Naturally Occurring Glasses: Analogues for Radioactive Waste Forms

**Rodney C. Ewing
Richard F. Haaker**

April 1979

**Prepared for the U.S. Department of Energy
under Contract EY-76-C-06-1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from

National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.00
026-050	\$4.50
051-075	\$5.25
076-100	\$6.00
101-125	\$6.50
126-150	\$7.25
151-175	\$8.00
176-200	\$9.00
201-225	\$9.25
226-250	\$9.50
251-275	\$10.75
276-300	\$11.00

3 3679 00049 3611

NATURALLY OCCURRING GLASSES: ANALOGUES
FOR RADIOACTIVE WASTE FORMS

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ACKNOWLEDGEMENTS

This report has benefitted from the efforts of Ms. Kathleen Affholter.

As this report is necessarily a compilation of the work of others, the authors are particularly indebted to Dr. John A. O'Keefe for the data available in Tektites and Their Origin and to Dr. Sydney P. Clark, editor of Geological Society of America Memoir 97: Handbook of Physical Constants.

INTRODUCTION

Glass, primarily the borosilicate type, has received major consideration as the primary waste form for the disposal of high level radioactive wastes (Grover and Chidley, 1962; Grover, 1972; Blasewitz and others, 1972; Mendel and McElroy, 1972; Platt and McElroy, 1973-1974; Mendel, 1977). One criteria in selecting glass as a waste form, in preference to other ceramic or glass-ceramic waste forms, is the evaluation of its long-term "geologic" stability. The waste form is considered unstable should physical changes occur which cause significant increased radionuclide mobility. These transformations may include devitrification of the glass, alteration effects or radiation damage which produce new, and perhaps, unexpected phases of undetermined physical and chemical properties. Work presently in progress is designed to predict the appearance of such phases (e.g. Turcotte and Wald, 1978)

The long-term effects of alteration and radiation damage on the waste glass form as a result of interaction with the geologic environment are difficult to assess in time-limited laboratory experiments. Therefore, it becomes important to look at naturally occurring analogues of waste forms to evaluate their long-term stability. Age distributions and alteration effects observed in natural glasses in different geologic environments provide insight into variables controlling the rates of devitrification, alteration and radiation damage.

This report describes the properties and occurrence of natural glasses (volcanic glasses, tektites, and lunar glasses). Much of the data on the

physical and chemical properties of glasses are taken from Clark (1966), an excellent reference for geologic materials. Particular attention is paid to the compositional variations, age distributions and alteration effects of these natural glasses in different geologic environments. Radiation damage effects are difficult to evaluate in natural glasses as uranium and thorium concentrations are quite low (1-30 ppm). A description of radiation effects in natural glasses and the metamict state will be the subject of a later report.

Although the compositions of the synthetic waste glass form are quite different from those of naturally occurring glasses, these natural materials provide excellent benchmark standards for comparison to the synthetic glasses, and they may serve as checks on the data of time-limited laboratory experiments that must be extrapolated to estimate long-term stability. A discussion of experimental studies of natural glasses is included.

Since much of the appropriate data are taken from the geologic and mineralogic literature, certain terms may be unfamiliar. A glossary is therefore provided at the end of this report.

NATURAL GLASSES

Naturally occurring silicate glasses are of three main types: (1) volcanic glasses, (2) tektites and (3) lunar glasses. A less important category of natural glasses are fulgurites, an irregular, glassy, often tabular or rod-like structure or crust produced by the fusion of loose sand by lightning. Petrographic properties of each of these glass types are summarized in Table 1.

Volcanic glasses (see Table 11 for typical compositions) are associated with extrusive volcanic rocks that have been undercooled so quickly that crystalline phases have not had an opportunity to form. These "chilled" zones may be as much as 10 to 20 meters thick and are a common feature of the volcanic belts that circle the earth.

Tektites are natural silicate glasses ranging in size from fractions of a millimeter to tens of centimeters in size. Their shape may be irregular and blocky, but the majority occur as spheres or dumbbell and lense shaped buttons. They seldom occur as isolated objects but rather, are found as members of large associations, strewn fields, which may cover areas up to 10,000 km wide. Their origin, terrestrial or extraterrestrial, is still the subject of much debate.

Lunar glasses occur as a common constituent of the lunar microbreccias and fines. The individual glass bodies may be perfectly spherical, oblate spherules, or dumbbell shaped. Aside from the small amount of residual glass in the lunar basalts, all lunar glasses have been ascribed to shock-induced melting of preexisting rocks due to meteorite impacts, possibly at

Table 1: Petrographic Properties of Natural Glasses

Type of Glass	Color	Range of Bulk Specific Gravity	Range of Index of Refraction	Homogeneity	Structure
Obsidians	Black, grey to red	2.30-2.46	1.47-1.53	Crystallites are commonly present but contain no glass inclusions of composition different from the bulk glass, generally dense.	Banded or lamellar structure generally due to bands of oriented crystallites. Strain birefringence generally not pronounced.
Tektites	Black, dark brown, to bottle green	2.21-2.80	1.4798-1.51	Contain no crystallites but inclusions of siliceous glass are nearly ubiquitous; generally dense to slightly vesicular.	Pronounced flow structure consisting of schlieren of glasses of slightly different composition, accompanied by strain birefringence.
Lunar Glasses	Varies from colorless to green or deep red brown	2.5-3.0	1.56-1.70	Generally very homogeneous with only minor streaking. Inclusions are rare, but metallic spheres of iron and spherulites of clinopyroxenes and plagioclase may be present.	Flow structure may be well developed. Streaks of glass of different refractive indices are not uncommon.
Fulgurites	Light gray to greenish gray	Generally less than 2.2	1.46	Crystallites locally present; siliceous inclusions are also present. Sand grains or mineral fragments can usually be detected; highly vesicular.	Generally tubular-shaped with adhered sand grains. Flow structure present but only locally developed.

pressures in the megabar range. This splattering effect is responsible for the common glass crusts found on both Apollo 11 and Apollo 12 samples.

The physical properties, compositional variations, age distributions and alteration, devitrification and hydration effects for each of these natural glass types are discussed separately in the following sections.

VOLCANIC GLASSES:

Volcanic glass is a common and highly characteristic constituent of volcanic rocks. In basic rocks ($\text{SiO}_2 = 47 \text{ wt. } \%$), the parent magma of which has a relatively low viscosity, glass is typically present in subordinate amounts in the groundmass or is altogether lacking. In acidic lavas ($\text{SiO}_2 = 72 \text{ Wt. } \%$), glass is an important constituent material. These acidic lavas are granitic (compositionally equivalent to a rhyolite) and the dark glasses are called obsidian. Pitchstone is similar to obsidian, except that it has a resinous rather than glassy luster with a highly variable color and composition. Pitchstone usually has a higher water content (6 to 10 wt. %) than obsidian (1 wt. %). The obsidian glasses are seldom homogeneous or monolithic and often contain swarms of crystallites or spherulites. In many instances it is apparent that the spherulites have grown after the flow of the magma had ceased and after it had reached an essentially glassy state. The devitrification and recrystallization of volcanic glasses is quite common. In their place are uniformly fine-grained (aphanitic or cryptocrystalline) volcanic rocks (felsites and rhyolites), with persistent perlitic cracks that evidence the former glassy state. Hence glassy rocks are rare, though not unknown, in Paleozoic (ages greater than 225 million years) as compared with Tertiary formations (less than 65 million years). The specific age distributions of volcanic glasses will be discussed in a later section.

Physical Properties:

The physical properties of typical volcanic glasses have not been determined for well documented standard glasses. Clark (1966) has summarized the physical properties of volcanic glasses from a number of different sources. These properties are summarized in Tables 2-10. The original sources of the data are given in Clark (1966).

Composition:

Volcanic glasses can be quite variable in composition (Table 11). Although volcanic glasses of basaltic composition ($\text{SiO}_2 = 52 \text{ wt. } \%$) exist in limited quantities as thin selvages and as fragments in volcanic ash, the most common composition is granitic ($\text{SiO}_2 = 72 \text{ wt. } \%$), as illustrated in the histogram in Figure 1.

Age Distributions:

The long-term stability of a natural glass is apparently limited by its tendency to devitrify or recrystallize. If one assumes that volcanic glasses are stable over long periods of geologic time and that volcanism has been continuous throughout geologic time, then one would expect to find volcanic glasses preserved throughout the geologic rock record, covering a span of at least 570 million years since the end of the Precambrian. A literature search of dates for volcanic glasses of North America provides 245 dated volcanic glasses. The age dating methods included fission track dating (11 data points), obsidian hydration dating (184 data points) and K/Ar radiometric dating (50 data points). Over half of the dates are less

Table 2: Average Densities of Natural Glasses (Clark, 1966)

Glass	Range of Density	Mean Density
Rhyolite obsidian	2.330-2.413	2.370
Trachyte obsidian	2.435-2.467	2.450
Pitchstone	2.321-2.37	2.338
Andesite glass	2.40-2.573	2.474
Leucite tephrite glass	2.52-2.58	2.55
Basalt glass	2.704-2.851	2.772

Table 3: Density of Crystalline Rock and Corresponding Glass, Artificially Prepared (Clark, 1966)

	Density		Difference per cent of rock density
Rock		Glass	
Granite	2.656	2.446	7.90
Granite	2.630	2.376	9.66
Syenite	2.724	2.560	6.02
Tonalite	2.765	2.575	6.87
Diorite	2.833	2.680	5.40
Diorite	2.880	2.710	5.90
Gabbro	2.940	2.791	5.07
Olivine dolerite	2.889	2.775	3.95
Dolerite	2.800	2.640	5.71
Dolerite	2.925	2.800	4.27
Diabase	2.975	2.761	7.19
Diabase	2.96	2.76	6.8
Eclogite	3.415	2.746(?)	19.6

Table 4: Glass and Glassy Rocks; Compressibility
 $(V_0 - V)/V_0 = aP - bP^2$, P in megabars (Clark, 1966)

	T, °C	a	b	P _{max} (kb)
Obsidian				
Lipari, Italy	25	3.01		0.6
	15	2.76	mean to →	10
	139	2.79		
	294	2.75		
	25	2.78-2.89		dynamic
Ascension Island	30	2.56	mean to →	dynamic
Yellowstone Park, Wyoming	25	2.85		
Modoc, Calif.	25	2.76		
Pitchstone, Meissen, Germany	30	2.54	4.3	12
Tachylite, Torvaig, Skye	30	1.906	10	12
	75	1.945	10	
Kilauea, Hawaii	30	1.348	8	12
	75	1.397		
	25	1.44		12
Diabase glass	0	1.59	6.5	12
artificial	100	1.61	.4	
	12	1.60	mean to →	10
	140	1.65		
	300	1.62		
Melts of natural diabase	25	1.36-1.53		dynamic

Table 5: Glass and Glassy Rocks:
Elastic Constants: Effect of Pressure on G (Clark, 1966)

	E (mb)	G (mb)	σ	$\frac{1}{G} \frac{\Delta G}{\Delta P}$ (mb ⁻¹)
Obsidian				
Modoc, Calif.	.656	.303	(.08)	-5.3
Lipari, Italy	.652	.278	(.17)	
Lipari, Italy	.695			
Arnafels, Iceland	.718	.303	(.18)	
Feldspar glass	.899			
An ₇₀				
Diabase glass	.90-.96	.35-.38	.26-.30	

Table 6: Glass: Effect of Temperature on Elastic Constants (Clark, 1966)

T, °C	E/E ₀	Silica glass G/G ₀	σ	Pyrex glass E/E ₀	Obsidian Lipari E/E ₀	Diabase Glass E/E ₀
0	1.000	1.000	.187	1.000	1.000	1.000
100	1.019	1.010	.198	1.027	1.003	.991
200	1.035	1.019	.205	1.044	1.005	.983
300	1.044	1.029	.205	1.059	1.007	.973
400	1.057	1.037	.210	1.068		.961
500	1.073	1.044	.220			.945
600	1.084	1.051	.225			.924
700	1.089	1.057	.222			
800	1.090	1.060	.220			

Table 7: Strength of Hollow Cylinders of Glass Under External Hydrostatic Pressure (Clark, 1966)

From room-temperature tests on rubber-jacketed specimens with a 5.5 wall ratio. Cylinder axes of single crystals parallel to optic axes

Material	Pressure (kb)	Type of Failure
Glass	12.0	Random fracturing. No spalling.

Table 8: Shearing Strength Under High Confining Pressure

Average shearing strength at different average normal pressures of lensoidal powder specimens pressed between a piston and steadily rotating anvil. Double 60-degree rotation in about 10 seconds. (Clark, 1966)

Mineral or Rock Name	Shear strength (kb)					Remarks
	At normal pressure of (kb)					
	10	20	30	40	50	
Basalt glass (artificial)	2.9	7.5	13	14	17	Rotates with snapping

Table 9: Conductivity of Glass (Clark, 1966)

Glass	Temperature °C	Conductivity (10^{-3} cal/cm sec°C)
Obsidian, Modoc, Calif.	0	3.21
	100	3.48
	200	3.74
	300	4.00
	400	4.26
	500	4.52
Diabasic glass (artificial)	0	2.74
	100	3.00
	200	3.27
	300	3.53

Table 10: Viscosity of Miscellaneous Glasses (Clark, 1966)

Composition, weight per cent		Temperature °C	Viscosity, poise
SiO ₂	78.28	843	3.50×10^6
Na ₂ O	11.76	892	7.83×10^5
MgO	9.30	1010	5.21×10^4
CaO	.91	1100	1.09×10^4
Al ₂ O ₃		1195	3.06×10^3
Fe ₂ O ₃		1425	2.43×10^2
SiO ₂	72.05	500	8.33×10^{12}
Na ₂ O	20.62	600	7.44×10^9
Al ₂ O ₃	6.85	674	1.56×10^8
CaO	.20	730	8.15×10^6
Fe ₂ O ₃		909	3.68×10^4
		1180	8.96×10^2
		1388	1.86×10^2
SiO ₂	71.56	550	1.43×10^{12}
Na ₂ O	15.28	700	2.08×10^8
Al ₂ O ₃	12.69	797	5.56×10^6
CaO	.31	1000	2.78×10^4
Fe ₂ O ₃		1190	4.55×10^3
		1390	6.27×10^2
SiO ₂	74.96	750	3.56×10^7
CaO	9.36	800	2.91×10^6
MgO	.28	890	9.35×10^4
Na ₂ O	14.88	995	1.03×10^4
Al ₂ O ₃	.42	1100	1.66×10^3
Fe ₂ O ₃	.16	1200	6.50×10^2
		1305	3.18×10^2
		1400	1.63×10^2

Table 10: Viscosity of Miscellaneous Glasses (continued)

Composition, weight per cent		Temperature °C	Viscosity, poise
SiO ₂	76.68	742	3.56×10^7
CaO	.14	796	4.60×10^6
MgO	6.87	902	1.59×10^5
Na ₂ O	15.78	998	2.11×10^4
Al ₂ O ₃	7.10	1100	4.23×10^3
Fe ₂ O ₃	.36	1198	1.24×10^3
		1304	4.48×10^2
		1400	1.80×10^2
SiO ₂	73.98	770	1.94×10^7
CaO	7.10	858	1.08×10^6
Al ₂ O ₃	7.10	995	3.15×10^4
Na ₂ O	11.66	1085	7.31×10^3
Fe ₂ O ₃	.10	1198	1.97×10^3
		1308	8.63×10^2
		1400	5.52×10^2

Table 11: Typical Compositions for Volcanic Glasses (Washington, 1916)

	1	2	3	4	5
SiO ₂	73.16	74.59	72.14	60.76	59.92
Al ₂ O ₃	11.97	12.88	15.93	20.08	18.09
Fe ₂ O ₃	2.23	0.80	1.99	4.46	4.52
FeO	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	1.08	0.30	0.40	trace	0.44
CaO	2.67	0.76	1.93	2.07	2.19
Na ₂ O	3.55	3.30	3.97	5.70	6.23
K ₂ O	4.56	5.35	2.55	6.31	7.24
H ₂ O+	0.16	1.03	n.d.	1.37	1.17
P ₂ O ₅	0.18				
MnO			0.43		
Total	99.56	99.01	99.34	100.75	99.80
S.G.	2.359	2.324			
¹ Rhyolite					
² Rhyolite					
³ Rhyolite					
⁴ Trachyte					
⁵ Leucite tephrite					

Figure 1: Silica content of 159 volcanic glasses (after Washington, 1916), including pitchstones, obsidians, perlites, marekanites, tholeiites, tachylites, palagonites, and rocks with the prefixes vitro- and hyalo- (from Marshall, 1961).

Figure 2: Age distributions of volcanic glasses as determined by fission track dating, obsidian hydration dates and K/Ar radiometric techniques.

than 2 m.y. old (Figure 2). Of the two oldest dates, 40 ± 13 m.y. B.P.* (Isochron/West, no. 11, Dec. 1974) and 71 ± 23 m.y. B.P. (Isochron/West, no. 11, Dec. 1974), the latter is probably in error. Thus, the vast majority of volcanic glasses are quite young, the older glasses having recrystallized to fine-grained volcanic rocks (e.g. rhyolite).

Although the age distribution data supports the thesis that volcanic glasses are metastable and thus recrystallize over relatively short periods of geologic time, there are certain qualifications to the data that must be noted:

(1) Most of the samples (184) were dated using obsidian hydration techniques. This technique is popularly used by archaeologists, and most of the samples of interest to archaeologists would be less than two million years old.

(2) Rocks of older age are more likely to have been eroded away, so that as one proceeds back into the rock record, that record becomes less complete. If the half-life of extrusive volcanic rocks is approximately the same as that of sedimentary rocks, then half of the volcanic rock record is removed every 130×10^6 years (Blatt and Jones, 1975). This means that the record of crystalline, as well as glass, rock types becomes more incomplete with increasing age, due to the agents of erosion.

(3) One must consider the possibility that volcanic activity has not been equally continuous throughout geologic time. Kennet and Thunell (1975) have suggested that explosive volcanic activity has much increased during the past two million years, as recorded in ash layers preserved in deep sea drilling cores. However, Ninkovich and Donn (1976) note that

*m.y.B.P. $\equiv$ million years before present

such records have been modified by the motion of tectonic plates, and hence may not be a representative record.

Due to the above limitations on the absolute age distribution data for volcanic glasses, it becomes important to compare the age distribution of volcanic glasses to the age distribution of volcanic rocks erupted during the same period of volcanic activity. If volcanic glasses recrystallize over short periods of geologic time, then the age distribution of the remaining volcanic glasses should be shifted to younger ages relative to those of the volcanic rocks of that area. Snyder, Dickinson and Silberman (1976) have compiled a data set of 2100 radiometrically dated igneous rocks of the western U.S., representing a time interval of 80 m.y. B.P. to the present. For each of the dated samples, the rock type is identified. Histograms (Figures 3-6) plotting the age distributions for each rock type may be compared. Note, the mean age of rhyolite and obsidian glasses is approximately 18 m.y. B.P. (Figure 3). The mean age for crystalline rhyolite (Figure 4) and tuff, ash flow and pumice (Figure 5) are 18 m.y. B.P. and 17 m.y. B.P., respectively. The preserved glasses are not distinctly younger than their crystalline compositional equivalents, indicating, at least in this suite of samples, very little recrystallization. The andesite diorite ages (Figure 6) are slightly older, 20 m.y. B.P., perhaps indicating recrystallization of older glasses to this compositional crystalline equivalent.

It is very apparent from these data that although metastable, natural volcanic glasses may exist in the rock record for periods of time up to 40 million years. This observation, however, does not address the question

Figure 3: Age distribution for rhyolite and obsidian glasses
(m.y.B.P. $\equiv$ million years before present)

Figure 4: Age distribution for rhyolites
(m.y.B.P. $\equiv$ million years before present)

Figure 5: Age distribution for tuff, ash flows, and pumice.
(m.y.B.P. $\equiv$ million years before present)

Figure 6: Age distribution for andesite and diorite
(m.y.B.P. $\equiv$ million years before present)

of whether these glasses exist in a substantially unaltered state. As one might expect, alteration and hydration effects may be of considerable importance in volcanic glasses.

Alteration:

The alteration of volcanic glasses has been an area of research for geologists and mineralogists for a number of very different reasons: (1) It has been important to establish the effect of weathering and alteration on age dating techniques (e.g. the loss of Ar in K/Ar radiometric dating; annealing of fission tracks; climatic and compositional effects on hydration rates). (2) Both in continental and submarine metallic deposits, leaching of metals (e.g. U, Th, Pb, Zn, Mn, Mg, Cr, Ni, K) from volcanic rocks has been suggested as the original metal source for hydrothermal and syngenetic metallic deposits. (3) Igneous petrologists have considered glass compositions to be "frozen" samples of melt compositions prior to crystallization. (4) Variations in weathered layers on natural and synthetic glass have been used to reconstruct past climatic conditions. This report will not attempt to summarize the data from all of these different types of studies, but rather will discuss several studies that will be directly pertinent to radioactive waste disposal questions. These alteration studies are empirical as well as experimental.

In an attempt to determine whether rhyolite glass is a source of uranium Zielinski (1978) and Zielinski, Lipman and Millard (1977) have completed a detailed analysis of minor-element abundances in obsidian,

perlite and felsite of calc-alkalic rhyolitic composition. The data include neutron activation analyses for twenty-four elements (Na, K, Cs, Cr, Mn, Fe, Co, Sc, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Lu, Zr, Hf, La, Sb and Th) and U analyses by delayed-neutron activation. Among the important conclusions are: (1) Obsidians and coexisting perlites have identical ($\pm 5\%$) uranium concentrations (5 to 46 ppm), confirming that little or no uranium is lost during hydration; (2) Felsites show uranium depletions as high as 80% relative to coexisting obsidians and perlites, indicating that uranium depletion seems to increase with age, with different depletion rates for calc-alkaline (slowest) and peralkaline (fastest) compositions; (3) The leached uranium is associated with concentrations of Fe-Ti-Mn oxides, especially along fractures or flow layers; (4) Uranium loss seems to be largely controlled by low temperature processes (ion exchange, differential solution, and absorption by secondary phases) over long periods of time.

The same type of data for elements such as Fe, Mn, Cu and Zn are available from experimental hydrothermal studies of seawater-basalt reactions (Seyfried, 1977; Seyfried and Bischoff, 1977). This type of approach may serve as a model for laboratory studies of brine and waste form interactions and is of particular interest if the waste canisters are exposed to a brine solution, either in bedded salt deposits or on the sea floor. Important conclusions from this type of study include: (1) The chemical exchange that results from the interaction of seawater and basaltic glass is more distinct than that of holocrystalline basalt-seawater interaction;

(2) The chemical exchange between seawater and basaltic glass at 260°C and 500 bars is such that heavy metals (Cu, Zn and Ba) are transferred in significant proportions to the aqueous phase; (3) The precipitates that form are strongly influenced by the degree of mixing and the ratio of water to rock.

Devitrification:

In addition to information on the alteration of glasses, devitrification rates have been calculated using simple rate theory and experimental data to set an approximate lower limit to the time required for thermal reconstruction of natural glasses as a function of temperature (Marshall, 1961). The time required for a glass at 300°C to devitrify to a crystalline feldspar is estimated to be at least a million years (Figure 7) and at 400°C at least several thousand years. The diffusion of water is presumed to control the rate of hydrothermal reconstruction. The diffusion constant at 20°C is estimated to be 10^{-23} cm²/sec, with an activation energy of 30 Kcal/mole. In contrast to simple thermal reconstruction, devitrification in the presence of water requires only a short time at temperatures less than 300°C (Figure 8). Lofgren (1970, 1971) in devitrification studies of obsidian in the temperature range of 240°-700°C and .5 to 4 kb has produced devitrification textures (e.g. spherulites) and granophyric textures with no evidence of the glassy precursors. The devitrification rate was substantially increased in the presence of Na- or K-rich solutions. [Recent hydrothermal studies of waste glasses (Westsik and Turcotte, 1978) suggest devitrification rates in salt brine are slower than in deionized water.]

Figure 7: Minimum time required for thermal reconstruction of natural glass plotted against temperature. (Marshall, 1961)

Figure 8: Time required for the hydrothermal reconstruction of perlite to a depth of 100 μ as a function of temperature (Marshall, 1961)

Hydration:

There is considerable data available on the hydration rates of volcanic glasses, as this is an important archaeological age dating technique (Friedman and Trembour, 1978; Friedman and Smith, 1960; Lanford, 1977; Michels and Bebrich, 1971). The obsidian dating method is based on the fact that volcanic glasses initially contain 0.1 to 0.3% water by weight, but the glasses absorb more water from the atmosphere along freshly broken surfaces. The resulting hydration rim increases in thickness with the passage of time. The glass that has absorbed the water has a higher refractive index than the original glass. The increased volume of the glass which has absorbed water causes mechanical strain which is visible as strain birefringence in polarized light. Thicknesses of the hydration rind may vary from 1 to 50 microns and may be related to the time that has passed since the fresh surface was exposed to the air (Figure 9). The hydration rate (which may vary from 1 to 20 $\mu\text{m}^2/1000 \text{ yrs.}$) becomes the critical value. Hydration rates were initially determined by measuring the thickness of the hydration rinds on samples that could be dated using ^{14}C radiometric techniques.

Experimental hydration rates were measured for obsidians of different compositions at elevated temperatures in order to accelerate the hydration process (Figure 10). Hydration rates can be determined from obsidian artifacts of known age under different climatic conditions (Figure 11) and this data can be combined with experimental data to construct an activation energy of hydration plot (Figure 12) (Friedman, Smith and Long, 1966). Additional data on the effect of climatic variations are available from archaeological studies (Bell, 1977; Findlow and others, 1975).

Figure 9: Experimental hydration rate curve for obsidian at 100°C (Friedman, Smith and Long, 1966)

Figure 10: "The relationship between the chemical composition of the obsidian - expressed as $\text{SiO}_2 - 45(\text{CaO} + \text{MgO}) - 20(\text{H}_2\text{O}^+)$ where the various oxides are expressed in weight percent and where H_2O^+ is water that is expelled at temperatures in excess of 110°C (bound water) - and the hydration rate - expressed in μm^2 per 100 years - is given as a function of temperature. These data were derived by experimentally hydrating obsidians of different chemical composition at elevated temperatures to speed up the hydration, and extrapolating the data so obtained to lower temperatures." (Friedman and Trembour, 1978)

Figure 11: Hydration rate curves for obsidian artifacts of known age formed under varying climatic conditions. (Friedman, Smith and Long, 1966)

Figure 12: Activation energy of hydration curve. Data from Figures 9 and 11. (Friedman, Smith and Long, 1966)

Jezek and Noble (1978) have used the electron microprobe to study the process of hydration and ion exchange. The water content was estimated by difference-of-sum of oxide components between associated non-hydrated glass and its hydrated equivalent. Hydration occurred along small microfractures and was accompanied by appreciably higher K_2O and appreciably lower Na_2O contents. The hydration is an early stage in the eventual formation of secondary argillic or zeolitic assemblages.

The most important feature of these studies is that finite rates of hydration can be determined as a function of glass composition and climate. The data from laboratory experiments at elevated temperatures can be extrapolated to the low-temperature, long-term effects observed in natural specimens. Such an approach confirms an experimental technique which allows the long-term prediction of the hydration rates of glasses, whether volcanic or a radioactive waste form.

TEKTITES:

Tektites are glassy objects, fractions of a millimeter to tens of centimeters in size, that are scattered across the earth's surface in discrete arrays up to tens of thousands of kilometers across. They are composed of a highly siliceous glass, devoid of crystalline phases, except rare coesite, nickel-iron spherules and particles of lechatelierite, a pure silica glass. The origin of tektites is a subject of much controversy. Some authors (Faul, 1966; King and others, 1970; Urey, 1971) have maintained a terrestrial origin for tektites, while others (Taylor and Kaye, 1969;

O'Keefe, 1976) an extraterrestrial origin.

The recent summary of the literature and data on tektites by O'Keefe (1976) will provide the basis for this section of the report.

Physical Properties:

Selected data on the physical properties of tektites are summarized in Tables 12 and 13. Most of these properties will vary as a function of composition (particularly SiO₂ content). Specific values for each of the physical properties as a function of composition are referenced in O'Keefe (1976).

Composition:

Typical compositions of tektites are listed in Table 14. Tektites differ from volcanic glasses mainly in their high SiO₂ content, low water content (.01 wt. %), low ferric/ferrous ratio and lower abundances of volatile elements. Among terrestrial rocks, the intermediate igneous rocks and sandstones are compositionally the most similar to tektites.

Age Distribution:

Tektites range in age from hundreds of thousands of years to approximately 35 million years (Table 15). Of the six known tektite strewn fields, their ages are: (a) Australasian, 0.75 m.y. B.P.; (b) Ivory Coast, 0.9 m.y. B.P.; (c) Aouelloul, 3 m.y. B.P.; (d) Moldavite, 15 m.y. B.P.; (e) Libyan Desert, 28 m.y. B.P.; and (f) North America, 35 M.Y. B.P. A literature

Table 12: Selected Physical Properties of Tektites (from O'Keefe, 1976)

Refractive Index: 1.48 - 1.54

Specific Gravity: 2.21 - 2.80

Hardness: 6 - 7 (Moh's Hardness)
900 - 1200 g/micron²

Tensile Strength: .6 - 1.0 Kbar

Linear Coefficient of
Thermal Expansion
(100°-500°C): 40×10^{-7}

Transformation Temperatures (T_g): 650°C

Viscosity (SiO₂ = 76 wt. %):

$$\log \eta = \frac{27.620}{T-262} - 10.09 \text{ [Nsec/m}^2\text{]}$$

T = absolute Temperature

Nsec/m² = 10 poise

Specific Heat (SiO₂ = 76 wt. %):

$$C_p = 0.953 + 0.00025T - \frac{27000}{T^2} \text{ [KJ Kg}^{-1} \text{ }^\circ\text{K}^{-1}\text{]}$$

T = absolute Temperature

Table 13: Elastic Constants (from O'Keefe, 1976)

		Moldavite	Indochinite
Longitudinal velocity	(km/sec)	5.918	5.999
Shear velocity	(km/sec)	3.627	3.638
Poisson's ratio		0.1991	0.2090
Density	(g/cm ³)	2.373	2.424
Bulk modulus	(kbar)	414.8	444.4
Shear modulus	(kbar)	312.2	320.9
Young's modulus	(kbar)	748.8	775.9

Table 14: Average Composition of Tektites (Friedman and Smith, 1960)

	Philippine Tektites	Texas Tektites	Moldavites	Indochinites	Australites
SiO ₂	71.21	75.64	79.60	73.14	73.33
Al ₂ O ₃	12.57	14.59	11.02	12.48	12.75
Fe ₂ O ₃	1.47	0.41	0.15	0.19	0.50
FeO	4.19	4.00	2.24	4.98	4.25
MgO	2.90	1.28	1.30	2.00	1.98
CaO	3.19	0.05	1.92	2.51	3.01
Na ₂ O	1.52	1.36	0.51	1.45	1.25
K ₂ O	1.93	1.85	3.00	2.40	2.05
H ₂ O+	0.37		0.07	0.28	0.19
H ₂ O-		0.05	0.04	0.10	0.09
TiO ₂	0.89	0.81	0.80	0.94	0.67
MnO	0.11	0.01	0.11	0.13	0.16
Total	100.35	100.05	101.39	100.60	100.23

Table 15: K-Ar and Fission-Track Ages of Tektite Strewn Fields
(from O'Keefe, 1976)

Materials	K-Ar ($\times 10^6$ years)	Fission Track ($\times 10^6$ years)
<u>Australasian</u>		
Australites	0.72 ± 0.06	0.7 ± 0.1
Indochinites	0.73 ± 0.06	
Philippinites	0.70 ± 0.07	
Thailandites	0.72 ± 0.06	
billitonites		
javanites		
Borneo tektites		
Darwin glass		0.72 ± 0.1
Muong Nong		0.7 ± 0.1
Microtektites		0.71 ± 0.1
<u>Ivory Coast</u>		
Land tektites	1.1 ± 0.1	1.02 ± 0.1
Microtektites		1.09 ± 0.20
Bosumtwi glasses	1.3 ± 0.3	
Ata glass		1.04 ± 0.2
<u>Moldavites</u>	14.7 ± 0.7	14.1 ± 0.6
<u>Ries glasses</u>	14.7 ± 0.6	14.0 ± 0.6
<u>Libyan Desert glass</u>		26.6 ± 6.3
		$- 1.3$
		28.5 ± 2.3
<u>North American tektites</u>		
Cuban		35
Bediasites	34.2	34.2 ± 2.0
Martha's Vineyard		36.4 ± 1.5
Georgia		1.0 ± 0.1
		6.3 ± 0.7
Microtektites		34.6 ± 4.2

Table 15: K-Ar and Fission-Track Ages of Tektite Strewn Fields (continued)

Materials	K-Ar ($\times 10^6$ years)	Fission Track ($\times 10^6$ years)
<u>Aouelloul</u>	18.6	0.46 $\pm$ 0.10
		0.38 $\pm$ 0.08
		0.16 $\pm$ 0.06
		0.16 $\pm$ 0.05
		0.49 $\pm$ 0.09
		0.50 $\pm$ 0.16
		0.57 $\pm$ 0.1
		0.59 $\pm$ 0.1
		0.61 $\pm$ 0.1
		3.3 $\pm$ 0.5

search indicated that over 40% of the dated tektites are less than five million years old.

Alteration, Hydration and Devitrification:

It is important to note that in over 900 published studies of tektites, there is only limited mention of alteration, hydration or devitrification effects. Although compositions of single tektites may vary considerably within the tektite (for an australite SiO_2 content may vary from 60 to 80 wt. %), electron microprobe analyses (Al, Fe, Mg, Ca, Ti, Mn, Ba, Na, K, P) reveal no systematic difference in composition between the core and flange of the tektite (Glass, 1970) indicating no later alteration or weathering effects. Similarly, hydration rims have not been described for tektites. Devitrification textures have been observed in tektites that were subjected to fires in Manila during World War II (Barnes and Russell, 1966). Experiments show that a similar amount of devitrification and partial collapse of bubbles takes place in tektites heated for approximately four days at 825°C. Certain tektite compositions showed no devitrification effects after heating for seven days at 825°C. The devitrification textures seem to be associated with minute amounts of water (2 ppm) which has dissolved into the glass after its formation. Yagi (1966) has noted that at 900°C, quartz is the end product of devitrification, while at 1000°C, after 48 hours, cristobalite and calcic plagioclase are the end products.

LUNAR GLASSES:

A very special category of naturally occurring glasses are the lunar glasses. Aside from the small amount of residual glass in the lunar basalts,

all the Apollo 11 and 12 glasses have been ascribed to shock-induced melting of preexisting rocks due to meteorite impacts, possibly at peak pressures in the megabar range. At the site of impact, large quantities of melt are ejected as a fine spray, which form droplets. In some cases the molten glass is splashed on nearby rocks and produces the common glass crusts found on lunar samples (Grieve and Plant, 1973). The rounded glass bodies are a common feature of lunar microbreccias and fines, their shapes reminiscent of tektites. Most are totally glassy, although some show evidence of partial crystallization or incomplete melting.

The glasses are colorless to green to deep red brown. Some of the glasses are not homogeneous, the refractive index as well as the color may vary in bands across a single sample. Bulk densities range from 2.5 to 3.0 g/cc.

The compositions of the lunar glasses may be variable, depending on the proportions of major minerals that have been melted at any single impact event (Table 16) (von Engelhardt and others, 1973; Ridley and others, 1973). The compositions of the minerals melted indicate temperatures in excess of 1550°C. The loss of silicon and sodium during volatilization is apparent when glass compositions are compared to the parent rock compositions.

Alteration and hydration rims have not been observed, but devitrification textures are not unusual (Lofgren, 1971; Wosinski and others, 1973). Approximately 5% of the glass spheres present in lunar soil and breccias are found to be either partially or wholly devitrified. Most commonly the devitrification products are spherulites. In most spheres the spherulites nucleated on the outer edge and grew radially inward. Much less commonly

Table 16: Microprobe Analyses of Various Apollo 11 Glasses
(Mason and Melson, 1970)

	1	2	3	4	5	6	7
SiO ₂	46	45.4	46.0	40	41.1	55.4	43.5
TiO ₂	0.8	0.1	0.4	9	9.2	0.9	0.4
Al ₂ O ₃	24	34.5	24.6	11	10.3	1.4	6.9
FeO	7	0.3	5.9	19	18.9	10.4	22.1
MnO	0.08		0.1	0.20	0.3		0.3
MgO	8	0.2	8.0	10	6.8	16.7	17.4
CaO	13	19.0	15.1	11	10.5	20.1	8.4
Na ₂ O	0.6	0.8	0.2	0.5	0.5		0.2
K ₂ O	0.1	0.1	0.1	0.1	0.2		0.1
Sum:	99.58	100.4	100.4	100.80	97.8		99.3

¹ Average of 13 colorless to green glasses.

² Glass of anorthite composition. Index of refraction = 1.5701.

³ Feldspathic glass. Index of refraction = 1.5942.

⁴ Average composition of 13 yellow, brown, red or violet glasses.

⁵ Titaniferous glass. Index of refraction = 1.7001.

⁶ Pyroxene glass. Duke et al. (1970), p. 649

⁷ Glass rich in olivine component.

the devitrification products are mats of randomly oriented acicular fibers or sheafs of fibers that may form a crust that encloses a glassy core. The devitrification probably occurred during heating events on the lunar surface, perhaps later meteorite impacts.

Most importantly, lunar glasses are very old. The inferred radiometric ages of the fines and microbreccias are an average age of the various crystalline and glassy fragments that compose them. They do not indicate the age of fragmentation that produced the fine material. Radiometric techniques indicate an age for these fragments of 4.6 billion years. This presents some problems, as the age of the original rock material that produced the fragments is estimated to be 3.7 billion years. This older age may in part be due to the addition of meteoritic fragments. Fission track dates on individual spherules, provide dates of 8.5×10^8 (Durrani and others, 1973) and 7.5×10^8 years (Durrani and Khan, 1972). These dates probably represent the actual ages of the glass phases. It should be noted that due to the intense interest in the age of lunar material, a considerable volume of literature is available on track registration parameters as a function of the type of radiation damage, the type of damaged material and annealing rates. Etch rates for different types of tracks have also been measured (Durrani and others, 1973).

SUMMARY

Volcanic glasses, the most common of the naturally occurring glasses, are very often altered by weathering and leaching (crystalline phases may show similar effects) and recrystallize to their fine-grained compositional equivalents (rhyolites and felsites). The oldest volcanic glasses are dated at 40 million years before the present, but the majority of the dated glasses are much younger. Experimental studies have produced devitrification textures; and laboratory experiments as well as empirical measurements have determined hydration rates for volcanic glasses as a function of composition, temperature and climate. The presence of water and the temperature are the most important rate controlling variables. Even material that may still be described as glassy often exhibits evidence of alteration and recrystallization. Of the volcanic glasses that are preserved in the geologic record, it would be rare to describe such a glass as pristine.

Despite the common alteration and recrystallization effects observed in volcanic glasses, glasses formed as a result of impact, tektites and lunar glasses, may occur in substantially unaltered form. In the case of tektites, their resistance to alteration is a result of their high SiO_2 content and low alkali content. Lunar glasses have been preserved for hundreds of millions of years because they exist in an environment with a low oxygen fugacity and an extremely low water vapor partial pressure. Thus one might expect glasses of particular compositions or in specific types of environments to be stable for long periods of time.

APPLICATION TO RADIOACTIVE WASTE DISPOSAL

It will probably not be possible to extract from the data available on natural glasses, direct information on how waste glasses might behave over geologic periods of time. The obvious reason for this lies in the very dissimilar compositions of natural volcanic and waste glasses as compared in Table 17. Virtually all waste glasses compositions now being studied are melted at relatively low temperatures (1050°C). Often they contain appreciable alkali and boron to achieve the appropriate viscosity. It is probable that these low silica glasses will not have the durability of natural glasses, but natural glass properties might be thought of as an achievable range. Certainly, by lowering the waste loading and developing higher temperature melting processes, comparable or better glasses could be prepared.

In this regard, it is worthwhile to consider the as yet hypothetical conditions waste glasses might be subjected to. Assume that a natural volcanic glass is the barrier to radionuclide dispersion. Figure 13 and Table 18 show thermal and hydrologic conditions that might be assumed, for purpose of discussion. Probable repository conditions have not in fact been established. The temperatures shown in Figure 13 relate to wastes from a hypothetical reprocessing facility where heat generation can be much higher than in existing defense wastes. This temperature history has been used by Turcotte and Wald (1978) to evaluate devitrification of a waste glass. Irrespective of conditions which will actually exist, our interest in this section is only to show how data on natural glasses might be applied. When specific repositories are identified and likely conditions defined, further analyses can be undertaken.

In the following subsections, several time periods are considered with respect to anhydrous devitrification, hydrothermal alteration and leaching.

For volcanic glasses, relevant data such as anhydrous devitrification rates in the appropriate temperature range are not available. Dissimilar compositions of volcanic and waste glasses necessarily limit information (such as leaching data) on the elements of interest. Much of this discussion will be based on data presented by Marshall (1961) and Lofgren (1970).

Table 17: Comparison of the major compositional differences between a typical synthetic borosilicate glass (76-68) and a typical natural volcanic glass.

OXIDE	BOROSILICATE GLASS	VOLCANIC GLASS
SiO ₂	40.0	73.16
Al ₂ O ₃	--	11.97
B ₂ O ₃	9.5	--
ZnO	5.0	--
Fe ₂ O ₃	9.0	2.23
MgO	--	1.08
CaO	2.0	2.67
Na ₂ O	7.5	3.55
K ₂ O	--	4.56
SrO	0.3	--
BaO	0.5	--
P ₂ O ₅	0.4	0.18
ΣRE ₂ O ₃	4.1	--
UO ₂	3.9	--
H ₂ O	--	1.00
Remaining oxides*		--

*Remaining oxides include Cr₂O₃, NiO, Rb₂O, Y₂O₃, ZrO₂, MoO₃, RuO₂, Rh₂O₃, PdO, Ag₂O, CdO, TeO₂, Rb₂O, Cs₂O, TiO₂, TeO₂.

Table 18: Assumed Waste Repository Conditions

-
-
1. Repository is 'dry' for 20 years after sealing (i.e., $t = 0$ at maximum temperature in Figure 13).
  2. Beyond 20 years, the repository is 'saturated', with water-flow conditions as given below.

Repository type:

Salt. No flow, a volume of water equal to the glass volume surrounds the glass.

Figure 13: Assumed canister thermal history as a function of time after vitrification (after Turcotte and Wald, 1978).

0 to 30 Hours:

During this period the canister centerline temperature will vary from a maximum of approximately 900°C to a minimum temperature of approximately 400°C. No water will be present. The rate of devitrification will be a function of the nucleation and crystallite growth rate. The maximum rate of crystal growth is usually reached about one hundred degrees below the liquidus temperature of the glass. This is supported by the size distribution of crystallites in typical volcanic glasses. The canister cooling rate is much greater than that found in volcanic glass flows, thus the extent of nucleation and crystal growth during this period would be minimal. In experimental studies, volcanic glasses may be completely devitrified if temperatures are held between 850°C and 1100°C for 700 hours. In such a case, (Marshall, 1961) crystallites as long as 30 microns are formed. Such excessive temperatures for extended periods of time are not expected for the waste canisters.

30 Hours to 20 Years:

The canister centerline temperature will vary between a maximum of 500°C and a minimum of 300°C. Again, conditions are anhydrous. Assuming an activation energy of 50 Kcal/mole and a frequency factor of 10^{20} microns/million years (Marshall, 1971; see Figure 7 of this report), devitrification would occur in a few years at 500°C, 1700 years at 400°C, 10^6 years at 300°C and 10^7 years at 275°C. These times are the minimum times required for complete devitrification (i.e., a mean crystallite size of 10 microns). The activation energy for most natural glasses is probably closer to 100 Kcal/mole. For this case, complete devitrification would require 10^9 years at 750°C, or 10^{60} years at 25°C. Thus,

under anhydrous conditions, devitrification would not be expected. This is what is observed in meteorite glasses, which may be as old as 4.5×10^9 years.

20 Years to 200 Years:

During this time period the waste canisters would cool from 300°C to 60°C, but the waste glass may have been exposed to water. Without water, of course, devitrification would require a minimum of 10^6 years. The presence of water substantially increases the rate of devitrification or recrystallization (Marshall, 1961; see figure 8 of this report). The hydrothermal reconstruction of natural glasses at 300°C may occur in less than 10 years, and at temperatures of 100°C may require as much as 10^8 years. The rate of hydrothermal devitrification is also dependent on the composition of the glass and the composition of the hydrothermal solutions. Estimated times of devitrification for basaltic glasses are about 20 percent less than the estimated times for granitic glasses. Experimental studies by Lofgren (1970) on devitrification rates of rhyolite glasses in Na or K rich solutions, such as might be found in the brines of salt repositories, suggest that the diffusion of Na or K into the glass promotes crystallization. The devitrification rate is increased by four to five orders of magnitude and the hydration rate increases by one to two orders of magnitude. Complex patterns of ion exchange (Jezek and Noble, 1978; Tsong, et al., 1978) are common in the hydrated areas. The effects of hydration on radionuclide concentrations in glass waste forms has to be evaluated separately from that observed in volcanic glasses, as compositions are so different.

RECOMMENDATIONS

It is difficult and inappropriate to make direct comparisons between naturally occurring glasses and glass waste forms, as their compositions and thermal histories are very different; however the previously summarized studies of naturally occurring glasses offer several possibilities for future research:

- (1) Any characterization scheme for waste form glasses which attempts to determine the "integrity" of the glass should be applied to well documented and dated glasses for the purpose of comparison. This report has attempted to compile data for the physical and chemical properties of volcanic glasses. The natural specimens would serve as standards or "benchmarks" of comparison. If a particular volcanic glass is known to have been stable for several million years and the waste form glass exhibits the same degree of "integrity", then this, to a first approximation, is an indication that the waste glass form may be stable at surface conditions for similar periods of time.

In order to provide for comparative studies of natural and synthetic glasses, well-documented natural glasses, of various ages, have been collected from the following localities:

1. Glass Mountain, Skiyou County, California (77-GM-01). Rhyolite-dacite flow less than 500 years old. The glass is described in detail by Friedman (1968) and Eichelberger (1974).
2. Obsidian Mound, Mono County, California (77-OM-01) Rhyolite approximately 5,000 years old.

3. Long Valley Caldera, Mono County, California (72G-004), Pyroxene-rhyolite, $670,000 \pm 14,000$ years old. Petrology and geochemistry are presently under study by Roy Bailey, Branch of Field Geochemistry and Petrology, U.S. Geological Survey, Reston, Virginia. (See Bailey and others, 1976; Krauskopf and Bateman, 1977).

- (2) A major problem in selecting an appropriate waste form is the evaluation of its long-term stability. The extrapolation of time-limited laboratory experiments over long periods of geologic time is often difficult to justify. Experimental studies of volcanic glasses (some of which are summarized in this report) have successfully surmounted this obstacle. Hydration rates at elevated temperatures in time-limited laboratory experiments have been related to hydration rates observed in naturally occurring materials that are thousand of years old. Alteration or weathering rates can be similarly determined in the laboratory and by empirical studies on natural materials. Two very recent studies on natural volcanic glass include those of Jezek and Noble (1978) and Tsong et al. (1978). The validation of these techniques using naturally occurring materials, should provide well tested experimental techniques for the evaluation of long-term effects in glass waste forms.

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GLOSSARY

The glossary that follows provides definitions for the geologic and mineralogic terms used in this report. Definitions have been adopted from the Glossary of Geology published by the American Geological Institute.

As an additional aid to an understanding of the definitions of the various rock types, the reader is referred to Table 19 and Figure 14. Table 19 lists typical chemical analyses in constituent oxides for certain types of igneous rocks. Figure 14 shows in a general way the mineralogical constitution to these igneous rocks.

Table 19: Average Chemical Analyses of Certain
Types of Igneous Rocks

(Totals reduced to 100.00)
(Clark, 1966)

	GRANITE	GRANODIORTTE	DIORITE	GABBRO	PLATEAU BASALT
	Number of Analyses Averaged				
	546	40	70	41	43
SiO ₂	70.18	65.01	56.77	48.24	48.80
TiO ₂	.39	.57	.84	.97	2.19
Al ₂ O ₃	14.47	15.94	16.67	17.88	13.98
Fe ₂ O ₃	1.57	1.74	3.16	3.16	3.59
FeO	1.78	2.65	4.40	5.95	9.78
MnO	.12	.07	.13	.13	.17
MgO	.88	1.91	4.17	7.51	6.70
CaO	1.99	4.42	6.74	10.99	9.38
Na ₂ O	3.48	3.70	3.39	2.55	2.59
K ₂ O	4.11	2.75	2.12	.89	.69
H ₂ O*	.84	1.04	1.36	1.45	1.80
P ₂ O ₅	.19	.20	.25	.28	.33

*Since most of the analysts neglected the effect of the absorption of water by their specimens when pulverized, the proportion given for this oxide is in general somewhat too high. On the whole, about three fourths of the total water indicated was driven off at temperatures no higher than 105°C.

Figure 14: Major mineralogical constituents of igneous rocks (Compton, 1977)

ACIDIC One of four subdivisions of a widely used system for classifying igneous rocks on the basis of silica content. It does not imply properties as would be used by a chemist. Applied loosely to any igneous rock composed predominantly of light-colored minerals having a low specific gravity and less than 65% silica.

ANDESITE A dark-colored, fine grained extrusive rock that when porphyritic, contains phenocrysts composed primarily of zoned plagioclase and one or more of the mafic minerals (e.g., biotite, hornblende, pyroxene) and a ground-mass composed generally of the same minerals as the phenocrysts.

APHANITIC Said of the texture of an igneous rock in which the crystalline components are not distinguishable by the unaided eye; both microcrystalline and cryptocrystalline textures are included.

ASH Fine pyroclastic material from volcanoes (under 4.0 mm diameter). The term usually refers to the unconsolidated material.

BASALT A dark-to-medium-dark-colored, commonly extrusive, mafic igneous rock composed chiefly of calcic plagioclase and clinopyroxene in a glassy or fine-grained ground-mass.

BASIC Said of an igneous rock having a relatively low silica content, sometimes delimited arbitrarily as less than 54%.

CALC-ALKALIC Said of an igneous rock, or group of igneous rocks, in which the weight percentage of silica is between 56 and 61 when the weight percentages of CaO and $K_2O + Na_2O$ are equal.

CRYPTOCRYSTALLINE Said of the texture of a rock consisting of crystals that are too small to be recognized and separately distinguished even under an ordinary microscope.

DIABASE An intrusive rock whose main components are plagioclase and pyroxene and which is characterized by an ophitic texture.

DOLERITE A synonym of diabase.

ECLOGITE Rock formed at extremely high pressures and temperatures which are considered to be required for the origin of the high density mineral association of omphacite and garnet plus rutile, kyanite, enstatite and diamond

EXTRUSIVE Said of igneous rock that has been ejected onto the surface of the Earth.

FELDSPAR A group of abundant rock forming minerals of general formula $MA_1(A_1, -Si)_3O_8$, where M = K, Na, Ca, Ba, Rb, Sr, and Fe. Feldspars are the most widespread of any mineral group and constitute 60% of the Earth's crust.

FELDSPATHOID A group of comparatively rare rock-forming minerals consisting of aluminosilicates of sodium, potassium, or calcium and having too little silica to form feldspar.

FELSITE A light-colored, fine grained extrusive or hypabyssal rock with or without phenocrysts and composed chiefly of quartz and feldspar.

FINES Very small particles, especially those smaller than the average in a mixture of particles of various sizes.

FULGURITE An irregular, glassy, often tubular or rod-like structure or crust produced by the fusion of loose sand by lightning.

GABBRO A group of dark-colored, basic, intrusive igneous rocks composed principally of plagioclase and clinopyroxene with or without olivine and orthopyroxene. It is the approximate intrusive equivalent of basalt.

GRANITE A plutonic rock in which quartz constitutes 10 to 50 percent of the felsic components and in which the alkali feldspar/total feldspar ratio is generally restricted to the range of 65 to 90 percent.

GRANOPHYRIC A term applied to the texture of a porphyritic igneous rock in which the phenocrysts and groundmass mutually penetrate each other, having crystallized simultaneously.

GROUNDMASS The interstitial material of a porphyritic igneous rock. It is relatively more fine-grained than the phenocrysts and may be glassy.

HOLOCRYSTALLINE Said of an igneous rock composed entirely of crystals, having no part glassy.

HYPABYSSAL Pertaining to an igneous intrusion or to the rock of that intrusion, which occurs at intermediate to shallow depths.

HYDROTHERMAL Of or pertaining to heated water, to the action of heated water, or to the products of the action of heated water. It is generally used for any heated water but has also been restricted to heated water of magmatic origin.

INTRUSIVE Of or pertaining to a rock which crystallizes below the surface.

LEUCITE A white or gray mineral of the feldspathoid group:
 KAlSi_2O_6 .

MAFIC Said of an igneous rock composed chiefly of one or more ferromagnesian, dark-colored minerals.

MAREKANITE Obsidian that occurs as rounded to subangular bodies, usually less than two inches in diameter and having indented surfaces. These bodies occur in masses of perlite and are of special interest because of their low water content as compared with the surrounding perlite, the ratio often being as small as one to ten.

MICROBRECCIA A poorly sorted aggregate containing relatively large and sharply angular sand size particles in a very fine matrix.

OBSIDIAN A black or dark-colored volcanic glass, usually of rhyolite composition characterized by conchoidal fracture.

OLIVINE An olive-green or brown orthorhombic mineral: $(\text{Mg,Fe})_2\text{SiO}_4$.

OPHITIC An igneous rock in which lath shaped plagioclase crystals are partially or completely included in pyroxene crystals.

PALAGONITE An altered tachylite, brown to yellow or orange and found in pillow lavas as interstitial material.

PALEOZOIC An era of geologic time, from the end of the Precambrian (570 m.y.) to the beginning of the Mesozoic (225 m.y.).

PERALKALINE Said of an igneous rock in which the molecular proportion of aluminum oxide is less than that of the sodium and potassium oxides combined.

PERLITE A volcanic glass having the composition of rhyolite, perlitic texture, and a generally higher water content than obsidian.

PHENOCRYST A relatively large, conspicuous crystal in a finer-grained igneous rock.

PITCHSTONE A volcanic glass, usually intrusive, with a waxy, dull, resinous pitchy luster. Its color and composition vary widely; it contains a higher percentage of water than obsidian.

PLAGIOCLASE A group of triclinic feldspars of the general formula: $(\text{Na,Ca})\text{Al}(\text{Si,Al})\text{Si}_2\text{O}_8$.

PLUTONIC Pertaining to igneous rocks formed at great depth.

PORPHYRITIC Said of the texture of a igneous rock in which larger crystals (phenocrysts) are set in a finer groundmass which may be crystalline or glassy or both.

PRECAMBRIAN All geologic time, and its corresponding rocks, before the beginning of the Paleozoic (570 m.y.). It encompasses about 90% of geologic time.

PUMICE A light-colored, vesicular, glassy rock commonly having the composition of a rhyolite.

PYROCLASTIC Pertaining to clastic rock material formed by volcanic explosion or aerial expulsion from a volcanic vent.

PYROXENE A group of dark, rock-forming silicate minerals closely related in crystal form and composition and having a general formula: ABSi_2O_6 , where $\text{A} = \text{Ca, Na, Mg or Fe}^{+2}$ and $\text{B} = \text{Mg, Fe}^{+3}$, or Al with silicon sometimes replaced in part by aluminum. It is characterized by a single chain of tetrahedra with a silicon:oxygen ratio of 1:3.

QUARTZ DIORITE A group of plutonic rocks having the composition of diorite but with an appreciable amount of quartz.

RHYOLITE A group of extrusive igneous rocks, generally porphyritic and exhibiting flow texture, with phenocrysts of quartz and alkali feldspar in a glassy to cryptocrystalline groundmass.

SCHILIEREN In some igneous rocks, irregular streaks or masses that contrast with the rock mass but have shaded borders. They may represent segregations of dark or light minerals, or altered inclusions, elongated by flow.

SELVAGE A marginal zone of a rock mass, having some distinctive feature of fabric or composition (e.g. the chilled border of an igneous mass).

SYNGENETIC Said of a mineral deposit formed contemporaneously with the enclosing rocks.

TEKTITE A small (usually walnut-sized), rounded, pitted, jet-black to olive-greenish or yellowish body of silicate glass of nonvolcanic origin, found usually in groups in several widely separated areas of Earth's surface and bearing no relation to the associated geologic formations. Most tektites have uniformly high silica (68-82%) and very low water contents (average 0.005%).

TERTIARY The first period of the Cenozoic era thought to have covered the span of time between 65 and two to three million years ago.

THOLEIITE A group of basalts primarily composed of plagioclase pyroxene and iron oxide minerals as phenocrysts in a glassy groundmass.

TONALITE A synonym for quartz diorite.

TRACHYTE A group of fine-grained, generally porphyritic, extrusive rocks having alkali feldspar, minor mafic minerals (biotite, hornblende, or pyroxene) as the main components.

VESICULAR Said of the texture of a rock especially a lava, characterized by abundant voids formed as a result of the expansion of gases during the fluid stage of the lava.

ZEOLITE A large group of white or colorless (sometimes red or yellow) hydrous aluminosilicates that are analogous in composition to the feldspars, with sodium, calcium, and potassium as their chief metals (rarely barium or strontium) that have a ratio of (Al + Si) to nonhydrous oxygen of 1:2 and that are characterized by their easy and reversible loss of water of hydration.

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