Co-crystallization, deuterium accessibility and high-temperature thermal stability of nanocelluloses containing lignin

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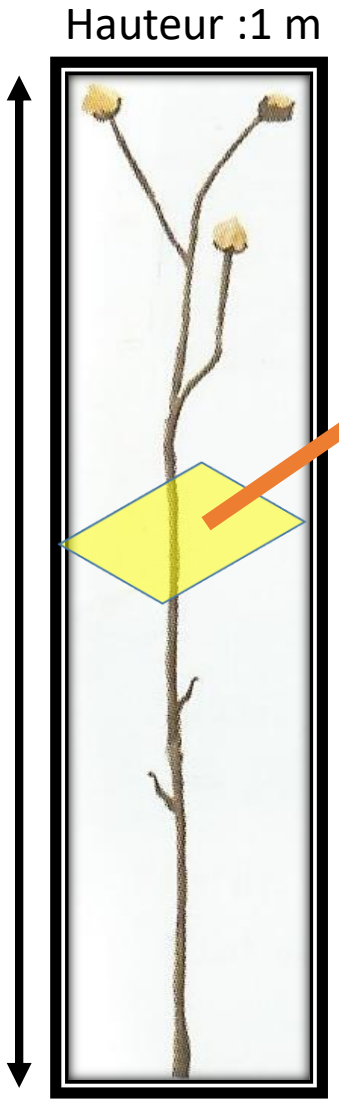
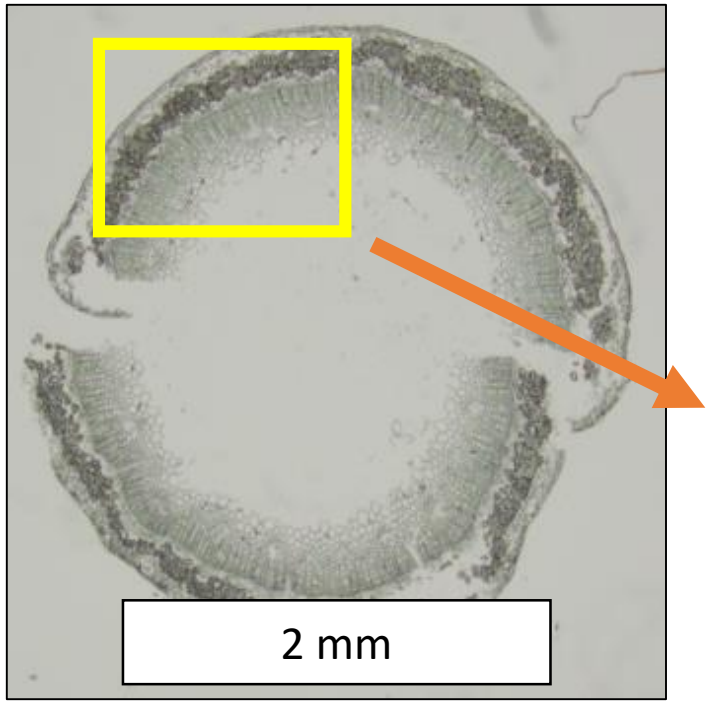
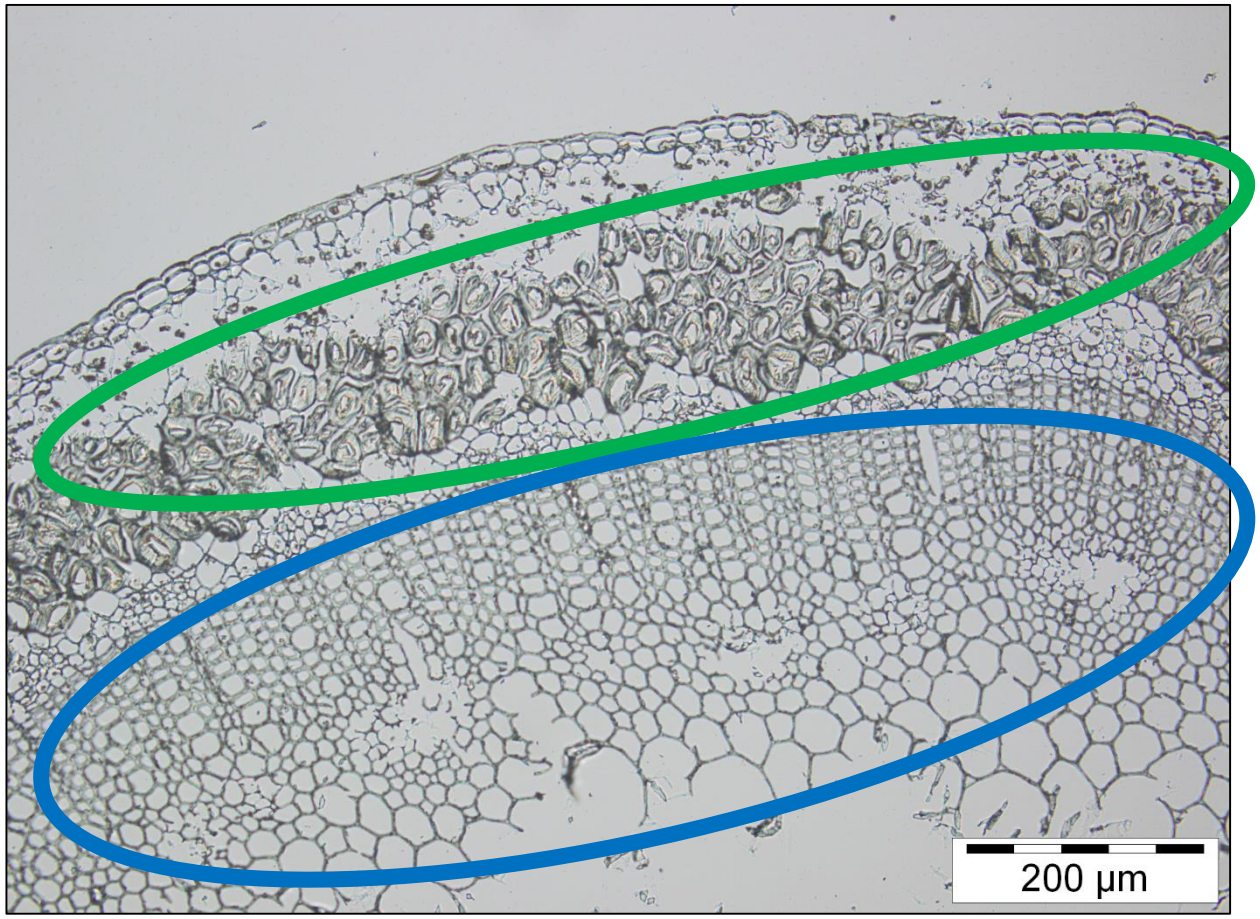
Les fibres et les anas







del Río, J. C (2011)
Sain, M. & Fortier, D (2002)
Kim, J.-W. & Mazza, G. (2006)

Fibres
65 % de cellulose
20 % de polysaccharide non cellulosique
Très peu de lignine

Anas
34-53% de cellulose
13-26% d'hémicelluloses
23-31 % de lignines

La composition (prétraitement)

Anas broyés (300 µm)

Décirage

Toluène - éthanol (2:1 v/v) pendant 20h

Traitement à la soude

5% NaOH, 24h puis 90°C pendant 5h

Blanchiment

4% H_2O_2, 6h, 45°C, milieu basique

Anas blanchis

Etape	Rendement	Rendement total
Décirage	91 %	91 %
Traitement à la soude	61 %	55 %
Blanchiment	98 %	54 %

Source	cellulose	hémicelluloses	Lignine	Autres
Lin anas	39 %	20 %	40 %	1%

Probable présence de lignine au blanchiment

Composition (FTIR et RMN)

Hémicellulose

Lignine

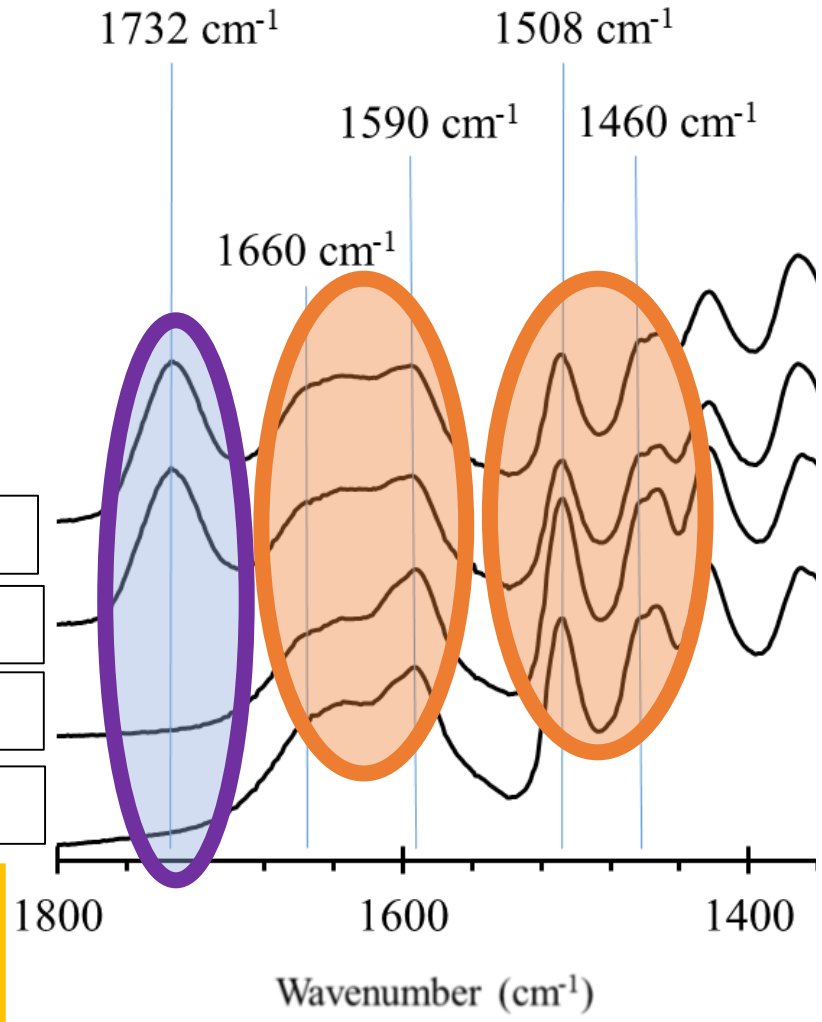
Anas broyés

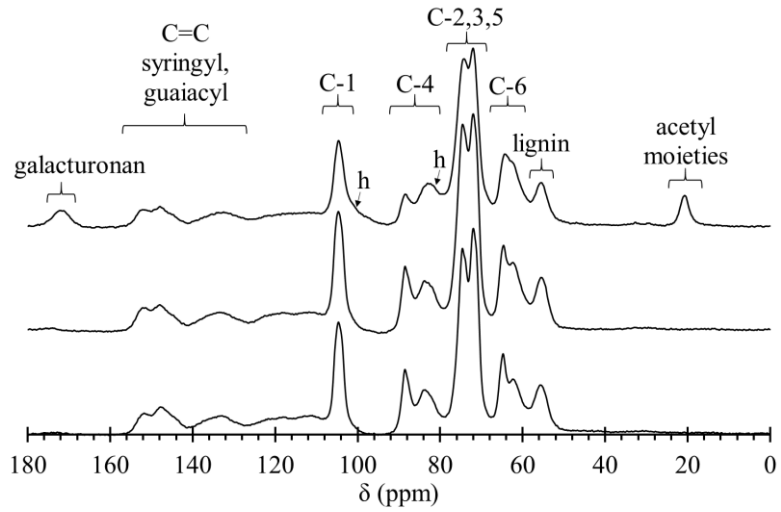
Anas décirés

Anas NaOH

Anas blanchis

Présence de lignine confirmée



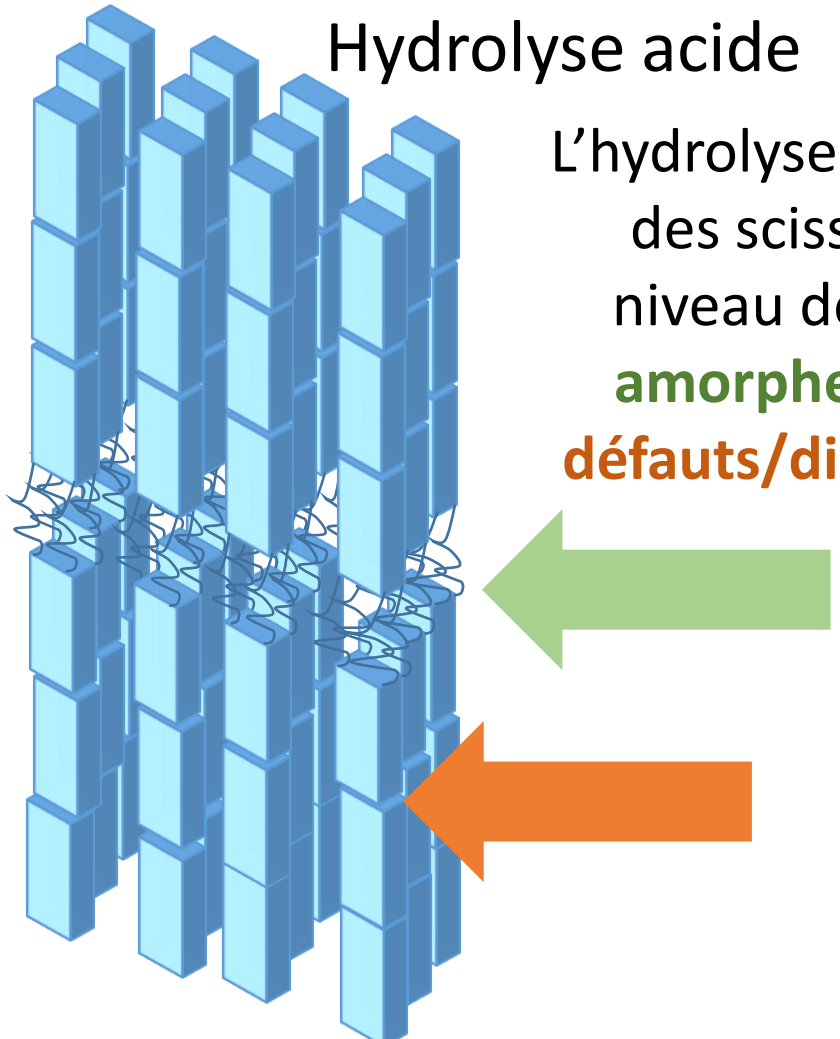


Nuclear magnetic resonance spectra of “raw” ground flax shives (top), the reference non-hydrolyzed sample (middle) and the sample that was hydrolyzed for 8 h (bottom). The C-1 to C-6 carbons are cellulose bands. The “h” letter indicates typical hemicellulose shoulders. All other bands are explicitly attributed.

Les nanocristaux

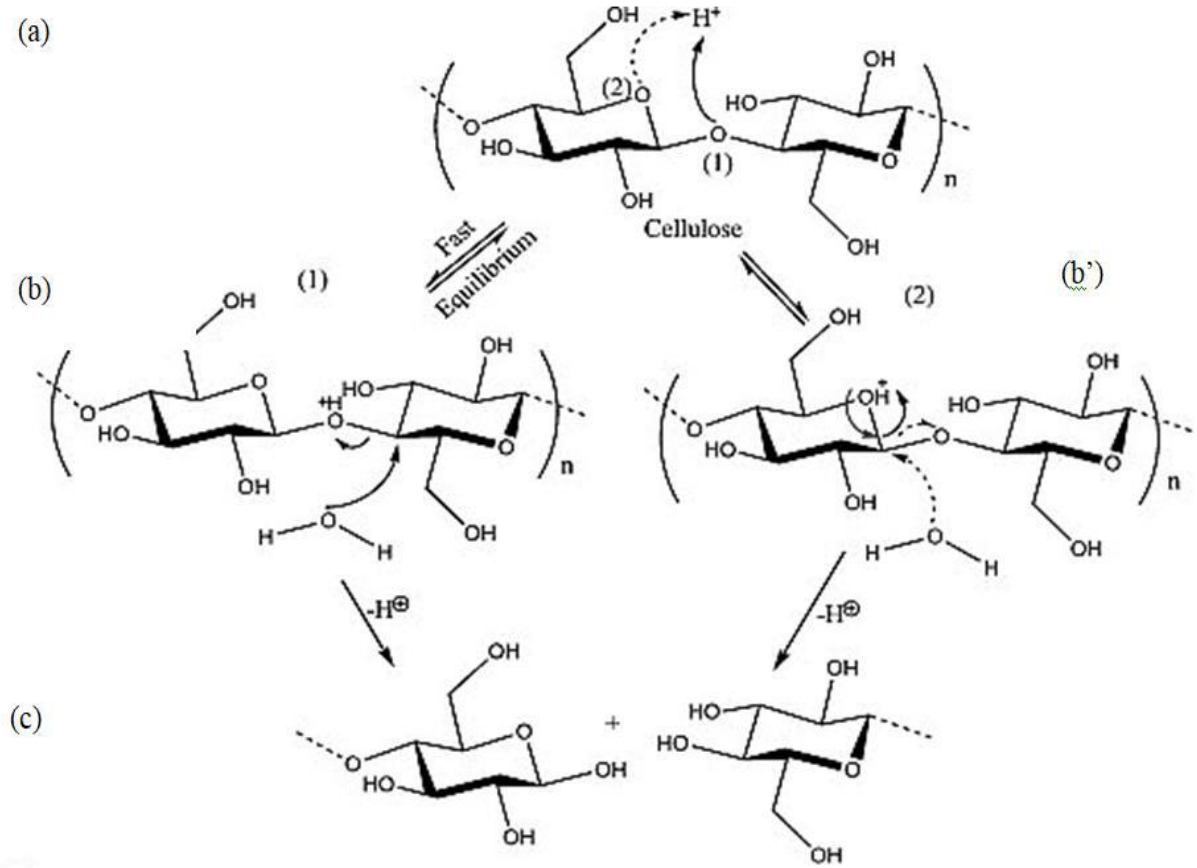
Mis en évidence par Rånby en 1949

Hydrolyse acide



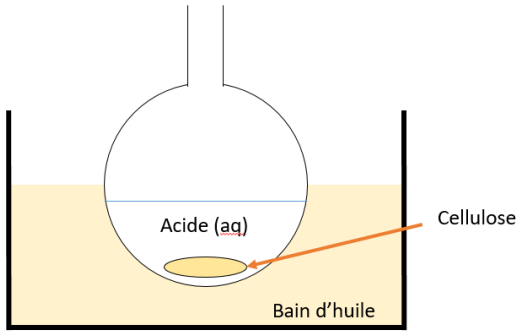
L'hydrolyse acide crée des scissions au niveau des **zones amorphes** et des **défauts/dislocations**

L'hydrolyse a lieu préférentiellement au niveau de la liaison glycosidique β-1,4

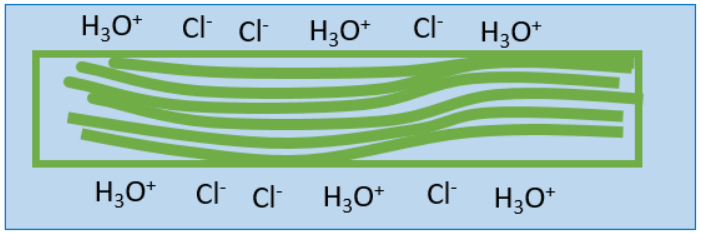


Fonctionnement de l'hydrolyse

Phase liquide



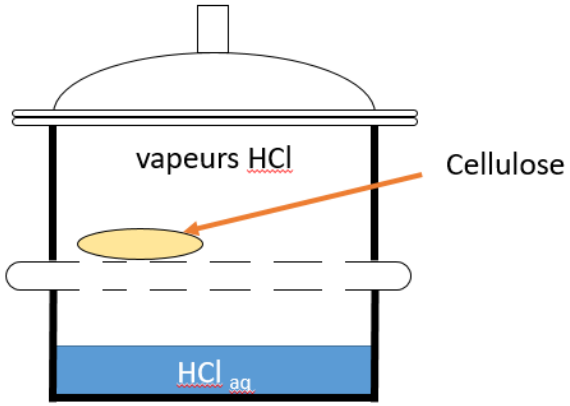
Fibre cellulosique (composé de fibrilles) immergée dans de l'acide chlorhydrique: diffusion, pression osmotique, etc



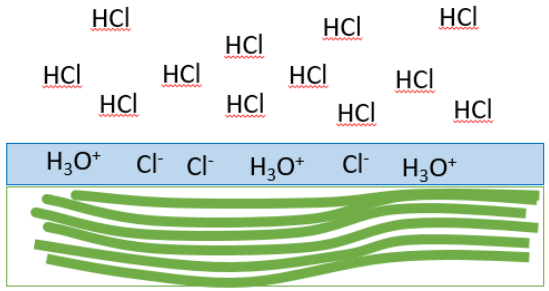
Le point important est l'accessibilité.

Kontturi *et al*. (*Angew Chem* 2016) ont démontré que les vapeurs d'acide atteignent facilement la surface des microfibrilles dans de la cellulose « sèche », permettant un rendement optimum avec un protocole facilité.

Phase vapeur



Les vapeurs d'acide s'adsorbent sur les fibres, qui sont recouverte d'une fine couche d'eau. L'acide peut se dissocier et catalyser la réaction d'hydrolyse, pour atteindre le LODP efficacement (Lorenz, 2018)



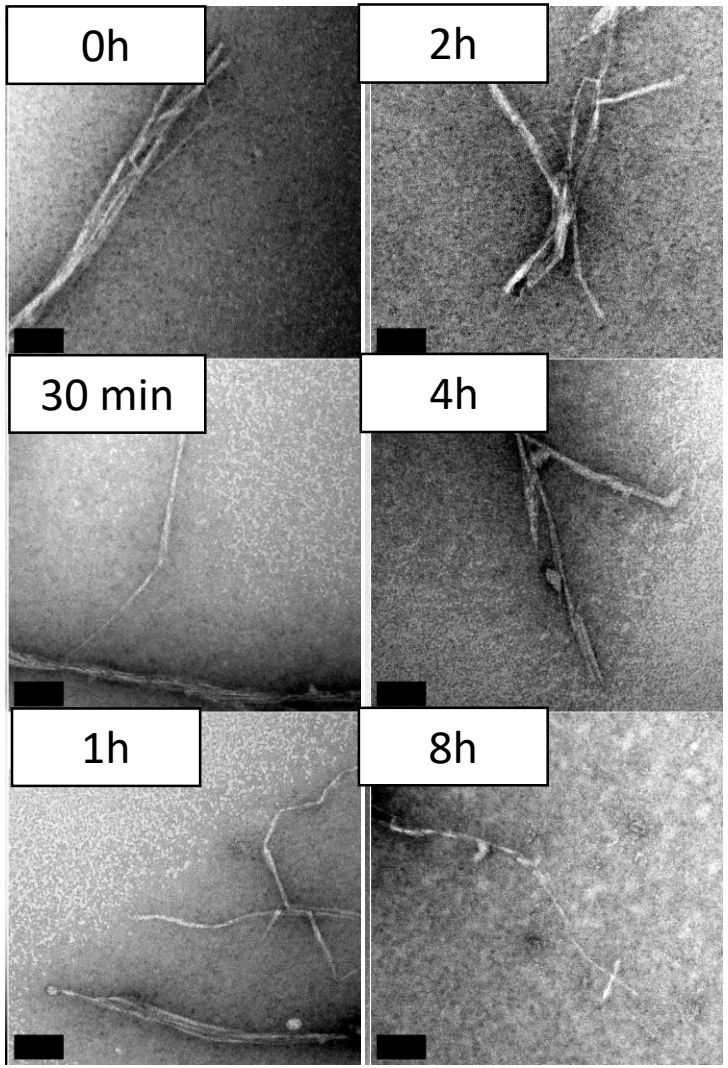
Atmosphère HCl

Fine couche d'eau sur la fibre

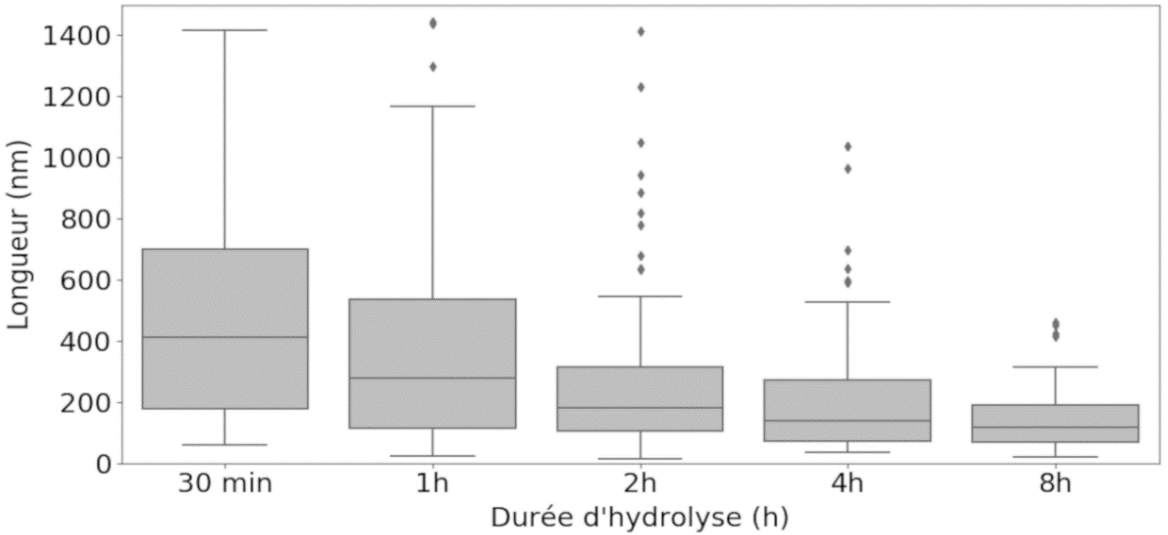
Fibre cellulosique (composé de fibrilles)

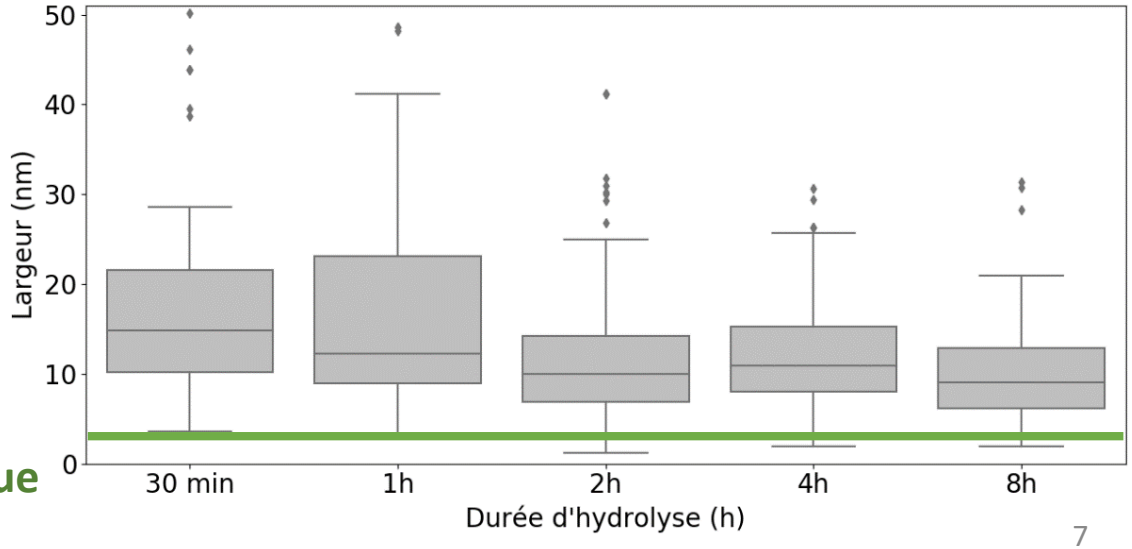
Dimensions (MET)

Barre d'échelle : 40 nm



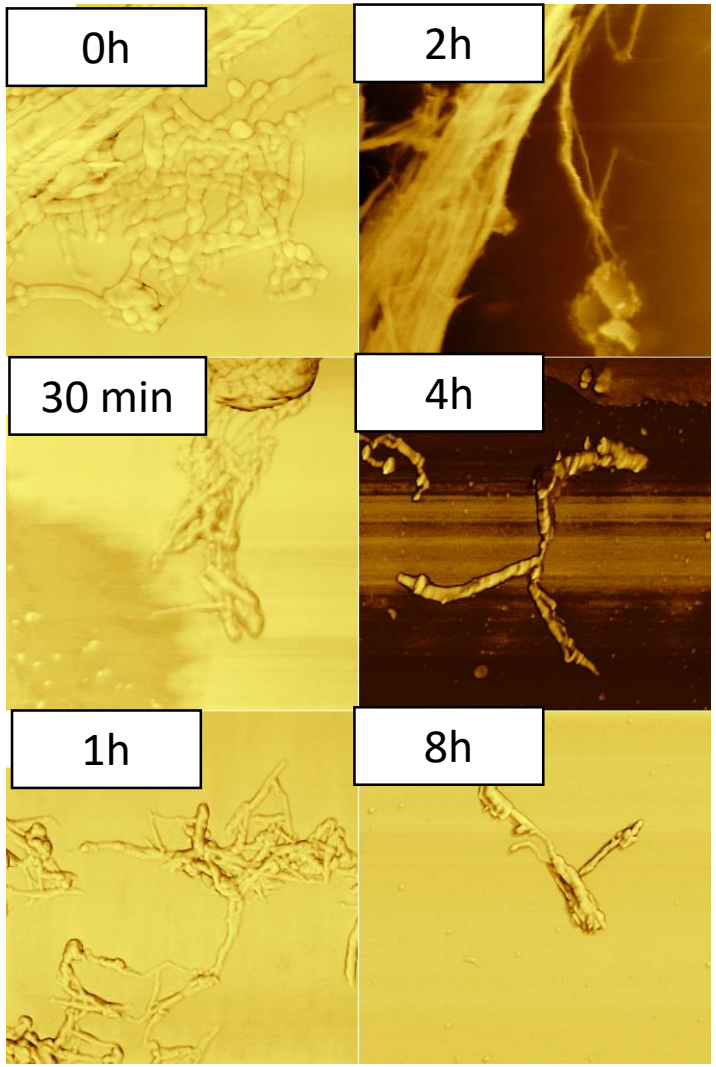
Dimensions mesurées



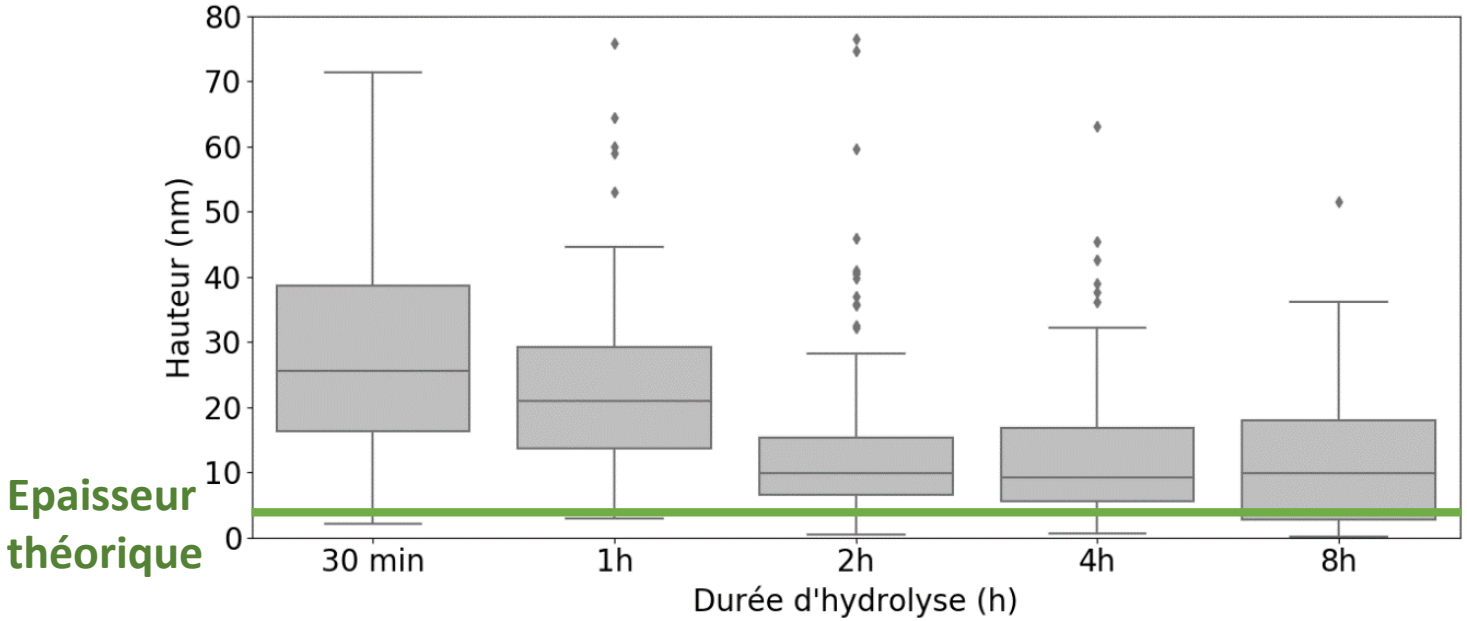


Largeur théorique

Dimensions (AFM)

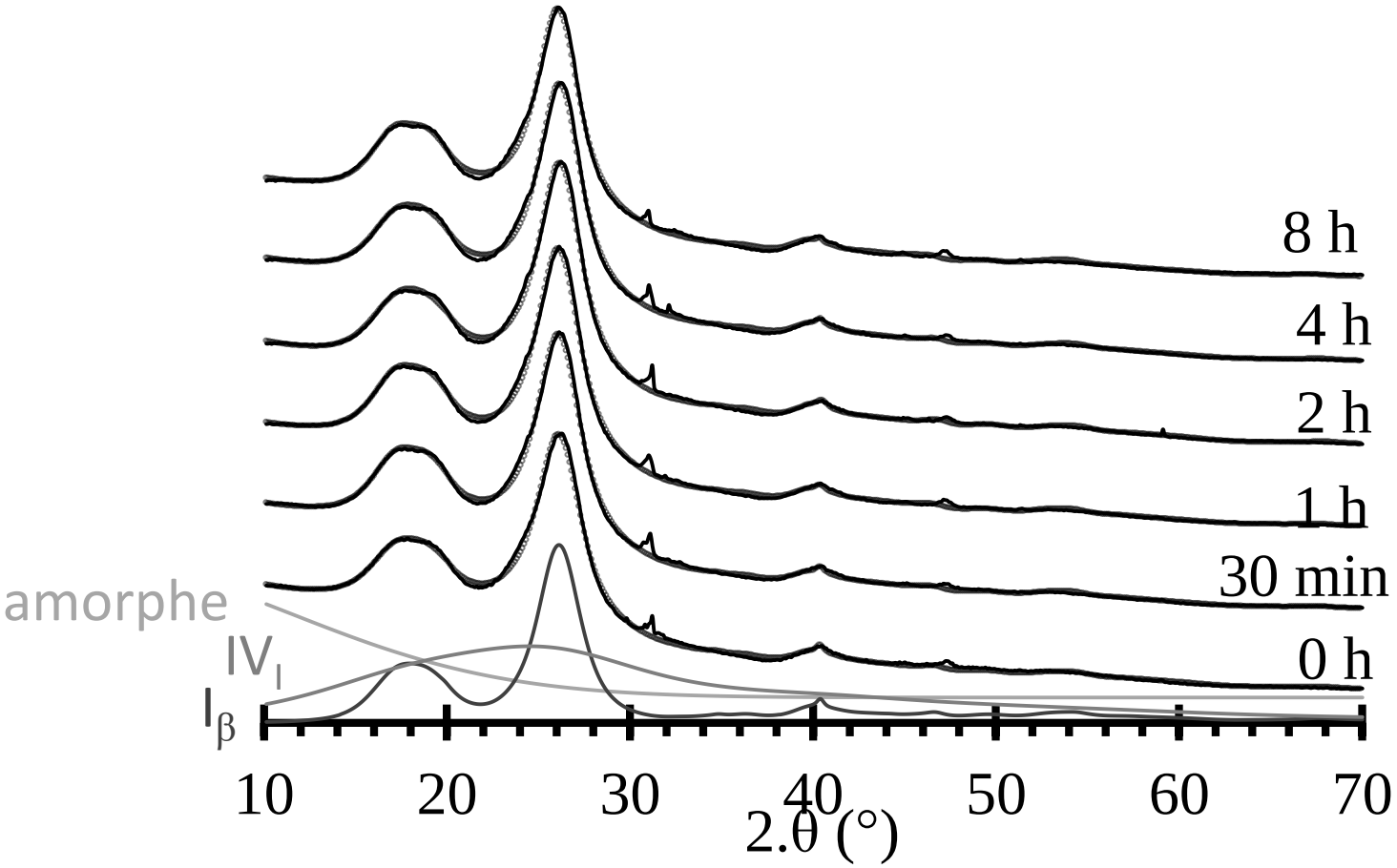


Dimensions mesurées



Ordre (DRX)

Méthode interne :
Size, shape, orientation and crystallinity of cellulose I_β by X-ray powder diffraction using a free spreadsheet program
Duchemin, B. Cellulose (2017)

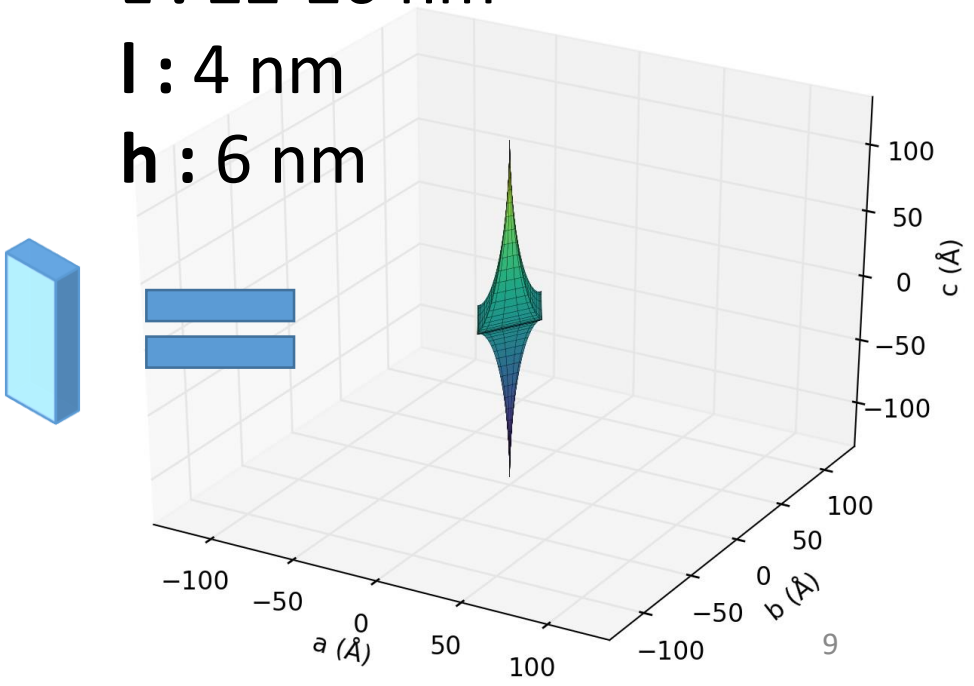


Forme: bipyramide allongée

L : 22-26 nm

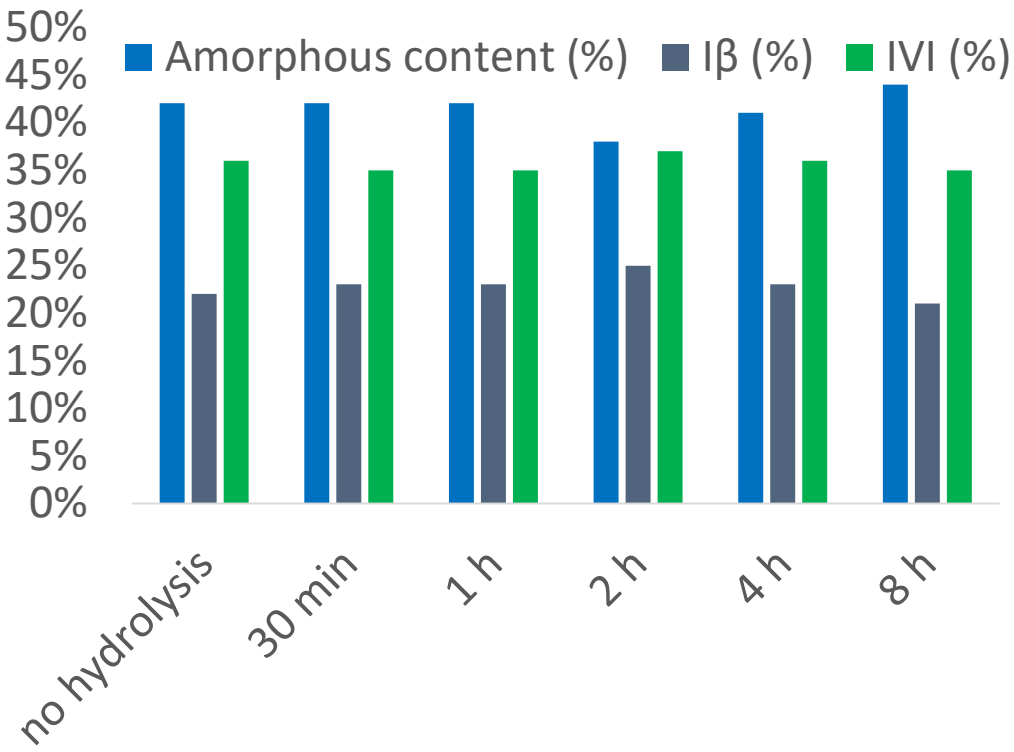
l : 4 nm

h : 6 nm



Ordre (DRX)

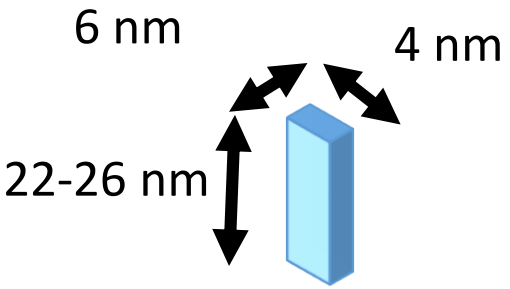
Hydrolysis time	no hydrolysis	30 min	1 h	2 h	4 h	8 h
Segal's CrI (%)	53%	55%	56%	57%	57%	56%
Superellispoid Rx (Å)	18	18	18	19	19	19
Superellispoid Ry (Å)	27	28	29	27	30	33
Superellispoid length Rz (Å)	113	114	102	82	129	129
Cell IV_I size (Å)	7,4	7,8	7,8	7,3	7,6	8,0
Correlation coefficient	0,998	0,999	0,999	0,999	0,998	0,999
R-pattern	1,97 %	1,76 %	1,83 %	1,86 %	1,90 %	2,05 %

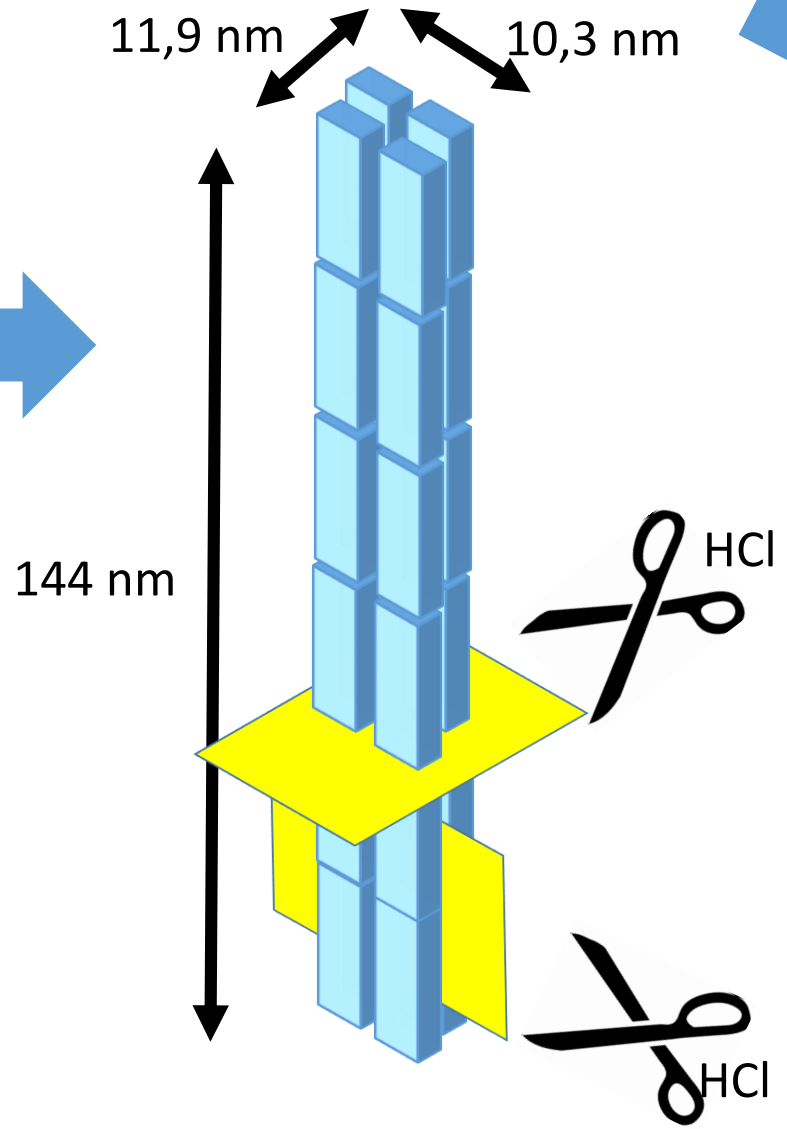


- **Invariance de la cristallinité**
- **Légère augmentation de la taille latérale des cristallites**

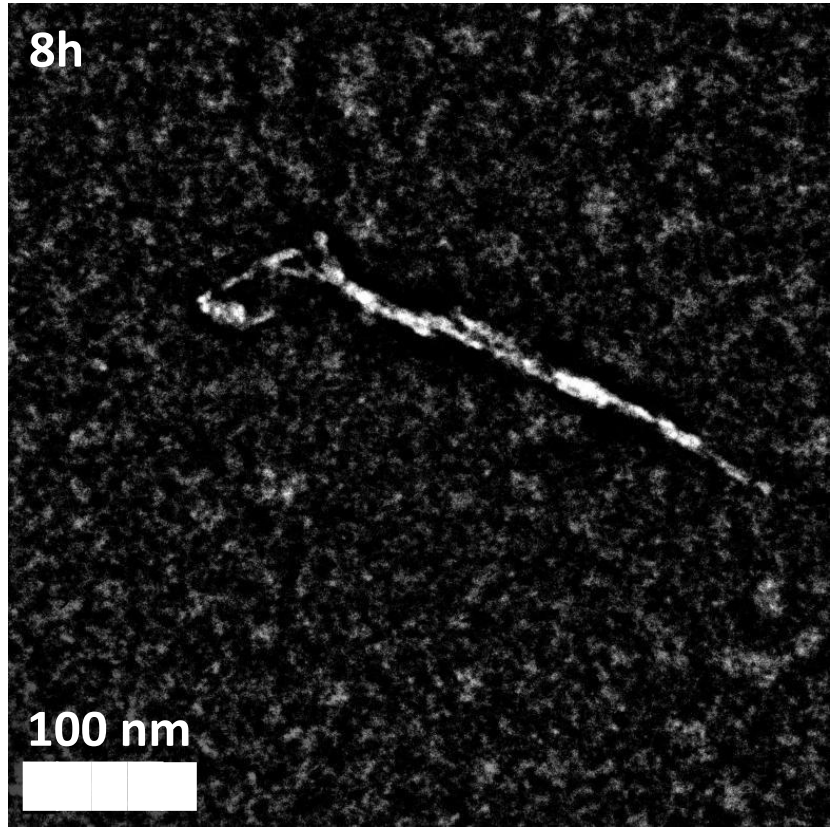
Dimensions des nanoparticules (MET et AFM)

Dimensions des nanocristaux invariante (DRX)





Agrégation des CNC côte à côte



Nanocristaux ≠ nanoparticules

Thermal-FTIR, isotopic labelling

grinding → bleaching → hydrolysis for 8 h (**nanosized**)
no hydrolysis (**microsized, control**)
US, stabilization 75%RH H_2O

1

→ D_2O exchange, N_2 drying
+ stabilization 75%RH D_2O

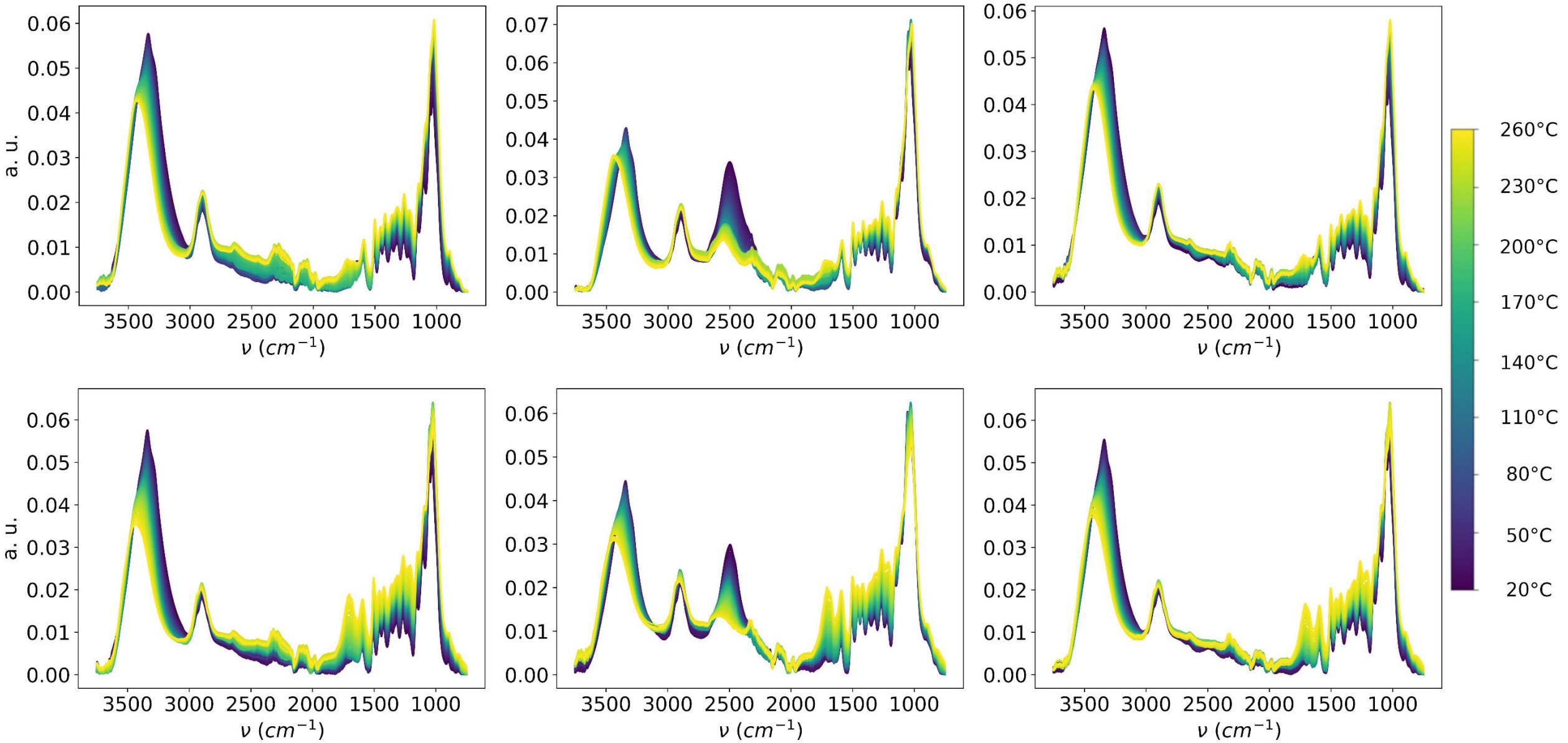
2

→ H_20 re-exchange, N_2 drying
+ stabilization 75%RH H_2O

3

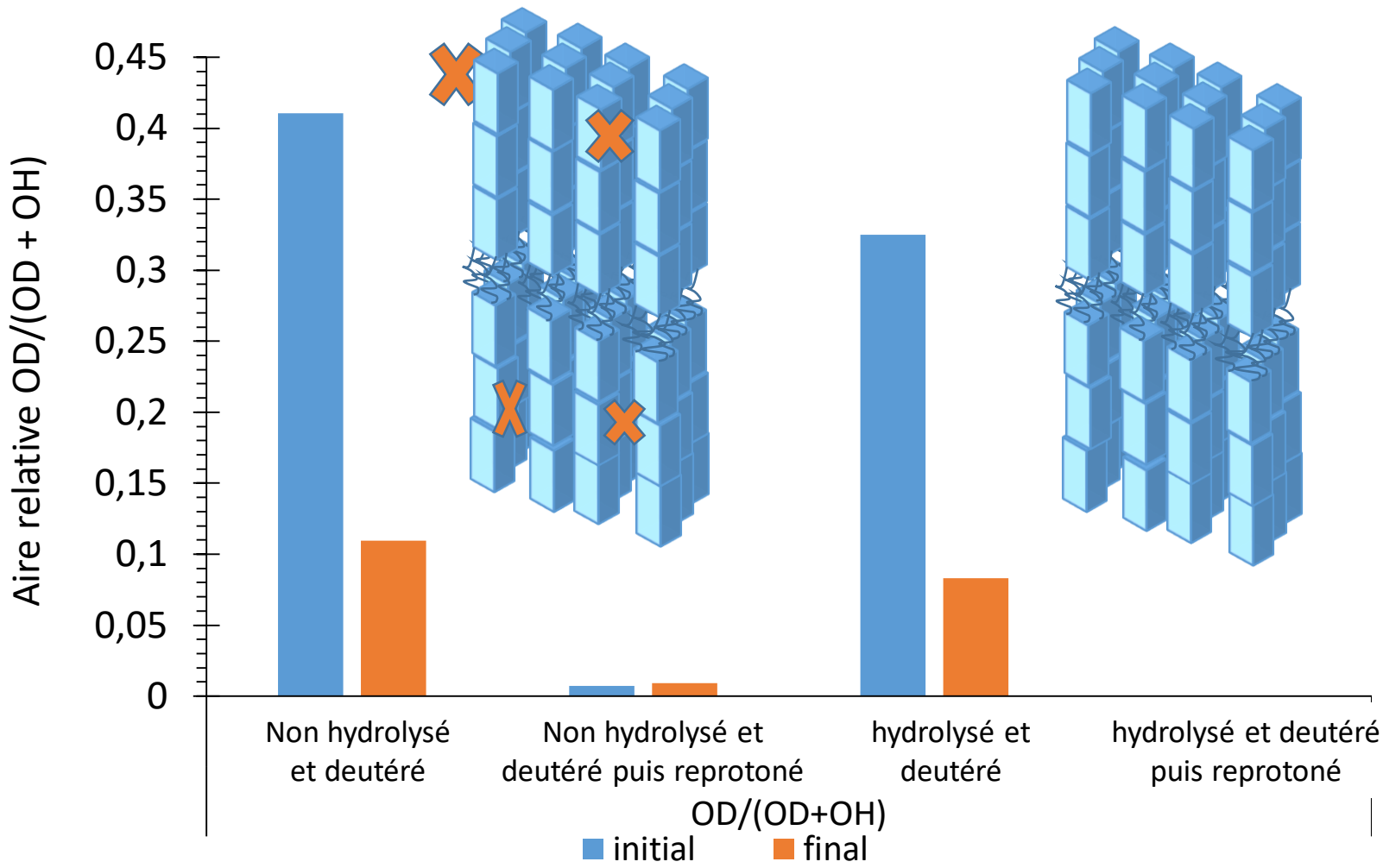
FTIR spectrometer (Nicolet iS50 FT-IR, Thermo scientific) equipped with a temperature-controlled ATR cell (diamond ATR "golden gate high temperature", SPECAC).

The measurements were performed by applying a 2°C/min temperature ramp from room temperature (**initial**) to 260°C and one spectrum was recorded every 40 s. Each spectrum resulted from the accumulation of 64 scans at a 4 cm^{-1} resolution. One spectrum was recorded after cooling to room temperature (**final**).



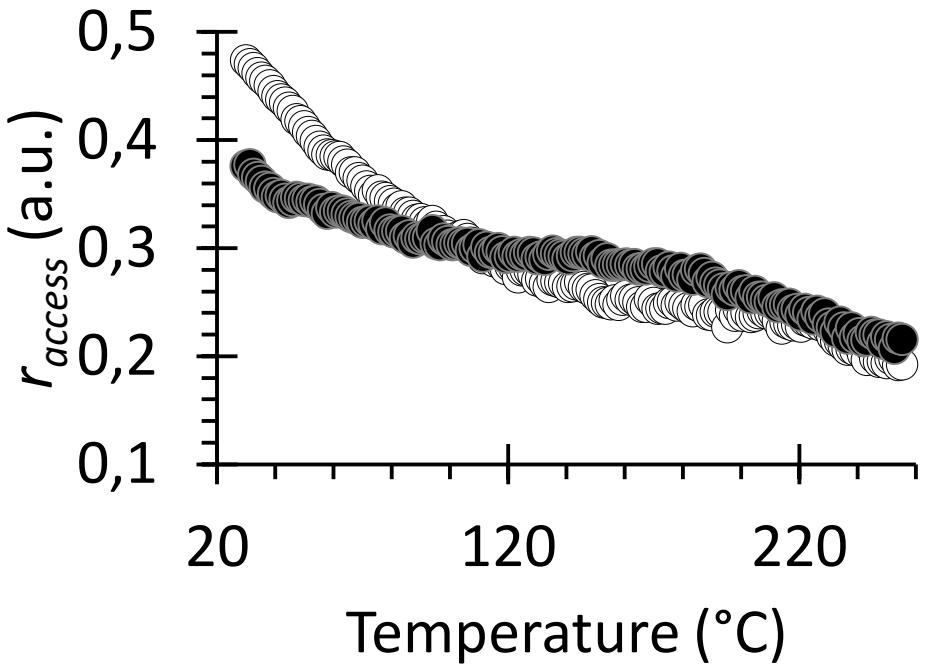
Absorbance FTIR spectra of the control sample (top row) and 8 h hydrolyzed sample (bottom row) as obtained after the deuterium-free control process (first column), after isotopic labelling with D_2O (second column) and after an isotopic labelling, drying, and hydrogen re-exchange (third column). The measurements were performed between room temperature and 260 °C

Aire relative du pic de deutérium avant et après le processus de chauffe : après deutération et après ré-échange

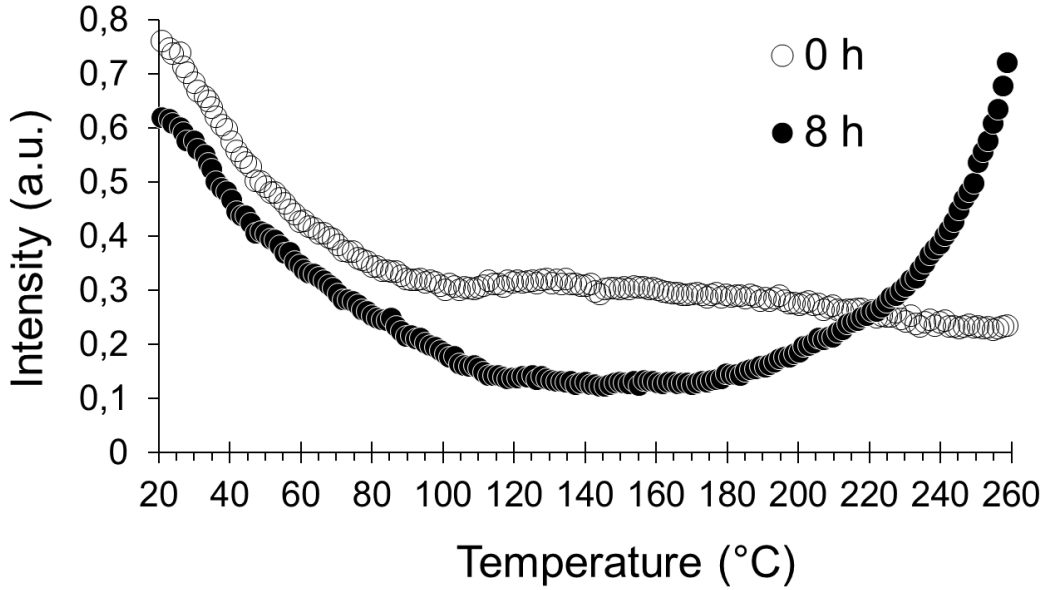


Echange isotopique plus important sur matériau non hydrolysé : interroge « l'accessibilité » car surface spécifique *a priori* plus importante *et* **cristallinité équivalente -> rôle eau confinée en espace poral**

Après hydrolyse, pas de piégeage de D_2O lors d'un cycle séchage/reprotonation/séchage -> effet d'hystérèse annulé



Crossover of OD/(OD+OH) near 100-120°C: transient porosity and it doesn't necessarily depend on the crystallinity.



Intensity of the molecular water maxima near 1640 cm^{-1} as a function of the temperature for the sample that was not hydrolyzed (open circle) and the sample that was hydrolyzed for 8 h (filled circle). The signals were normalized with respect to intensity of the –CH band near 2900 cm^{-1}. The intensity increase observed after 180 °C for the hydrolyzed sample is attributed to the onset of cellulose dehydration.

-> NATURE OF THE LABELLED SITES

Conclusions

Thermal FTIR demonstrated that isotopic labelling of cellulose sources to qualify the accessibility can produce *false positives* when conducted at room temperature and thermal FTIR can unambiguously distinguish between labelled cellulose groups and free deuterium oxide, which is paramount when measuring the higher accessibility of the nanocelluloses

This result also means that hygroscopic moisture can induce an important bias in the quantitative assessment of accessibility (or “crystallinity”) by deuterium labelling. In this work, two materials with very close crystallinities but with different morphologies (fibres and nanoparticles) had very different accessibilities, meaning that deuterium labelling cannot measure crystallinity. Thermal ATR-FTIR also evidenced small hysteretic effects of the hydrogen bond network and cellulose backbone (C–O stretching region) to temperature variations after hydrolysis.

Merci pour votre attention

Pour aller plus loin/citer:

Leboucher, Jonathan, Philippe Bazin, Didier Goux, Hussein El Siblani, Arnaud Travert, Antoine Barbulée, Joel Bréard, et Benoit Duchemin. « High-Yield Cellulose Hydrolysis by HCl Vapor: Co-Crystallization, Deuterium Accessibility and High-Temperature Thermal Stability ». *Cellulose* 27, nº 6 (1 avril 2020): 3085-3105. https://doi.org/10.1007/s10570-020-03002-2.

(également disponible sur HAL et researchgate)