VAPOR HYDRATATION OF NUCLEAR WASTE GLASS

SUBATECH Department
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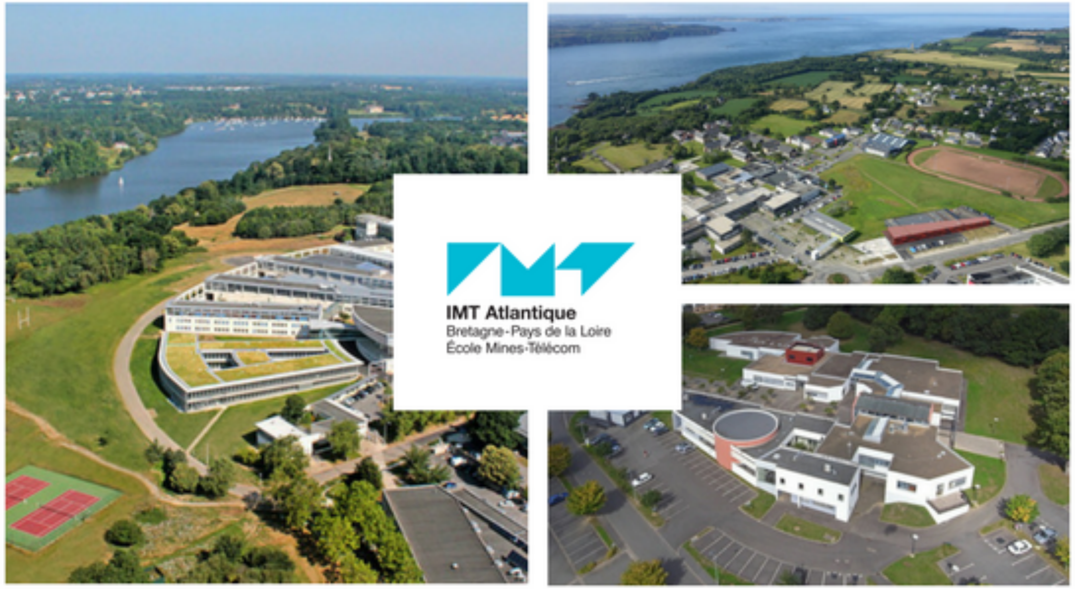
IMT Atlantique



IMT Atlantique is an engineering school of the French ministry of industry located in the north-west of France, member of the Institut Mines-Télécom

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Biography

- Pr. of Radiochemistry at IMT Atlantique (since 2000)
- Adjunct Pr. at MODY Univ. (Rajasthan, India)
- Adjunct Pr. at IFCEN (Sun Yat-sen Univ., Zhuhai, China)
- Head of Radiochemistry Group (44 staff)
- Head of SNEAM Nuc. Eng. Master program (since 2011)
- Coordinator of EMJMD Nuc. Eng. SARENA (since 2018)

- H.D.R. in Radiochemistry 2004 (Univ. Nantes, France)
- PhD in Geochemistry 1996 (Univ. Strasbourg, France)

Subatech Laboratory

From fundamental to applications and health

The UNIVERSE at HIGH ENERGY

- Quark Gluon plasma
- Cosmic rays
- Dark matter
- Radio-detection
- Theory, Simulation of ion collisions
- Detectors for CERN

SUBATECH
Shared research unit
IMT Atlantique
CNRS/IN2P3
Nantes University

NUCLEAR - ENVIRONMENT
Energy and Materials

- Radiochemistry
- Waste storage
- Migration studies
- Radiolysis
- Transmutation
- Reactor modelling
- Non-proliferation
- Instrumentation
- Detectors
- SMART (environmental monitoring)
- Cyclotron

NUCLEAR - HEALTH

- Radionuclides
- Imaging: 3g,Xe liq.
- Nanomedecine
- Cyclotron

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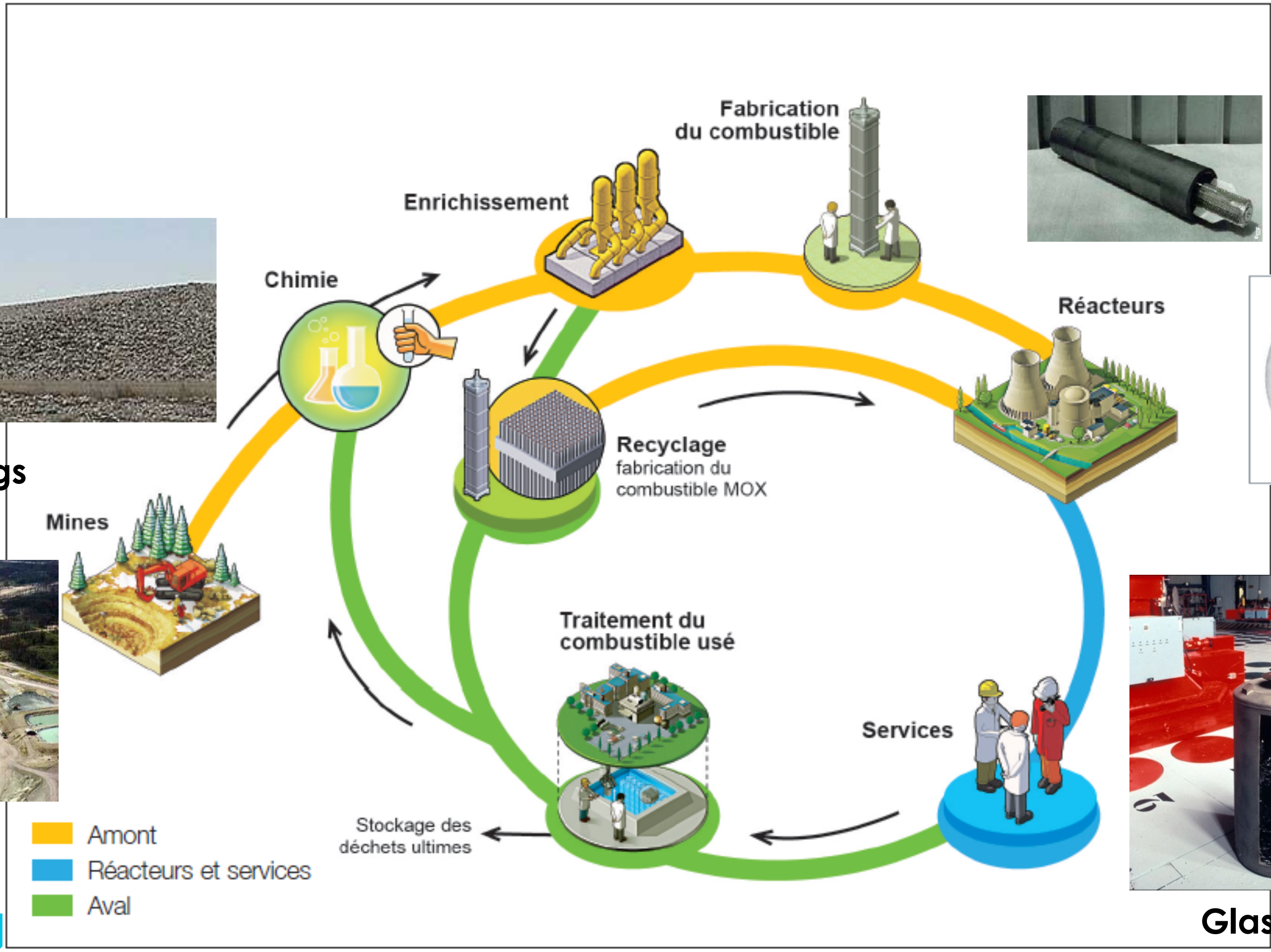
Fuel Cycle

The DU penetrator of a 30 mm round

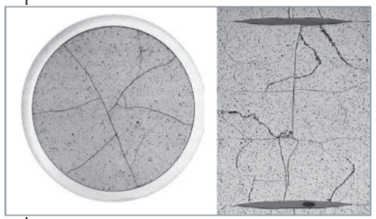
Filters

Ventilation



Resins

Mill tailings



Spent fuel

Open mine

Glass

Cladding…

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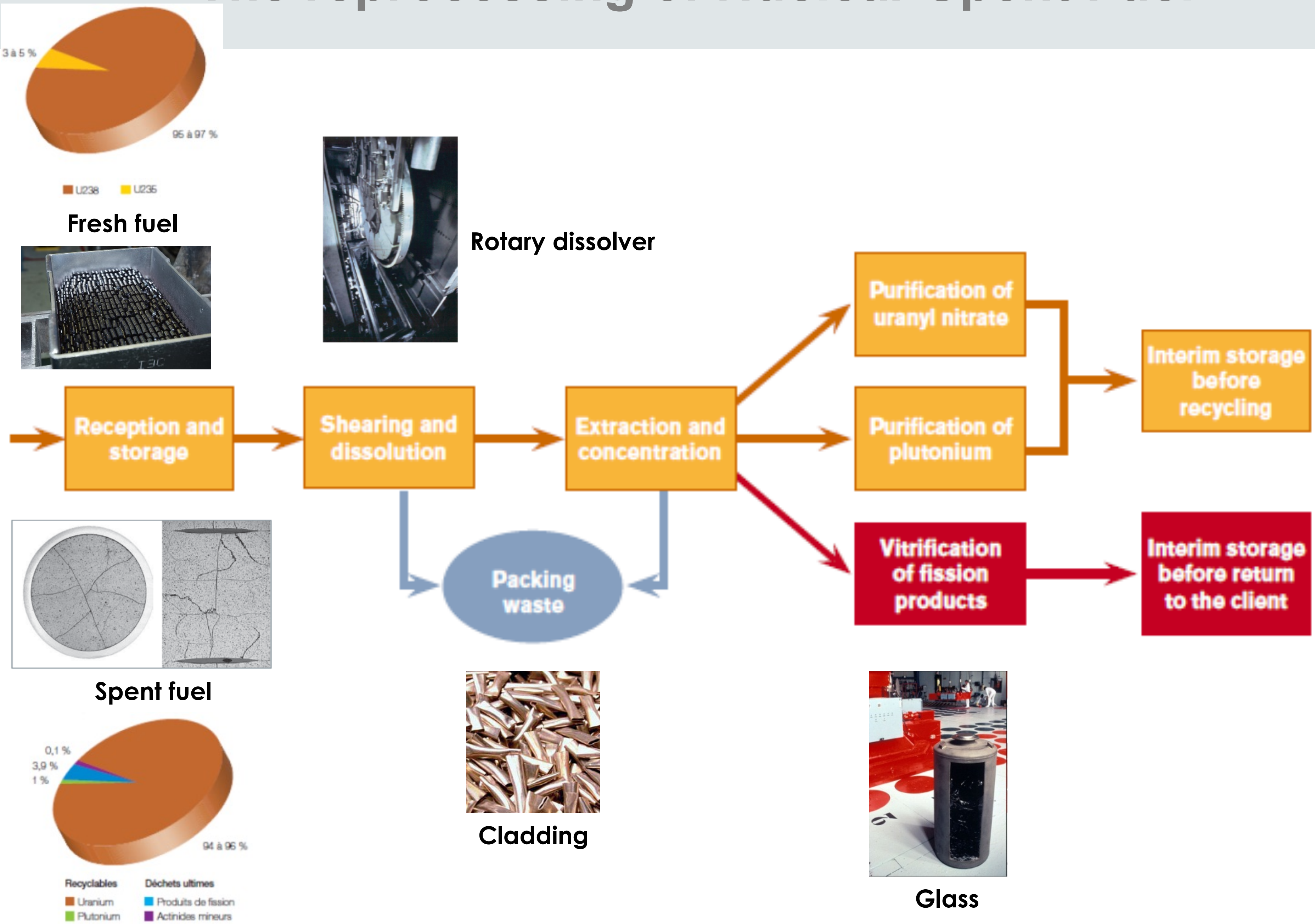
The reprocessing of Nuclear Spent Fuel



Waste Inventory in France (m^3)

Waste category	Forecasts made in 2013
HLW	10 000
ILW-LL	72 000
LLW-LL	180 000
LILW-SL	1 900 000
VLLW	2 200 000
TOTAL	4 300 000

Forecasts at the end of all facilities service life

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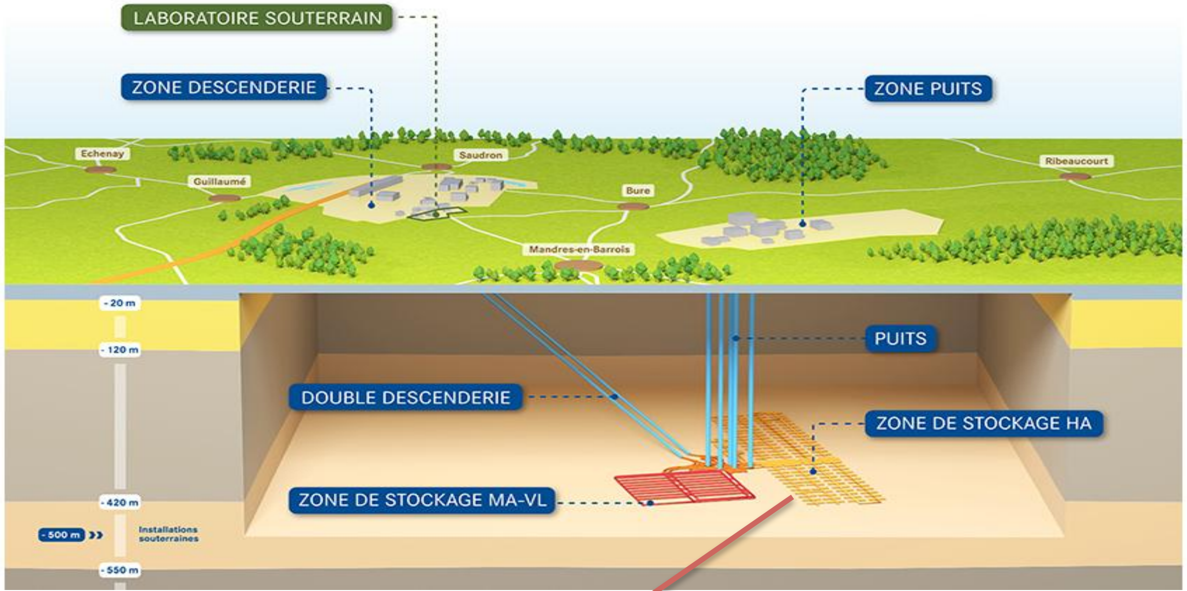
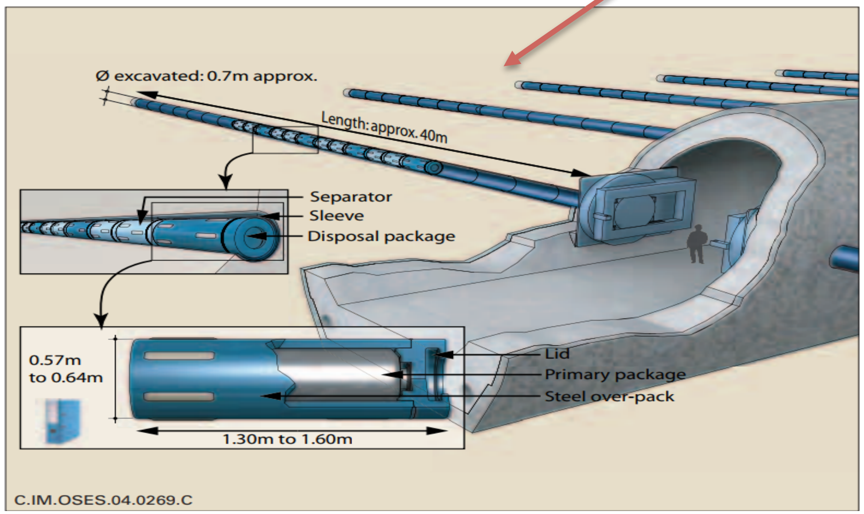
Geological Disposal

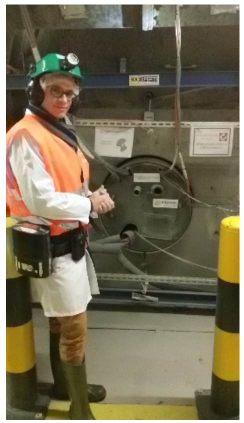
(ANDRA 2005)

HLW glass containing radionuclides

Stainless steel primary envelope







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Repository Evolution

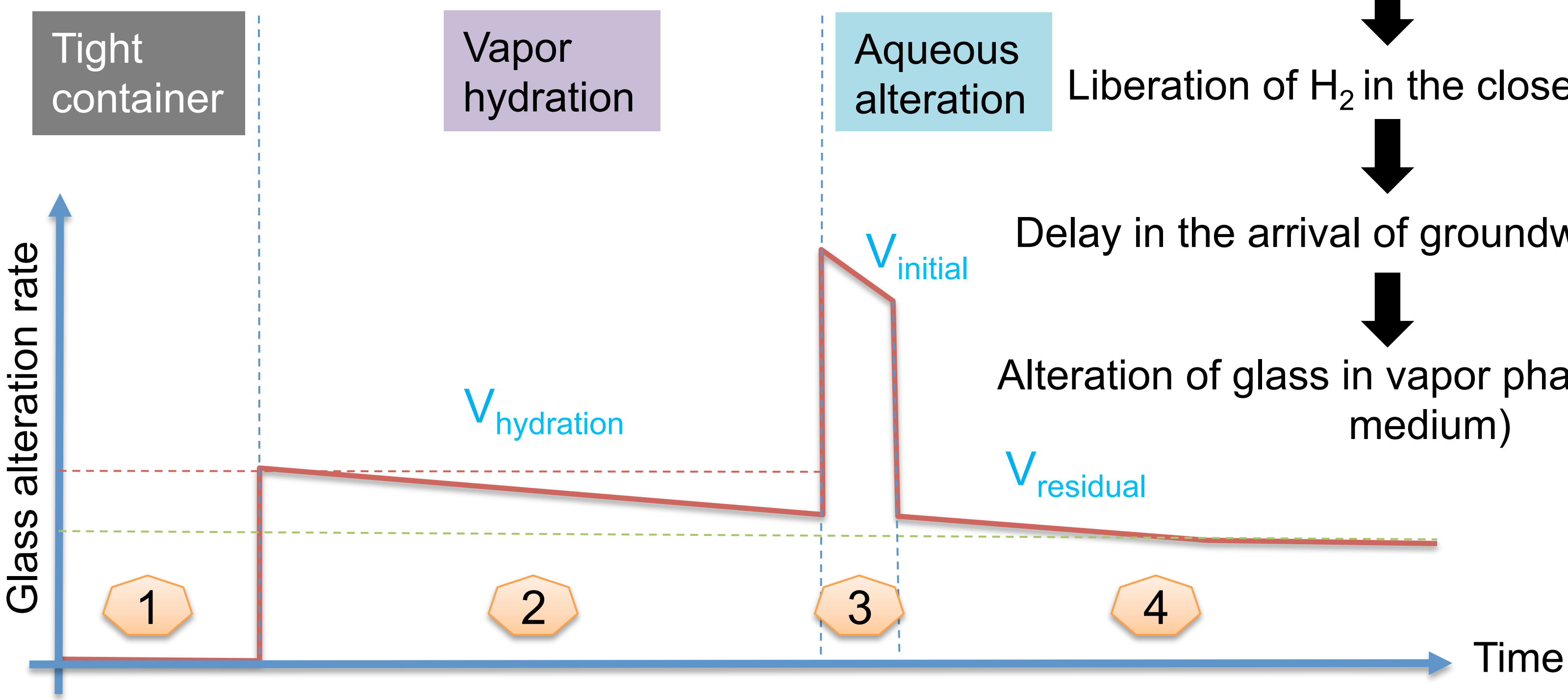
- 4 phases during glass alteration in the repository:

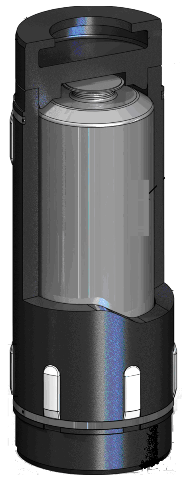
Corrosion of steel over-packs and concrete reinforcements

Liberation of H_2 in the closed repository

Delay in the arrival of groundwater to the site

Alteration of glass in vapor phase (unsaturated medium)





- ✓ Alteration mechanisms, secondary phases formation and role, effect of radiolysis, modeliing, effect of near-field materials etc.

Glass Vapor Hydration

Glass vapor phase hydration can be defined as the process of altering the chemical and/or physical properties of surface by means of exposure to water vapor in contrast to exposure to liquid water, which leads to elemental dissolution and leaching.

History of Glass Hydration – Natural Glasses

Interest in hydration of glasses was first driven by Friedman and coll. during the 60s for development of new dating method for artifacts made from obsidian.

$$l = k \times t^{1/2}$$

where l is the thickness of the hydration layer, t is the hydration time, and k the proportionality constant, which describes the temperature dependence of the process.

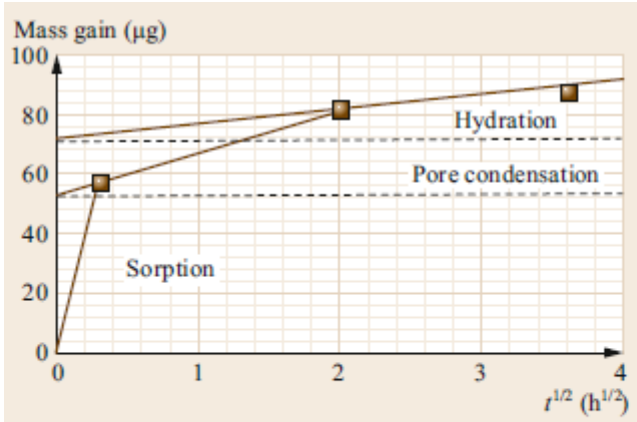
Obsidian - Wikipedia
en.wikipedia.org

I. Friedman, R.L. Smith: A new dating method using obsidian: Part I, The development of the method, Am. Antiq. ***25****, 476–493 (1960).*

History of Glass Hydration – Natural Glasses

Two parameters were highlighted as important for obsidian hydration:

- **The temperature,**
- **Relative humidity.**



Water sorption expressed as mass gain (µg) of obsidian hydrated at 23°C and 84% RH

Still a reliable method for obsidian dating

- Increase of accuracy of depth measurement (SIMS, FTIR)

W.L. Ebert et al., "The sorption of water on obsidian and a nuclear waste glass," Phys. Chem. Glasses., 32 [4] 133-137 (1991).

History of Glass Hydration – Commercial Glasses

- ✓ **Moriya and Nogami studied in 1980 the hydration of silicate glasses in steam atmosphere.**
  - **Water speciation in the glass matrix using FTIR**
  - **The role of oxides (Na, Ca) on hydration rates**

- ✓ **In early 80s Bates and coll. Applied first the vapor hydration methodology on nuclear waste glasses.**
  - **Safety analysis of HLW repository**

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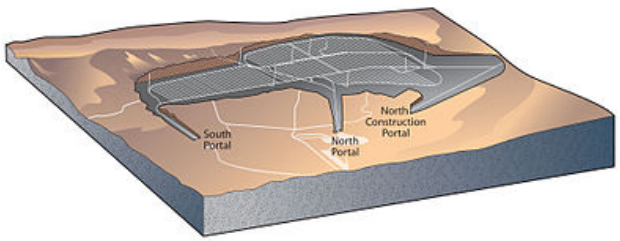
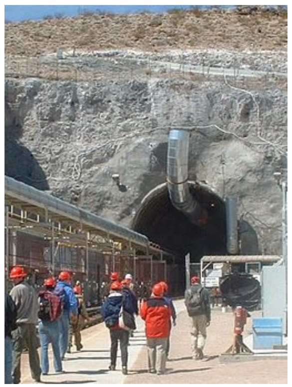


The proposed design

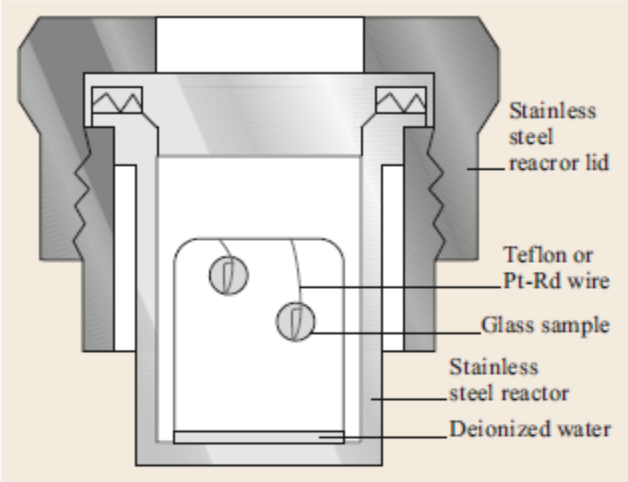


Wikipedia - en.wikipedia.org

History of Glass Hydration – Commercial Glasses

- ✓ **The essential early work on nuclear waste glasses hydration was done during the 1980s and early 1990s by Bates and collaborators.**
- ✓ **Bates et al. proposed the methodology to perform the hydration tests and presented the first results of glass hydration.**

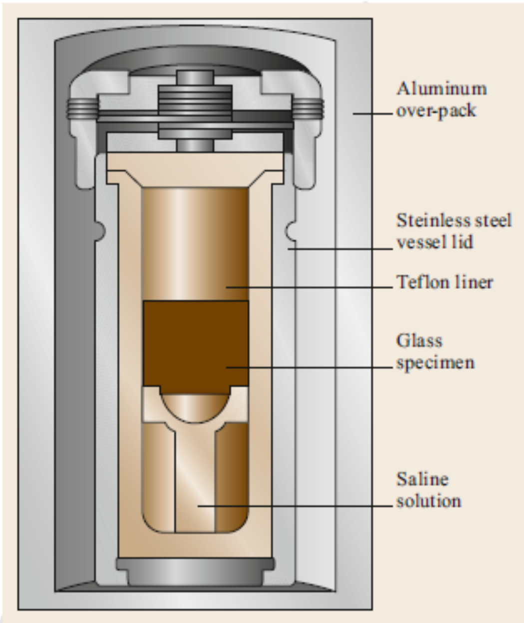
Experimental apparatus for glass vapor hydration developed by Pacific Northwest National Laboratory (PNNL), USA.



A. Abdelouas, J. Neeway, B. Grambow: Chemical durability of glasses, Handbook of Glass, Springer (2019).

History of Glass Hydration – Commercial Glasses

- ✓ **French scientists with the support of WMO (ANDRA) restarted in late 2000s R&D on nuclear waste glasses vapor hydration according to refined evolution scenarios (H_2 migration).**
- ✓ **Abdelouas and coll. proposed a new methodology to perform the hydration tests with a fine control of RH.**



Experimental apparatus for glass vapor hydration developed by SUBATECH Laboratory, France.

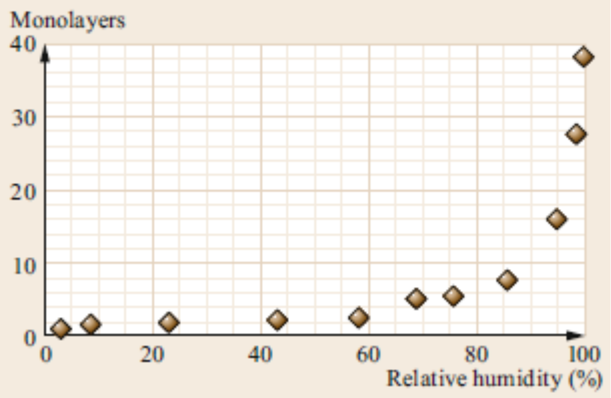
J. Neeway et al.: Vapor hydration of SON68 glass from 90 °C to 200 °C: A kinetic study and corrosion products investigation, J. Non-Cryst. Solids 358, 2897–2905 (2012).

Water Sorption on Silicate Glasses

✓ **A major study on water sorption on obsidian and the SRL165 borosilicate nuclear waste glass was conducted by Ebert et al.**

- **The water sorption occurs primarily at silanol (SiOH) sites and the sorption to other sites remaining very low.**
- **A water film is generated at RH above 95%.**

Water sorption isotherms on the SRL165 borosilicate nuclear waste glass at 23°C. Data were obtained with experiments using increasing or decreasing humidity techniques.

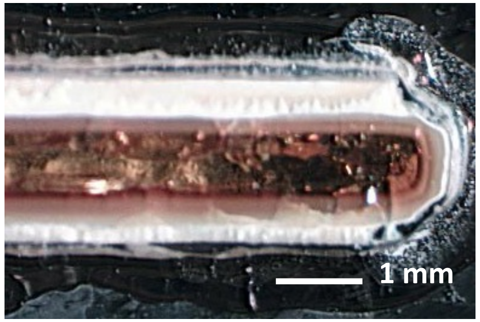


W.L. Ebert et al., "The sorption of water on obsidian and a nuclear waste glass," Phys. Chem. Glasses., 32 [4] 133-137 (1991).

Methodology for Measurement of Hydration Layer

- ✓ **The absence of leachate makes the determination of hydration rate limited to glass surface analysis (depth measurement).**
  - **Light microscope measurement based on the difference in refractive index between the pristine glass and hydrated glass.**

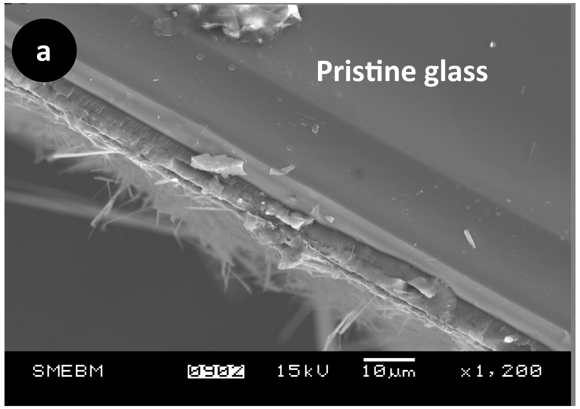
Hydrated HLP-09 low-activity waste glass at 300°C for 3 d, adapted from Schulz et al.

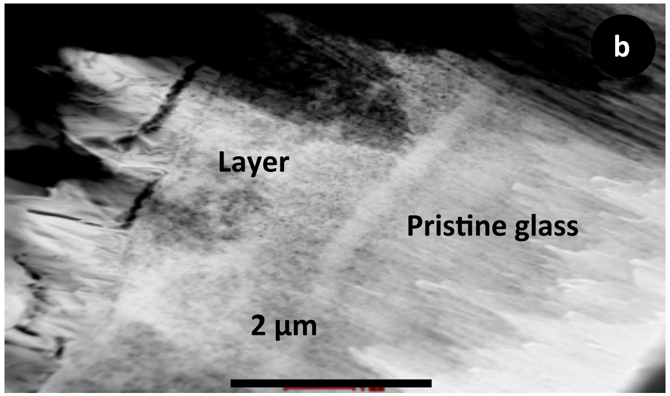


R.I. Schulz et al.: Hanford immobilized LAW product acceptance: tanks focus area testing data package II. Pacific Northwest National Laboratory. PNNL-13344 (2000).

Methodology for Measurement of Hydration Layer

- **Scanning and transmission electron microscope measurements.**



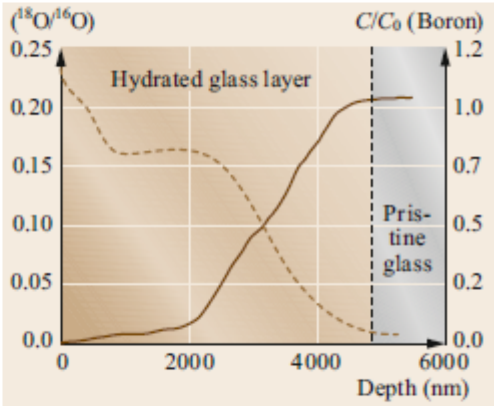


SEM (a) and TEM (b) picture of SON68 glass hydrated at 200°C and 92% RH.

J. Neeway: The alteration of the SON68 reference waste glass in silica saturated conditions and in the presence of water vapor. PhD Thesis, University of Nantes, France (2011).

Methodology for Measurement of Hydration Layer

- **Time-of-flight secondary ions mass spectrometry (ToF-SIMS).**

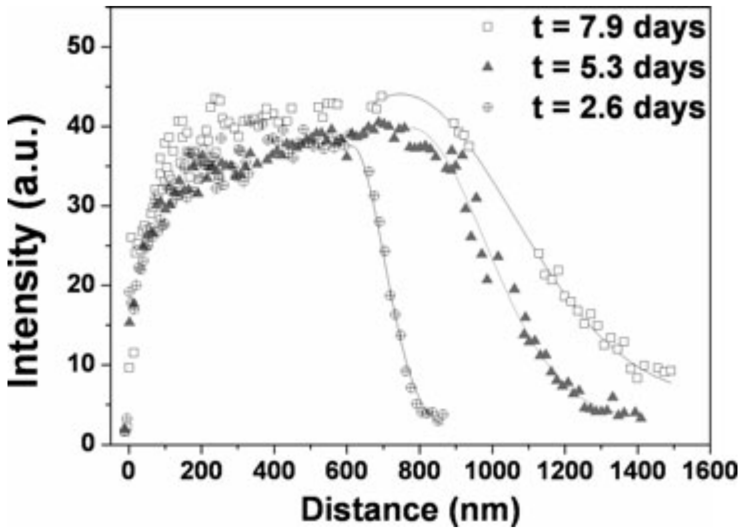


ToF-SIMS profile of boron and $^{18}O/^{16}O$ isotopic ratio for SON68 glass hydrated at 125°C and 95% RH for 600 d. The depth profile is about 5 µm.

R. Bouakkaz, A., Abdelouas, B. Grambow. Kinetic study and structural evolution of SON68 nuclear waste glass altered from 35 to 125 °C under unsaturated H_2O and D_2O_{18} vapour conditions. Corrosion Science 134, 1-16 (2018).

Methodology for Measurement of Hydration Layer

- **Nuclear Reaction Analysis (NRA).**
  - ✓ **Water diffusion coefficients of 2.31–7.34 × 10^{-21} m^2/s**

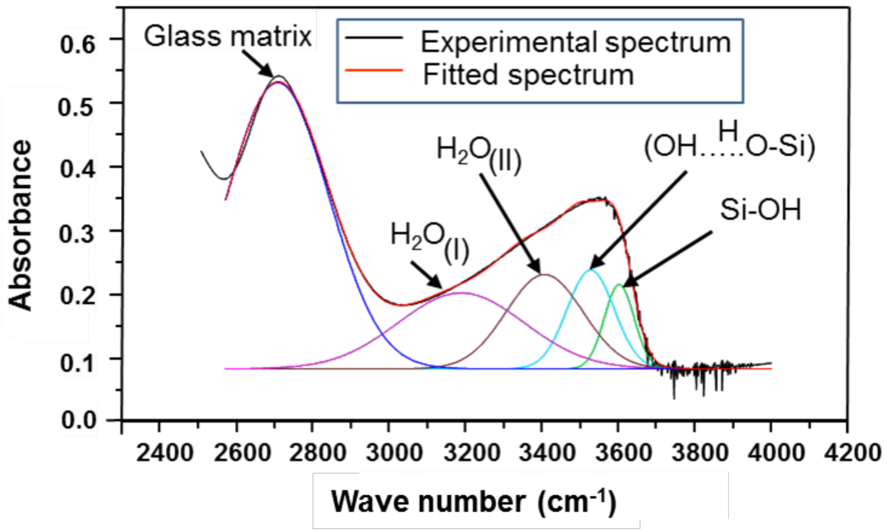


Protons profile in ISG borosilicate glass hydrated at 175°C at 98% RH.

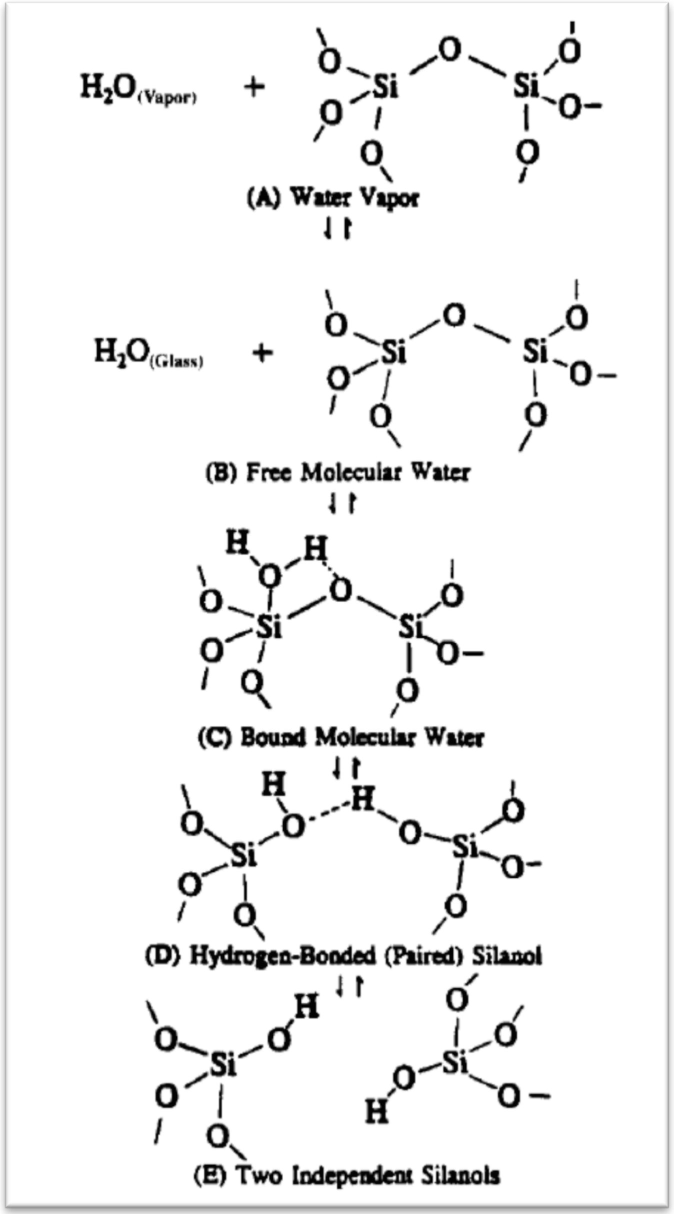
A. Abdelouas et al.: A preliminary investigation of the ISG glass vapor hydration, Intern. J. Appl. Glass Sci. 4, 307-316 (2013).

Methodology for Measurement of Hydration Layer

- **Fourier Transform Infra-Red spectroscopy (FTIR).**



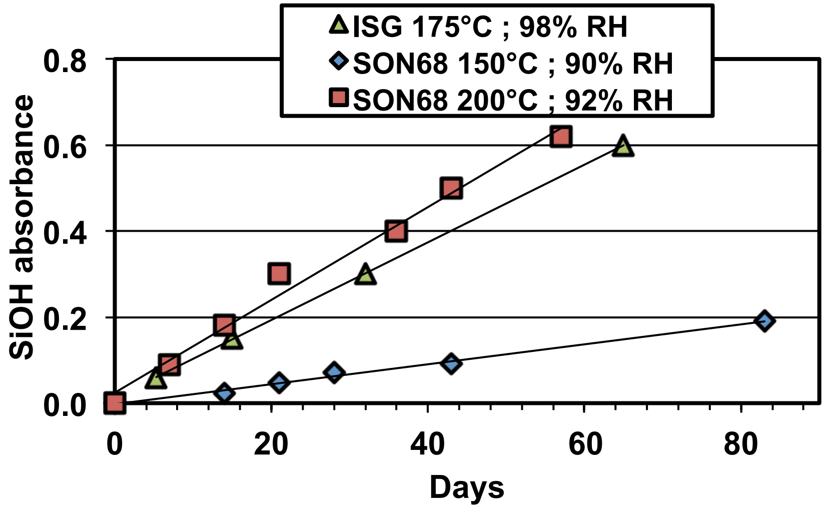
Experimental and deconvoluted FTIR spectra of SON68 glass hydrated at 125°C and 95% RH.



- *H. Tomozawa, M. Tomozawa: Diffusion of water into a borosilicate glass, J. Non-Cryst. Solids 109, 311-317 (1989)*
- *Efimov et al. J. Non-Cryst. Solids., 332 93-114 (2003).*

Methodology for Measurement of Hydration Layer

- **Fourier Transform Infra-Red spectroscopy (FTIR).**
  - ✓ **0.1 absorbance = 1 µm of hydration layer**

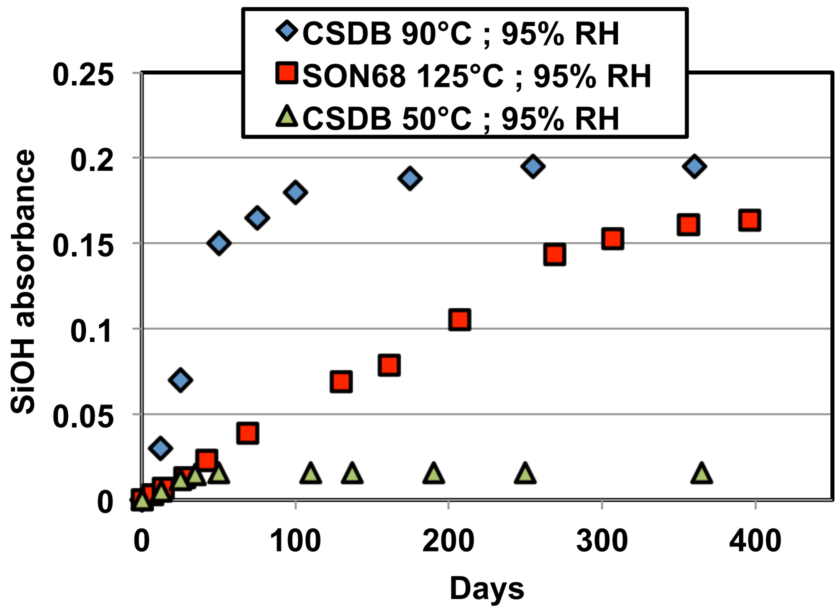


The growth of the SiOH peak at 3595 cm^{-1} for the SON68 and ISG glasses hydrated at different temperatures and relative humidity values.

- *A. Abdelouas et al.: A preliminary investigation of the ISG glass vapor hydration, Intern. J. Appl. Glass Sci. 4, 307-316 (2013).*
- *J. Neeway et al.: Vapor hydration of SON68 glass from 90 °C to 200 °C: A kinetic study and corrosion products investigation, J. Non-Cryst. Solids 358, 2897–2905 (2012).*

Methodology for Measurement of Hydration Layer

- **Fourier Transform Infra-Red spectroscopy (FTIR).**

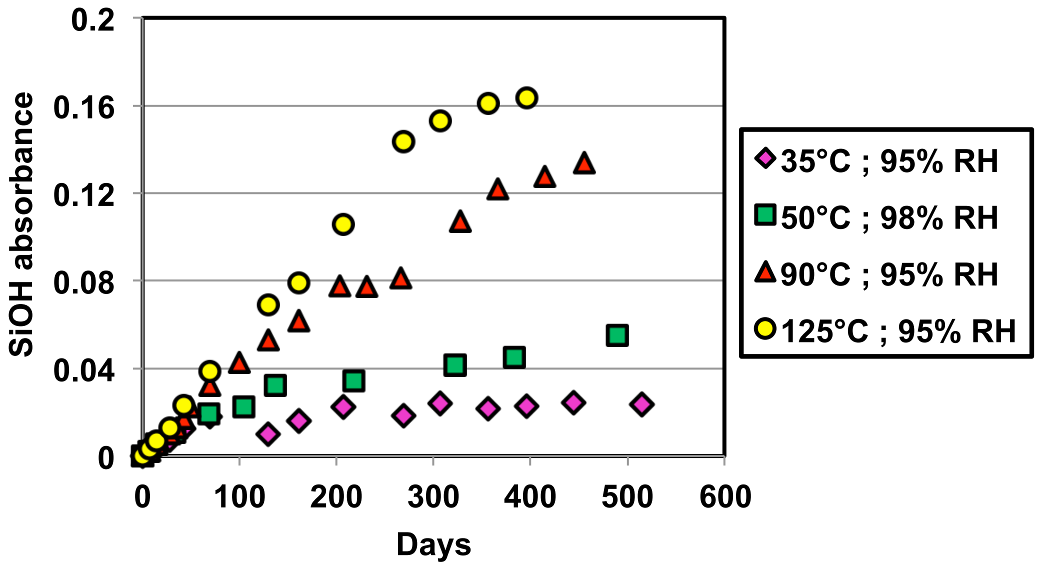


The growth of the SiOH peak at 3595 cm^{-1} for the French CSDB intermediate-level nuclear waste glass and SON68 high-level nuclear waste glass and ISG glasses hydrated at different temperatures and relative humidity values.

- *A. Aït Chaou et al.: Vapor hydration of a simulated borosilicate nuclear waste glass in unsaturated conditions at 50°C and 90°C. RSC Adv. 5, 64538-64549 (2015).*
- *R. Bouakkaz: Altération aqueuse et hydratation en phase vapeur du verre SON68 à basse température (35-90°C). PhD Thesis, University of Nantes, France (2014).*

Effect of Temperature on Glass Hydration

- **Arrhenius model applied for different glasses (obsidian, borosilicate nuclear glasses)**

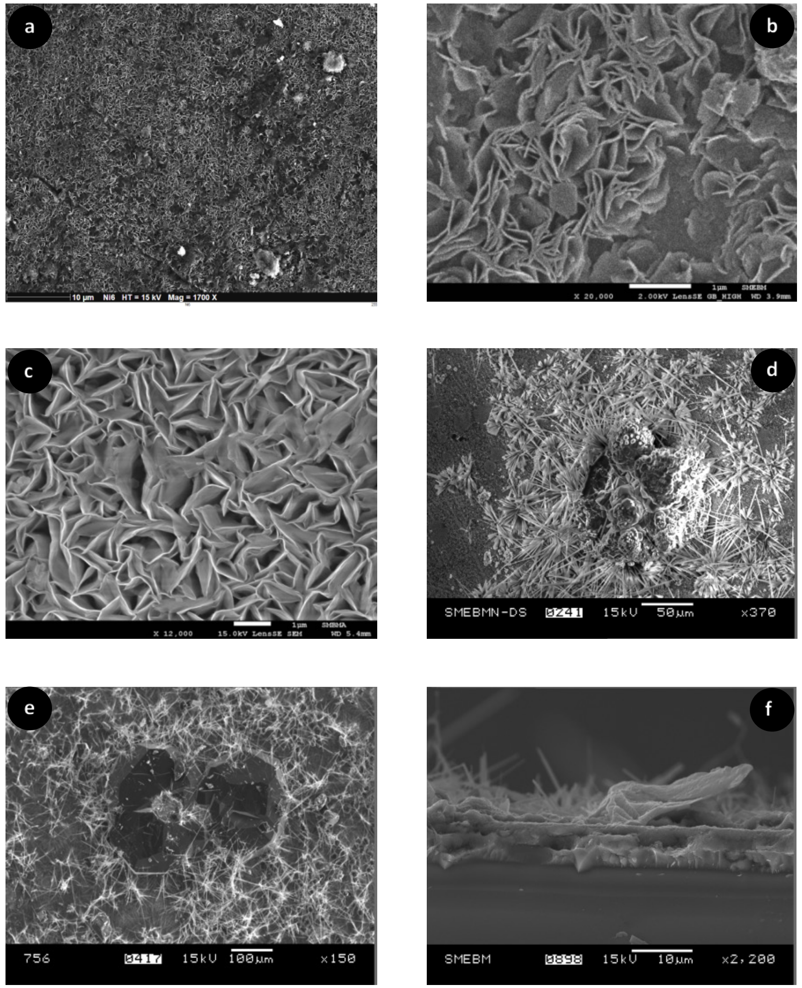


The growth of the SiOH peak at 3595 cm^{-1} for the SON68 glass hydrated at different temperatures.

R. Bouakkaz: Altération aqueuse et hydratation en phase vapeur du verre SON68 à basse température (35-90°C). PhD Thesis, University of Nantes, France (2014).

Effect of Temperature on Glass Hydration

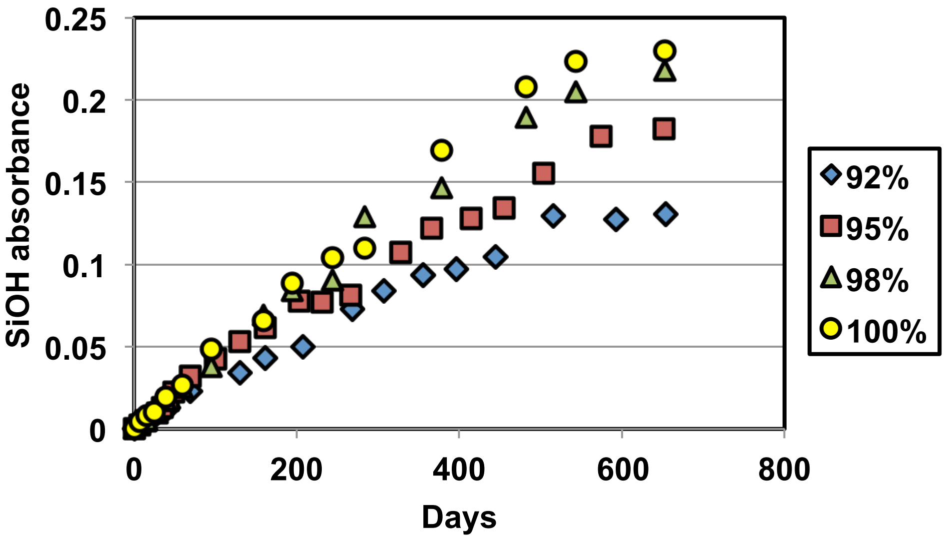
- **The nature of secondary phases depends on temperature and time**



SEM photos of SON68 glass hydrated at (a) 35°C, 95% RH for 654 d, (b) 125°C, 92% RH for 154 d, (c,d) 175°C, 95% RH for 99 d, (e) 175°C, 98% RH for 99 d, and (f) 200°C, 92% RH for 57d.

Effect of RH on Glass Hydration

- **The hydration rate is proportional to relative humidity (number of water monolayers)**



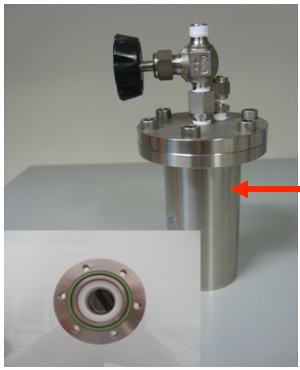
The growth of the SiOH peak at 3595 cm^{-1} for the SON68 glass hydrated at 90°C and different relative humidity values.

R. Bouakkaz: Altération aqueuse et hydratation en phase vapeur du verre SON68 à basse température (35-90°C). PhD Thesis, University of Nantes, France (2014).

Effect of pH on Glass Hydration

- **Development of an experimental set up to control the water film pH**
  - ✓ **Use of different gases (NH_3, H_2S, CO_2 and argon)**

T°C	RH (%)	Vol. (mL)	Gas	pH	Time (d)
175°C	98%	8	H_2S 1% / Ar	4.9	365
175°C	98%	8	CO_2 60% / Ar	4.5	365
175°C	98%	8	Pur Ar	5.7	290
175°C	98%	8	NH_3 8% / Ar	9.1	98



Reactor

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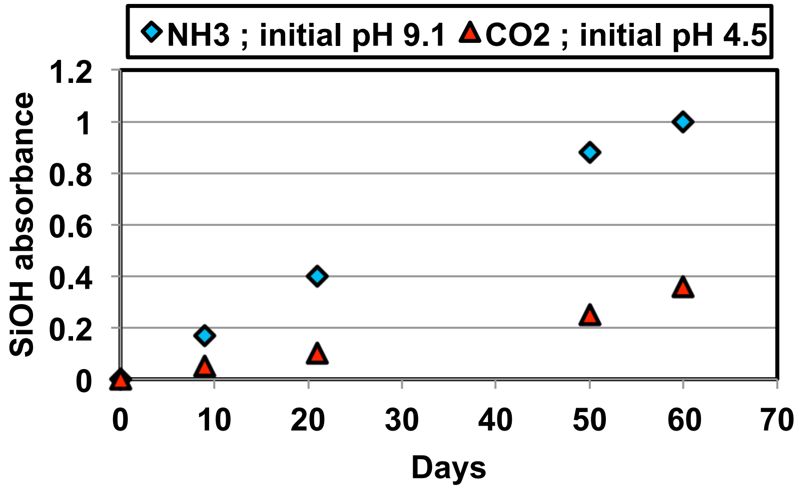
Effect of pH on Glass Hydration

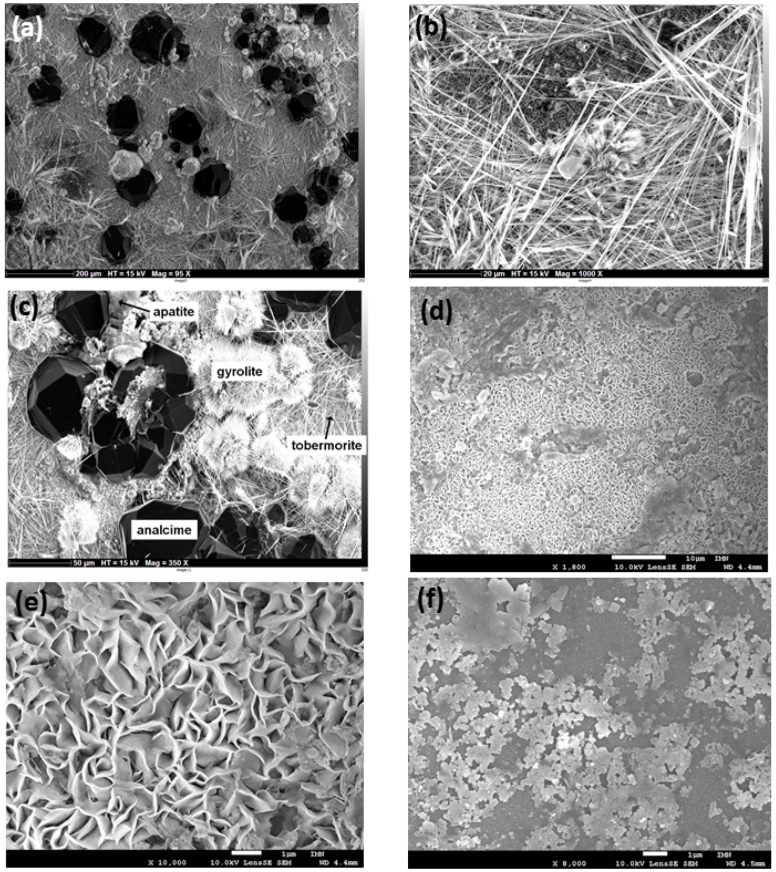
- **Increase of glass hydration with increasing pH**



The growth of the SiOH peak at 3595 cm^{-1} for the SON68 glass hydrated at 175°C and 98% relative humidity under acidic (H_2S equilibrated water vapor) and alkaline (NH_3 equilibrated water vapor) conditions.

A. Aït Chaou, A. Abdelouas, Y. El Mendili, C. Martin: The role of pH in the vapor hydration at 175°C of the French SON68 glass, Appl. Geochem. 76, 22–35 (2017).

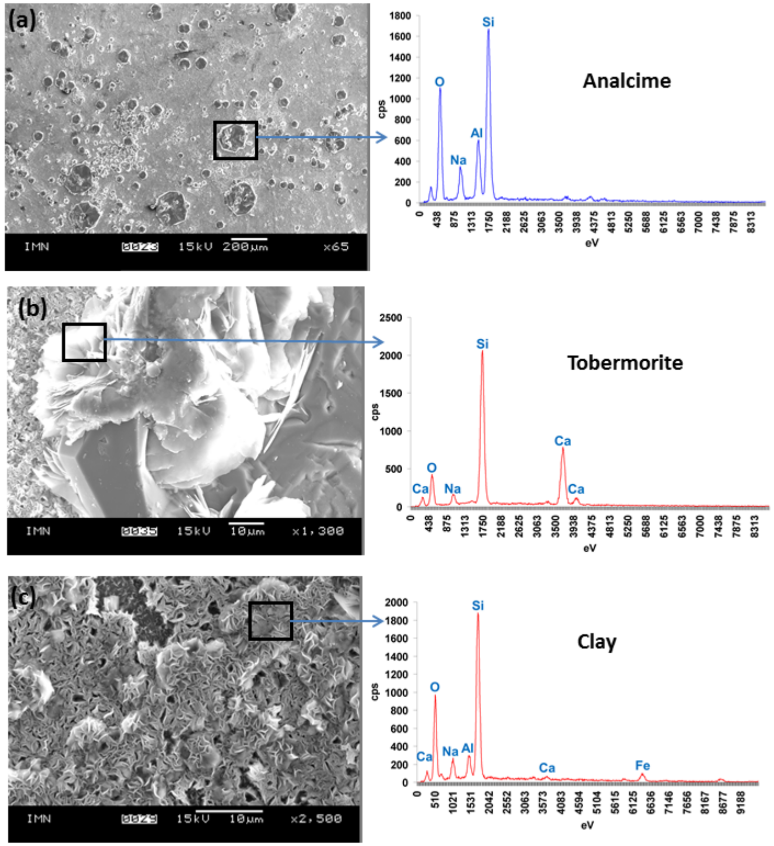
Alteration Products Formation



The surface of SON68 glass hydrated under 98% of RH at 175°C: for 290 days under argon (a, b and c), for 365 days under CO_2 (d and e) and for 365 days under H_2S (f).

A. Aït Chaou et al.: Vapor hydration of a simulated borosilicate nuclear waste glass in unsaturated conditions at 50°C and 90°C. RSC Adv. 5, 64538-64549 (2015).

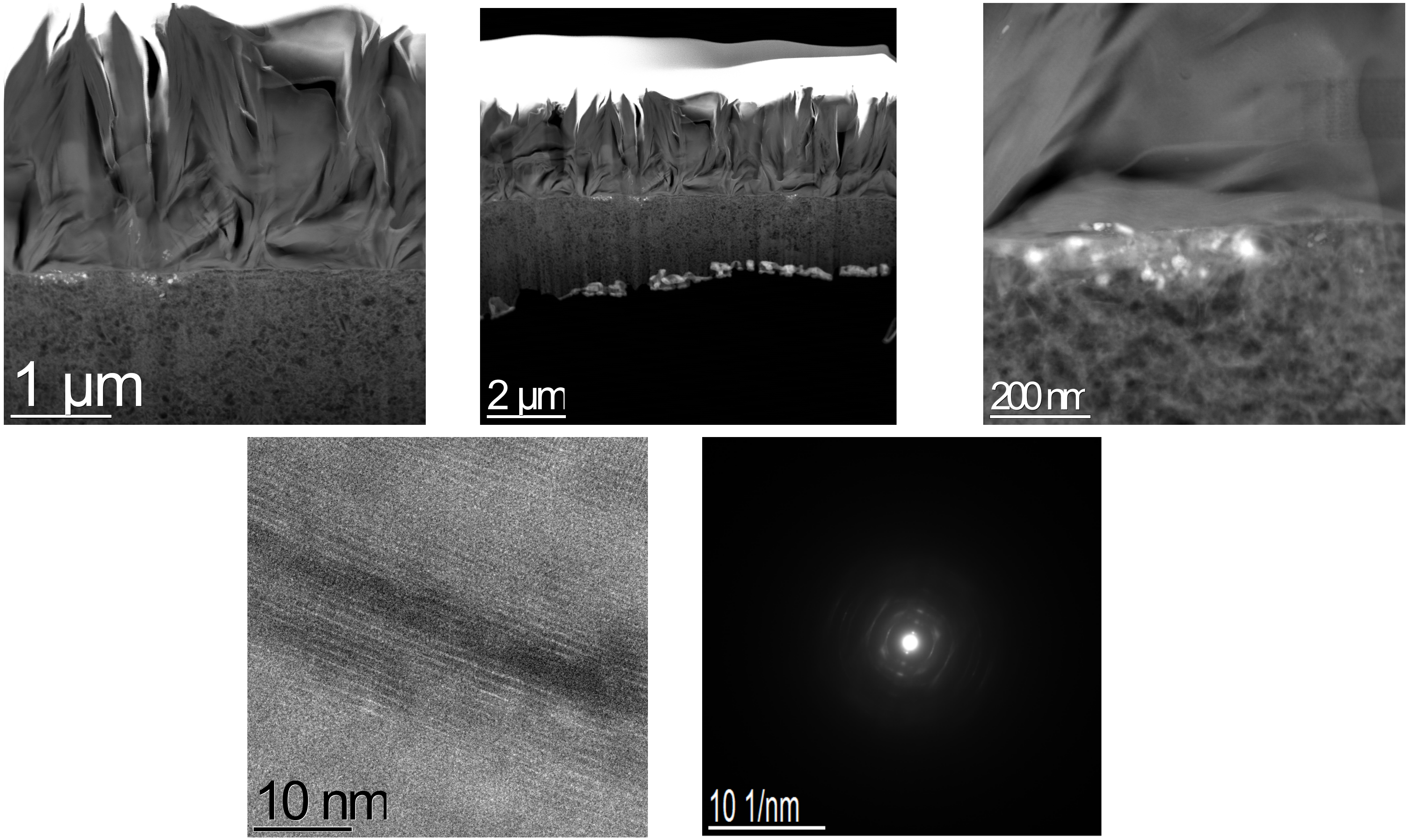
Alteration Products Formation



SEM photographs and EDX spectra of SON68 glass hydrated for 98 days at 175°C and 98% of RH under NH_3 showing the surface of the glass with analcime phase (a), tobermorite (b) and clay (c).

A. Aït Chaou et al.: Vapor hydration of a simulated borosilicate nuclear waste glass in unsaturated conditions at 50°C and 90°C. RSC Adv. 5, 64538-64549 (2015).

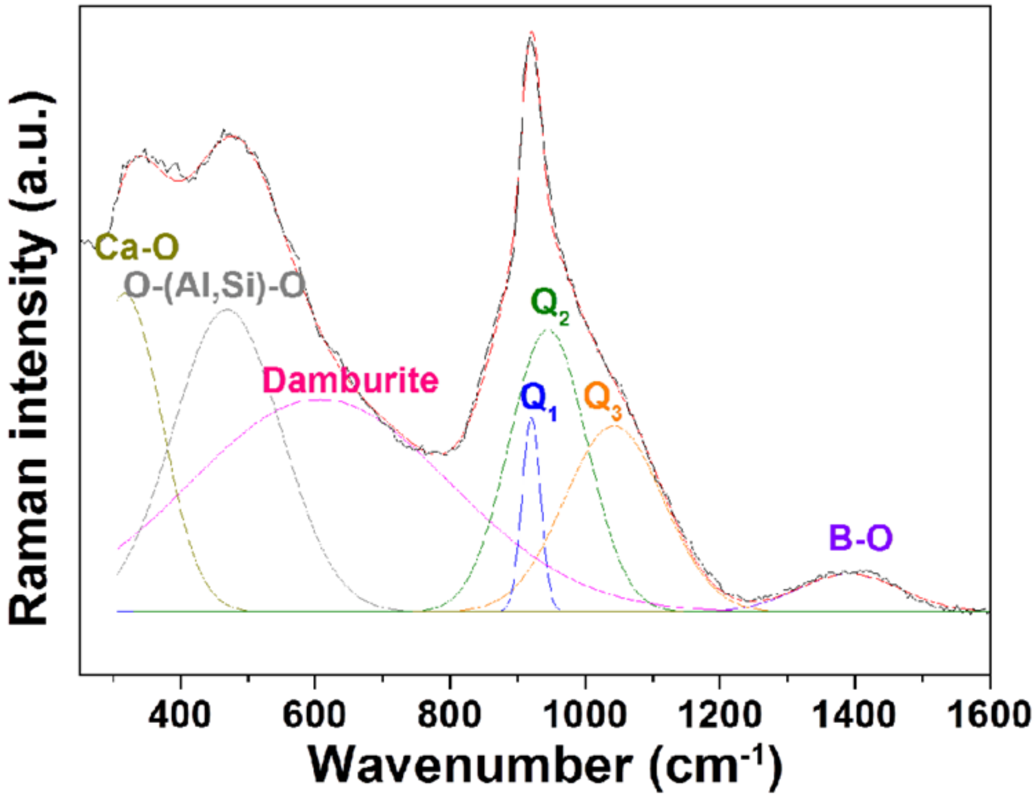
Alteration Products Formation



TEM micrographs of SON68 glass hydrated for 98 days at 175°C and 98% of RH under NH_3 showing a tick layer of clay minerals.

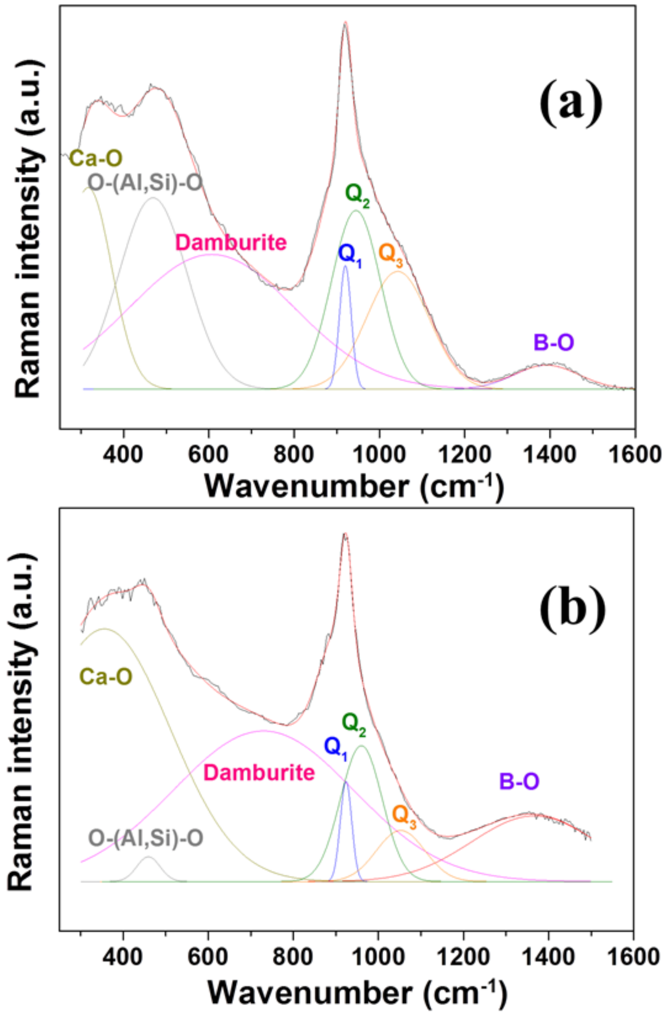
Alteration Products Formation

- **Raman spectroscopy for structural analysis of hydration layer**



Raman spectrum of the pristine SON68 glass. Example of Raman spectrum deconvolution with 7 Gaussian.

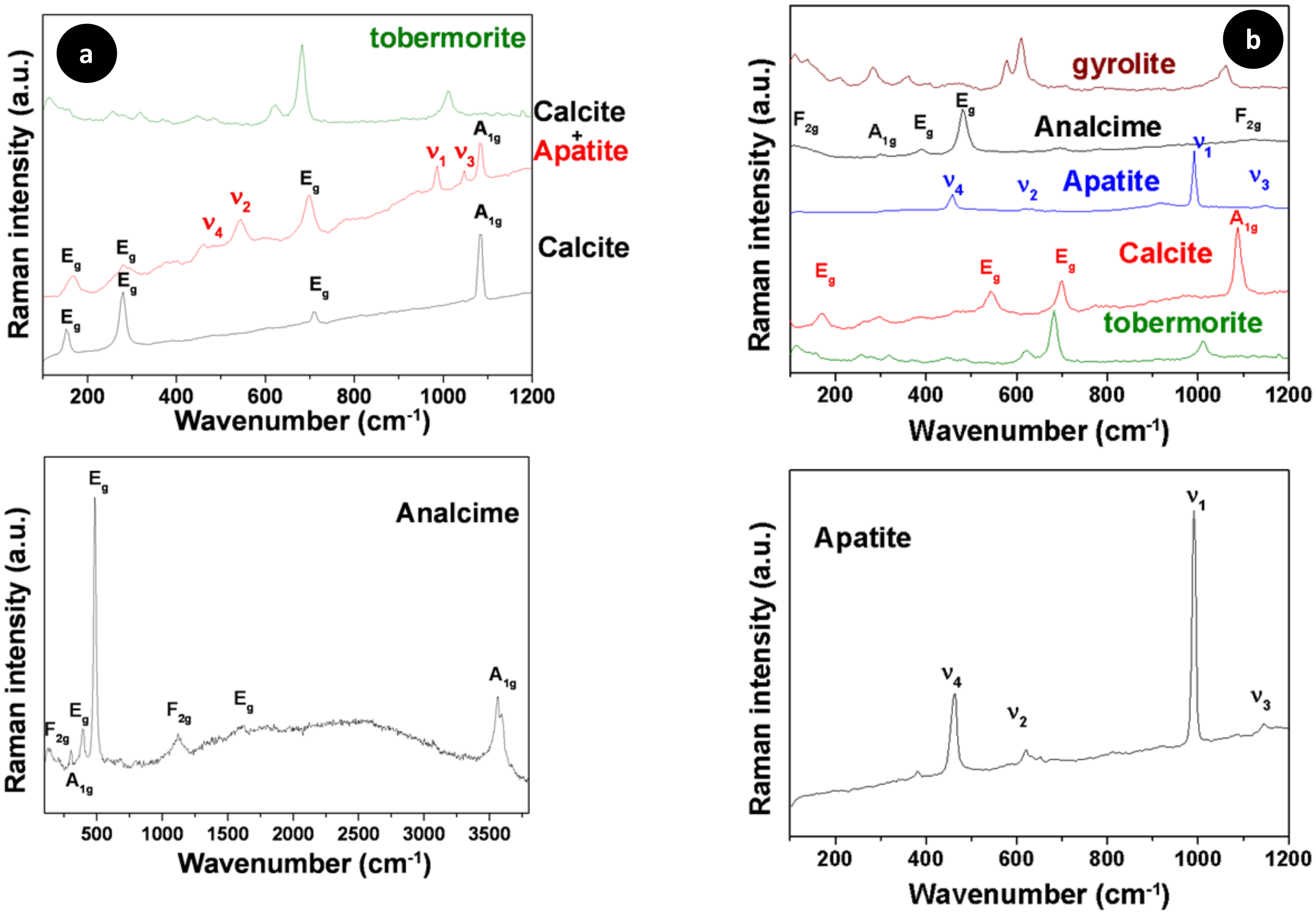
Alteration Products Formation



	Vibration mode	% of species in pristine glass	% of species in hydrated glass
1	Q3	11.5	6
2	Q2	13.7	10.2
3	Q1	2.3	6.1

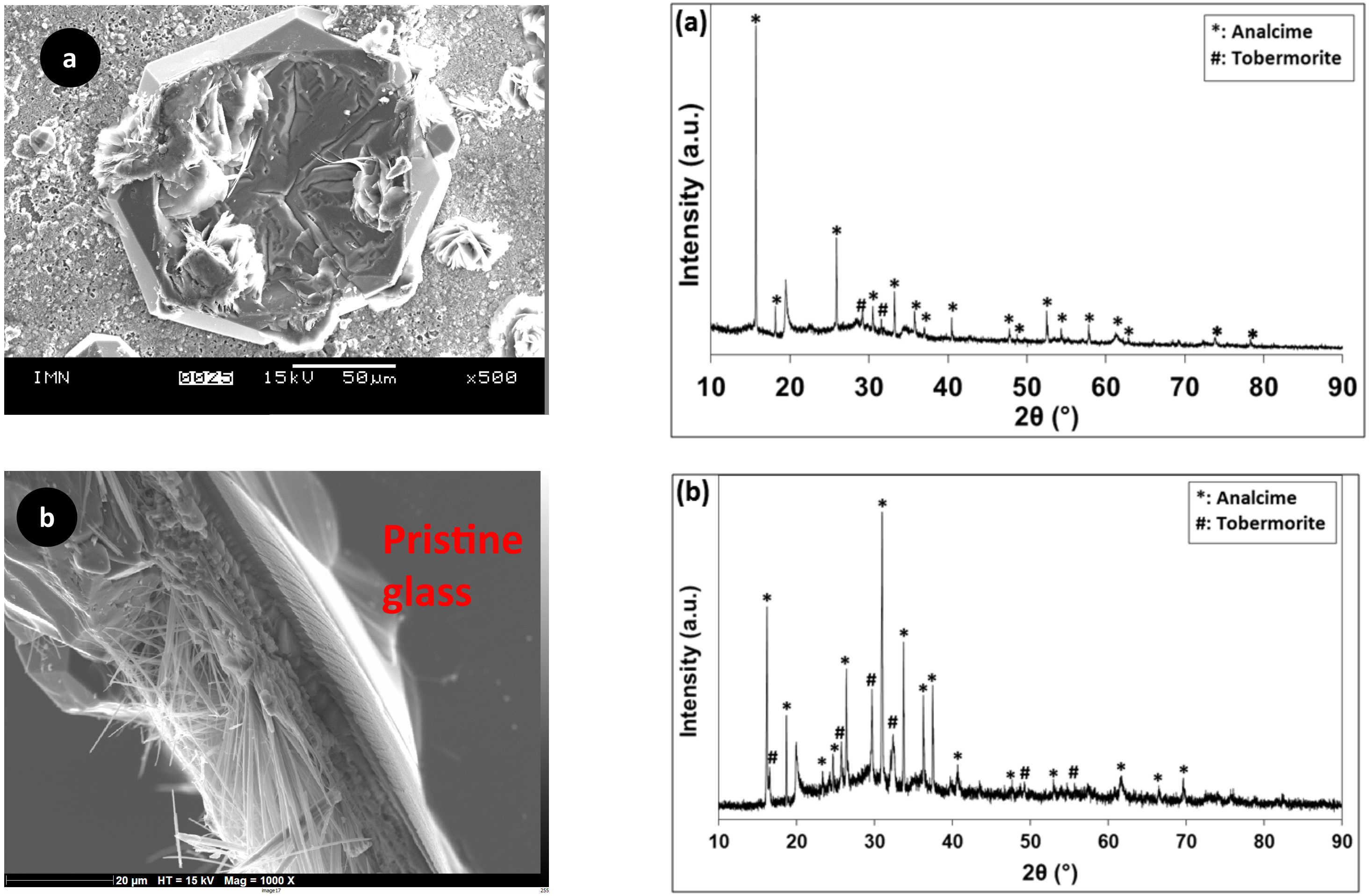
Raman spectra of SON68 glass before (a) and after (b) 365 days of vapor hydration under H_2S.

Alteration Products Formation



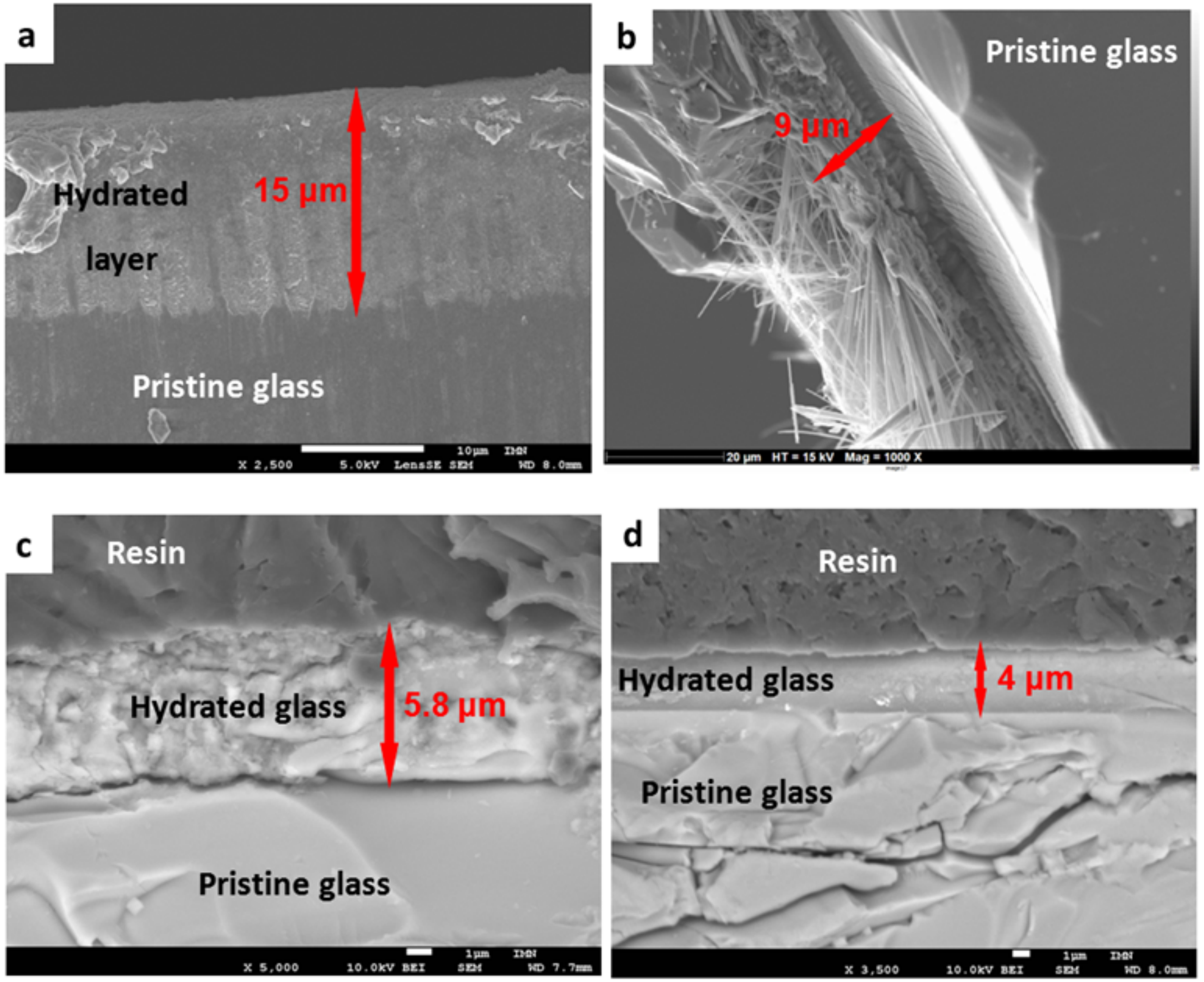
Raman spectra of SON68 glass hydrated at 98% RH under NH_3 for 98 days (a) and under argon for 290 days (b).

Alteration Products Formation



SEM and XRD images of SON68 glass hydrated at 175°C: 98 days under NH_3 (a) and 290 days under argon (b).

Alteration Products Formation



Cross section of a SON68 glass hydrated at 175°C and 98% RH, (a): 98 days of hydration under NH_3, (b): 290 days of hydration under argon, (c): 365 days of hydration under CO_2, (d): 365 days of hydration under H_2S.

Effect of Radiolysis on Glass Hydration

- **Use of alpha- (actinides) an beta (^{99}Tc-) doped glasses, and external gamma irradiation (USA scientists ANL, PNNL)**
  - ✓ **Increase of hydration rates of doped/irradiated glasses (4-15 times increase) due to the increase to water vapor acidification.**
  - ✓ **Reduction of 'soluble form' of ^{99}Tc (TcO_4^-) to insoluble TcO_2.**

- *D.J. Wronkiewicz, L.M. Wang, J.K. Bates, B.S. Tani: Effect of radiation exposure on glass alteration in a steam environment, Mater. Res. Soc. Symp. Proc. 294, pp. 183-190 (1993).*
- *A.C. Buechele, D.A. McKeown, W.W. Lukens, D.K. Shuh, I.L. Pegg: Tc and Re behavior in borosilicate waste glass vapor hydration tests II, J. Nuc. Mater. 429, 159-165 (2012).*

Effect of Composition on Glass Hydration

Study of influence of glass composition on vapor phase hydration of nuclear waste glasses

Glasses studied : 6

Atelier de Vitrification de Marcoule (AVM) glasses : Mg-containing glasses produced at CEA Marcoule facility

(mol%)	SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	MgO	Other
AVMV4	48,17	16,71	18,61	7,15	0,04	7,15	2,17
AVM6	49,29	18,64	16,65	5,88	0,24	6,28	3,02
AVM10	43,5	16,33	16,43	8,32	0,24	10,41	4,77
Q	57,48	15,28	19,17	8,07			
QCa	52,67	14,6	19,01	7,49	**6,23**		
QMg	52,6	15,02	18,83	7,74		**5,81**	

Sathya NARAYANASAMY PhD (defense scheduled on November 2019).

Complex glasses(>20 oxides) ;

AVM6 – Glass alteration in water highest at 50°C;

AVM10 – Glass alteration in water lowest at 50°C;

AVMV4 – Representative composition of active AVM glass

Simple glasses (4 or 5 oxides);

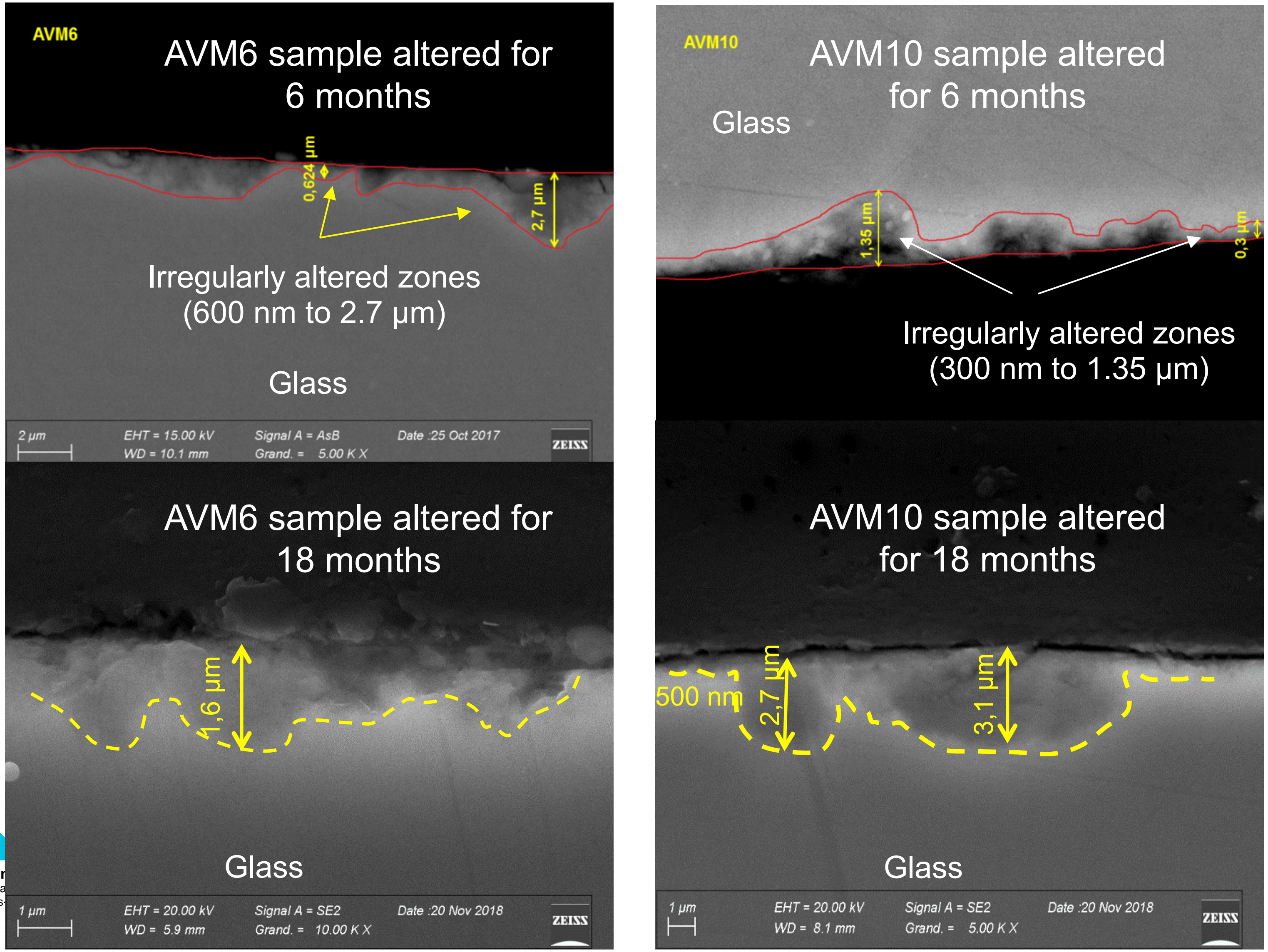
Q – Simple quaternary glass based on Si/Al ratio of AVMV4;

QCa – Specific effect of Ca (Q+CaO);

QMg – Specific effect of Mg (Q+MgO)

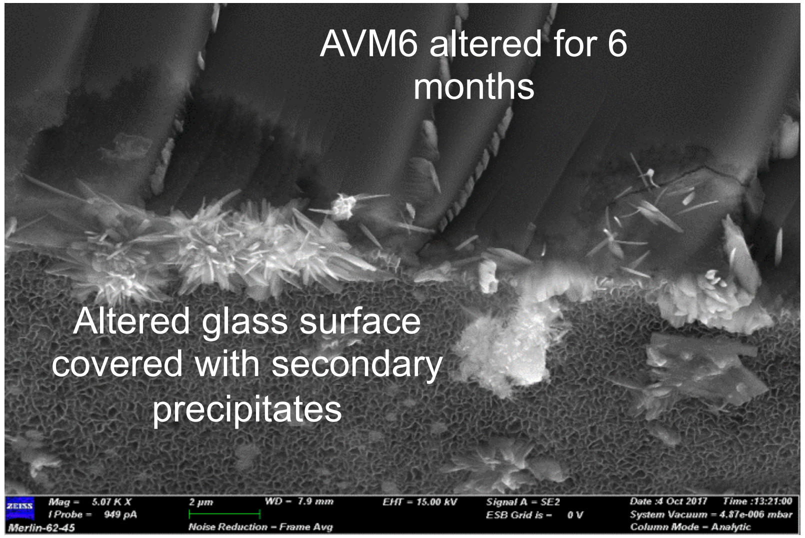
Effect of Composition on Glass Hydration

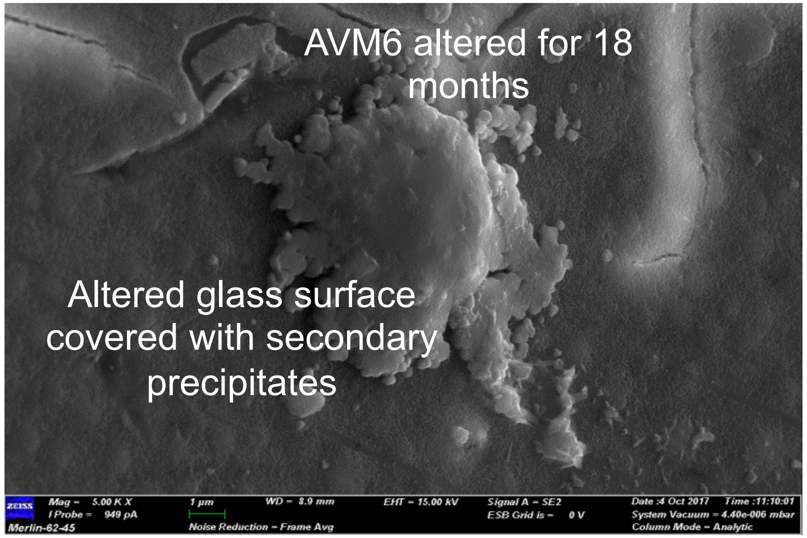
AVM6 & AVM10 - Heterogeneous altered layer (SEM images)

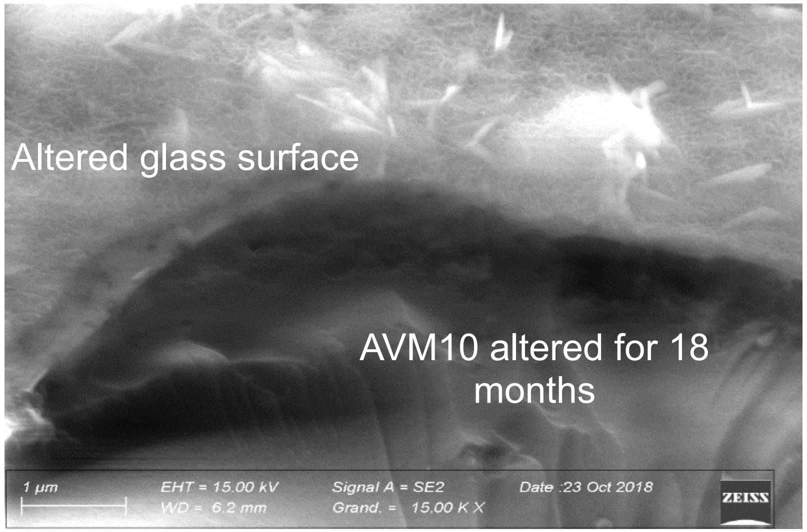


Effect of Composition on Glass Hydration

Surface covered with secondary precipitates (AVM6 & AVM10)

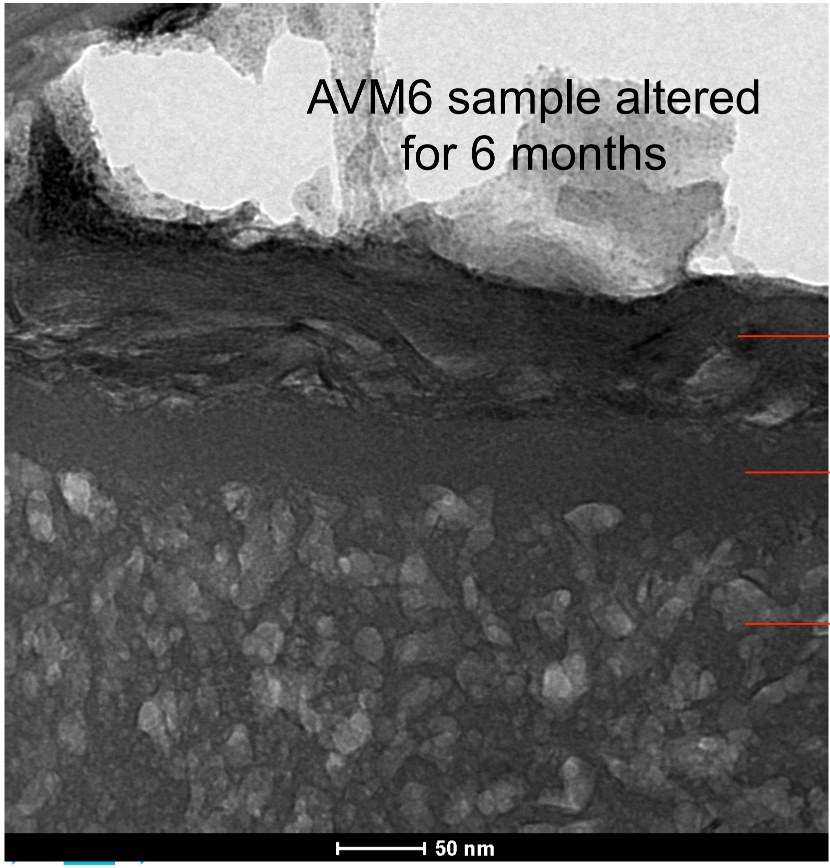






Effect of Composition on Glass Hydration

TEM analysis revealed a different morphology of the altered AVM6 and AVM10 glasses



A layer of phyllosilicates (70 nm thick approx.). Interfoliate distance seems to be around 1.5 nm

Homogeneous continuous gel layer of 50 nm thickness approx.

A very porous irregularly shaped discontinuous altered zone

The homogeneous gel is present even in zones where the irregular and porous altered zones are absent

Effect of composition on Glass Hydration

Study of influence of glass composition in Mg-containing glasses

- ❑ In the case of AVM6 & AVM10, Mg has a negative effect on vapor hydration rate due to formation of Mg-silicates (under given conditions)
- ❑ In the case of AVMV4 & QMg, negative effect of Mg has been attenuated by the addition of Al
- ❑ In the case of QCa, negative effect of Ca is also not noticeable (possibly attenuated by Al) ***(Al_2O_3/CaO >1)***
- ❑ This also insinuates that the 10-20 times faster vapor hydration of AVM6 and AVM10 glasses is *driven by secondary phase precipitation*
  - ❑ *Two types of altered layer morphologies* (irregular porous zones & uniform continuous altered layer) formed on the same glass
  - ❑ Each type of altered layer could be formed by separate processes in the same glass

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Conclusions

- **Glass vapor hydration is a complex phenomenon depending on many parameters:**
  - ✓ **Temperature, relative humidity, glass composition, radiolysis, etc.**
- **More studies are needed for :**
  - ✓ **A better identification of secondary phases.**
  - ✓ **Hydration mechanisms (diffusion vs hydrolysis).**
  - ✓ **Experimental determination of pH of the water film.**
  - ✓ **Role of ionizing radiation.**
  - ✓ **Effect of near-field (steel, clay, concrete)**
  - ✓ **Modeling….**

Thanks

- **All the colleagues, students and interns who contributed into this nice journey on glass hydration and still many work to come.**

- **Jim Neeway, R. Bouakkaz, A. Aït Chaou, G. Karakurt, Y. El Mendili, S. Utsunomiya, B. Grambow, S. Naranayanasamy, P. Jllivet, N. Godon, S. Gin, H. Zhang, T. Suzuki, etc.**