Altération de verres silicatés en phase vapeur

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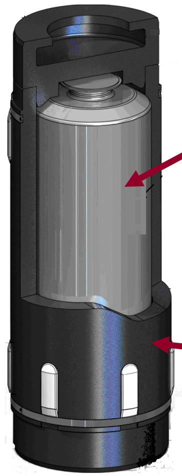
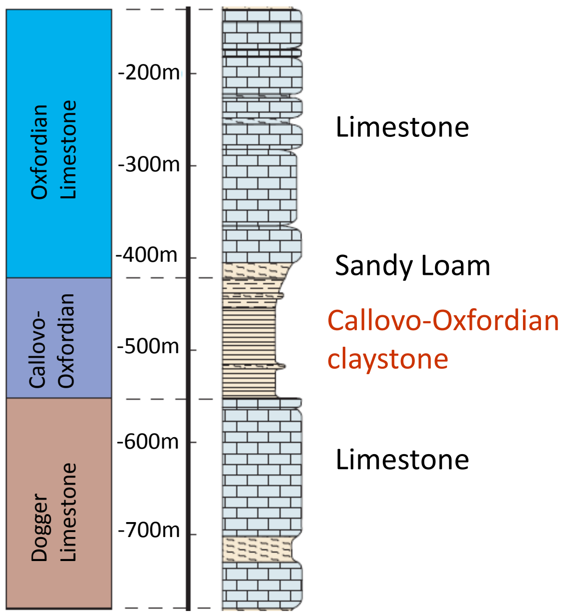
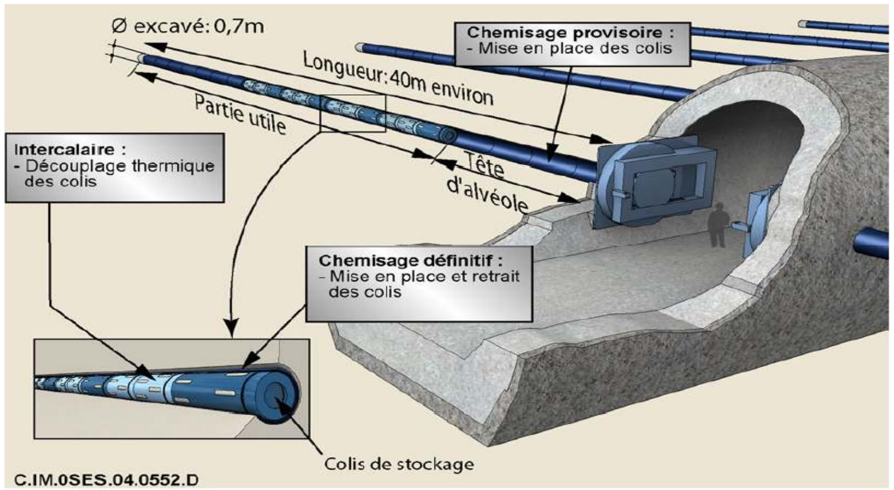
HLW geological storage



Stainless steel canister

Carbon steel overpack





Geological disposal concept of HLW in France (ANDRA 2005)

Water under-saturation may last for thousands of years due to venting and hydrogen production.

What methodology?

- **Use reliable experimental set-up with reproducible outcome particularly in terms of relative humidity control.**

- **Estimate with a reasonable accuracy the hydration rate by only studying the solid in preference by using a simple method.**

Literature Review

J.K. Bates et al., "The relevance of vapor phase hydration aging to nuclear waste isolation," *Nucl. Chem. Waste. Man.*, 5 63-73 (**1984**).

J.K. Bates et al., "The hydration alteration of a commercial nuclear waste glass," *Chem. Geol.*, 51 79-57 (**1985**).

T.A. Abrajano Jr. et al., "Aqueous corrosion of natural and nuclear waste glasses I. Comparative rates of hydration in liquid and vapor environments at elevated temperatures," *J. Non-Cryst. Solids.*, 84 [1–3] 251-257 (**1986**).

T.A. Abrajano Jr. et al., "Aqueous corrosion of natural and nuclear wastes glasses," *J. Non-Cryst. Solids*, 108 269-288 (**1989**).

B.M. Biwer et al., "Comparison of the layer structure of vapor phase and leached SRL glass by use of AEM," *Mat. Res. Symp. Proc.*, 176 255-263 (**1990**).

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

W.L. Gong et al., "Analytical electron microscopy study of surface layers formed on the French SON68 nuclear waste glass during vapor hydration at 200°C," *J. Nucl. Mater.*, 254 249-265 (**1998**).

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 2894-2905 (**2012**).

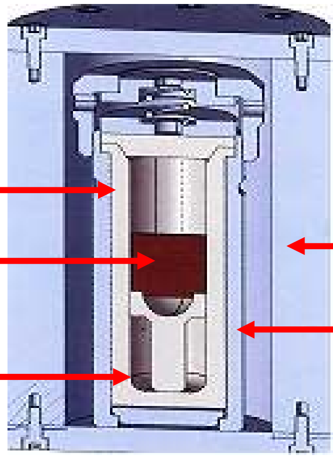
Abdelouas et al., "A preliminary investigation of the ISG glass vapor hydration," *Intern. J. App. Glass Sci.,* 4 307-316 (**2013**).

Experimental set up

- **Use of Stainless Steel autoclave with a Teflon liner. Use of a thick Al container to minimize water condensation.**
- **Use of NaCl solutions with increasing salinity.**

% RH	80%	85%	95%
% NaCl	25%	18%	6%

- **Use of different gas atmospheres to control the pH.**



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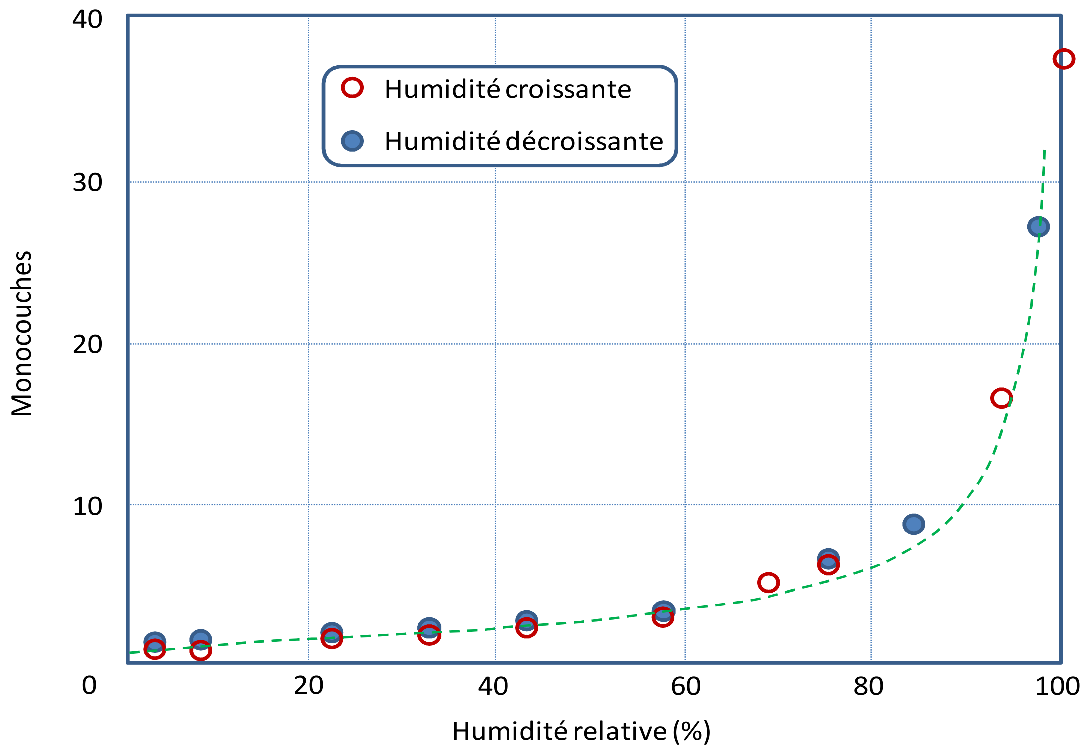
Water Sorption on Borosilicate Glasses



Sorption isotherm of water on the SRL 165 borosilicate glass at 23°C
(after *Ebert et al.*, 1990)

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Water Sorption on Borosilicate Glasses

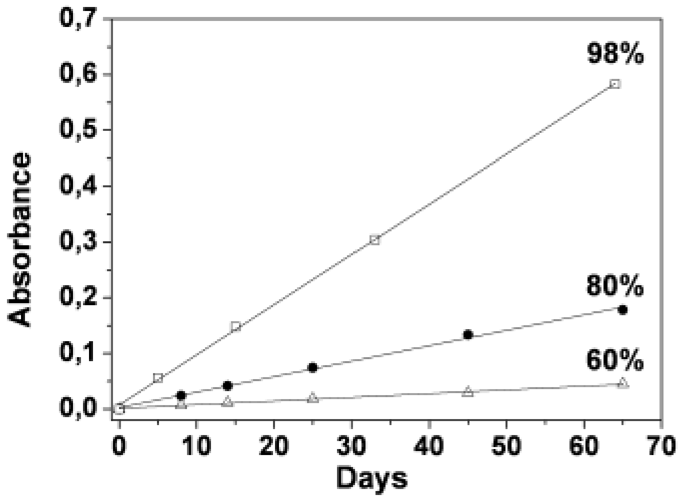


Fig. 5. Evolution with the alteration time of the absorbance band around 3600/cm assigned to SiOH for the ISG glass hydrated at 175° C under different relative humidities (60%, 80%, and 98%).

Table IV. Ratios of SiOH Absorbance Units of ISG Glass Hydrated for 65 days at 175°C, and 60%, 80%, and 98% RH Compared with Ratios of the Number of Water Monolayers, Corresponding to 60%, 80%, and 98% RH, and Expected to be Sorbed on ISG Glass According to Ebert *et al.*[2]

Experiment	Ratio of SiOH Absorbance Units	Ratio of Number of Water Monolayers
98%: 80%	3.6	4.75
98%: 60%	11.6	10.84
80%: 60%	2.6	2.3

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

Solid analysis

- **SIMS**

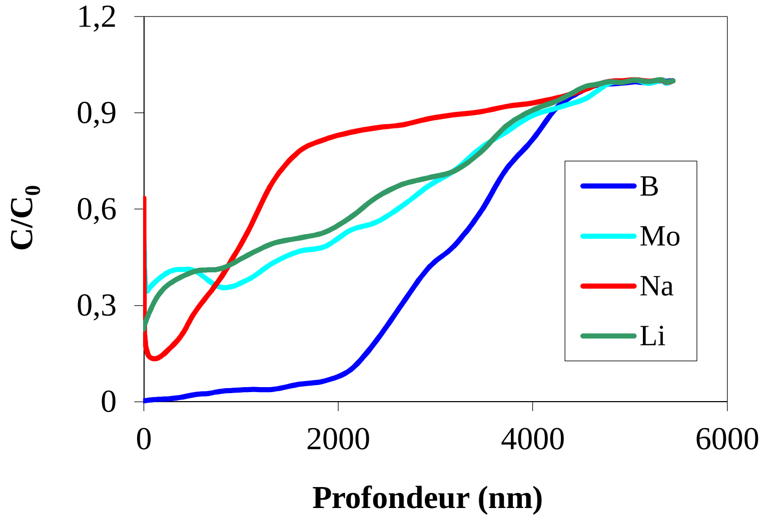
(Secondary Ions Mass Spectrometry)

R. Bouakkaz (2014)

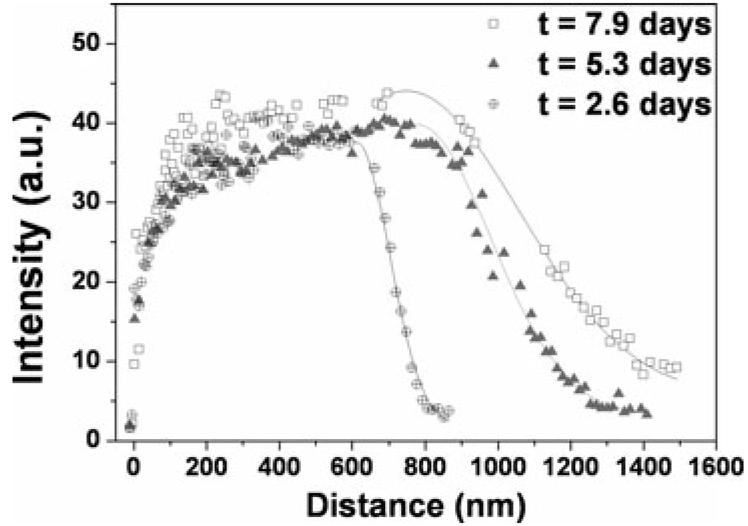
- **NRA**

(Nuclear Reaction Analysis)

Abdelouas et al. (2013)



SON68 glass hydrated at 125°C

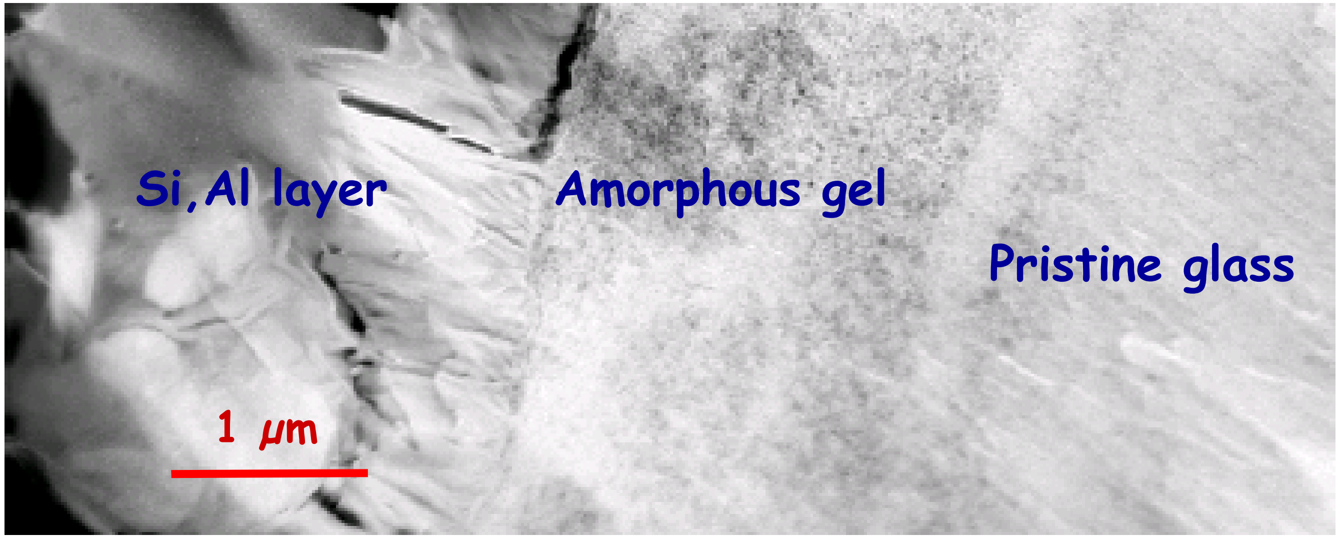


ISG glass hydrated at 175°C

Solid analysis

- **MET**

Duration: 99d, T: 175°C, 95% RH



Neeway et al. (2012)

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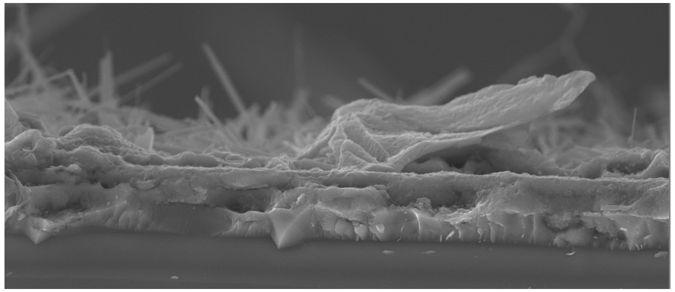
Solid analysis

- **MEB**

Duration: 57d, T: 200°C, 92% RH

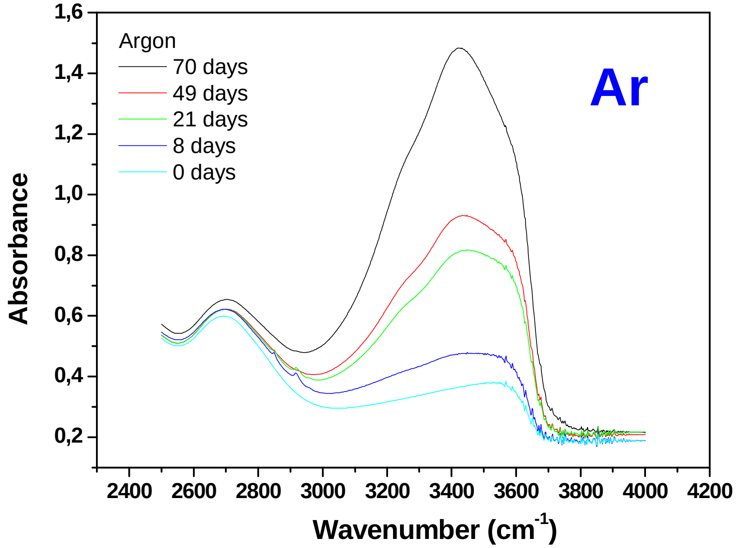


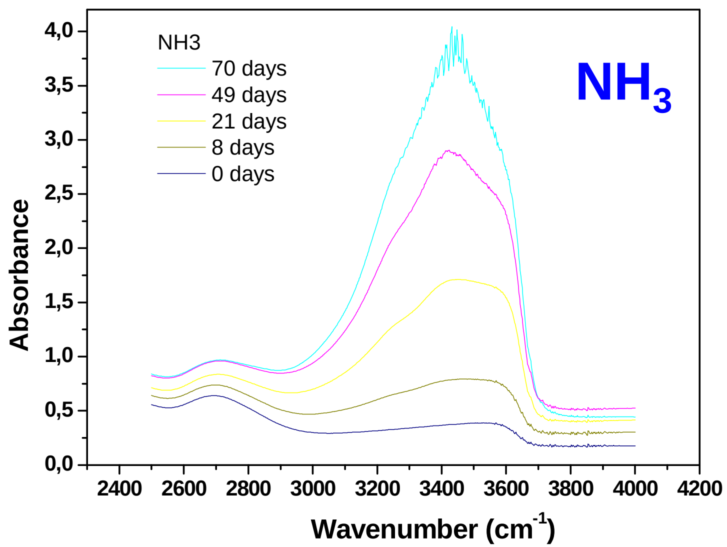
Duration: 57d, T: 200°C, 92% RH

Neeway et al. (2012)

Solid analysis

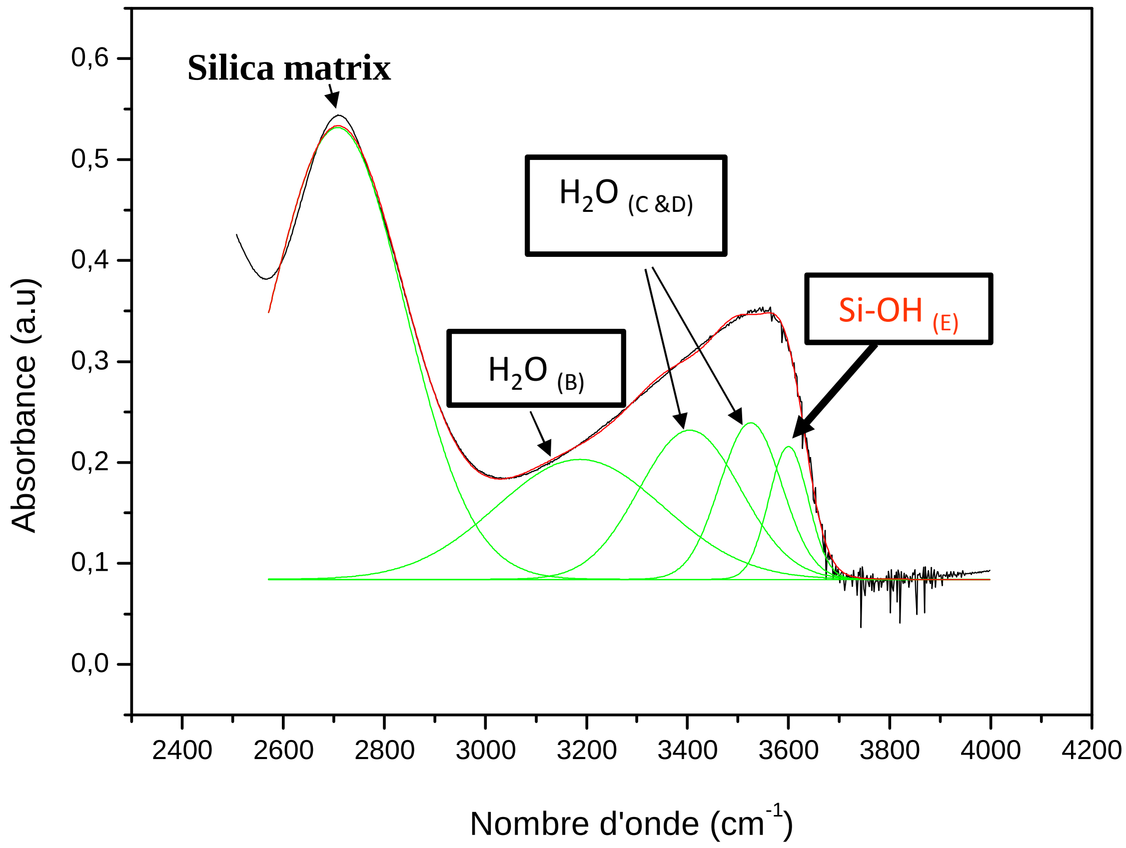
- **FTIR** (Fourier Transform Infra Red spectroscopy)



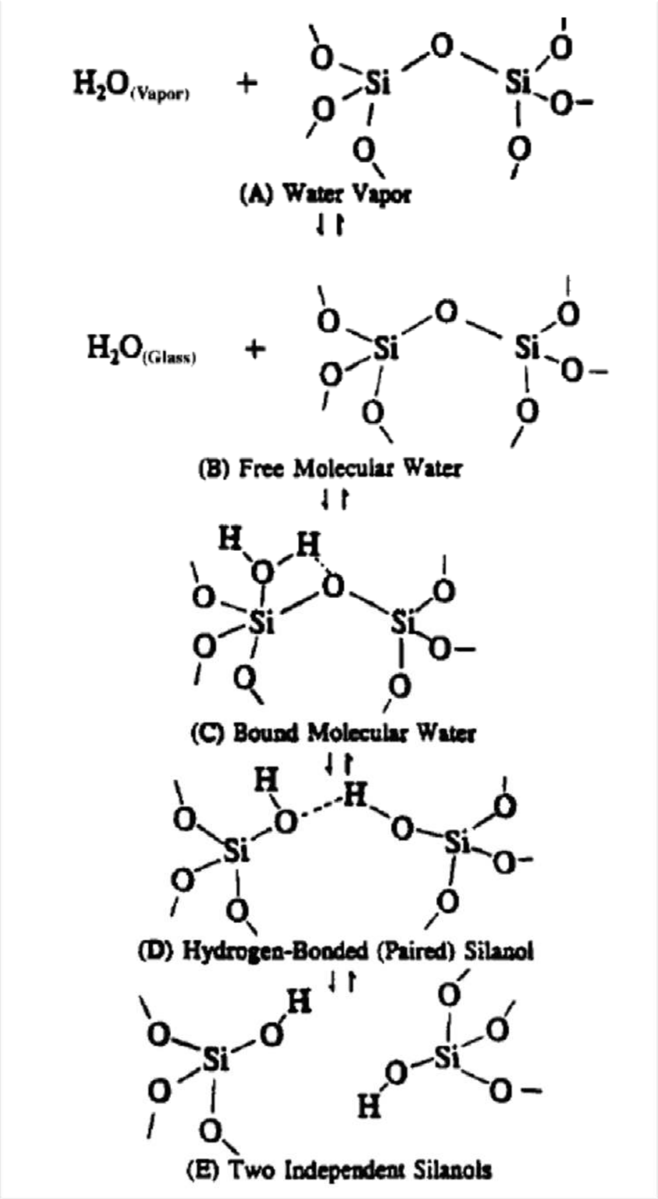


SON68 glass, T: 175°C, 98% RH

Solid analysis



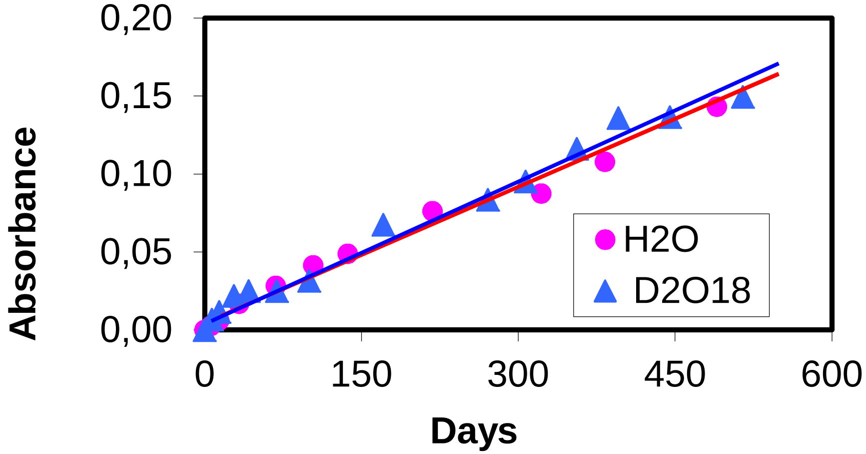
Efimov et al. J. Non-Cryst. Solids., 332 93-114 (2003)



Solid analysis

- **3 borosilicate glasses were used:**
  - SON68 glass
  - CSD-B glass
  - ISG glass
- **Temperature:** 35,50,90, 150, 175, 200°C
- **% relative humidity:** 60-100%

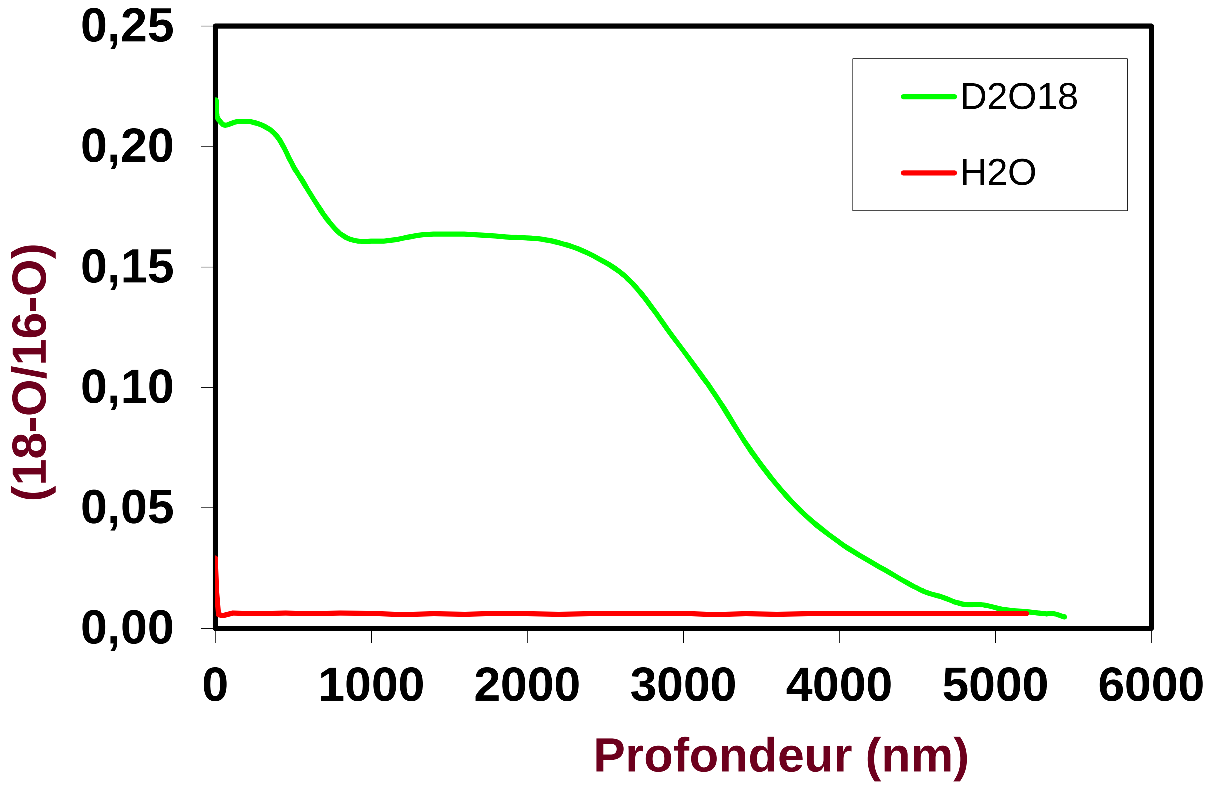
R. Bouakkaz (2014)



The FTIR main result is the correspondence between SiOH absorbance and the hydration layer

0.1 absorbance = 1 µm of hydration layer

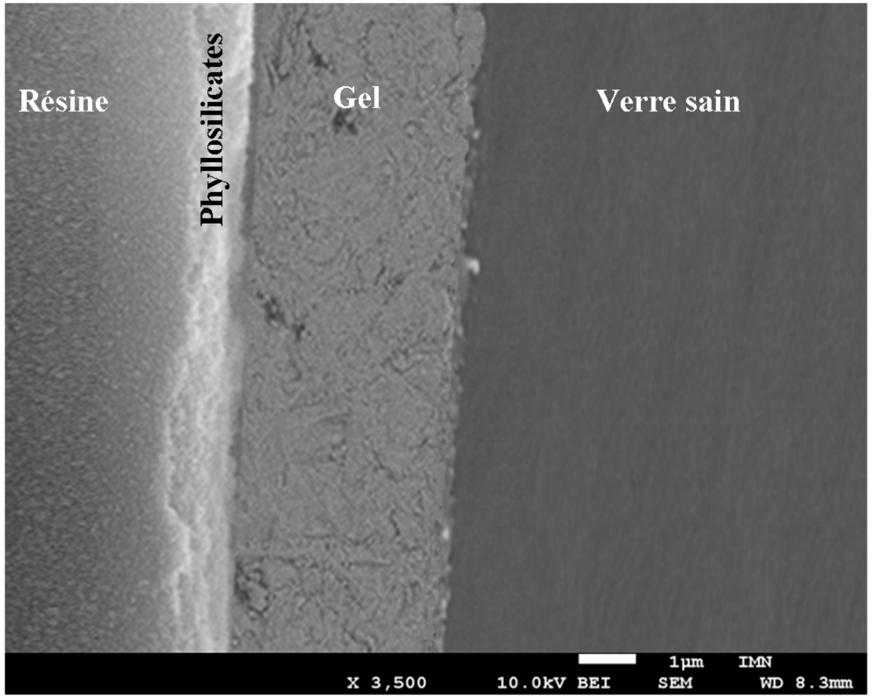
SON68 glass hydration - SIMS



SON68 glass hydrated at 125°C, RH 95% during 593°C

R. Bouakkaz (2014)

SON68 glass hydration - SEM

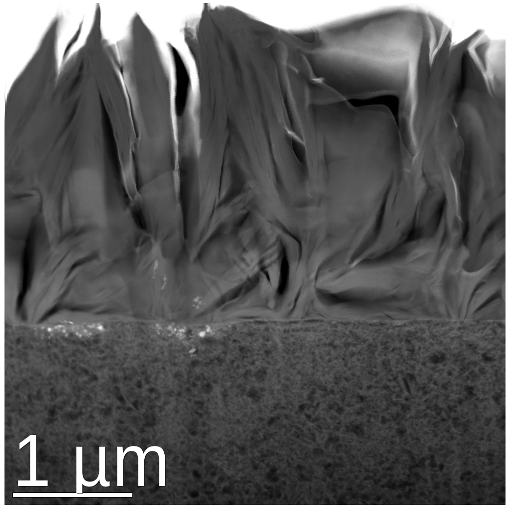


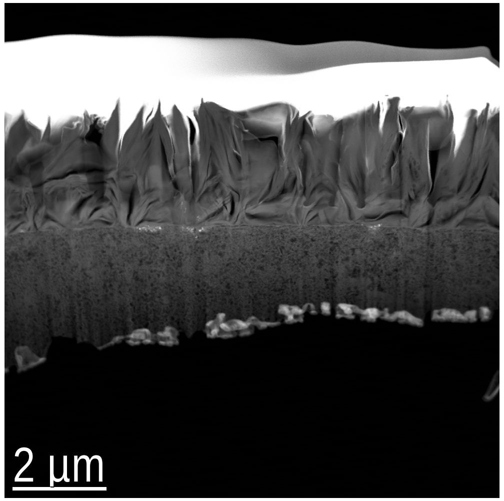
SON68 glass hydrated at 125°C, RH 95% during 593°C

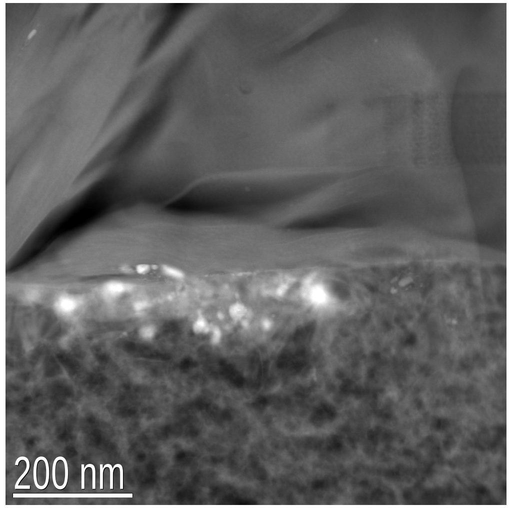
R. Bouakkaz (2014)

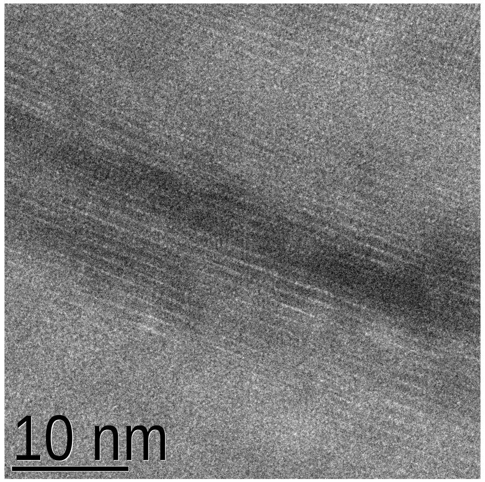
SON68 glass hydration - TEM

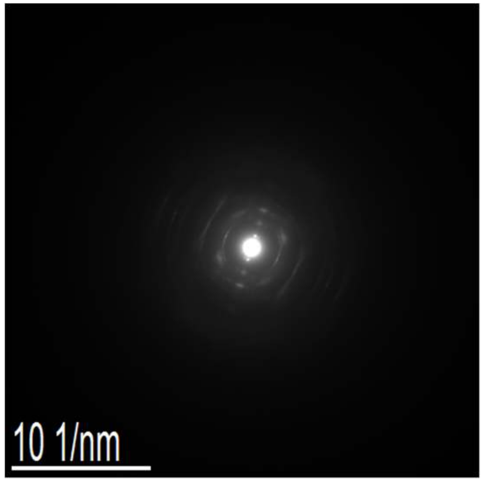
Surface of hydrated glass under NH_3 for 98d





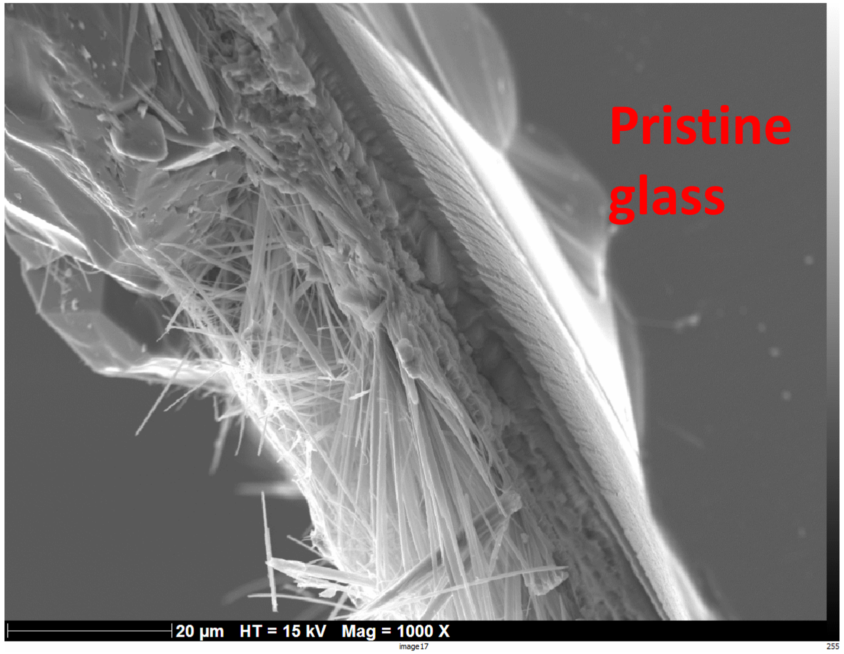


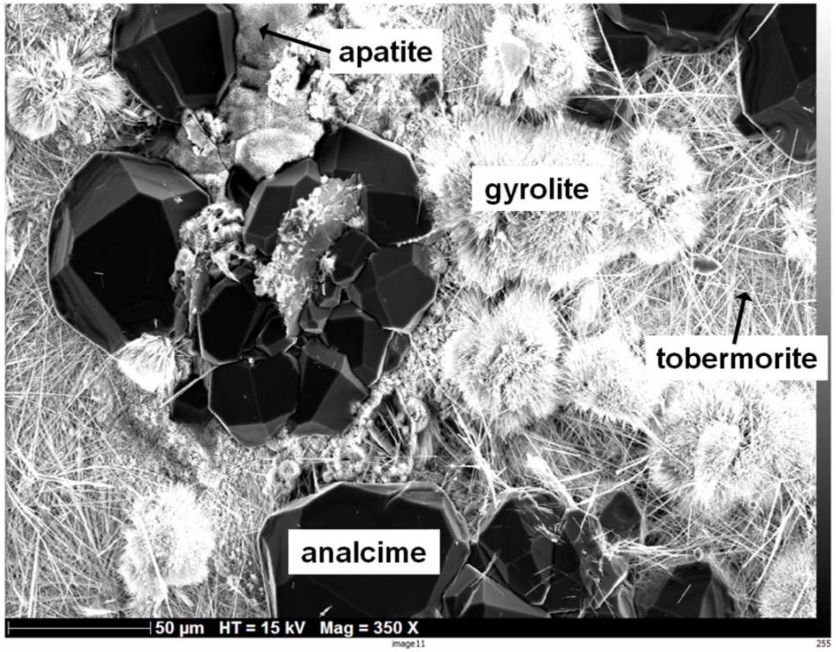




Hydration at high temperature

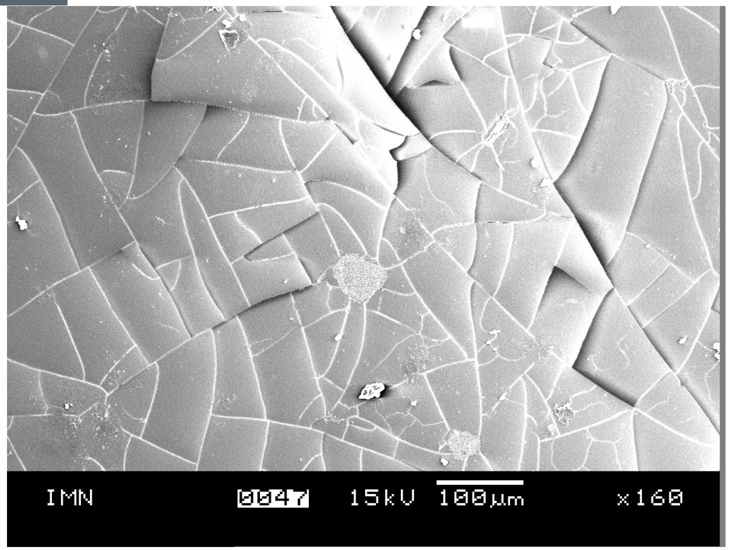
Surface of hydrated SON68 glass under Ar for 290d

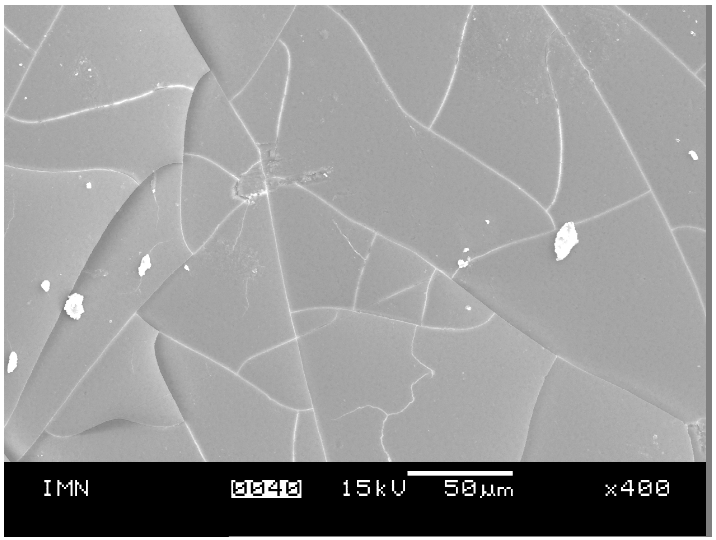




Massive precipitation of CSH

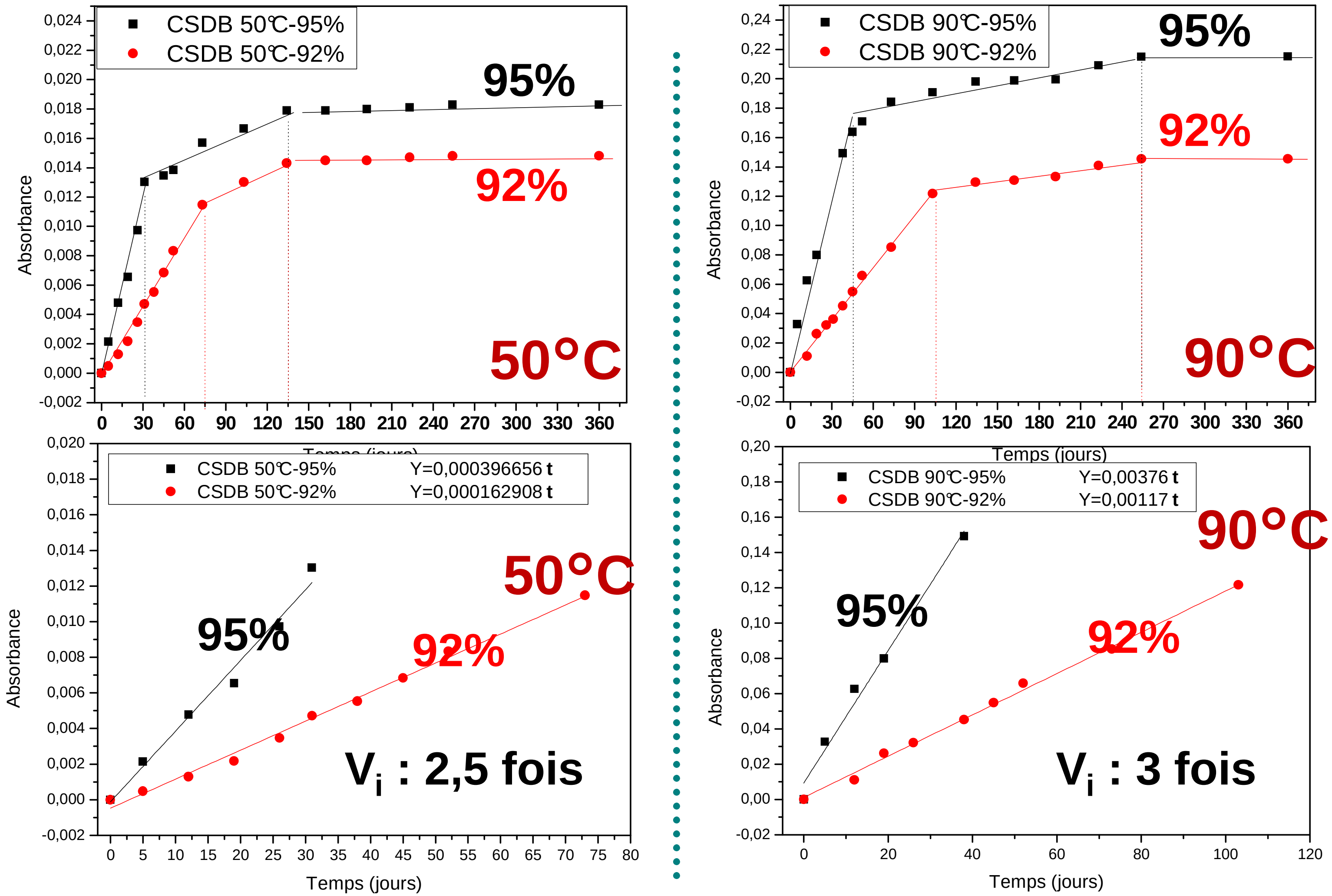
Hydration at low temperature (CSD-B; 90°C)



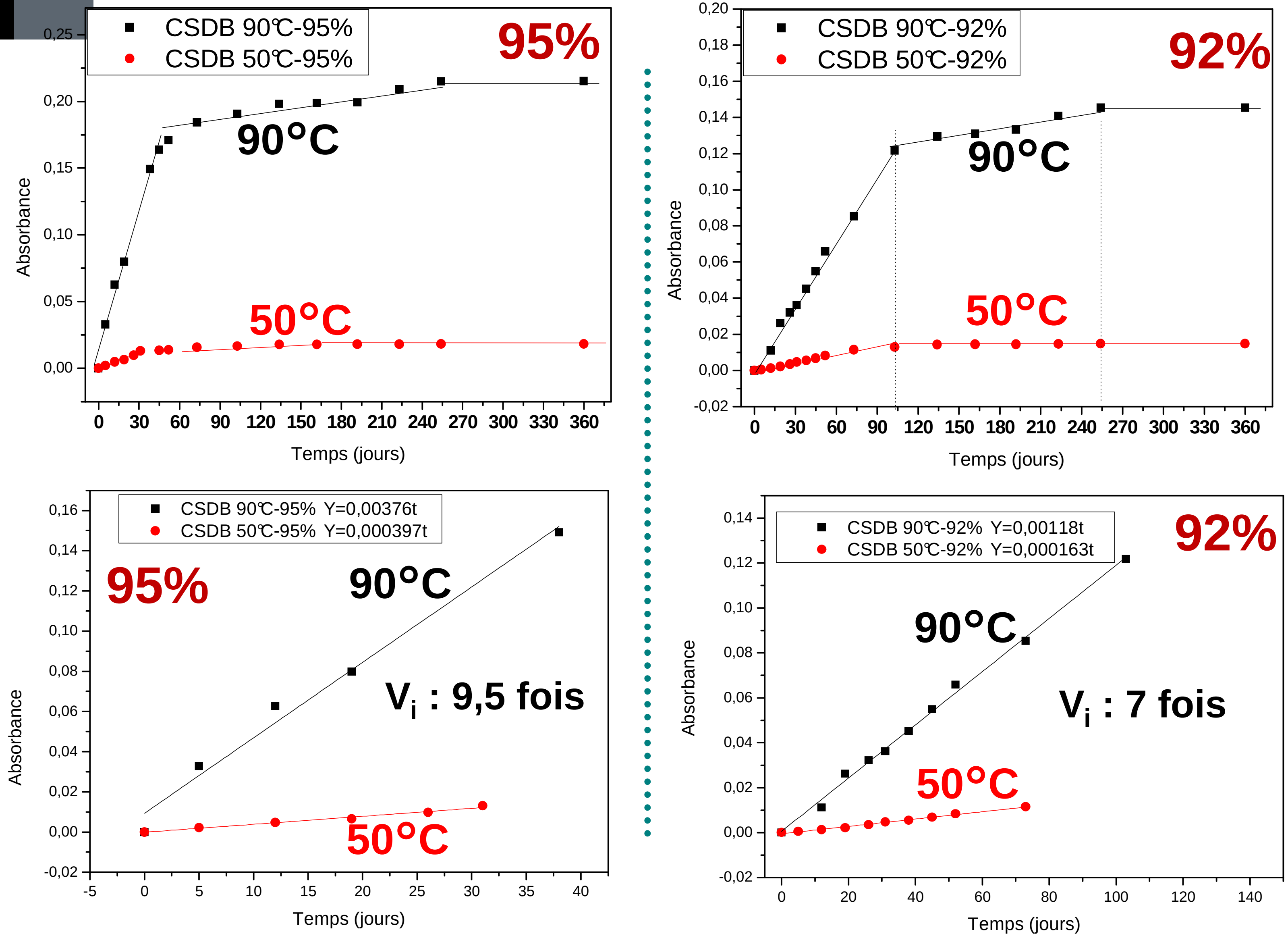


Oxides	Pritine glass	92 % RH, 90°C, 365 d
SiO_2	63.56	67.9
Al_2O_3	10.74	12.76
Na_2O	12.30	6.76
Cr_2O_3	0.31	0.28
CaO	3.80	1.48
Fe_2O_3	3.20	3.89
P_2O_5	0.41	0.69
NiO	0.34	0.45
ZrO_2	3.19	2.98
La_2O_3	0.20	0.12
Ce_2O_3	1.23	1.34
Nd_2O_3	0.71	0.85
RuO_2	0.01	0.08
Total	100	100

CSD-B glass hydration



CSD-B glass hydration



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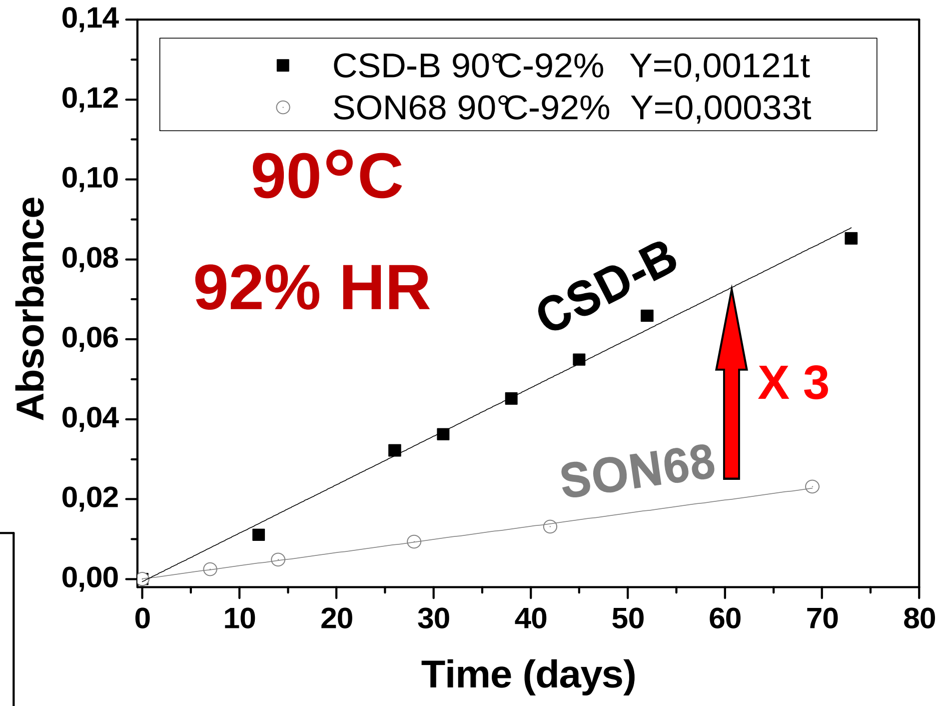
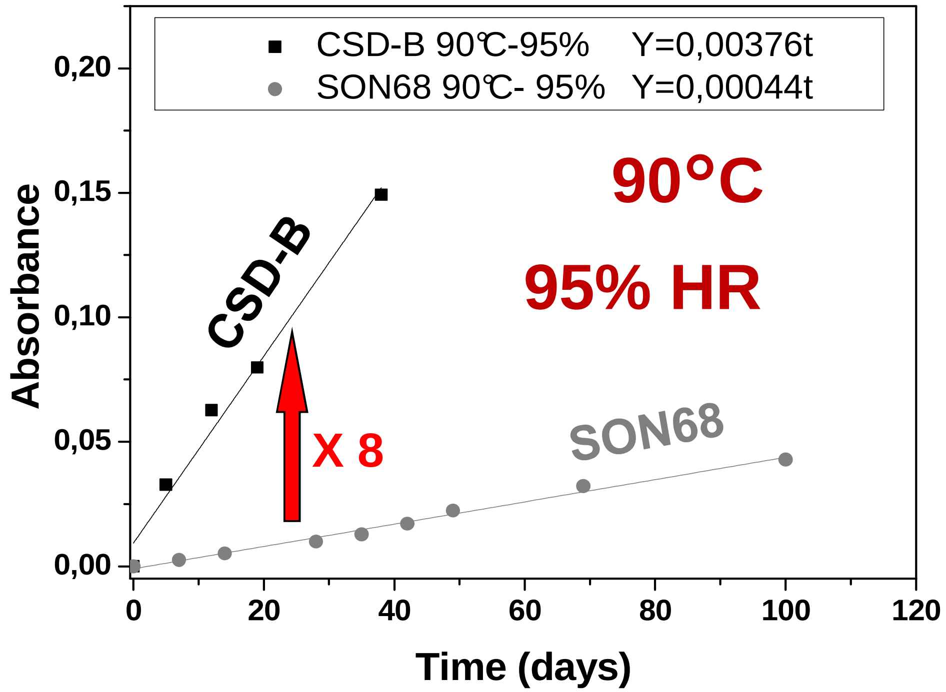
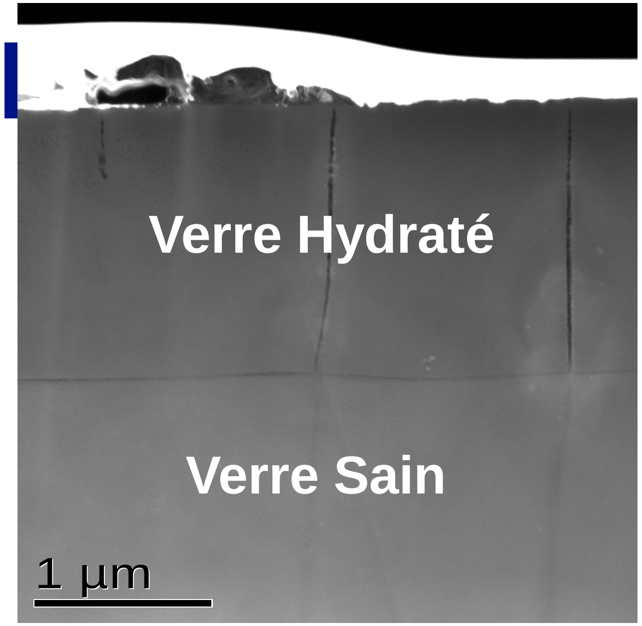
CSD-B and SON68 glasses hydration

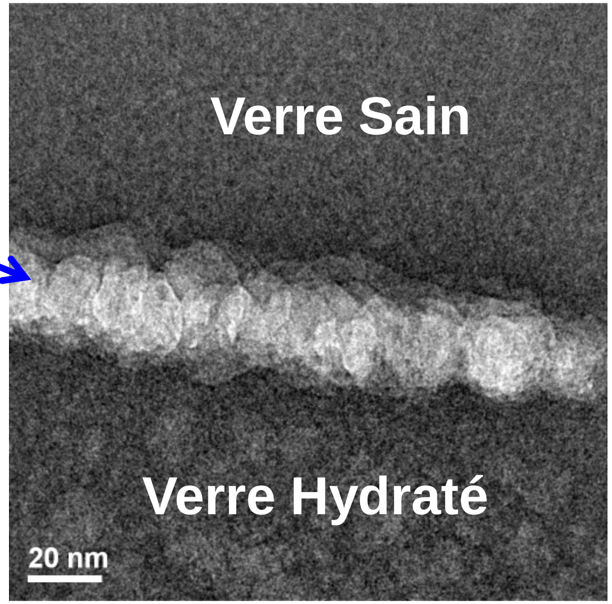


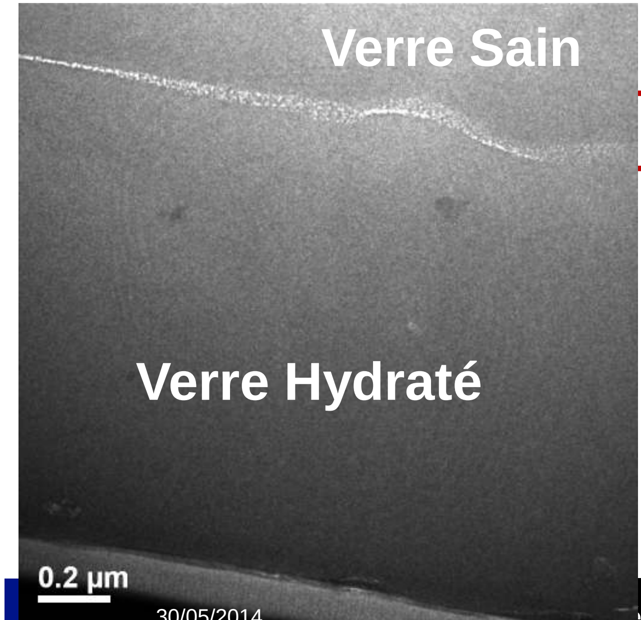




90°C, 95 % HR, 1 an

Front d'hydratation



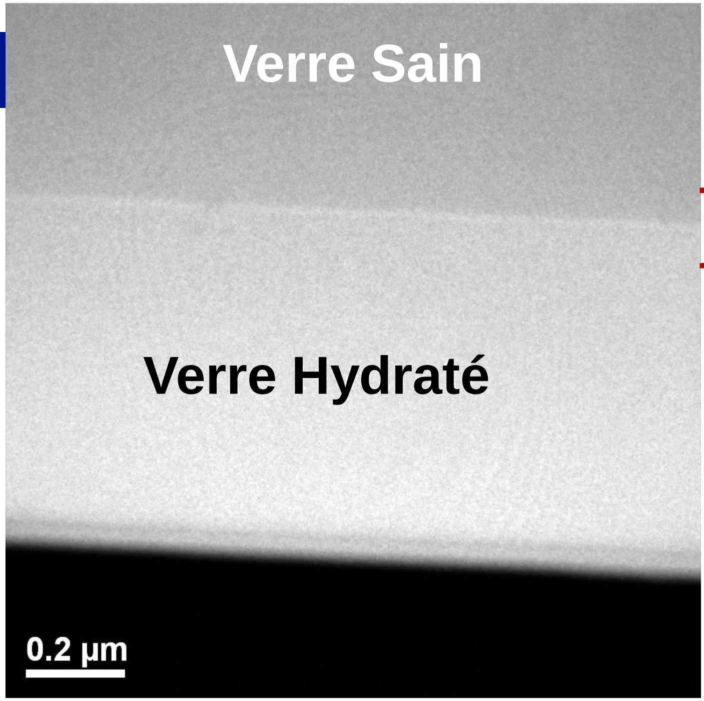


Epaisseur de la couche hydratée :

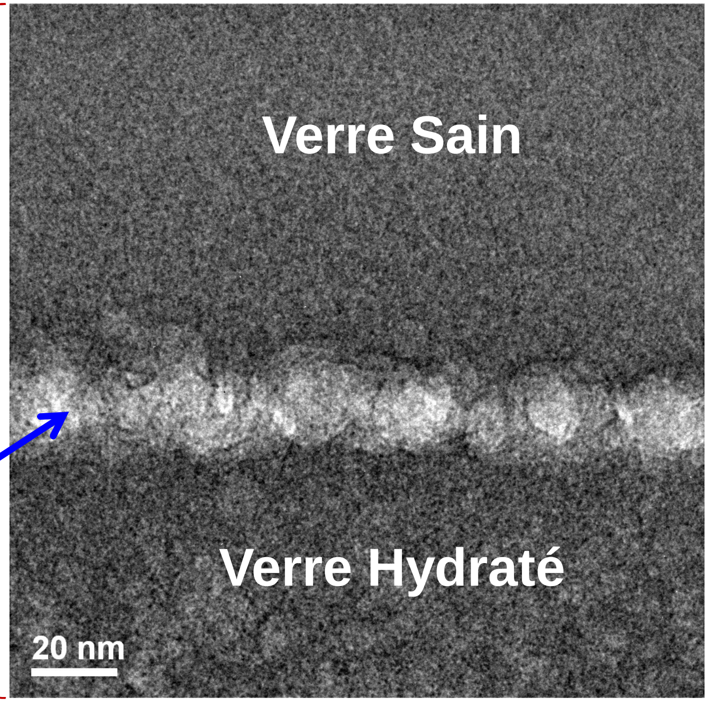
IMN : 1,5 µm

Japon : 1,6 µm

90°C, 92% HR, 1 an



Front d'hydratation



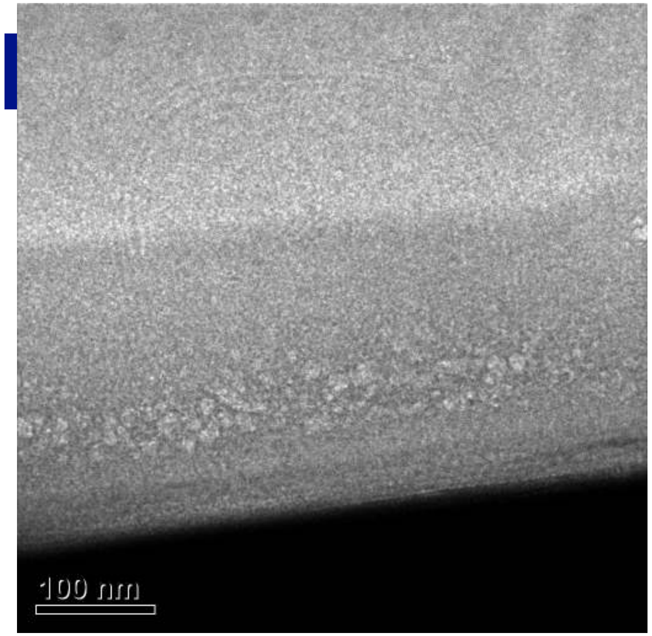
Epaisseur de la couche hydratée :

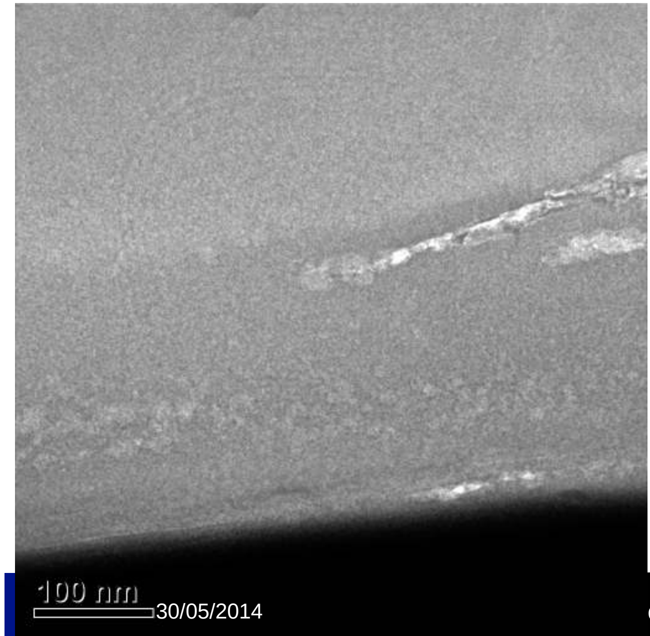
IMN (Nantes) : 680 nm

Japon : 710 nm

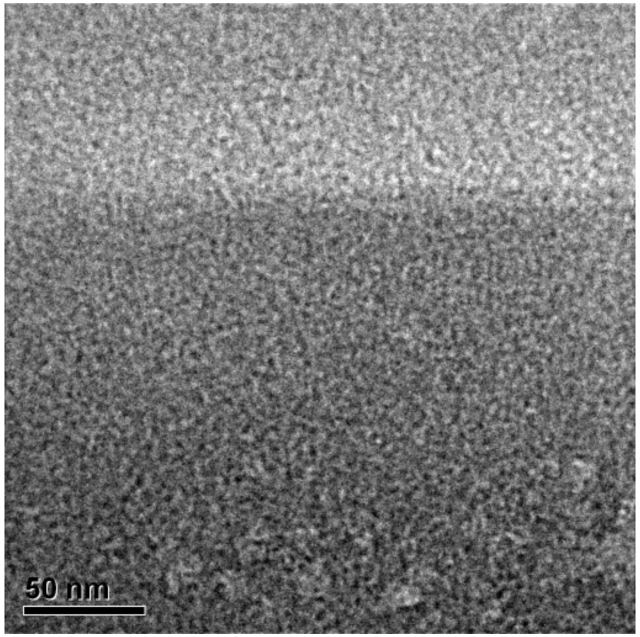
Pas de porosité importante dans la partie hydratée comparé au verre sain

90°C, 95 % HR, 1 mois





Pas de porosité importante dans la partie hydratée



Epaisseur de la couche hydratée :

200 nm

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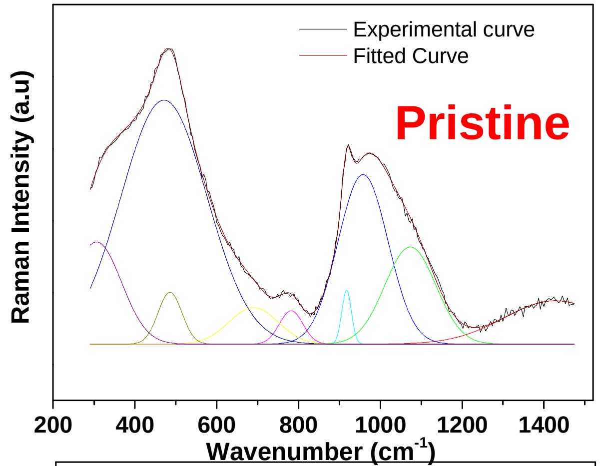
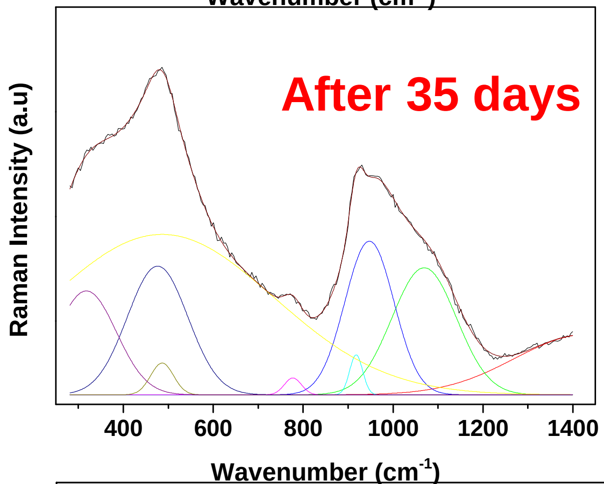
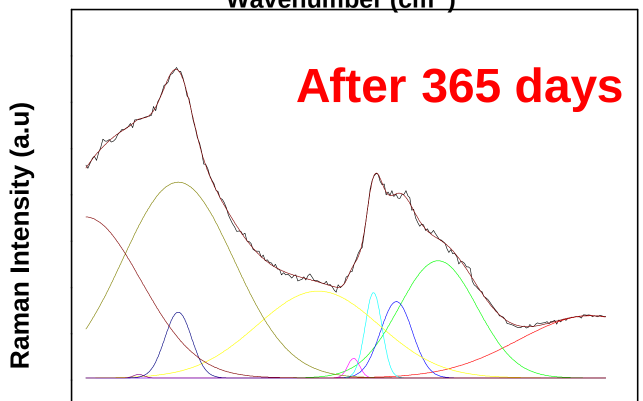


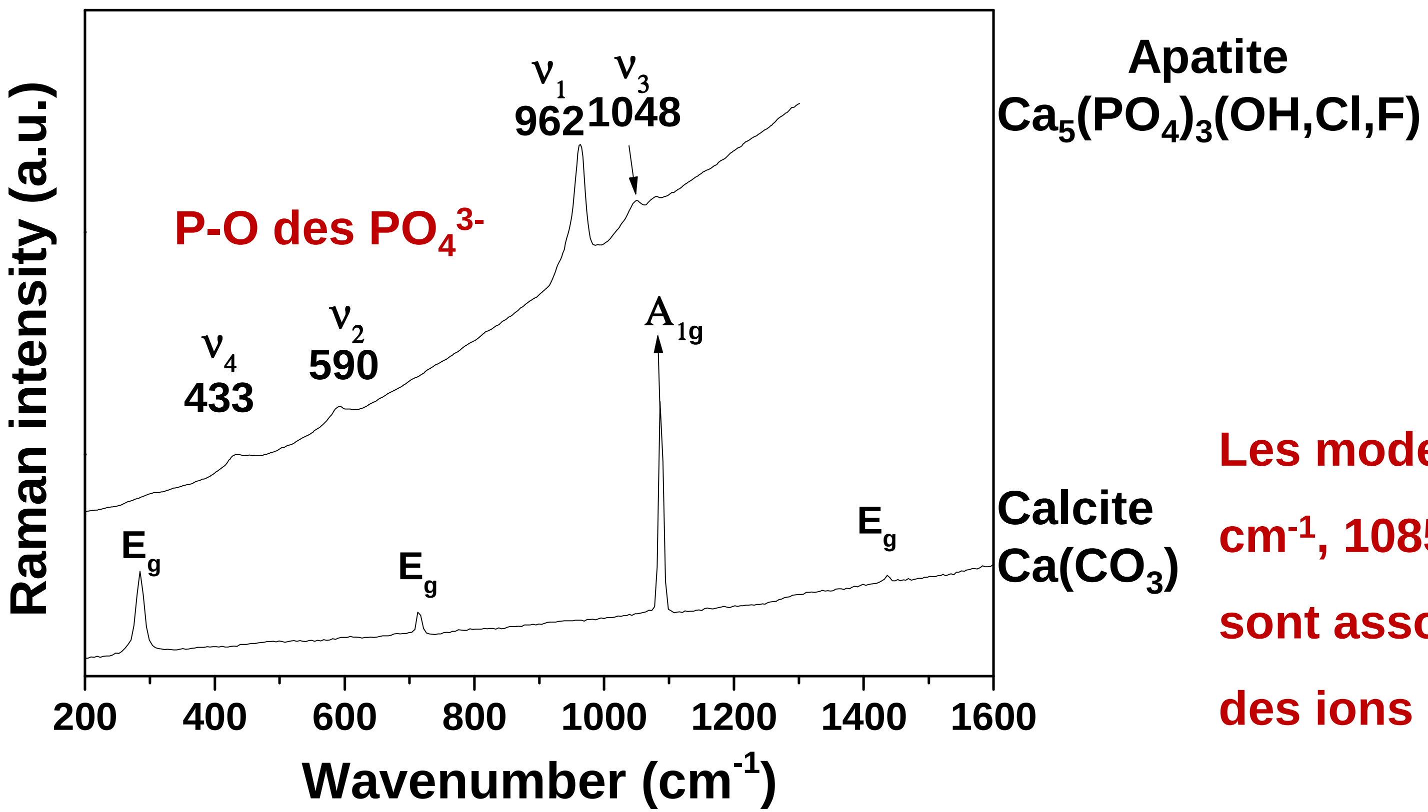




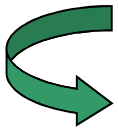
Raman analysis

Peaks	Vibration mode	Center	%		
			Pristine	After hydration (35 days)	After hydration (356 days)
1	BO-binding	1427-1430	9.2	11.3	12.1
2	Q_3	1060-1072	10.2	10.8	12.7
3	Q_2	952-963	17.6	9.94	3.3
4	Q_1	916-917	1.1	1.3	1.9
5	Q_0	875			0.4
6	Si–O stretching	779-791	1.6	2.38	14.3
7	Danburite B_2O_7-Si_2O_7	690	3.7	0	0
8	Si-O-Si stretching	485	2.5	2.95	2.4
9	O—(Al, Si)—O bending	475-477	43.4	47.4	29.9
10	Ca-O polyhedra	316-320	10.6	8.22	0.05
11	P-O bending Ru-Ru Bending	280	0	0	24.1

90°C, 95% HR, 35 days



Les modes à 282 cm^{-l}, 712 cm^{-1}, 1085 cm^{-l}, et 1434 cm^{-l} sont associés à la vibration des ions carbonate CO_3^{2-}



Présence de calcite et d'apatite en faible quantité

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Conclusions

- **La méthodologie des études d'altération des verres borosilicatés en phase vapeur est validée avec une bonne reproductibilité des résultats.**
- **Des paramètres comme le pH, l'humidité relative, la température et la re-condensation (D_2O^{18}) sont faciles à tester.**
- **Les analyses des verres hydratés par FTIR, faciles à mettre en œuvre, permettent d'obtenir des vitesses d'hydratation validées par d'autres techniques.**
- **A basses températures (35-90°C) un effet de saturation est observable (cimentation?).**

Conclusions

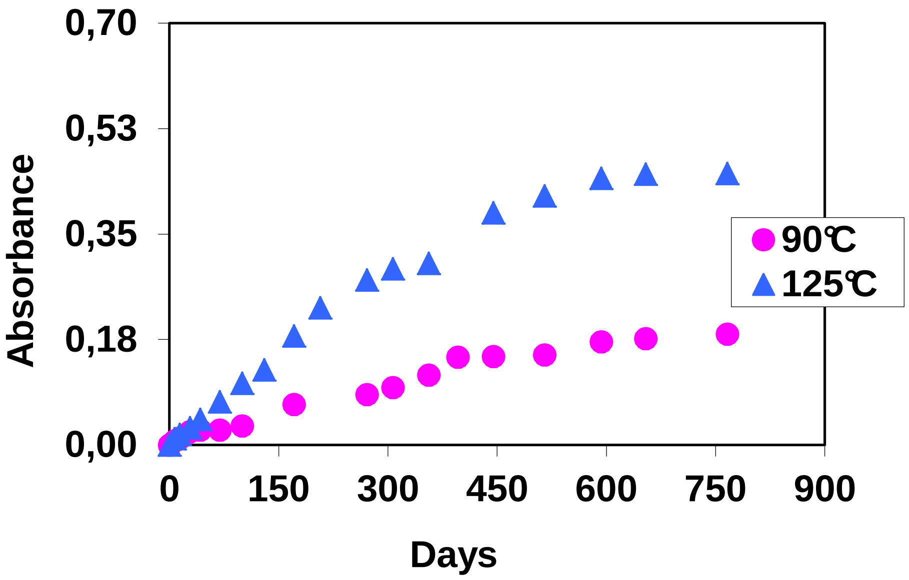
- **Un gros travail de caractérisation des surfaces hydratées à l'échelle nanométrique est nécessaire pour mieux comprendre les mécanismes d'hydratation et re-condensation (sonde atomique?).**
- **Des expériences à long-terme sont nécessaires afin de tester l'hypothèse de la reprise d'altération via la formation des zéolithes.**
- **Etudier des compositions de verres simples pour mieux évaluer le rôle de certains éléments.**
- **Un effort de modélisation géochimique reste à fournir mais ça ne sera pas facile (rapport S/V très élevé).**

Autres applications pertinentes pour le stockage

- **Effet de la radiolyse sur la tenue des gels d'altération. L'impact augmenterait avec HR. La radiolyse serait très importante dans les pores de taille nanométrique. Utilisation de sources d'irradiation externe.**

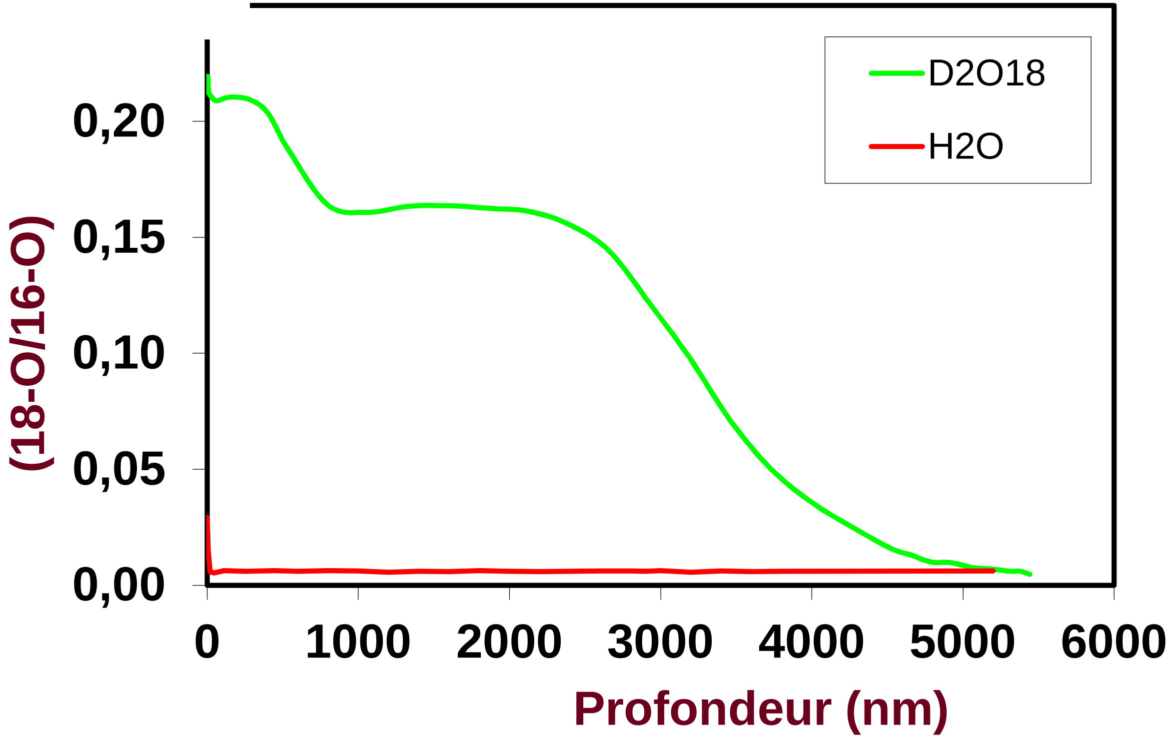
- **Altération d'autres matériaux en particulier les bétons et rôle de la radiolyse.**

- **Hydratation des aciers.**



SON68, 90°C, 95% HR

R. Bouakkaz (2014)



Merci à toute l'équipe

- J. Neeway (PNNL)
- R. Bouakkaz, G. Karakurt, Y. El Mendili, A. Ait Chaou, B. Grambow (SUBATECH)
- S. Utsunomiya (Univ. Kyushu), H. Matsuzaki (Univ. Tokyo)

Un merci aussi à l'ANDRA pour le soutien financier et au CEA.

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