Cellulose microfibrils are extracted from biomass using chemical treatments and mechanical defibrillation. Our study aimed at characterizing the effect of ultrasonication on the morphology and crystal structure of model cellulose microfibrils and nanocrystals dispersed in water. Algal cellulose microfibrils were extracted from *Glaucocystis* and *Valonia* cell walls. Shorter nanocrystals were obtained by sulfuric acid hydrolysis of these microfibrils. Nanocrystals from tunicin, the cellulose found in *Halocynthia*, a marine animal, were prepared as well. 0.1 wt% aqueous suspensions of microfibrils or nanocrystals were submitted to low and high frequency ultrasounds (20 and 600 kHz, resp.). The suspensions were sonicated for 3 h, their temperature being thermoregulated at 25-30°C. Negatively stained preparations were observed before and after sonication by transmission electron microscopy (TEM). Thin films were prepared by air-drying concentrated suspensions and X-ray diffraction (XRD) patterns were recorded. Solid-state $^{13}$C NMR spectra were recorded from dry powders using magic angle spinning and cross-polarization (CP/MAS) techniques. *Glaucocystis* (Fig. 1a) and *Valonia* cellulose microfibrils were initially rectilinear and nearly defect-free. The damage resulting from sonication was extensive for low-frequency treatments and due to the many defects (kinks, subfibrillation), the general impression was that the microfibrils had lost their rigidity (Fig. 1b). 600 kHz sonication seemed to induce a smaller number of defects which remained separated by linear segments (Fig. 1c). Native cellulose is a mixture of two allomorphs: $\alpha$ (triclinic) and $\beta$ (monoclinic, thermodynamically more stable). Tunicin is $\beta$-rich (90%) while *Glaucocystis* and *Valonia* cellulososes are $\alpha$-rich (90 and 65%, resp.). XRD profiles revealed that the structure of the latter two specimens changed during sonication (Fig. 1d), the effect being stronger at low frequency. The decreasing distance between 100 and 010 peaks indicated a transition to the $\beta$ structure while the shift of the 110 peak to lower angles would be due to the high number of defects and lower crystallinity. The quantitative analysis of the CP/MAS NMR spectra allowed to evaluate the $\alpha/\beta$ ratio in the samples and showed that the transition was incomplete. The origin of the structural transition has not been fully identified yet and several hypotheses exist [Briois et al., Cellulose 20 (2013), 597-603]. Damage would be caused by the shocks and shears generated by acoustic cavitation that may also induce longitudinal translations along some crystal planes, resulting in the structural change. In addition, so-called “hot spots” are known to occur near cavitation bubbles which may promote a thermal transition in cellulose.

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Fig. 1: Negatively stained Glaucocystis cellulose microfibrils (GCMs): initial (a), sonicated for 3 h at 20 and 600 kHz (b,c); d) XRD profiles of GCMs and tunicin nanocrystals (TNs): initial GCMs (1); GCMs sonicated for 3 h at 20 and 600 kHz (2,3); initial TNs (4); TNs sonicated for 3 h at 20 kHz (5). t and m refer to triclinic and monoclinic indexations.