

Moisture-related changes in the nanostructure of woods studied with x-ray and neutron scattering

Electronic supplementary material

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Table S1 Mass stability (dm/dt) with a 1 h regression window of wood samples measured with DVS at different RHs during subsequent desorption and adsorption isotherms (columns from left to right), with error estimates (least significant digit shown in parentheses) based on standard deviation from two or more specimens

Sample	Drying state	dm/dt ($\mu\text{g g}^{-1} \text{min}^{-1}$) at different RHs (%)				
		88.7(3)	43.5(1)	12.57(3)	43.05(6)	88.4(2)
Beech	Never-dried	−8(4)	−21(4)	−5(1)	1.6(3)	16(2)
	Dried/rewetted	−10.64(6)	−18(2)	−5(2)	2.5(4)	14(1)
Beech TW	Never-dried	−42(9)	−30(10)	−5(1)	1.4(6)	14(2)
	Dried/rewetted	−27(9)	−19(5)	−5.6(5)	0(1)	13(4)
Fir EW	Never-dried	−0.67	−14	−6.9	3.0	7.0
	Dried/rewetted	0.81	−18	2.2	4.8	15
Fir LW	Never-dried	−7(5)	−17.8(4)	−6.5(7)	0.973(9)	11(1)
	Dried/rewetted	2.3	−19	−7.4	1.9	12
Spruce EW	Never-dried	4(4)	−22(3)	−6.8(5)	1.87(2)	10(2)
	Dried/rewetted	1.2	−12	−6.3	2.6	13
Spruce LW	Never-dried	−2.6	−16	−6.2	1.8	12
	Dried/rewetted	14	−16	−6.7	2.5	9.4

Table S2 Results from fits of Eq. 1 to equatorial, anisotropic SANS intensities from never-dried and dried/rewetted wood samples, with fixed parameters $\Delta R/\bar{R} = 0.2$ and $\alpha = 4.0$ and uncertainty of the least significant digit shown in parentheses

Sample	A	$2\bar{R}$ (nm)	a (nm)	$\Delta a/a$	B	$\sigma (\times 10^{-2} \text{ \AA}^{-2})$	$C (\times 10^{-7})$
Beech, never-dried	0.77(1)	2.09(1)	2.74(1)	0.371(4)	1.45(2)	2.06(2)	7.55(3)
Beech, dried/rewetted	0.71(2)	2.08(2)	2.67(2)	0.411(5)	0.69(1)	2.53(2)	9.88(3)
Beech TW, never-dried	0.67(1)	2.00(2)	6.44(5)	0.38(1)	4.67(2)	3.36(2)	12.00(4)
Beech TW, dried/rewetted	0.590(8)	2.08(1)	6.54(4)	0.344(8)	4.84(2)	3.53(1)	11.23(3)
Fir LW, never-dried	0.63(4)	1.91(9)	4.4(1)	0.30(1)	0.6(1)	1.7(2)	3.926(3)
Fir LW, dried/rewetted	0.76(5)	1.99(8)	4.3(1)	0.31(1)	0.28(5)	2.1(2)	7.166(2)
Spruce LW, never-dried	0.694(6)	2.05(1)	4.37(1)	0.307(1)	0.175(9)	2.13(4)	8.41(3)
Spruce LW, dried/rewetted	0.82(1)	2.06(1)	4.29(2)	0.326(2)	0.59(2)	1.62(2)	12.47(4)

Table S3 Results from fits of Eq. 1 (plus constant) to equatorial, anisotropic SAXS intensities from wood samples at various moisture conditions, with fixed parameters other than $\Delta a/a = 0.4$ and $\alpha = 4.0$ marked with asterisk

Sample	Drying state	$A (\times 10^3)$	$2\bar{R}$ (nm)	$\Delta R/\bar{R}$	a (nm)	$B (\times 10^3)$	$\sigma (\times 10^{-2} \text{ \AA}^{-2})$	$C (\times 10^{-3})$	Constant
Beech, TL	Never-dried	5.15	2.352	0.22*	2.92	1.99	2.8	0.33	2.4
	RH 90% (d)	1.74	1.958	0.22*	3.62	1.78	5.7	3.51	14.8
	RH 45% (d)	0.81	1.967	0.22*	3.25	1.46	6.6	6.31	7.0
	RH 15%	0.57	1.946	0.22*	3.21	1.61	7.1	6.36	2.4
	RH 45% (u)	0.66	1.970	0.22*	3.18	1.36	7.0	6.21	5.2
	RH 90% (u)	1.21	1.951	0.22*	3.32	1.48	6.5	5.52	14.3
	Dried/rewetted	3.81	2.344	0.22*	2.77	1.34	2.8	0.23	–
Beech, RL	Never-dried	3.58	2.480	0.20*	3.49	0.49	1.8	0.15	5.0
	RH 90% (d)	4.99	2.519	0.20*	3.70	0.67	1.8	3.14	6.7
	RH 45% (d)	1.49	2.405	0.20*	3.68	1.03	7.9	3.90	4.5
	RH 15%	1.22	2.402	0.20*	3.76	1.49	8.0	4.20	3.3
	RH 45% (u)	1.26	2.386	0.20*	3.72	1.09	8.1	4.07	4.2
	RH 90% (u)	3.12	2.458	0.20*	3.74	0.53	7.8	4.19	8.5
	Dried/rewetted	4.74	2.471	0.20*	3.33	1.10	1.7	0.26	1.1
Beech TW, TL	Never-dried	2.99	1.997	0.20*	6.22	20.64	3.6	0.48	8.6
	RH 90% (d)	1.19	1.831	0.20*	5.98	3.58	4.8	5.37	16.4
	RH 45% (d)	0.33	1.747	0.20*	4.67	0.98	6.4	9.59	9.2
	RH 15%	0.22	1.760	0.20*	3.83	1.03	6.9	8.98	4.6
	RH 45% (u)	0.26	1.765	0.20*	4.33	0.93	6.7	9.45	7.4
	RH 90% (u)	0.67	1.786	0.20*	4.54	2.48	5.7	8.41	15.6
	Dried/rewetted	2.88	2.006	0.20*	6.07	23.66	3.9	0.52	11.3
Beech TW, RL	Never-dried	2.24	1.990	0.20*	6.26	17.54	3.5	0.20	5.4
	RH 90% (d)	1.03	1.829	0.20*	5.96	3.31	4.2	2.20	11.3
	RH 45% (d)	0.26	1.732	0.20*	4.64	0.96	5.5	2.70	3.1
	RH 15%	0.24	1.891	0.20*	4.25	1.00	5.9	2.88	2.6
	RH 45% (u)	0.19	1.717	0.20*	4.26	0.80	6.1	2.67	2.5
	RH 90% (u)	0.59	1.843	0.20*	5.33	2.29	4.7	2.40	9.9
	Dried/rewetted	1.06	2.046	0.20*	6.15	13.17	3.6	0.20	0.6
Fir, EW	Never-dried	1.70	2.438	0.22*	3.98	–	–	0.23	4.3
	RH 90% (d)	1.29	2.493	0.22*	3.47	–	–	3.16	–
	RH 45% (d)	0.58	2.555	0.22*	2.35	0.35	8.9	4.25	–
	RH 15%	0.44	2.388	0.22*	2.25	0.54	7.4	4.20	–
	RH 45% (u)	0.46	2.710	0.22*	2.27	0.34	9.3	4.21	–
	RH 90% (u)	1.21	2.547	0.22*	3.23	–	–	3.28	–
	Dried/rewetted	1.54	2.482	0.22*	4.18	–	–	0.19	1.0
Fir, LW	Never-dried	3.43	2.453	0.22*	3.89	–	–	0.11	4.2
	RH 90% (d)	3.61	2.483	0.22*	3.58	–	–	2.43	4.7
	RH 45% (d)	1.58	2.362	0.22*	2.83	1.49	6.1	3.64	–
	RH 15%	0.91	2.234	0.22*	3.46	2.30	6.0	3.81	–
	RH 45% (u)	1.19	2.319	0.22*	2.90	1.57	6.2	3.26	–
	RH 90% (u)	3.54	2.547	0.22*	3.00	–	–	2.92	–
	Dried/rewetted	4.42	2.474	0.22*	4.04	–	–	0.17	4.5
Spruce, EW	RH 90% (d)	1.62	2.487	0.22*	3.63	–	–	6.54	–
	RH 45% (d)	0.48	2.323	0.22*	2.82	0.34	7.6	7.27	–
	RH 15%	0.33	2.348	0.22*	2.11	0.38	8.4	7.07	–
	RH 45% (u)	0.38	2.457	0.22*	2.43	0.33	9.2	7.68	–
	RH 90% (u)	1.22	2.478	0.22*	3.35	–	–	7.20	–
	Dried/rewetted	1.62	2.599	0.22*	4.01	–	–	0.14	–
	Never-dried	3.75	2.522	0.22*	3.97	–	–	0.20	2.1
Spruce, LW	RH 90% (d)	2.95	2.465	0.22*	3.74	–	–	7.96	3.4
	RH 45% (d)	1.09	2.318	0.22*	2.83	0.89	6.9	11.38	–
	RH 15%	0.60	2.216	0.22*	2.90	1.40	7.2	12.24	–
	RH 45% (u)	0.81	2.288	0.22*	2.76	0.85	7.4	11.36	–
	RH 90% (u)	2.61	2.507	0.22*	3.18	–	–	9.60	–
	Dried/rewetted	3.81	2.527	0.22*	4.03	–	–	0.17	2.9

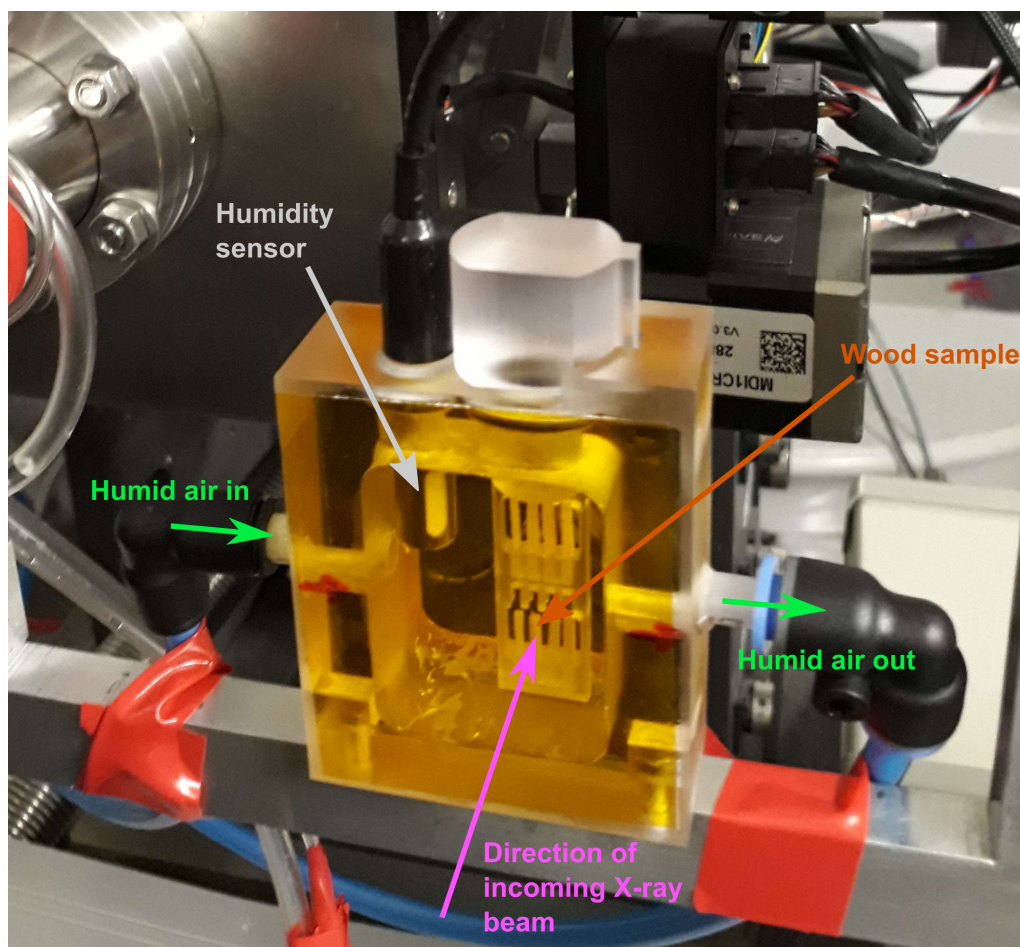


Fig. S1 Photograph of the humidity chamber used in the SAXS and WAXS measurements at the D2AM beamline of the European Synchrotron Radiation Facility (ESRF)

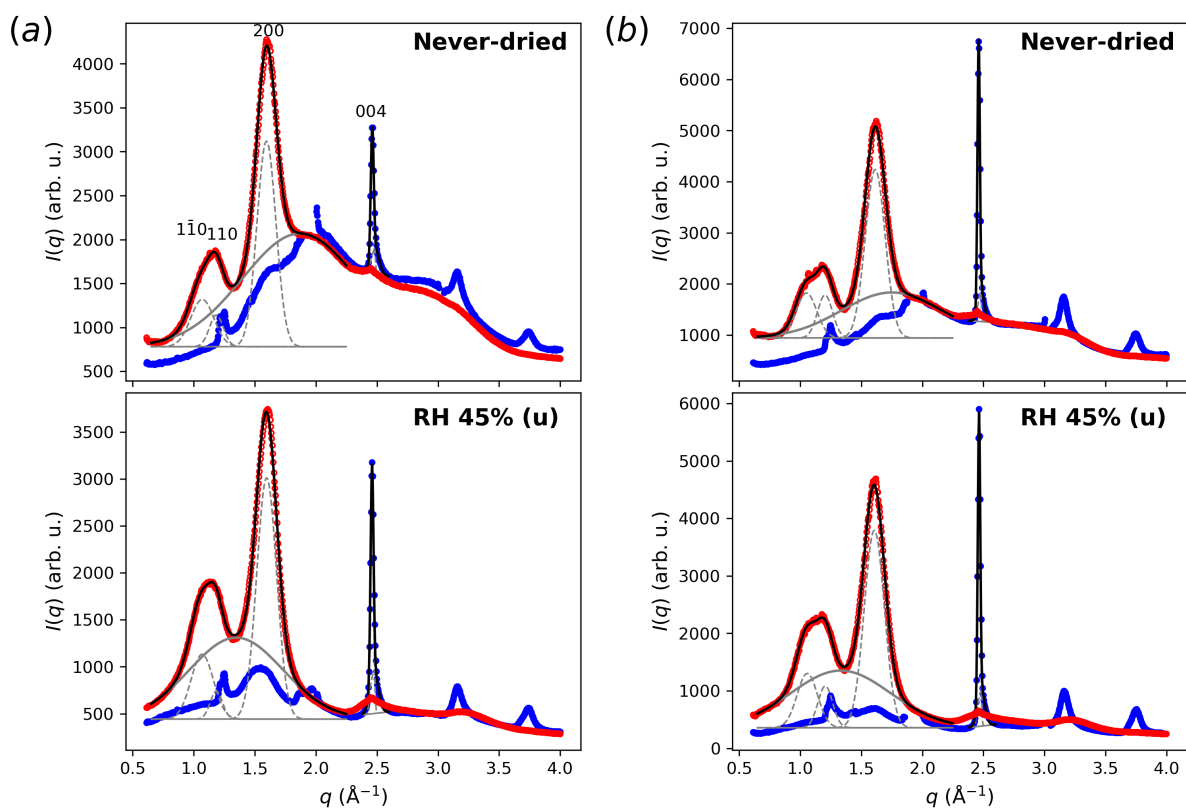


Fig. S2 Examples of WAXS fits to **a** Beech, TL and **b** Fir LW, with equatorial (*unfilled, red symbols*) and meridional (*filled, blue symbols*) intensities shown together with the fit components (*dashed line* for diffraction peaks, *thick solid line* for less-ordered/water background and *thin solid line* for linear background)

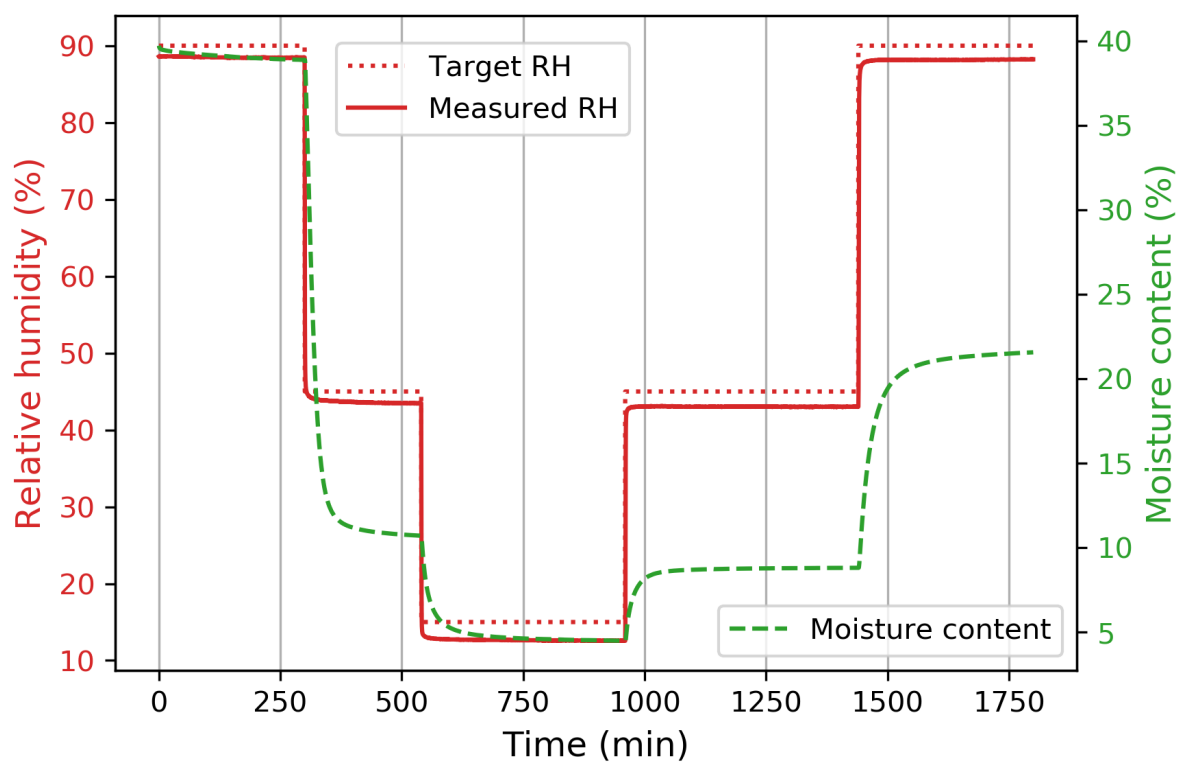


Fig. S3 Relative humidity (RH) cycle used in the DVS measurements (*vertical axis on the left*) and the measured moisture content of a beech sample as a function of time (*vertical axis on the right*)

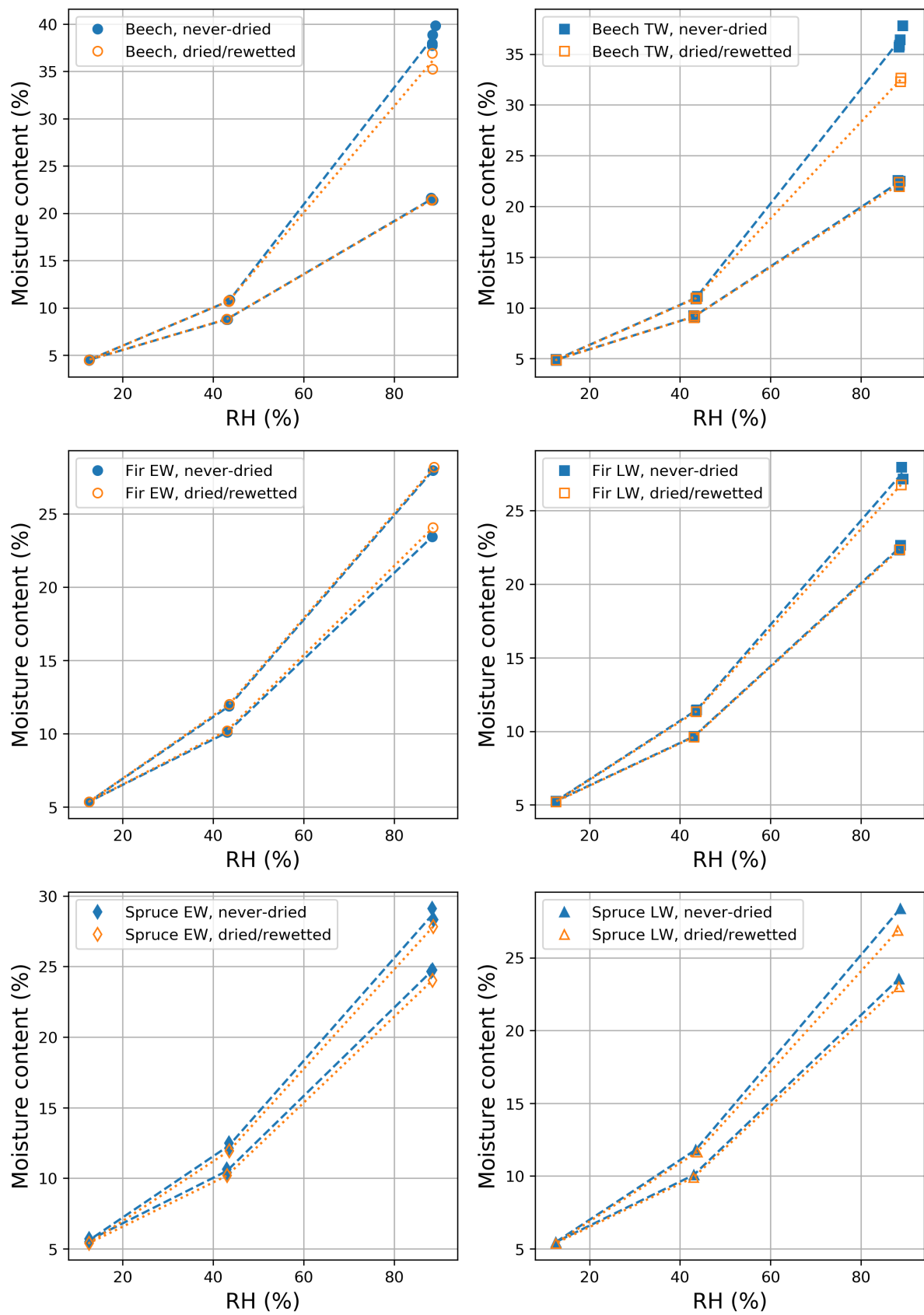


Fig. S4 Sorption isotherms of all wood samples

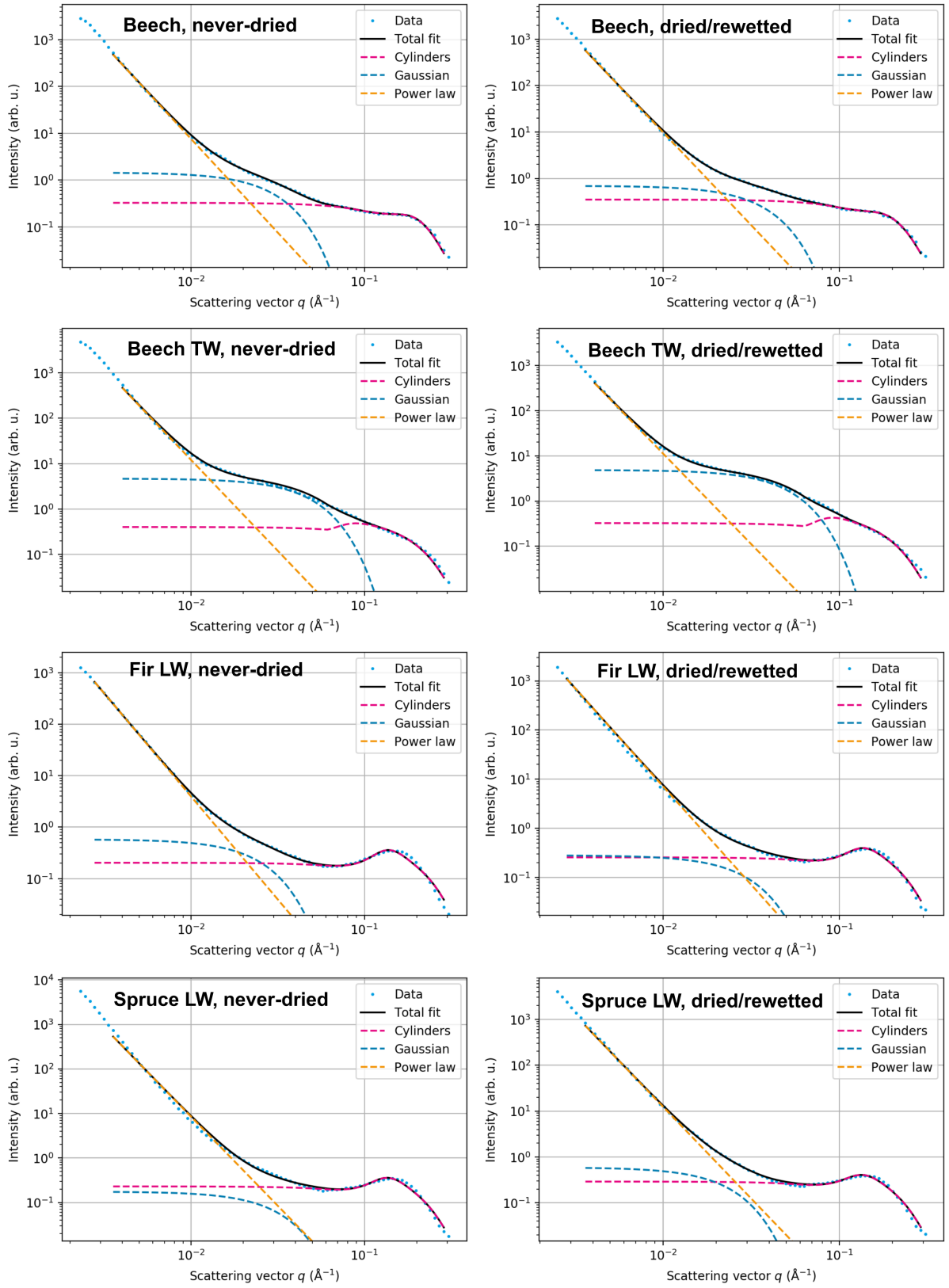


Fig. S5 Equatorial, anisotropic SANS intensities from wood samples, together with fits of Eq. 1 and the different contributions of the fit

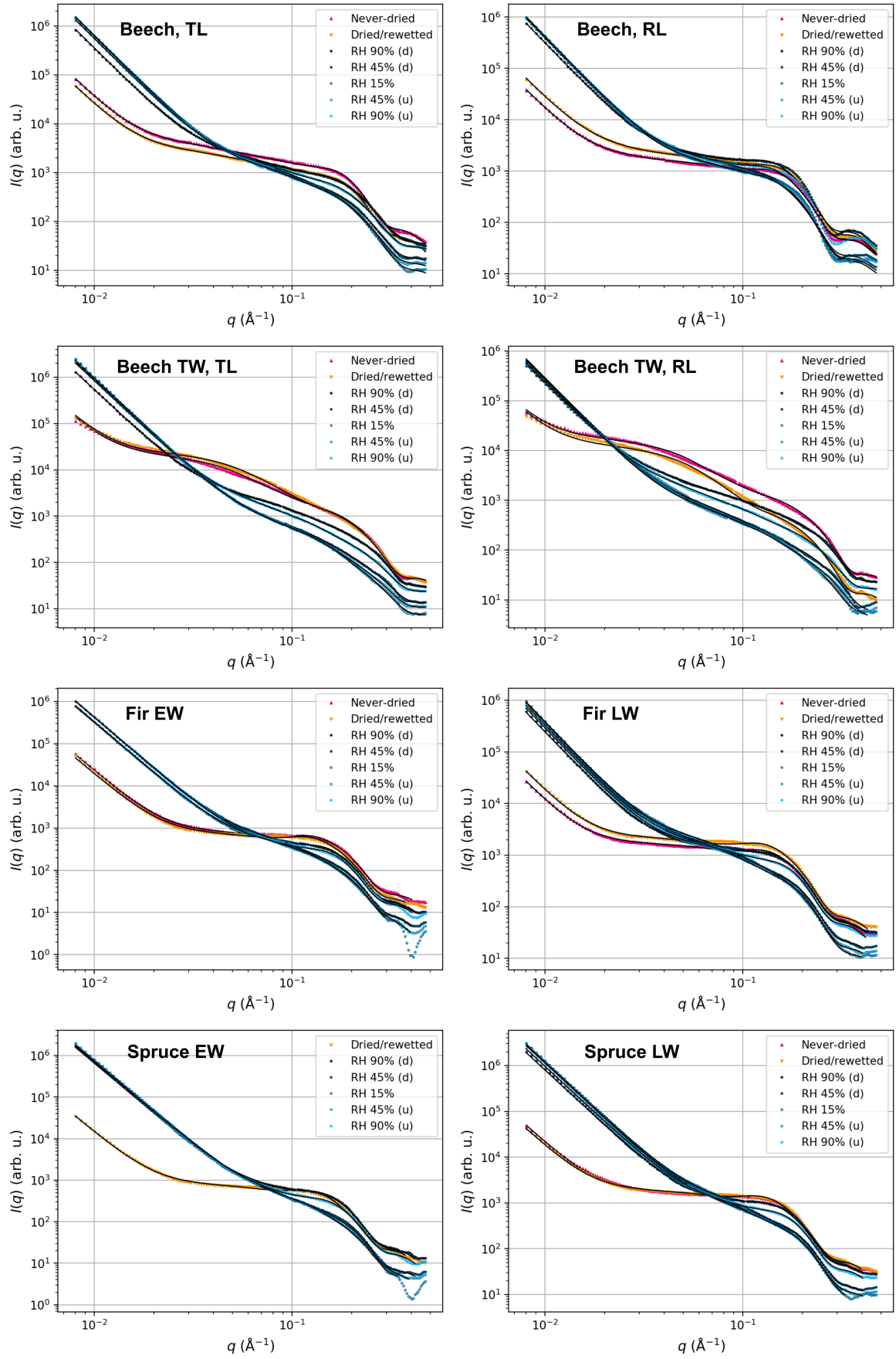


Fig. S6 Equatorial, anisotropic SAXS intensities from wood samples at various moisture conditions (*symbols*), together with fits of Eq. 1 (*solid lines*)

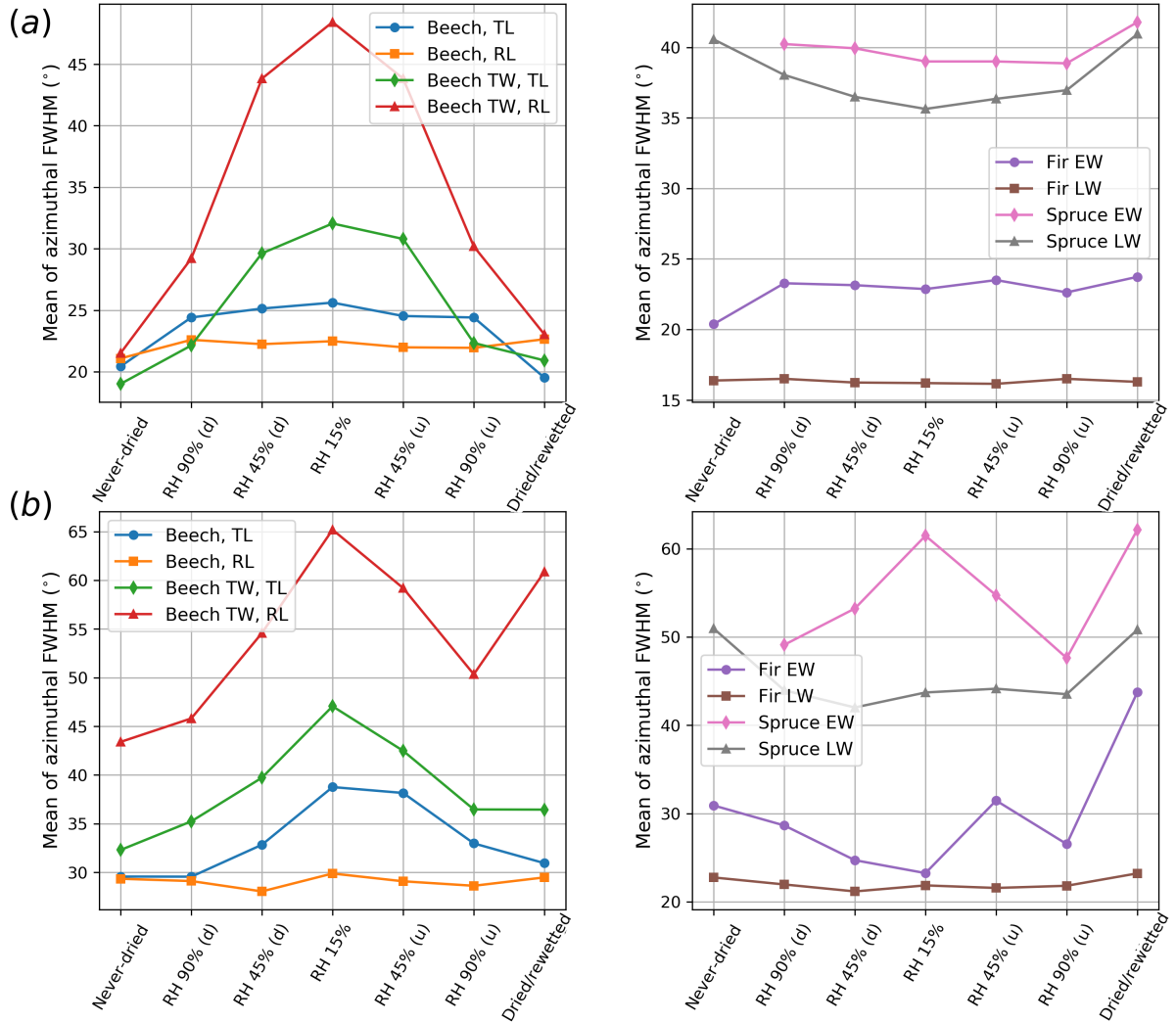


Fig. S7 Mean azimuthal widths (FWHM) of equatorial streaks in SAXS intensities from wood samples at various moisture conditions, averaged over a q range **a** from $0.02 \text{ \AA}^{-1}$ to $0.2 \text{ \AA}^{-1}$ and **b** from $0.2 \text{ \AA}^{-1}$ to $0.5 \text{ \AA}^{-1}$

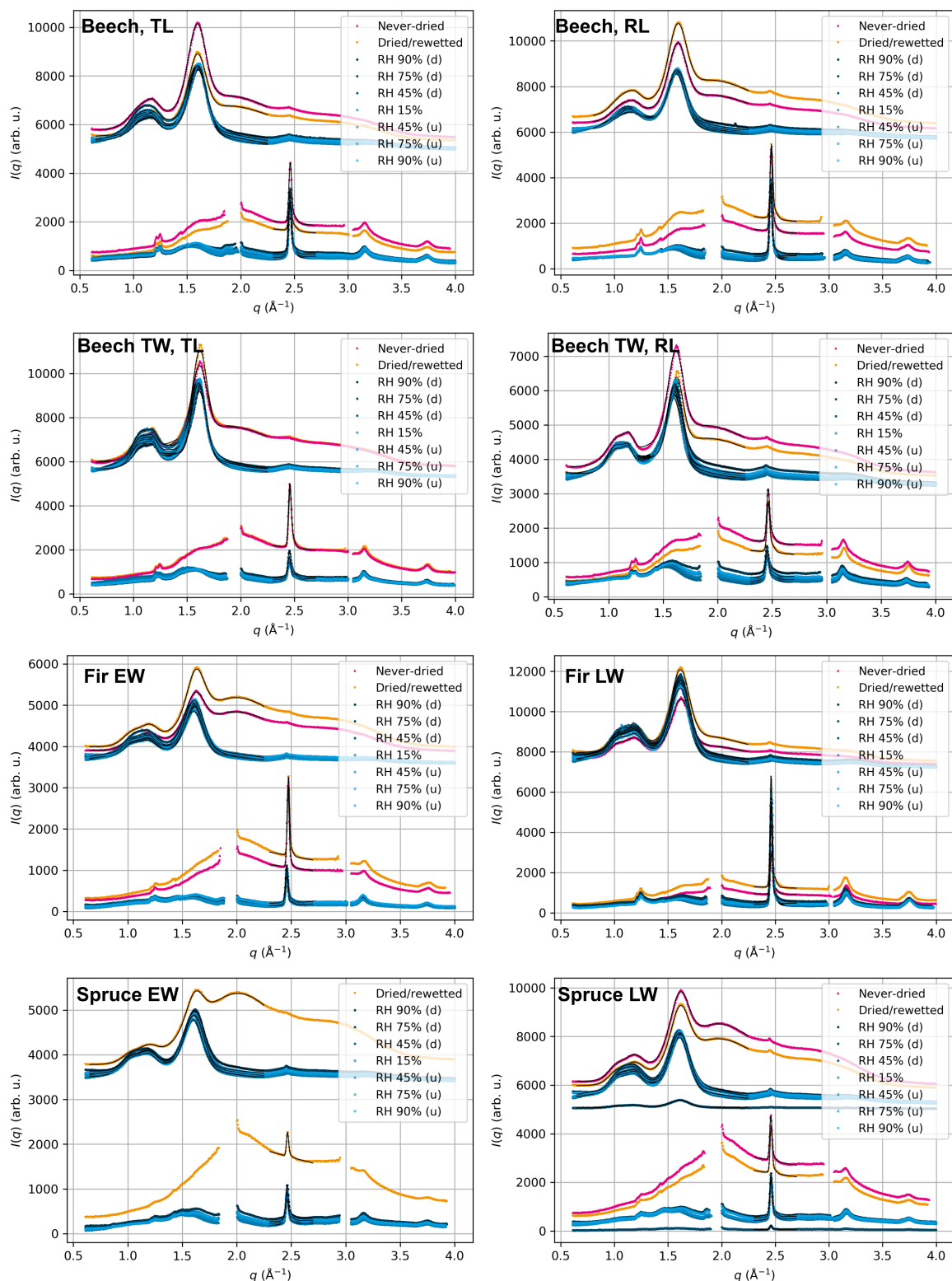


Fig. S8 Equatorial (*above, vertically shifted*) and meridional (*below*) WAXS intensities from wood samples at various moisture conditions and fits used to determine crystal size and lattice spacings (*solid lines*)

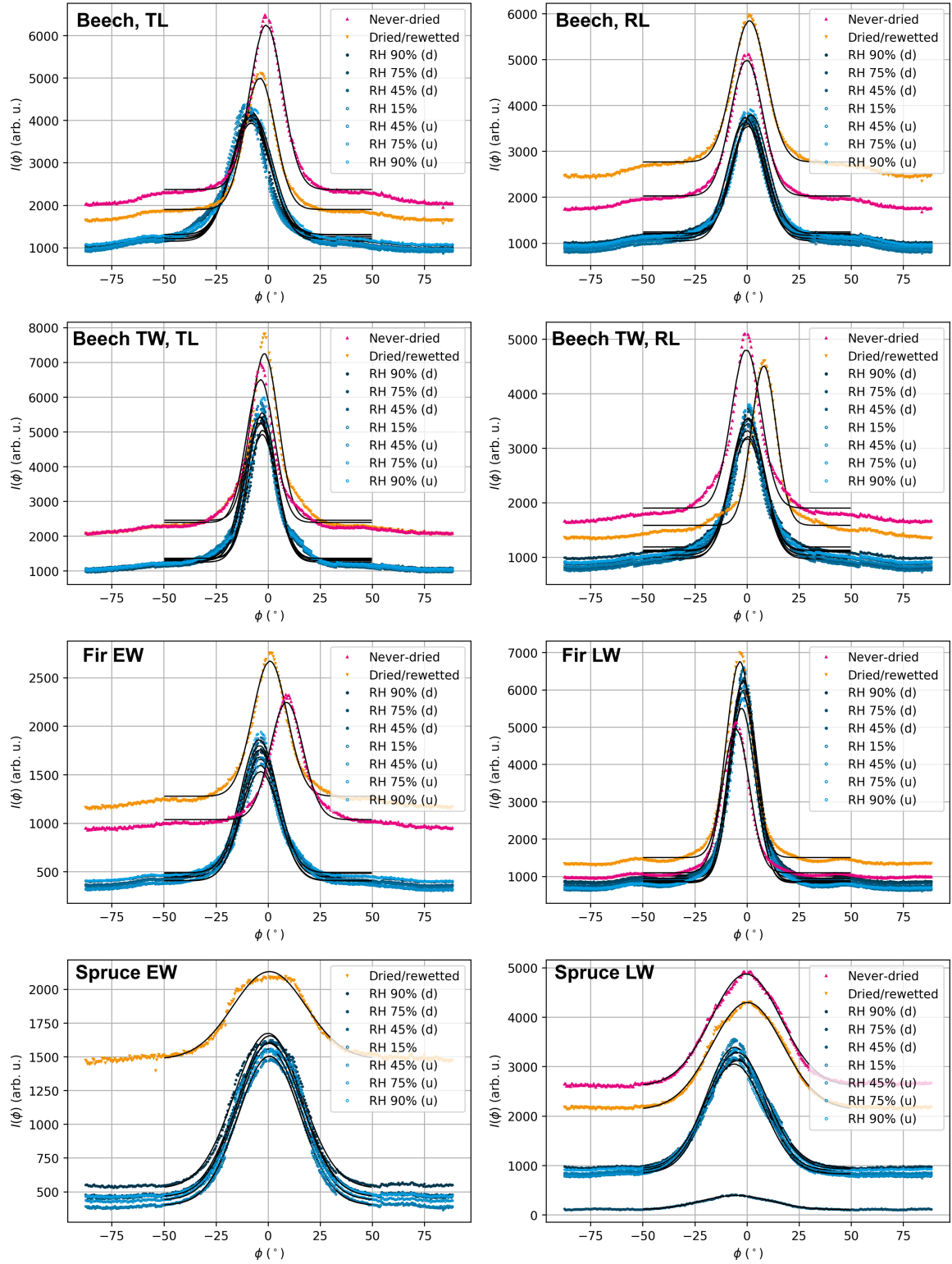


Fig. S9 Fits of Gaussian functions (*solid lines*) to azimuthal WAXS intensity distributions (*symbols*) from wood samples at various moisture conditions, averaged around the 200 diffraction peak of cellulose I_β (q range approximately from $1.6 \text{ \AA}^{-1}$ to $1.7 \text{ \AA}^{-1}$)

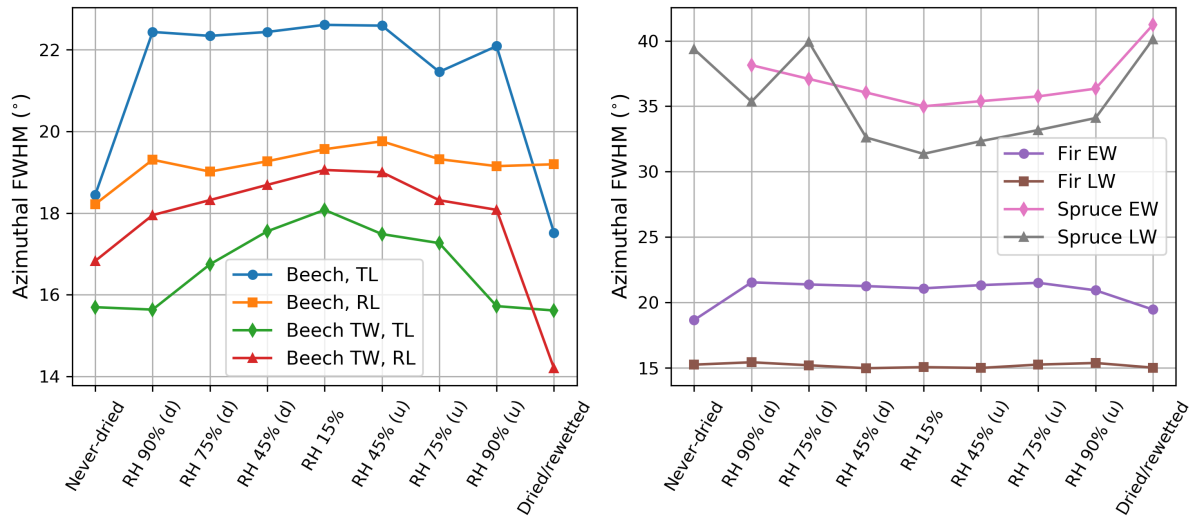


Fig. S10 Azimuthal widths (FWHM of Gaussian fits in Figure S9) of equatorial streaks in WAXS intensities from wood samples at various moisture conditions, averaged around the 200 diffraction peak of cellulose I_β (q range approximately from $1.6 \text{ \AA}^{-1}$ to $1.7 \text{ \AA}^{-1}$)

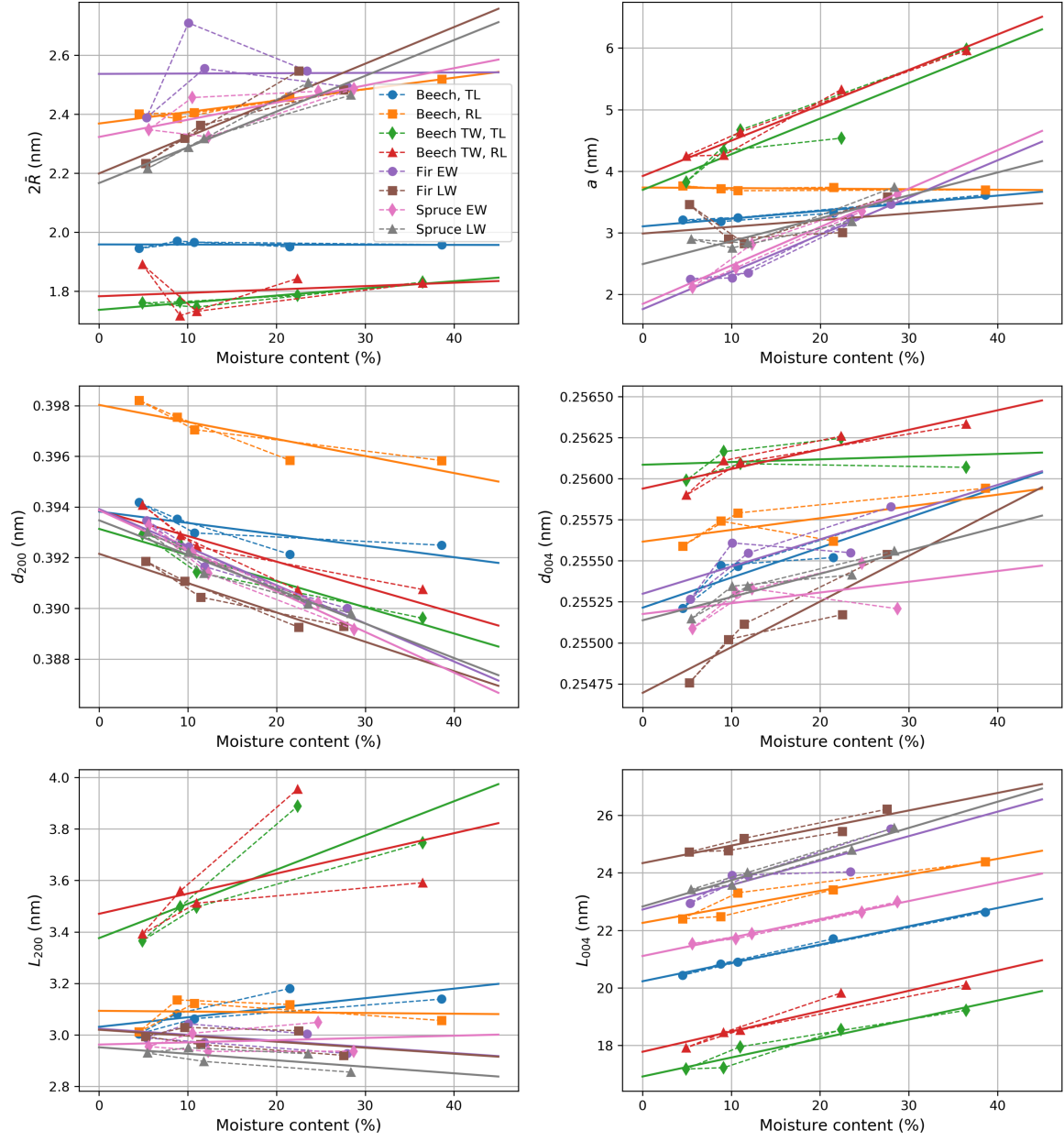


Fig. S11 Variation of nanostructural parameters determined with SAXS ($2\bar{R}$, a) and WAXS (d_{200} , d_{004} , L_{200} , L_{004}) for wood samples at RH values between 15% and 90%, with linear fits presented by *solid lines*