0.031	13.1	0.534
FeO	0.04	0.033	0.120	0.064	0.285	0.020	0.063
Al_2O_3	0.03	0.016	0.418	0.042	0.000	0.000	3.26
TiO_2	-	1.02	1.02	0.000	0.549	1.72	0.000
SiO_2	31.0	29.7	60	30.8	60	32.3	60
Na_2O	51.0	68.9	122±4	78±5	134±6	57±4	128±2
K_2O	4.9	6.00	7.68	3.51	10	5.02	10
		22°C	152°C	22°C	152°C	22°C	152°C
	Oxide	Element		Element		Element	

More data is required to reconcile these reactions. The behavior of titanium and aluminum appears not to be predictable from the water data available. It would be possible with the available data to back-calculate the water chemistry of various stratigraphic zones on the basis of ion behavior with respect to dissolution of volcanic glass. This exercise, however, is plagued with various uncertainties and admits to requiring more base-line information than is presently available (e.g., zeolite and clay data presented here are from different stratigraphic zones).

Terrestrial-environment obsidian reactions during high-temperature devitrification favor the formation of quartz and its polymorphs, authigenic feldspars rather than zeolites (dependent upon phase temperature), and interlayered smectite-illite and illite and chlorites. At lower temperatures approaching ambient and at ambient conditions the devitrification reactions favor smectites, zeolites, and ferromanganese oxyhydroxides (larger more expandable and looser structures). The energy applied to the system during devitrification of glass is most probably a controlling factor in the number of bonds and which bonds, with respect to former and modifier, are broken. Apparently, the greater number of bonds collapsed, the more compact are the monomer structures released for recombination. In addition, the degree of freedom for recombination is increased, accounting for more varied structures. Those structures (authigenic minerals) formed at high temperatures are stable with respect to their formational environment.

At ambient, diagenetic conditions, autocatalytic-hydration diffusion provides a more significantly confined authigenic-mineral assemblage. The chemistry of these reactions requires scrutiny with respect to the relative ion sinks within the authigenic minerals; for Yucca Mountain glasses those data for the zeolites and clays are shown on the following table.

TABLE 6. Activity Ratio for Clay and Zeolite as Preferential and Relative Sinks

	ZEOLITE	CLAY
CaO	1.57	-
FeO**	0.00 none	all
Al_2O_3	-	1.83
TiO_2**	0.00 none	all
SiO_2	1.22	-
Na_2O	-	4.91
K_2O	3.36	-

---

* 1.00 oxide is sinked into each structure equally above. 1.00 is a multiplier of the relative sinking of that oxide in that particular structure relative to the other structure. Example: for sodium, 3.91 times more sodium is linked in the clay structure than in the zeolite structure (4.91 - 1.00 equality = 3.91).

** For Fe and Ti, the clays take all of these elements relative to the zeolites; however, other structures are probably important such as the oxides and hydroxides for which we have shown no data. In addition, these elements may transport as ions in the aqueous phase some distance from the zone of reaction prior to precipitation.

PROPOSED AUTOCATALYTIC REACTIONS FORMING MONOMERS AND AUTHIGENIC MINERALS

In consideration of previous data and arguments, the following six reactions are proposed as a means to examine the hydration mechanism. These are by no means the total limit of possible reactions. They do, however, provide an understanding of the various structural possibilities. The state of hydrogen and oxygen as sourced from the aqueous phase or the solid phase will assist in isotope work which could be utilized to characterize the source of the aqueous phase in a particular environment.

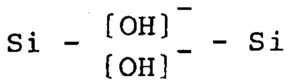
Model reactions for the silanol formation probably involve an alternate jumping of protons and hydroxyl groups. In addition, for the alkali, one might envision a base exchange of Ca^+ for $2K^+$ freeing calcium to the aqueous phase. The hydroxyl contribution to the glass may come from the associated hydroxyl with potassium in the aqueous phase. In this scenario, we would be looking at a hydroxyl and alkali reaction with water tagging behind for a proton source for the silanol group.

In reality, the nature of the diffusing species has not been established. The model proposed here looks at alkali ions, protons, and hydroxyl ions as the diffusing species. The potential for hydrogen atoms, hydrogen molecules, oxygen atoms, oxygen molecules, and water molecules is also significant and must be left open for consideration. In addition, if isotope studies are of interest, diffractionation must be sorted out for each of the proposed reactions.

1. The formation of bridging silanol groups:

Glass Structure	Reaction
Si - O - Si	$\underset{\mathrm{Aq}}{2[\mathrm{HOH}]} + \underset{\mathrm{G\ G\ G}}{\mathrm{Si\text{-}O\text{-}Si}} \longrightarrow \underset{\mathrm{G\ AqAq}}{2[\mathrm{SiOH}]} + \underset{\mathrm{AqGAq}}{[\mathrm{HOH}]}$

New Structure



$$\mathrm{Si} - \begin{matrix}[\mathrm{OH}]^- \\ [\mathrm{OH}]^-\end{matrix} - \mathrm{Si}$$

2. The formation of nonbridging-silanol groups: same reaction as above.

New Structure

Si - OH OH - Si

3. Reaction at a network modifier of potassium:

Glass Structure

$\mathrm{Si - O - \overset{K^+}{K^+} - O - Si}$

Reaction

$$\underset{Aq}{[HOH]} + 2\underset{G}{[K^+]} \longrightarrow 2\underset{G\ Aq}{[KOH]} + \underset{Aq}{2H^+}$$

$$\underset{Aq}{2H^+} + 2\underset{G\quad G}{[Si-O]} - 2\underset{G\ GAq}{[SiOH]}$$

Products are 2[KOH] + 2[SiOH] The silanol groups can be bridging or non bridging and as combined or uncombined with KOH>

4. Reaction at a network modifier of calcium:

Glass Structure

$\mathrm{Si - O - Ca^{++} - O - Si}$

Reaction

$$2\underset{Aq}{[HOH]} + \underset{G}{[Ca]} \longrightarrow \underset{G\ Aq}{Ca[OH]_2} + \underset{Aq}{H_2^+}$$

$$\underset{Aq}{2H^+} + 2\underset{G\quad G}{[Si-O]} \longrightarrow 2\underset{G\ GAq}{[SiOH]}$$

Products are $Ca(OH)_2$ + 2[SiOH] The silanol groups can be bridging and as combined or uncombined with $Ca(OH)_2$.

5. Reaction at a network modifier of calcium with double diffusion:

Glass Structure

$Si - O - Ca^{++} - O - Si$

Reaction

$2[HOH] + [Ca] \longrightarrow Ca[OH]_2 + H_2^+$

Aq G G Aq Aq

$2[K]^+ + Ca(OH)_2 \longrightarrow 2K[OH]_2 + Ca^{++}$

Aq G Aq Aq Aq G

$2H^+ + 2[Si-O] \longrightarrow 2[SiOH]$

Aq G G G GAq

Products are $2KOH + 2SiOH + Ca^{++}_{sol}$

6. Reaction at an Fe site with oxidation.

Glass Structure

$Si - O - Fe^{=} - O - Si$

Reaction

$2[HOH] + Fe \longrightarrow Fe[OH]_2 + 2H^+$

Aq G G Aq

$2H^+ + 2[Si-O] \longrightarrow 2\ [SiOH]$

Aq G G G GAq

$Fe[OH]_2 + O_2 \longrightarrow Fe_2O_3$ " H_2O

G Aq Aq G Aq AqAq

Products are ferrous hydroxide to geothite by oxidation and two silanol groups.

The reactions proposed here are attempts to look at the disengagement of glass bonds at the edge of layer former-network structure. We see no evidence in either the glasses or their products to presume that most of the bridging bonds are broken during diagenetic reactions. Rather, as previously stated, it is more energy efficient to free larger monomer building blocks. The pH of the reacting aqueous phase apparently controls, in part, the number of bonds which are broken and, consequently, the size of the monomers available for reorganization to authigenic phases, such as zeolites or smectites.

CONCLUSION

It is apparent that there is sparsity of data concerning the actual reactions for the transition of glass to authigenics, even though there seem to be various theories for the mechanism(s) of the reactions. A very rough model has been developed here which assists in explaining portions of the physical and chemical observations. The model admits to revision and is provided as a testing platform for determining the actual parameters controlling the reactions, reaction-rates, and products, as both authigenic minerals and aqueous solutions.

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29 Freidman, I., 1976. In: Advances in Obsidian Glass Studies, ed: Taylor, pp. 173-180.

APPENDIX A:

Review by Roger Aines, June 16, 1985

Department of Energy
Nevada Operations Office
P. O. Box 14100
Las Vegas, NV 89114-4100

AUG 12 1985

Robert R. Loux, Jr., Manager
Nuclear Waste Project Office
Office of the Governor
Capitol Complex
Carson City, NV 89710

STATE REPORTS

On April 29, 1985, you sent me six reports prepared by your office covering the work that we have done. I subsequently passed them on to a number of technical experts that support this Project. In the spirit of the protocol that we established last year, I am passing on the comments provided to me regarding these reports.

Donald L. Vieth

Donald L. Vieth, Director
Waste Management Project Office

WMPO:DLV-1413

Enclosure:
As stated

cc w/encl:
M. B. Blanchard, WMPO, DOE/NV
V. F. Witherill, WMPO, DOE/NV
J. C. Rotert, WMPO, DOE/NV
J. R. Barner, WMPO, DOE/NV
V. J. Cassella, DOE/HQ (RW-22) FORSTL
A. B. Benson, DOE/HQ (RW-25) FORSTL
C. M. Smith, DOE/HQ (RW-43) FORSTL

June 16, 1985

To: L. Ramspott

From : Roger Aines

Subject: Review of Desert Research Institute Report #1, "Physics and Chemistry of the Transition of Glass to Authigenic Minerals"

//

This paper seems to be operating on two levels. First, the majority of the paper is simply a review of some of the reaction mechanisms for the alteration of volcanic glass with an emphasis on the dating of glasses using reaction rims. Second, the paper occasionally addresses issues of glass hydration at Yucca Mountain. No new insight regarding Yucca Mountain processes is presented; the author reiterates several points which were made in the Yucca Mountain EA regarding unresolved issues. This paper might be an appropriate introduction to the field if it were up to date, but it is consistently about 10 to 15 years behind the current literature and oversimplified with regard to the application of glass alteration. The author's main point is that the alteration rates can not be predicted for the remaining volcanic glass in Yucca Mountain. The EA agrees that prediction is difficult but gives evidence to show that the rate is very small.

Most of the comments below are addressed to the authors points regarding Yucca Mountain conditions, which are a small part of the paper.

Specific Comments

Forward.

The author states that items (1) and (2) are contradictory and unsupported. It is difficult to understand how he arrived at this conclusion since he does not give specific page number references from the EA; perhaps he did not read the pertinent sections. Item (1), the current extent of volcanic glass, has been extensively investigated as part of the determination of the mineralogy of the units in Yucca Mt. This has been determined from surface and drilling investigations (pages 6-148 to 6-150, references therein, and figure 6-4).

Item (2), the probable fate of remaining glass, is not subject to direct determination and as such there is some uncertainty. However, the author's assessment that the EA states that "zeolites could form from as yet unreacted glass during the transport of water from the repository" is incorrect in detail. Page 6-149 clearly states that although more zeolites could form from remaining vitric tuff, this is not a process that has occurred at a substantial rate during the Quaternary period and it is not expected to be important in the next 100,000 years.

There is no contradiction in these two statements, as the author suggests. There is still some volcanic glass within the repository block; that material could convert to zeolites under the proper conditions but the rate under the expected conditions is very small to zero. The author states that it is not possible to determine the extent of radionuclide retardation which would result from the zeolitization of remaining glass; the EA makes no claims for retardation from this material. The issue of the long term devitrification of remaining glass is interesting but the author has made no case whatsoever that the placement of a repository in Yucca Mountain would affect that devitrification in such a way as to make it occur to a substantial degree in 100,000 years. Even if it did occur, it is not shown by the author that it would have any negative effects on repository performance, as discussed on page 6-149.

Introduction

This review of glass hydration and alteration is outdated and incomplete with regard to possible processes that might occur at or near the water table in Yucca Mountain. Glass hydration studies underwent a revolution in the 1970's and 1980's which the author is unaware of. In particular it has been shown that hydrated glasses contain both water and hydroxyl groups and that diffusivities are directly correlated to viscosity which is a function both of the original state of polymerization of the melt and the depolymerization that results from hydroxyl incorporation (for good reviews see Stolper, 1982; Bartholomew et al. 1980; Wolters and Verweij, 1980). The alteration of glass has received a tremendous amount of scrutiny recently because of the obvious corrolary between the long term behavior of nuclear waste glass and that of similar natural glasses. The conclusions of the author are in general accord with more recent work with regard to the migration of alkali elements. However, further devitrification of glass in Yucca Mountain is only expected to occur in the presence of substantial amounts of liquid water, and as such the system considered by the author is oversimplified. The solubilities and reactivities of all phases present must be considered in such an interactive system. If the author has evidence to suggest that devitrification will occur at a substantial rate under the present conditions, he should present it.

Page 12 ; The statement in lines 7-9 is unsubstantiated in the text and is incorrect according to current understanding. A similar statement is made in line 24. There is no evidence that hydroxyl concentration affects glass hydration rates of which the reviewer is aware; if such evidence exists the author should refer to it. There is a very substantial difference between the hydration of a glass and the alteration of that glass to a material such as palagonite. In the latter case, a new phase forms from the reaction of water and glass under pseudo-equilibrium conditions, and the composition of the fluid may be expected to affect the reaction rate.

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APPENDIX B:

RESPONSE:

To review of this report by R. Aines, U.S. Department of Energy.

Prepared by:

Martin Mifflin
Water Resources Center
Desert Research Institute
University of Nevada System

February 1986

APPENDIX B:

Response to the Review: R. Aines (June 16, 1985).

The format of this appendix is a response to the Review by R. Aines (LLNL) on a comment-by-comment basis.

The review by R. Aines operates from a context that: 1) the high temperature experimental glass data produced during the 1970's - 1980's provides specific insight to the behavior of volcanic glass hydration during diagenesis at ambience or slightly above ambience and 2) that the DEA adequately deals with this subject matter. The reviewer (Aines) provides several interesting citations, and perhaps identifies the state of the DOE's conceptual investigative approach to volcanic and waste-glass problems.

1. Comment: Page 1, paragraph 1, lines 1 to 6, page 1.

> "This paper seems to be operating on two levels. First, the majority of the paper is simply a review of some of the reaction mechanisms for the alteration of volcanic glass with an emphasis on the dating of glasses using reaction rims. Second, the paper occasionally addresses issues of glass hydration at Yucca Mountain." R. Aines (1985, page 1).

Response:

The report is designed to review, in a general sense, the potential reaction mechanisms for volcanic glass hydration during diagenesis, through the authigenic production of secondary minerals. No new research has been accomplished. Rather, data provided by Kerrisk, et al., (1983) from Yucca Mountain were found to be conforming to other glass reactions and of significant value in their utility in predicting glass behavior for Yucca Mountain. The paucity of data from Yucca Mountain is in itself responsible for the less than intensive treatment given by the report reviewed by R. Aines.

2. Comment: Page 1, paragraph 1, lines 6 to 9, page 1.

> "No new insight regarding Yucca Mountain processes is presented; the author reiterates several points which were made in the Yucca Mountain EA regarding unresolved issues." R. Aines (1985, page 1).

Response:

The comment is somewhat pretentious in that the DEA is presumed to have mastered the subject matter; where in reality, the DEA falls short of a conservative presentation. If the issues raised had been previously recognized, one might expect to see at least one DOE publication delineating this topical area from the standpoint of low-temperature diagenesis.

3. Comment: Page 1, paragraph 1, lines 9 to 12.

"This paper might be an appropriate introduction to the field if it were up to date, but it is consistently about 10 to 15 years behind the current literature and oversimplified with regard to the application of glass alteration." R. Aines (1985, page 1).

Response:

The subject matter of the reviewed report deals with diagenetic hydration of glass, which is not the same mechanism as syngenetic hydration. Although, both topics provide significant data concerning the behavior of glass during hydration, the emphasis was not on syngenesis. The comment by the reviewer (Aines) points out our potential failing in the syngenetic area.

4. Comment: Page 1, paragraph 1, lines 12 to 16.

"The author's main point is that the alteration rates can not be predicted for the remaining volcanic glass in Yucca Mountain. The EA agrees that prediction is difficult but gives evidence to show that the rate is very small." R. Aines (1985, page 1).

Response:

We fail to locate the "evidence to show that the rate is very small." The following quotes are taken from the DEA.

DRAFT ENVIRONMENTAL ASSESSMENT, YUCCA MOUNTAIN SITE, NEVADA RESEARCH AND DEVELOPMENT AREA, NEVADA (December 1984).

page (6-147):

"Clinoptilolite and mordenite now present in Yucca Mountain are assumed to have been there for at least 10 million years."

page (6-149):

"Petrofabric studies of the altered rocks, combined with information about the tectonic history of the area, indicate that the zeolitic alteration of glasses at Yucca Mountain predated the Quaternary Period (Bryant and Vaniman, 1984). A separate episode of zeolitizaton, localized in the lower Topopah Spring Member of the Paintbrush Tuff was probably related to the original cooling of the unit and therefore also predated the Quaternary Period (Levy, 1984b). Because this geochemical process was probably not operating during the Quaternary Period (Bryant and Vaniman, 1984) its Quaternary rate is inferred to be close to zero. Barring climatic changes that would significantly increase ground-water recharge or raise the static water level at Yucca Mountain, zeolitization should be inoperative or minor during the next 100,000 years. However, zeolitization could occur either in the upper tuffaceous beds of Calico Hills or in stratigraphically higher rock units if the environment becomes wet enough for these rocks to become saturated."

page (7-29):

"At Yucca Mountain, no heat-induced alteration of the tuff is expected. Alteration would require the presence of water and free silica, and the tuff would alter to zeolite, which would favorably affect the sorption of radionuclides."

page 6-133:

> "On the other hand, a decrease in effective porosity by the precipitation of minerals in fractures would be more than offset by increased sorption; fracture coatings (zeolites, smectites, and manganese oxides) have very reactive surfaces that greatly increase retardation."

We find no compelling evidence from those data presented nor from the cited references to the indicated presence of either a documented rate of hydration of volcanic glass or of the rate(s) of authigenic mineral production.

The literature (Friedman, et al., 1966; Friedman, 1976; and W. Ambrose, 1976; among others) indicate that glass will hydrate in environmental settings that are not saturated with water; consequently, zeolitization as well as smectite production might be accomplished even if saturation is not present in the tuffs. The points made in our report are that:

1. The rates of glass hydration for Yucca Mountain are not presently known.
2. The rates of glass hydration for already altered obsidian have not been determined.
3. The rates for authigenic mineral production have not been determined.

4. The diagenetic minerals which might form from the hydration process of volcanic glass have not been determined.

5. The DEA has not treated these topics in a comprehensive manner.

5. <u>Comment</u>: <u>Page 1, paragraph 3, lines 1 to 9;</u>
<u>Page 1, paragraph 4, lines 1 to 2 and</u>
<u>Page 2, lines 1 to 8; and</u>
<u>Page 2, paragraph 1, lines 1 to 5.</u>

"The author states that items (1) and (2) are contradictory and unsupported. It is difficult to understand how he arrived at this conclusion since he does not give specific page number references from the EA; perhaps he did not read the pertinent sections. Item (1), the current extent of volcanic glass, has been extensively investigated as part of the determination of the mineralogy of the units in Yucca Mt. This has been determined from surface and drilling investigations (pages 6-148 to 6-150, references therein, and figure 6-4)."

"Item (2), the probable fate of remaining glass, is not subject to direct determination and as such there is some uncertainty. However, the author's assessment that the EA states that: "zeolites could form from as yet unreacted glass during the transport of water from the repository" is incorrect in detail. Page 6-149 clearly states that although more zeolites could form from remaining vitric tuff, this is not a process that has occurred at a substantial rate during the Quaternary Period and it is not expected to be important in the next 100,000 years."

"There is no contradiction in these two statements, as the author suggests. There is still some volcanic glass within the repository block; that material could convert to zeolites under the proper conditions but the rate under the expected conditions is very small to zero." R. Aines (1985, pp. 1-2).

Response:

We note in the DEA on page 7-20 (previously cited in the response #4): "Alteration would require the presence of water and free silica, and the tuff would alter to zeolites, which would favorably affect the sorption of radionuclides." Might not the tuff also alter to other authigenic minerals such as smectites? Which zeolites - if formed - would produce favorable sorption of which radionuclides? As an example, would the actinides sorb in K-clinoptilolite? Or in any of the zeolites? How can the reviewer's (Aines') statements be accurate given the paucity of hydrogeochemical data in the vadose zone?

6. Comment: Page 2, paragraph 1, lines 5 to 8.

"The author states that it is not possible to determine the extent of radionuclide retardation which would result from the zeolitization of remaining glass; the EA makes no claims for retardation from this material." R. Aines (1985, page 2).

Response:

See: Response for Comment #5. See: DEA, pages 6133 and 7-29.

7. Comment: Page 2, paragraph 1, lines 8 to 15.

"The issue of the long term devitrification of remaining glass is interesting but the author has made no case whatsoever that the placement of a repository in Yucca Mountain would affect that devitrification in such a way as to make it occur to a substantial degree in 100,000 years. Even if it did occur, it is not shown by the author that it would have any negative effects on repository performance, as discussed on page 6-149." R. Aines (1985, page 2).

Response:

The task of the DOE Program is to provide an accurate and conservative assessment. A point has been raised questioning whether this has been accomplished - in truth - with respect to the DEA (not necessarily with respect to the actual DOE program). The DEA has stated that, and we reiterate:

1. Most of the available glass in the proximity of the repository horizon has been already hydrated; and authigenic minerals which could form have already done so.

2. The glass could hydrate if conditions regarding vadose and saturated zone water changed so that more water was available for reaction.

3. The tuffs, if they alter, would alter to zeolites which would favorably affect the sorption of radionuclides. This condition could exist due to heat-induced mineral alteration; and it is like-

> ly to be favorable or not to adversely affect the repository. (DEA, page 7-20).

On the basis of the work thus far published in the DOE program, one might contend that:

1. The rates of glass hydration have not been determined.
2. The rates of authigenic mineral production have not been determined.
3. The mineralogy which would form (if it did at all) from the hydration of volcanic glass has not been determined by the DOE program. The hydrogeochemical environment where reactions might take place has not been characterized.
4. The assumptions made in the DEA are not conservative, because they are based on assumptions rather than on data; and the assumptions are not well supported by the available literature.

Further, this apparent problem with the DEA could be rectified; such that, the document presented a conservative picture of the extant knowledge with respect to authigenic-mineral production. The expectation that glass will not hydrate given the presumed conditions does NOT address the issues raised. Finally, the DOE program as exemplified by the DEA has not recognized the technical data required for confident site selection at Yucca Mountain; consequently, there is a disappointing paucity of well-based technical information upon which to assess the probable suitability of the Yucca Mountain Site, as a High-Level Nuclear Waste (HLW) Repository.

8. Comment: Page 2, paragraph 2, lines 1 to 11.

"This review of glass hydration and alteration is outdated and incomplete with regard to possible processes that might occur at or near the water table in Yucca Mountain. Glass hydration studies underwent a revolution in the 1970's and 1980's which the author is unaware of. In particular it has been shown that hydrated glasses contain both water and hydroxyl groups and that diffusivities are directly correlated to viscosity which is a function both of the original state of polymerization of the melt and the depolymerization that results from hydroxyl incorporation (for good reviews see Stolper, 1982; Bartholomew, et al. 1980; Wolters and Werweij, 1980). R. Aines (1985, page 2).

Response:

Stolper (1982) provided an excellent study of water in silicate glasses with contents ranging from 0.06 to 6.9 weight percent. There were no ambient hydrated glasses studied. Stolper noted that:

1. "The linear relationship between water fugacity and the square of the mole fraction of total dissolved water observed for silicate melts at

low water contents and the observed deviations from this linear relationship at high total water contents can be accounted for by this hypothesis." Stolper (1982, page 1. Our underlining).

2. The hypothesis: "It is proposed that the speciation of water in silicate glass formed by rapid quenching from melt equilibrated at high temperature reflects that of the melt." Stolper (1982, page 1).

3. "The $Na_2Si_3O_7$ glasses studied by Takata et al. (1981) show similar ratios of these two species at given total water content, but the glasses studied by Bartholomew et al. (1980) have significantly higher ratios of molecular water to hydroxyl groups for total water contents greater than 4 weight percent. It is significant that the glasses studied by Bartholomew et al. (1980) were prepared at low temperatures (300°C) while those studied by Takata et al. (1981) and in this work were all quenched from much higher temperatures." Stolper (1982, pages 11-12. Our underlining.).

Cerling, *et al.*, (1985) found, and we quote:

"However, molecular water (H-O-H) is clearly dominant over hydroxyl groups (M-O-H) in this low-temperature alteration. The hydroxyl hydrogen makes from 10% to 25% of the total hydrogen content (as

> H_2O^+) in these glasses. This is in contrast to the findings of Stolper (1982) that the high-temperature glasses have more water present as hydroxyl water than as molecular water below 4 wt. % total water. Thus, the relative speciation of water in glasses is different at high and low temperature." (Cerling, et al., 1985, page 289).

The reviewer's (Aines') statement (1985, page 2, paragraph 2, lines 5 to 10) that:

> "In particular it has been shown that hydrated glasses contain both water and hydroxyl groups and that diffusivities are directly correlated to viscosity which is a function both of the original state of polymerization of the melt and the depolymerization that results from hydroxyl incorporation..."

does not adequately treat the subject matter. Based upon Cerling, et al., (1985), one may very well doubt whether the reviewer's (Aines') statement adequately characterizes low-temperature (ambient) diagenetic hydration, which is the subject matter of the reviewed report.

These and other works clearly indicate that both water and hydroxyl groups are contained in volcanic glass. Che-Kuang Wu (1980) concluded that: "The diffusion species of water, in silicate glasses under a saturated steam atmosphere at high temperatures is molecular water. (It is well known that the diffusion species of water in anhydrous glasses are H^+ and OH^-)." Che-Kuang Wu (1980, page 457). Scholtz (1966, Part Two, page 625) showed that as the alkali content is increased, diffusivity increased because the viscosity decreased. The mechanism of diffusion was stated as an auto-co-diffusion of OH groups and the alkali ions. Thus, in the simplest case, the diffusion is inversely proportional to the viscosity. These data are not a product of the reviewer (Aines'), 1970's - 1980's glass revolution rather they are a consequence of careful studies of many years of research and are reported during the 1960's.

In the subject report dated November 1984, we did not have the Cerling (1985) data to work from, as it had not yet been published. Nevertheless, on page 26, we stated:

> "In reality, the nature of the diffusing species has not been established. The model proposed here looks at alkalic ions, protons, and hydroxyl ions as the diffusing species. The potential for hydrogen atoms, hydrogen molecules, oxygen atoms, oxygen molecules, and water molecules is also significant and must be left open for consideration. In addition, if isotope studies are of interest, fractionations must be sorted out for each of the proposed reactions."

We still believe that the above is a fair and accurate statement as the information (citations) provided by the reviewer (Aines) do not characterize the behavior of the diagenetic transition of glass during hydration. The Cerling (1985) data has now, however, modified our conceptual view.

Further, the conceptual argument that the reviewer (Aines) provides is that the Stolper (1982) and related literature adequately and accurately depict the behavior of all (or most) glass reactions, including glasses undergoing hydration - during low-temperature (ambient) diagenesis. This position has been shown by the recent work of Cerling (1985) to be incorrect. Based upon the reviewer's (Aines') premise, he proposes that our report is out-of-date. However, the "revolution" in the 1970's and 1980's concerning glass hydration studies, which the reviewer (Aines) expounds upon, omits studies on perlitization and palagonitization, which of course, is the subject matter of concern. Additionally, both the reviewer's (Aines') and our report failed to note some excellent works on these topical areas during this period of time (See: Staudigel and Hart (1980); Dibble and Tiller (1981); Hawkins (1981); among others).

9. Comment: Page 2, Paragraph 2, Lines 11 to 15.

> "The alteration of glass has received a tremendous amount of scrutiny recently because of the obvious corollary between the long term behavior of nuclear waste glass and that of similar natural glasses." R. Aines (1985, page 2).

Response:

The alteration of waste glass was not a topic which was under discussion in the reviewed report. The issues raised by the reviewer (Aines), however, suggest that this topic should receive intensive scrutiny for the following reasons:

1. At low temperatures above ambience (300° C) the behavior of glass may not follow the Stolper (1982) speciation concept. Proposed near-field repository conditions do not admit to temperatures much higher than this.

2. Prior to reaching the higher temperature regimes and after going through temperature peaking the wasteform temperatures could and probably would be significantly lower than 300° C.

3. Temperatures may even approach the normal ambient geotherm at various times. Under these potential conditions, wasteform glass devitrification (*via* hydration) would probably not proceed under the

apparent mechanisms suggested by the reviewer (Aines). In the absence of the characterization of the wasteform under non-melt conditions, the existence of a reasonably comprehensive understanding of both the wasteform behavior and its ability to act effectively as a retardation barrier over the life of the repository is obviously questionable.

4. Boulos and Kyeidl (1972) found that neutron and gamma irradiation in the presence of hydrogen provided mechanisms for the introduction of hydration to glass (See: their figure 1, page 84). Thus radiation effects need to be considered in addition to the above (1 to 3) concerns. This includes the effects of radiation on the aqueous phases, in addition to alpha decay from the recoil nuclei and transmutation of the fission products.

5. McVay, et al., (1981) in their review of the behavior of waste glass state:

   a. Predictive models and/or results derived from simple silicate glasses should not be used to predict the behavior of complex borosilicate glasses.

   b. If air or nitrogen is present, radiolysis effects can produce nitric acid which greatly enhances elemental removal at all temperatures.

   c. The effects of pH on elemental leach rates are significantly different for simple silicate glasses than the borosilicate waste glass. The simple silicate glasses suffer large-scale attack in the basic pH range (significant above 8.5); whereas, the borosilicate glasses show poor acid resistance.

d. It is important not to extrapolate high-temperature results to lower temperature reactions for predictive purposes.

e. Leachate compositions can modify the pH and significantly affect the leaching. Leachates that have complexing anions can enhance actinide removal from glass; and solutions of high ionic strength can enhance alkali and alkaline earth removal from glass.

f. The leaching rate of elements of more than one valence state can be affected by the electron activity in the solution.

10. Comment: Page 2, paragraph 2, lines 15 to 22.

"The conclusions of the author are in general accord with more recent work with regard to the migration of alkali elements. However, further devitrification of glass in Yucca Mountain is only expected to occur in the presence of substantial amounts of liquid water, and as such the system considered by the author is oversimplified. The solubilities and reactivities of all phases present must be considered in such an interactive system." R. Aines (1985, page 2).

Response:

One would greatly appreciate knowing precisely which studies have shown that "substantial amounts of liquid water" are necessary to hydrate volcanic glass.

I. Friedman and R. L. Smith (1960) report that obsidian in the dry atmosphere of Egyptian pyramid tombs hydrate at a rate only slightly lower than obsidian from the contrasting moist tropical soils of Coastal Ecuador. One would normally presume that the vadose zone of Yucca Mountain contains at least, if not more, liquid and vapor water than do Egyptian Tombs.

The diagenetic hydration of obsidian at Yucca Mountain should theoretically proceed at rates dependent upon temperature, alkalinity of the vadose and saturated zone water, and the bonding chemistry of the glass. In a theoretical sense, Kastner and Stonecipher (1976) suggest: "If hydration of volcanic glass by either diffusion of water molecules or dissolution-precipitation is an essential primary step prior to zeolite formation, at low temperatures basaltic glass will be more susceptible to palagonitization and zeolite formations than rhyolitic glass will be to hydration, and zeolite formation from volcanic glass will be favored in higher pH environments." (Kastner and Stonecipher, 1976, page 214). Thus, in a relative sense for zeolite formation there should be less "reactivities and solubilities", as the reviewer (Aines) put it with the Yucca Mountain volcanic glass, than with sideromelane in an ocean setting. However, this does not lend credence to the concept that not much glass is expected to hydrate at Yucca Mountain. The authigenic production of clay minerals (dominantly - smectites), ferromanganese oxyhydroxides, and polymorphic varieties of quartz would not be expected to form under the same hydrogeochemical conditions as zeolites. Hay (1966), and Velde (1977), among others have adequately treated this issue. Thus, when the reviewer (Aines) states that the chemistry of the system needs to be taken into account, one can certainly concur. And simultaneously, one must be cognizant that this applies to the devitrification of the glass in the sense of hydration to produce perlitic material and the sequential production of authigenic minerals. The saturation conditions ("substantial amounts of water") as suggested by the reviewer (Aines) as the controlling parameter of glass hydration is, in fact, the oversimplification which consistently finds little if any support in the existing literature. Further, Scholze (1966, Part II, page 626) has shown that even carbon dioxide contents in glass can affect the reacting chemistries. Scholze concludes that: in glass, carbonate ions are present and that with increasing alkali content and decreasing temperature, the carbon dioxide solubility rises steeply. Under such conditions, carbonate formation is favored.

11. Comment: Page 2, paragraph 2, lines 22 to 23 and continued on page 3, line 1.

"If the author has evidence to suggest that devitrification will occur at a substantial rate under the present conditions, he should present it." R. Aines (1985, pages 2 - 3).

Response:

As DOE contractors have been the only bodies designated by DOE to obtain raw scientific data from Yucca Mountain to date or to design and execute investigative programs to address site specific issues, there have been no opportunities to obtain appropriate information as the reviewer (Aines) is kind enough to suggest. The recent (2 December 1985) Ninth Circuit Court of Appeals' decision, however, changes the entire picture; and we may now do our utmost to collect the appropriate field data necessary to address these questions. The glass hydration literature suggests that the glass at Yucca Mountain should undergo hydration as long as it is not encapsulated (e.g., that the glass is exposed). The reviewer (Aines) suggests that the glass can not hydrate unless there are "substantial amounts of water" (substantial is undefined). We are left with a situation which admits that there is a need to accurately define the reactions beyond the present state of assumptions, conceptual arguments, and expectations.

12. Comments: Page 3, lines 2 to 4.

"Page 12; The statement in line 7-9 is unsubstantiated in the text and is incorrect according to current understanding. A similar statement is made in line 24." R. Aines (1985, page 3).

Lines 7 - 9 (of subject report by M. Morgenstein, 1984).

"As the alkalic concentration increases, or the basicity of alkalis increases, the amount of bonded [OH] is increased and the diffusion rate of water into the glass is also increased." M. Morgenstein (1984, page 12).

Line 24 (of subject report by M. Morgenstein, 1984).

"As high hydroxyl concentrations favor zeolitization they also favor increase [HOH] diffusion rates." M. Morgenstein (1984, page 12).

Response:

Hay (1966) states:

> "The pH and salinity of subsurface water probably increase progressively with time through solution and hydrolysis of glass. When the pH and salinity are sufficiently high, glass probably dissolves at an accelerated rate, and zeolites rather than montmorillonite are formed." R. Hay (1966, page 82).

> "Alkalic, silica poor glass reacts more rapidly and at much shallower depths than does siliceous glass with circulating water. This fact is illustrated by the pattern of zeloitic alteration in land-laid nephelinite tuffs erupted from the Salt Lake group of craters on Oahu, Hawaii." R. Hay (1966, page 82).

Surdam and Sheppard (1976) state:

> "Table 1 suggests that the important compositional parameters in zeolite genesis are cation ratios, Si/Al ratios, and H_2O activity. All of these parameters will be greatly affected by changes in salinity and/or alkalinity. For example, experiment work by Mariner and Surdam (1970) indicated that the Si/Al ratio of zeolites formed by the hydration and solution of glass is related to the pH of the solution. Hay (1966) showed that the rate of solution of silicic glass increases with increasing salinity and alkalinity." Surdam and Sheppard (1976, page 155).

"Thus, the important chemical parameters during the glass-to-zeolite reaction are cation ratios, Si/Al ratios, and activity of H_2O, whereas the most significant parameters affecting the solution of glass are salinity and pH." Surdam and Sheppard 1976, page 155).

Other sources of data that suggest that both alkalinity of the glasses and the fluids as well as the pH of the fluids control the reaction rates are offered by: Dibble and Tiller (1981, DEA reference no. 915); Hawkins (1981, DEA reference no. 917); and Mariner (1971).

13. Comment: Page 3, lines 7 to 12.

"There is a very substantial difference between the hydration of a glass and the alteration of that glass to a material such as palagonite. In the latter case, a new phase forms from the reaction of water and glass under pseudo-equilibrium conditions, and the composition of the fluid may be expected to affect the reaction rate." R. Aines (1985, page 3).

Response:

The precise meaning and intention of both of these sentences are very difficult to determine. If the reviewer (Aines) is suggesting that hydration at high temperatures may add a slight quantity of water to sideromelane, without the accompanying reorganization of the structures (e.g., the formation of hydrated sideromelane which by definition is palagonite), then, one would perhaps suggest that this would have to take place in a regime equating to a glass-melt; however, this is not a topic under consideration in the report in question. If on the other hand, the reviewer (Aines) is suggesting that the glass is undergoing solution (etching of its surface), without the fixation of hydrated species within its structure, then, perhaps one would not call it hydration with confidence.

The topic matter of the reviewed report has been: the hydration of volcanic glass; the transition of that glass to perlite and/or palagonite; and the continued diagenetic hydration of those components to authigenic minerals. The fact that the reviewer (Aines) recognizes that the composition of the water can affect and probably does affect the rate of these reactions (sideromelane to palagonite) suggests that he (Aines) does agree with the contents of the report. However, the reviewer (Aines) suggests that water composition does not play an important role in the hydration of glass. If he (Aines) is referring to "dissolution" (or dissolution-precipitation) of glass, then, unfortunately, we can not be in agreement. D. B. Hawkins (1981) suggests that the glass-dissolution rate was affected by the carbonate concentration - the higher the carbonate concentration the faster the dissolution rates (Hawkins, 1981, page 336). "This effect may be due in part to the catalytic effect of the hydroxide ion (OH^-) on the dissolution of silica (Fyfe et al., 1978)." (Hawkins, 1981, pages 336 to 337). In his review, Aines states: "There is no evidence that hydroxyl concentration affects glass hydration rates of which the reviewer is aware; if such evidence exists the author should refer to it." The Hawkins (1981) paper is referenced in the DOE DRAFT ENVIRONMENTAL ASSESSMENT for Yucca Mountain (reference no. 917). Consequently, one must presume that the reviewer (Aines) is quite familiar with this reference. The reviewer (Aines) makes the distinction between the hydration of glass and the alteration of glass to form palagonite. He (Aines) suggests that during palagonitization the chemistry of the fluids can be expected to affect the reaction rate. Therefore, during the hydration of glass (Aines' non-palagonite or perlitic hydration of glass), the reviewer (Aines) suggests that the hydroxyl does not affect the rate; yet, the DOE literature of which the reviewer (Aines) should be familiar refutes his (Aines') arguments. In addition to this, Kastner and Stonecipher (1976), Hay (1966), Velde (1977), Surdam and Sheppard (1976), Ericson et al. (1976), Morgenstein and Rosendahl (1976), among others support the conclusions of Hawkins (1981).

AN OVERVIEW:

> "Nature fits all her children with some thing to do,
> He who would write and can't write, can surely review."
>
> James Russell Lowell.

The reviewer (Aines) is correct, in that, the report requires some support citations and a few updated references. This would certainly clarify the purpose of the report, and perhaps, make it more meaningful. The high temperature glass melt data is historically of interest and should have been included in the report. However, we feel that this may be somewhat beyond the scope of the report, at present. This is a failing of the author, not of the reviewer. However, it is, perhaps, myopic to conclude that this information predominantly explains the processes of the hydration of volcanic glass. Although the conceptual aspects of Aines' review are in fact eloquent, Cerling et al. (1985) have indicated that the melt data is nonconformable to the ambient temperature hydration behavior of volcanic glass. Others (e.g., Hay, 1966; Dibble and Tiller, 1981; Mariner, 1971) have shown that the hydrogeochemistry has significant bearing on the rates of glass reactions. And still others (e.g., Surdam and Sheppard, 1976) have indicated that the mineralogies produced during diagenesis are greatly dependent upon the hydrogeochemical components.

Finally, the DOE's DEA statements have not appropriately treated the important issues. Rather, the DOE's presentation has relied upon gross generalities, which are yet to be systematically supported by experimental evidence.

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