Supplementary Material to

Water sorption in wood cell walls – data exploration of the underlying physicochemical mechanisms

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Details of the results of the statistical analysis using backward elimination are given in the following. Table S1 shows the sequence in which non-significant parameters (physical and chemical characteristics) were removed from the analysis until only statistically significant parameters ($P < 0.05$) remained. Table S1 covers both the analysis of the full dataset as well as four subsets of data, while the *F*- and P-values of the final set of statistically significant parameters are described in Tables S2-S6. The residuals of each analysed set of data are shown in Fig. S1 along with the actual versus predicted values of the normalised moisture content. Table S7 gives the estimates for the statistically significant parameters, whereas Table S8 illustrates the weight of these parameters in predicting the variation in normalised cell wall moisture content between specimens.

Fig. S2-S3 illustrates the rate of sorption during conditioning to the different levels of relative humidity (RH) in the 20-95% range. Fig. S4 shows the correlation between moisture content and cellulose crystallinity, whereas Fig. S5 shows the correlation between hydroxyl accessibility and cellulose crystallinity. Both of these figures are derived from literature data. Fig. S6 shows an example of the Gaussian peak fitting of the experimental data from powder XRD to determine cellulose crystallinity.

Table S1. Gradual removal of non-significant parameters in predicting the normalized moisture content of cell walls. Initially, the following parameters were excluded from the analysis: ash content, extractives content, and density after extraction

Dataset	Order of parameter removal	P-value
All RH levels	1. Hemicelluloses	0.8261
	2. Density before extraction	0.5795
	3. Microfibril angle, S2	0.4413
20-80% RH	1. Hemicelluloses	0.6818
	2. Microfibril angle, S1 & S3	0.6966
	3. Microfibril angle, S2	0.2192
80-100% RH	1. Hemicelluloses	0.7716
	2. Density before extraction	0.6314
	3. Microfibril angle, S2	0.2283
95-100% RH	1. Hemicelluloses	0.8024
	2. Density before extraction	0.6720
	3. Microfibril angle, S2	0.1950
100% RH	1. Hemicelluloses	0.7716
	2. Density before extraction	0.6314
	3. Microfibril angle, S2	0.2283
	4. Hydroxyl accessibility	0.1515

Table S2. Statistically significant parameters in predicting the normalised moisture content at all levels of relative humidity (RH)

Parameter	*F*-value	*P*-value
RH level	108.96	< 0.0001
Cellulose content	24.91	< 0.0001
Microfibril angle, S1 & S3	21.92	< 0.0001
Cellulose crystallinity	8.56	0.0039
Lignin content	7.88	0.0055
Hydroxyl accessibility	5.49	0.0202

Table S3. Statistically significant parameters in predicting the normalised moisture content at 20%-80% relative humidity (RH)

Parameter	*F*-value	*P*-value
RH level	253.78	< 0.0001
Cellulose crystallinity	94.09	< 0.0001
Lignin content	85.02	< 0.0001
Hydroxyl accessibility	60.05	< 0.0001
Cellulose content	19.09	< 0.0001
Density before extraction	4.65	0.0341

Table S4. Statistically significant parameters in predicting the normalised moisture content at 80%-100% relative humidity (RH)

Parameter	*F*-value	*P*-value
RH level	88.74	< 0.0001
Cellulose content	49.20	< 0.0001
Microfibril angle, S1 & S3	34.04	< 0.0001
Lignin content	24.35	< 0.0001
Cellulose crystallinity	5.53	0.0204
Hydroxyl accessibility	4.10	0.0453

Table S5. Statistically significant parameters in predicting the normalised moisture content at 95%-100% relative humidity (RH)

Parameter	*F*-value	*P*-value
Cellulose content	67.10	< 0.0001
Microfibril angle, S1 & S3	44.56	< 0.0001
Lignin content	35.65	< 0.0001
RH level	22.80	< 0.0001
Cellulose crystallinity	6.00	0.0161
Hydroxyl accessibility	4.06	0.0465

Table S6. Statistically significant parameters in predicting the normalised moisture content at 100% relative humidity (RH)

Parameter	*F*-value	*P*-value
Lignin content	114.62	< 0.0001
Cellulose content	65.77	< 0.0001
Microfibril angle, S1 & S3	39.41	< 0.0001
Cellulose crystallinity	4.28	0.0418

Table S7. Estimates and standard error (both multiplied by 10^2) of the statistically significant parameters in predicting the normalised moisture content at various levels of relative humidity (RH)

Wood characteristic	Relative humidity range (%)				
	20-100	20-80	80-100	95-100	100
Bulk density		0.001 ± 0.000			
Microfibril angle, S1 & S3	-0.126 ± 0.027		-0.192 ± 0.033	-0.222 ± 0.033	-0.222 ± 0.035
Cellulose	-0.449 ± 0.090	0.115 ± 0.026	-0.775 ± 0.111	-0.913 ± 0.112	-0.988 ± 0.122
Lignin	-0.452 ± 0.161	0.404 ± 0.044	-0.974 ± 0.197	-1.189 ± 0.199	-1.559 ± 0.146
Hydroxyl accessibility	-1.348 ± 0.575	-1.247 ± 0.161	-1.426 ± 0.704	-1.432 ± 0.710	
Cellulose crystallinity	0.598 ± 0.204	0.558 ± 0.058	0.589 ± 0.251	0.620 ± 0.253	0.259 ± 0.125

Table S8. Partial R^2-values for the statistically significant parameters in predicting the normalised moisture content at various levels of relative humidity (RH) as well as the R^2-value for the total model

Wood characteristic	Relative humidity range (%)				
	20-100	20-80	80-100	95-100	100
Bulk density		0.004			
Microfibril angle, S1 & S3	0.021		0.062	0.121	0.140
Cellulose	0.024	0.015	0.090	0.183	0.233
Lignin	0.008	0.068	0.044	0.097	0.407
Hydroxyl accessibility	0.005	0.048	0.007	0.011	
Cellulose crystallinity	0.008	0.075	0.010	0.016	0.015
RH level	0.731	0.807	0.485	0.124	0.000
R^2-value for total model	0.825	0.936	0.790	0.733	0.709

Table S9. Fitting parameters and constraints for the seven Gaussian peaks used for the peak deconvolution of the XRD-Data for calculating the crystallinity index. The crystallinity index was calculated as ratio of areas of the peaks: CI=1-Area(P2)/Area(P0-6)

Gaussian peak	assignment		position p (2θ)	rel. height h	width w (2θ)
P0	(1-10)	min	14.9	0.1	1
		max	15.4	0.5	3
P1	(110)	min	16.2	0.1	1
		max	16.9	0.5	2.5
P2	amorphous cell wall	min	18	0.2	1
		max	20	1	12
P3	(200)	min	22.2	0.2	1
		max	22.8	1	2.5
P4	(004) + high. order	min	34.5	0.03	1
		max	35.5	0.4	12
P5	higher order	min	38	0.02	1
		max	42	0.2	12
P6	higher order	min	44	0.02	1
		max	47	0.2	12

Inter peak constraints: w(P0)=w(P1), h(P0)=h(P1)

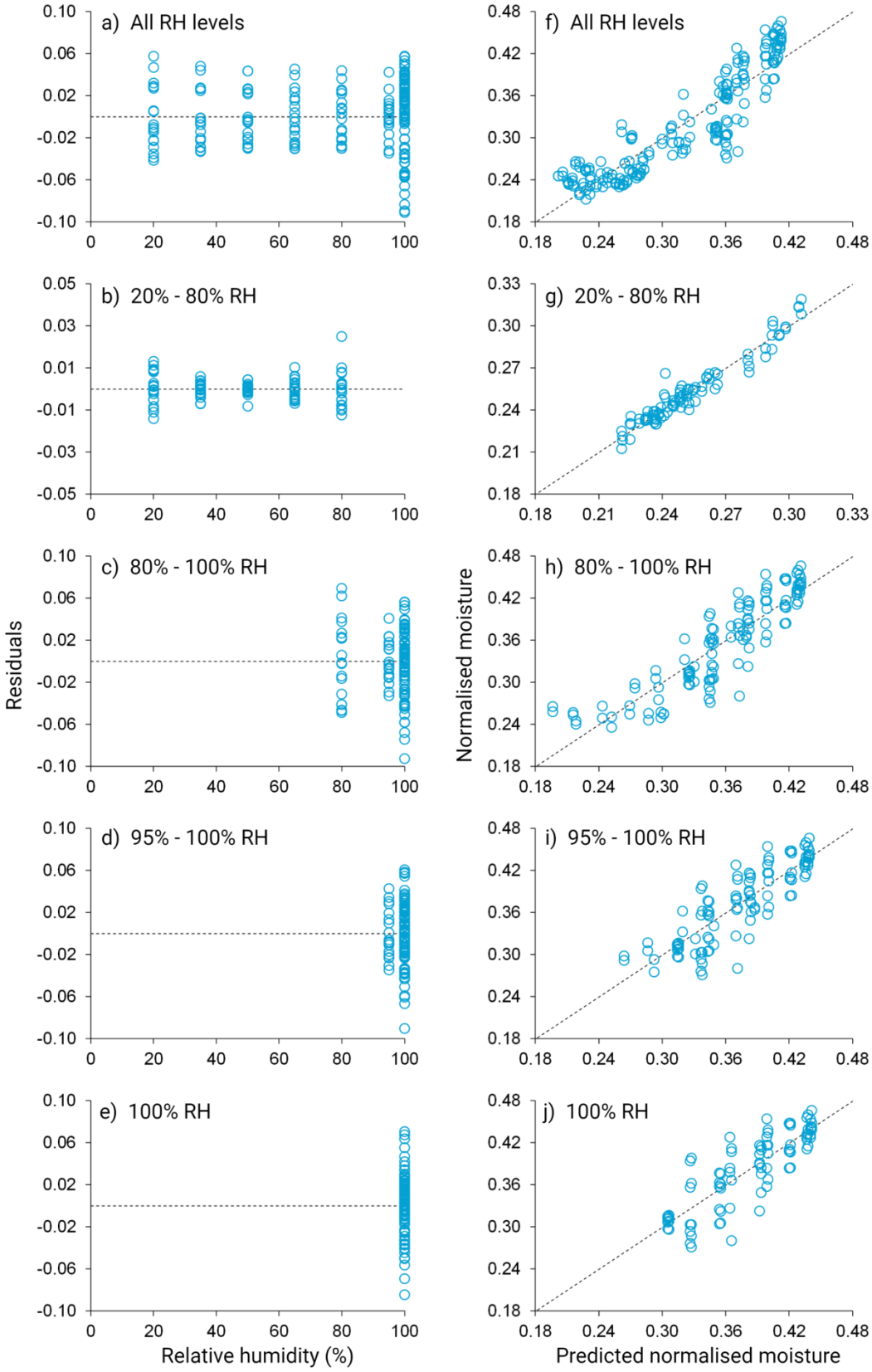

Fig. S1. a)-e) Residuals after statistical analysis of the different data subsets, f)-j) Actual vs. predicted normalised moisture content for the same data subsets as in a)-e)

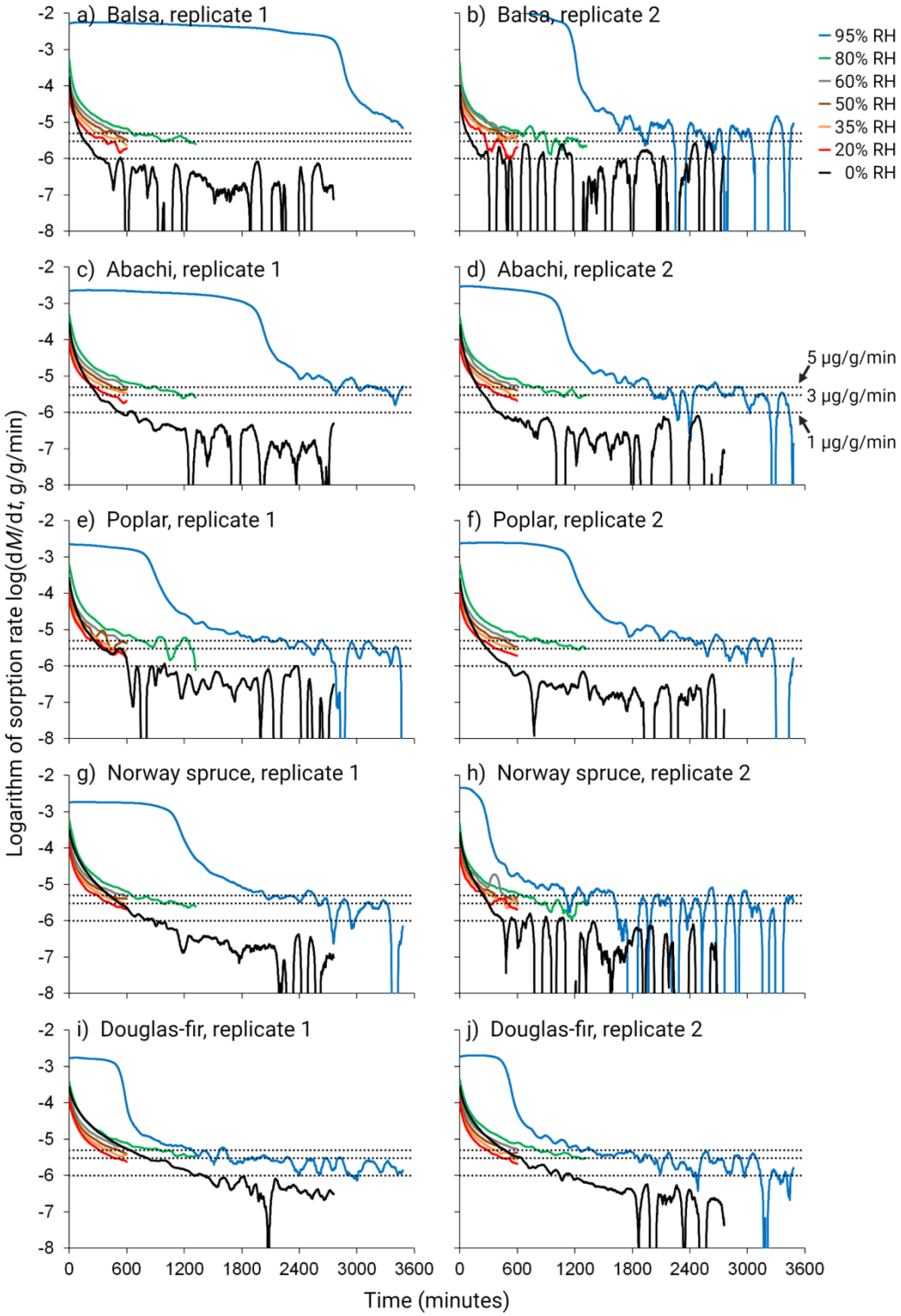

Fig. S2. Rate of sorption, dM/dt, as function of time in the conditioning to different levels of relative humidity (RH) for a-b) balsa, c-d) abachi, e-f) poplar, g-h) Norway spruce, and i-j) Douglas-fir. Dotted lines indicate three mass stability criteria

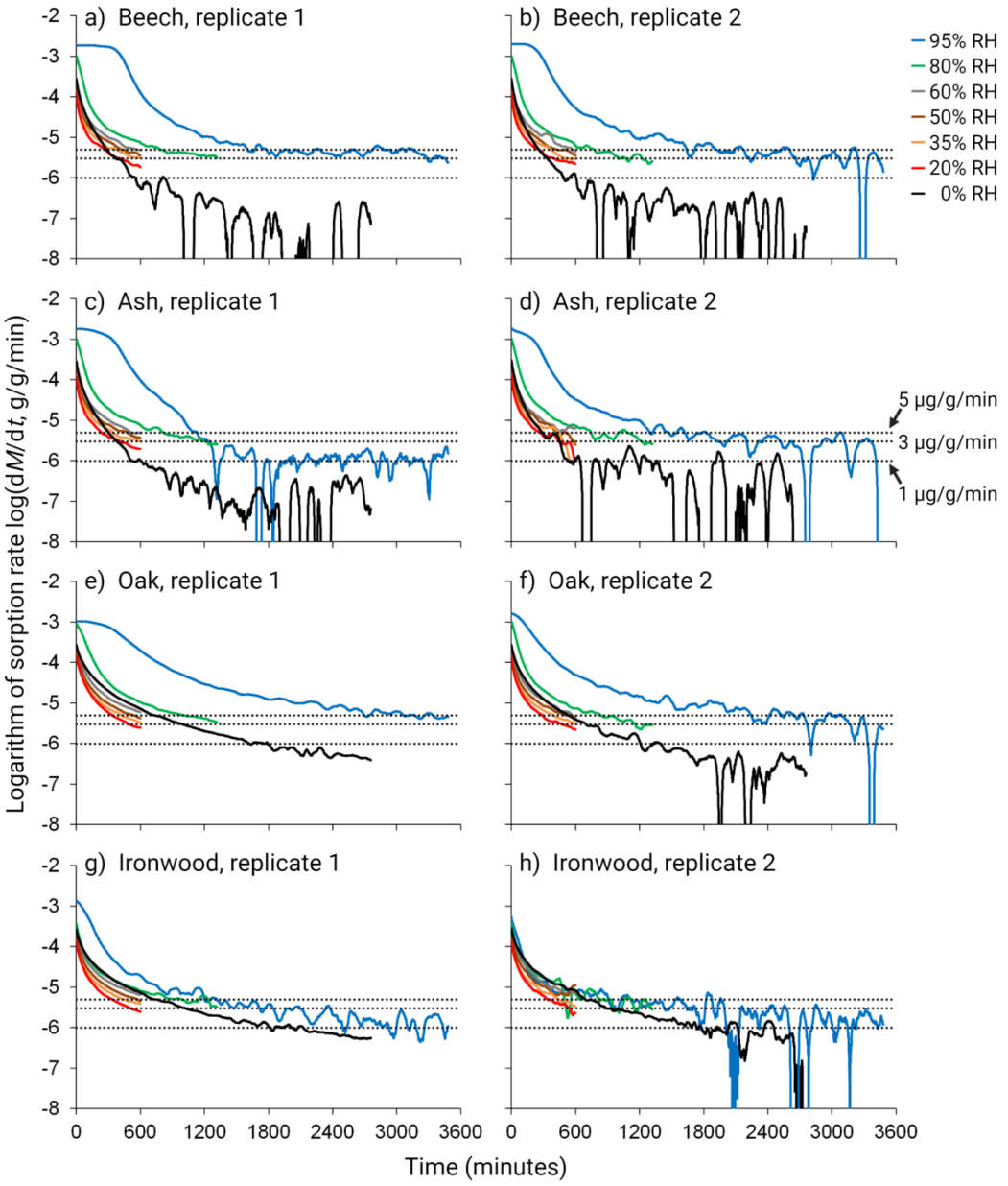

Fig. S3. Rate of sorption, dM/dt, as function of time in the conditioning to different levels of relative humidity (RH) for a-b) beech, c-d) ash, e-f) oak, and g-h) ironwood. Dotted lines indicate three mass stability criteria

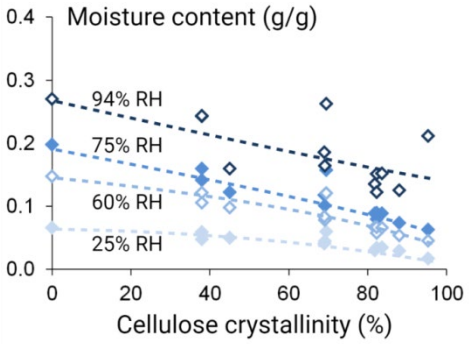

Fig. S4. Correlation between moisture content and crystallinity of cellulose from different sources and treatments at four levels of relative humidity (RH). Based on experimental sorption isotherm data at 23-25 °C from (Hatakeyama et al. 1987; Kocherbitov et al. 2008; Mihranyan et al. 2004; Xie et al. 2011), which for data from (Hatakeyama et al. 1987; Kocherbitov et al. 2008; Xie et al. 2011) was linearly interpolated to the illustrated levels of relative humidity

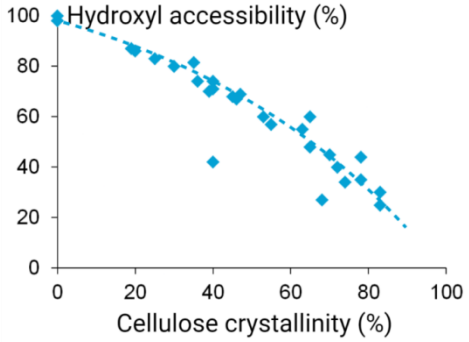

Fig. S5. Correlation between hydroxyl accessibility and crystallinity of cellulose from different sources and treatments. Based on experimental data from (Howsmon 1949; Lang and Mason 1960; Loelovitch and Gordeev 1994; Mann and Marrinan 1956; Pennings et al. 1961; Schroeder et al. 1986)

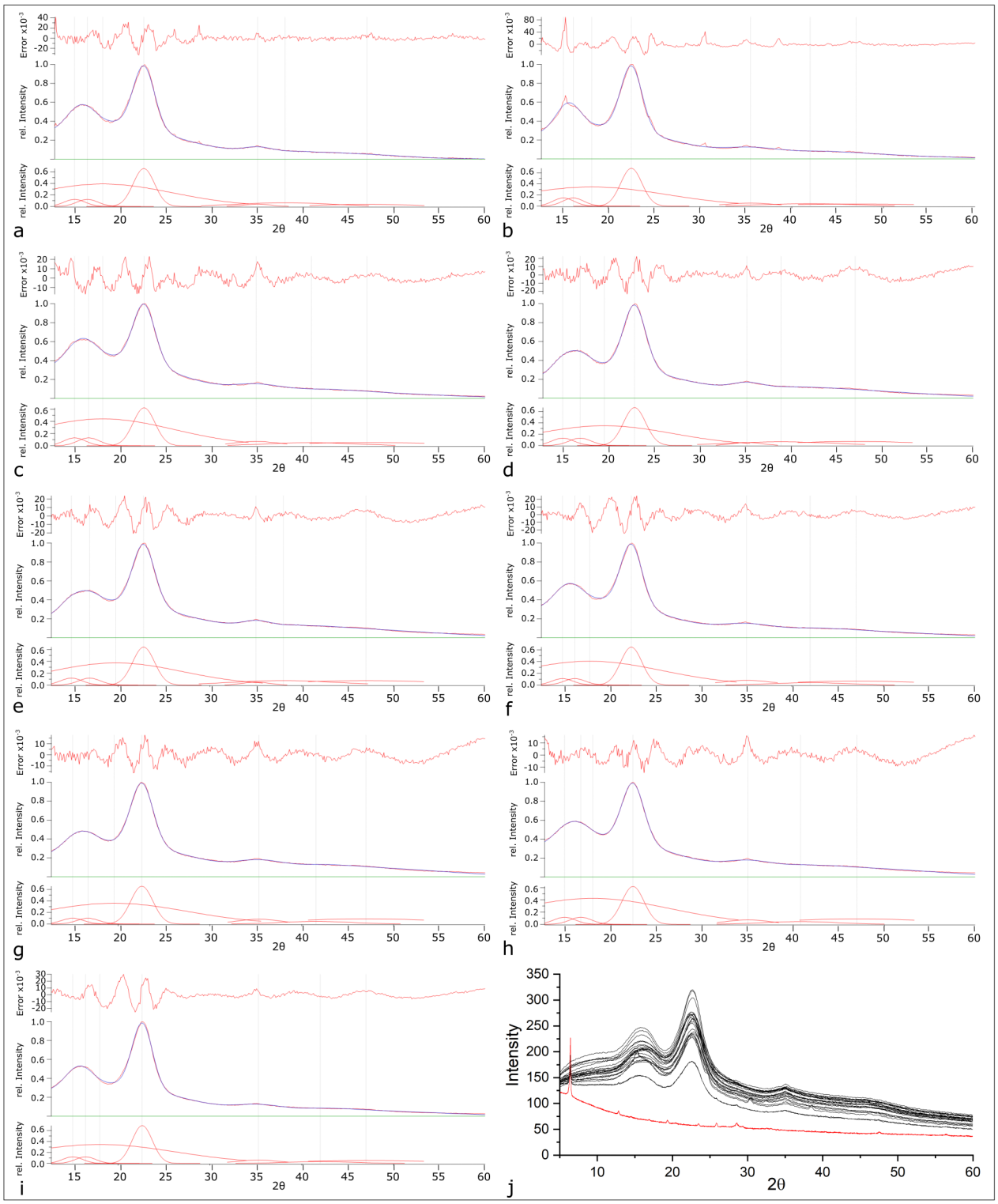

Fig. S6. Peak fitting of diffraction data for calculating crystallinity index. The parameters for the seven Gaussian peaks used to deconvolute the diffraction data are given by the table Table S9. a-i) fitted data of the nine wood species: a) Balsa, b) Abachi, c) Poplar, d) Spruce, e) Douglas-fir, f) Beech, g) Ash, h) Oak, i) Ironwood; midline graphs: truncated (2theta range: 12.5-60°) data (red, background subtracted), fitted intensity (blue), zero line (green), lower line graphs: deconvoluted data showing the seven Gaussian peaks, upper line graphs: residual error j) Raw data as obtained from the diffractometer for the different wood species (black) and for the blank runs for background subtraction (red).

References

Hatakeyama T, Ikeda Y, Hatakeyama H (1987) Effect of bound water on structural change of regenerated cellulose. 188:1875-1884 https://doi.org/10.1002/macp.1987.021880811

Howsmon JA (1949) Water sorption and the poly-phase structure of cellulose fibers. 19:152-163 https://doi.org/10.1177/004051754901900303

Kocherbitov V, Ulvenlund S, Kober M, Jarring K, Arnebrant T (2008) Hydration of microcrystalline cellulose and milled cellulose studied by sorption calorimetry. 112:3728-3734 https://doi.org/10.1021/jp711554c

Lang ARG, Mason SG (1960) Tritium exchange between cellulose and water - accessibility measurements and effects of cyclic drying. 38:373-387 https://doi.org/10.1139/v60-053

Loelovitch M, Gordeev M (1994) Crystallinity of cellulose and its accessibility during deuteration. 45:121-123 https://doi.org/10.1002/actp.1994.010450211

Mann J, Marrinan HJ (1956) The reaction between cellulose and heavy water .2. Measurement of absolute accessibility and crystallinity. 52:487-492 https://doi.org/10.1039/tf9565200487

Mihranyan A, Llagostera AP, Karmhag R, Strømme M, Ek R (2004) Moisture sorption by cellulose powders of varying crystallinity. 269:433-442

Pennings AJ, Prins W, Hale RD, Rånby BG (1961) Inter- and intramolecular order in regenerated cellulose. 5:676-684

Schroeder LR, Gentile VM, Atalla RH (1986) Nondegradative preparation of amorphous cellulose. 6:1-14

Xie YJ, Hill CAS, Jalaludin Z, Sun DY (2011) The water vapour sorption behaviour of three celluloses: analysis using parallel exponential kinetics and interpretation using the Kelvin-Voigt viscoelastic model. 18:517-530