ÚJV Řež, a. s.

Natural glasses as natural analogues for vitrified HLW

Václava Havlova

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Presentation outline

1. **Borosilicate glass for RWM, incl. CZ**
2. **Glass – history, structure and types**
3. **Glass durability**
4. **Processes, influencing glass durability**
    1. Dissolution
    2. Leaching
    3. Devitrification
    4. Radiation impact
    5. Others
5. **Sources of analogy**
    1. Natural glasses
    2. Dissolution rates
6. **Conclusions**

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1. Borosilicate glass

- widely used as the matrix for HLW immobilisation.
- a massive, stable and durable material.
- can chemically incorporate high levels of RW, can physically tolerate large radiation doses and can accept wide variations in the composition of the waste streams.
- however, devitrifies with time

- the long half-lives of many fission products and actinides in HLW requires that they must be isolated from the biosphere for log time periods (10^6 y) and the safety has to be proved

- most tests - short-term in lab.
- long-term stability: possible use of ANALOGUES

Source: *(www.civildigital.com)*

1. Czech Republic: vitrified waste

- disposal concept: DIRECT DISPOSAL OF SNF

- transfer of highly enriched SNF from research reactors to the country of its origin (2007, 2013)
- US DOE – Russian Federation – IAEA program
  - Czech Republic, Poland, Ukraine, Belarus, Serbia, Hungary, Bulgaria, Vietnam, Uzbekistan

- SNF transferred to Mayak (RF) and reprocessed (112 SNF assemblies with enrichm. up to 36%)

- vitrified waste will be transferred back after 2024 in Al – Na phosphate glass form (0,586 m^3)

- Will be most probably disposed in DGR
- Part of the source term for SA

Transport of SNF from Vietnam

2. Glass history

- **first appearance: approx. before 3,500 years (Egypt and Mesopotamia)**
- **glass blowing** (approximately 50 – 0 BC)
- s**oda-lime glass around 1000 AD** when potassium-lime glass started to be produced in Northern and Western Europe.
- **11th century**: new ways of making sheet glass by blowing spheres were introduced in Germany (perfected in the 13th century on the Venetian island of Murano)
- around 1688, a process for casting glass = more commonly used material.
- invention of the glass-pressing machine (1827): **mass production of inexpensive glass articles**.
- cylinder method of creating flat glass (USA, 1820s) commercial production of window glass. This and other types of hand-blown sheet glass were replaced in the 20th century by rolled plate.

2. Glass structure

- amorphous solid substance formed from a melt by cooling below its melting, or liquidus point, without crystallization or spinoidal decomposition with viscosity greater than 10 Pa

- the basic structural unit for silicate glass is tetrahedral $(SiO_4)^{4-}$
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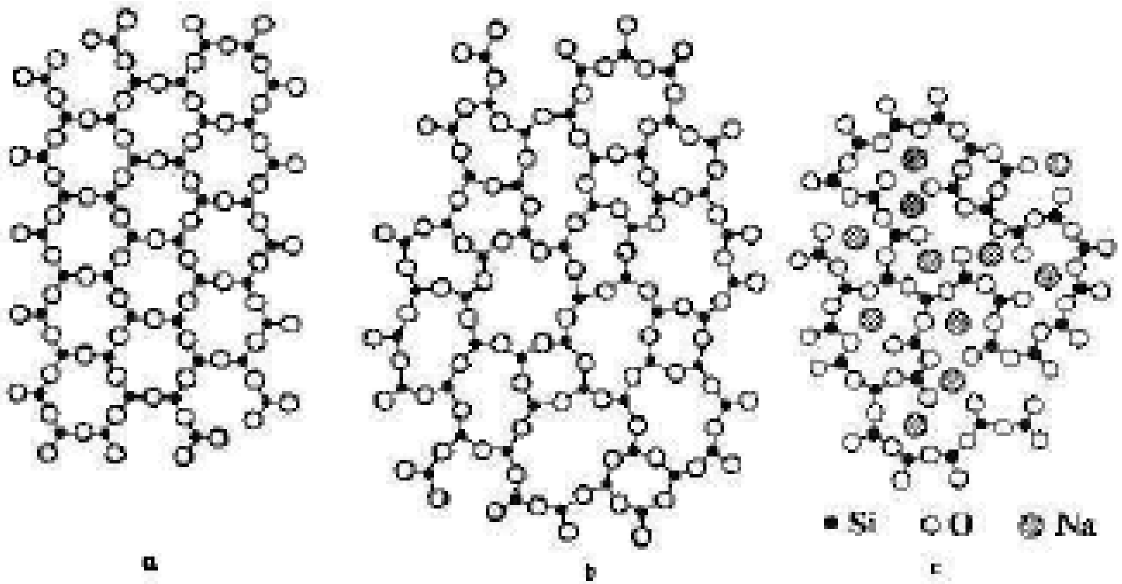

Structure of a) SiO2 (quartz) regular lattice, b) irregular quartz glass lattice and c) Na quartz glass structure (Hlavac, 1988)

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1. Glass types

Oxides used for glass production can be divided into net-forming (SiO_2, B_2O_3, P_2O_5, GeO_2) and modifiers (CaO, BaO, Na_2O, K_2O)

Glass types

a) soda calcic glass (basic glass - sheet glass, bottles etc.);

b) borosilicate glass (containing borax B_2O_3);

c) lead glass (optical use);

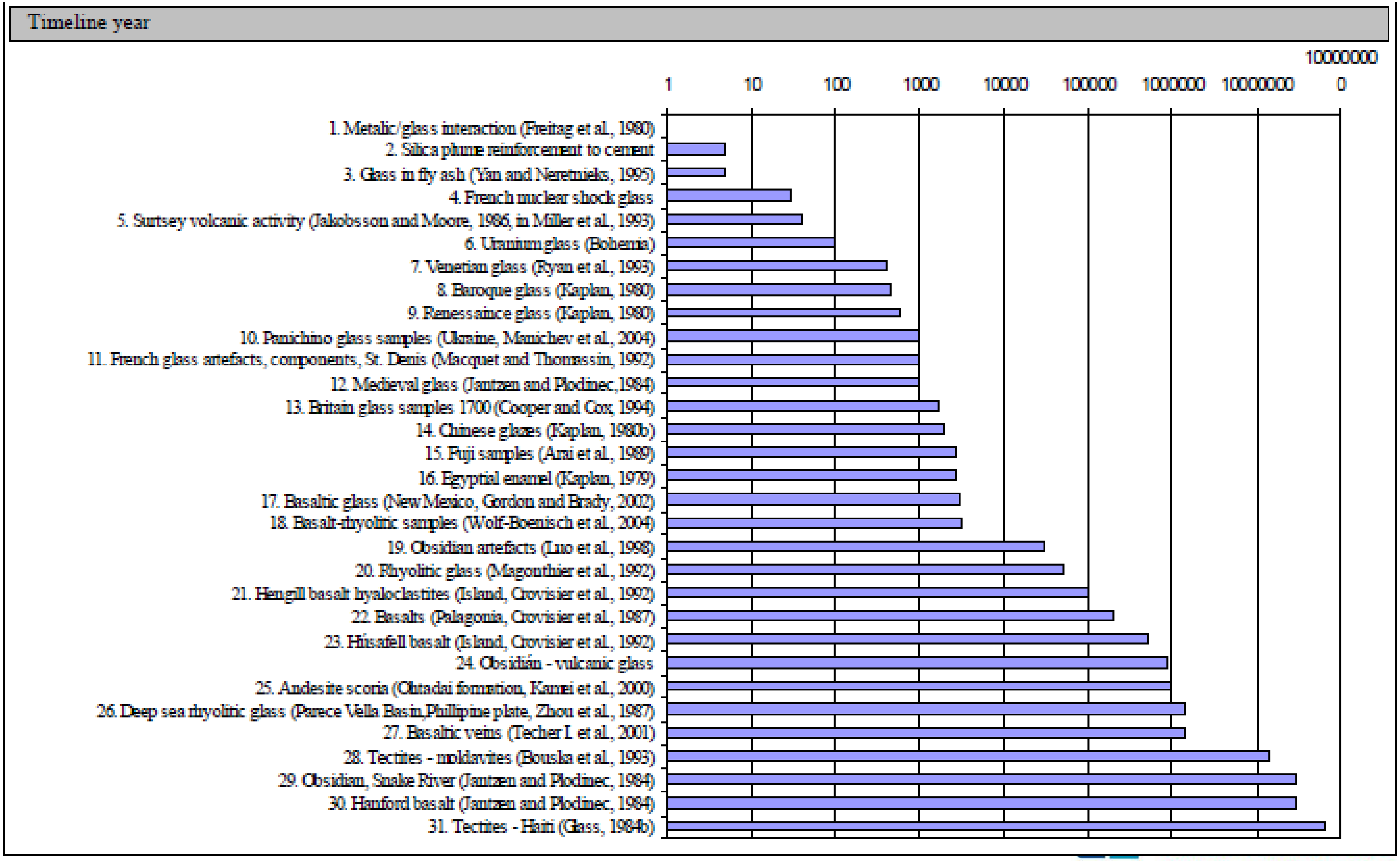
d) other oxide glasses (aluminosilicate glass, orthophosphate glass etc.).

3. Glass durability

Glass durability depends on many variables

- glass composition
- SiO_2 content
- surface area
- volume and pH of the leaching solution
- ions present in the corrosive solutions and their concentrations
- humidity and temperature of the environment etc.

3. Glass durability



The timescales of the most representative glass analogues (Havlová et al., 2009)

4.1 Glass dissolution

Essential role plays

- temperature
- pH
- ratio of glass surface area to volume of solution (SA/V)
- flow rate (groundwater flux)
- glass composition (Si content)
- solution composition (concentration of Si and alkali ions)

4.1 Glass dissolution

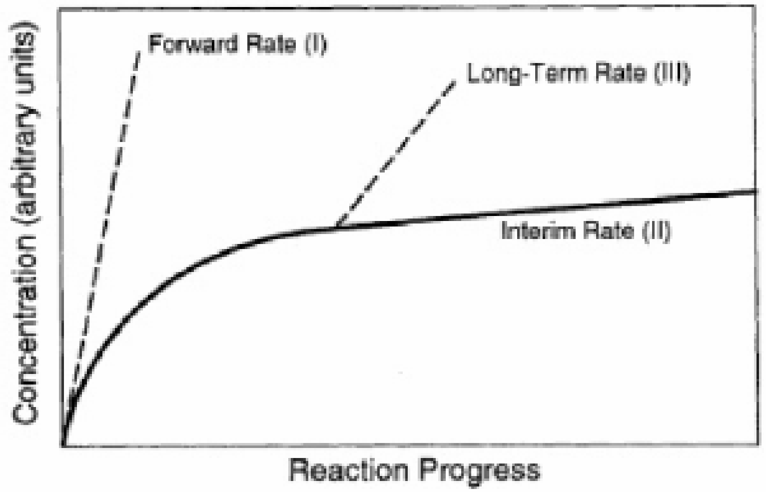
Stage I. - release rate of elements is congruent and linear because the elemental concentrations in solution are lower than the solubility limits of most phases.

Stage II - after loss of silica from the glass, when the dissolution rate decreases as the silica concentration in solution reaches a higher level.

- glass reaction during *Stages I* and *II* : formation of a reaction layer that may or may not be partially crystalline - *palagonite* - mixture of a hydrated glass matrix with authigenic minerals.

Stage III glass dissolution process as the precipitation of aluminosilicates (e.g. zeolites)

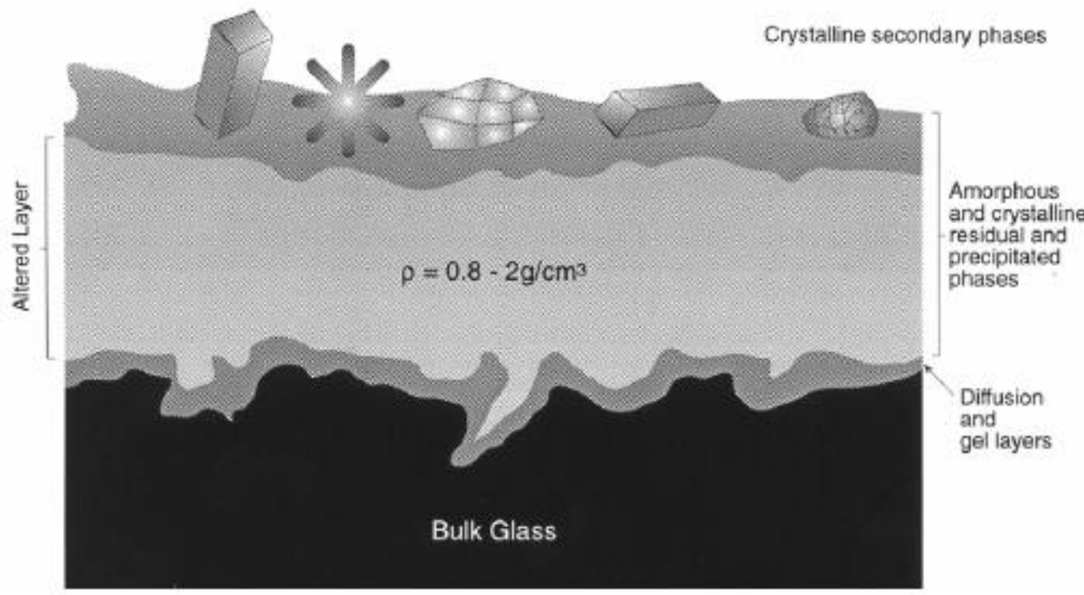
removes silicon from solution. The phases formed are dependent not only on glass composition but also on the composition of the water in contact with the glass



Schematic representation of reaction progress for glass dissolution (after Bates et al., 1996, and Grambow, 1991)

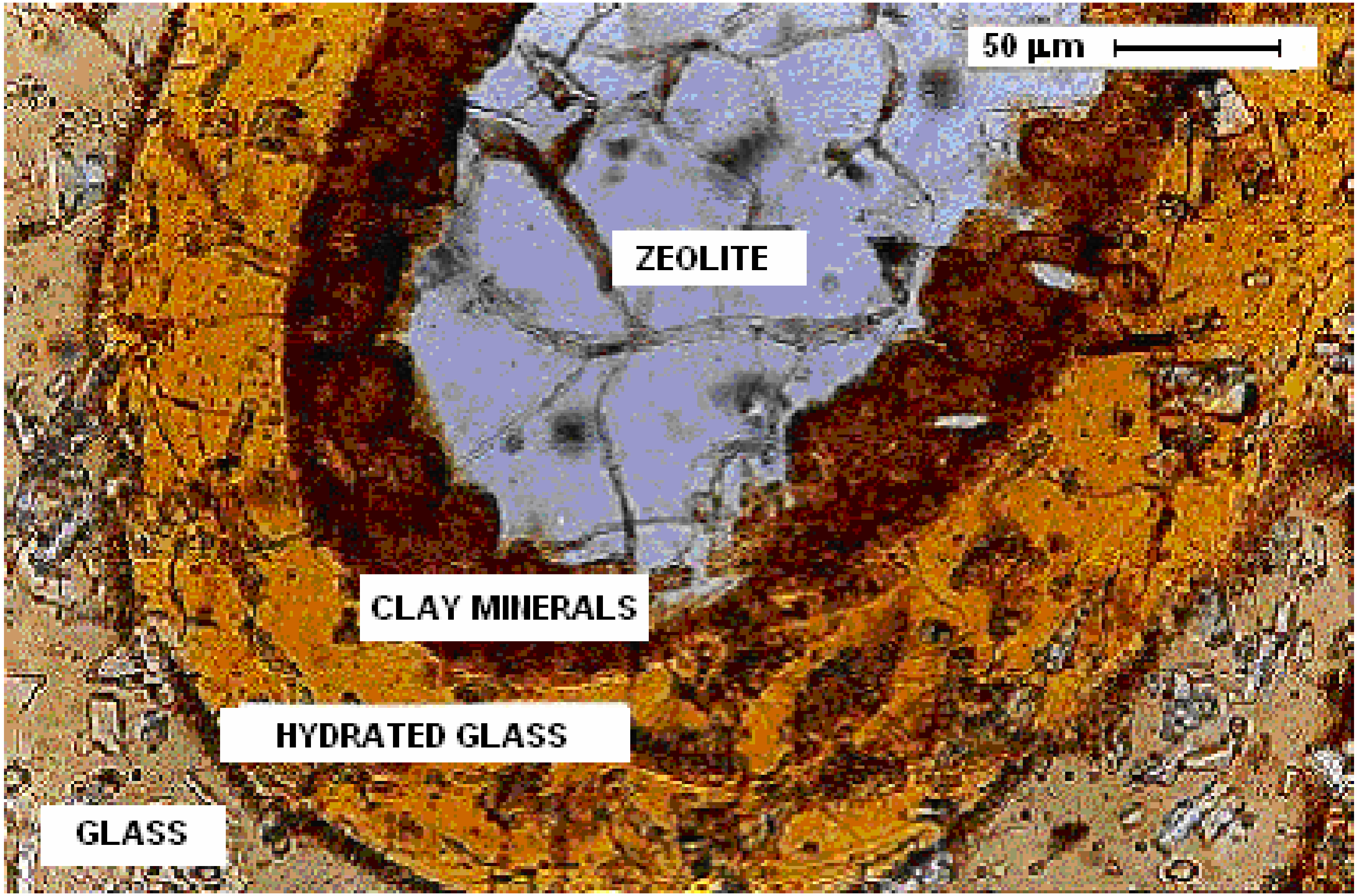
4.2 Glass leaching

- elements incorporated into the glass matrix can be leached out and released into solution.
- slow and dependent on the flux of water
- alteration/palagonite layer may become a chemical sink for released radionuclides due to the precipitation of phases, or it may be a physical barrier to diffusive loss of radionuclides.
- short-term laboratory hydration and leaching experiments suggested that the alteration products act to retain a range of elements, including iron, REEs and actinides (Petit et al., 1989; Trotignon et al., 1992; Ribet et al., 2007).
- non-selective dissolution (all the glass elements are hydrated at the same time) but becomes incongruent, i.e. not all the elements enter solution
- the elements recombine *in situ* to form an amorphous surface "gel" layer.



From Lutze and Ewing (1988)

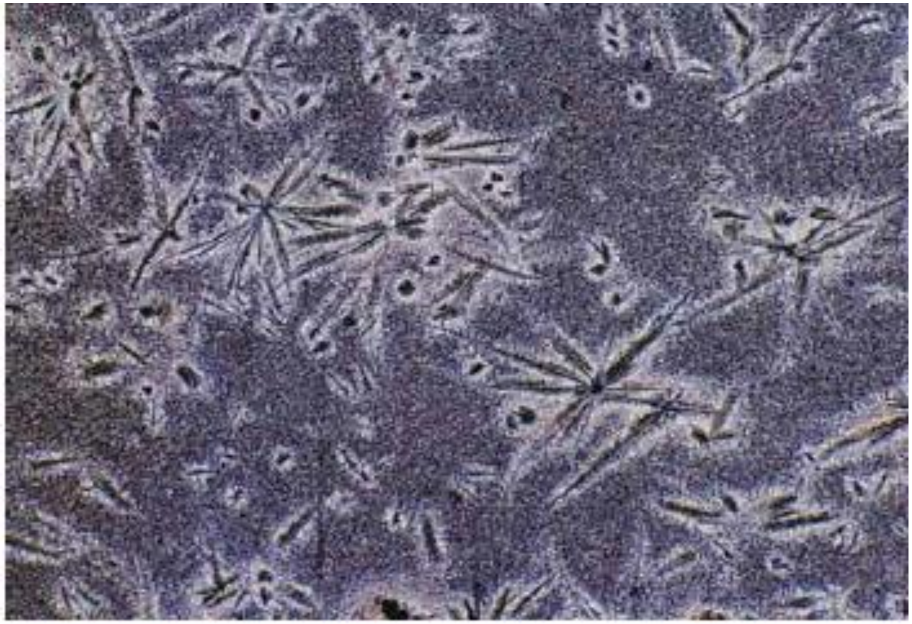
4.2 Glass alteration



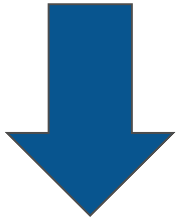
Altered layers in Iceland volcanic glass (Bernotat, 2001).

4.3 Glass devitrification

- nucleation and crystalisation
- can affect silicate or oxyhydroxide gels that are likely to form during the alteration of the waste matrices (Marshall, 1961)
- similar process to "**crizzling**", observed for historical glasses
- under low T and in the presence of a very small amount of water devitrification takes a long time.
- abundant water supply devitrification requires only a short time)



Photomicrograph of a natural volcanic glass from Scotland. From Miller et al. (2000)



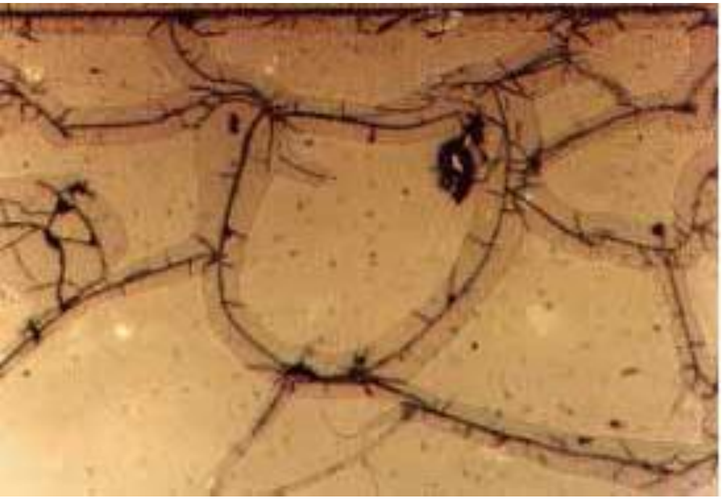
- severely limited existence of volcanic glasses.
- <u>no known volcanic glasses or tektites older than those of the late Cretaceous (65 Ma, Marshall, 1961; Bouska et al., 1993) and most are less than 25 Ma</u>.

4.4 Radiation induced effects

- In some cases, radiation damage has been observed in natural glass in close proximity to radionuclide-bearing minerals (Miller et al., 2000)
- but it does not make any sense to upscale such observations to the high radiation doses experienced by the vitrified waste matrices.

Uranium glass (Bohemia, 19th century)

- a century long doping experiment
- not too much under research
- in one case, bubbles in uranium-bearing glasses were identified that could have been caused by irradiation and could contain O_2 (Laciok, 2004).
  However, the actual content and origin remained unknow
- In 70ties a research: it was noted that U was not leached out of the glass and appears strongly locked in its structure (research)



Samples of uranium glass from the Czech Republic (left) and altered glass surface (parallel nicols; right; Laciok, 2004).

4.5 Other processes

- Thermal cracking
- Wheeping
- Crizzling
- Pittling
- Layering
- Crusting

4.5 Crizzling and wheeping

Glass goblet, Venice, 17th century, displaying advance stages of deterioration. Victoria and Albert museum

17th century glass goblet displaying early signs of instability (‘weeping glass’). Droplets are visible on the surface. Victoria and Albert museum.

5. Sources of analogy

	French vitrified HLW (Savage,1995)	UK vitrified HLW (Defra, 2005)*
SiO_2	45.2	47.2
Al_2O_3	4.9	
Na_2O	9.8	8.6
K_2O		
CaO	4.0	
MgO		
FeO		
Fe_2O_3	2.9	
LiO_2		2.0
B_2O_3	13.9	17.3
Waste oxides	19.3	24.9

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5. Sources of analogy for borosilicate glass

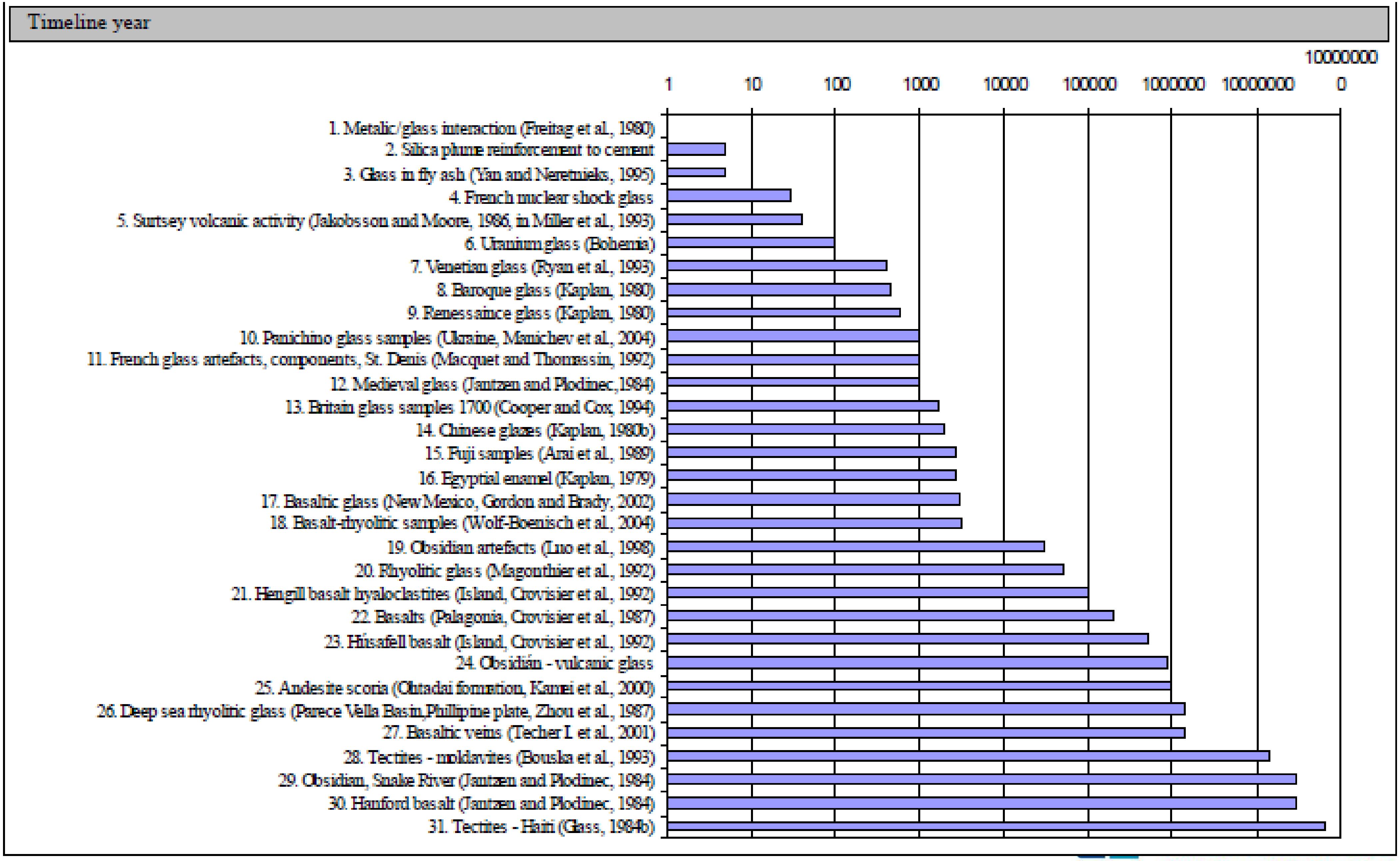
- Natural glasses
  - Basaltic glass
  - Rhyolitic glas
  - Tectites
- Natural shock glasses
- Nuclear shock glasses
- Archeological artifacts
- Industrial materials

5.1 Natural glasses

- Natural glasses

	Basaltic glass (Mazer, 1994)	Rhyolitic glass (Mazer, 1994)	Tektite (Mazer, 1994)	French vitrified HLW (Savage,1995)	UK vitrified HLW (Defra, 2005)*
SiO_2	50.7	74.9	74.4	45.2	47.2
Al_2O_3	11.7	14.2	12.17	4.9	
Na_2O	4.5	4.68	1.32	9.8	8.6
K_2O	0.7	4.59	2.61		
CaO	10.6	0.53	1.52	4.0	
MgO	6.7	0.02	1.85		
FeO	-	0.49	-		
Fe_2O_3	13.1	0.29	5.58	2.9	
LiO_2					2.0
B_2O_3				13.9	17.3
Waste oxides	0.0	0.0	0.0	19.3	24.9

5.1 Timescales of the most representative glass analogues



The timescales of the most representative glass analogues (Havlová et al., 2009)

5.1 Natural glasses

Basaltic glass

- the most similar to vitrified HLW (chemical
- composition - silica content, alteration products, alteration structure and morphology
- similar processes of degradation and palagonite layer

Basaltic glass (Hawaii, Smithsonian National Museum of Natural History)

Rhyolitic glass (obsidian)

- the SiO_2 in obsidian is much higher than for vitrified HLW.
- still have value as analogues of vitrified HLW as follows:
  - chemical composition (durability of high Si glasses = upper limit of the durability of nuclear waste glasses);
  - enrichment in Fe (analogy for secondary phases);
  - enrichment in incompatible elements, such as the REEs, U and Th (analogous to radiotoxic elements; Magontier et al., 1992);

Obsidian (earthsciences.hku.hk)

5.1 Natural glasses

Tectites

- slightly exotic glasses, formed by cooling of molten material (usually assumed to be due to asteroid impact. Those are usually acidic silicate (SiO_2 content higher than 65%) glasses with high melting point. (Bouska et al., 1993).
- Australasia (australites), the Czech Republic (moldavites), the Ivory Coast and North America (Glass, 1984; McCall, 2001).
- Studied tektites vary in age from 0.7 Ma australites to the oldest known 65 Ma samples from Haiti

Typical forms of tektites (generally 2.5 – 5 cm across). Image courtesy of Mila Zinkova (http://home.comcast.net/~milazinkova/Fogshadow.html).

5.1 Stability of natural glasses

Rate (mol cm^{-2} s^{-1})	Glass/solution	Comments	Reference
$10^{-19} – 10^{-18.3}$	Basalt glass	Huallai Volcano (3kyr) 10 – 20 °C	Gordon and Brady (2002)
$10^{-16.2} – 10^{-15.7}$	Nepheline – syenite glass	Field rates (1 – 9 a)	Melnyk et al., 1983*)
$10^{-11.5} – 10^{-13.5}$	Nepheline – syenite glass	Lab rates (1 – 100 days)	Melnyk et al., 1983*)
$10^{-14.8}$	Basalt (minerals + glass)	10 °C seawater rate estimated from measured activation energy and higher T rates	Brady and Gislason, 1997*)
$10^{-13.55}$	Basalt glass	25 °C meteoric water, pH 9.4	Gislason and Eugster, 1987*)
$10^{-13.9}$	Basalt glass	25 °C in seawater	Crovisier et al., 1987
$10^{-13} – 10^{-11}$	SiO_2	25 °C	Wirth and Gieskes, 1979*)
$10^{-14} – 10^{-10}$	Various compositions	25 °C	Grambow et al., 1985*)
$10^{-12} – 10^{-10}$	Glass phase of coal fly ash	25 °C	Yan and Neretnieks, 1995
1,250 – 6,250 µm/1000a	Uranium glass	Bohemia	Procházka et al. 2002a

Examples of glass dissolution rates under different conditions (references marked with *) are referred in Gordon and Brady, 2002)

5.2 Dissolution rates of natural glasses

- it is clear that dissolution rates of basaltic and other glass are low

- less than 50 µm/1000a and the rate appears to diminish with time in continental and oceanic environments the glass dissolution rates

- This decrease may be related to a diffusion mechanism involving key chemical species and controlled by the mineralogy of the palagonite layer

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5.2 Comparison of lab and analogy based dissolution rates

Form of data	Dissolution rate ($g\ m^{-2}\ d^{-1}$)	Reference	Comments
Short-term lab	$1x10^{-3}$	JNC (2000)	H12 reference value
Short-term lab	$1x10^{-3}$	Nagra (1994)	K-1 reference value
Short-term lab	$1x10^{-1}$	Nagra (1994)	K-1 model sensitivity value
Short-term lab	$1.5x10^{-2}$	Nagra (2002)	BNFL glass
Short-term lab	$2x10^{-3}$	Nagra (2002)	Cogema glass
Short-term lab (initial rates)	0.75	Crovisier et al. (2003)	Synthetic basaltic glass leached in the lab in low-silica solution (quasi-analogue)
Short-term lab (initial rates)	0.75	Crovisier et al. (2003)	SON68 'nuclear' glass leached in low-silica solution
Short-term lab (initial rates)	$3.5x10^{-3}$	Techer (1999)	Synthetic basaltic glass leached in high-silica solution
Short-term lab (initial rates)	$3.5x10^{-3}$	Techer (1999)	SON68 'nuclear' glass leached in high-silica solution
Natural analogue	$1.0x10^{-8} – 1.5x10^{-5}$	Techer (1999)	Basaltic glass in contact with clays
Natural analogue	$1.5x10^{-7} – 1.5x10^{-6}$	Grambow et al. (1985)	Lowest rates calculated from 'isolated' basaltic glass tektites in marine sediments

Havlová et al. (2009)

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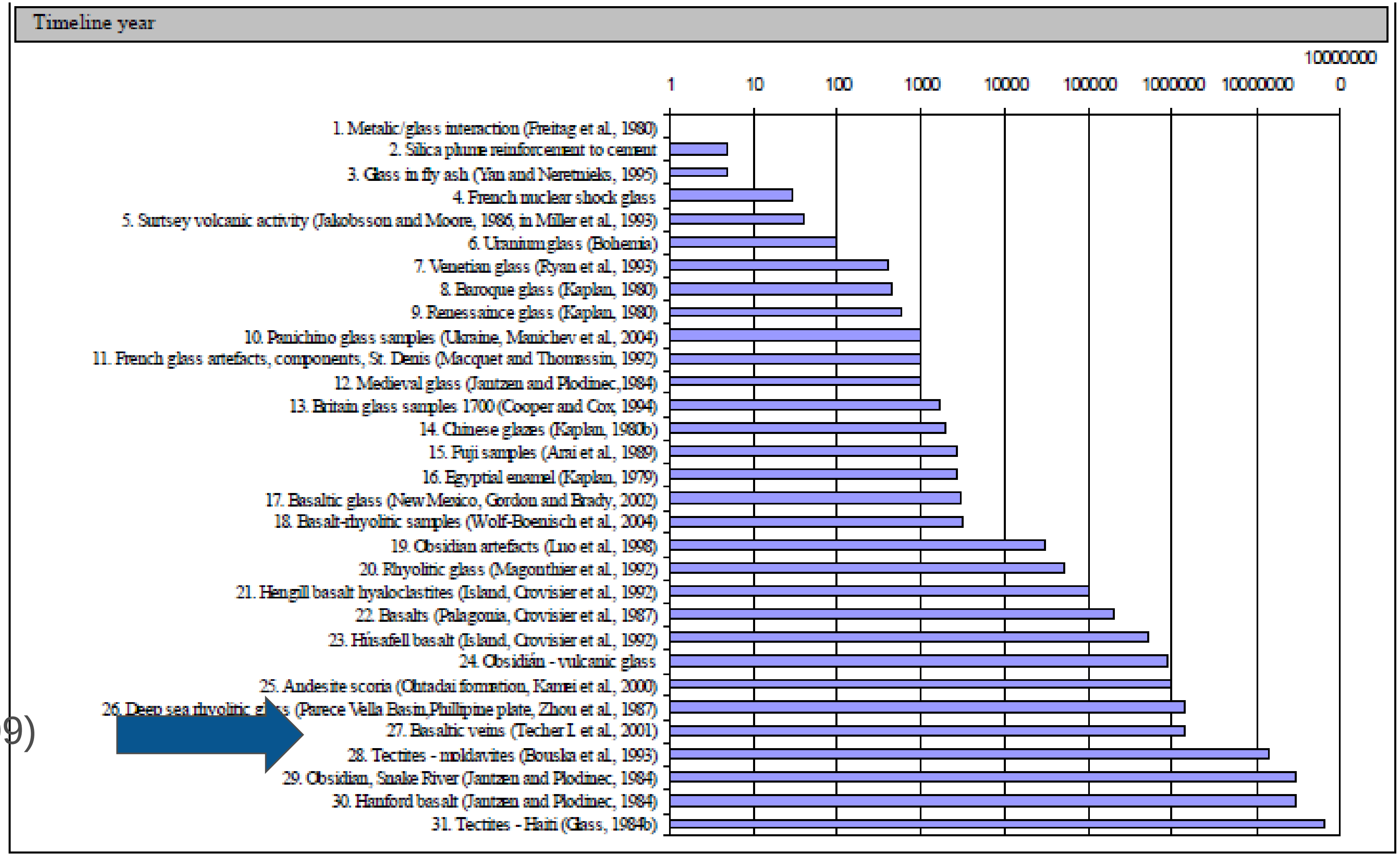
6. Conclusions

- basaltic glass was recognised as good analogy for HLW waste
- long durability of basaltic glass under natural can provide an argument for long term durability of borosilicate glass



Havlová et al. (2009)

6. Conclusions

- Some materials (archaeological glass, ferrite material etc.) could also provide useful information, **mainly about processes that the glass matrix undergoes** but the analogy is not always as clear.

- Archaeological glasses can be used as analogues for long-term behaviour only with caution, due to their different composition and relatively short time span involved

- **Not all processes could be addressed satisfactorily using glass analogues**: for example radiolysis, thermal fracturing, interaction with metals, cement and other engineered barriers remain without ideal analogues.

7. Conclusions concerning vitrified waste in CZ

- different composition (Al-Na phosphate glass)
- declared leachability
  - max. 10^{-6} g/cm^2/day = **10^{-2} g/m^2/day**
  - **can be considered as an initial rate**
- at least expert judgement or research of potential behaviour under DGR onditions should be needed

Form of data	Dissolution rate ($g\ m^{-2}\ d^{-1}$)	Reference	Comments
Short-term lab	$1x10^{-3}$	JNC (2000)	H12 reference value
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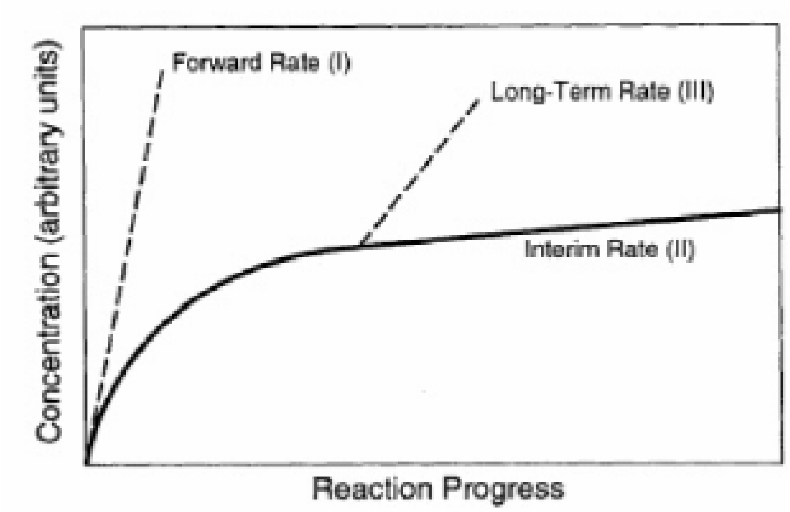

Schematic representation of reaction progress for glass dissolution (after Bates et al., 1996, and Grambow, 1991)

8. Further steps

- Small volume of waste in comparison with other waste, hence at least short study would be recommended

- Evaluation of natural or industrial glass composition concerning phosphate glass
- Evaluation of available information about durability, leaching rates, deterioriation of identified glass
- Laboratory experiments
- Expert evaluation of available information in order to determine long-term leaching rates and availablity of radionuclides, fixed in the matrix

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Acknowledgement

The presentation was based on the report Havlová et al. (2008) **Analogue evidence relevant to UK HLW glass wasteforms,** compiled for NDA, with a kind support of Jon Knight and Cherry Tweed.

HAVLOVA, V., LACIOK, A., CERVINKA, R. AND VOKAL, R. 2008 Natural analogue evidence relevant to UK HLW glass waste forms. *UK Nirex Report 509009, RWM Ltd, Harwell, UK.*

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