

NATURAL GLASSES AS ANALOGUES TO ASSESS THE LONG-TERM STABILITY OF SOME ARTIFICIAL GLASSES

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Abstract: Twenty samples of natural glasses (volcanic glasses, impact glasses, tektites and fulgurites) are described and compared with twenty artificial glasses and ceramics proposed for packing of high level radioactive waste. The weathering indices tested both groups of samples. There is a negative correlation between the sum of net-forming oxides and the weathering index I_{ko} (and IPW or I_w). According to these indices, Pyrex is the synthetic glass which is the most resistant to weathering. It has an analogue in the Libyan Desert glass. Some pairs of both natural and synthetic types of glass have been found with similar values of weathering indices. On the basis of comparison of the weathering stability of various natural glasses and glasses used for vitrification, the following glasses have the highest stability as suitable natural analogues: an obsidian, tektites and the Libyan Desert glass.

Key words: natural glasses, waste glasses, crystalline ceramics, indices of weathering.

Introduction

Natural glasses of terrestrial, meteoritic and lunar origin are currently the subject of extensive study because of their industrial uses and the origin of some glasses in underground nuclear blasts. Theoretical and experimental work has been concerned with the kinetics of processes in glasses and phase relations in rocks containing glass. All natural glasses are thermodynamically unstable under conditions on the Earth's surface and tend to be chemically weathered or recrystallized (devitrified). In spite of this, some natural glasses of Precambrian age have survived unaltered. If the critical factors governing the preservation of such glasses could be understood, it may be useful in establishing a standard etalon for glasses used in high level radioactive waste repositories.

The factors controlling the degradation of natural glasses are the subject of this paper which summarizes the results of investigations carried out at the Faculty of Science, Charles University in Prague, in close cooperation with the Nuclear Research Institute, Řež.

Data on natural glasses and their stability are summarized in monographs by Bouška et al. (1993), Strnad (1986) and Lutze & Ewing (1980) and in numerous special studies, notable among which is that by Mazer (1994). It deals with natural glasses as analogues in designing stable glasses for use in high level radioactive waste repositories.

To assess the reactivity and weathering of glasses, the weathering index has been applied. In using this approach,

analyses of all types of natural glasses and suitable synthetic glasses and ceramics already proposed for immobilization in high level repositories were selected from a wide range of published data. Some ceramic material and synthetic glasses from the ancient Roman and Egyptian periods and the Tiffany window glass were also used for comparison.

Weathering indices based on available geochemical and petrological data were used to calculate and compare the reactivity of natural and synthetic glasses. The next step involved comparison of the properties of natural glasses and those used for vitrification.

Natural glasses

Natural glasses are classified according to the time required for their formation: a) fulgurite glass, b) diaplectic glass formed during impact by a pressure shock wave, c) impact glass formed by thermal fusion of the original minerals and rocks during an impact on the Earth or Moon, planets and meteorites, d) tektites, and e) terrestrial, lunar and planetary volcanic glass. In general, the homogeneity of natural glasses increases with the duration of the extreme conditions under which they were formed. This criterion for classifying natural glasses has not been retained throughout this study as the time factor need not necessarily be decisive. The natural glasses selected for study were chosen on the basis of the importance of the individual types and especially according to the mechanism of their origin.

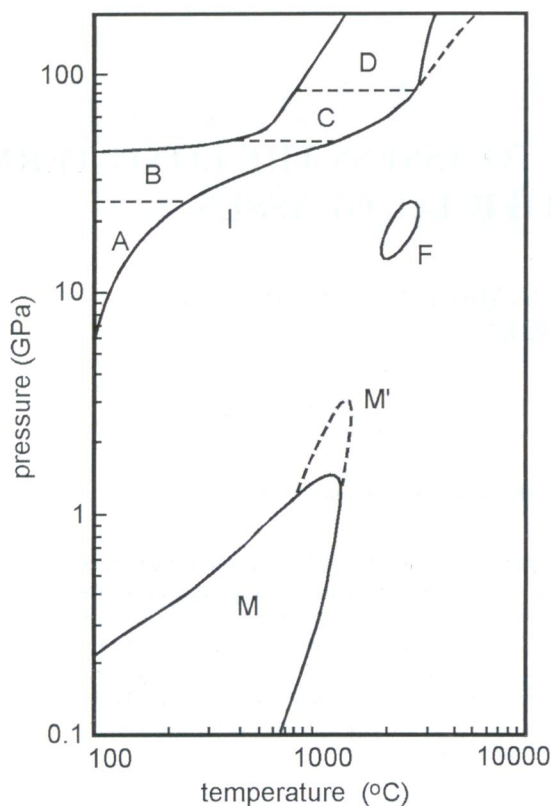


Fig. 1. Diagram of pT conditions for the natural processes. I — field of impact process (A — zone of planar deformation and changes of physical properties of minerals, B — diaplectic glasses, C — melts, D — zone of vaporization), M — field of geological processes (magmatic, hydrothermal, metamorphic, sedimentary, weathering, earthquakes), M' — crystallization of high pressure melts in upper mantle conditions, F — field of fulgurites.

The definition of natural glasses

Natural glasses are formed from the liquid state by supercooling, as condensates from a rapidly cooled sublimate or by pressure destruction of the crystal structure of substances. The chemical composition, bonding energy, melt temperature, cooling rate and crystallization kinetics all participate in the complex process of glass formation. The energetic balance of the formation of natural glasses vs. natural processes is shown in a diagram (Fig. 1). Water and volatile components in general reduce the viscosity of melts and increase the diffusion rate of dissolved oxides. Nearly all natural glasses are in some degree anisotropic due to inner strain, induced by rapid cooling, however, they appear amorphous in X-ray studies. They are solid substances with nonperiodic structure. Some authors consider them to be supercooled liquids that cannot crystallize because of their high viscosity. Glasses formed from a melt by cooling it below its melting or liquidus point show viscosity greater than 10^{12} Pa.s. The boundary between the crystalline and the amorphous state of the substance is not sharp. Structural

analysis has revealed regions in glasses that have an ordered structure with dimensions less than 3–5 nm.

The formation of glass depends on the chemical composition of the parent melt. For instance, hot (about 1200 °C) and fluid basaltic magmas allow a rapid growth of crystals. Glass with this composition is relatively rare and is a maximum of several centimetres thick even when the melt was rapidly cooled by effusion into deep sea regions. On the other hand, less tempered (about 800 °C) and highly viscous rhyolite melts can yield glass layers that are up to several metres thick.

Glasses with nonperiodic structure can also be formed by condensation of vapours on a cooled surface, by sintering a gel, amorphization of crystalline substances by nuclear radiation or shock waves and other processes.

Types of natural glasses and conditions of their formation

Volcanic glasses

Volcanic glasses according to their chemical composition can be divided into basaltic, intermediate and silicic.

Basaltic and intermediate glasses originated under a limited range of conditions. The glass is usually formed during extremely fast cooling of the magma melts. Such conditions especially occur during volcanic activity in an aqueous environment, e.g. along the oceanic rift zones. This glass can be of extrusive, effusive or explosive character. Fresh unaltered types of glass are called tachylite, partly altered as sideromelane. The fibrous basaltic glass in the Hawaiian Islands is known as Peleé's hair, and the lapilli of basaltic glass as Peleé's tears. The porosity of basaltic glass is between 20 and 60 %, the SiO_2 content varies in the range of 49–54 wt %. Complete chemical analyses of selected basaltic volcanic glasses are summarized in Table 1b. The density of these glasses varies between 2.8 and 2.9 g.cm⁻³. The refractive index is affected by the contents of SiO_2 and FeO (total iron), and decreases with increasing SiO_2 and decreasing FeO. The water content in compact basaltic glass can vary from 0.04 to 0.21 wt % but can be even more, especially when the glass has undergone alterations connected with hydration and palagonitization. Abundant basaltic volcanic glass is known from Iceland and the Hawaiian Islands.

Silicic volcanic glasses are much more abundant on the Earth's surface relative to those of basaltic chemistry. They are connected particularly with rhyolite volcanism including ignimbrites. These glasses are also more resistant to weathering providing they did not undergo postvolcanic alteration. The deposits of acidic volcanic glass are connected with effusive and explosive processes or with intrusive magmatism. The individual types of acidic volcanic glass are usually designated according to their structural and textural properties as

compact obsidian, perlite, obsidian-perlite, pitchstone (silicic volcanic glass with a high content of water ranging between 6 and 16 wt %), and pumice. Obsidians usually contain 71–72 wt % SiO_2 , and about 1 wt % water. The density of obsidian varies in the range 2.27–2.40 g.cm^{-3} , and the refractive index from 1.480 to 1.493. Porosity of pumice is as high as 89.5 %. Chemical analyses of silicic glass-obsidians are summarized in Table 1b. Perlite has a characteristic texture. When struck, perlite breaks to form tiny, shiny, iridescent spheres. The most widely found perlites have water contents in the range 2.6–6 wt %. Dark and light grey perlites from Slovakia have a refractive index of 1.493–1.501 and density of about 2.346 g.cm^{-3} (Šalát & Ončáková 1964; Lajčáková 1980).

Impact glasses

There are about 120 craters on the Earth's surface which originated in collisions between a cosmic body and the surface of our planet at a velocity exceeding 12 km.s^{-1} . They are called meteorite or impact craters or astroblemes. These phenomena occur in a very short peri-

od of time, of the order of one to a few tens of seconds. The temperature varies between 2000 and 3000 °C and/or 5000 °C in the case of large structures. The pressure at the front of shock wave varies between 10 and 150 GPa and may be even higher which is far greater than that in volcanic explosions which does not exceed 0.3–0.4 GPa. The energy of the whole phenomenon of the formation of impact craters has been estimated to be of the order of 10^{13} – 10^{23} J. Underground nuclear explosions exhibit a similar energy. For example, the explosion of a 1 Tg nuclear bomb releases an energy of about 10^{15} J. Impact craters are distributed erratically over the Earth's surface, and are of various age ranging from the Precambrian till the present times.

Impact glasses were formed by rapid melting of the target rocks and minerals at a high temperature. A varying degree of selective evaporation of the elements occurs. Basilevskii & Yakovlev (1984) established the sequence of evaporation: $\text{Na, K} > \text{Fe} > \text{SiO} > \text{Mg} > \text{Ca, TiO} > \text{Al, Al}_2\text{O}_3, \text{AlO}$. Impact glasses are not homogeneous but have a chemical composition closer to that of their parent rocks than to impact glasses found in various craters. Impact glass is either monomineral or polymineral depending on

Table 1a: Chemical analyses of synthetic glasses and ceramics (in wt%).

No.	Samples	n	SiO_2	TiO_2	ZrO_2	Al_2O_3	B_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Li_2O	Na_2O	K_2O	P_2O_5	H_2O^+	Total	Note
1	Waste gl. A, France	1	42.17				23.16							9.17				100.00	a
2	Waste gl. B, France	1	45.61			4.91	14.06	2.91				4.04	1.98	12.38				99.99	b
3	Waste gl. C, France	1	29.85			25.86	15.15	0.25						23.88				100.00	c
4	Waste gl. SRL 165, USA	1	68.00		1.00		10.00				1.00		7.00	13.00				100.00	
5	Waste gl. SRL 165, USA	1	52.86	0.14	0.66	4.08	6.76	11.74		2.79	0.70	1.62	4.18	10.85	0.19	0.02	0.10	97.54	d
6	Waste gl. SON68, France	1	54.90			5.90	16.90					4.90	2.40	11.90				99.90	e
7	Waste gl. SM 5 39, Germany	1	45.50				33.00					6.50	4.50	10.50				100.00	
8	Waste gl. SM 5 13, Germany	1	58.60	5.10		3.00	14.70				2.30	5.10	4.70	6.50				100.00	
9	Waste gl. UK 209	1	68.50				15.00						5.40	11.20				100.10	
10	Waste gl. AVM, France	1	56.10				25.30							18.60				100.00	
11	Waste gl. PO422, Japan	1	61.00			5.00	19.90					2.80	4.30	1.40	2.80			100.00	f
12	Waste gl. PNL 76-68, USA	1	59.40	4.50			14.30					2.90		11.30				100.00	g
13	Waste gl. GP 98 /12, Germany	1	58.50	3.60		1.60	11.00				3.30	4.50		17.50				100.00	
14	Waste gl. SRL 131, USA	1	56.00	1.04	0.45		14.90				2.10		5.50	15.00				95.44	h
15	Waste gl. Pyrex	1	81.00			2.00	13.00					1.00		4.00				101.00	
16	Cryst.ceramics, Synroc B	1		59.40	10.90	6.50						15.20						100.00	ch
17	Cryst.ceramics, Synroc D	1	0.50	18.70	4.90	19.90		24.20				4.70		3.40				93.10	i
18	Roman bottle g.	1	68.48			2.61			0.29	0.65	0.68	6.74		19.73	0.77			100.00	j
19	Egyptian gl.	1	64.75			0.62		0.31		0.02	2.53	7.23		19.43	1.66			98.10	k
20	Tiffany window glass	1	43.30	0.10		2.00	11.50		0.09		0.03	0.35		0.20	2.70	0.26		99.52	l

Table 1b: Chemical analyses of natural glasses (in wt %).

No.	Samples	n	SiO ₂	TiO ₂	ZrO ₂	Al ₂ O ₃	B ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Li ₂ O	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O+ Total	Note
21	Basaltic volcanic glass, Tolbachik, Kamchatka	1	50.98	1.45	16.50			7.56	0.16	4.42	8.98		3.60	1.85	0.35	6.40	102.25	m
22	Basaltic volcanic glass, Kilauea,Hawaii Islands	9	51.70	2.88	13.28			10.94	0.17	6.13	10.22		2.75	0.64	0.31		99.02	n
23	Basaltic volcanic gl., Mid-atlantic rift zone, Miocene	10	50.63	1.47	14.97			9.71	0.18	7.85	11.39		2.77	0.13	0.14		99.28	o
24	Basaltic volcanic gl., Maria Celesta trench, Ind. Ocean	1	50.47	2.75	15.30			9.90		8.52	9.95		2.85	0.13			99.87	p
25	Obsidian, Eastern Slovakia	3	75.14		13.74		0.66	1.74	0.19	0.24	1.30		2.98	4.31	0.17	0.18	100.65	
26	Obsidian, Kogudoro-Bosano, Sardinia	11	68.99	0.57	15.22		2.94	0.15	0.11	0.81	2.60		3.36	4.12	0.13		98.70	
27	Obsidian, Milos, Greece	1	74.59	0.11	13.37		0.53	0.95	0.02	0.53	0.67		4.47	4.51	0.02	0.32	100.31	q
28	Obsidian, Armenia	6	73.80	0.13	13.77		0.98	0.83	0.06	0.29	1.09		3.97	3.98	0.02	0.33	99.30	r
29	Impact glass, Lonar crater, India	1	51.60	2.90	13.70			13.80		5.40	9.70		2.20	0.60			99.90	s
30	Impact glass from suevite, Ries, Germany	88	64.01	0.79	15.25			5.22	0.08	3.04	3.96		3.02	4.01	0.21		99.59	t
31	Impact glass, Zhamanshin, Kazakhstan	16	54.34	0.87	20.59			7.45		2.73	8.45		3.94	1.40	0.22		99.99	u
32	Libyan Desert glass	11	97.92	0.19	1.37		0.20	0.19		0.05	0.21		0.26	0.02	0.01	0.03	100.45	
33	Australasian microtektites	60	66.40	0.70	14.70			5.70	0.10	5.90	3.40		1.00	1.70			99.60	u
34	Australites	52	70.70	0.68	13.23		0.64	4.64	0.10	2.48	3.77		1.63	2.03	0.04		99.94	
35	Moldavites, Radomilice region, CZ	11	83.17	0.33	8.04		0.26	0.70	0.08	1.89	2.23		0.30	2.50			99.50	
36	Moldavites, Č. Budějovice region, CZ	89	79.97	0.33	9.95		0.33	1.50	0.08	1.97	2.71		0.46	3.39			100.69	
37	Moldavites, Moravian region, CZ	37	79.25	0.39	10.84		0.33	2.07	0.09	1.53	1.89		0.55	3.35			100.29	
38	Moldavites, H Ca/Mg	8	77.70	0.25	9.02			1.64	0.09	2.37	4.85		0.43	3.72			100.07	u
39	Brown glass from meteorite ALPHA 81005	1	44.54	0.22	26.91			5.24		6.82	15.60		0.28	0.06			99.81	v
40	Fulgurite from soil, Křenice, CZ	1	74.00	0.86	12.68		1.50	2.74	0.09	1.04	2.55		1.02	2.62		0.05	99.15	

Notes to tables 1a and 1b (in wt %)

a) including oxides of fission products and actinides – 25.50, b) including oxides of fission products and actinides – 12.28 and other components 1.82, c) including oxides of fission products and actinides – 2.37 and other components 2.64, d) NiO = 0.85, e) ZnO = 3.0, f) ZnO = 2.8, g) ZnO = 7.6, h) La₂O₃ = 0.45, ch) BaO = 8, i) MnO₂ = 7.5, Na₂SO₄ = 0.4, Cs₂O = 0.3, SrO = 0.4, BaO = 1.4, NiO = 3.1, CeO₂ = 0.4, Gd₂O₃ = 0.4, Nd₂O₃ = 0.4, Eu₂O₃ = 0.4, UO₂ = 2.1, j) CuO < 0.06, k) CuO = 1.55, l) CuO = 0.06 %, PbO = 38.93, m) FeO = FeO_{tot}, n) FeO = FeO_{tot}, o) Cr₂O₃ = 0.04, FeO = FeO_{tot}, p) FeO = FeO_{tot}, q) CO₂ = 0.22, r) S = 0.05, s) FeO = FeO_{tot}, t) FeO = FeO_{tot}, u) FeO = FeO_{tot}, v) FeO = FeO_{tot}, Cr₂O₃ = 0.14

References to Tables 1a and 1b

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the number of original components which were melted. In general, the composition of impact glasses is similar to that of the host rocks, but the Al, Ti, Mg, Ca and sometimes K contents are enhanced whereas Si and Na decreased. These glasses are porous, with fluidal texture, and form glass bombs, lenses or veinlets. Monomineral glasses consist of quartz (lechatelierite). Some impact glasses contain grains of fused quartz (melting point 1723 °C), baddeleyite (a product of thermal decomposition of zircon at 1775–1900 °C), magnetite and rutile (about

1860 °C). In general, the melting point of impact glasses varied between 1300° and 1900 °C).

Chemical analyses of selected impact glasses of various chemistry and from diverse target rocks are summarized in Table 1. More detailed data are given in the books by Bouška et al. (1987 and 1993).

Impact glasses are mostly strongly inhomogeneous and envelope relics of unmelted high-temperature minerals. The impact glass easily undergoes recrystallization and hydration, fresh glass is rare. Hydrothermal solutions as

an after-effect of impact processes seems to facilitate recrystallization and hydration of impact glasses. The Libyan Desert glass is one of the oldest impact glasses. Its radiometric age is 28.5 Ma (Storzer & Wagner 1977). Libyan Desert glass is a pure lechatelierite and represents rather an exception among impact glasses. Similar features are found in blocks of lechatelierite glass in the Zhamanshin crater in northern Kazakhstan. Relatively fresh impact glasses are known from impact craters max. 3.5 million years old (El'gygytyn, Chukotski peninsula, dark brown glass bombs), and from younger craters (Lunar 0.05 Ma, Zhamanshin 1.07 Ma, Monturaqui, Chile, 1 Ma, and others).

Impact metamorphism leads to the formation of diaplectic glass. Pressure destruction of the crystal structure of minerals leads to the formation of diaplectic glass in the solid state. The shape of the original crystals or grain boundaries or twin lamellae and cleavage are retained. Pressure wave induced destruction of the crystal structure but the temperature is thought to have been lower than the melting point of the given substances. Isotropization of quartz occurs in a shock wave at a pressure varying between 26 and 30 GPa (refractive index decreases from 1.5487 to 1.470). Quartz is converted into a diaplectic glass at a pressure of 50 GPa with $n = 1.458$. Shock isotropization of feldspars occurs in a pressure wave of 42 to 45 GPa (maskelynite). Diaplectic glass has been observed for quartz, plagioclase, potassium feldspar, cordierite and coesite (Stähle 1973).

Due to hydrothermal processes accompanying impact events these processes lead to decomposition of glass and formation of clay minerals, micas, chlorites or carbonates. As the majority of impact glasses are of intermediate character, the products of weathering often consist of smectite or chlorite. Some impact glasses contain tiny spherules of reduced iron metal and/or iron and nickel. Impact glasses which are not devitrified or only slightly hydrated occur merely in younger craters from the Neogene until recent years otherwise due to their porosity and inhomogeneity, the glasses are easily exposed to hydration.

The most renowned impact structures include the Meteor crater in Arizona, Ries crater near Stuttgart, Popigai structure in Russia, Lunar crater in India and others.

Tektites

Tektites are usually rounded, natural, acidic silicate glasses with a high melting point ranging from 1055° to 1530°C. They are impact glasses, but in contrast to regular impact glasses, they have flown through the atmosphere after their ejection from the parent crater. Tektites are homogeneous. In spite of their different age, all tektites have been found in thin layers of surface sediments at a depth not exceeding 10 m below the surface. Tektites are not known in older geological formations. If older tektites existed, they were probably de-

stroyed by transport or completely dissolved. Tektites do not exhibit any recrystallization or hydration, thus representing relatively stable materials occurring on the Earth's surface. However, their surface has been exposed to chemical corrosion leading to rich sculptural forms and deep grooving marks due to etching in alkaline or acid environment after their deposition in the sediment. Their distribution over the surface of the Earth is erratic.

Tektite glass can be basically divided into four major types: a) Muong Nong (named according to the type locality) represents layered tektite found primarily in China, Laos and Thailand. These tektites are usually large irregular pieces. The layering appears in the color and distribution of bubbles, in the composition, density and refractive index of the individual layers.

b) Shaped tektites — the shape was obtained through rotation of the viscous melt shortly before its fall on the Earth's surface. These tektites have the shape of a sphere, ellipsoid, disk, teardrop, etc. The sculpture is a characteristic feature of these tektites. The etching of moldavites has been studied by Knobloch et al. (1991). Lechatelierite grains or schlieren appear to be more resistant to chemical corrosion than the remaining glass of the tektites. Therefore, lechatelierite fibres sometimes emerge from the tektite surface (Rost 1972; Knobloch et al. 1981). The glass is likely to have been ejected in a tongue-like form from the formation site and parts could have been separated during their passage along a ballistic path at a velocity of at least 4–5 km.s⁻¹, attaining their final shape and internal strain during solidification.

c) Tektites with ablation phenomena. These forms are actually shaped tektites modified by atmospheric ablation at their rims during remelting as they re-entered the Earth's atmosphere (O'Keefe 1963). These ablation rims (flanges) are typically developed on australites.

d) Microtektites are shaped identically to other tektites but are defined as bodies less than 1 mm in diameter (Glass et al. 1979). Microtektites are found in deep sea sediments. Except for microirghizites, the microtektites were not found in continental conditions.

Tektites are found in several regions on the Earth's surface, called strewn fields. Six main strewn fields were distinguished and can be ordered according to their radiometric age and geographical distribution:

1. North American tektites and microtektites (bediasites, georgianites, tektite from Martha's Vineyard and a tektite from Cuba).

Localities: Texas, Georgia, Martha's Vineyard in Massachusetts, Cuba, Barbados, sediments from the bottom of Pacific Ocean in an area elongated in the E-W direction, the Caribbean Sea, the Gulf of Mexico, and along the east coast of the U.S.A. Radiometric age was established at 34.5 Ma. Estimated total amount: 10¹⁰ tons (Glass 1984).

2. Urengoites, (microtektites are not known). Locality: Novyi Urengoi, West Siberia. Radiometric age: 24 Ma.

Only three pieces were found (Masaitis et al. 1988). As for their age they seem to be connected with the impact structure of Haughton Dome in Canada.

3. Moldavites, (microtektites are not known). Localities: Southern Bohemia, Prague-Kobylisy, South-Western Moravia, the Cheb region, Lusatia in Germany, around Radessen in Austria. Radiometric age: 15 Ma. Estimated amount: 3000 tons (Bouška & Rost 1968).

4. Tektites and microtektites from the Ivory Coast. Localities: Ivory Coast and neighbouring regions of sediments from the bottom of the Atlantic Ocean. Radiometric age: 1.1 Ma. Estimated total amount: 10^7 tons (Glass 1984).

5. Irghizites and microirghizites. Locality: the Zhaman-shin crater, Kazakhstan. Radiometric age: 0.81–1.07 Ma (Florenskii et al. 1979; Kolesnikov et al. 1987). Estimated total amount: tens of tons (Florenskii 1975).

6. Australasian tektites and microtektites (australites, indochinites, billitonites, thailandites, javanites, philippinites, malaysianites). Localities: Australia, Indonesia (Borneo, Java, Sumatra, Belitung), Malaysia, Indochina (Vietnam, Cambodia, Laos), Thailand, Southern China, the Philippines, microtektites from boreholes drilled on the bottom of the Pacific and Indian Oceans. Radiometric age: 0.7 Ma which is synchronous with the Brunhes/Matuyama geomagnetic boundary. Estimated total amount: 10^8 metric tons (Glass 1984).

Tektites are silicate glasses with SiO_2 contents exceeding 65 wt %. The silica content in tektites is greater than would be expected on the basis of the content of mafic oxides. This corresponds more closely to sediments of the upper layers of the Earth's crust as the source material than to igneous rocks. The water content in tektites is very low, much lower than for terrestrial volcanic or impact glasses. The water content in tektites is lower than one hundredth of a per cent, usually in thousandths or tenthousandths of a per cent. The glass formed in an experimental explosion at Alamogordo in New Mexico contained 0.05 wt %. Common volcanic glasses (obsidians) contain up to 1 wt %. The average chemical composition, i.e. the relative proportions of major elements, contents of trace elements, isotopic composition and the distribution of REE, suggest that the tektites were formed through melting of sediments such as greywackes, sandstones and clays, thus the rocks confined to the uppermost layers of the crust at the impact site.

Chemical analyses of selected microtektites, australites and moldavites are summarized in Table 1b. More details on the subject are given in several books, e.g. by Bouška et al. 1987 and 1993.

Fulgurites

They originated during the strike of lightning on soil, sand or crystalline rock. Fulgurites form glassy tubes in soil and sands and glassy crusts in crystalline rocks.

Fulgurites are formed at temperatures ranging from 1900° to 2700 °C and pressures between 15 and 22 GPa (Bouška & Vrána 1993). Time data for the formation of fulgurites agree on a value of about 1 ms (Switzer & Melson 1972). A selective melting takes place during the formation of fulgurite glass. Fulgurites, due to their rare occurrence, can hardly be considered analogues of glasses used for vitrification in deposition of radioactive waste. However, one sample of fulgurite glass from soil near Křenice has been included in Table 1b summarizing various natural glasses.

Other natural glasses

This group includes all types of lunar glasses, glass from meteorites and other natural glasses such as glass from the gabbro boundary facies or glass from ultramafic xenoliths, glass found in contact metamorphic rocks, or glasses which originated during selfignition of plant material or during oil fires. A brown glass from the ALHA 81005 meteorite has been used in our calculations (Tab. 1) as this glass can serve as an analogue.

Distribution of natural glasses on the Earth's crust and their age

Among natural glasses, volcanic glasses seem to be best preserved on the Earth's surface (in the upper parts of the Earth's crust). Most of the volcanic glass that is found today was formed in the Tertiary and Quaternary and is thus usually not more than 65 Ma old. Older volcanic glass is rather exceptional unless it was exposed to postvolcanic metamorphism. Among them the following can be quoted: the Permian pitchstone from Saxony (Pietzch 1962), Permo-Triassic glass in the Ubagar structural zone of the Targay fold (Korobov & Chernyayeva 1981), Jurassic to Early Cretaceous volcanic glass from Cisbaikalia (Lebedeva 1981), etc. Volcanic glasses in general may occur in amounts which are viable for mining.

Most volcanic basaltic glass has been found in Iceland where it is part of the Pleistocene Moberg Formation, in the Hawaiian Islands where it represents a product of oceanic intraplate volcanism. Silicic volcanic glass occurs in the Sierra Madre Occidental region in Western Mexico, in the Great Basin in Nevada, Mobollon-Datil in New Mexico and in San Juan Mts in Colorado, then in the Central Andes and New Zealand. In Europe, the volcanic glasses are associated with the rhyolitic and andesitic complexes in North-West Sardinia, in the islands of Milos and Lesbos (Greece). The Carpathian-Rhodopian volcanic zone of Paleogene and Neogene ages is also important for the occurrence of volcanic glasses. Numerous deposits of volcanic glass in the Western Carpathians occur in the Kremnické and Štiavnické vrchy Mts, in the

Slánské vrchy Mts and near Viničky in the Zemplínské vrchy Mts in Eastern Slovakia, and also in the Tokajské vrchy Mts. Important deposits of obsidian occur in the East-Arabian rift zone near Aburra and in Armenia. For us, the most accessible deposits of obsidian and perlite are located in Central and Eastern Slovakia (Šalát & Ončáková 1964) and Armenia (Nasedkin 1978).

The following part of this text deals with some glasses which were found in old Paleozoic and Precambrian formations. The Permo-Triassic glasses or Permian pitchstone have already been mentioned earlier. They are usually very rare. Paleozoic glasses occur mostly as a constituent of volcanic rocks, e.g. diabase but are mostly completely devitrified. Similarly, the glasses of Precambrian diabases are also devitrified. The glass in offshoots of Precambrian diabase found in Orivesi in Southern Finland (Liquist & Laitakari 1980) is an exception because it suffered only slight devitrification even though it has a high content of water. Similar Precambrian glass has been described from a diabase dike near Häme, Alanda and Satakunta in Finland (Mäkipää 1979). Precambrian diabase offshoots containing glass are only 1 cm thick, and form the terminations of diabase dikes. The age of these glasses is something extraordinary. This may be explained by the fact that these glasses were preserved beneath the Earth's surface and were not in contact with the atmosphere or aqueous solutions until glacial erosion exposed them during the Quaternary. Of the tektites, the North American tektites and microtektites are the oldest with a radiometric age of 35 Ma. The microtektites and tektites from Haiti (Beloc), from the boreholes DSDP 540 and 546 drilled in Wyoming (Dogie Creek and Teapot Dome), and from Mexico (Arroyo el Minebral) are of the age of the Cretaceous-Tertiary boundary. Spherules of microtektite glass of Late Devonian age have recently been described from Senzeille and Hony in the Dinant Basin in Southern Belgium (Claeyes et al. 1992). The glass spherules were found along the Frasnian-Famenian boundary which, as early as in the 1980s, was considered by some authors to be associated with an iridium anomaly and extinction of some organisms (e.g. Raup & Sepkoski 1982).

In the section at Hony, the glass spherules were found at the very base of the first conodont zone of the Famenian with *Palmatolepis triangularis*, thus about 5 to 10 cm above the Frasnian-Famenian boundary. Glass spherules from Hony and Senzeille are on average from 50 mm to 1 mm in size. They are colorless, yellowish, reddish or exhibit a grey metallic luster. Their shape is mostly perfectly rounded. Spherules of oval shape, teardrops or dumbbell-like particles are less abundant.

The spherules are often coated with a thin layer of calcite and clay minerals. This protective cover together with the low content of water in spherules (0.009 wt %) is thought to have contributed to their preservation over 367 Ma. According to Claeyes & Casier (1993), fast burial also may have contributed to their preservation.

The chemical composition of glasses varies slightly more than that of microtektites. Glasses are also rich in aluminium or iron or calcium. Spherules high in silica are known from the locality Hony. This may indicate remelted quartz grains (lechatelierite) which are known from tektites and microtektites. Glass spherules are interpreted as microtektites produced by an impact. Similar microtektite glass was described from a Famenian section at Qidong in China (Wang 1992) and from the Yukon Territory (Boundy-Sanders 1992). High contents of calcium and magnesium in these glasses indicate that their source rock must have been rich in a carbonate component. More data on Devonian glass spherules are given in Bouška et al. (1993).

The phenomena described infer that even though glass is an unstable material under superficial conditions, it may be preserved under certain favourable conditions without recrystallization or decomposition due to weathering processes. The Devonian microtektite glasses described above serve as an example.

Reactivity, stability and degradation of natural glasses

Natural glasses are much rarer on the surface of the Earth than crystalline minerals or rocks. The reasons for this lie in the contents of water and other volatiles in the parental melt. Water and volatile components reduce the viscosity of terrestrial magmas and increase the diffusion rate of dissolved oxides, thus enabling crystal growth. This is why the glasses are rare under terrestrial conditions.

Decomposition and dissolution of natural glasses depends on the conditions under which they were deposited. Besides the chemistry of glass, the environmental conditions (p, t, pH, Eh, water regime etc.) control the degradation of glass. In particular, the presence or absence of water and the degree of drainage are important. Water is a common constituent of some natural glasses. The interaction between water and glass results first in the formation of hydroxide groups which bond with oxygens. This process leads to breakage of the strong Si-O-Si bonds creating more non-bridging oxygens and the Si-O group then reacts with another molecule of water. The excess of $(OH)^-$, which originates during this reaction at higher pH leads to dissolution of the glass through an autocatalytic process. Depending on the drainage the hydrated layer thus formed along the glass surface is exposed to circulating ground water and chemical dissolution results. The rate of transfer of silica and other major components into solution has a linear trend whereas the release of Na, K, Ca and Mg initially shows a parabolic course (Hawkins 1981). The relative degree of ion hydration is directly proportional to the ratio of charge to the radius. Mostly alkalis, alkaline earths and SiO_2 are released into neighbouring solutions during the decomposition of glasses. Alkalis are the most mobile ions. Among trace elements, Li, Ba, Mn, Sr and P are readily leachable. The chemical

reaction between water and glass proceeds in two stages (Doremus et al. 1983). The first stage involves release of the alkalis into solution through ion exchange. The second stage involves release of alkaline earths together with dissolution of the other glass components.

Hydration of the glass leads to breaking of the bonds between alkali metals and the nonbridging oxygens with formation of silanol groups Si-OH and the released alkali elements can migrate. Extremely high values of pH lead to dissolution of the glass skeleton. Aluminosilicates contain sodium atoms with two different mobilities arising from their different position in the glass structure. The ion compensating the charge deficit resulting from the bonding of Al in 4-coordination has lower mobility, while that associated with the Si-O⁻ groups migrates readily.

Two different hydrosilicate layers are formed on the glass surface in this second hydration stage. These consist of a hydrosilicate gel, and a cracked, brittle layer of hydrosilicate. The outer gel layer has a constant water content and constant alkali concentration. Diffusion is faster here than in the transition zone bordering directly on the fresh glass. In the direction towards the inner part of the glass, this gel layer passes into a transition zone with a thickness that is dependent on the weathering time. The water content in this layer decreases from the site of contact with the outer gel layer towards the contact with the fresh glass.

A brittle hydrosilicate layer is formed on the surface of the glass in a noncorrosive environment under mild conditions. Fine cracks are clearly visible, caused by tension strain. This hydrosilicate layer mostly consists of hydromica. This layer can be removed by the motion of the surrounding solution and the fresh glass surface is again exposed to the action of the extracting solution. If this layer remains on the glass, then the sharp boundary between the hydrated and unhydrated glass moves at a certain velocity into the inner parts of the glass. A palagonite instead of hydromica layer is formed in basaltic glasses. The rate of resistance of glasses having the same content of SiO₂ decreases with the increasing concentration of alkalis and water because the higher content of water favours hydration of Si-O bonds (Tomozava et al. 1982). Fair draining leads to the corrosion of natural glasses which has been studied by Knobloch (1992).

The stability of tektites during weathering in a continental environment is much greater than that of obsidian or basaltic glass. The weathered zone on basaltic glass from basaltic tuffs formed after hydration is termed palagonite. The regular interaction of basaltic glass with water at 25 °C leads to the formation of the palagonite layer at a rate of approximately 0.07 mm per year. Basaltic glass, which is very unstable, could be completely altered after several thousands of years or maximum some tens of thousand years.

The rate of hydration of rhyolite glass, which is considerably lower than that of basaltic glass, decreases with increase in the content of SiO₂ and is three to four orders higher than the rate of devitrification. In all cases, devitrifi-

cation, i.e. crystallization, is slower in natural glasses than hydration processes. Basaltic and other inhomogeneous glasses are more easily devitrified than silicic glasses. Crystallization nuclei of cristobalite are known to occur in some obsidians which are older than the Neogene. The formation of cristobalite microcrystals is sometimes dependent on the cooling temperature of the rhyolite melt. All devitrified glasses, with only a few exceptions, e.g. pitchstone from Saxony, are older than the Mesozoic. However, the numerous Triassic and Jurassic glasses have undergone at least partial devitrification.

The lattice energy, representing the degree of polymerization of the melt, which correlates with an overall change in the Gibbs energy of hydration of the glass, depends on the number of nonbridging oxygens. This can be determined from the chemical composition of the given glass. The nonbridging oxygens are formed during the hydration of glass by breaking of the siloxane bonds by hydroxide ions which results in the release of silicon from the structure. Further reaction with water leads to the formation of silanol bonds on the surface of the glass and the simultaneous release of hydroxide ions. When calculating the number of nonbridging oxygens in a synthetic borosilicate glass it is clear that this glass is very similar to basaltic glass, both having 0.55 nonbridging oxygens. In contrast, the number of nonbridging oxygens in silicic volcanic glass varies around 0.05 (Borovec & Bouška 1992).

The stability of glass in high level radioactive waste repositories is the subject of intense study at the present time. The majority of glasses utilized in these repositories is of borosilicate composition. The long-term stability of these glasses is established by extrapolation of results obtained in short term experiments on hydration of glasses at different temperatures. The results obtained are compared with analogues of natural glasses. Some authors consider basaltic glass to be an appropriate natural analogue of synthetic borosilicate glass. The processes and products of hydration in natural basaltic glass are known in some detail (Borovec 1987; Morgenstein & Shettel 1994). However, these authors have not taken into account the differences in the basicity of these two types of glass. As boron is an acid-forming element with geochemical properties similar to silicon, it replaces silicon, and occasionally aluminum, in aluminosilicates. It is not only adsorbed on the surface but also forms part of the inner tetrahedral structure in which it replaces silica. This element is not readily extracted from the aluminosilicate structures, even by hot mineral acids.

Tektites represent a special group of very homogeneous natural glasses which were formed by rapid supercooling of high temperature melts. Therefore it may be easier to search for analogues of the above mentioned synthetic glasses among silicic volcanic glasses which are more similar in their velocity of cooling and original temperature of the parent melt. It is well known that the content of alkalis, boron and water decreases the melt liquidus

Table 2: Indices of stability (weathering).

$M_1 = \frac{\text{FeO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO}}$	
$M_2 = \frac{\text{Al}_2\text{O}_3}{\text{FeO} + \text{MgO}}$	
$M = \frac{\text{K}_2\text{O} + \text{Al}_2\text{O}_3}{\text{Na}_2\text{O} + \text{MgO}};$	Björlyke (1974)
$MV = \frac{\text{Al}_2\text{O}_3 + \text{K}_2\text{O}}{\text{MgO} + \text{CaO} + \text{Na}_2\text{O}};$	Vogt (1927)
$\text{Petti} = \frac{\text{Al}_2\text{O}_3}{\text{Na}_2\text{O}};$	Pettijohn (1957)
$A = \frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}};$	
$\text{IPW} = \frac{100 \times (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO} - \text{H}_2\text{O})}{(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO} + \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)};$	Reiche (1943)
$K_{\text{alk}} = \frac{\text{Na} + \text{K} + \text{Li} + \text{Ca} + \text{Mg} + \text{Ba} + \text{Sr}}{\text{Si} + \text{Ti} + \text{Al} + \text{Fe}^{\text{II}} + \text{Fe}^{\text{III}} + \text{Mn} + \text{Na} + \text{K} + \text{Li} + \text{Ca} + \text{Mg} + \text{Ba} + \text{Sr}};$	Adamová (1991)
where meaning of chemical formula is n/m (mol/100 g of rock sample)	
$I_{\text{ko}} = \frac{200 \times X}{Y};$	Konta (1982)
where $X = \text{sum } (n/m \times Z/r)$ of oxides of group A - $(n/m \times Z/r)$ of group C $Y = \text{sum } (n/m \times Z/r)$ of oxides of groups A and B	
$I_w = \frac{100 \times U}{Z};$	this paper
where $U = \text{sum } (n/m \times r/Z)$ of oxides of group A - $(n/m \times r/Z)$ of group C $Z = \text{sum } (n/m \times r/Z)$ of oxides of groups A and B	
Group A: FeO, MnO, MgO, CaO, SrO, BaO, NiO, Li ₂ O, Na ₂ O, K ₂ O, P ₂ O ₅ Group B: SiO ₂ , ThO ₂ , ZrO ₂ , TiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , Cr ₂ O ₃ , B ₂ O ₃ , V ₂ O ₅ Group C: H ₂ O	

of the aluminosilicate or silicate glass. However, the stability and rate of hydration or devitrification should be similar. Acidic silicate melts are able to dissolve a certain amount of water without any structural changes. Such water has nothing in common with secondary water of hydration. The basic parameter controlling the stability of glass is the bonding energy of individual elements towards oxygen. In common with crystalline silicates, the strongest bond in the silicate glasses is that between Si and O. The position of amphoteric aluminum in silicate glasses is also important. It is strongly affected by the presence of trivalent iron. In glasses containing no iron, aluminum enters tetrahedral coordination and behaves as a glass-forming oxide with a strong bond Al-O. Some experiments showed that glasses high in aluminum are even hydrophobic. Nevertheless, certain volcanic glasses high in aluminum also have high water contents (Adams 1984).

The degree of oxidation of iron present in the glass also affects the rate of hydration. Trivalent iron behaves as a structure-forming element but divalent iron functions as a modifier allowing hydration.

The comparison of properties of natural and artificial glasses

As follows from the previous text, the nearest natural analogues of synthetic borosilicate glasses are volcanic glasses,

both silicic and basaltic, and tektites. They exhibit similar chemical stability and mechanical properties. Basaltic volcanic glass in particular shows similar behaviour during weathering and contains nonbridging oxygens. Silicic glasses show chemical similarities, as boron is linked with silicon and aluminum in the structure of the glass. Numerous authors have determined the basicity of synthetic glasses according to the content of SiO₂. However, boron is also an acid-forming element which is even more acidic than silica. Natural borosilicates such as tourmaline and datolite are very resistant to weathering and often occur in heavy mineral assemblages in placers. According to Stubičan and Roy (in Walker 1968), the diadochy substitution B-Si and Al-B occurs in clay minerals in which boron enters the tetrahedral positions in these structures. The bond is so strong that its extraction is impossible even when using even hot mineral acids. On the other hand, boron released from the structure of the borosilicate glass into a weathering zone can migrate because borate salts are more soluble than silicates though less soluble than phosphates. If the contents of B₂O₃, SiO₂ and Al₂O₃ in borosilicate glasses are summed, then we obtain silicic glasses comparable with silicic volcanic glasses and tektites. The latter have almost no water and a minimum of alkali metals. The diadochy of P-Si is assumed to exist in phosphoric glass used in Russia for vitrification of radioactive waste (Lutze & Ewing 1988).

The chemical stability of silicates and silicic glasses during weathering processes is controlled by the contents of SiO_2 and Al_2O_3 . This is due to the strong bonding energy between Si and O in tetrahedrons (770 kJ.mol^{-1}). The energy of B-O bonds (807 kJ.mol^{-1}), Zr-O bonds (758 kJ.mol^{-1}) and Ti-O bonds (662 kJ.mol^{-1}) are more or less similar. Al-O bonds (486 kJ.mol^{-1}), Fe-O bonds (402 kJ.mol^{-1}) and the major alkaline earth bonds Ca-O (352 kJ.mol^{-1}) and Mg-O (331 kJ.mol^{-1}) are lower. Alkali metals and oxygen exhibit low values of bonding energy (Li-O: 327 kJ.mol^{-1} , Na-O: 255 kJ.mol^{-1}) and K-O: 239 kJ.mol^{-1}). The above mentioned values are taken from Weast (1984). Keller (1957) points out that the bonding energy between Fe^{3+} and O is stronger than that between Fe^{2+} and O.

Altogether 15 specimens of synthetic glass from France, the UK, Germany, the USA and Japan intended for vitrification were selected for assessment of the stability of borosilicate glasses and other materials used for disposal of radioactive waste. Two ceramic materials and another 3 types of synthetic glass were also assessed (cf. Table 1). The above-mentioned materials were compared with the main types of natural glass. The behaviour of individual glasses was expressed in terms of various indices of weathering commonly used in the geochemical and petrological literature. Of the 36 published equations, only those summarized in Table 2 were used. These equations provide the most suitable proportions of metals to establish the stability of individual glasses. The best suited equations include oxides of alkali metals, alkali earths and aluminium trioxide and/or ferrous oxide. Among the first indices formulated is the index of potential weathering introduced by Reiche (1943) which decreases with in-

creasing mutual bonds of Si-O tetrahedrons and increasing resistance to weathering. The coefficient of alkalinity (K_{alk}) has also been used in constructing a series of maps of reactivity of rocks at a scale of 1:50,000 published in sequence since 1985 by the Czech Geological Survey (Adamová 1991). Natural materials with low reactivity were rich in SiO_2 but extremely low in alkali metals and alkaline earths.

An index of the relative stability of silicates was defined by Konta (1982). The index I_{KO} includes the content of the constituent oxides (in mols) and their properties expressed by multiplying their values by the ion potential Z/r of the given element. The relative degree of hydration of ions in an aqueous medium varies in direct proportion to the ionic charge and inversely with the ionic radius. Therefore, the multiple of a sum of moles of oxides is useful to express relations of ions belonging to a certain chemical group (e.g. alkali metals or alkaline earths). When assessing two or more groups of ions, e.g. alkali metals or alkaline earths, it is better and more realistic to divide the pertinent sum of moles of individual oxides by the value of ionic potential Z/r of the element concerned. It was established that the trend remained the same but the calculated indices differed considerably (Fig. 2). This is why it was possible to plot I_{KO} against the sum of $\text{SiO}_2 + \text{TiO}_2 + \text{ZrO}_2 + \text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3$ in wt % (see Fig. 3). For this reason all samples investigated were listed in Table 3 in order of increasing sum of the above-mentioned oxides.

The results shown in tables and diagrams (Figs. 2 and 3) were firstly evaluated from the viewpoint of the validity and coherency of the data obtained. Some indices of weathering, valuable in geochemical studies of the maturity of sediments

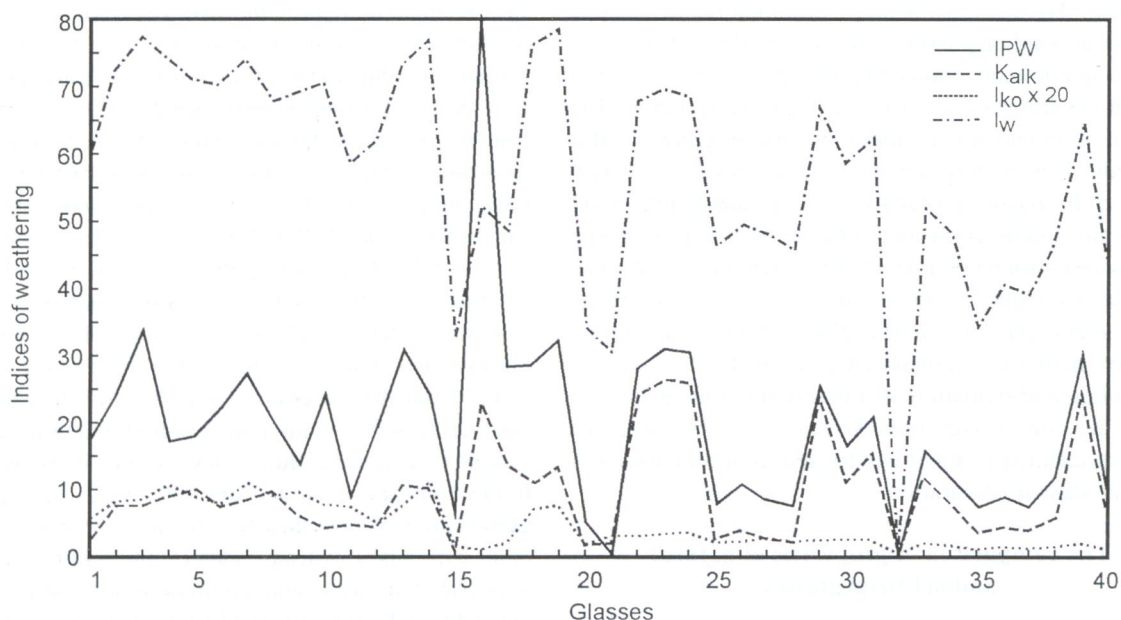


Fig. 2. Comparison of the values of IPW, K_{alk} , I_{KO} , I_{w} indices of studied glasses and ceramics. Numbers of samples correspond to Table 1.

Table 3: Calculated indices of weathering arranged according to the sum of $\text{SiO}_2 + \text{TiO}_2 + \text{ZrO}_2 + \text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3$ in wt%.

Glasses	M1	M2	M	MV	Petti	A	IPW	K_{alk}	I_{ko}	I_{w}	Total	No.
Cryst.ceramics, Synroc D	3.59	0.64	3.56	1.41	3.56		28.09	0.12	13.59	47.88	44.00	17
Tiffany window glass	0.57	9.82	14.96	4.73	6.08	8.88	4.99	0.08	1.47	34.07	56.90	20
Waste gl. SRL 165, USA	0.99	0.24	0.20	0.19	0.23	0.01	17.90	0.45	10.32	71.41	64.50	5
Waste glass B, France	0.31	1.32	0.24	0.18	0.24		24.77	0.43	8.03	72.83	64.58	2
Waste glass A, France							17.41	0.30	2.60	60.30	65.33	1
Egyptian glass	0.16	0.09	0.08	0.05	0.02	0.06	32.50	0.40	13.56	79.07	65.37	19
Basaltic volcanic gl., Midatlantic rift zone, Miocene	1.91	0.45	3.14	0.33	3.29	0.03	30.97	0.18	26.38	70.10	67.07	23
Basaltic volcanic glass, Kilauea, Hawaii Islands	1.86	0.43	2.93	0.36	2.94	0.15	28.01	0.16	24.30	68.79	67.86	22
Impact glass, Lonar crater, India	2.14	0.41	3.96	0.41	3.79	0.18	25.99	0.14	24.05	68.15	68.20	29
Basaltic volcanic gl., Maria Celesta trench, Ind.Ocean	2.22	0.43	3.29	0.35	3.26	0.03	30.58	0.19	25.95	69.05	68.52	24
Basaltic volcanic glass, Tolbachik, Kamchatka	1.58	0.75	3.01	0.55	2.79	0.34	-0.57	0.17	1.85	30.22	68.93	21
Waste glass C, France	0.67	81.01	0.66	0.66	0.66		33.88	0.43	8.03	77.69	70.86	3
Roman bottle glass	0.10	1.22	0.10	0.07	0.08	0.03	28.46	0.36	10.83	76.76	71.09	18
Brown glass from meteorite ALPHA 81005	1.79	1.09	58.56	0.59	58.42	0.14	31.04	0.12	24.74	65.73	71.67	39
Waste gl. SRL 131, USA	0.22						23.99	0.57	10.43	77.14	72.39	14
Waste gl. GP 98/12, Germany	0.27	0.19	0.06	0.04	0.06		31.00	0.38	10.82	74.09	74.70	13
Impact glass, Zhamanshin, Kazakhstan	1.63	1.18	3.41	0.77	3.18	0.23	21.15	0.14	15.84	63.40	75.80	31
Cryst.ceramics, Synroc B	0.24			0.24			80.96	0.06	23.06	52.63	76.80	16
Waste gl. SON68, France	0.21		0.30	0.21	0.30		22.33	0.41	7.41	70.56	77.70	6
Waste gl. PNL76-68, USA							19.14	0.26	4.39	62.13	78.20	12
Waste gl. SM 539, Germany							27.37	0.55	8.59	74.59	78.50	7
Waste gl. SRL 165, USA	0.12						17.17	0.55	9.14	74.76	79.00	4
Impact glass from suevite, Ries, Germany	1.84	1.01	3.85	0.99	3.07	0.87	16.34	0.15	10.97	59.06	80.05	30
Waste gl. SM 513, Germany	0.44	0.52	0.28	0.12	0.28		20.11	0.45	10.02	67.94	81.40	8
Waste gl. AVM, France							24.33	0.39	4.23	70.82	81.40	10
Australasian microtektites	3.90	0.64	9.25	0.73	8.94	1.12	16.18	0.13	12.72	52.19	81.80	33
Waste gl. UK 209							13.68	0.49	6.11	69.69	83.50	9
Australites	2.29	0.97	5.46	0.98	4.93	0.82	11.88	0.09	8.31	48.39	84.61	34
Obsidian, Kogudoro-Bosano, Sardinia	1.44	2.53	3.46	1.60	2.75	0.81	11.11	0.13	4.17	49.59	84.78	26
Waste gl. PO422, Japan	0.48		3.49	1.09	2.17	1.32	8.77	0.38	4.87	58.53	85.90	11
Moldavites, H Ca/Mg, CZ	1.28	1.08	15.59	0.84	12.75	5.69	12.18	0.09	6.52	47.50	86.97	38
Fulgurite from soil, Křenice, CZ	2.31	1.50	8.59	1.73	7.56	1.69	7.61	0.07	4.54	39.71	87.54	40
Obsidian, Armenia	1.32	4.35	2.73	1.96	2.11	0.66	7.63	0.13	2.17	45.58	87.70	28
Obsidian, Milos, Greece	1.24	3.97	2.47	1.84	1.82	0.66	8.37	0.14	2.45	48.22	88.07	27
Obsidian, Eastern. Slovakia	1.48	3.51	3.56	2.34	2.80	0.95	7.47	0.11	3.12	45.68	88.88	25
Moldavites, Č. Budějovice region, CZ	1.87	1.32	15.62	1.28	13.15	4.85	8.95	0.08	4.75	40.78	90.25	36
Moldavites, Moravian region, CZ	2.27	1.50	13.99	1.76	11.98	4.01	7.52	0.07	4.23	39.04	90.48	37
Moldavites, Radomilice region, CZ	1.95	1.32	17.66	1.15	16.29	5.48	7.46	0.07	3.78	34.23	91.54	35
Waste gl. Pyrex	0.24		0.30	0.24	0.30		5.68	0.09	1.26	32.03	96.00	15
Libyan Desert glass	2.43	2.10	3.25	1.49	3.20	0.05	0.47	0.01	0.24	4.03	99.48	32

or their stability and reactivity under natural conditions, turned out to be unsuitable for our purposes. These unsuitable indexes include: M_1 , M_2 , M , MV , $Petti$ and A . The reason for this is that they include oxides which are completely missing or occur in very small amounts in synthetic materials. Therefore, the results obtained using these indices are difficult to evaluate.

The index K_{alk} is also not sensitive to significant variations within the range of compositions investigated. The plot of this alkalinity index (Fig. 2) is uniform and similar

for both the synthetic and natural glasses. Some samples were excluded from our calculations and interpretations because of their anomalous behaviour. One was sample no. 21, the basaltic glass from Tolbachik in Kamchatka. This strongly weathered glass has 6.4 wt % H_2O and negative values of the IPW index (Table 3, Fig. 2). These parameters lead to the distortion of other indices of weathering. This would also distort and consequently favour this glass as far as its stability is concerned. Among synthetic glasses and ceramic materials samples which showed markedly

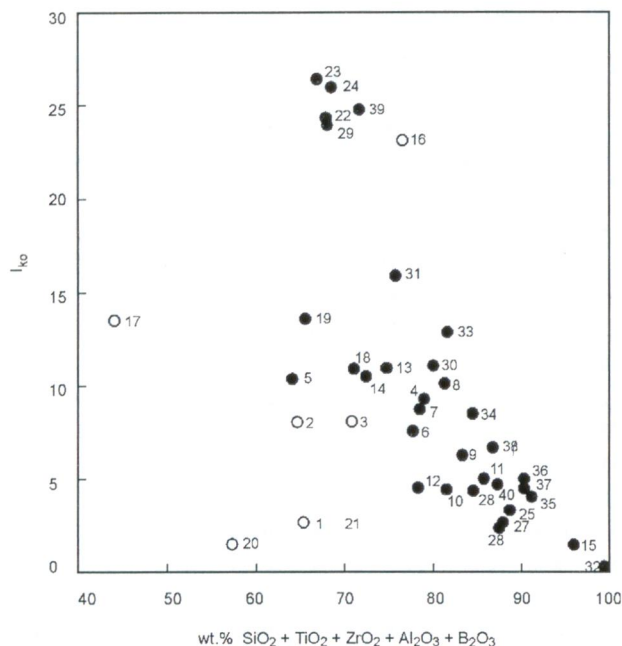


Fig. 3. Correlation between the index of weathering I_{ko} and the sum of glass net-forming oxides. Numbers of samples correspond to Table 1.

different chemical composition were excluded. For instance, sample no.1 showed 25.50 wt % fission products and actinides, sample no. 2 and no. 3 have a similar composition (see Table 1, note b, c). Ceramic materials nos. 16 and 17 were excluded for very different compositional reasons (see notes in Table 1), and also the Tiffany glass (sample no. 20) which contained 38.93 wt % PbO. Although it was still possible to recalculate analyses to 100 wt % after deduction of water, fission products and actinides or other strange components, this operation would confuse the whole system, improve the stability of these glasses and finally lead to distorted results.

The values of weathering indices for individual glasses are plotted in Fig. 2. Excluding the K_{alk} index as a less suitable parameter, the other indices show comparable trends but at different levels. The classification of samples according to the sum of their net-forming oxides was found very useful. These oxides actually form the skeleton of the glass structure whereas the modifiers such as Na_2O , K_2O , CaO , etc., tend to break the continuity of the network, causing depolymerization which leads to its irregularity, and are carriers of the glass's stability.

After elimination of the above-mentioned samples (marked by circles in Fig. 3), an indirect correlation exists between the sum of net-forming oxides and the weathering index I_{ko} . Similar correlations would exist between the sum of the net-forming oxides and the index of potential weathering IPW and the weathering index I_w . Only some shift in values would occur but this is not crucial.

Sample no. 15 (Pyrex), which is a borosilicate glass, appears to be the glass which is most resistant to weathering. Moreover, it has an analogue in the Libyan Desert glass

(sample no. 32). The parameters of both samples are shown in Fig. 2, and particularly in Fig. 3. The synthetic glasses nos. 10, 12, 11, 9 and/or sample no.6 are relatively stable. Their analogues can be found in tektites (samples nos. 35, 37, 36, 38), silicic volcanic glasses (nos. 28, 27, 25, 26), and fulgurite glass (no. 40). Plots on Fig. 3 show pairs which have similar resistance to weathering. In particular, samples no.10 and 11 can be correlated with sample no. 26 or sample no. 9 with no. 38, and no. 15 with no. 32.

The least resistant to continental weathering are basaltic volcanic glasses (nos. 23, 24, 22), brown glass from the ALHA 81005 meteorite and the impact glass from the Lonar crater (no. 29).

The study of stability of natural and synthetic glasses intended for vitrification of the radioactive waste based upon different weathering indices showed that some synthetic borosilicate glasses (nos. 15, 10, 12, 11 and 9) display high stability comparable with silicic volcanic glasses, tektites and the Libyan Desert glass.

Conclusions

The weathering indices tested in petrology and geochemistry and also used in the construction of maps of the reactivity of rocks in the Czech Republic were applied to natural and artificial borosilicate glasses. The investigation carried out so far has focussed on the comparison of basaltic and borosilicate glasses taking into account similarities in content of SiO_2 and similar reaction rims originating during weathering. It is notable that boron is also acid-forming like silicon and has a strong bond energy when combined with oxygen in the polymeric structure of glasses and therefore it is necessary to re-consider silicic volcanic glasses (obsidians) and tektites as suitable analogues for artificial borosilicate glasses, providing boron forms tetrahedrons with oxygen in these glasses.

Comparing the stability and weathering indices of various types of natural glasses and glasses used for vitrification, the following glasses exhibit the highest stability as suitable natural analogues: obsidian (localities: Slovakia, North Caucasus), tektite-moldavites (South Bohemia), and the Libyan Desert glass.

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