Obsidians : origins

Obsidian is a silicic rhyolite glass formed from quenched magmatic liquid which cools to form a solid glassy rock and is found worldwide near many volcanic vents.   It is a super cooled magma formed from viscous lava flows.

It exhibits conchoidal fracture which is a smoothly curving fracture surface of fine-grained materials which have no planar surfaces (i.e. no cleavage. This type of curving fracture surface is characteristic of amorphous/glassy and brittle materials without defined crystal structure.

NanoMEGAS
Advanced Tools for electron diffraction

Obsidians : more than 10.000 years old history

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Review

Fifty years of obsidian hydration dating in archaeology

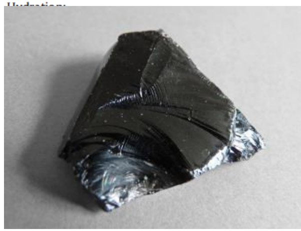
Ioannis Liritzis *, Nikolaos Laskaris

University of the Aegean, Laboratory of Archaeometry, Department of Mediteranean Studies, Rhodes 85100, Greece

A R T I C L E I N F O

Article history:
Received 2 October 2010
Received in revised form 22 February 2011
Available online 23 March 2011

Keywords:
Obsidian;



A B S T R A C T

About fifty years ago Friedman and Smith [1] recognized the obsidian hydration phenomenon and proposed an empirical dating method based on the conversion of the optically measured hydration depth to an absolute age. They and subsequent researchers developed distinct versions of obsidian hydration method consisting of both empirical rate and intrinsic rate development, thus refining the method. However, in spite the accurately measured rinds beyond digital optical microscopy employing infrared spectroscopy and nuclear analysis, the traditional empirical age equation produce occasionally satisfactory results but still fail to produce a reliable chronometer. In the last ten years, secondary ion mass spectrometry (SIMS) has been employed to accurately define the hydration profile. By modeling the profile of the surface hydrogen concentration versus depth the age determination is reached via equations describing the diffusion process. Finite difference modeling and essential assessments of the novel SIMS-SS (surface saturation) phenomenological method produce a sound basis for the new diffusion age equation and provides promising results. This review refers on the development of obsidian hydration dating (OHD) and diffusion process in glass and reckons future directions of SIMS applications in obsidians.

SIMS

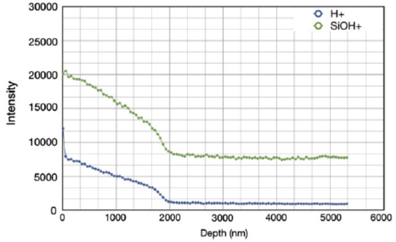
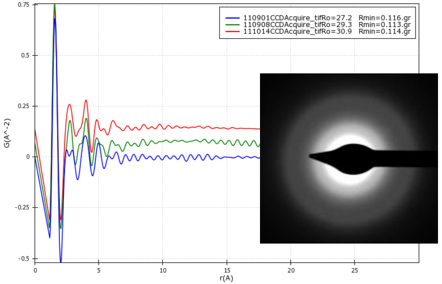


Fig. 9. Depth profile of Hydrogen (H) and silanol groups (SiOH).

TEM



MOTIVATION : OBSIDIAN HYDRATION DATING WITH TEM MICROSCOPY

NanoMEGAS
Advanced Tools for electron diffraction

Obsidians : more than 10.000 years old history

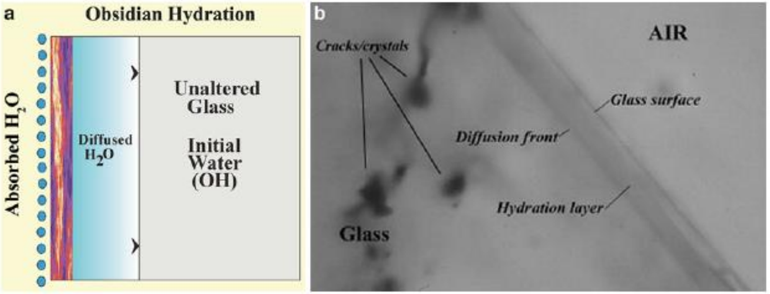
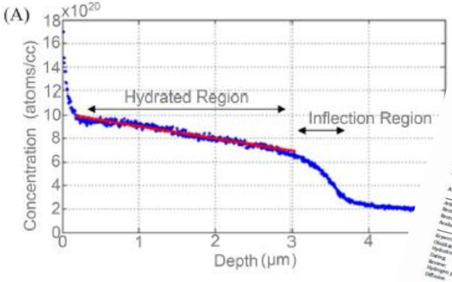
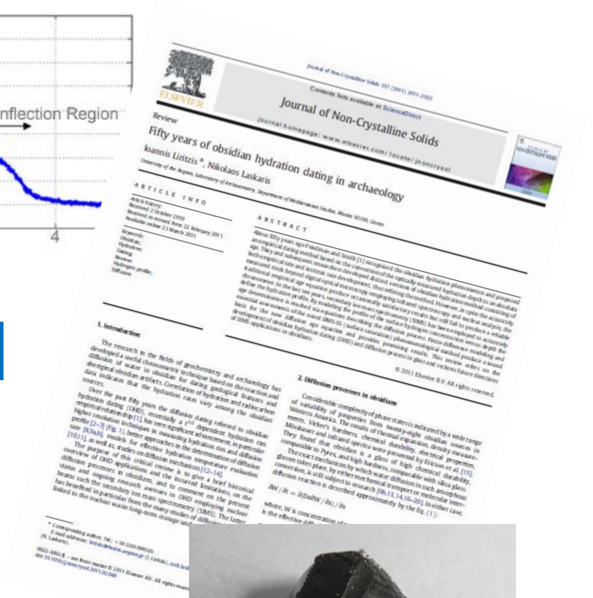


Fig. 1 (a) Schematic diagram of obsidian hydration of diffused water, (b) obsidian hydration rim seen through optical microscopy





OBSIDIAN HYDRATION DATING WITH SIMS

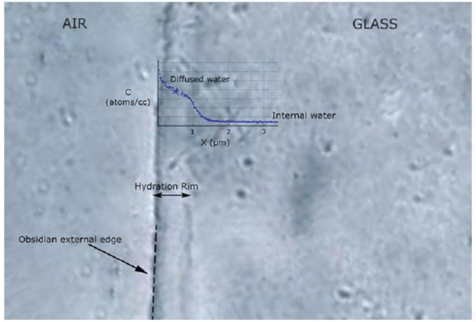


Fig. 3 Overlapping of SIMS H$^+$ profile in atoms/cc versus depth, on the hydration layer (rim), into the obsidian glass (Liritzis and Laskaris 2011)

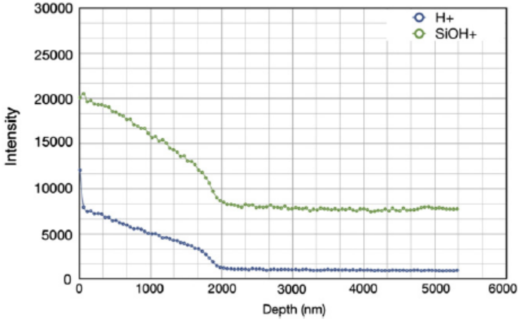
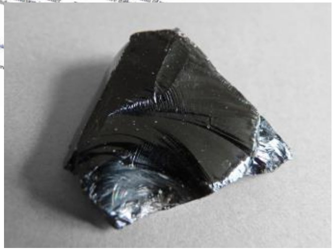
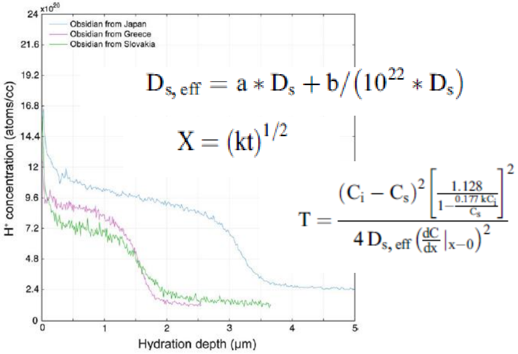


Fig. 9. Depth profile of Hydrogen (H) and silanol groups (SiOH).



NanoMEGAS
Advanced Tools for electron diffraction

Obsidians : more than 10.000 years old history



$$D_{s,\,eff} = a * D_s + b/(10^{22} * D_s)$$

$$X = (kt)^{1/2}$$

$$T = \frac{(C_i - C_s)^2 \left[\frac{1.128}{1 - \frac{0.177\,kC_i}{C_s}}\right]^2}{4\,D_{s,\,eff} \left(\frac{dC}{dx}\Big|_{x-0}\right)^2}$$

Fig. 2 SIMS H+ profiles for three samples from Greece, Japan, and Slovakia

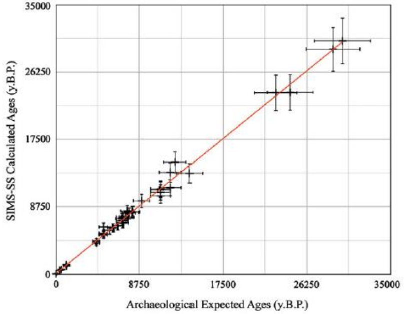
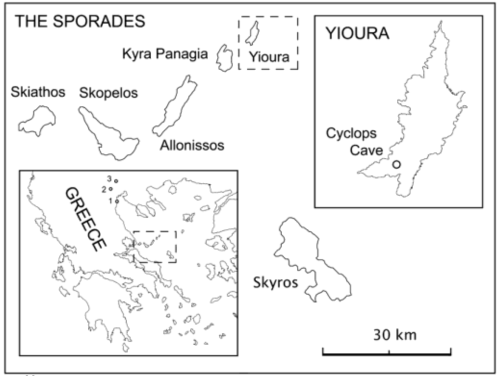


Fig. 5 SIMS-SS versus ^{14}C/archaeological ages for obsidians all over the world (Liritzis and Laskaris 2011)

CASE STUDY : OBSIDIAN HYDRATION DATING FROM GREECE



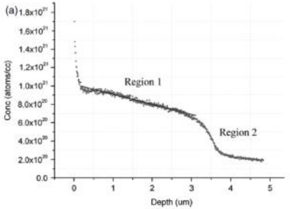
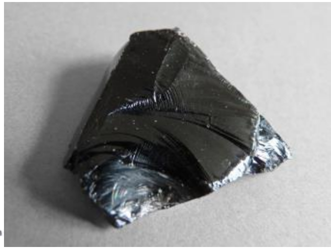
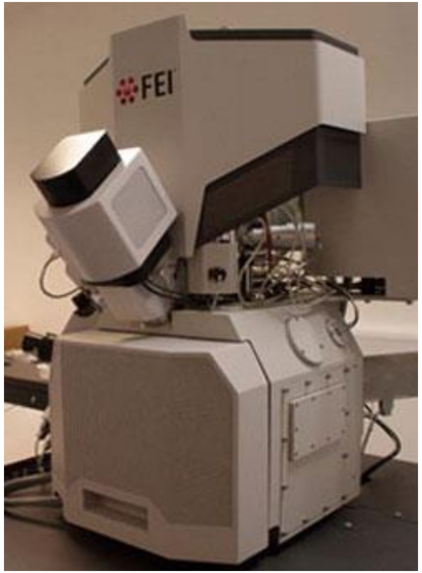


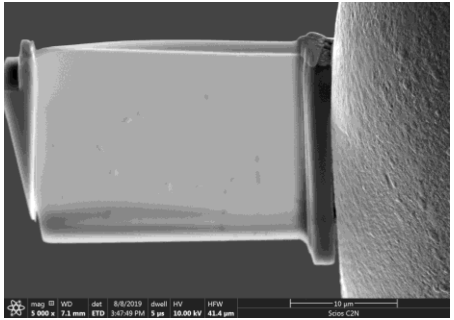
Figure 3. (a) SIMS profile of YR-2 from Yali island, with the linear regression Diffusion regions 1 and 2, are shown (see text).



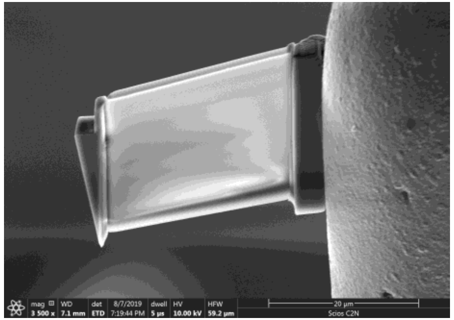
Cyclops cave, Gioura island, Greece

Obsidians : FIB Specimen preparation

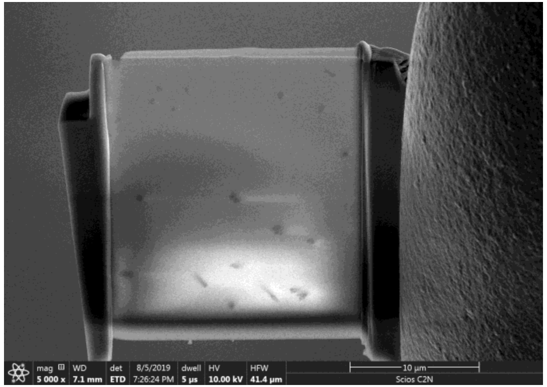




Sample SAR 9



Sample Rho 1024



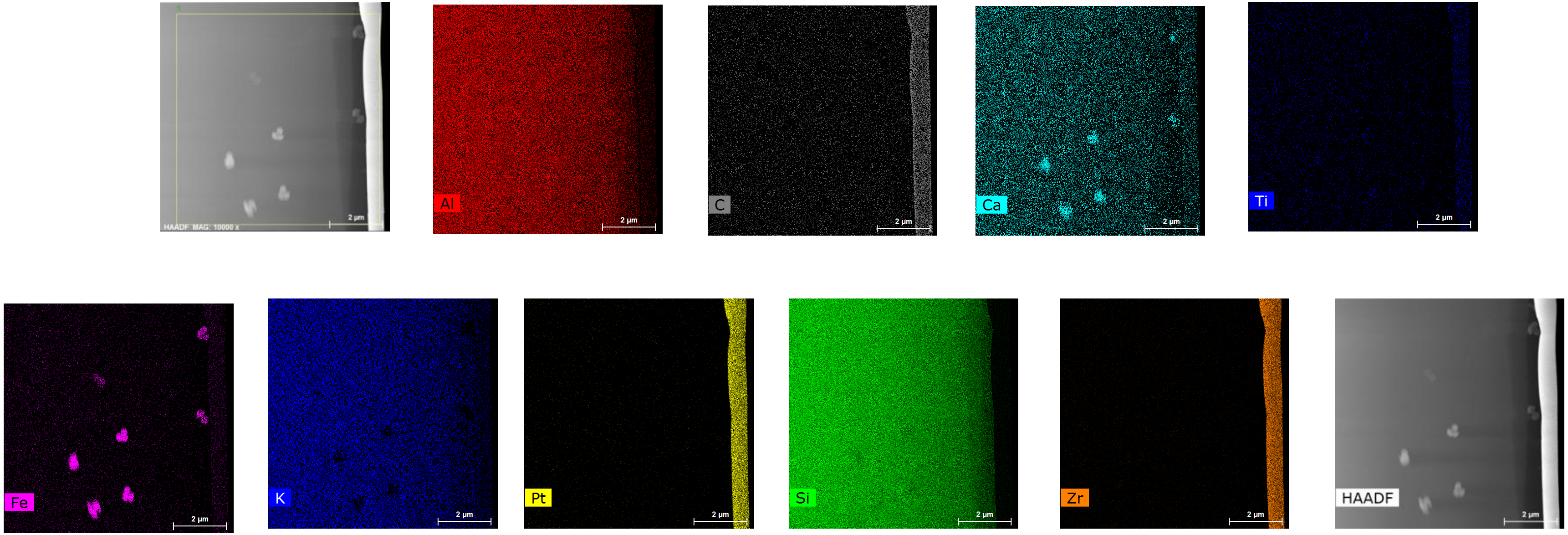
Sample YR-3

NanoMEGAS
Advanced Tools for electron diffraction

Obsidians : more than 10.000 years old history

Samples	Depth µm	AGE y BP	SIMS	AFM	TOF-SIMS	SEM
Desf / Rho- 1024, Desfina near Delphi	2,2	10635	✓		✓	
YR-3, Youra Cave of Cyclops	3,5	12017	✓	✓		✓

Sample YR-3 EDS map area 1

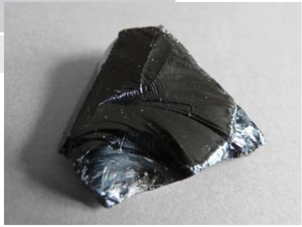


NanoMEGAS
Advanced Tools for electron diffraction

Obsidians : more than 10.000 years old history

Average composition obtained on a large area (about 6µm2), avoiding large precipitates.

Element	AN	series	Net	[wt.%]		[norm. at.%]	Error in wt.% (1 Sigma)
Oxygen	8	K-series	162376	47,28269		61,52257	1,448319
Silicon	14	K-series	202302	39,7055		29,43097	0,115098
Aluminium	13	K-series	38231	5,462957		4,214995	0,053124
Sodium	11	K-series	12316	2,408474		2,180938	0,100444
Potassium	19	K-series	15929	3,214235		1,711417	0,125128
Calcium	20	K-series	5377	1,147026		0,595804	0,063234
Iron	26	K-series	1941	0,564252		0,210334	0,046227
Magnesium	12	K-series	471	0,093784		0,080328	0,030157
Titanium	22	K-series	480	0,121079		0,052644	0,031609
			Sum:	100		100	



NanoMEGAS
Advanced Tools for electron diffraction

Amorphous Obsidians : Structural characterization by e-PDF

Eur. J. Mineral.
2006, **18**, 745–752

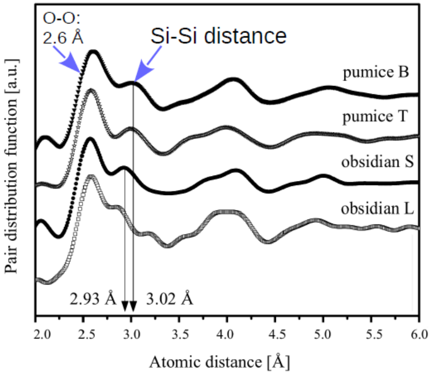
Amorphous and partly ordered structures in SiO_2 rich volcanic glasses. An ED study

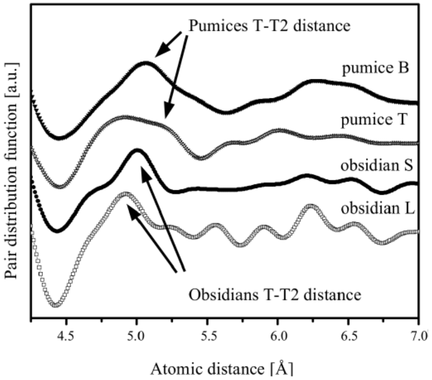
VIKTÓRIA KOVÁCS KIS[1, 2,*], ISTVÁN DÓDONY[2] and JÁNOS L. LÁBÁR[1]

[1]Research Institute for Technical Physics and Materials Science, P.O.Box. 49, 1525 Budapest, Hungary
[2]Department of Mineralogy, Eötvös Loránd University, Pázmány Péter sétány 1/c, 1117 Budapest, Hungary
*Corresponding author, e-mail: kis@mfa.kfki.hu

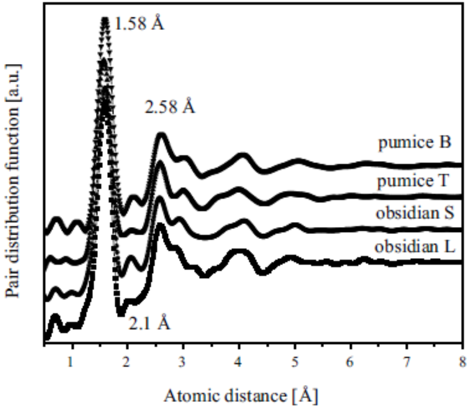
Abstract: Glass structures of obsidian and pumice samples were measured using electron diffraction. Amorphous, partly ordered, and nanocrystalline regions were distinguished and analysed separately. The deconvoluted atomic distances obtained from experimental diffraction patterns through total pair-distribution functions are consistent with distances for ideal SiO_4 tetrahedra. Partly ordered structures in pumices are composed of plate-like fragments of tridymite/cristobalite layers, whereas obsidian contains quartz nanocrystals with abundant moganite-like planar faults. The validity of the structure-model of Goodman for silica glasses is discussed and an alternative interpretation is proposed for silicic volcanic glasses.

Key-words: glass structure, obsidian, pumice, electron diffraction.





Kis et al. (2006)



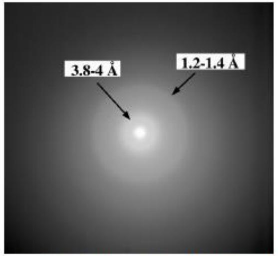
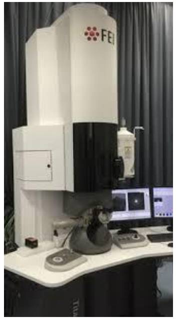


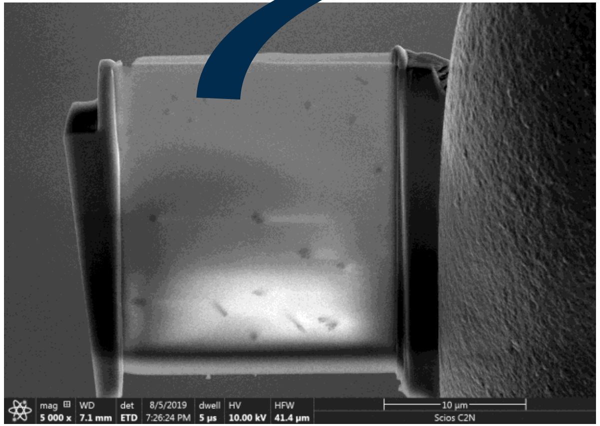
Fig. 3. Typical ED pattern of a poorly ordered glass (major component of both pumices and obsidians). The arrows show two diffuse rings. The scale of intensities is logarithmic (sample pumice T).

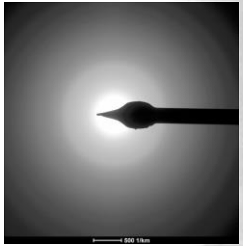
	Si-O	Si-Si		Si-Si2		Si-Si3	
	Å	Å	Si-Si/Si-O	Å	Si-Si/Si-O	Å	Si-Si/Si-O
Quartz	1.59	3.04	1.91	4.36	2.74	5.76	3.62
				4.72	2.97		
				4.91	3.09		
Tridymite	1.55	3.11	2.01	5.05	3.26	5.93	3.83
				5.06	3.26		
Cristobalite	1.55	3.10	2.00	5.06	3.26	5.90	3.81
Pumice B	1.58	3.01	1.91	5.07	3.21	5.91	3.74
Pumice T	1.57	3.00	1.91	4.91	3.13	6.02	3.83
				5.11	3.25		
Obsidian S	1.58	2.93	1.85	4.73	2.99	5.95	3.77
				4.99	3.16		
Obsidian L	1.58	2.88	1.82	4.91	3.11	5.91	3.74
		3.19	2.02				

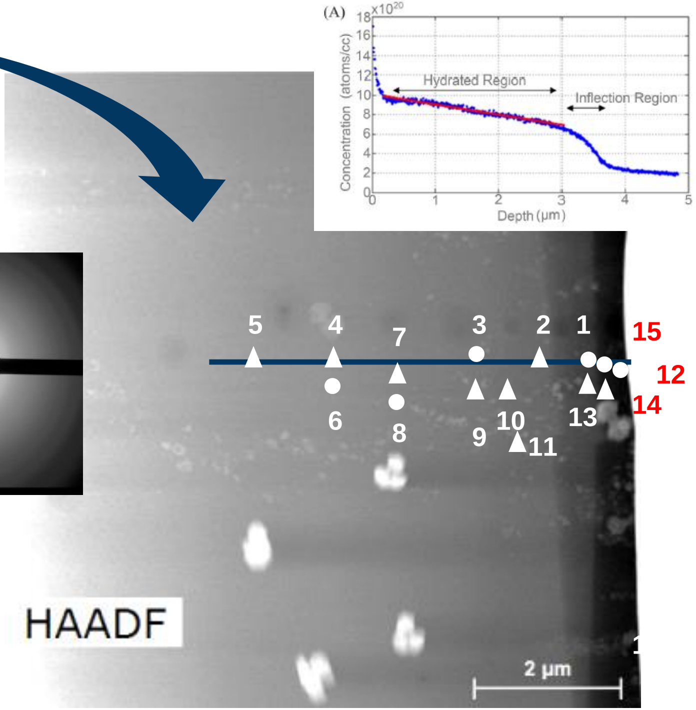
NanoMEGAS
Advanced Tools for electron diffraction

Obsidians : sampling for ED and e-PDF



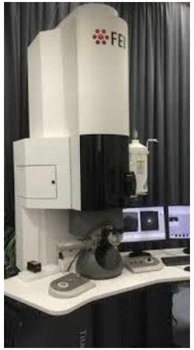


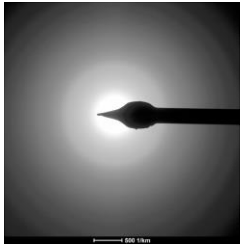


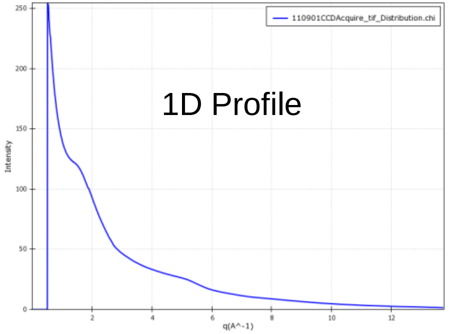


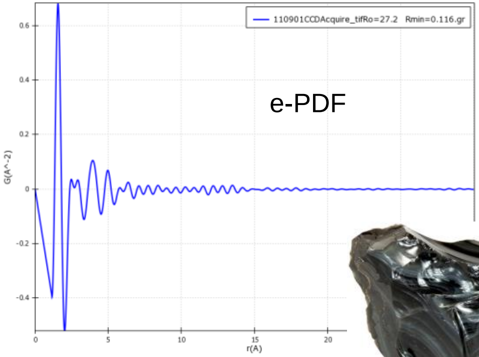
Idea : correlate atomic distances determined from e-PDF with hydration layer and presence of structural H_2O

Amorphous Obsidians : Structural characterization by e-PDF





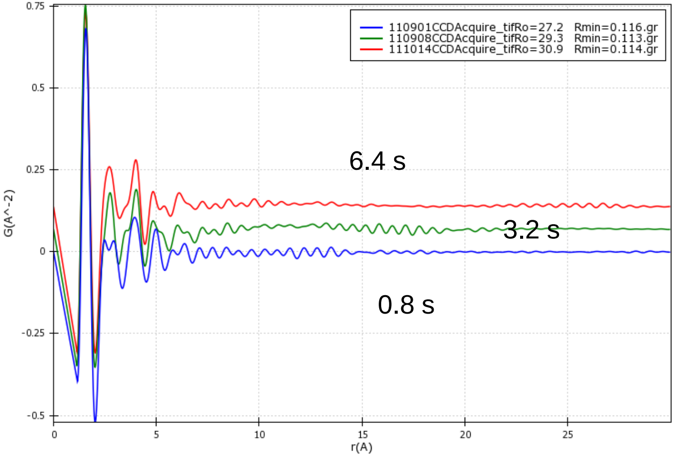




<u>Position 1</u>
672 nm   from surface

e-PDF calculated from 3 data sets

11.09.01   0.8 s
11.09.08   3.2 s
11.10.14   6.4 s



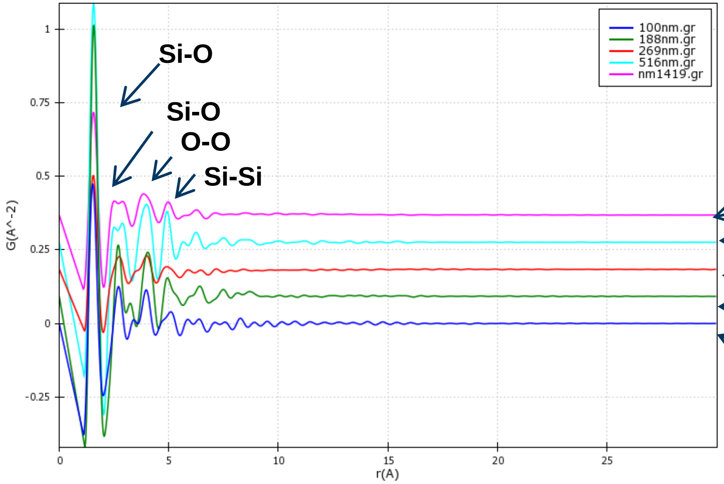
Q values for all the data varies 12-13 Å-1

e-PDF has been calculated using e-PDF suite and Process Diffraction software

Datasets from different exposure times can be added in condition that are collected in the same experimental conditions (eg beam focus is not changed between different exposures)

NanoMEGAS
Advanced Tools for electron diffraction

Amorphous Obsidians : Structural characterization by e-PDF



Correlate atomic distances determined from e-PDF with hydration layer and presence of structural H_2O

Position11 (1419 nm from surface)

Position13 (516nm from surface)

Position14 (269 nm from surface)

Position15 (188 nm from surface)

Position12 (100 nm from surface)

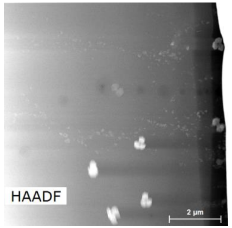
Away from surface

ED pattern and e-PDF from each position

Table 1. Interatomic distances [Å] from SAED measurements and selected X-ray-based data from literature. Some tetrahedral cation (T) and oxygen (O) distances are assigned according to literature (Zotov *et al.* 1989). The O-O2 distances fall into the range of 4.5–5.0 Å, close to the T-T2 ones, they are listed together. The errors in the interatomic distances derived from SAED are ±0.02–0.03 Å.

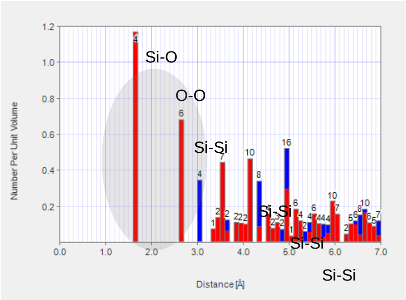
sample	T-O1		O-O1	T-T1			T-T2 O-O2				
pumice B	1.58	2.09	2.59	3.01	3.56	4.06	5.07		5.91	6.26	6.5
pumice T	1.57	2.06	2.58	3.01	3.67	3.98	4.91; 5.11	5.68	6.02		6.44
obsidian S	1.58	2.05	2.56	2.93	3.83	4.08	4.73; 4.99	5.41	5.95	6.21	6.52
obsidian L	1.58	2.01	2.58	2.88; 3.19	3.58	4	4.91; 5.24	5.56	5.91	6.22	6.53
Perlite[a]	1.61–1.62		2.65–2.68	3.15–3.18		4.12–4.16	5.13–5.26				
Obsidian[b]	1.64			3.1		4.13	5.05				

[a]Zotov et al. (1989)
[b]Deganello et al. (1998)

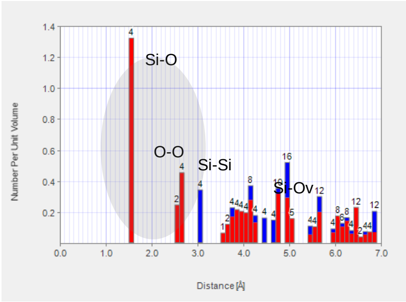


NanoMEGAS
Advanced Tools for electron diffraction

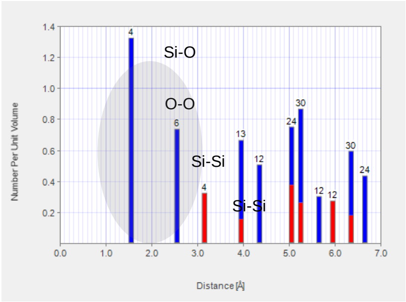
Quartz (alpha) @298K



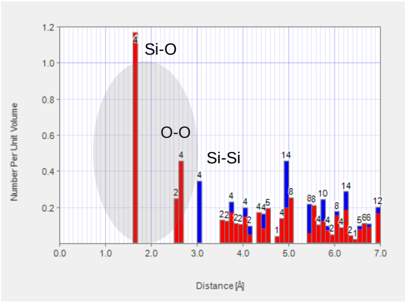
Quartz (beta) @1078K



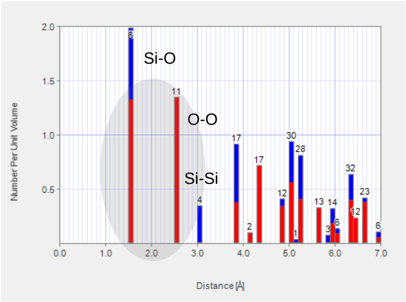
cristobalite-0 (idea#DA8C6.cif



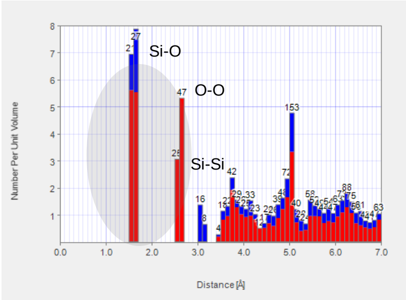
Cristobalite-I (alpha).



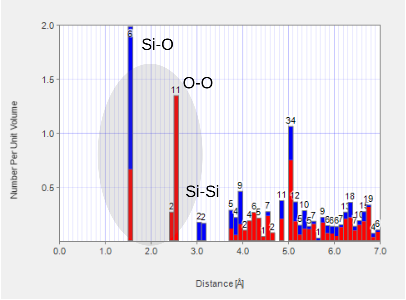
Tridymite (HP-hexagonal)



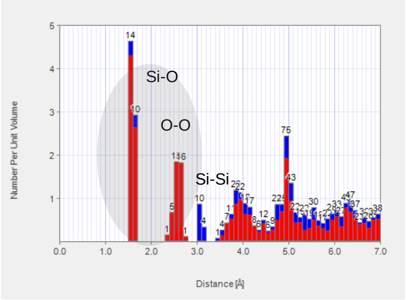
Tridymite (MP-monoclinic)



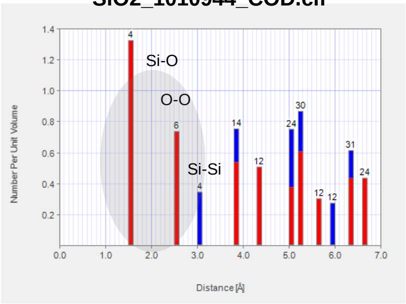
Tridymite (OC-orthor)



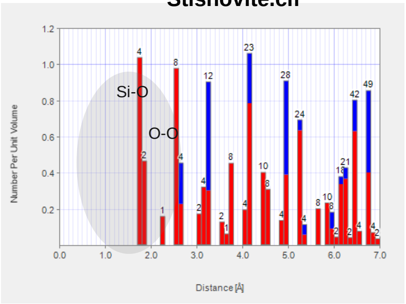
Tridymite (OC-orthor)

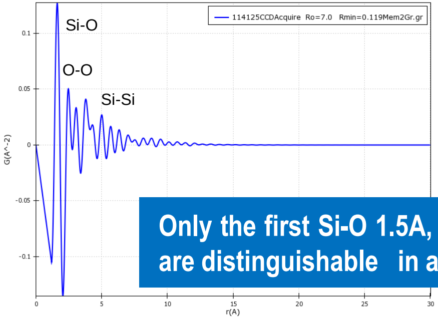


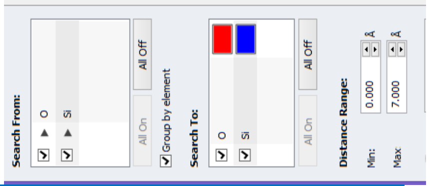
SiO2_1010944_COD.cif



Stishovite.cif

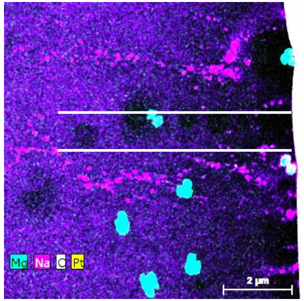






Only the first Si-O 1.5A, 2.4A O-O and 3.4A Si-Si distances are distinguishable in all SiO2 polymorphs

We examine experimental variations of ONLY reliable Si-O 1.5 A and 2.4 A O-O distances from e-PDF with distance from surface



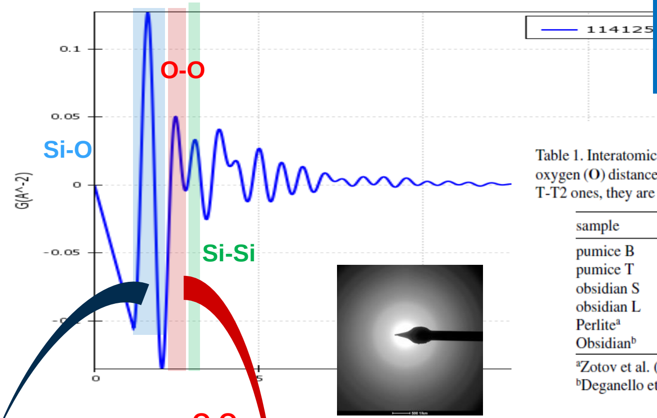


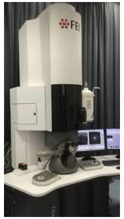
Table 1. Interatomic distances [Å] from SAED measurements and selected X-ray-based data from literature. Some tetrahedral cation (**T**) and oxygen (**O**) distances are assigned according to literature (Zotov *et al.* 1989). The O-O2 distances fall into the range of 4.5–5.0 Å, close to the T-T2 ones, they are listed together. The errors in the interatomic distances derived from SAED are ±0.02–0.03 Å.

sample	T-O1		O-O1	T-T1			T-T2 O-O2				
pumice B	1.58	2.09	2.59	3.01	3.56	4.06	5.07		5.91	6.26	6.5
pumice T	1.57	2.06	2.58	3.01	3.67	3.98	4.91; 5.11	5.68	6.02		6.44
obsidian S	1.58	2.05	2.56	2.93	3.83	4.08	4.73; 4.99	5.41	5.95	6.21	6.52
obsidian L	1.58	2.01	2.58	2.88; 3.19	3.58	4	4.91; 5.24	5.56	5.91	6.22	6.53
Perlite[a]	1.61–1.62		2.65–2.68	3.15–3.18		4.12–4.16	5.13–5.26				
Obsidian[b]	1.64			3.1		4.13	5.05				

[a]Zotov et al. (1989)
[b]Deganello et al. (1998)

Si-O

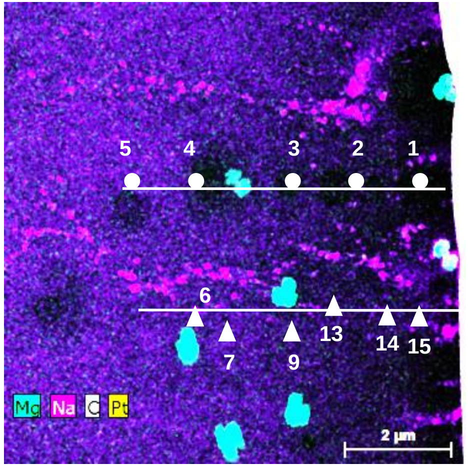
O-O

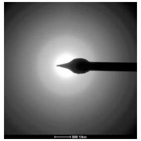


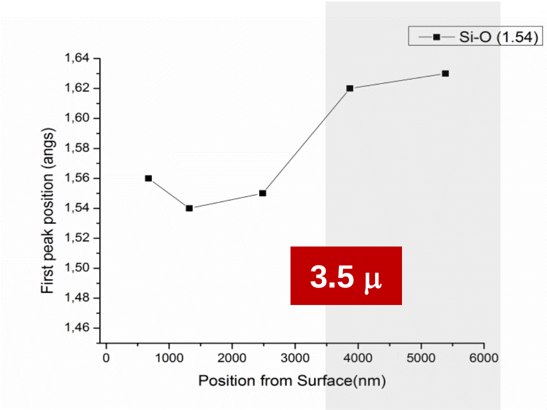
O1(X1)	A(X2)	B(Y2)	C(Y2)	D(Y2)	M1(Y2)	N1(Y2)	E(Y2)	F(Y2)	G(Y2)	H(Y2)	I(Y2)	J(Y2)	K(Y2)	L(Y2)
nm		angstrom		angstrom		angstrom		angstrom		angstrom		angstrom		angstrom
nm	Position	Si-O (1.54)		O-O (2.52)		Si-Si (3.08)		Si-O (3.87)		O-O (4.36)		O-O/Si-Si (5.03)		Si-O/O-O (5.26/5.63)
672	Position1	1,56	Position1	2,4	Position1		Position1	3,44	Position1	4,04	Position1	4,81	Position1	5,44
1322	Position2	1,54	Position2	2,31	Position2	2,86	Position2	3,53	Position2	4,13	Position2	4,86	Position2	5,53
2484	Position3	1,55	Position3	2,4	Position3	2,99	Position3	3,68	Position3	4,27	Position3	4,97	Position3	5,65
3870	Position4	1,62	Position4	2,4	Position4	3,05	Position4	3,72	Position4	4,35	Position4	5,01	Position4	5,69
5387	Position5	1,63	Position5	2,41	Position5	3,07	Position5	3,75	Position5	4,36	Position5	5,01	Position5	5,68
3710	Position6	1,52	Position6	2,33	Position6	2,94	Position6	3,62	Position6	4,21	Position6	4,91	Position6	5,64
3065	Position7	1,54	Position7	2,3	Position7	2,83	Position7	3,46	Position7	4,04	Position7	4,77	Position7	5,35
3000	Position8	1,58	Position8	2,22	Position8	2,71	Position8	3,29 & 3.88	Position8	4,46	Position8	5,03	Position8	5,59
2484	Position9	1,6	Position9	2,43	Position9	3,1	Position9	3,83	Position9	4,49	Position9	5,1	Position9	[illegible]
1645	Position10	1,52	Position10	2,65	Position10	3,31	Position10	3,96	Position10	4,66	Position10	5,21	Position10	[illegible]
1419	Position11	1,59	Position11	2,35	Position11	2,89	Position11	3,45 & 3.95	Position11	4,52	Position11	5,04	Position11	[illegible]
1000	Position12	1,55	Position12	2,53	Position12	3,33	Position12	--	Position12	4,02	Position12	4,95	Position12	[illegible]
516	Position13	1,58	Position13	2,39	Position13	3	Position13	3,8	Position13	4,93	Position13	--	Position13	[illegible]
269	Position14	1,56	Position14	2,4	Position14	3,4	Position14	4,02	Position14	4,8	Position14	5,42	Position14	[illegible]
188	Position15	1,58	Position15	2,49	Position15	3,31	Position15	4,05	Position15	4,86	Position15	--	Position15	[illegible]
--	--	--	--	--	--	--	--	--	--	--	--	--	--	[illegible]
--	--	--	--	--	--	--	--	--	--	--	--	--	--	[illegible]
--	--	--	--	--	--	--	--	--	--	--	--	--	--	[illegible]
188	Position15	1,58	Position15	2,49	Position15	3,31	Position15	4,05	Position15	4,86	Position15	--	Position15	[illegible]
269	Position14	1,56	Position14	2,4	Position14	3,4	Position14	4,02	Position14	4,8	Position14	5,42	Position14	[illegible]
516	Position13	1,58	Position13	2,39	Position13	3	Position13	3,8	Position13	4,93	Position13	--	Position13	[illegible]
672	Position1	1,56	Position1	2,4	Position1	--	Position1	3,44	Position1	4,04	Position1	4,81	Position1	[illegible]
1000	Position12	1,55	Position12	2,53	Position12	3,33	Position12	--	Position12	4,02	Position12	4,95	Position12	5,85
1322	Position2	1,54	Position2	2,31	Position2	2,86	Position2	3,53	Position2	4,13	Position2	4,86	Position2	5,53
1419	Position11	1,59	Position11	2,35	Position11	2,89	Position11	3,45 & 3.95	Position11	4,52	Position11	5,04	Position11	5,61
1645	Position10	1,52	Position10	2,65	Position10	3,31	Position10	3,96	Position10	4,66	Position10	5,21	Position10	5,88
2484	Position3	1,55	Position3	2,4	Position3	2,99	Position3	3,68	Position3	4,27	Position3	4,97	Position3	5,65
2484	Position9	1,6	Position9	2,43	Position9	3,1	Position9	3,83	Position9	4,49	Position9	5,1	Position9	5,88
[illegible]	[illegible]	1,58	Position8	2,22	Position8	2,71	Position8	3,29 & 3.88	Position8	4,46	Position8	5,03	Position8	5,59
[illegible]	[illegible]	1,54	Position7	2,3	Position7	2,83	Position7	3,46	Position7	4,04	Position7	4,77	Position7	5,35
[illegible]	[illegible]	1,52	Position6	2,33	Position6	2,94	Position6	3,62	Position6	4,21	Position6	4,91	Position6	5,64
[illegible]	[illegible]	1,62	Position4	2,4	Position4	3,05	Position4	3,72	Position4	4,35	Position4	5,01	Position4	5,69
[illegible]	[illegible]	1,63	Position5	2,41	Position5	3,07	Position5	3,75	Position5	4,36	Position5	5,01	Position5	5,68

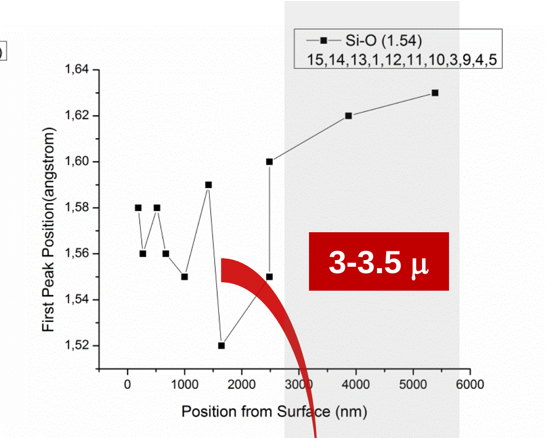
NanoMEGAS
Advanced Tools for electron diffraction

Amorphous Obsidians : Hydration layer by e-PDF ?

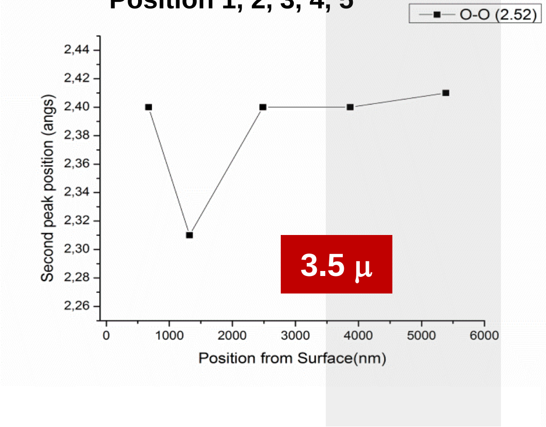


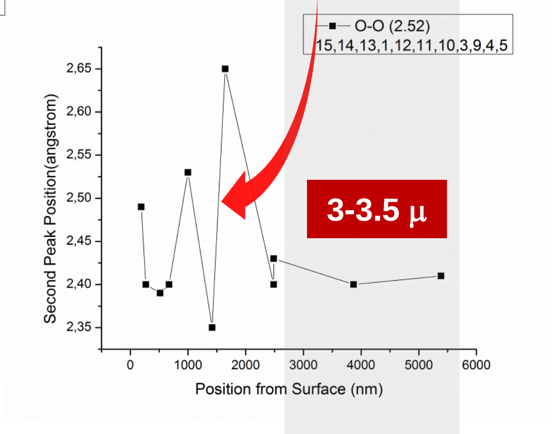






Position 1, 2, 3, 4, 5



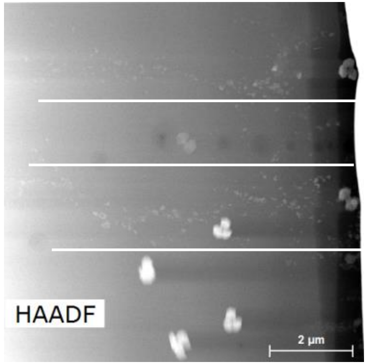


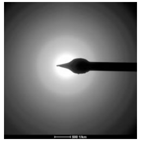
Local variations of Si-O and O-O distances show variations with distance from surface; such variations may depend on local water content and also local defects/change stoichiometry (arrow)

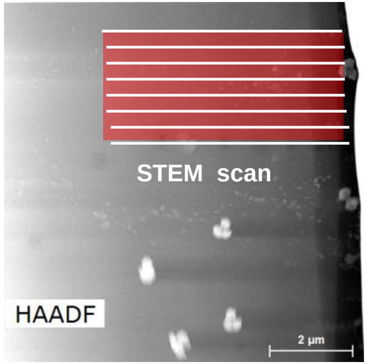
Local Si-O and O-O variations show probable stabilization after 3,5 µ (in agreement with SIMS) probably related to limit of hydration layer ?

NanoMEGAS
Advanced Tools for electron diffraction

CONCLUSIONS – FURTHER EXPERIMENTAL STUDY

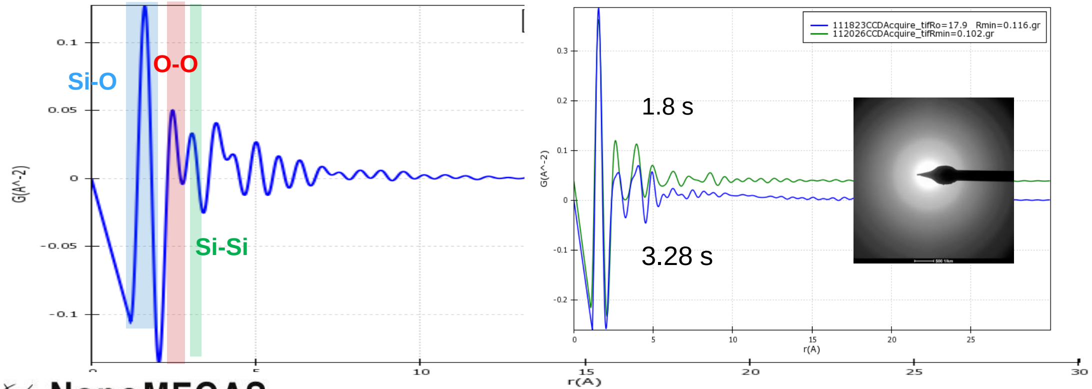






Amorphous Obsidians : further confirm hydration layer by e-PDF

NEED for take ED patterns from various data points along "a line" from the surface up to 6 micron deep inside ; an area can be also scanned with STEM to generate e-PDF maps.
ALL ED patterns shoud be away from defects, precipitates & structural inhomogeneities.



To have more reliable e-PDF (eg distinguish clearly Si-Si 3.3A distances on ALL e-PDF spectra we need to increase ED exposure time

NanoMEGAS
Advanced Tools for electron diffraction