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**NATURAL GLASS ANALOGUES TO ALTERATION OF
NUCLEAR WASTE GLASS: A REVIEW AND
RECOMMENDATIONS FOR FURTHER STUDY**

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INTRODUCTION

The purpose of this report is to review previous work on the weathering of natural glasses; and, to make recommendations for further work with respect to studying the alteration of natural glasses as it relates to quantifying rates of dissolution. The first task was greatly simplified by the published papers of Jercinovic and Ewing (1987) and Byers, Jercinovic, and Ewing (1987). The second task is obviously the more difficult of the two and the author makes no claim of completeness in this regard. Glasses weather in the natural environment by reacting with aqueous solutions producing a rind of secondary solid phases. It has been proposed by some workers that the thickness of this rind is a function of the age of the glass and thus could be used to estimate glass dissolution rates. However, Jercinovic and Ewing (1987) point out that in general the rind thickness does not correlate with the age of the glass owing to the differences in time of contact with the solution compared to the actual age of the sample. It should be noted that the rate of glass dissolution is also a function of the composition of both the glass and the solution, and the temperature. Quantification of the effects of these parameters (as well as time of contact with the aqueous phase and flow rates) would thus permit a prediction of the consequences of glass-fluid interactions under varying environmental conditions.

Defense high-level nuclear waste (DHLW), consisting primarily of liquid and sludge, will be encapsulated by and dispersed in a borosilicate glass before permanent storage in a HLW repository. This glass containing the DHLW serves to dilute the radionuclides and to retard their dispersion into the environment. DHLW is temporarily being stored at the Savannah River Plant in South Carolina, the Hanford Reservation in Washington, and the Idaho National Engineering Laboratory in Idaho. This HLW is primarily from the production of nuclear materials. In addition to the defense waste, there is a small amount of civilian liquid HLW at West Valley, New York that will also be converted to glass before permanent storage. This civilian waste was created by some limited reprocessing of spent fuel rods.

The Nuclear Regulatory Commission regulations (10 CFR 60) state that the containment of HLW within the waste packages must be substantially complete for a period of 300 to 1,000 years after permanent closure of the geologic repository; and that the release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1,000 years following permanent closure, or as otherwise approved by the Commission.

The requirement to predict materials performance and the geological environment over long periods of time is unprecedented. Field and laboratory experiments are carried out for only short periods of time relative to the period over which a repository must maintain integrity. Consequently the prediction of radionuclide release rates from the waste form ("source terms") must be made by models that extrapolate data obtained in short-term experiments, such as glass leaching rates, to longer times. Such an extrapolation from tests lasting from months to years to predicting the consequences over 10,000 years must be demonstrated to be valid.

NATURAL ANALOGUES

Natural analogs in general can be useful in extrapolating short-term experiments to longer time frames. However it is doubtful that natural analogs can provide all the needed quantitative data to reasonably assure that a HLW repository will maintain its integrity over long periods of time. Nevertheless, studies of natural analogs should provide information regarding the reasonableness of projections about repository integrity. Natural analogs have been proposed for the glass waste form, metal containers, and for radionuclide movement. The latter natural analogs will only be briefly mentioned here as the focus of this report is on natural glass analogues to alteration of nuclear waste glass.

Metal objects such as naturally occurring pure copper, pure iron, and iron meteorites have been preserved in the geologic record for millions of years. Some iron meteoritic material has been extant since the time of the Egyptian Pharaohs in the form of a dagger with a blade resembling stainless steel. The blade is quite high in nickel and cobalt content and upon etching or corrosion reveals a Widmanstätten pattern that is unique to iron meteorites. This material is of particular interest owing to the present plans to store nuclear waste in stainless steel, also an iron alloy containing nickel.

The natural analog of radionuclide movement in the earth's crust that probably is the most similar to an actual nuclear waste repository is the uranium deposit at Oklo in Gabon (reviewed by Brookins, 1987). Other than at Oklo, natural uranium ores throughout the world yield values of near 0.71% ^{235}U . Oklo ores range as low as 0.3% ^{235}U . Evidence points to the ^{235}U at Oklo being consumed by neutron-induced fission when the deposit became a natural reactor about 2 billion years ago since there are also present fission products found associated with the depleted ore. Details remain unclear on how the ore at Oklo became high grade, enriched in ^{235}U to greater than 2-3%, and with a water content at between 12-16% - all necessary to achieve criticality. Water at much less than 12% would be too little to serve as an efficient moderator and water much greater than 16% would allow the neutron flux to become too diffuse. Natural fission reactors are therefore expected to be exceedingly rare and indeed only Oklo has thus far been found in the geologic record. Oklo is an uniquely important natural analog owing to the fact that actinides are produced during fissioning whereas most actinides (exceptions being thorium and uranium) are generally present only in trace amounts in nature. Furthermore the actinide elements have no non-radioactive elements that can serve as proxies as is the case for other elements such as strontium, where both radioactive and non-radioactive isotopes behave chemically similar. Thus other than introducing actinides into a repository, one of the few places to obtain actinide migration rates in a natural setting is at Oklo.

Natural glasses similar in bulk composition to that of the HLW glass are found in nature and have been subjected to conditions similar to that expected if the repository is flooded with water and the canisters are breached allowing groundwater to react with the glass waste form. Careful study of these natural analogues could provide the necessary link between theoretical models and short-term laboratory tests to provide information regarding the long-term integrity of the glass-waste form. In other words models developed to extrapolate data obtained in short-term experiments could be validated by careful observation of the geologic record which has preserved information for time frames from hundreds to millions of years. This long-term information is not obtainable from laboratory experiments, in situ tests, or,

presently, *ab initio* calculations. Geochemical modeling codes such as Path (R. G. Berman and T. H. Brown, pers. comm., 1988), Gt (C. Bethke, pers. comm., 1988), and EQ3/6 (Wolery, 1979) are not presently capable of predicting the changes resulting from rock-water-glass interactions owing to the restrictions imposed by an inadequate data base, particularly in regards to the thermodynamic properties of relevant mineral phases and rate constants for reactions, and an inadequate conceptual model to account for components in the glass. In addition the coupling of hydrologic flow with chemical reactions (reactive transport) has not been successfully achieved.

NATURAL GLASSES

A variety of glasses are not man-made but have formed naturally: basaltic glasses, rhyolitic glasses, lunar glasses, meteoritic glasses, and tektites (Ewing, 1978; Ewing and Haaker, 1979) and these glasses have ages from months to millions of years. Samples of meteoritic glasses are relatively rare and albeit interesting will not be discussed further in this report.

Tektites occur as glassy bodies, bottle-green to blackish, and range in size from fractions of a millimeter to tens of centimeters in diameter. They generally are found strewn across wide areas up to 10,000 km wide and range in age from a few hundreds of thousands of years to more than 35 million years. Their origin is thought to be associated with the impacts of giant meteorites. It is rare that any alteration, hydration, or devitrification of tektites is noted. This is the case even for tektites observed in older sediments recovered from deep-sea cores and which were subjected to seawater for periods up to millions of years. This durability is generally attributed to the high silica content (> 65 wt %), high silica + alumina (usually > 80 %), low alkali and alkaline earth oxide content, and low water content (< 0.01 wt %) (Ewing and Jercinovic, 1987). However, there is a class of tektites that are much lower in silica content. Bottle-green tektites have compositions that extend to 50% silica and lower (Glass, 1972) which is in the range of silica composition proposed for high-level nuclear waste glass. The average depth of corrosion of tektites from the deep oceans was found by Glass to be about 2 ± 2 micrometers for tektites of 72% silica to about 14 ± 5 micrometers for tektites of 54 % silica. The tektites with low silica values were found only in areas with ages of less than one million years. Barkatt et al. (1984; 1986) conducted leaching experiments on these glasses and found that the rates were 30 times greater in deionized water compared to that in seawater and that extrapolated laboratory tests are in approximate agreement with field observations of tektite corrosion. Barkatt's group (see Maggs, 1988) have proposed that magnesium serves to protect the glasses from rapid corrosion. Crovisier and Honnorez (1988) have questioned the role of magnesium in reducing corrosion rates and have stated that it is not presently possible to conclude that any one factor will lead to a decrease in glass corrosion.

Lunar glasses are of interest as they have remained stable for up to 4 billion years and show no traces of alteration or crystallization (Roedder and Wieblen, 1971). The utilization of lunar glasses for natural analogue studies is precluded owing to the high cost of field collections. Nevertheless, the observed stability of lunar glasses substantiates the notions that glasses can disappear in the natural environment by two mechanisms:

- Glasses can react with water which in turn increases the concentration of glass components in solution and also produces secondary non-glassy mineral phases

such as clays and zeolites - a process that some workers term glass dissolution or corrosion.

- Glasses can convert to a more stable crystalline state - a process known as devitrification.

In the case of an anhydrous environment, it is expected that glasses would be subject only to devitrification over time. Under anhydrous conditions and at low temperatures (<25°C), the time required for devitrification exceeds the age of lunar glasses by many orders of magnitude (Marshall, 1961). At high temperatures Rutley (1886) demonstrated that natural glasses could be readily devitrified by heating a sample of obsidian from Ascension Island. Crystals up to 30 microns grew in less than a month when the obsidian was heated to between 850°C and 1100°C.

Rhyolitic glasses typically contain approximately 70 wt% silica. Although these glasses have been studied relatively intensely (e.g., Marshall, 1961; Friedman and Trembour, 1978; Dickin, 1981; Zielinski, 1979; and White, 1983), they are of presently less concern with respect to the focus of this report owing to their high silica composition. We could however learn more regarding the overall compositional dependency of the glass on corrosion rates by further study of these siliceous glasses.

It has been suggested that basaltic glasses could serve as natural analogues for nuclear waste glasses (e.g., Ewing, 1978; Ewing and Haaker, 1979; Adams, 1979; Zielinski, 1980; Dickin, 1981; Bates et al., 1982; Allen, 1982; Plodinec, 1984; and Malow, et al., 1984) owing to similar compositions between the glasses and the observed increasing alteration of the natural glasses with time. Two recent studies on basaltic glasses stand out: the JCC study of basaltic glasses from Iceland and the deep sea (Jercinovic and Ewing, 1987) and the Argonne study of basaltic glasses (Byers, Jercinovic, and Ewing, 1987). Following a discussion of palagonitization and secondary mineralization, these two studies will be reviewed in some detail as they represent the most thorough work published to date regarding the dissolution rates of basaltic glass and how this relates to the glass waste form for high-level nuclear waste.

PALAGONITIZATION

W. Sartorius von Waltershausen (1845) coined the term palagonite when he described a brown material in the groundmass of a tuff from Palagonia in Sicily. Initially it was used to describe a wide range of scales of material from deposits (Pjetursson, 1900) to that on a microscopic scale such as sideromelane (basaltic) glass (Peacock, 1926; Peacock and Fuller, 1928). Palagonite is now used to describe the reddish to yellow-brown, gel-like material that is the alteration product of sideromelane glass (Nayudu, 1964; Hay and Iijima 1968a, 1968b; Allen et al., 1981).

As reviewed by Jercinovic and Ewing (1987), the physical and chemical properties of palagonite have been studied by numerous researchers (e.g., Hay and Iijima 1968a, 1968b; Honnorez, 1972; Jakobsson, 1972; Singer, 1974; Furnes 1978, 1980, 1984; Furnes and El-Anbaawy, 1980; Allen et al., 1981; Staudigel and Hart, 1983). The glass-palagonite contact is generally sharp (Hay and Iijima, 1968b; Geptner, 1978), characterized by pitted or etched glass surface (Hay and Jones, 1972; Allen et al., 1981), and sometimes exhibits penetration by microchannels (Staudigel and Hart, 1983) which may be the same as the "rootlet intergrowth" observed by Geptner (1978). The refractive index of palagonite ranges in values from 1.46 to 1.70 (Hay and Iijima

1968a, 1968b; Stokes, 1971) and the specific gravity of palagonite ranges in values from 1.93 to 2.42 (Hay and Iijima 1968a, 1968b; Furnes, 1978).

Mechanisms proposed for palagonitization include: solution precipitation, or hydrogen-ion metasomatism, (Hay and Iijima 1968b; Hay and Jones, 1972), hydration (Peacock, 1926; Morgenstein and Riley, 1974), and solid-state diffusion accompanied by hydration (Moore, 1966). Palagonitization has been observed over a wide temperature range and time scales from almost instantaneous to thousands of years. For example, Bonatti (1965) observed immediate palagonitization associated with magma eruption at high temperatures, Hay and Iijima (1968a, 1968b) observed palagonitization at low temperatures associated with sediments and that the palagonitization took place over thousands of years, and Jakobsson (1978) and Jakobsson and Moore (1986) observed palagonitization on Surtsey volcano at temperatures from 40°C to 150°C a few years after eruption. Thus as expected the rate of palagonitization increases with temperature which is in agreement with experimental studies (Moore, 1966; Moore, et al., 1985). Jercinovic and Ewing (1987) reached the following conclusions from reviewing the general characteristics of palagonite that are evident from published data (e.g., Bonatti, 1965; Hay and Iijima 1968a, 1968b; Hay and Jones, 1972; Muffler et al., 1969; Honnorez, 1972; Jakobsson, 1972; Melson, 1973; Singer, 1974; Furnes, 1978, 1980, 1984; Juteau et al., 1979; Furnes and El-Anbaawy, 1980; Ailin-Pyzik and Sommer, 1981; Allen et al., 1981; Staudigel and Hart, 1983; and Jakobsson and Moore, 1986):

- palagonitization is not a simple hydration process and is a non-isochemical (metasomatic) process;
- palagonite composition varies from one occurrence to another; and,
- palagonites of chemically different composition can be derived from chemically and physically similar glasses, indicating the importance of solution composition, temperature, flow rate, etc.

In general most elements are depleted during palagonitization with only minor losses observed in most cases for aluminum, iron, and titanium. Concentrations of elements that form relatively insoluble substances and are enriched in the glass phase are found in greater abundance in the palagonite formed from such a glass. For example, glasses that are rich in iron and titanium form palagonites that are more concentrated in these elements than are palagonites formed from glasses relatively depleted in iron and titanium (Furnes and El-Anbaawy, 1980). Palagonites produced in a marine environment can be enriched in more mobile elements such as potassium and sodium (Andrews, 1977; Baragar et al. 1977; Bonatti, 1965; Melson, 1973; Pritchard et al., 1978; Juteau et al., 1979; Staudigel and Hart, 1983; and Scarfe and Smith, 1977). Jercinovic and Ewing (1977) have summarized that the composition of palagonite results from three factors:

- the chemical composition of the glass and its physical properties;
- the chemical composition of the aqueous solution [and the attendant temperature and pressure under which the palagonitization occurs]; and,
- the duration during which alteration of the glass takes place - this is particularly important in systems where the water-rock ratio is extremely small which in turn will greatly effect the composition of the liquid phase.

Rates of palagonitization have been estimated in "fresh" water and seawater at temperatures from 5 to 50°C in the natural environment and range in value from 3 to 30 microns/1000 years (Moore, 1966; Morgenstein and Riley, 1974; Hekinian and Hoffert, 1975; Moore, et al. 1985; Grambow et al. 1985; and, Jakobsson and Moore, 1986). Experimental palagonitization studies have also resulted in estimates for rates of palagonitization (Furnes, 1975; Malow et al., 1984; Crovisier, 1985; and Crovisier et al. 1986) which are somewhat higher than estimates from the natural environment - up to 180 microns/1000 years

Furnes (1975) observed in his experimental work over 14 months that the rate of palagonitization increases dramatically with temperature and was not linear with time. For alkali basalt glass the rate was about 0.3 microns/month for the first 10 months at temperatures from 20 to 70°C, and increased to 3.3 microns/month after 10 months for temperatures greater than 70°C. Studies of the Surtsey cores (Jakobsson and Moore, 1982, 1986) have also indicated the rapid increase in palagonitization with an increase in temperature. At 40°C the rate at Surtsey was 15 microns/1000 years whereas at 120°C the rate doubled. Moore et al. (1985) made similar observations at Hawaii where they found that the rate increased 1.8 times for a temperature increase of 100°C.

As noted by Jercinovic and Ewing (1987), if one assumes a rate of 2 microns/1000 year as being a good estimate for palagonitization, centimeter-thick glassy rims on a pillow basalt would be completely palagonitized in less than five million years; and hyaloclastites with an average grain size less than 2 mm would be completely palagonitized in less than one million years. There are, however, abundant observations that fail to corroborate these estimates. For example fresh glass is found in drill core samples of much greater age: in Deep Sea Drilling Program (DSDP) Hole 408 glass was found that was 20 m.y. (Luyendyk et al. 1978); DSDP 407, 35 m.y., (Luyendyk et al., 1978); DSDP 382, 70 to 80 m.y. (Tucholke et al., 1979), and DSDP 417 and 418, 105 to 110 m.y. (Donnelly et al., 1979). In addition there is unaltered glass found in the Miocene Frenchman Springs Flow of the Wanapum Basalts, 12 to 14 m.y., in the Columbia River Basalt Group (Jercinovic, Ewing, and Byers, 1986), in submarine-produced hyaloclastics, now subaerially exposed, in the Hound Island Volcanics that are about 200 m.y. (Muffler, et al., 1969), and in the 340 m.y. Lahn Dill deposits (Schmincke and Pritchard, 1981). Therefore one cannot assume a singular, linear alteration rate to explain the persistence of glass through geologic time for all glasses. Schmincke et al. (1978) postulate that a sealing process has preserved glasses in the deep ocean sediments. Muffler et al. (1969) suggested that calcite precipitation has protected the glasses found at the Hound Island volcanics from alteration. Keith and Staples (1985) observed that sealing could also account for the preservation of glasses that are 35 to 55 million years old found in the Siletz River volcanics of western Oregon.

SECONDARY MINERALIZATION

Zeolites, smectites, and calcite are the most common minerals associated with palagonitization. Analcime, phillipsite, and chabazite are the most commonly observed zeolites (Jercinovic and Ewing, 1987) and it is likely that the particular zeolite formed is a function of glass composition, fluid composition, and temperature. Mordenite, heulandite, stilbite, and epistilbite are found in tholeiite basalts (Kristmannsdottir, 1978) whereas chabazite, thomsonite, and mesolite-scolecite are

found in the less siliceous olivine-tholeiite basalts. Mordenite, heulandite, stilbite, epistilbite, chabazite, thomsonite, and mesolite-scapolite are found where temperatures were less than 100°C whereas they are replaced by laumontite in the temperature interval of 100 to 120°C (Kristmannsdottir, 1978) and all zeolites disappear above 230°C (Tomasson and Kristmannsdottir, 1972).

Chlorite, montmorillonite, Fe-saponite, and nontronite are the most commonly observed clays associated with palagonitization. Nontronite, as well as celadonite, appear to form at low temperature in the deep oceans and under oxidizing conditions (Kurnusov et al., 1982) whereas saponite forms at higher temperatures under non-oxidative conditions (Stakes and O'Neil, 1982). Chlorite is found in only those glasses that have been hydrothermally altered (Tomasson and Kristmannsdottir, 1972).

JCC STUDY OF BASALTIC GLASSES FROM ICELAND AND THE DEEP SEA

This study (Jercinovic and Ewing, 1987) focused on the alteration process and products from natural basaltic glasses. Amorphous leached layers were examined using analytical electron microscopy (AEM) which revealed that the leached layers are not completely amorphous, but contain a relatively high proportion of crystalline phases, primarily as smectite-type clays. In addition there were found channels through the layers which provide access for solutions to react with the fresh glass/alteration layer interface. Jercinovic and Ewing conclude that glasses are not "protected" from further reaction by the formation of a surface layer.

Corrosion rates were not readily extracted from the examination of natural samples owing to the fact that the contact time of the solution with the glass was difficult to establish accurately. Nevertheless the authors concluded that there was evidence that corrosion proceeds at two rates: (1) an initial rate, k^+ , in silica-undersaturated environments and (2) a long-term rate, k , in silica-saturated environments. This evidence is based on the long-term survival of glass once buried. Pore fluids in buried oceanic sediments approach saturation with respect to silica. Jercinovic and Ewing felt that this was significant as it supported the fundamental premises of the GLASSOL model (Grambow, 1987), but also supports the notion that there is no change in corrosion rates over long time periods. The long-term corrosion rate estimated for natural basalt glasses exposed to sea water on the ocean floor was a minimum of 0.01 microns/1000 year.

Basaltic glasses from submarine deposits near the coast of Iceland and from subglacial-volcanic deposits were analyzed for alteration. Palagonite was the main alteration product regardless of the environment or age of the sample, and forms rinds on the glass surface as a reddish, vitreous product. It is suggested by petrographic examination that palagonitization is isovolumetric, with the possible exception of some deep sea palagonites that are relatively concentrated in iron and depleted in silica. The subglacial-volcanic palagonites form a rind that is composed of colloidal material that could be natronite. Jercinovic and Ewing observed that palagonite appears to be amorphous by Scanning Electron Microscopy (SEM) and optical microscopy whereas Analytical Electron Microscopy (AEM) detects crystallinity and microstructure and zoning of these features as well as zoning in chemical composition within the palagonite rinds.

Palagonite formed in seawater is enriched in alkalis and iron compared to palagonite formed in fresh water. The potassium enrichment for seawater palagonites suggest that they may be more like an illite. There is some titanium depletion, especially in deep sea samples, relative to the parent glass for which the cause is presently not known. No major compositional difference was found between samples on the ocean floor collected by dredging or samples from oceanic drill cores suggesting that the drill core glasses may have undergone palagonitization in the open ocean before burial. Nevertheless, there were found compositional gradients in the rinds which were more strongly developed in the palagonites that formed zeolites and were low in aluminum. The calcium and aluminum concentrations increase toward the interior and later-formed parts of the rinds with iron and magnesium concentrations decreasing correspondingly. The gradients were thought to be due to the varying solution composition, such as pH, as hydrolysis of the glass takes place in a closed system. There was also found some zoning where zeolites were not associated with the rinds, but although similar in pattern the zoning was lower in magnitude.

Jercinovic and Ewing observed that aluminum must be depleted in the rind relative to the parent glass in order for zeolites to form. Zeolites in general form in closed or nearly closed systems when flow rates are slow and following high reaction progress suggesting a high pH. It was observed that relatively thick rinds result from high dissolution rates at correspondingly high pH, or if the glass was subjected to very long exposure to the solution. If significant aluminum is leached during palagonitization accompanied by a large water/glass ratio, zeolites may not form. It was found that saponite will precipitate before zeolite if the release rate of magnesium + iron exceeds that of calcium during leaching. Although phillipsite is not common in zeolitized Iceland samples, it is present in some oceanic palagonitized glasses. The dominant zeolite in all the subglacial-volcanic glasses was chabazite, and, for all glasses, analcime was observed to be the last zeolite to form owing to the consumption of calcium and potassium by the earlier-formed zeolites in a closed system. Little mass loss occurs when zeolites are formed based on mass balance calculations and elements required to form these authigenic phases probably come entirely from glass dissolution. There was observed a net mass loss of silicon, magnesium, calcium, sodium, and potassium if zeolites or clays do not form.

Jercinovic and Ewing concluded that the rind thickness of the palagonite does not correlate with age owing to the differences in time of contact with the solution compared to the actual age of the sample. As was pointed out above, the rates of palagonitization will also vary as a function of pH and silica concentration in the solution. Minimum palagonitization rates were estimated to be between 0.01 to 1 microns/1000 years and there were not any consistent differences in rind thickness between dredge and drill core samples despite the differences in silica concentrations in the interstitial waters compared to that in the sea water.

ARGONNE STUDY OF BASALTIC GLASSES

The alteration of natural basalt and nuclear waste glasses was studied by the University of New Mexico and Argonne National Laboratory (Byers, et al., 1986). Workers at the University of New Mexico characterized the reaction products associated with a variety of natural basaltic glasses and described in detail the alteration process of fresh glasses to those coated with authigenic materials. ANL conducted experiments attempting to mimic the natural alteration process using synthetic glasses of basaltic composition. Where the glasses were subjected to water vapor at temperatures above 90°C there was found a similarity in alteration to that of

the natural glasses altered in the natural environment. In addition a similar alteration process was found when synthetic nuclear waste glass (SRL 165) was subjected to similar conditions. The conclusion was that both the natural alteration of basaltic glass and water-vapor experiments can be used as an analogue in assessing the durability of HLW glass under conditions as could be found in a repository.

Samples of basaltic glasses collected included those altered by seawater, and fresh water (lakes, streams, groundwater, and glacial melt). The glass occurred as rims on pillow basalts or as vitric tuff, agglomerate, breccia, or tephra deposits (hyaloclastite). Ages of the samples ranged from recent to 350 million years and glass compositions ranged in silica content from 45 to 55 wt % and alkali oxide content between 2 and 5 wt %. Both the glasses and the alteration products were analyzed with the aim of determining the physical, mineralogical, and chemical results of palagonitization. The results of these studies showed that the glass alters to first an amorphous reaction layer (palagonite) followed by some degree of secondary mineral formation. It was difficult to correlate the amount and rate of palagonitization with specific geologic conditions, but it was found that the reaction progress is a function of both time and temperature. General conclusions reached by Byers et al. include:

- All samples were palagonitized to some degree regardless of environment or age and palagonite was found to replace basaltic glass on exposed surfaces such as pillow surfaces, grain edges along fractures, and vesicles. In some cases the only secondary alteration product observed was palagonite, which compositionally resembles smectite - Fe-saponite or nontronite.

- Si, Mg, Ca, Na, K, and Mn are depleted in the palagonitic rind relative to the glass in fresh water settings whereas in seawater environments the rinds are enriched in K and total alkalis. Generally, the titanium and iron are immobilized in the rinds as sparingly soluble oxides. Al can be depleted in some rinds and enriched in others, but depleted Al rinds are often accompanied by silica enrichment relative to the glass composition.

- The most-common alteration minerals are clays which occur as a replacement of the palagonite and as cement. The clays observed are smectite-kaolinite clays and Fe-rich smectites. Fe-saponite is found in samples of all environments and ages and is the most commonly found clay. Although clays are found in samples that are relatively little palagonitized, where there clearly is a contribution of material from the solution or non-glass sources. In general the composition of the clays represent the relative proportions of material leached from the glass. The next most common authigenic minerals are zeolites and calcite. The compositions of the zeolites reflect the proportions of elements released during palagonitization or that remaining after the formation of clays. The formation of zeolites does not appear to be directly related to the amount of glass reacted owing to the fact that if Ca and Al are not dissolved during the palagonitization process or when clay replaces palagonite, zeolites do not form.

- The rates for low-temperature alteration of glass which were estimated from the correlation of thickness and age for rinds from samples collected in subglacial volcanoes in British Columbia and Iceland are 3 to 10 micrometers/1000 years. These rates were considered to be minimum rates as the actual exposure time are not known.

Basaltic glass that was reacted in water vapor at elevated temperatures ($>90^{\circ}\text{C}$) formed first an amorphous layer and then secondary minerals formed which included a smectite-type clay, analcime, gyrolite, thomsonite, aragonite, and reyerite. These same secondary phases had been previously identified in natural samples. There was extensive depletion of alkalis: relatively high depletion of Si, Al, and Ca; and, immobilization of Ti and Fe - all consistent with natural palagonitization.

When the SRL 165 glass was reacted with hot water vapor, the results were similar to that of the basaltic glass with the exception that the rate of reaction for the SRL 165 glass was greater than that for the basaltic glass. Despite the differences in rates, the ANL group concluded that the same processes that control the vapor-phase alteration of the SRL 165 glass are also the processes that control the vapor-phase alteration of the basaltic glass owing to the similarity in alteration products and their compositions.

Byers et al. concluded that natural glass alters first to palagonite and then to a series of authigenic minerals. However the correlation of palagonitization and geologic conditions was difficult to generalize because of the variability of the environmental conditions with time. There was observed a similarity in the alteration of natural basaltic glass, synthetic basaltic glass, and nuclear waste glass (SRL 165) and therefore the natural alteration of basaltic glass can be used as an analogue for assessing the performance of HLW glass insofar as placing approximate limits on the extent of reaction and to model alteration as a function of environmental conditions. It was also concluded that the laboratory tests involving the reaction of HLW glass with water vapor at high temperatures can serve to simulate the effects of long-term subaerial alteration that would be expected for these glasses in a repository.

RECOMMENDATIONS FOR FURTHER STUDY

The search for a better scientific understanding of the dissolution of natural glasses should continue by the employment of the three approaches utilized in previous studies:

- inquiry by careful observation of natural processes in the field;
- inquiry by physicochemical *experimentation* in the laboratory and in situ; and,
- inquiry by *theoretical* modeling.

It is not expected that any one of these approaches can fully explain the details of a system or process. Nevertheless, scientific inquiry by means of such a tri-pronged attack generally exceeds the sum of the individual components in producing meaningful results.

FIELD STUDIES

Two different types of field studies are proposed:

1) **Search for well-constrained natural analogues.** This work would place emphasis on the collection of well-constrained samples with respect to age, homogeneity of the glass, constant composition of fluid with time, total immersion, etc. This probably can't be accomplished by a review of the literature, but will entail considerable field work and in all likelihood drilling activities. For example, sample quenched flows in Hawaii for datable carbon content as well as an eye towards constancy in fluid flow and composition over time, glass homogeneity, etc.. Owing to the proposed composition of the waste glass, this study will focus primarily on natural basaltic glasses as they are similar in composition to that of the waste glass. It will be required to chemically analyze the unaltered glass, fluid, and the composition and relative amounts of alteration products. The latter will require considerable development work in analysis owing to the fact that present state-of-the-art methods are generally not capable of identifying phases in extremely fine-grained or cryptocrystalline material.

It has been proposed (W. L. Bourcier, pers. comm., 1988) that geothermal holes drilled near Kilauea could be studied with respect to natural analogues for glass dissolution. The fluid phases have been collected and analyzed in some detail by Thomas (1987), but relatively little has been done in characterizing the solid phases which include altered basaltic glass. Bottom hole temperatures range from 320-370°C and alteration minerals include zeolites, clays, chlorite, and epidote. Following characterization of the solid phases, Bourcier points out that geochemical modeling could be validated by correctly predicting the observed paragenesis. Bourcier also notes that there are some problems with the Kilauea site including the lack of age control on the lava flows and the inability to correlate fluid samples with specific rock horizons.

It has been proposed (H. F. Shaw, pers. comm., 1988) that the collection of glass formed by underground nuclear tests could prove useful. Some tests were performed below the water table and some have been subjected to water interaction over 20 years. There are three major drawbacks to this idea: (1) sampling would involve relatively expensive drilling costs, (2) the glass could be too rich in silica to be directly compared to the proposed HLW glass composition, and (3) the thermal history is complex in that there was a high-temperature period following the detonation of the nuclear weapon followed by a cooling period and finally a period of ambient temperatures. Most of the glass alteration would have presumably taken place during the higher-temperature period. Nevertheless, we would know the composition of the flowing fluid would have been constant and that the temperature of the system has not changed after the glass cooled - putting some constraints on these samples where it might be difficult to do likewise for natural basaltic samples. In addition, radionuclide migration could be monitored.

It could also be useful to extend the work of previous workers in regards to field collections of medieval, man-made glasses. Samples would be sought out that vary in composition, age, and that were subjected to varying environmental conditions. This work could provide a crucial time link from laboratory tests of a year or so duration to basalts that are hundred of thousands to millions of years old.

2) Quantitatively evaluate the survival rates of natural glasses in the environment. I noted that a histogram of observations of 245 dated volcanic glasses in the western United States is exponential in shape with the vast majority of glasses being quite young, less than 3 million years old (Ewing, 1979). If the following rather, broad assumptions are made:

- The observations are proportional to the actual amounts of glasses of different ages.

- Glasses disappear solely by burial or dissolution.

- Devitrification is not a major destruction mechanism for glass owing to the very slow diffusion rates to form microcrystallites at low temperatures.

- Vulcanism and the amount of glasses produced has been constant over this time period in this region.

The decay curve of glass dissolution would represent a dissolution rate for geological-averaged-over-time conditions for "average" glass compositions. Or, one could view this curve as representing the probability of finding glasses of certain ages, or the probability of glasses surviving for certain time periods. Data to be collected to put this idea on firm footing would be the production and present abundance of volcanic glasses over the past 50-100 million years.

EXPERIMENTAL STUDIES

Two broad types of experimental studies could augment and complement previous experiments on glass dissolution conducted over the past 50 years:

1) Experimental studies that provide quantitative information on the dependency of glass dissolution on the composition of the glass. At present there are few well-constrained experiments regarding the dependency of glass dissolution on the composition of the glass. It may be that geochemical modeling will not be possible without such a data set owing to the fact that such compositional data will probably be required to build realistic theoretical models. In addition should the composition of the proposed HLW glass change markedly, compositional data will allow long-term predictions of glass durability for the new glass composition(s) without having to repeat experiments for each composition.

2) Experimental studies on the dissolution of natural basaltic glass. It will be required to conduct further hydrothermal alteration experiments on unaltered natural basaltic glass and to identify the composition, and relative amounts of alteration products as well as monitor the composition of the solution. These experiments are necessary to assess the suitability of accelerated (e.g., higher temperature, high or low pH, large water/glass ratios, high glass surface areas, etc.) tests in modeling long-term dissolution rates.

THEORETICAL STUDIES

Two broad areas of theoretical studies are proposed:

1) Geochemical modeling. One approach to studying the dissolution of glass is to experimentally determine the rates of dissolution as a function of various

parameters: pH, temperature, aqueous silica concentration, etc. Although this approach may be useful to guide theoretical modeling, it is clear that this approach cannot be used alone to make long-term predictions of glass dissolution rates. Large, multi-component geochemical systems are simply not amenable to analysis based on a few variables. All variables, in general, must be considered simultaneously.

Improvements in conceptual models for glass dissolution must be made for any meaningful modeling computations. For example one model is that the early stages of glass dissolution is characterized by rapid dissolution of alkalis from the surface owing to activated surfaces and a ready supply of the more soluble components of the glass at the surface. This is followed by the buildup of a palagonitic rind layer (diffusion controlled) until the rind thickness becomes constant and dissolution is then controlled by transport through the rind. Transport across this rind becomes more difficult and glass dissolution rates decrease. Questions to be answered to substantiate this model includes:

- Is a constant thickness rind layer achieved with time observed in experiments or in natural glasses?
- Does the rind layer become increasingly impervious with time?
- What is the interrelationship between diffusion in the glass and mass transport across the rind layer?
- Is diffusion an important process in the rind layer, across the rind layer at later stages of dissolution maturity?
- Can the early gel-like rind layer be characterized thermodynamically?

It is clear that the rate of interaction between a glass and a fluid depend on several physical and chemical parameters. The composition of the glass and fluid, the surface area of the solid, the water-rock ratio, and the temperature and pressure are obvious candidates to consider regarding dissolution rates. Much has been made of the fact that glass is not a stable phase and is somewhat different from other solids that are weathered on the earth's surface. In fact all igneous and metamorphic and most sedimentary rocks in the near crustal environment are in disequilibrium with their surrounding environment and thus are also not stable phases. It is thus conceivable that much is to be learned regarding glass dissolution by looking at the work of others who have studied mineral-water reaction rates (e.g., Wood and Walther, 1983).

In 1983, Walther and Wood contended that the rates of mineral dissolution at high temperature for virtually all minerals from orthosilicates through tectosilicates dissolve with essentially the same rate constant under near-neutral conditions when the rate constants were normalized to gram-atoms of oxygen per square centimeter per second which translates to multiplying each molar rate by the number of oxygens per mole. For glasses we would have to determine how to normalize the experimental measured rates of dissolution. It is apparent that, in general, the rates of dissolution are less for glasses that contain oxide components with a greater proportion of oxygen. For example silica-rich glasses dissolve more slowly than glasses rich in alkali or alkaline earth oxides.

At 25°C, Walther and Wood (1986) propose that there is a relationship between the reaction rate and the relative entropies per unit volume or gram atom of oxygen. It was observed that minerals with high entropy per unit volume (S^0/V^0) dissolve more rapidly than those with low entropy per unit volume. As above the rates were normalized to a constant gram atom of oxygen basis. Although the correlation observed by Walther and Wood was far from perfect, the approach may be useful in interpreting the dependency of glass dissolution rates on the composition of the glass. As interpreted by Walther and Wood, their correlation of reaction rates with entropies is based on the fact that different silicates produce different concentrations of the activated surface complex and that the most unstable silicate (that with the greater entropy) produces the more abundant activated complexes. Thus the more unstable minerals will dissolve at higher rates than the more stable minerals because they produce greater concentrations of activated complexes on the mineral surface. Glass components with lower entropies per volume, in general dissolve more slowly than those components with higher entropies per volume with a few exceptions (e.g., MgO seems "out of order").

A comparison of EQ3/6 (Wolery, 1979) calculations involving 91 day leach waters from SRL-165 glass and glass of basaltic composition indicated general agreement. The same components were chosen as those by Bourcier (1988). Components were chosen similar to that of "hydration theory thermodynamic model" of Paul (1977), but picked so that they had the same coordination number of the metal as that in the glass. Metamorphic phases such as andalusite and wollastonite were thus included despite the fact that these phases are not expected phases to crystallize from melts of basaltic composition. In addition preliminary calculations were made involving J-13 water and basaltic glass and SRL-165 glass at 90 and 150°C using Gt (C. Bethke, 1988). Again there was general agreement between the types of glasses. In this case oxides were chosen as solid components. Despite these encouraging exploratory calculations, there are problems to resolve in modeling glass dissolution which includes:

- How does one choose components for the glass? Are simple oxides as components realistic, or metamorphic phases? Perhaps CIPW normative phases would be more realistic. Or phases that would be expected to crystallize out of glass of basaltic composition. It could be fruitful to look into following an approach similar to that used by modelers of high temperature crystallization from a melt (e.g., Ghiorso, 1987; Berman and Brown, 1987), but in this case reacting the glass with a fluid phase at lower temperatures.

- Are the chosen components part of a solid solution and if so how is it modeled?

- How does one account for the differing rates of dissolution for these solid components?

- Are there sufficient thermodynamic data available on the components in the glass, secondary stable phases formed, and unstable gels formed?

2). **Assessment, development, and use of theoretical methods for estimation and correlation of thermochemical data.** Theoretical investigations that predict thermochemical systematics and properties are essential since the potential experimental test matrix is too prohibitively large to allow laboratory measurements to be made for all needed thermochemical data and also

provide a means for estimating thermochemical properties where experiments are difficult or impossible to conduct. There is presently insufficient thermochemical data to allow comprehensive modeling of glass dissolution in nature or in the laboratory. Hence it is not presently possible to use geochemical modeling computer codes such as EQ3/6, Gt, or PATH, in predicting or estimating the long-term durability of the glass waste form.

Most of the thermodynamic data for common minerals presently used in geochemical computations are from the compilation by Helgeson et al. (1978) and do not take into account recent experimental results. In addition Helgeson and co-workers used multiple linear regression in deriving their dataset which results in a sensitivity to the order or path of data analysis. All experimental results involving a given phase therefore do not necessarily contribute to the refinement of the thermodynamic properties for that phase. Mathematical programming methods (Berman, et al. 1986) that extended the linear programming approach of Gordon (1973) have been used to update part of the thermodynamic data set for minerals utilizing recent calorimetric and phase equilibrium data. This new set of internally consistent thermodynamic data for minerals (Berman et al., 1985; Berman, et al., 1986; Brown, pers. comm., 1988) differs in part from the earlier data set for minerals of Helgeson et al. (1978). There presently needs to be a careful evaluation of these data in order to select which thermodynamic data for minerals are to be used in modeling calculations.

It is equally important to know the thermodynamic properties of aqueous species associated with rock-forming minerals and are commonly found in groundwaters as well as those of radionuclides in order to calculate solubilities. As is the case with laboratory determinations of thermochemical properties of minerals, the test matrix to determine experimentally all the necessary thermochemical properties for species of interest is prohibitively large. It is therefore often necessary to rely on theoretical models to predict thermochemical properties in cases where data is lacking or difficult or impossible at this time to measure. The principle of corresponding states (e.g., Criss and Cobble, 1964) that represents thermodynamic properties at a given temperature and pressure as linear functions of the corresponding property at another temperature and pressure is very useful where there is extensive experimental data set. Where such an extensive experimental dataset is lacking, application of semiempirical electrostatic/nonelectrostatic models and continuum theory to describe thermodynamic properties can be employed (e.g., Helgeson, et al., 1981). Both approaches could be used to evaluate recent experimental data and to refine the thermochemical parameters needed to carry out geochemical modeling computations. Evaluation of the data would in addition provide improvement in concepts as well as algorithms that represent fundamental parameters of aqueous species.

BIBLIOGRAPHY¹

- Aagaard, P., and Helgeson, H. C., 1982, Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions. I. Theoretical considerations, *Am. J. Sci.*, **282**, p. 237-286. HQS.80517.2373.
- Abrajano, Jr., T. A., and Bates, J. K., 1987, Transport and reaction kinetics at the glass-solution interface region: results of repository-oriented leaching experiments, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 533-545. NNA.90125.0106.
- Abrajano, Jr., T., Bates, J., Ebert, W., and Gerding, T., 1986, *The effect of gamma radiation on groundwater chemistry related to the NNWSI repository site*, Lawrence Livermore National Laboratory Report, UCRL-15825, 12 p. HQS.880517.2375.
- Adams, P. B., 1979, in, *Int. Symp. Ceramics in Nuclear Waste Management*, Chikalla, T. D. and Mendel, J. E., eds., American Ceramic Society, Columbus, OH, p. 233-237. NNA.900306.0021.
- Adams, P. B., 1984, Glass corrosion a record of the past? A predictor of the future?, *J. Non-Cryst. Solids*, **67**, p. 193-205. NNA.900215.0002.
- Adiga, R. B., Akomer, E. P., and Clark, D. E., 1985, Effects of flow parameters on the leaching of nuclear waste glass, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 45-54. NNA.900125.0107.
- Ailin-Pyzik, I. B., and Sommer, S. E., 1981, Microscale chemical effects of low temperature alteration of DSDP basaltic glasses, *J. Geophys. Res.*, **86**, p. 9503-9510. NNA.900306.0022.
- Aines, R. D., 1986, *Estimates of radionuclide release from glass waste forms in a tuff repository and the effects on regulatory compliance*, Lawrence Livermore National Laboratory Report, UCRL-93735, 12 p. HQS.880517.2377.
- Aines, R. D., 1986, *Application of EQ3/6 modeling of nuclear waste glass behavior in a tuff repository*, Lawrence Livermore National Laboratory Report, UCID-20895, 11 p. NNA.900215.0004.
- Aines, R. D., 1987, *Plan for glass waste form testing for NNWSI*, Lawrence Livermore National Laboratory Report, UCID-21190, 29 p. NNI.881209.0026.
- Aines, R. D., Weed, H. C., and Bates, J. K., 1987, Hydrogen speciation in hydrated layers on nuclear waste glass, *Mat. Res. Soc. Symp. Proc.*, **84**, p. 547-558. NNA.900125.0108.
- Allen, C. C., 1980, Icelandic subglacial volcanism: thermal and physical studies, *J. Geol.*, **88**, p. 108-117. NNA.900306.0023.
- Allen, C. C., 1982, Stability and alteration of naturally occurring low silica glasses: implications for the long term stability of waste form glasses, in, *Scientific Basis for Nuclear Waste Management*, Lutze, W., ed., Elsevier, New York, p. 57-68. NNA.900215.0005.

¹ This bibliography is more extensive than normally would have been prepared for a review of this nature. The reason for this is twofold. First the author of this report could not find in the open literature a previously prepared bibliography. And second the nature of this report required a review of a very wide range of material including mechanisms proposed for glass dissolution in general; and, field, laboratory, and theoretical studies of glass durability. The intent of including this bibliography in this report is to provide other interested workers a jumping off point for entrance into the literature.

Allen, C. C., Gooding, J. L., Jercinovic, M., and Keil, 1981, Altered basaltic glass: A terrestrial analog to the soil of mars, *Icarus*, 45, p. 347-369. NNA.900306.0024.

Allen, C. C., Lane, D. L., Johnston, R. G., Marcy, A. D., and Adece, R. R., 1985, Hydrothermal studies of simulated defense waste glass plus basalt, *Mat. Res. Soc. Symp. Proc.*, 44, p. 451-458. NNA.900125.0109.

Allenhein, F. K., Lutze, W., Malow, G., 1981, The mechanism for hydrothermal leaching of glass and glass-ceramic nuclear waste forms, *Mat. Res. Soc. Symp. Proc.*, 3, p. 32-38. NNA.900312.0143.

Ambrose, W., 1976, Intrinsic hydration rate dating of obsidian, in, *Advances in Obsidian Glass Studies*, Taylor, R. E., ed., Noyes Press, Park Ridge, NJ, p. 81-105. NNA.900405.0455.

Andrews, A. J., 1977, Low temperature fluid alteration of oceanic Layer 2 basalts, DSDP Leg 37, *Can. J. Earth Sci.*, 14, p. 911-926. NNA.900306.0025.

Apted, M. J., and Adiga, R., 1985, The effect of groundwater flow on release rate behavior of borosilicate glass, *Mat. Res. Soc. Symp. Proc.*, 44, p. 163-170. HQS.880517.2379.

Arndt, J., and Haberle, F., 1973, Thermal expansion and glass transition temperatures of synthetic glasses of plagioclase-like compositions, *Contrib. Min. Petrol.*, 39, p. 175-183. NNA.900306.0026.

Arnold, G. W., 1985, Ion implantation damage processes in nuclear waste glass and other silicate glasses, *Mat. Res. Soc. Symp. Proc.*, 44, p. 617-622. NNA.900125.0110.

Bach, H., 1988, Estimation of the enthalpies of formation for leached subsurface layer materials from ion beam sputtering and analysis, *J. Non-Cryst. Solids*, 102, p. 43-49. NNA.900215.0007.

Bacon, C. R., 1977, High temperature heat content and heat capacity of silicate glasses: experimental determination and a model for calculation, *Am. J. Sci.*, 277, p. 109-183. NNA.900306.0272.

Baer, D. R., Pederson, L. R., and McVay, G. L., 1984, Glass reactivity in aqueous solutions, *J. Vac. Sci. Technol.*, A2(2), p. 738-743. NNA.900215.0006.

Banba, T., Murakami, T., and Kimura, H., 1985, Moving boundary model for leaching of nuclear waste glass, *Mat. Res. Soc. Symp. Proc.*, 44, p. 113-120. NNA.900125.0111.

Banks, H. H., 1972, Iron-rich saponite: additional data on samples dredged from the Mid-Atlantic Ridge, 22°N, *Smithsonian Contrib. Earth Sci.*, 9, p. 39-42. NNA.900312.0144.

Baragar, W. R. A., Plant, A. G., Pringle, C. J., and Schau, M., 1977, Petrology and alteration of selected units of mid-atlantic ridge basalts sampled from sites 332 and 335, DSDP Leg 37, *Can. J. Earth Sci.*, 14, p. 837-874. NNA.900306.0027.

Barkatt, Aa., Barkatt, Al., Pehrsson, P. E., Szoke, P., and Macedo, P. B., 1981, State and dynamic tests for the chemical durability of nuclear waste glass, *Nucl. Chem. Waste Management*, 2, p. 151-164. NNA.900306.0028.

Barkatt, Aa., Boulous, M. S., Barkatt, Al., Sousanpour, W., Broomand, M. A., Macedo, P. A., and O'Keefe, J. A., 1984, The chemical durability of teckites - A laboratory study and correlation with long-term corrosion behavior, *Geochim. Cosmochim. Acta*, 48, p.363-372. NNA.900306.0029.

Barkatt, Aa., Gibson, B. C., and Brandys, M., 1985, A kinetic model of nuclear waste glass dissolution in flowing water environments, *Mat. Res. Soc. Symp. Proc.*, 44, p. 229-236. HQS.880517.2385.

Barkatt, Aa., Macedo, P. B., Gibson, B. C., and Montrose, C. J., 1987, Modelling of waste form performance and system release, *Mat. Res. Soc. Symp. Proc.*, 44, p. 3-14. NNA.900125.0112.

Barkatt, Aa., Macedo, P. B., Sousanpour, W., Barkatt, Al., Boroomand, M. A., Fisher, C. F., Shirron, J. J., Szpke, P., and Rogers, V. L., 1983, The use of a flow test and a flow model in evaluating the durability of various nuclear waste-form materials, *Nucl. Chem. Waste Management*, 4, p. 153-169. NNA.900306.0030.

Barkatt, Aa., Saad, E. E., Adiga, R., Sousanpour, W., and Barkatt, Al., 1986, Leaching of microtektite glass compositions in seawater, *Adv. Ceram.*, 20, p. 681. NNA.900320.0143.

Barkatt, Az., Simmons, J. H., and Macedo, P. B., 1981, Corrosion mechanisms and chemical durability of glass media proposed for the fixation of radioactive wastes, *Chemical Waste Management*, 2, p. 3-23. NNA.900215.0008.

Barkatt, Aa., Simmons, J. H., and Macedo, P. B., 1981, Evaluation of chemical stability of vitrification media for radioactive waste products, *Phys. Chem. Glasses*, 22, p. 73-85. NNA.900306.0031.

Barkatt, Aa., Sousanpour, W., Barkatt, Al., and Boroomand, M. A., 1984, Effects of metals and metal oxides on the leaching of nuclear waste glass, *Mat. Res. Soc. Symp. Proc.*, 26, p. 689-696. NNA.900215.0009.

Barkatt, Aa., Sousanpour, W., Barkatt, Al., Boroomand, M. A., and Macedo, P., 1984, Leach behavior of SRL TDS-131 defense waste glass in water at high/low flow rates, *Mat. Res. Soc. Symp. Proc.*, 26, p. 643-653. NNA.900215.0010.

Barrett, N. T., Antonini, G. M., Thornley, F. R., Greaves, G. N., and Manara, A., 1987, Structural changes around uranium at the surface of waste glasses caused by leaching, *Mat. Res. Soc. Symp. Proc.*, 84, p. 571-576. NNA.900125.0113.

Bart, G., Aerne, E. T., Grauer, R., Linder, H., Z'berg, D., and Zwicky, H. U., 1985, Surface film characterization of corroded HLW glass specimens, *Mat. Res. Soc. Symp. Proc.*, 44, p. 213-220. NNA.900125.0114.

Bartholomew, R. F., 1983, High-water containing glasses, *J. Non-Cryst. Solids*, 56, p. 331-342. NNA.900306.0032.

Bartholomew, R. F., Tick, P. A., and Stookcy, S. D., 1980, Water glass reactions at elevated temperatures and pressures, *J. Non-Cryst. Solids*, 38/39, p. 637-642. NNA.900215.0012.

Bates, J. K. and Gerding, T. J., 1986, One-year results of the NNWSI unsaturated test procedure: SRL 165 glass application, Argonne National Laboratory report, ANL-85-41, 78 p. NNA.870903.0081.

Bates, J. K., and Gerding, T. J., 1985, NNWSI waste form performance test development, *Mat. Res. Soc. Symp. Proc.*, 44, p. 295-302. NNA.900125.0115.

Bates, J. K., and Gerding, T. J., 1988, The performance of actinide-containing SRL 165 type glass in unsaturated conditions, *Mat. Res. Soc. Symp. Proc.*, 112, p. 651-662. NNA.900306.0033.

Bates, J. K., Gerding, T. J., Abrajano, Jr., T. A., 1986, *NNWSI waste form testing at Argonne National Laboratory*, Lawrence Livermore National Laboratory Report, UCRL-15801, 57 p. HQS.880517.2393.

Bates, J. K., Jardine, L. J., and Steindler, M. J., 1982, Hydration: aging of nuclear waste glass, *Science*, 218, p. 51-53. NNA.891101.0005.

Bates, J. K., Seitz, M. G., and Steindler, M. J., 1984, The relevance of vapor phase hydration aging to nuclear waste isolation, *Nucl. Chem. Waste Management*, 5, p. 63-73. NNA.900306.0034.

Bates, J. K., and Steindler, M. J., 1983, Alteration of nuclear waste glass by hydration, *Mater. Res. Soc. Symp. Proc.*, 15, p. 83-90. NNA.900306.0035.

Bates, J. K., Steindler, M. J., Tani, B., and Purcell, F. J., 1985, The hydration alteration of a commercial nuclear waste glass, *Chem. Geol.*, 51, p. 79-87. NNA.900306.0036.

Bates, J. K., and Oversby, V. M., 1985, The behavior of actinide containing glasses during gamma irradiation in a saturated tuff environment, *Mat. Res. Soc. Symp. Proc.*, 44, p. 257-264. NNA.891101.0010.

Baucke, F. G. K., 1974, Investigation of surface layers, formed on glass electrode membranes in aqueous solutions, by means of an ion sputtering technique, *J. Non-Cryst. Solids*, 14, p. 13-24. NNA.900306.0037.

Bazan, F., and Rego, J., 1985, Parametric testing of a DWPF borosilicate glass, *Mat. Res. Soc. Symp. Proc.*, 44, p. 303-310. NNA.870407.0185.

Berman, R. G. and Brown, T. H., 1987, Development of models for multicomponent melts: Analysis of synthetic systems, *Rev. Mineralogy*, 17, p. 405-442. NNA.900312.0145.

Berman, R. G., Brown, T. H., and Greenwood, H. J., 1985, *An internally-consistent thermodynamic data base for minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂*: Atomic Energy Canada Tech. Rpt. 377, 62 p. NNA.900312.0146.

Berman, R. G., Engi, M., Greenwood, H. J., and Brown, T. H., 1986, Derivation of internally-consistent thermodynamic data by the technique of mathematical programming: a review with application to the system MgO-SiO₂-H₂O, *Jour. of Petrology*, 27, p. 1331-1364. NNA.900306.0038.

Bibler, N. E., and Jantzen, C. M., 1987, Materials interactions relating to long-term geologic disposal of nuclear waste glass, *Mat. Res. Soc. Symp. Proc.*, 84, p. 47-66. NNA.900125.0116.

Bibler, N. E., and Jurgensen, A. R., 1988, Leaching Tc-99 from SRP glass in simulated tuff and salt groundwaters, *Mat. Res. Soc. Symp. Proc.*, 112, p. 585-594. NNA.900306.0039.

Bihler, N. E., Wicks, G. G., and Oversby, V. M., 1985, Leaching Savannah River Plant nuclear waste glass in a saturated tuff environment, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 247-256. NNA.900125.0117.

Bickford, D. F., and Jantzen, C. M., 1984, Devitrification behavior of SRL defense waste glass, *Mat. Res. Soc. Symp. Proc.*, **26**, p. 557-565. HQS.880517.2400.

Bickford, D. F., and Pellaring, D. J., 1987, Large scale leach testing of DWPF canister sections, *Mat. Res. Soc. Symp. Proc.*, **84**, p. 509-518. HQS.880517.2401.

Bidoglio, G., Offermann, P., De Plano, A., and Lazzari, G. P., 1988, Influence of groundwater composition on glass leaching and actinide speciation, *Mat. Res. Soc. Symp. Proc.*, **112**, p. 621-630. NNA.900306.0040.

Bischoff, J. L., and Dickson, F. W., 1975, Seawater-basalt interaction at 200°C and 500 bars: Implications for origin of sea-floor heavy-metal deposits and regulation of seawater chemistry, *Earth Planet. Sci. Lett.*, **25**, p. 385-397. NNA.900306.0041.

Boksay, Z., Bouquet, G., and Dobos, S., 1967, Diffusion processes in the surface layer of glasses, *Phys. Chem. Glasses*, **8**, p. 140-144. NNA.900306.0042.

Boksay, Z., Bouquet, G., and Dobos, S., 1968, The kinetics of the formation of leached layers on glass surfaces, *Phys. Chem. Glasses*, **9**, p. 69-71. NNA.900215.0014.

Bonatti, E., 1965, Palagonite, hyaloclastites and the alteration of volcanic glass in the ocean, *Bull. Volc.*, **28**, p. 257-269. NNA.900306.0043.

Boulos, E. N., DePaula, R. P., El-Bayoumi, O. H., Lagakos, N., Macedo, P. B., Moynihan, C. T., and Rekhson, S. M., 1980, Crystallization of nuclear waste disposal glass, *Am. Ceram. Soc. Bull.*, **63**, p. 496-501. NNA.900306.0044.

Brookins, D. G., 1987, Coupled processes at the Oklo natural reactor, in, Tsang, Chin-Fu, ed., *Coupled Processes Associated with Nuclear Waste Repositories*, p. 237-248. NNA.900430.0046.

Bruton, C. J., 1988, Geochemical simulation of dissolution of West Valley and DWPF glasses in J-13 water at 90°C, *Mat. Res. Soc. Symp. Proc.*, **112**, p. 607-620. NNA.891006.0181.

Bunker, B. C., 1987, Waste glass leaching: chemistry and kinetics, *Mat. Res. Soc. Symp. Proc.*, **84**, p. 493-507. NNA.900125.0118.

Bunker, B. C. and Arnold, G. W., 1983, The effect of solution pH and iron concentration on leaching of silicate glass, *Mat. Res. Soc. Symp. Proc.*, **15**, p. 151-158. NNA.900306.0045.

Bunker, B. C., Arnold, G. W., Beauchamp, E. K., and Day, D. E., 1983, Mechanisms for alkali leaching in mixed Na-K silicate glasses, *Jour. Non-Cryst. Solids*, **58**, p. 295-322. NNA.900215.0015.

Bunker, B. C., Arnold, G. W., Day, D. E., and Bray, P. J., 1986, The effect of molecular structure on borosilicate glass leaching, *Jour. Non-Cryst. Solids*, **87**, p. 226-253. NNA.900215.0016.

Bunker, B. C., Headly, T. J., and Douglas, D. C., 1984, Gel structures in alkali silicate glass, *Mat. Res. Soc. Symp.*, **32**, p. 41. NNA.900306.0046.

Bunker, B. C., Tallant, D. R., Headley, T. J., Turner, G. L., and Kirkpatrick, R. J., 1988, The structure of leached borosilicate glass, *Phys. Chem. Glasses*, **29**, no. 3, p. 106. NNA.900215.0017.

Byerly, G. R., and Sinton, J. M., 1979, Compositional trends in natural basaltic glasses from Deep Sea Drilling Project holes 417D and 418A, in, *Initial Reports of the Deep Sea Drilling Project 53*, Donnelly, T. et al., eds., U. S. Printing Office, Washington, D.C., p. 957-971. NNA.900315.0281.

Byers, C. D., Jercinovic, M. J., and Ewing, R. C., 1987, *A study of natural glass analogues as applied to alteration of nuclear waste glass*, Argonne National Laboratory, ANL-86-46 (or NUREG/CR-4842), 150 p. NNA.900215.0018.

Byers, C. D., Jercinovic, M. J., Ewing, R. C., and Keil, K., 1987, Basalt glass: an analogue for the evaluation of the long-term stability of nuclear waste form borosilicate glasses, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 583-590. NNA.900125.0119.

Carmichael, I. S. E., Nicholls, J., Spera, F. J., Wood, B. J., and Nelson, S. A., 1977, High-temperature properties of silicate liquids: applications to the equilibration and ascent of basic magma, *Phil. Trans. Roy. Soc. Lond.*, **A286**, P. 373-431. NNA.900306.0047.

Caurel, J., Beaufort, D., and Vernaz, E. Y., 1988, Mineral phase identification along two profiles from the LWR French reference glass: Use of an x-ray position sensitive detector, *Mat. Res. Soc. Symp. Proc.*, **112**, p. 663-672. NNA.900306.0048.

Chick, L. A., and Pederson, L. R., 1984, The relationship between reaction layer thickness and leach rates for nuclear waste glasses, *Mat. Res. Soc. Symp. Proc.*, **26**, p. 635-642. NNA.900215.0019.

Christensen, H., Hermansson, H. P., Clark, D. E., and Werme, L., 1984, Surface reactions occurring on simulated nuclear waste glass immersed in aqueous solutions containing bentonite, granite, and stainless steel corrosion products, in, *Advances in Ceramics 8*, Nuclear Waste Management, Wicks, G. G., and Ross, W. A., eds., The American Ceramic Society, Columbus, Ohio, p. 346-357. NNA.900315.0282.

Clark, D. E. and Hench, L. L., 1983, Theory of corrosion of alkali-borosilicate glass, *Mat. Res. Soc. Symp. Proc.*, **15**, p. 113-124. NNA.900306.0049.

Clement, S. C., and Ribbe, P. H., 1973, New locality, formula, and proposed structure for reyerite, *Am. Mineral.*, **58**, p. 517-522. NNA.900306.0051.

Clark, D. E. and Hench, L. L., 1982, An overview of the physical characterization of leached surfaces, *Nucl. Chem. Waste Management*, **2**, p. 93-101. NNA.900306.0050.

Coles, D. G., Simonson, S. A., Thomas, L. E., Schramke, J. A., and McKinley, S. G., 1985, Investigation of the hydrothermal interaction of ⁹⁹Tc-doped glass with basalt repository nuclear waste package components, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 323-332. NNA.900125.0120.

Conradi, R., Roggendorf, H., and Scholze, H., 1985, A contribution to the modelling of the corrosion process for HLW glasses, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 155-162. NNA.900125.0121.

Conradi, R., Roggendorf, H., and Scholze, H., 1985, Investigations on the role of surface layers in HLW glass leaching, *Mat. Res. Soc. Symp. Proc.*, **50**, p. 203-210. NNA.900306.0052.

Cowan, R., and Ewing, R. C., 1986, Alteration products of basaltic glass, Hanauma Bay, Oahu, Hawaii, in, *Microbeam Analysis - 1986*, Romig, A. D., and Chambers, W. F., eds., San Francisco Press, San Francisco, p. 131-134. NNA.900215.0020.

Criss, C. M., and Cobble, J. W., 1964, The thermodynamic properties of high-temperature aqueous solutions, *J. Am. Chem. Soc.*, **86**, p. 5385-5393. NNA.900306.0053.

Crovisier, J. L., and Eberhart, J. P., 1985, Apports de la microscopie electronique a l'etude des couches d'alteration formees a la surface des verres, *J. Microsc. Spectrosc. Electron.*, **10**, p. 171-180. NNA.900312.0148.

Crovisier, J. L., Eberhart, J. P., Thomassin, J. H., Juteau, T., Touray, J. C., and Ehret, G., 1982, Interaction eau de mer-verre basaltique a 50°C. Formation d'un hydroxy-carbonate et de produits silicates amorphes (Al, Mg) et mal cristallises (Al, Fe, Mg). Etude en microscopie electronique et par spectrometrie des photoelectrons (E.S.C.A.), *C. R. Acad. Sci.*, **294**, ser. II, p. 989-993. NNA.900306.0054.

Crovisier, J. L., Fritz, B., Grambow, B., and Eberhart, J. P., 1985, Disolution of basaltic glass in seawater: Experiments and thermodynamic modelling, in, *Scientific Basis for Nuclear Waste Management IX*, Werme, L., ed., p. 273-280. NNA.900306.0055.

Crovisier, J. L., and Honnorez, 1988, Nuclear waste under glass, reconsidered, *EOS Trans. AGU*, **69**, p. 628. NNA.900306.0056.

Crovisier, J. L., Honnorez, J., and Eberhart, J. P., 1987, Dissolution of basaltic glass in seawater: Mechanism and rate, *Geochim. Cosmochim. Acta*, **51**, p. 2977-2990. NNA.900215.0021.

Crovisier, J. L., Thomassin, J. H., Juteau, T., Eberhart, J. B., Touray, J. C., and Baillif, P., 1983, Experimental seawater-basaltic glass interaction at 50°C: Study of early developed phases by electron microscopy and x-ray photoelectron spectrometry, *Geochim. Cosmochim. Acta*, **47**, p. 377-387. NNA.900306.0057.

Dibble, W. E., and Tiller, W. A., 1981, Kinetic model of zeolite paragenesis in tuffaceous sediments, *Clays Clay Mins.*, **29**, p. 323-330. NNA.870406.0093.

Dibble, W. E., and Tiller, W. A., 1981, Non-equilibrium water rock interactions I. Model for interface-controlled reactions, *Geochim. Cosmochim. Acta*, **45**, p. 79-92. NNA.900306.0058.

Dickinson, A. P., 1981, Hydrothermal leaching of rhyolite glass in the environment has implications for nuclear waste disposal, *Nature*, **294**, p. 342-345. NNA.900215.0022.

Donnelly, T., et al., 1975, *Initial Reports of the Deep Sea Drilling Project 51-53*, U. S. Government Printing Office, Washington, D. C., p. 1613. NNA.900315.0283.

Doremus, R. H., 1979, Chemical durability of glass, in, *Treatise on Materials Science and Technology 17*, Tomozawa, M. and Doremus, R. G., eds., Academic Press, New York, p. 41-69. NNA.900306.0059.

Doremus, R. H., 1983, Diffusion controlled reaction of water with glass, *J. Non-Cryst. Solids*, **55**, p. 143-147. NNA.900306.0060.

Doremus, R. H., Mehrotra, Y., Lanford, W. A., and Burman, C., 1983, Reaction of water with glass: Influence of a transformed surface layer, *J. Mater. Science*, **18**, p. 612-622. NNA.900215.0023.

Dran, J-C, Langevin, Y., Doorhyec, E., and Petit, J-C., 1987, Modelling of the dissolution of silicate glasses by a monte-carlo code (ETCH), *Mai. Res. Soc. Symp. Proc.*, **84**, p. 559-569. NNA.900215.0024.

Dran, J.-C., Petit, J.-C., and Brousse, C., 1986, Mechanism of aqueous dissolution of silicate glasses yielded by fission tracks *Nature*, 319, p. 485-487. NNA.900312.0150.

Dubrovo, S. K., and Schmidt, Yu. A., 1953, *Bull. Acad. Sci. USSR Div. Chem. Sci.*, 403, p. 535. NNA.900405.0456.

Ebert, W. L., Bates, J. K., Gerding, T. J., and Van Konynenburg, R. A., 1987, The effects of gamma radiation on groundwater chemistry and glass reaction in a saturated tuff environment, *Mat. Res. Soc. Symp. Proc.*, 84, p. 613-622. NNA.89212.0005.

El-Shamy, T. M., Lewins, J., and Douglas, R. W., 1972, The dependence on the pH of the decomposition of glasses by aqueous solutions, *Glass Tech.*, 13, p. 81. NNA.900306.0061.

Ethridge, E. C., Clark, D. E., and Hench, L. L., 1979, Effects of glass surface area to solution volume ratio on glass corrosion, *Phys. Chem. Glasses*, 20, p. 35-40. NNA.900306.0062.

Ewing, R. C., 1978, Natural glasses: analogues for radioactive waste forms, in, *Scientific Basis for Nuclear Waste Management*, McCarthy, G. J., ed., Plenum, New York, p. 57-68. NNA.900215.0025.

Ewing, R. C., and Haaker, R. F., 1979, Natural glasses: analogues for radioactive waste forms, *Battelle PNL Report 2776/UC-70*, 71 p. NNA.900315.0277.

Ewing, R. C., and Jercinovic, M. J., 1987, Natural Analogues: their application to the prediction of the long-term behavior of nuclear waste forms, *Mat. Res. Soc. Symp. Proc.*, 84, p. 67-83. NNA.900215.0026.

Feng, X., and Barkatt, A., 1987, Effects of aqueous phase composition on the leach behavior of nuclear waste glasses, *Mat. Res. Soc. Symp. Proc.*, 84, p. 519-531. NNA.900215.0027.

Feng, X., and Barkatt, A., 1988, Structural thermodynamic model for the durability and viscosity of nuclear waste glass, *Mat. Res. Soc. Symp.*, 112, p. 543-554. NNA.900306.0063.

Feng, X., Barkatt, A., and Jiang, T., 1988, Systematic composition studies on the durability of waste glass WY205, *Mat. Res. Soc. Symp. Proc.*, 112, p. 673-684. NNA.900306.0064.

Flintoff, J. F., and Harker, A. B., 1985, Detailed processes of surface layer formation in borosilicate waste glass dissolution, *Mat. Res. Soc. Symp. Proc.*, 44, p. 147-154. NNA.900215.0028.

Freude, E., Grambow, B., Lutze, W., Rabe, H., and Ewing, R. C., Long-term release from high-level waste glass - part IV: the effect of leaching mechanism, *Mat. Res. Soc. Symp. Proc.*, 44, p. 99-106. HQS.880517.2439.

Friedman, I., and Smith, R. L., 1960, A new dating method using obsidian - Part I. The development of the method, *Am. Antiquity*, 25, p. 476-522. NNA.900312.0152.

Friedman, I., Smith, R. L., and Long, W. D., 1966, Hydration of natural glass and formation of perlite, *Geol. Soc. Am. Bull.*, 77, p. 323-328. NNA.900306.0065.

Friedman, I., and Long, W., 1976, Hydration rate of obsidian, *Science*, 191, p. 347-352. NNA.900306.0066.

Friedman, I., and Trembour, F. W., 1978, Obsidian: the dating stone, *Amer. Sci.*, 66, p. 44-51. NNA.900306.0067.

Furnes, H., 1974, Volume relations between palagonite and authigenic minerals in hyaloclastites and its bearing on the rate of palagonitization, *Bull. Volc.*, **38**, p. 173-186. NNA.900312.0153.

Furnes, H., 1975, Experimental palagonitization of basaltic glasses of varied composition, *Contrib. Mineral. Petrol.* **50**, p. 105-113. NNA.900215.0029.

Furnes, H., 1978, Element mobility during palagonitization of a subglacial hyaloclastite in Iceland, *Chem. Geol.*, **22**, p. 249-264. NNA.900306.0068.

Furnes, H., 1980, Chemical changes during palagonitization of an alkaline olivine basaltic hyaloclastite, Santa Maria, Azores, *N. Jahr. Mineral. Abh.*, **138**, p. 14-30. NNA.900315.0284.

Furnes, H., 1984, Chemical changes during progressive subaerial palagonitization of subglacial olivine tholeiite hyaloclastite: A microprobe study, *Chem. Geol.*, **43**, p. 271-285. NNA.900215.0030.

Furnes, H., and El-Anbaawy, M. I. H., 1980, Chemical changes and mineral formation during palagonitization of a basaltic hyaloclastite, Gran Canaria, Canary Islands, *Neues Jahrbuch*, **139**, p. 279-302. NNA.900315.0285.

Garland, J. A., and White, W. B., 1985, Determination of early stages of glass dissolution by pH titration, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 81-88. NNA.900215.0031.

Garrels, R. M., and Christ, C. L., 1965, *Solutions, Minerals and Equilibria*, Harper and Row, New York, p. i-v. NNA.900315.0286.

Garlick, G. D., and Dymond, J. R., 1970, Oxygen isotope exchange between volcanic materials and ocean water, *Geol. Soc. Amer. Bull.*, **81**, p. 2137-2141. NNA.900306.0069.

Geptner, A. R., 1978, Palagonite and the process of palagonitization, *Litoligiya i Poliznye Iskopaemye*, **5**, p. 113-130 (in Russian). NNA.900312.0154.

Ghiorso, M. S., 1987, Modeling magmatic systems: Thermodynamic Relations, *Rev. Mineralogy*, **17**, p. 443-466. NNA.900312.0155.

Gignac, L. M., Altstetter, C. J., and Brown, S. D., 1985, A nuclear reaction analysis technique to determine the penetration of hydrogenic species into glasses exposed to leaching solutions, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 107-112. NNA.900215.0032.

Glass, B. P., 1972, Bottle-green microtektites, *J. Geophys. Res.*, **77**, p. 7057-7064. NNA.900215.0033.

Glass, B. P., 1982, *Solution of naturally occurring glasses in the geological environment*, NASA Contract. Rep. 170518, NASA/GSFC, Greenbelt, Md. NNA.900312.0156.

Gordon, T. M., 1973, Determination of internally consistent thermodynamic data from phase equilibrium experiments, *J. Geol.*, **81**, p. 199-208. NNA.900306.0070.

Grambow, B., 1982, The role of metal ion solubility in leaching of nuclear waste glasses, *Mat. Res. Soc. Symp. Proc.*, **11**, p. 93-102. NNA.900306.0071.

Grambow, G., 1984, Geochemical modeling of the reaction between glass and aqueous solution, in, *Advances in Ceramics Proc. Amer. Ceram. Soc. Symp. 85th*, Wicks, G. G., and Ross, A., eds., 8, p. 474-481. NNA.900315.0287.

Grambow, B., 1984, Ein physikalisch-chemisches Modell für den Mechanismus der Glaskorrosion unter besonderer Berücksichtigung simulierter radioaktiver Abfallgläser, Theses, Freien Universität Berlin, 255 p. NNA.900215.0034.

Grambow, B., 1985, A general rate equation for nuclear waste glass corrosion, *Mat. Res. Soc. Symp. Proc.*, 44, p. 15-27. HQS.880517.2447.

Grambow, B., 1987, *Nuclear waste dissolution: mechanism, model, and application*, JSS Project Technical Report-87-02, Swedish Nuclear Fuel and Waste Management Co., 112 p. NNA.900215.0035.

Grambow, B., Jercinovic, B. J., Ewing, R. C., and Byers, C. D., 1985, Weathered basalt glass: a natural analogue for the effects of reaction progress on nuclear waste glass alteration, *Mat. Res. Soc. Symp. Proc.*, 50, p. 263-272. NNA.900306.0072.

Grambow, B., Lutze, W., Ewing, R. C., and Werme, L. O., 1988, Performance assessment of glass as a long-term barrier to the release of radionuclides into the environment, *Mat. Res. Soc. Symp. Proc.*, 112, p. 531-542. NNA.900306.0073.

Grambow, B., and Strachan, D. M., 1984, Leach testing of waste glasses under near-saturation conditions, *Mat. Res. Soc. Symp. Proc.*, 26, p. 623-634. NNA.870406.0329.

Grambow, B., and Strachan, D. M., 1988, A comparison of the performance of nuclear waste glasses by modeling, *Mat. Res. Soc. Symp. Proc.*, 112, p. 713-724. NNA.900215.0036.

Haaker, R., Malow, G., and Offermann, P., 1985, The effect of phase formation on glass leaching, *Mat. Res. Symp. Proc.*, 44, p. 121-128. NNA.900215.0037.

Harvey, K. B., and Litke, C. D., 1984, Model for leaching behavior of aluminosilicate glasses developed as matrices for immobilizing high-level wastes, *J. Am. Cer. Soc.*, 67, p. 553-61. NNA.900306.0074.

Harvey, K. B., Litke, C. D., and Boase, C. A., 1986, The dissolution of a simple glass. Part 1. Initial model and application to an open glass/water system, *Phys. Chem. Glasses*, 27, p. 15-21. NNA.900306.0075.

Hawkins, D. B., and Roy, R., 1963, Experimental hydrothermal studies on rock alteration and clay mineral formation, *Geochim. Cosmochim. Acta*, 27, p. 1047-1054. NNA.900306.0078.

Hay, R. L., 1966, Zeolites and zeolitic reactions in sedimentary rocks, *Geol. Soc. Am. Special Paper* 85, 130 p. NNA.900315.0288.

Hay, R. L., and Iijima, A., 1968a, Petrology of palagonite tuffs of Koko Craters, Oahu, Hawaii, *Contrib. Mineral. Petrol.*, 17, p. 141-154. NNA.900306.0076.

Hay, R. L., and Iijima, A., 1968b, Nature and origin of palagonite tuffs of the Honolulu Group on Oahu, Hawaii, *Geol. Soc. Am. Mem.* 116, p. 331-376. NNA.900312.0157.

Hay, R. L., and Jones, B. F., 1972, Weathering of basaltic tephra on the island of Hawaii, *Geol. Soc. Am. Bull.*, 83, p. 317-332. NNA.900306.0077.

Helgeson, H. C., 1971, Kinetics of mass transfer among silicates and aqueous solutions, *Geochim. Cosmochim. Acta*, 35, p. 421-469. NNA.900306.0079.

Helgeson, H. C., Delany, J. M., Nesbitt, H. W., and Bird, D. K., 1978, Summary and critique of the thermodynamic properties of the rock-forming minerals, *Am. Jour. Sci.*, 278A, p. 1-228. HQS.880517.2457.

Helgeson, H. C., Kirkham, D. H., and Flowers, G. C., 1981, Theoretical prediction of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb, *Am. Jour. Sci.*, 281, p. 1249-1516. NNA.891006.0200.

Hench, L. L., 1975, Characterization of glass corrosion and durability, *J. Non-Cryst. Solids*, 19, p. 91-109. NNA.900306.0080.

Hench, L. L. and Clark, D. E., 1978, Physical chemistry of glass surfaces, *J. Non-cryst. Solids*, 28, p. 83-105. NNA.900306.0081.

Hodder, A. P. W., 1984, Effect of composition on hydration kinetics in volcanic glasses: Implications for dating, *J. Colloid Interface Sci.*, 103, p. 45-49. NNA.900306.0082.

Honnorez, J., 1969, La palagonitisation. Un aspect du volcanisme sous marin: l'alteration du verre basique de Palagonia (Sicile). These Sci. Nat. Univ. libre Bruxelles, 131 p. NNA.900320.0144.

Honnorez, J., 1984, Generation of phillipsites by palagonitization of basaltic glass in sea water and the origin of K-rich deep-sea sediments, in, *Natural Zeolites: Occurrence, Properties and Use*, Sand, L. B., and Mumpton, F. A., eds., Pergamon Press, Oxford, p. 245-258. NNA.900306.0083.

Houser, C. A., and Pantano, C. G., 1985, Early stages of film formation during the leaching of radioactive waste glasses, *Mat. Res. Soc. Symp. Proc.*, 44, p. 205-212. NNA.900215.0038.

Iijima, A., and Harada, K., 1969, Authigenic zeolites in zeolitic palagonite tuffs on Oahu, Hawaii, *Am. Min.*, 54, p. 182-197. NNA.900306.0084.

Iler, R. K., 1955, *Colloid Chemistry of Silica and Silicates*, Cornell University Press, Ithaca, NY, p. v-xii; 301-324. NNA.900320.0145.

Isard, J. O., Allnatt, A. R., and Melling, P. J., 1982, An improved model of glass dissolution, *Phys. Chem. Glass*, 23, p. 185. NNA.900215.0039.

Jacquet-Francillon, N., Pacaud, F., and Queille, 1982, An attempt to assess the long-term crystallization rate of nuclear waste glasses, *Mat. Res. Soc. Symp. Proc.*, 11, p. 249-259. NNA.900306.0085.

Jakobsson, S. B., 1972, On the consolidation and palagonitization of the tephra of the Surtsey Volcanic Island, Iceland, *Surtsey Res. Progr. Rep. VI*, p. 121-128. NNA.900312.0159.

Jakobsson, S. P., 1977, Environmental factors controlling the palagonitization of the Surtsey tephra, Iceland, *Bull. Geol. Soc. Denmark*, 27, p. 91-105. NNA.900312.0158.

Jakobsson, S. P., and Moore, J. G., 1986, Hydrothermal minerals and alteration rates at Surtsey Volcano, Iceland, *Geol. Soc. Am. Bull.*, 97, p. 648-659. NNA.900306.0086.

Jantzen, C. M., 1984, Effects of Eh (Oxidation potential) on borosilicate waste glass durability, in, *Advances in Ceramics 8*, Wicks, G. G. and Ross, W. A., eds., The American Ceramic Society, Columbus, OH, p. 385-393. NNA.900315.0290.

Jantzen, C. M., 1986, Prediction of nuclear waste glass durability from natural analogs, *Advances in Ceramics*, 20, p. 703-712. NNA.900215.0040.

Jantzen, C. M., 1988, Pourbaix diagram for the prediction of waste glass durability in geologic environments, *Mat. Res. Soc. Symp. Proc.* 112, p. 519-530. NNA.900215.0041.

Jantzen, C. M., 1988, Nuclear waste glass durability: I. Predicting environmental response from thermodynamic (Pourbaix) diagrams, presented at the 89th American Ceramic Society Meeting, Pittsburgh, PA, ms. NNA.900215.0042.

Jantzen, C. M., and Bibler, N. E., 1985, The role of groundwater oxidation potential and radiolysis on waste glass performance in crystalline repository environments, *Mat. Res. Soc. Symp. Proc.*, 50, p. 219-230. NNA.900215.0043.

Jantzen, C. M., and Bickford, D. F., 1985, Leaching of devitrified glass containing simulated SRP nuclear waste, *Mat. Res. Soc. Symp. Proc.*, 44, p. 135-146. NNA.900215.0044.

Jantzen, C. M., Bickford, D. F., and Karraker, Time-temperature-transformation kinetics in SRL waste glass, in, *Advances in Ceramics 8*, Wicks, G. G. and Ross, W. A., eds., The American Ceramic Society, Columbus, OH, p. 30-38. NNA.900315.0289.

Jantzen, C. M., and Plodinec, M. J., 1984, Thermodynamic model of natural, medieval, and nuclear waste glass durability, *J. Non-Cryst. Solids*, 67, p. 207-223. NNA.900215.0045.

Jantzen, C. M., and Wicks, G. G., 1985, Control of oxidation potential for basalt repository simulation tests, *Mat. Res. Soc. Symp. Proc.*, 44, p. 29-35. NNA.900215.0046.

Jercinovic, M. J. and Ewing, R. C., 1987, *Basaltic glasses from Iceland and the deep sea: Natural analogues to borosilicate nuclear waste-form glass*, JSS [Joint Japanese (CRIEP), Swiss (NAGRA), Swedish (SKB) project managed by Swedish Nuclear Fuel and Waste Management Co.] Technical Report 88-01, 221 p. NNA.900215.0045.

Jercinovic, M. J., Ewing, R. C., and Byers, C. D., 1987, Alteration products of basalt glass from the Frenchman Springs Flow, Wanapum Basalts, Hanford, Washington, in, *Advances in Ceramics 20: Nuclear Waste Management II*, The American Ceramic Society, Columbus, OH, p. 671-679. NNA.900320.0151.

JSS, 1987, *Experimental and modelling studies of HLW glass dissolution in repository environments*, JSS [Joint Japanese (CRIEP), Swiss (NAGRA), Swedish (SKB) project managed by Swedish Nuclear Fuel and Waste Management Co.] Technical Report 87-01. NNA.900215.0048.

Juteau, T., Noack, Y., Whitechurch, H., and Courtois, C., 1980, Mineralogy and geochemistry of alteration products in Holes 417A and 417D basement samples (DSDP Leg 51), *Init. Rept. DSDP LI, LII, LIII*, part 2, p. 1273-1297. NNA.900430.0051.

Keith, T. E. C., and Staples, L. W., 1985, Zeolites in Eocene basaltic pillow lavas of the Siletz River Volcanics, Central Coast Range, Oregon, *Clays Clay Min.*, 33, p. 135-144. NNA.900306.0087.

- Kim, J. I., Treiber, W., Lierse, Ch., and Offerman, P., 1985, Solubility and colloid generation of plutonium from leaching of a HLW glass in salt solutions, *Mat. Res. Soc. Symp. Proc.*, 44, p. 359-368. NNA.900215.0049.
- Kohyama, N., Shimoda, S., and Sudo, T., 1985, Iron-rich saponite (ferrous and ferric forms), *Clays Clay Mins.*, 21, p. 229-237. NNA.900312.0161.
- Kristmannsdottir, H., 1976, Types of clay minerals in hydrothermal altered basaltic rocks, Reykjanes, Iceland, *Jokull*, 26, p. 30-39. NNA.900315.0291.
- Kristmannsdottir, H., 1978, Alteration of basaltic rocks by hydrothermal activity at 100-300°C, in, *International Clay Conference, Developments in Sedimentology* 27, Mortland, M. M., and Farmer, V. C., eds., Elsevier, New York, p. 359-367. NNA.900315.0292.
- Kuhn, W. L. and Peters, R. D., 1983, Leach models for a commercial nuclear waste glass, *Mat. Res. Soc. Symp. Proc.*, 15, p. 167-174. NNA.900306.0088.
- Laidler, K. J., 1965, *Chemical Kinetics*, McGraw-Hill, New York, p. vii-ix, 542-566. NNA.900315.0293.
- Lanford, W. A., Davis, K., Lamarche, P., Lauresen, T., Groleu, R., and Doremus, R. H., Hydration of soda-lime glass, *J. Non-Cryst. Solids*, 33, p. 249-266. NNA.900306.0089.
- Lanza, F., and Ronsecco, 1982, Influence of a backfilling material on borosilicate glass leaching, in, *Scientific Basis for Nuclear Waste Management V*, Lutze, W., ed., North Holland, New York, p. 173-180. NNA.900306.0090.
- Lanza, F., Conradi, R., Hall, A. R., Malow, G., Trocellier, P., Van Iseghem, P., 1985, Mechanisms of leaching and corrosion of vitrified radioactive waste forms, in, *Radioactive Waste Management and Disposal: Proceedings of the Second European Community Conference*, Luxembourg, Simon, R., ed., Cambridge University Press. NNA.900315.0294.
- Lanza, F., Manara, A., Mammarella, L., Blasi, P., and Ceccone, G., 1988, Borosilicate HLW glass leaching in silica saturated solution, *Mat. Res. Soc. Symp. Proc.*, 112, p. 685-692. NNA.900306.0091.
- Lasaga, A. C., 1984, Chemical kinetics of water-rock interactions, *J. Geophysical Res.*, 89, p. 4009-4025. NNA.900216.0060.
- Lasaga, A. C., and Kirkpatrick, R. J., 1981, Kinetics of Geochemical Processes, *Reviews in Mineralogy*, 8, Mineralogical Society of America, p. i, vii-x. NNA.900430.0042.
- Lee, Cheng-Tsin., 1986, Surface and solution chemistry of glass/water interactions, Unpub. Ph.D. dissertation, University of Florida, 274 p. NNA.900216.0080.
- Lee, C. T., and Clark, D. E., 1985, Electrokinetics, adsorption and colloid study of simulated nuclear waste glasses leached in aqueous solutions, *Mat. Res. Symp. Proc.*, 44, p. 221-228. NNA.900215.0050.
- Lehman, R. L., and Kuchinski, F. A., 1985, The effect of various lead species on the leaching behavior of borosilicate waste glass, *Mat. Res. Soc. Symp. Proc.*, 44, p. 179-186. NNA.900215.0051.

Lewis, R. A. and Segali, R. L., Pressure dependence of glass dissolution and nuclear waste disposal, *Nature*, **299**, p. 140-141. NNA.900312.0162.

Lindqvist, K., and Laitakari, I., 1980, Glass and amygdulites in Precambrian diabases from Orivesi, southern Finland, *Geol. Soc. Finland Bull.*, **52**, p. 221-229. NNA.900405.0458.

Lutze, W., Malow, G., Ewing, R. C., Jercinovic, M. J., and Keil, K., 1985, Alteration of basalt glasses: implications for modelling the long-term stability of nuclear waste glasses, *Nature*, **314**, p. 252-255. NNA.900215.0052.

Lutze, W., Muller, R., and Montserrat, W., 1988, Chemical corrosion of cogema glass R7T7 in high saline brines, *Mat. Res. Soc. Symp. Proc.*, **112**, p. 575-584. NNA.900306.0092.

Lutze, W., and Schubert, P., 1988, Chemical corrosion of lead-iron phosphate glass, *Mat. Res. Soc. Symp. Proc.*, **112**, p. 641-650. NNA.900306.0093.

Luyendyk, B. P., et al., 1978, *Initial Reports of the Deep Sea Drilling Project 49*, U. S. Government Printing Office, Washington, D. C., p. 1020. NNA.900315.0295.

Machiels, A. J. and Pescatore, C., 1983, The functional dependence of leaching on the surface area-to-solution volume ratio, *Mat. Res. Soc. Symp. Proc.*, **15**, p. 209-216. NNA.900306.0094.

Maggs, W. W., 1988, Mg may protect waste under glass, *EOS Trans. AGU*, **69**, p. 49. NNA.900312.0163.

Malow, G., Lutze, W., and Ewing, R. C., 1984, Alteration effects and leach rates of basaltic glasses: implications for the long-term stability of nuclear waste form borosilicate glasses, *J. Non Cryst. Solids*, **67**, p. 305-322. NNA.900215.0053.

Manara, A., Lanza, F., Ceccone, G., Della Mea, G., and Salvagno, G., 1985, Application of XPS and nuclear technique to the study of the gel layers formed under different redox conditions on leached glasses, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 63-71. NNA.900215.0054.

Mark, T. D., and Ritter, W., 1987, Radiation damage and its annealing in sodium silica glass, *Mat. Res. Soc. Symp. Proc.*, **84**, p. 659-669. NNA.900215.0055.

Mark, T. D., and Walder, G., 1988, Annealing and leaching studies with natural and artificial obsidian glass, *Res. Soc. Symp. Proc.*, **112**, p. 693-702. NNA.900306.0095.

Marshall, R. R., 1961, Devitrification of natural glass, *Geol. Soc. Am. Bull.*, **72**, p. 1493-1520. NNA.900215.0056.

Mazer, J. J., 1987, Kinetics of glass dissolution as a function of temperature, glass composition, and solution pHs, Unpub. Ph.D. dissertation, Northwestern University, 179 p. NNA.900216.0062.

McCarthy, G. J., Scheetz, B. E., Komarneni, S., Smith, D. K., and White, W. B., 1980, Hydrothermal stability of simulated radioactive waste glass, in, *Solid State Chemistry: A Contemporary Overview*, Holt, S. L., Milstein, J. B., and Robbins, M., eds., The American Chemical Society Advances in Chemistry Series **186**, p. 349-398. NNA.900315.0297.

McGrail, B. P., 1988, Modeling the dissolution behavior of defense waste glass in a salt repository environment, *Mat. Res. Soc. Symp. Proc.*, **112**, p. 595-606. NNA.900306.0096.

McGrail, B. P., Kumar, A., and Day, D. E., Sodium diffusion in the and leaching of simulated nuclear waste glass, *J. Amer. Cer. Soc.*, 67, p. 463-467. NNA.900312.0164.

McKenzie, W. F., Wolery, T. J., Delany, J. M., Silva, R. J., Jackson, K. J., Bourcier, W. L., Emerson, D. O., 1986, *Geochemical Modeling (EQ3/6) Plan, Office of Civilian Radioactive Waste Management Program*, Lawrence Livermore National Laboratory, UCID-20864, 75 p. NNI.881209.0024.

McVay, G. L., and Buckwalter, C. Q., 1983, Effect of iron on waste-glass leaching, *J. Am. Cer. Soc.*, 66 (3), p. 170-184. NNA.900306.0097.

Melnik, T. W., Walton, F. B., and Johnson, L. H., 1984, High-level waste glass field burial test: Leaching and migration of fission products, *Nucl. Chem. Waste Management*, 5, p. 49-62. NNA.900306.0097.

Melson, W. G., 1973, Basaltic glasses from the Deep Sea Drilling Project. Chemical characteristics, compositions of alteration products, and fission tract "ages", *Trans. Am. Geophys. Union*, 54, p. 1011-1014. NNA.900306.0099.

Melson, W. G., and Thompson, G., 1973, Glassy abyssal basalts, Atlantic seafloor near St Paul's Rocks: petrography and composition of secondary clay minerals, *Geol. Soc. Am. Bull.*, 84, p. 703-716. NNA.900306.0100.

Melson, W. G., Byerly, G. R., Nelen, J. A., O'Hearn, T., Wright, T. L., and Vallier, T., 1977, A catalog of the major element chemistry of abyssal volcanic glasses, *Smithsonian Contrib. Earth Sci.*, 19, p. 31-60. NNA.900312.0165.

Mendel, J. E., 1982, The measurement of leach rates: A review, *Nucl. Chem. Waste Management*, 3, p. 117-123. NNA.900312.0166.

Michels, J. W., Tsong, I. S. T., and Nelson, C. M., 1983a, Obsidian dating and East African archaeology, *Science*, 219, p. 361-366. NNA.900312.0168.

Michels, J. W., Tsong, I. S. T., and Smith, G. A., 1983b, Experimentally derived hydration rates in obsidian dating, *Archaeometry*, 25, p. 107-117. NNA.900312.0167.

Moore, J. G., 1966, *Rate of palagonitization of submarine basalt adjacent to Hawaii*, U. S. Geol. Survey Prof. Paper 550-D, p. D163-D171. NNA.900312.0169.

Moore, J. G., Forni, D. J., and Clague, D. A., 1985, *Basalts from the 1877 submarine eruption of Mauna Loa, Hawaii: New data on the variation of palagonization rate with temperature*, U. S. Geol. Survey Bull. 1663, 11 p. NNA.900315.0298.

Morgenstein, M., and Piley, T. J., 1975, Hydration-rind dating of basaltic glass: A new method for archeological chronologies, *Asian Perspectives*, 17, p. 145-159. NNA.900315.0299.

Morgenstein, M., and Rosendahl, P., 1976, Basaltic glass hydration dating in Hawaiian archaeology, in, *Advances in Obsidian Glass Studies*, Taylor, R. E., ed., Noyes Press, Park Ridge, NJ, p. 141-164. NNA.900405.0459.

Moriya, Y., and Nogami, M., 1980, Hydration of silicate glass in steam atmosphere, *J. Non-Cryst. Solids*, 38/39, p. 667-672. NNA.900306.0101.

- Mottl, M. J., and Holland, H. D., 1978, Chemical exchange during hydrothermal alteration of basalt by seawater - I. Experimental results for major and minor components of seawater, *Geochim. Cosmochim. Acta*, **42**, p. 1103-1115. NNA.900306.0102.
- Mouché, E., and Vernaz, E., 1988, Aqueous corrosion of the French LWR solution reference glass: First generation model, *Mat. Res. Soc. Symp. Proc.*, **112**, p. 703-712. NNA.900306.0103.
- Muehlenbachs, K. and Clayton, R. N., 1972, Oxygen isotope studies of fresh and weathered submarine basalts, *Can. J. Earth Sci.*, **9**, p. 172-184. NNA.900306.0104.
- Muffer, L. J. P., Short, J. M., Keith, T. E. C., and Smith, V. C., 1969, Chemistry of fresh and altered basaltic glass from the Upper Triassic Hound Island volcanics, southeastern Alaska, *Am. J. Sci.*, **267**, p. 196-209. NNA.900306.0105.
- Murakami, T. and Banba, T., 1984, The leaching behavior of a glass waste form-Part I: The characteristics of surface layers, *Nucl. Technol.*, **67**, p. 419-428. NNA.900312.0170.
- Murakami, T., Ewing, R. C., and Bunker, B. C., 1988, Analytical electron microscopy of leached layers on synthetic basalt glass, *Mat. Res. Soc. Symp. Proc.*, **112**, p. 737-750. NNA.900306.0106.
- Natland, J. H., and Melson, W. G., 1980, Composition of basaltic glasses from the East Pacific Rise and Siqueiros fracture zone, near 9°N, in, *Initial Report of the Deep Sea Drilling Project 54*, Rosendahl B. R. et al., eds., U. S. Government Printing Office, Washington, D. C., p. 705-723. NNA.900315.0300.
- Nayudu, Y. R., 1964, Palagonite tuffs (haloclastites) and the products of post-eruptive processes, *Bull. Volc.*, **27**, p. 391-410. NNA.900306.0107.
- Newton, R. G., and Paul, A., 1980, A new approach to predicting the durability of glasses, *Glass. Tech.*, **21**, p. 301. NNA.900215.0063.
- Nogues, J. L., Vernaz, E. Y., and Jacquet-Francillon, N., 1985, Nuclear glass corrosion mechanisms applied to the French LWR reference glass, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 89-98. NNA.900212.0057.
- Nogues, J. L., Vernaz, E. Y., Jacquet-Francillon, N., and Pasquini, S., 1985, Alterability of the French LWR solution reference glass in repository conditions, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 195-204. NNA.900215.0058.
- O'Keefe, J. A., Barkatt, A., Glass, B. P., and Alterescu, S., 1988, Nuclear Waste under glass, further discussion, *EOS Trans. AGU*, **70**, p. 860. NNA.900215.0059.
- Ougouag, A. M., and Machiels, A. J., 1985, Effects of radiation-induced stress on the chemical durability of nuclear waste glass, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 609-616. NNA.900215.0060.
- Palmer, H. C., Tazaki, K., Fyfe, W. S., and Zhou, Z., 1988, Precambrian glass, *Geology*, **16**, p. 221-224. NNA.900215.0061.
- Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980, *PHREEQE- A computer program for geochemical calculations*, Water-resources Investigations 80-96, U. S. Geological Survey, Reston, VA, 210 p. HQS.880517.2817.
- Paul, A., 1977, Chemical durability of glasses: A thermodynamic approach, *J. Materials Science*, **12**, p. 2246-2268. HQS.880517.2522.

Paul, A., 1982, *Chemistry of Glasses*, Chapman and Hall, 293 p. NNA.900216.0063.

Paul, A., and Zeman, M. S., 1978, The relative influence of Al_2O_3 and Fe_2O_3 on the chemical durability of silicate glasses at different pH values, *J. Materials Science*, 13, p. 1499-1502. NNA.900306.0108.

Peacock, M. A., 1926, The volcano-glacial Palagonite Formation of Iceland, *Geol. Mag.*, 63, p. 385-399. NNA.900312.0173.

Peacock, M. A., and Fuller, R. E., 1928, Chorophaeite, sideromelane, and palagonite from the Columbia River Plateau, *Am. Min.*, 13, p. 260-282. NNA.900312.0172.

Pederson, L. R., Baer, D. R., McVay, G. L., and Engelhard, M. H., 1986, Reaction of soda lime glass in isotopically labelled water, *Jour. Non-Cryst. Solids*, 86, p. 369-380. NNA.900306.0109.

Pederson, L. R. and McVay, G. L., 1983, Influence of gamma irradiation on leaching of simulated nuclear waste glass: Temperature and dose rate dependence in deaerated water, *J. Am. Ceram. Soc.*, 66, p. 863-867. NNA.900306.0110.

Pederson, L. R. and McVay, G. L., 1984, Effect of gamma radiolysis on waste glass leaching on brines, in, *Advances in Ceramics 8*, Wicks, G. G. and Ross, W. A., eds., The American Ceramic Society, Columbus, OH, p. 49-56. NNA.900315.0301.

Pescatore, C., and Machiels, A. J., 1983, Mechanistic approach to modelling of nuclear waste form leaching, in, *Advances in Ceramics 8*, Nuclear Waste Management, Wicks, G. G. and Ross, W. A., eds., Amer. Cer. Soc., Columbus, OH, p. 509-518. NNA.900215.0062.

Petit, J. C., Langevin, Y., Lameille, J. M., and Dran, J. C., 1982, On the leaching behavior of a simple borosilicate glass in a confined environment, *Mat. Res. Soc. Symp. Proc.*, 11, p. 203-210. NNA.900306.0111.

Pjetursson, H., 1900, The glacial palagonite formation of Iceland, *Scottish Geog. Mag.*, 16, p. 265-293. NNA.900312.0174.

Plodinec, M. J., Jantzen, C. M., and Wicks, G. G., 1984a, Thermodynamic approach to prediction of the stability of proposed radwaste glasses, *2nd Int. Symp. Ceramics in Nuclear Waste Management*, Wicks, G. G. and Ross, W., eds., American Ceramic Society, p. 491-495. NNA.900215.0064.

Plodinec, M. J., Jantzen, C. M., and Wicks, G. G., 1984b, Stability of radioactive waste glasses assessed from hydration thermodynamics, *Mat. Res. Soc. Symp. Proc.*, 26, p. 755-762. NNA.900215.0065.

PNL, 1984, *Final report of the defense high level waste leaching mechanisms program*, PNL-5157, Pacific Northwest Laboratory, August, 1984. HQS.880517.2498.

Pritchard, R. G., Cann, J. R., and Wood, D. A., 1978, Low temperature alteration of basalts, Leg 49, in, Cann, J. R. et al., eds., *Initial Reports of the Deep Sea Drilling Project*, 49, U. S. Government Printing Office, Washington, D. C., p. 709-714. NNA.900315.0302.

Rana, M. A., and Douglas, R. W., 1961a, The reaction between glass and water, Part 1. Experimental methods and observations, *Phys. Chem. Glasses*, 2, p. 179-195. NNA.900312.0175.

- Rana, M. A., and Douglas, R. W., 1961b, The reaction between glass and water, Part 2. Discussion of the results, *Phys. Chem. Glasses*, 2, p. 196-205. NNA.900312.0176.
- Richet, P., and Bollinga, Y., 1986, Thermochemical properties of silicate glasses and liquids: A review, *Reviews of Geophysics*, 24, p. 1-25. NNA.900215.0066.
- Rimstidt, J. D. and Barnes, H. L., 1980, The kinetics of silica-water reactions, *Geochim. Cosmochim. Acta*, 44, p. 1623-1699. HQS.880517.2528.
- Robinson, P. T., Melson, W. G., O'Hearn, T., and Schmincke, H. -U., 1983, Volcanic glass compositions of the Troodos ophiolite, Cyprus, *Geology*, 11, p. 400-404. NNA.900306.0113.
- Rutley, F., 1886, Notes on alteration induced by heat in certain vitreous rocks, *Royal Soc. London Proc.*, 40, p. 1071-1089. NNA.900315.0303.
- Sales, B. C., White, C. W., Begun, G. M., and Boatner, L. A., 1984, Surface layer formation on corroded nuclear waste glasses, *J. Non-Cryst. Solids*, 67, p. 245-264. NNA.900306.0112.
- Savage, D., Robbins, J. E., and Merriman, R. J., 1985, Hydrothermal crystallization of radioactive waste storage glass, *Min. Mag.*, 49, p. 195-201. NNA.900312.0178.
- Scarfe, C. M. and Smith, D. G. W., 1977, Secondary minerals in some basaltic minerals from DSDP Leg 37, *Can. J. Earth Sci.*, 14, p. 903-910. NNA.900312.0179.
- Scheetz, B. E., Freeborn, W. P., Smith, D. K., Anderson, C., Zolensky, M., and White, W. B., 1985, The role of boron in monitoring the leaching of borosilicate glass waste forms, *Mat. Res. Soc. Symp. Proc.*, 44, p. 129-134. NNA.900215.0068.
- Scheidegger, K. F., and Stakes, D. S., 1979, X-ray diffraction and chemical study of secondary minerals from Deep Sea Drilling Project Leg 51, Holes 417A and 417D, in, *Init. Rep. DSDP 51, 52, 53*, Donnelly, J. et al., eds., p. 1253-1263. NNA.900430.0051.
- Schindler, P. W., Furst, B., Dick, R., and Wolf, P. U., 1976, Ligand properties of surface silanol groups. I. Surface complex formation with Fe^{3+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , *J. Colloid and Interface Science*, 55, p. 469-475. NNA.900306.0114.
- Schmincke, H. -U., 1983, Ash layers, hyaloclastites, and alteration of basaltic glass, Leg 65, in, *Initial Reports of the Deep Sea Drilling Project 65*, Lewis, B. T. R., et al., eds., U. S. Government Printing Office, Washington, D. C., p. 477-483. NNA.900315.0304.
- Schmincke, H. -U., and Pritchard, G., 1981, Carboniferous volcanic glass from submarine hyaloclastite, Lahn-Dill area, Germany, *Naturwissenschaften*, 67, p. 615. NNA.900312.0181.
- Schmincke, H. -U., Robinson, P. T., Ohrmacht, W., and Flower, M. F. J., 1978, Basaltic hyaloclastites from Hole 396B, DSDP Leg 46, in, *Initial Reports of the Deep Sea Drilling Project 46*, Dmitriev, L. et al., eds., U. S. Government Printing Office, Washington, D. C., p. 341-355. NNA.900315.0305.
- Scholze, H., 1988, Glass-water interactions, *J. Non-cryst. solids*, 102, p. 1-10. NNA.900215.0067.
- Scholze, H., Conradi, R., Engelke, H., and Roggendorf, H., 1982, Determination of the corrosion mechanism of high-level waste containing glass, in, *Scientific Basis for Nuclear Waste Management V*, Lutze, W., ed., North Holland, New York, p. 173-180. NNA.900306.0115.

Schramke, J. A., Simonson, S. A., and Coles, D. G., 1985, ^{237}Np and ^{239}Pu solution behavior during hydrothermal testing of simulated nuclear waste glass with basalt and steel, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 343-350. NNA.900306.0116.

Seyfried, W. E., and Bischoff, J. L., 1979, Low-temperature basalt alteration by seawater: An experimental study at 70°C and 150°C, *Geochim. Cosmochim. Acta*, **43**, p. 1937-1947. NNA.900306.0117.

Shade, J. W., Pederson, L. R., and McVay, G. L., 1983, Waste glass-metal interactions in brines, in, *Advances in Ceramics 8*, Nuclear Waste Management, Wicks, G. G., and Ross, W. A., eds., The American Ceramic Society, Columbus, Ohio, p. 358-367. NNA.900320.0152.

Singer, A., 1974, Mineralogy of palagonitic material from the Golan Heights, Israel, *Clays Clay Min.*, **22**, p. 231-240. NNA.900306.0118.

Smets, B. M. J., and Lommen, T. P. A., 1982, The leaching of sodium aluminosilicate glasses studied by secondary ion mass spectrometry, *Phys. Chem. Glasses*, **23**, p. 83-87. NNA.900215.0069.

Smets, B. M. J., Tholen, M. G. W., and Lommen, T. P. A., 1984, The effects of divalent cations on the leaching kinetics of glass, *J. Non-Cryst. Solids*, **65**, p. 319-332. NNA.900215.0070.

Smets, B. M. J., and Tholen, M. G. W., 1985, The pH dependence of the aqueous corrosion of glass, *Phys. Chem. Glasses*, **26**, p. 60-63. NNA.900215.0071.

Stakes, D. S., and O'Neil, J. R., 1982, Mineralogy and stable isotope geochemistry of hydrothermally altered oceanic rocks, *Earth Planet. Sci. Lett.*, **57**, p. 285-304. NNA.900306.0119.

Staudigcl, H., and Hart, S. R., 1983, Alteration of basaltic glass: Mechanisms and significance for the oceanic crust-seawater budget, *Geochim. Cosmochim. Acta*, **47**, p. 337-350. NNA.900215.0072.

Stokes, K. R., 1971, Further investigations into the nature of the materials chlorophaeite and palagonite, *Min. Mag.*, **38**, p. 205-214. NNA.900312.0183.

Stone, J. A., 1981, An overview of factors affecting the leachability of nuclear waste forms, *Nucl. Chem. Waste Management*, **2**, p. 113-118. NNA.900306.0120.

Strachan, D. M., 1984, Effect of flow rate on the leaching of nuclear waste glass, in, *Advances in Ceramics 8*, Wicks, G. G. and Ross, W. A., eds., The American Ceramic Society, Columbus, OH, p. 12-18. NNA.900320.0146.

Strachan, D. M., Krupka, K. M., and Grambow, B., 1984, Solubility interpretations of leach tests on nuclear waste glass, *Nuclear and Chemical Waste Management*, **5**, p. 87-99. HQS.880517.2547.

Sturchio, N. C., and Seitz, M. G., 1985, Behavior of nuclear waste elements during hydrothermal alteration of glassy rhyolite in an active geothermal system: Yellowstone National Park, Wyoming, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 557-564. NNA.900215.0073.

Sullivan, T. M., and Machiels, A. J., 1984, Modeling chemical interactions in the hydrated layers of nuclear waste glasses, *Mat. Res. Soc. Symp. Proc.*, **26**, p. 597-604. NNA.900215.0074.

Thomas, D., 1987, *A geochemical model of the Kilauea East Rift Zone*, U. S. Geol. Surv. Prof. Pap. 1350, p. 1507-1525. NNA.900215.0075.

Tomasson, J., and Kristmannsdottir, H., 1972, High temperature alteration minerals and thermal brines Reykjanes, Iceland, *Contrib. Mineral. Petrol.*, **36**, p. 123-134. NNA.900306.0121.

Tsong, I. S. T., Smith, G. A., Michels, J. W., Wintenberg, A. L., Miller, P. D., and Moak, C. D., 1981, Dating obsidian artifacts by depth-profiling of artificially hydrated surface layers, *J. Nucl. Instrum. Meth.*, **191**, p. 403-407. NNA.900312.0184.

Tsukamoto, M., Bjorner, I., Christensen, H., Hermansson, H. -P, and Werme, L., 1988, Leaching of Am-241 from a radioactive waste glass corroded in the presence of stainless steel corrosion products and/or bentonite, *Mat. Res. Soc. Symp. Proc.*, **112**, p. 565-574. NNA.900306.0122.

Tucholke, B. E. et al., 1979, *Initial Reports of the Deep Sea Drilling Project*, **43**, U. S. Government Printing Office, Washington, D. C., p. xxiii-xxv. NNA.900320.0147.

Uhlmann, D. R., 1972, A kinetic treatment of glass formation, *J. Noncrystalline Solids*, **7**, p. 337-348. NNA.900306.0123.

Van Iseghem, P., and Grambow, B., 1988, The long-term corrosion and modelling of two simulated Belgian reference high-level waste glasses, *Mat. Res. Soc. Symp. Proc.*, **112**, p. 631-640. NNA.900306.0124.

Van Iseghem, P. Ph., Timmermans, and De Batist, R., 1985, Parametric study of the corrosion behaviour in static distilled water of simulated European reference high level waste glasses, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 55-62. NNA.900215.0076.

Velde, B., 1985, *Clay Minerals: A Physico-Chemical Explanation of their Occurrence*, Elsevier, Amsterdam, p. 1-6. NNA.900320.0148.

Vernaz, E. Y., Dussossoy, J. L., and Fillet, 1988, Temperature dependence of R7T7 nuclear waste glass, *Mat. Res. Soc. Symp. Proc.*, **112**, p. 555-564. NNA.900306.0125.

Walker, D. D., Wiley, J. R., Dukes, M. D., and LeRoy, J. H., 1982, Leach rate studies on glass containing actual radioactive waste, *Nucl. Chem. Waste Management*, **3**, p. 91-94. NNA.900312.0185.

Wallace, R. M., and Wicks, G. G., 1983, Leaching chemistry of defense borosilicate glass, *Mat. Res. Soc. Symp. Proc.*, **15**, p. 23-28. NNA.900306.0126.

Walters, H. V., and Adams, P. B., 1975, Effects of humidity on weathering of glass, *J. Non-Cryst. Solids*, **19**, p. 183-199. NNA.900312.0186.

Werme, L. O., and Grambow, B., 1987, Development, application and validation of models for waste package long-term performance: current trends, *Mat. Res. Soc. Symp. Proc.*, **84**, p. 29-43. NNA.900215.0077.

Werme, L. O., Hench, L. L., and Lodding, A., 1985, Nuclear waste glass interfaces after 1 year burial in Stripa, *Mat. Res. Soc. Symp. Proc.*, **44**, p. 37-44. NNA.900215.0078.

White, A. F., 1983, Surface chemistry and dissolution kinetics of glassy rocks at 25°C, *Geochim. Cosmochim. Acta*, **47**, p. 805-815. NNA.900312.0188.

White, A. F., and Claassen, N. C., 1980, Kinetic model for the short-term dissolution of a rhyolitic glass, *Chemical Geology*, **28**, p. 91-109. NNA.900306.0127.

- White, W. B., 1986, Dissolution mechanisms of nuclear waste glasses: Critical review, *Advances in Ceramics* 20, p. 431-442. NNA.900215.0079.
- Wicks, G. G., 1986, Nuclear waste vitrification - The geology connection, *J. Non-Cryst. Solids*, 84, p. 241-250. NNA.900215.0080.
- Wicks, G. G., Rankin, W. D., and Gore, S. L., 1985, International waste glass study - composition and leachability correlations, *Mat. Res. Soc. Symp. Proc.*, 44, p. 171-177. NNA.900215.0081.
- Wicks, G. G., Robnett, B. M., and Rankin, W. E., 1982, *Scientific Basis for Nuclear Waste Management*, 5, Lutze, W., ed., Elsevier, New York, p. 15. NNA.900306.0128.
- Wolery, T. J., 1979, *Calculation of chemical equilibrium between aqueous solutions and minerals: The EQ3/6 software package*, Lawrence Livermore National Laboratory Report UCRL-52658, Livermore, CA, 41 p. HQS.880517.2586.
- Wood, B. J., and Walther, J. V., 1983, Rates of hydrothermal reactions, *Science*, 222, p. 413-415. NNA.900312.0189.
- Yokoyam, H., Hermansson, H-P, Christensen, H., Bjorner, I-K, and Werme, L., Corrosion of simulated nuclear waste glass in a gamma radiation field, *Mat. Res. Soc. Symp. Proc.*, 44, p. 601-607. NNA.900215.0082.
- Zellmer, L. A., and White, W. B., 1985, Characterization of hydrated surface layers on nuclear waste glasses by infrared reflectance spectroscopy, *Mat. Res. Soc. Symp. Proc.*, 44, p. 73-80. NNA.900215.0083.
- Zhu, Bing-Fu, Clark, D. E., Hench, L. L., Wicks, G. G., and Werme, L., 1985, One-year leaching of three SRL glasses in granite, *Mat. Res. Soc. Symp. Proc.*, 44, p. 187-194. NNA.900215.0084.
- Zhou, Z., and Fyfe, W. S., 1988, A comparative experimental study of glass stability in seawater and distilled water, *Mat. Res. Soc. Symp. Proc.*, 112, p. 725-736. NNA.900306.0129.
- Zielinski, R. A., 1980, Stability of glass in the geologic environment: Some evidence from studies of natural silicate glasses, *Nuclear Technology*, 51, p. 197-200. NNA.900215.0085.