Glasses: natural

Description: Natural glasses frequently occur on Earth and include volcanic glasses, impact glasses and tektites, fulgurites and other rare forms (Bouska, 1993).

The analogue studies have been focused on assessment of stability and release of elements from natural glasses as analogues of the borosilicate glassform which is universally used for vitrification of HLW. The results are compared with laboratory and in-situ experiments with radioactive or simulant glass waste forms with the aim of reaching consistency in predicted degradation processes and degradation rates. Devitrification (crystallization of glass matrix), dissolution and alteration and retardation of species in secondary alteration products were also extensively studied since glass is thermodynamically unstable. The dissolution and alteration of glass in nature is a function of glass composition, temperature, water/glass ratio, interaction/contact time, solution chemistry and flow conditions.

Excluding studies of exotic glass forms (e.g. lunar material), the research activities were focused on frequently occurring silica-rich (volcanic and impact glasses) and silica-poor glasses (basaltic glasses), see Table 1. Basaltic glasses most resemble borosilicate waste forms with regards to chemical composition (silica content), alteration products, alteration structure and morphology and alteration rates derived from laboratory experiments. The age of studied samples covers the period from some tens of years to hundreds of millions of years. The studied environments span from ocean-floor and sub-ocean sediments to subglacial, hydrothermal and surface conditions.

Table 1: Example of chemical composition (wt. %) of typical natural glasses in comparison with radioactive waste glass (according to Mazer, 1994)

	Basaltic glass	**Rhyolitic glass**	**Tektite**	**SRL 165 waste glass**
SiO_2	50.7	74.9	74.4	52.86
Al_2O_3	11.7	14.2	12.17	4.08
Na_2O	4.5	4.68	1.32	10.85
K_2O	0.7	4.59	2.61	0.19
CaO	10.6	0.53	1.52	1.62
MgO	6.7	0.02	1.85	0.70
FeO	-	0.49	-	-
Fe_2O_3	13.1	0.29	5.58	11.74

In the past, the mechanistic and kinetic models (based on first-order law) were derived (see for example Vernaz et al., 2001 for review) mainly from laboratory experiments and natural glasses can therefore be considered a control if processes and rates are described adequately and sufficiently. Glass is transformed to thermodynamically more stable phases via complex of reactions. The processes leading to dissolution of silicate glasses in aqueous solution include mass transport, ion exchange and hydrolysis (Luo et al., 1998). These three processes can occur simultaneously and are mutually interlinked. Dissolution of glass is not solubility limited and is controlled by the kinetics of the alteration processes. Formation of gel layer (e.g. amorphous palagonite) and crystallization of secondary minerals (e.g. zeolites) were identified at many natural glasses, mainly of basaltic composition.

Rod Ewing was probably the first scientist to suggest the use of natural glasses as analogues of radioactive waste glasses in a systematic way, but early relevant works also appeared (for example Marshall, 1961). He performed first focused studies (compilation of ages of 425 samples from North America) accompanied by modelling, interpretations and also discussion of limitations of such analogues (Ewing, 1979, and later works).

The studies have been focused mainly on basaltic glasses that occur on the outer surface of volcanic flows of basaltic magma which have come into contact with air or water. Basaltic glasses also occur as ash particles and have variable colour. Such glasses were intensively studied in both laboratory and natural environments to elucidate the mechanisms and to derive the kinetics of alteration. Alteration of basaltic glasses generally results in the occurrence of alteration layers historically referred as palagonites (mixture of hydrated glass matrix with authigenic minerals). Basaltic glasses have been found in a wide range of environments (Ewing, 1979): sea-floor and ocean sediments, subglacial environments, exposed volcanic ash flows or active geothermal environments. Based on extensive literature review, Byers et al. (1987) refer to the following characteristics of palagonite: palagonitization is a non-isochemical alteration process and not simple hydration, the composition of palagonite commonly differs from sample to sample, chemically different palagonites can originate from chemically and physically similar glasses indicating thus the importance of the alteration environment. Extensive characterisation of palaginitization is also provided by Crovisier et al. (2003). Palagonitization frequently leads to occurrence of amorphous gel-like material. In other cases (generally in samples younger than 1 Ma) the alteration layer also contains a crystallized part consisting of clay minerals (smectite). alteration layers of samples older than 1 Ma also contain zeolites. Other minerals like opal, calcite or gibbsite have also been identified.

Many laboratory experiments with natural basaltic glasses have been performed to study the mechanisms of glass alteration and to check the consistency with data from experiments with borosilicate glasses and with data from natural observations. For example Crovisier et al. (1992) reacted artificial tholeitic glass with artificial seawater (60^0C, 1 and 350 bars, up to 595 days) and compared the results with natural samples from Palagonia. They found that for $2x10^5$ y of reaction the palagonitic layer does not constitute a diffusional barrier to the mass transfer between the glass and the bulk solution. The surface recession rate (130 μm/1000 y) derived from experimentally found dissolution rate was nearly two orders of magnitude higher than palaginitization rate measured for basalt glasses altered by open sea water. Series of experiments were performed by Thomassin et al. and Crovisier et al. with seawater and by Trichet in pure water (all references in Crovisier et al., 2003). The general conclusion of these experiments is that the dissolution is stoichiometric and can become incongruent (notably with higher temperature) following the precipitation of silicate phases. The palagonite layer is a product of glass alteration, however, the rate of palagonitization may not be representative of the rate of glass dissolution. The rate of palagonitization (thickness of palagonite layer divided by the age of glass) is a function of temperature and exposure time (period of contact with water). Therefore the apparent alteration rate is used (Crovisier et al., 2003) or reaction progress (the total mass of glass dissolved per kilogram of solution) derived by thermodynamic computer code like DISSOL (Crovisier et al., 1992) tend to be used instead.

The alteration of natural basaltic glasses was studied in a variety of environments: ocean, subglacial, subaerial, fully contained in clay and even in hydrothermal conditions. Unfortunately, not all studies also report details on environmental conditions (for example water chemistry and water flow).

Natural alterations in subglacial conditions were studied on samples mainly from Iceland (series of works of Crovisier) and on hyaloclastites from British Columbia (for example Grambow et al., 1986). Such samples have been altered by cold and fresh diluted melt and rain water, although some samples may have been subjected to alternately submarine and subglacial conditions due to the fluctuations of the sea level. Crovisier studied samples of various ages (0.09 - 2.4 Ma) and found mean alteration time ranging from 0.004 to 0.33 μm/1000 y (the studies of other authors derived the similar values). The hyaloclastites samples from British Columbia originated from subglacial eruptions during the late Pleistocene. The thickness of alteration layers was highly variable (2 - 138 μm) and derived apparent alteration rates from 0.1 to 13.8 μm/1000 y. Crovisier found sharp boundaries between palagonite and glass and the presence of etched pits supports a palagonitization mechanism of progressive glass dissolution with contemporaneous repprecipitation of phases at the glass surface. It is unclear, based on these examinations, whether the glass dissolution is congruent. Authigenic mineralization generally occurs during the late stage of palagonitization. Most zeolites were found to be Ca varieties. Redistribution of Rare Earth

Elements (REE), U, and Th in altered basaltic glasses (Figure 1) was characterized in a set of studies (Bernotat 2001; Bernotat et al., 2001). They used younger (2000 and 100 ka) and older samples (3-4 Ma) with alteration rims less than 50 μm and 200-300 μm, respectively. Derived alteration rates are higher for younger samples (around 1 μm/1000 y) and higher for older samples (around 0.05 μm/1000 y). REE are progressively enriched in gel due to higher solubility of other elements and light REE are incorporated in smectites easier than heavy REE. It was found that the formation of zeolites changes the process of glass dissolution considerably: the complete complete dissolution of glass and precipitation of smectite is replaced by the selective dissolution of glass, formation of glass layer and precipitation of smectite.

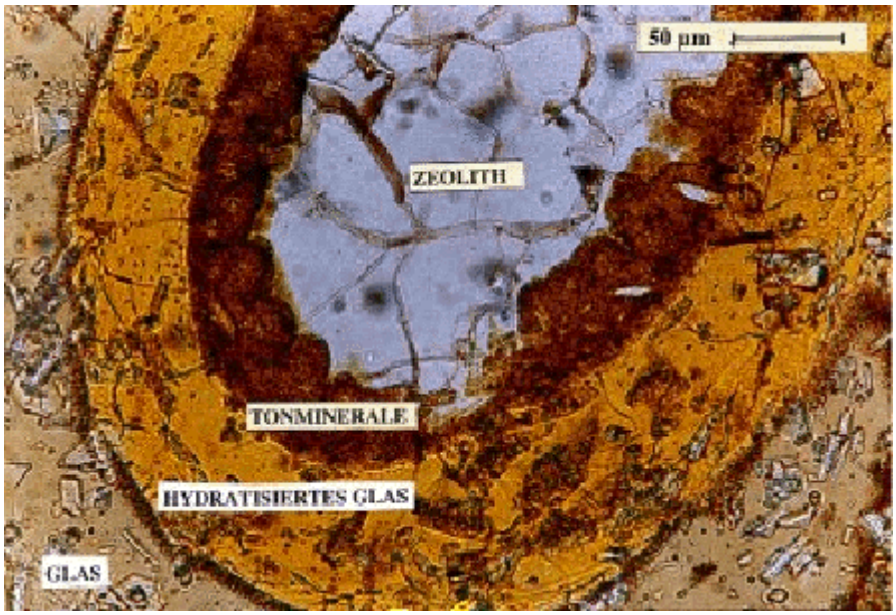

Figure 1: Altered layers in Icelandic volcanic glass (FZK, Germany).

Several studies have also been undertaken on the alteration of basaltic glasses in seawater (samples dredged from the surface of the ocean floor or recovered from the Deep Sea Drilling Project) - for example Grambow et al. (1986). The ages of samples are variable - up to 13 Ma. Very wide range of values of apparent alteration rates were derived - from 0.001 to 50 μm/1000 y.

In continental and oceanic environments glass dissolution rates are generally less than 50 μm/1000 y. Generally, the rate tends to diminish over time. This decrease may be related to a diffusion mechanism involving key chemical species and may also be controlled by the mineralogy of the palagonite layer.

Samples in subaerial conditions are exposed to unsaturated conditions and are corroded by rain water (directly at the surface or in soil or near surface sediments) and humid air. The ages of samples span from several hundred years to around 1 Ma. For example, Arai et al. (1989) studied 280- and 2,800-year old samples from the foot of Mount Fuji volcano. The alteration rate of this material is estimated to be several μm/1000 y. The palgonites formed in unsaturated conditions exhibit physical and chemical characteristics similar to those formed in subglacial conditions. The secondary precipitated minerals (occurring mainly in older samples) often include in such conditions smectite clays, phallipsite, chabazite, analcime and calcite.

Studies of the alteration of basaltic glasses in clay environment can examine palagonitization in the presence of clay that can be used an as analogue for the disposal of radioactive waste glass in clay-based engineered barrier or clay host rock. Techer et al. (2001) studied basaltic veins glassy rinds formed 1.4 Ma old in much older argillaceous sediment. They estimated an alteration rate from 0.014 to 2.14 μm/1000 y. Despite many uncertainties, these alteration rates are comparable to those measured immediately in contact of glass with aqueous media without clay material. Over a period of 1 Ma, no more significant alteration of the glass was observed in the presence of

Permian pelite. Kamei et al. (2000) studied volcanic glass around 1 Ma old with higher content of SiO_2 (around 60 wt. %) in marine argillaceous rocks that were uplifted above sea level around 0.5 Ma years ago. The lack of alteration in these conditions may be due to the aqueous silica and amorphous SiO_2 being in equilibrium which resulted in negligible dissolution of the glass matrix.

Alteration processes in hydrothermal conditions (Hawaii - up to 300^0C) were also studied, but the relevance of such studies for evaluation of disposal safety is questionable due to huge difference in predicted temperature evolution in a repository.

Rhyolitic acidic glasses (obsidians) occur after rapid cooling of magma of rhyolitic composition. Archaeologists and geologists have studied the hydration of rhyolitic glasses to develop a technique for dating obsidian artefacts (obsidian artefacts survived for more than 30,000 y in different environments). These studies have demonstrated that the rate of obsidian corrosion is controlled by a water diffusion process in humid environments and that the hydration of obsidian that occur in nature can be reproduced reasonably well in the laboratory Luo et al., 1998). Obsidians can be black, grey-green, brown, red, pinkish or even colourless.

Many studies performed in laboratory conditions with natural obsidians in laboratory and increased temperatures revealed that hydration (described by an ion-exchange model) involves inter-diffusion of H_3O^+ and alkali ions (for example McGrail et al., 1988). Hydration rates are proportional to the square of time, which suggest that the reaction is diffusion controlled (Mazer et al., 1992). It was also shown that the hydration rate is strongly affected by the initial water content of the glass and this that is the reason for extremely high durability of tektites and one of the reasons for predicted degradation of radioactive waste glass forms having only up to 0.1 wt. % of initial water. Alteration of obsidian samples in natural sub-aerial environments revealed the occurrence of hydrated altered layers known as perlite, ranging from 1 to 50 μm in thickness. Consistent with other studies, there is no evidence of the formation of secondary minerals during the corrosion of obsidian samples in terrestrial environment (Friedman and Long, 1984, and older works of Friedman). There are only a few studies assessing degradation of obsidians in water, partly due to the limited availability of such samples (Luo et al., 1998). A rare example is that of Magonthier and Petit (1992) who studied alteration of 52,000-year old rhyolitic glass by rain and subglacial melt waters. Unlike in terrestrial conditions, the alteration layer consisted of amorphous iron-rich alumosilicate and crystallized aluminium trihydroxide. Hydration rates derived from different sites were found at the level of units of $\mu m^2/1000y$. These field observations are consistent with general diffusion equation ($D = k \cdot t^{1/2}$) , but other dependencies have also been determined empirically ($D = k \cdot t^n$) from different data sets - these formulas are summarized in Luo et al. (1998).

Tektites are products of rock and soil melting after meteoritic impact. The four main strewn fields occur in Australasia, Czech Republic (Figure 2), Ivory Coast and North America (Glass, 1984b). They were formed millions of years ago (from 0.7 Ma old australites to 65 Ma old samples from Haiti) The colour is blackish to green. Tektites have usually fresh appearance without any large degradation layers due to their high silica content. Dissolution rates were quantified by Barkatt et al. (1984) at australites and indochinites in accelerated laboratory experiments (2.3 μm/1000 y; similar rates were found by other researchers) and hydration rates by Mazer et al. (1992). Deep-sea and sub-aerial alterations were studied Glass (1984a) at 170 microtektites and measured average thickness of dissolved glass span from 4.2 μm (North America microtektites) to 20.7 μm (micro-irghizites from Siberia) with absolute range 0.2 - 28 μm which corresponds to dissolution rates from $9x10^{-5}$ to $2.1x10^{-2}$ μm/1000 y. North American tektites have dissolution rates systematically two orders of magnitude lower in comparison with younger Australasian and Ivory Coast tektites despite their similar composition and deep sea environment. This discrepancy can be explained by possible burial in pelagic sediments that could drastically decrease dissolution due to reaching of saturation of Si in sedimentary pores. Tektites from terrestrial environment (micro-irghizites) have generally two to three orders of magnitude higher than australites (Glass, 1984a).

Figure 2: Typical sculptured tektite from Bohemia, the Czech Republic

Relevance: Glass is a most frequent waste form used for high-level waste (always used for solidification of liquid HLW from reprocessing of spent nuclear fuel) and is also proposed for solidification of low-level and mixed waste. Mainly borosilicate glass is utilised; phosphate type is used is Russia. Degradation of glass waste form and the release rate of elements is very important component of performance assessment.

Position(s) in the matrix tables: (Near-field) Concerning waste form (glass) and demonstration of near-field processes: barrier containment (physical and chemical integrity), nuclide release (dissolution and leaching), nuclides movement (diffusion) and nuclide retardation (precipitation of priority elements in surface layers).

Limitations: Differences in chemical composition of natural glasses and man-made borosilicate glasses are always present, even in the case of basaltic natural glasses. Consequences of ionising radiation on structure of glasses are not possible to evaluate due to their low content of natural radionuclides. Dissimilarities in geochemical conditions of deposition of natural glasses occur in many cases in comparison with expected near-field conditions (groundwater composition and other parameters).

Quantitative information: Alteration rates of basaltic glass materials were derived in the range of 0.001 to 100 μm/1000 years in a variety of environments. Based on integration of results from various types of observations and experiments, a two-stage model of glass degradation was proposed

Uncertainties: Uncertainties have mainly two sources: glass composition and properties and geochemical/hydraulic conditions of sites. Age of glass is known only approximately in many cases. Great discrepancies also stem from interchange of real alteration/degradation rates and apparent rates derived from the thickness of altered layer.

Time-scale: Very variable - from very young samples (some tens of years) from currently active volcanoes to many hundreds of millions of years (up to even around 1 billion years). Usual age of studied basaltic glasses span from some thousands to first millions of years.

PA/safety case applications: Analogues of natural glasses provide mainly qualitative and semi-quantitative information and enhance confidence that degradation processes are well understood and provided they have upper bounding limits to the degradation rates. Unfortunately, data used in performance assessment rely mainly on the results from laboratory experiments as can be documented in recently published performance assessment supporting documentation on glass dissolution parameters (Curti, 2003).

Communication applications: Frequently used for demonstration of stability and durability of glass waste forms for general public (longevity of occurrence despite of their meta-stable character).

References:

Barkatt A, Boulos MS, Barkatt A, Sousanpour W, Boroomand MA, Macedo PB and O'Keefe JA (1984) The chemical durability of tektites—A laboratory study and correlation with long-term corrosion behavior.- Geochimica et Cosmochimica Acta, 48, 2, 361-371.

Bernotat W (2001) Correlation between REE and Si content of smectites in altered basaltic glasses (natural analogue of radioactive waste glass). In FZKA-6629.

Bernotat W, Le Gal X and Crovisier J-L (2001) Retention of LREE and HREE by smectite and gel in altered basaltic glass (Natural analogue of vitrified radwaste). MIGRATION Conference, Bregenz, Austria.

Bouska V (1993) Natural glasses. Ellis Horwood, 354 pp.

Byers CD, Jercinovic MJ and Ewing RC (1987) A study of natural glass analogues as applied to alteration of nuclear waste glass. ANL-86-46 and NUREG/CR-4842.

Crovisier J-L, Honnorez et al. (1992) Dissolution of subglacial volcanic glasses from Iceland: laboratory study and modelling. Applied Geochemistry, Suppl. Issue No. 1, 55-81.

Crovisier J-L, Advocat T and Dussossoy J.-C (2003) Nature and role of natural alterations gels formed on the surface of ancient volcanic glasses (Natural analogs of waste containment glasses). Journal of Nuclear Materials, 321, 91-109.

Curti E (2003) Glass dissolution parameters: Update for “Entsorgungnachweis”. PSI Bericht 03-18.

Ewing R (1979) Natural analogues - analogues for radioactive waste forms. Materials Research Society Symposium Proceedings (I), 57-68.

Ewing RC and Jercinovic MJ (1987) Natural analogues: Their application to the prediction of the long-term bahavior of nuclear waste forms. Materials Research Society Symposium Proceedings (X), vol. 84, 67-83.

Friedman I and Long W (1984) Volcanic glasses, their origins and alteration processes. Journal of Non-Crystalline Solids, 67, 127-133.

Glass BP (1984a) Solution of naturally-occurring glasses in the geological environment. Journal of Non-Crystalline Solids, 67, 265-286.

Glass BP (1984b) Tektites. Journal of Non-Crystalline Solids, 67, 333-344.

Grambow B, Jercinovic MJ, Ewing RC and Bayers CD (1985) Weathered basalt glass: A natural analogue for the effects of reaction progress on nuclear waste glass alteration.- Materials Research Society Symposium Proceedings (IX), vol. 50, 263-272.

Kamei G, Yusa Y and Arai T (2000) A natural analogue of nuclear waste glass in compacted bentonite. Applied Geochemistry, 15, 141-155.

Luo JS, Abrajano TA Jr and Ebert WL (1998) Natural analogues of nuclear waste glass corrosion.- Argonne National Laboratory, Illinois, ANL-98-22.

Magonthier M-C and Petit CJ (1992): Rhyolitic glasses as natural analogue of nuclear waste glasses: Behavior of Icelandic glass upon natural aqueous corrosion. Applied Geochemistry, Suppl. Issue No. 1, 83-93.

McGrail BP, Pederson LR, Strachan DM, Ewing RC and Cordell LS (1988) Obsidian hydration dating - Field, laboratory, and modeling results. Materials Research Society Symposium - Materials Issues in Art and Archaeology, vol. 123 (Vandiver P. B., Druzik J. and Stevenson C., Eds.), 263-269.

Mazer JJ, Bates J, Stevenson CM and Bradley CR (1992) Obsidians and tektites: Natural analogues for water diffusion in nuclear waste glasses. Materials Research Society Symposium Proceedings (XV), vol. 257, 513-520.

Mazer JJ (1994) The role of natural glasses as analogues in projecting the long-term alteration of high-level nuclear waste glasses. Materials Research Society Symposium Proceedings (XVII), vol. 333, 159-165.

Techer I, Lancelot J, Clauer N, Liotard JM and Advocat T (2001) Alteration of a basaltic glass in an argillaceous medium: The Salagou dike of the Lodeve Permian Basin (France). Analogy with an underground nuclear waste repository- Geochimica et Cosmochimica Acta, 65, 7, 1071-1086.

Vernaz E, Gin S, Jegou C and Ribet I (2001) Present understanding of R7T7 glass alteration kinetics and their impact on long-term behaviour modeling. Journal of Nuclear Materials, 298, 27-36.

Added value comments: Better integration of data from laboratory experiments (both with borosilicate and natural glasses) and data from natural analogues studies performed in relevant conditions is desirable with the final aim to use in performance assessment calculations.

Potential follow-up work: The natural analogue studies will probably continue mainly in countries that produce HLW galls forms (France).

Keywords: Glass, dissolution, alteration, waste form

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