Standard Project

Experimental Report

Proposal title: Water mechanical properties under 1-D confinement, inside 100 to 5 nm-deep silicon nano-channels		**Proposal number:** 201403864
Beamline: CRG-IF	**Date(s) of experiment:** from: 27/08/2014 to: 02/09/2014	**Date of report:** 10th october 2013
Shifts: 18	**Local contact(s):** François RIEUTORD	*Date of submission:* 13th october 2013

Objective & expected results (less than 10 lines):
Our objective is to better understand how the thermodynamic properties of trapped liquid change due to the host channel size, with capillary and/or disjoining pressure effects, mimicking what arise in natural and technical settings. We hope to get quantitative information about the deformation of the monocrystalline container when the channels are entirely filled with water or only partially filled giving rise to capillary menisci (and then to capillary tension). The quantitative measurements obtained as a function of the channel sizes (4 µm wide, 3 mm long, 5 to 50 nm deep; Fig. 1) should result in a clear understanding of the role of capillarity, disjoining pressure, and solid-liquid adhesion on the water thermodynamics but also on channels geomechanics.
These measurements will give us entirely new insights about the dependency between the structure of one porous media, its drying-filling history, and the properties of the infilling solutions. In particular, the quantization of the channels size as a function of the local conditions, or the stress induced in the host solid by the guest liquid, with potential influence on the mechanical strength and permeability of the solid matrix, should greatly improve our understanding of the reactive transport in finely porous media, but has also interesting connections with the fatigue processes in solids.

Results and the conclusions of the study (main part):
The silicon wafers used during this experiment have the following design (Fig. 1).

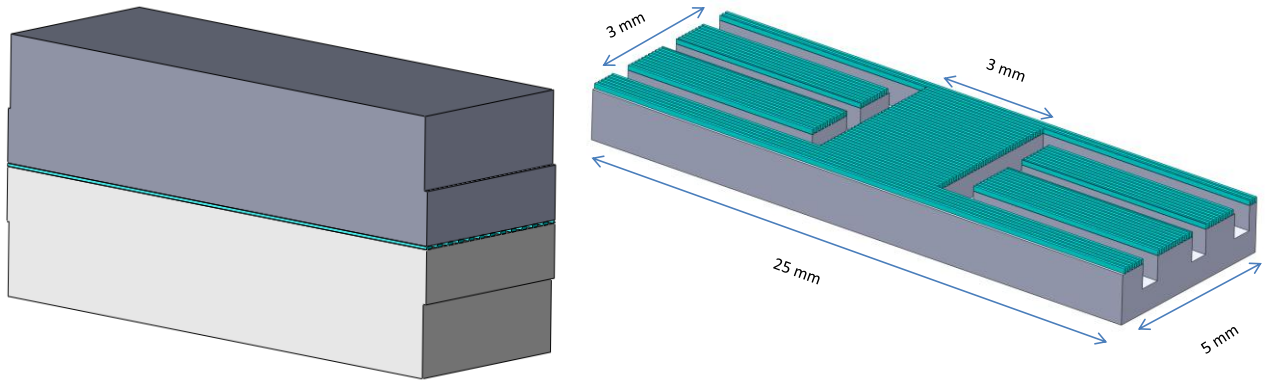


Fig. 1. Global view (left), and bottom wafer look at the one-chip size (right, with characteristic distances) after nano-channels patterning.

The principle was quite clear: measuring the fringe contrasts and fringe width as a function of the channels filling = i) dry air conditions, as trapped during the clean room fabrication, ii) liquid water conditions by continuous infilling from a connected reservoir, and then iii) liquid-air partitioning conditions after a drying stage simply induced by disconnecting the reservoir and connecting the two sides of the chips to a primary vacuum pump (1 mbar). Special sample holders with the required environment (parallel connections, primary pumps, etc.) were developed before the run for that filling/drying purposes at the ISTO workshop in Orléans: everything worked well on that respect.
The whole run proceeded in two steps (Fig. 2), the first was devoted to adjust different settings to homogeneize the protocole and make it exactly reproducible. This was the topic of the #16 to #395 records as reported in the left part of Fig. 2. The first key conclusion was about the settings of the “transversal z, trz” that ensures that the beam is always at the center of the chip when the grazing angle increases. Usually, this setting is of small importance because it only modifies the beam spreading along the 5mm width of the chip. In this case, due to the low signal and the relative importance of sides effects (not so well understood, btw), this positioning plays a strong role to obtain reproducible measurements from one filling step to the others. Also, we decided to measure the signal at three locations along the channels lenth: at the exact center of the 3 mm length (owing to a special procedure taking advantage of the beam diffusion in the deep entrance channel, see Fig. 1), and at ± 1 mm. That enables us to visualize the progression of the

saturation/drying “wave” along the channels. The second key conclusion was about the dry state preparation: we realized that even the chips maintained closed since their fabrication was slightly impregnated by water. We included therefore a preliminary heating stage under secondary vacuum (300°C, 10^{-5} mbar), and defined this as the “dry state”. Once the protocol tuned, the different chips have been measured successively after heating under vacuum (dry state), after filling by only one side (simple imbibition) and then under capillary state which was obtained by pumping on the two sides of the chips with a primary vacuum (around 1 mbar). Each filling state was maintained around 5h-6h, the time needed to measure the series. We made two variations around this theme: the 50 nm chip was re-wetted after a first capillarizing stage, this time by connecting the two sides to a water reservoir (dual imbibition), and then simply put under hutch atmosphere (40-50% RH) to capillarize the inner channels. In the meantime, the 12 nm chip was let under imbibition conditions for two weeks in order to appreciate the kinetics of the water infilling.

Taille canaux	Etat sec	Imbibition simple		Capillarité à l'air	Pompage double	Four 295° (au vz CEN du 50 nm)
50	#16-8	#65-6	#100-1	t_1 #105-6 t_2 #107-8 t_3 #109-10 #160-161	#234-5 vz0 #239 vz-1 #243 vz-2 #247 vz1 #251 vz2 (vz scan #330)	#571-2
30	#26+28 (→ 3°) #27+29	#70-1	#114-5	#165-6 #167	#263-4 vz0 #268 vz-1 #272 vz-2 #276 vz1 #280 vz2 (vz scan #281)	#576-7
20	#33-4	#75-6	#119-20	#172-3	#285-6 vz0 #290 vz-1 #294 vz-2 #298 vz1 #302 vz2 (vz scan #303)	#581-2
15	#38-9	#80-1	#124-5	#177-8	#307-8 vz0 #312 vz-1 #316 vz-2 #320 vz1 #324 vz2 (vz scan #?)	#586-7
12	#50-1	#85-6	#129-30	#182-3 #184 #186 vz1 #192-3 vz-1	#334-5 vz0 #339 vz-1 #343 vz-2 #347 vz1 #351 vz2 (vz scan #352)	#591-2
10	#55-6	#90-1	#134-5	#197-8 (vz -1)	#365-6 vzCEN #370 vz-1 #374 vz1	#596-7
5	#60-1	#95-6	#139 #143-4 #150-1 vz1 #155 VZ0	#202-3 vz0 #207-8 vz-1 #212 vz1 #217 vz-2 #222 vz2 vz scan #226	#388-9 vzCEN #392 vz-1 #395 vz1	#601-2

Barrettes d'origine, mises au four en sortie de boites

Alignement du barycentre de barrette par rapport au faisceau, au moins à partir des mesures en imbibition

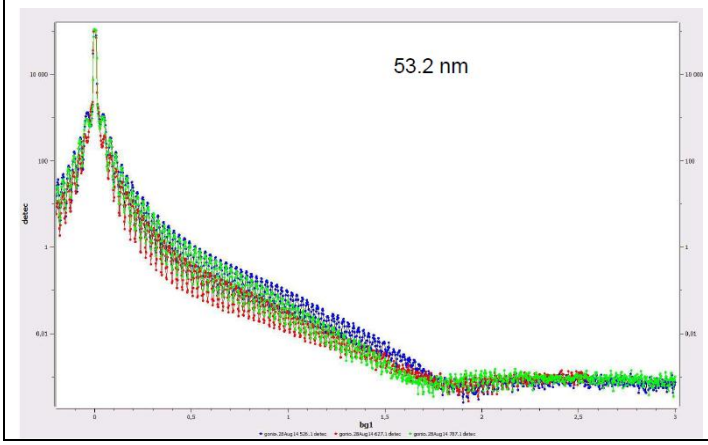
Taille canaux	Four 195° / 300° / 25° (au vz CEN du 50 nm)			Imbibition simple	Pompage double	Imbibition double	Capillarité à l'air
50	#456-7	#491-2	#526-7	#623 vz-1 #627 vzCEN #633 vz1	#787-8 vzCEN #792 vz1 #796 vz-1	#888-9 vzCEN #893 vz1 #897 vz-1	#1029-30 vzCEN #1036 vz1 #1042 vz-1
30	#462-2	#496-7	#531-2	#651-2 vzCEN #656 vz1 #660 vz-1	#807-8 vzCEN #812 vz1 #816 vz-1		#1057-8
20	#466-7	#501-2	#536-7	#679-80 vzCEN #684 vz1 #688 vz-1	#842-3 vzCEN #847 vz1 #851 vz-1		#1078-9
15	#471-2	#506-7	#541-2	#700-1 vzCEN #705 vz1 #709 vz-1	#946-7 vzCEN #958 vz1 #964 vz-1		
12	#476-7	#511-2	#546-7	#725-6 vzCEN #730 vz1 #734 vz-1		#866-7 vzCEN #871 vz1 #875 vz-1	
10	#481-2	#516-7	#551-2	#746-7 vzCEN #751 vz1 #755 vz-1	#978-9 vzCEN #985 vz1 #991 vz-1		#1092-3
5	#486-7	#521-2	#556-7	#767-8 vzCEN #772 vz1 #776 vz-1	#1004-5 vzCEN #1011 vz1 #1017 vz-1		#1108-9

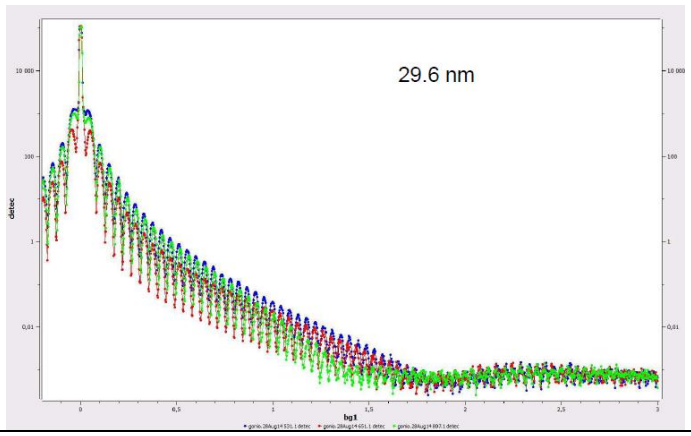
Fig. 2. Overview of all measurements perfomed during the run. The first part (left) were carried out to precisely tune the protocol and settings. To the right, the references measurements which will be treated to extract the parameters.

Figure 3 collects all the key measurements for the 6 chips ranging over one order of magnitude as for the channels depth (1D confinement). Two deviations, on the fringe contrast and on the fringe width, systematically arise at each stage, and are increasingly pronounced with the thinning of the channels:

- under saturation, the fringe contrast is around 25-30% of the dry state’s, in good agreement with the electronic densities in the air-filled and water-filled situations. Also, the fringe width decreases which was not expected meaning a corresponding swelling of the channels, most probably due to disjoining pressure effect.
- Under capillary conditions, the fringe contrast again increased (increasing air/water ratio) while the fringe width increased, displaying then the effect of capillary traction of water on the silicon layers. These two trends were highly expected, as well as a growing effect with decreasing channels depth which was also observed.

The whole series appears then as promising as expected, and the usual treatment (data inversion), already tested in the past, should result in a quantitative sketch of what is going on during water-filling cycles in thin slit-chaped channels.





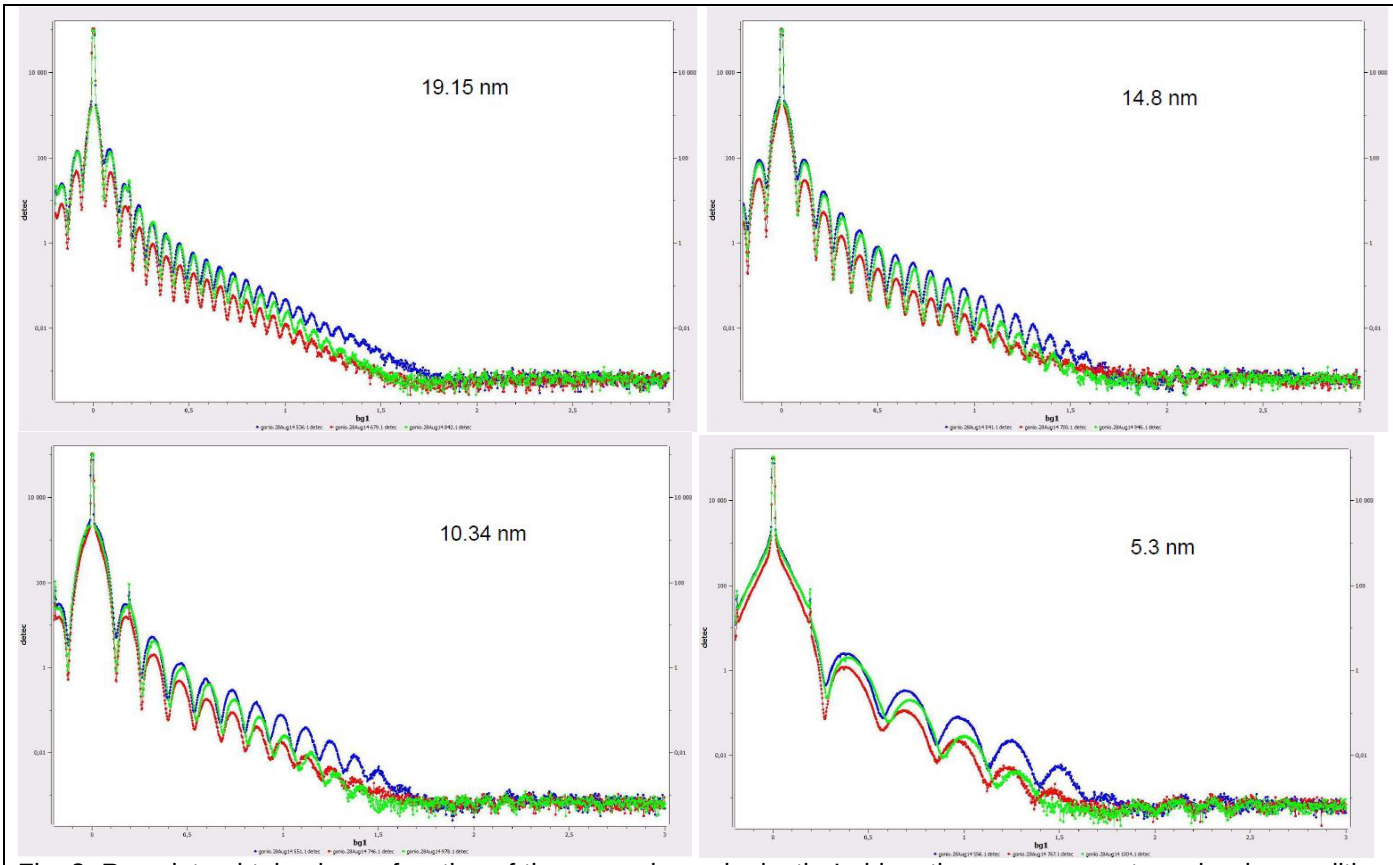


Fig. 3. Raw data obtained as a function of the nano-channels depth. In blue, the measurements under dry conditions, in red, those under fully-saturated conditions, and then, in green, the partially-filled (capillary) conditions.

The 12 nm chip let apart under imbibition conditions during the run was measured two weeks later (Fig. 4). The saturation slightly increased what is manifested by a small decrease of the fringes contrast but also by a tiny (though visible) decreasing fringes width. The two shifts, characterizing the saturation state, are then confirmed especially the surprising swelling at imbibition. After that, the chip was put under a dry N_2 gentle flush at the two extremities of the channels during one night, and the spectra systematically recorded (acquisition time: 50 min/1 hour) at three locations along the channels length. After some hours, the capillarization features (fringes width increasing) can be observed from the channels extremities, moving slowly towards the channels centre, at approximately constant fringe contrast. After some time, the fringes contrast started increasing (air/water ratio) and the fringes with (channels depth) started decreasing, what can be interpreted at first sight by an inner drying of the channels until recovering almost (not exactly) the initial features. Again, each shift confirmed the conclusions inferred previously and gives new insigth into the characteristic times and distances involved in the processes.

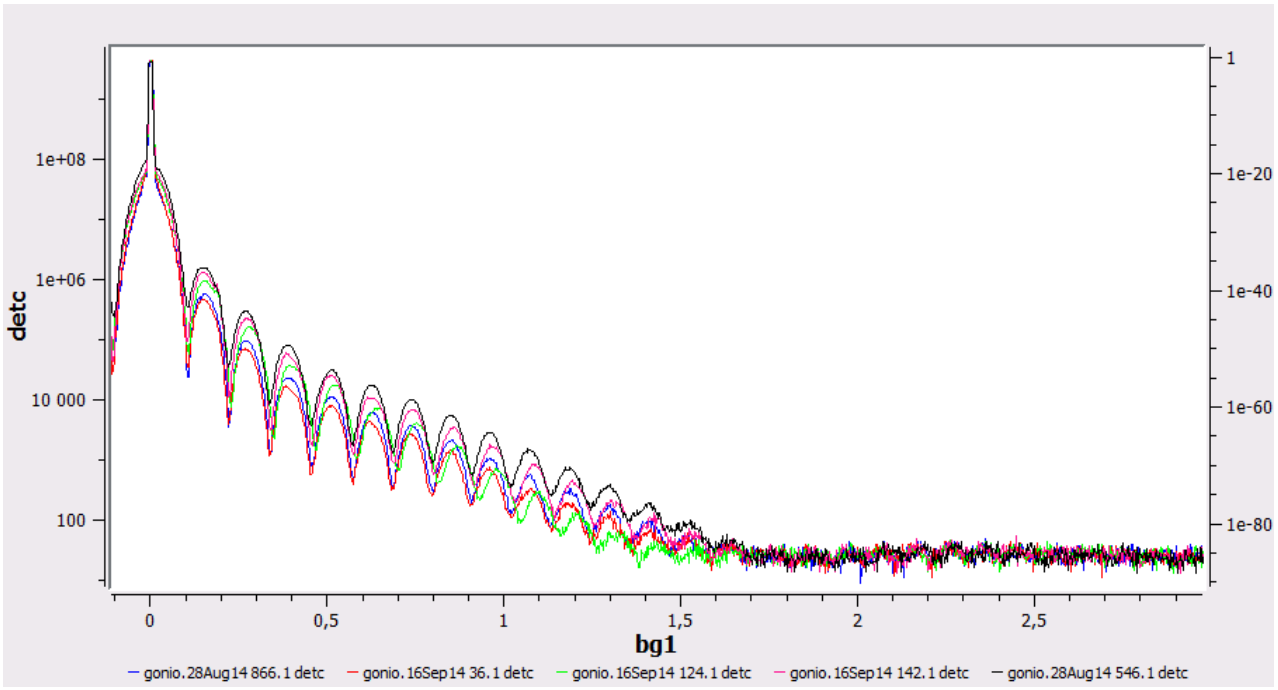


Fig. 4. Raw data obtained with the 12 nm deep nanochannels at constant saturation conditions during two weeks. Black curve was obtained under initially-dry conditions, blue (after hours) and red (after 2 weeks) under water-infilling conditions, green and pink under drying (capillary) conditions.

As a conclusion, the beamtime period has been particularly rich, giving impressive results and definite arguments to justify that wetting-drying cycles can significantly affect the local geomechanics of slit-shaped 1D-nano channels. This is a very interesting conclusion, demonstrating the coupling between saturation state in porous media and local geomechanical constraints. Another interesting track is about the fatigue effects in minerals, and how such cycles could lead to fissuration on solid matrix. At last, the existence and magnitude of capillary tension and disjoining pressure were indirectly measured meaning that any water model in porous mdia should take them into account.

Justification and comments about the use of beam time (5 lines max.)**:**
The brillance of ESRF radiation source was necessary because interfacial reflection experiments require high energies (27-30 keV typically) in a narrow beam (few 10 µm), due to the grazing angle conditions. As we are looking for minute effects (slight changes of electron density, very small thickness changes), getting access to large q_s was required to compensate for low reflectivity and the ESRF synchrotron high fluxes perfectly fited our needs. The collaboration with the local team was excellent (as usual), and offered the required assistance to optimize the conditions and reach the required high spatial resolution.

Publication(s):
- Mercury L., Rieutord F., Tardif S., Berenschot E., Tas N. (in prep.) Deformation and fatigue effects in porous media: the role of trapped liquid. Journal of Geophysical Research.