Studies on natural and archeological glasses
Opportunities to learn about long-term nuclear waste glass corrosion

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Since 2010: Assistant Professor at LISA, France
2009-2010: Post-doc at CRPG on Li isotopes to trace basaltic glass alteration
2005-2008: PhD at CEA on the Study of archaeological analog for the validation of nuclear glass long-term behavior models

Summer Board Meeting of the U.S. Nuclear Waste Technical Review Board
June 21, 2017 - Richland
Studies of ancient glasses

Basaltic glass
- Ewing (1979, 2001)
- Allen (1983)
- Birchard (1984)
- Lutze et al. (1985)
- Grambow et al. (1986)
- Ewing and Jercinovic (1987); Jercinovic and Ewing (1988)
- Cowan and Ewing (1989)
- Crovisier et al. (1989)
- Murakami et al. (1989)
- Arai et al. (1989)
- Werme et al. (1990)
- Techet et al. (2001, 2001a,b)
- Parruzot et al. (2015)

Obsidian
- Magonthier et al. (1992)
- Rani et al. (2013)

Chondrites
- Morlok and Libourel (2013)
- Libourel et al. (2011)

Tektites

Strachan & Pierce (2010) PNNL-19752 Report
Weaver et al. (2016)

Roman glass (shipwreck)
- Embiez
- Iulia Felix
- Verney-Carron et al. (2008, 2010a,b)
- Ryan et al. (in prep)
- Strachan et al. (2014)

Buried archaeological glass
- Macquet and Thomassin (1992) Saint-Denis

Vitreous slags
- Michelin et al. (2015)

Vitrified forts
- Sjöblom et al. (2013)
Objectives of analogs study

- **Features**: long-term durability, retention of elements, low contribution of cracks, ...
- **Similarities between ancient and nuclear glasses**
- **Demonstration of the predictive capacity of the models**

**REASONING BY ANALOGY**
- A is similar to C in certain known respects.
- A has some further feature B.
- Therefore, probably, C also has the feature B.
I.A. Properties: long-term durability of natural glass

Richet (2009) Verre

Rocks from Figeac (Lot, France) – 280 My

⇒ Old basaltic glasses despite tectonic and erosion

<table>
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<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe₂O₃</th>
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I.A. Properties: long-term durability of natural glass

⇒ Decrease of the apparent dissolution rate with time
⇒ Extrapolation of a linear residual rate measured at the laboratory consistent with ancient samples
Stained glass excavated from the site of Notre-Dame-de Bourg (Digne), 12th century

⇒ Retention of transition elements and heavy metals
I.C. Interactions between glass and iron

Comparison between experimental results (diamonds), modelling with sorption of Si (dashed lines) and sorption of Si + precipitation of iron silicates.

⇒ Iron increases glass alteration rate due to the precipitation of Fe-silicates

⇒ Formation of Fe-silicates
⇒ Alteration thickness = \( r_0/2 \)
⇒ Iron sustains a high alteration rate
I.C. Interactions between glass and iron

VITREOUS SLAGS

Site of Glinet (Normandy)
16th c.
Soil saturated with anoxic water

SiO₂ : 62 à 77 %, Al₂O₃ : 5 à 9 %,
CaO : 16 à 25 %

⇒ Analogy: vitreous slag / glass package and steel container
I.C. Interactions between glass and iron

⇒ Fe-silicates precipitation is a long-term mechanism but there is a drop in the alteration rate in cracks

Alteration thickness: ~ 20 µm (external cracks) / 2-6 µm (internal cracks)
II. Similarities?

- Composition
- Phenomenology

**NUCLEAR GLASS**

- Hydrated glass
- Rough interface (rim)
- Passivating layer
- Smectites, zeolites

**BASALTIC GLASS**

- Alteration front
- Gel palagonite
- Fibrous palagonite
- Smectites, calcite, oxides, zeolites

From Gin et al. (2017)
Gin et al. (2001)

⇒ Similar alteration facies

From Zhou & Fyfe (1989)
Zhou et al. (2001)
II. Similarities?

- Mechanisms: $^{29}\text{Si}$ tracing in solution

NUCLEAR GLASS  
$T = 90^\circ C$

STAINED GLASS  
$T = 30^\circ C$

$\Rightarrow$ Similar mechanisms far from saturation

Valle et al. (2010)

Verney-Carron et al. (2017)
ISG GLASS
T = 90°C, pH 7 and 9
Si saturated solution
t = 209 d

⇒ Weak interaction of $^{29}$Si with gel

BASATIC GLASS
T = 90°C, pH 7 (at 90°C)
Si saturated solution
t = 600 d

⇒ Enrichment in $^{29}$Si in the mixing zone

Ducasse et al. (in prep)
ISG : Gin et al. (2015, 2017)
II. Similarities?

(a) Quick interdiffusion and hydrolysis → release of Na and Ca and B
(b) Precipitation of clays (Si, Al, Fe, Mg, Ti) and SiO$_2$(am)
(c) The remaining silicate network dissolves and SiO$_2$(am) precipitates
(d) The layer of secondary phases grows up, sustaining glass dissolution

⇒ Differences with ISG Glass
ISG: selective dissolution → passivating layer (glass alteration is limited by water diffusion)

BG: congruent dissolution → clays (equilibrium)
The dissolution is controlled by the hydrolysis of the glass network and is sustained by the precipitation of secondary phases.
II. Similarities?

• Kinetics

NUCLEAR / BASALTIC GLASS

Forward dissolution rate

Residual rate

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<th>Basaltic glass data</th>
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⇒ Similar alteration rates

Parruzot et al. (2015)

- \( r_r \) (BG) = \( 9.6 \cdot 10^{-6} \) g/m\(^2\)/d (90°C)
- \( r_r \) (NG) = \( 2 \cdot 10^{-4} \) g/m\(^2\)/d (90°C)

Techer et al. (2000)
Summary

• To a unified understanding of glass alteration

• Similar alteration facies

• Similar mechanisms with a different contribution as a function of glass composition and environmental conditions (kinetics)

• Kinetics dependent of the glass composition and structure
III. Glass alteration modelling

- Experimental study (short-term)
  - Mechanisms
  - Kinetic parameters
  - Geochemical model of glass alteration

- Ancient glass characterization
  - Long-term simulation

- Simple geochemical model applied to Roman glass
  (Verney-Carron et al., 2008, 2010a,b)

- GRAAL model applied to basaltic glass
  (PhD Ducasse in progress)
III.A. Roman glass alteration modeling

Alteration for 1800 years
In a stable environment
(seawater at 15°C)

Morphological analogy
Border zone (BZ)
- Thick altered cracks
- Smectites
- 84% of total alteration

Internal zone (IZ)
- Thin altered cracks (5-20 µm)
- Hydrated glass (and smectites)
- Cracks density 6x higher
- 16% of total alteration

⇒ Low contribution of internal cracks to global alteration (+ sealing)
Experimental study (short-term)

Mechanisms
Kinetic parameters

Ancient glass characterization

Long-term simulation

Geochemical model of glass alteration
1st step: interdiffusion

Arch. glass
SiO$_2$ Na$_2$O
CaO Al$_2$O$_3$
Li$_2$O

\[
D_{Na} = 0.678 \cdot [H^+]^{0.37} \cdot \exp\left(\frac{-93600}{RT}\right)
\]

Leached glass
SiO$_2$ CaO
Al$_2$O$_3$

2nd step: dissolution/precipitation

Leached glass
SiO$_2$ CaO
Al$_2$O$_3$

\[
r = 6.73 \cdot 10^9 \cdot [H^+]^{0.32} \cdot \exp\left(\frac{-85600}{RT}\right) \cdot \left(1 - \frac{[H_4SiO_4]}{K_{Cristobalite}}\right)
\]

Secondary phases
LogK

Pure water: analcime, gyrolite, tobermorite
Seawater: saponite, calcite, aragonite
+ brucite, portlandite, gibbsite

GEOCHEMICAL MODEL

HYTEC software
Thermodynamic database (Chess – EQ3/6)
SUMMARY

✓ Alkalis and pH: good simulation
  pH is an important parameter of the coupling between chemistry and transport

✓ Ca: underestimated at low pH due to its release by interdiffusion
  However, Ca is highly concentrated in seawater

✓ Si: overestimated at high pH (interactions with Ca) and in seawater (stoichiometry)
  Change of the database (smectites)

⇒ The chemical model can be coupled with transport and tested on long-term
Experimental study (short-term)

Mechanisms
Kinetic parameters

Geochemical model of glass alteration

Ancient glass characterization

Long-term simulation
Simulation results of 2 cracks (≠ apertures a and ≠ distance from the external surface)

⇒ The external cracks are in contact with a diluted medium $r_0$

⇒ Good agreement between simulations and observations
⇒ Validation of the predictive capacity of the geochemical model

⇒ Strong coupling between chemistry and transport
If only the internal surfaces were leached, more than 650,000 years would be necessary for complete alteration of the Roman glass blocks, but external surfaces alteration would limit the lifetime to about 20,000 years.
Transposition to nuclear glass alteration

\[ S_{\text{geo}} = 1.7 \text{ m}^2 \]
\[ S_{\text{ext}} = 5 \times S_{\text{geo}} \]
\[ S_{\text{int}} = 40 \times S_{\text{geo}} \]
\[ T = 50^\circ \text{C (after 4000 years)} \]
\[ r_0 = 5.1 \mu \text{m/y} \]
\[ r_r = 0.008 \mu \text{m/y} \]
\[ D \ (50^\circ \text{C, pH 7}) = 6.8 \times 10^{-23} \text{ m}^2/\text{s} \]

⇒ If like for Roman glass, internal surfaces are controlled by diffusion, 5% of alteration after 100 000 years.
Outcomes

• Important to study other kinds of glasses
  → General understanding of glass alteration (even minerals)
  → Questions raised by the differences

• Important to continue the modeling work
  → To demonstrate the feasibility and the predictive capacity
  → To extend the range of applications of nuclear glass models