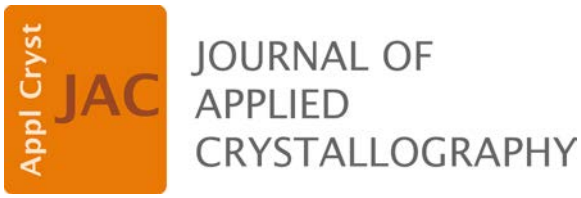

Volume 52 (2019)

Supporting information for article:

Wide angle x-ray scattering combined with pair distribution function analysis of pyrolyzed wood

Agnieszka Poulain, Capucine Dupont, Pablo Martinez, Chamseddine Guizani and Jakub Drnec

Table S1 Main properties of raw samples – full list including standards and elements with low concentration.

		Standard	Unit	Beech	Orchard apricot
	Ash	CEN/TS 14775	wt% dry basis	0.5	3.8
Elemental analysis	C	CEN/TS 15104	wt% dry basis	49.1	48.3
	H	CEN/TS 15104		5.7	6.3
	O	By difference		44.5	40.3
	N	CEN/TS 15104		0.15	1.25
	Al	EN 15290	mg.kg dry biomass^{-1}	53	104
	As	EN 15297		nm (*)	0.3
	B	NF EN ISO 11885		nm	14
	Ca	EN 15290		1243	10927
	Cd	EN 15297		nm	<0.4
	Cr	EN 15297		nm	1
	Cl	EN 15289		81	326
	Cu	EN 15297		nm	3
	Fe	EN 15290		50	88
	Hg	EN 15297		nm	<0.05
	K	EN 15290		862	7254
	Mg	EN 15290		279	1374
	Mn	EN 15297		193	20
	Na	EN 15290		24	41
	P	EN 15290		61	1161

	Pb	EN 15297		nm	<0.5
	S	EN 15289		450	819
	Si	Internal method		249	990
	Ti	EN 15290		6	9
	Zn	EN 15297		nm	17
Macromolecular constituents analysis	Extractives	Internal method	wt% dry basis (normalized)	3.0 (**)	20.9
	Cellulose	Internal method		43.3 (**)	27.0
	Lignin	TAPPI standard T222 om-83		22.0 (**)	27.9
	Hemicellulose	Internal method		31.0 (**)	20.5
	Glucan	TAPPI standard T249 cm-85 - ASTM E1758 standard method	wt% dry basis	nm	26.9
	Mannan			nm	1.2
	Xylan			nm	11.8
	Galactan			nm	2.6
	Arabinan			nm	3.4
	Acetates			3.0 (**)	20.9

Table S2 Overview of the microstructural parameters obtained after manual fitting of BFH and ASH series in CarbX. Layer structure: L_a – average graphene layer extent, $\langle l \rangle$ - average chord length, κ_a - polydispersity of chord length l, l_{cc} – average C-C bond length, σ_1 – standard deviation of the first neighbor distribution; Layer stacking: L_c – average stack height, κ_c – polydispersity of stack height, a_3 – average interlayer spacing, $a_{3,min}$ – minimum of interlayer spacing, σ_3 – standard deviation of interlayer spacing, $\langle N \rangle$ - number of graphene layers per stack, η – homogeneity of the stack, q – parameter of preferred orientation, Δ_{an} – parameter of anisotropy of the atomic form factor of carbon.

	BFH800	BFH1000	BFH1200		ASH1000	ASH1200	ASH1400	
L_a [Å]	10.3	17.2	17.9	↑	24.9	27.2	47.3	↑
$\langle l \rangle$ [Å]	7.7	13.8	15.4	↑	22.9	25.1	44.9	↑
κ_a	0.33	0.25	0.17	↓	0.09	0.08	0.05	↓
l_{cc} [Å]	1.40	1.40	1.40	-	1.40	1.40	1.40	-
σ_1	0.12	0.12	0.12	-	0.07	0.04	0.12	?
L_c [Å]	12.6	12.6	12.3	↓	9.6	11.7	13.1	↑
κ_c	0.25	0.28	0.26	?	0.10	0.09	0.41	?
a_3 [Å]	3.61	3.52	3.54	?	3.60	3.56	3.56	↓
$a_{3,min}$ [Å]	2.83	2.99	2.76	?	3.07	2.86	3.00	?
σ_3	0.50	0.47	0.47	↓	0.57	0.54	0.59	?
$\langle N \rangle$	2.8	2.8	2.7	↓	2.92	3.0	2.6	?
η	1.00	1.00	1.00	-	1.00	0.99	1.00	?
q	0.00	0.00	0.00	-	0.00	0.00	0.03	↑
Δ_{an}	61.5	52.5	48.0	↓	51	26.0	31.0	?

Table S3 Table S3. Summarized results of the PDF analysis of the BFH and ASH chars.

	BFH800	BFH1000	BFH1200	BFH1400 refined as a combination of the three components: calcite, graphene and fairchildite	direction of changes
c [Å]	7.22	7.04	7.08	7.08	↓
U_{33} [Å^2]	0.09±0.15	0.21±0.25	0.25±0.22	0.23±0.22 60% (calcite) 25% (graphene) 15% (fairchildite)	↑
R_w [%]	24.8	24.5	28.5	37.0	↑
sp diameter [Å]	7.2±1.5	10.3±2.6	11.5±2.4	13.3±3.3	↑
	ASH800 ASH800*	ASH1000 ASH1000*	ASH1200 ASH1200*	ASH1400	
c [Å]	7.20	7.20	7.12	7.12	↓
U_{33} [Å^2]	0.21±0.26 7.7%**	0.26±0.22 10.8%**	0.36±0.20 5.4%**	0.57±0.20	↑
R_w [%]	41.8 38.5***	41.7 36.2***	34.4 33.5***	34.4	↓
sp diameter [Å]	9.1±2.0	13.2±3.1	17.5±3.7	22.6±3.6	↑

* Ca(OH)2 added in the refinement; ** concentration of $Ca(OH)_2$; *** agreement factor after addition of $Ca(OH)_2$

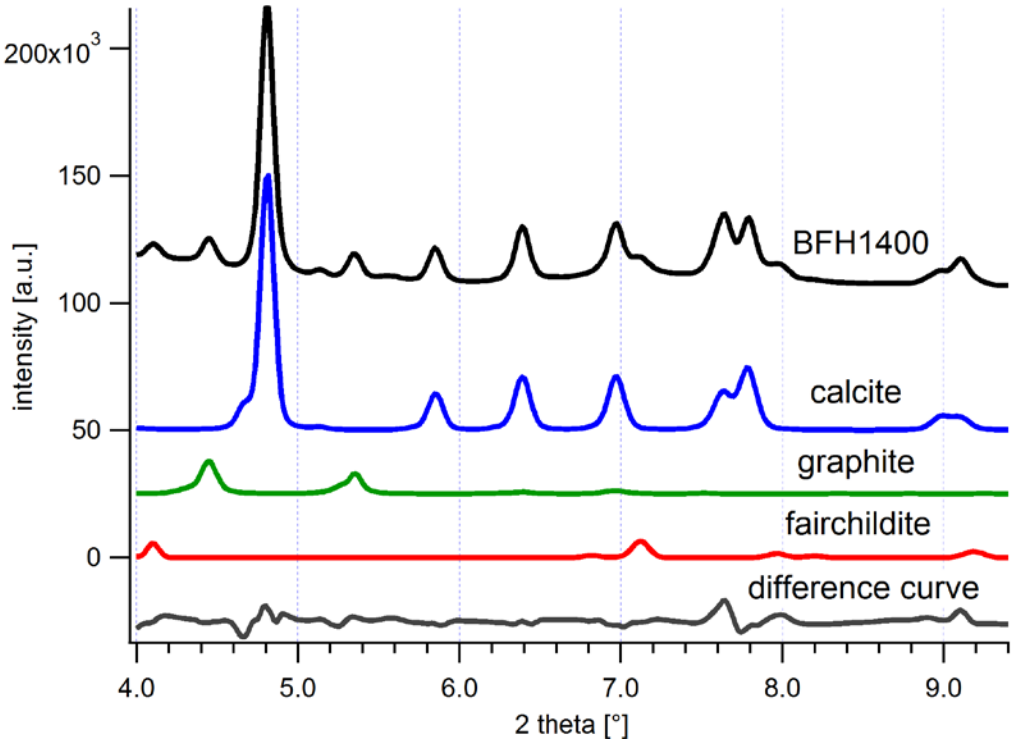

Figure S1 Modeling of the BFH1400 beech with calcite ($CaCO_3$, blue curve), graphite (final *c*=7.07 Å, black curve) and fairchildite ($K_2Ca(CO_3)_2$), green curve). Red curve represents the calculated sum of the three components. Offset introduced for sake of clarity.

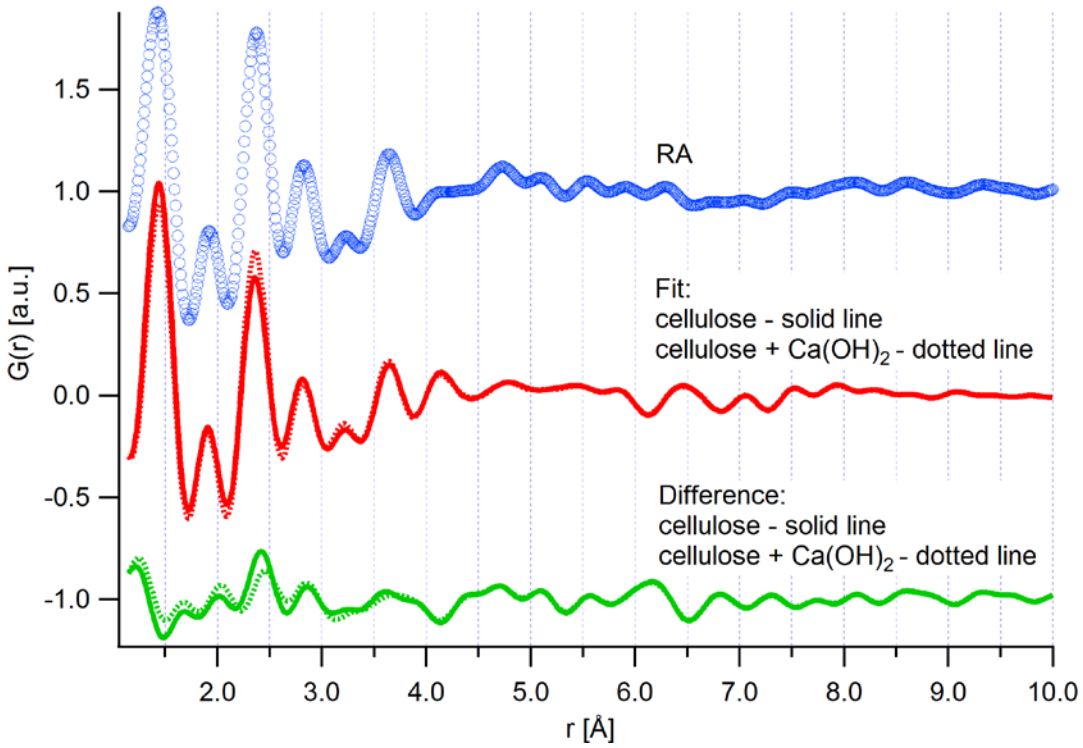

Figure S2 Modeling of the RA PDF with cellulose only and as a combination of cellulose and $Ca(OH)_2$. Blue circles – experimental data, red line – calculated, green line– difference. Offset introduced for sake of clarity.

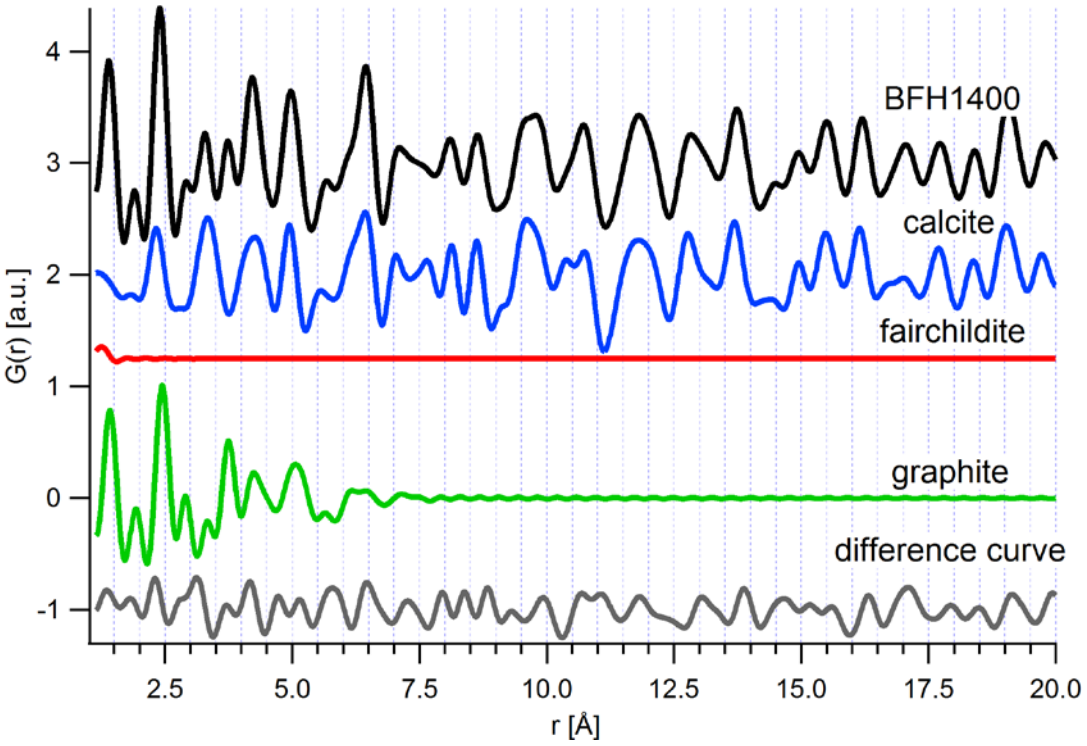

Figure S3 Final modeling of the experimental PDF of the BFH1400 using calcite, fairchildite and modified graphite structures. Color code is the same as in Figure S2. Little input from fairchildite comes from overestimation of calcite concentration, as both minerals have very similar composition. Calculated concentrations are 60 % ($CaCO_3$,), 25 % ($K_2Ca(CO_3)_2$) and 15 % (graphite). Offset introduced for sake of clarity.

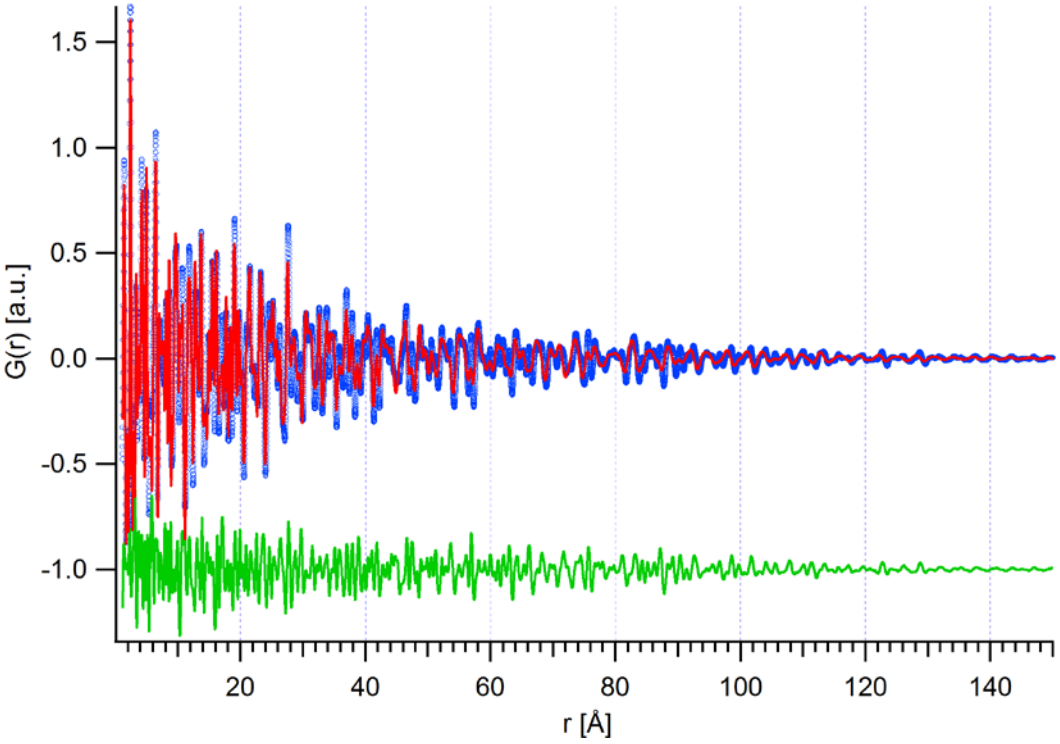

Figure S4 Long range order in the experimental PDF of BFH1400 coming from the crystallinity of calcite; blue circles – experimental, red line – calculated, green line– difference. Although the three phases contribute to the pattern, the main component is $CaCO_3$.