Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supplementary Information: Shaped mesoporous materials from fresh macroalgae

J. R. Dodson,V. L. Budarin, A. J. Hunt, P. Shuttleworth and J. H. Clark*

Materials and methods

Laminaria digitata (October), *Laminaria hyperborea* (August) and *Saccharina latissima* (October) samples came from Clachan Sound, Scotland collected in 2010. Following collection they were frozen, air dried and ground. *Ascophyllym nodosum* and *Fucus vesiculosus* were collected from St Edwards Bay and *Laminaria digitata* for shape studies was collected from Seaham beach, both near Newcastle (UK) in March 2012. The samples were air dried and either ground or separated into shaped samples. D-mannitol, laminarin, fucoidan and calcium alginate were purchased from Sigma Aldrich.

Expansion

Ground seaweed was mixed with distilled water (1:10 w/v) and stirred for 24 h at room temperature. The sample was washed with water and then exchanged with EtOH (1:10, 99 %) five times by shaking the sample in EtOH for 10 minutes before centrifuging and exchange. The expanded material was dried under vacuum at 40 °C overnight or using a Thar Technologies scCO_2 rig at 40 °C and 300bar for 4h with a CO_2 flow of 40g/min. The samples were depressurised overnight. In total two days were required to obtain the expanded materials from the dry sample.

Analysis

Nitrogen adsorption measurements were carried out at 77 K using an ASAP 2010 volumetric adsorption analyser from Micromeritics. Before the measurement the samples were outgassed for 3-4 h under vacuum at 150 °C. The BET (Brunauer, Emmett and Teller) specific surface areas were evaluated using adsorption data in the relative pressure range from 0.06 to 0.15. The BJH equation was used to determine the mesoporous volumes and pore size distribution of the expanded macroalgae materials. The micropore volumes and distributions were calculated using Dubinin-Radushkevich and MP methods. Infrared absorption spectra were recorded on powdered samples using a Bruker Vertex 70 FTIR spectrometer equipped with a MKII Golden Gate Single Reflection ATR System with a 45° diamond crystal. SEM micrographs were recorded using a JEOL JSM-649OL. Samples were sparsely scattered on a carbon tab and sputter coated with Au/Pd before analysis. The inorganic content of the materials and thermal decomposition were obtained on a Netzsch 409

Simultaneous Thermal Analyser based on triplicate measurements. Samples (~150 mg) were heated at 10 K min^{-1} from 20 °C to 550 °C under a flow of 150 mL min^{-1} air and 50 mL min^{-1} N_2 and held until no further mass loss was observed. The elemental composition was analysed by ICP-AES on acid digested samples (Yara Analytical Aervices).

Table S1: Literature data on the variation in chemical composition of macroalgae species

	Laminaria digitata,[1,2]	***Saccharina latissima***[1]	***Laminaria hyperborea***[3]	***Ascophyllum nodosum***[2]	***Fucus vesiculoses***[4]	**Comments**
Ash (%)[a]	21-44	22-44	15-33	15-25	14-21	Increases from autumn to spring
Alginic acid (%)[a]	16-45	13-21	22-35	15-30	14-17	Increases from autumn to spring
Laminaran (%)[a]	0-18	0-26	0-24	0-10	2-5	Increases from spring to autumn
Mannitol (%)[a]	4-22	6-22	6-18	5-10	8-16	Increases from spring to autumn
Fucoidan (%)[a]	2-4		2-4	5-10		
Crude proteins (%)[a]	8-15	6-13	5-15	5-10	6-15	Increases from autumn to spring
Fibre (%)[a]	6-8	5-7	5-11	5		Almost constant
Fat (%)[a]	1-2	0.5-3	0.5-1.5	2-7		Almost constant

[a] Dry weight basis

1 Black, W.A.P. The seasonal variation in weight and chemical composition of the common British Laminariaceae. *J. Mar. Biol. Assoc. U.K.* **29**, 45-72 (1950).
2 Guiry, M.D. & Garbary, D.J. A geographical and taxonomic guide to European Seaweeds of Importance. in *Seaweed Resources in Europe: Uses and Potential* (eds. Guiry, M.D. & Blunden, G.) Ch. 1 (John Wiley & Sons, Chichester, 1991).
3 Haug, A. & Jensen, A. Rapport. ser. A. no. 4: Seasonal Variations on the Chemical Composition of Alaria esculenta, Laminaria saccharina, Laminaria hyperborea and Laminaria digitata from Northern Norway. (Norsk Institutt for Tang- og Tareforskning, Oslo, 1954).
4 Black, W.A.P. Seasonal variation in chemical composition of some of the littoral seaweeds common to scotland. Part II. Fucus serratus. Fucus Vesiculosus. Fucus spiralis and pelvetia canaliculata. *Journal of the Society of Chemical Industry* **68**, 183-189 (1949).

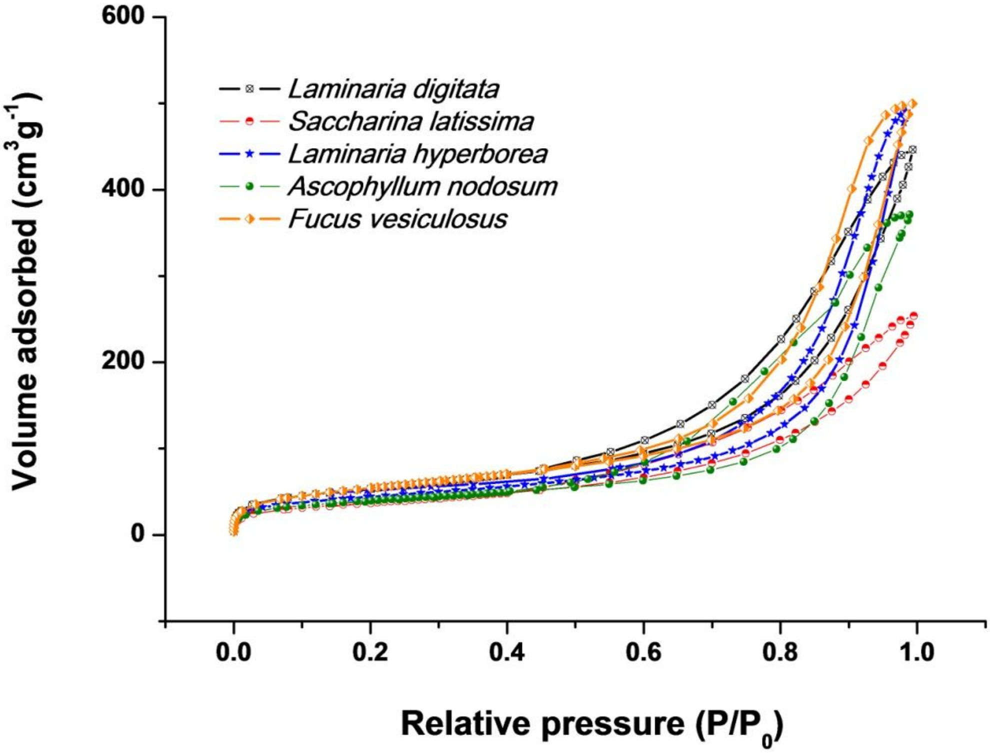


Figure S1: Nitrogen isotherms of ground macroalgae species following expansion and drying directly in a vacuum oven.

Table S2: Textural properties of expanded macroalgae using vacuum oven and $scCO_2$ drying

Seaweed species and collection month	Drying method	S_{BET} ($m^2\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	PD_{avg} (nm)
Laminaria digitata	$scCO_2$	210	0.80	0.10	10.7
	Vacuum oven	192	0.69	0.09	9.9
Saccharina latissima	$scCO_2$	139	0.48	n/a	15.0
	Vacuum oven	198	0.48	n/a	9.7
Laminaria hyperborea	$scCO_2$	205	0.74	0.10	10.3
	Vacuum oven	217	0.72	n/a	13.3
Ascophyllum nodosum	$scCO_2$	168	0.72	0.09	10.3
	Vacuum oven	138	0.57	0.08	9.2
Fucus vesiculosus	$scCO_2$	87.3	0.41	0.05	14.1
	Vacuum oven	196	0.77	0.12	12.0

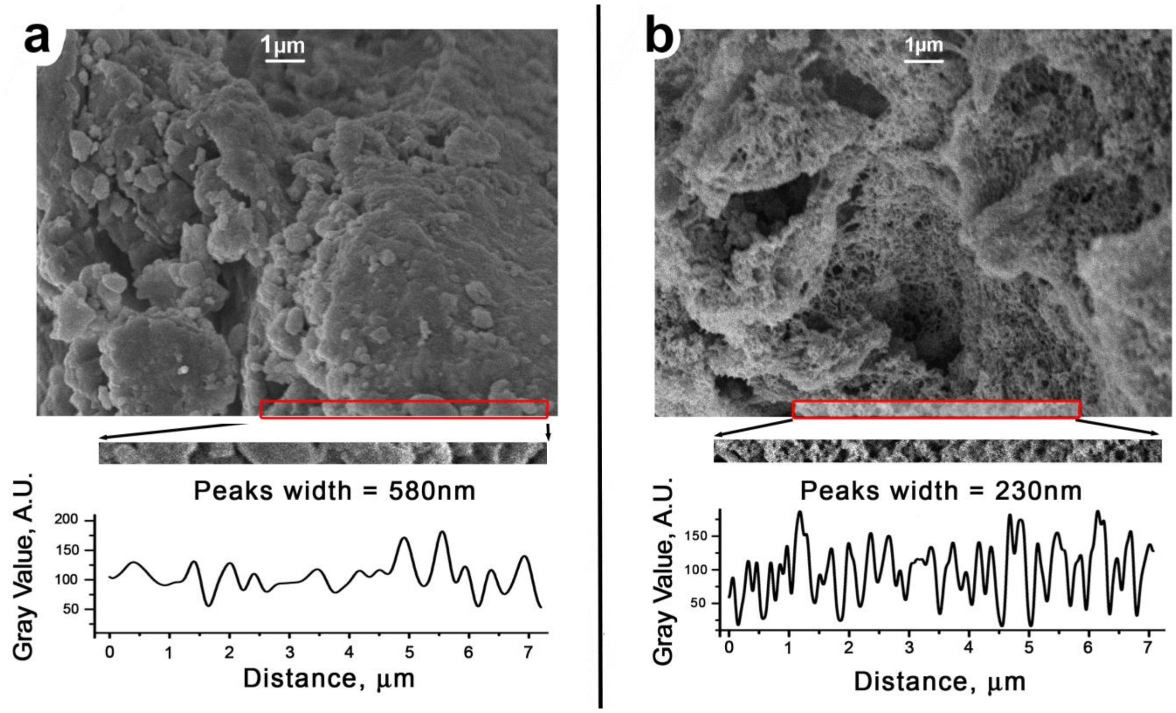


Figure S2: Comparison of textural properties of Laminaria digitata before (a) and after (b) expansion. Graphs of grey value versus distance give a semi-quantitative value on the roughness of the structure i.e. distance between average peak value.

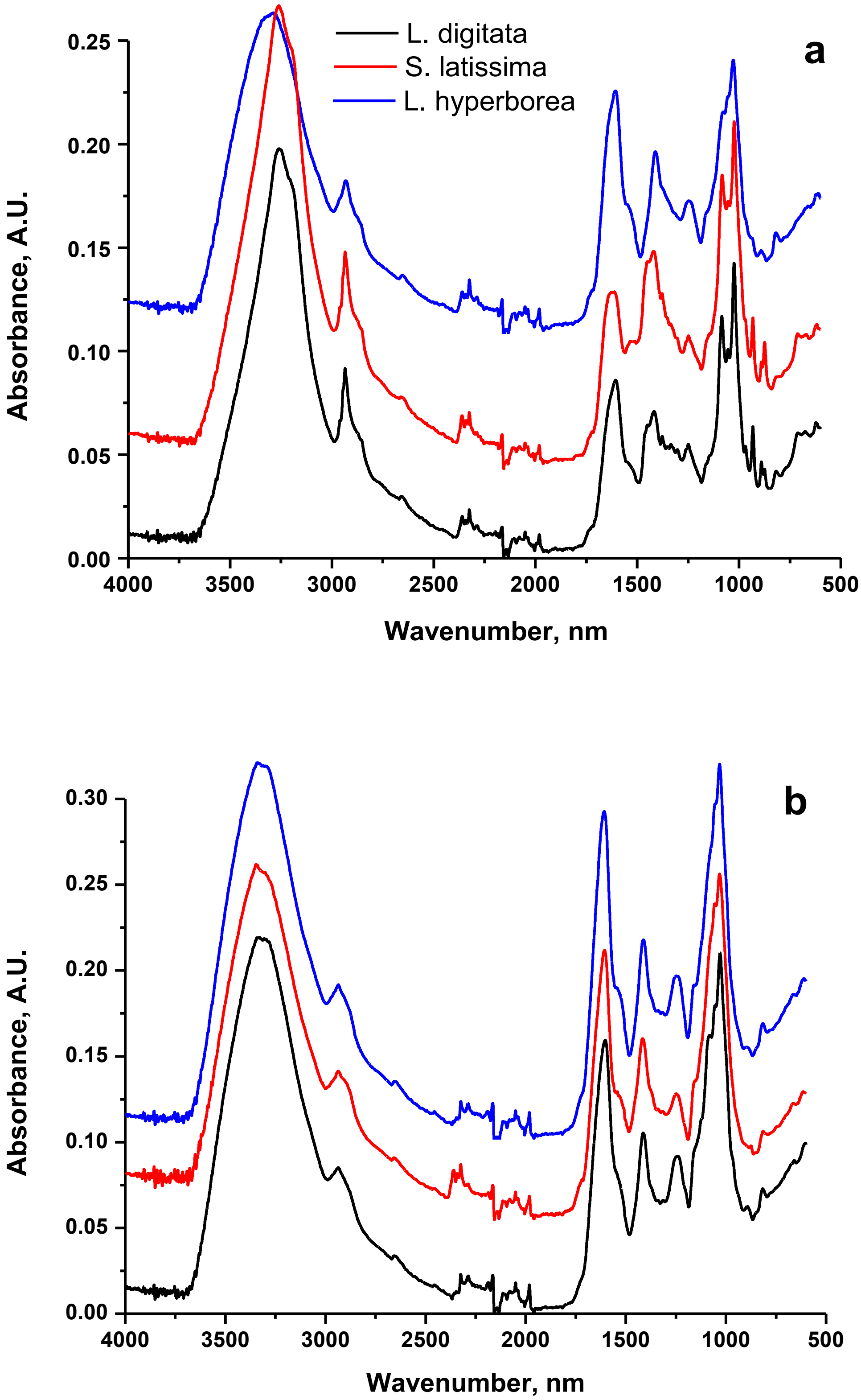


Figure S3: ATR-FTIR spectra of Laminariaceae ground seaweed before (a) and after (b) expansion

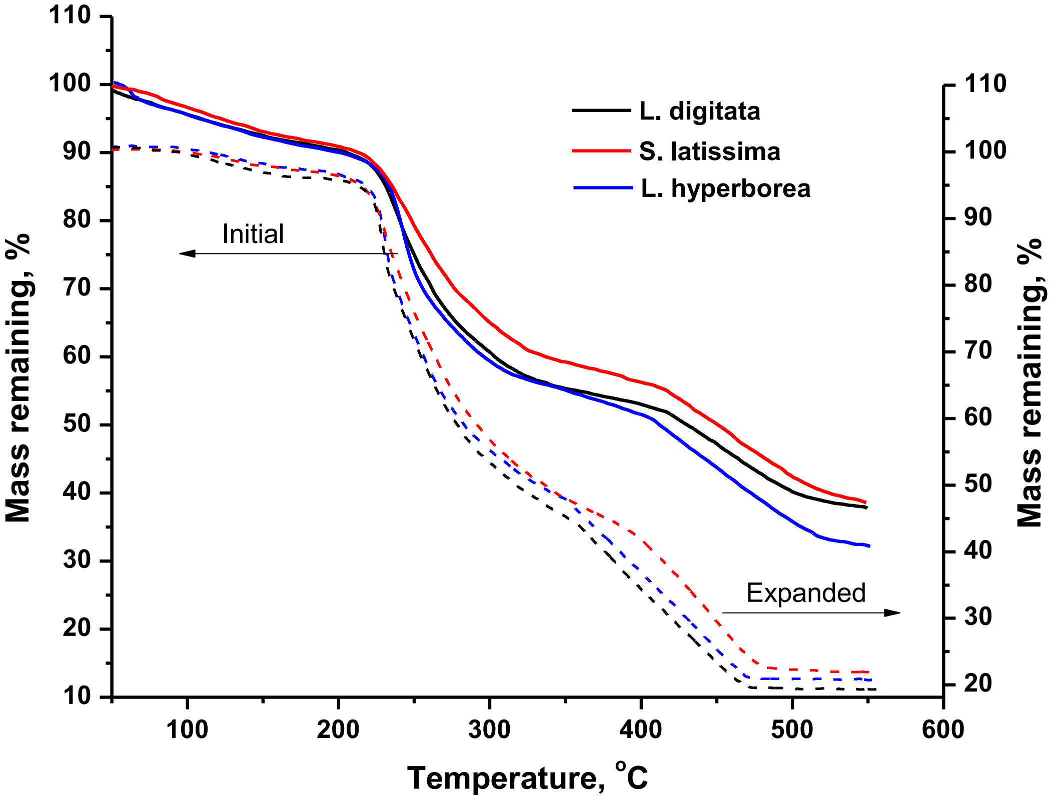
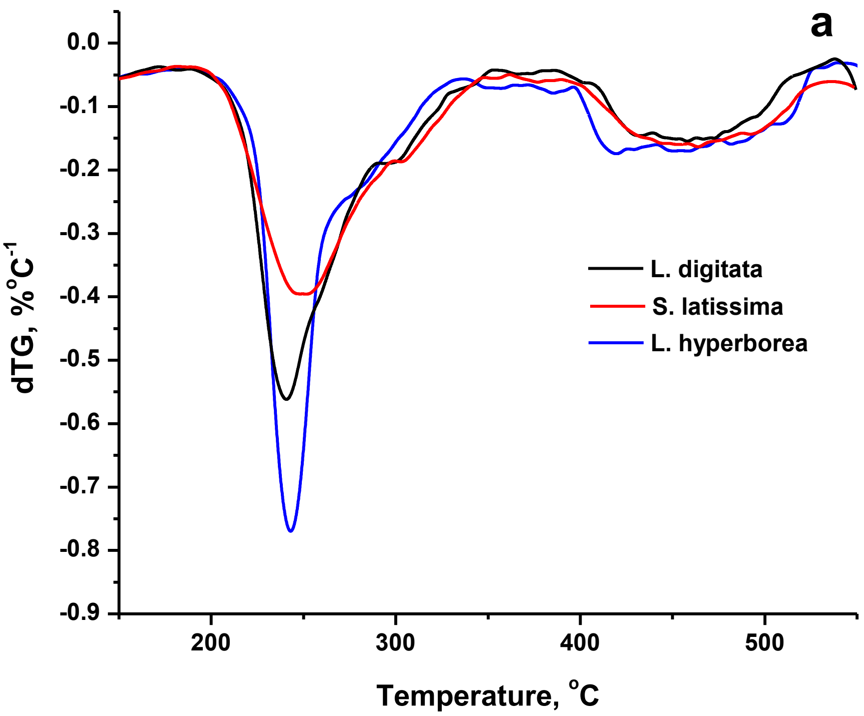


Figure S4: Thermogravimetric weight loss curves under air flow of Laminariaceae seaweed before and after expansion



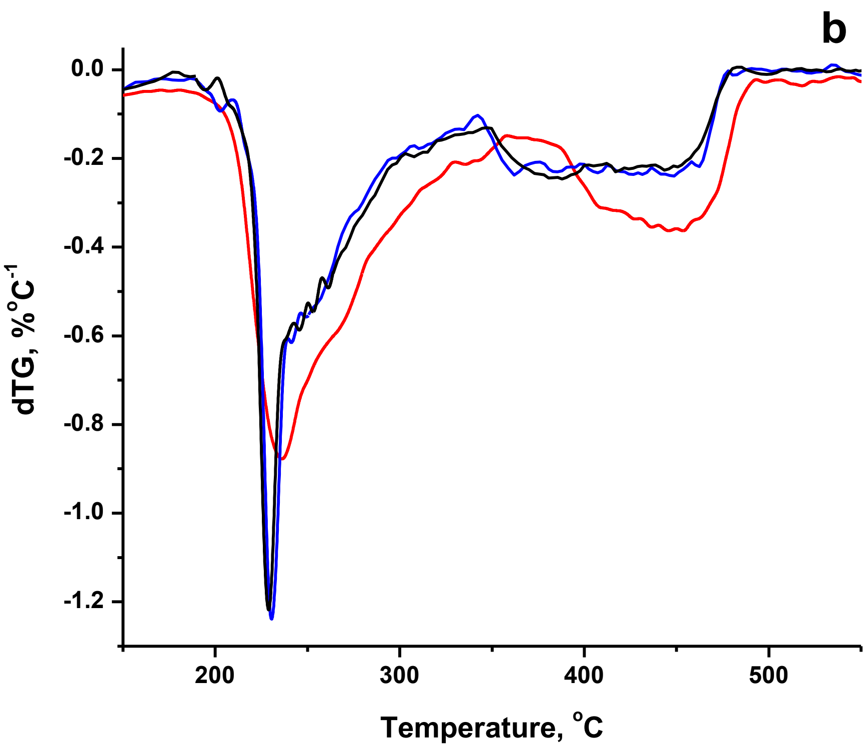


Figure S5: Thermogravimetric derivative of weight loss curve under air flow of Laminariaceae seaweed before (a) and after (b) expansion

Table S3: Infrared peak positions and assignments during the expansion of *Laminaria digitata*

Peak position (cm^{-1})	Initial[a]	Water washed[a]	Expanded[a]	Main component(s)	Assignment[b]
3300	***	***	***	All	υ(O-H)
2939	***	***	*	Mannitol and lipids	$υ_{as}$(C-H) CH_3, CH_2
2857	***	***	*	Mannitol and lipids	$υ_s$(C-H) CH_3, CH_2
1743	**	**	*	Lipids, chlorophyll, phlorotannins and fucoidan	υ(C=O)
1611	**	***	***	Alginate, fucoidan	$υ_{as}$(C=O) carboxylate
1459	**			Laminarin	
1412	**	***	***	Alginate	$υ_s$(C=O) carboxylate
1300-1400	**	*	*	Mannitol, laminarin, lipids	δ (C-H) CH_3, CH_2
1241	**	***	***	Fucoidan	υ(O=S=O)
1085	***	*	*	Mannitol	υ(C-OH)
1056	*	*	*		υ(C-OH)
1024 → 1030	***	**	**	Mannitol, laminarin, fucoidan, alginate	υ(C-O) glycosidic linkage
970	**			Mannitol	υ(C-C)
934	***			Mannitol	υ(C-C)
891	***	* (broad)	* (broad)	Mannitol (s), laminarin (b), fucoidan (b), alginate (b)	υ(C-C)
875	***	* (broad)	* (broad)	Mannitol (s), laminarin (b), fucoidan (b), alginate (b)	υ(C-C)
818	**	**	**	Fucoidan, alginate	υ(C-C)

[a] Number of stars indicates relative intensity of peak. (*** highest)

[b] s symmetric, as asymmetric, υ stretch, δ bend, s strong, b broad

Table S4: Ash content of Laminariaceae seaweed before and after expansion

	Laminaria digitata	*Saccharina latissima*	*Laminaria hyperborea*
Ash content initial seaweed (dry wt%)	37.5	37.2	33.2
Ash content expanded seaweed (dry wt%)	19.7	22.0	20.6

Table S5: Ash composition of initial and expanded Laminariaceae seaweed by ICP-AES analysis of digested samples

	Laminaria digitata			*Saccharina latissima*			*Laminaria hyperborea*		
Element	Initial seaweed (ppm)	Expanded seaweed (ppm)	Ratio	Initial seaweed (ppm)	Expanded seaweed (ppm)	Ratio	Initial seaweed (ppm)	Expanded seaweed (ppm)	Ratio
Al	47.2	119	2.5	273	514	1.9	43.7	4373.0	100.2
As	135.8	30.5	0.2	81.1	13.7	0.2	75.1	15.9	0.2
B	44.3	0.0	0.0	46.6	0.0	0.0	31.6	0.0	0.0
Ca	2337	5137	2.2	5738	15756	2.7	2654	5567	2.1
Fe	94.4	297	3.1	478.3	1277	2.7	120	272	2.3
K	20761	5935	0.3	18353	3881	0.2	18342	5605	0.3
Mg	1082	3847	3.6	1066	3543	3.3	1070	4455	4.2
Na	58741	16413	0.3	47668	10145	0.2	56342	18443	0.3
P	2571	1610	0.6	3082	2293	0.7	2933	1745	0.6
Rb	71.2	20.1	0.3	59.7	13.6	0.2	69.6	23.8	0.3
S	8248	10643	1.3	7463	7620	1.0	9078	10271	1.1
Si	65.5	122.3	1.9	37.1	235.0	6.3	46.3	176.5	3.8
Sr	150	411	2.7	170.9	491.1	2.9	302.5	646.3	2.1
Zn	26.7	57.1	2.1	16.3	33.7	2.1	33.2	62.2	1.9
Sum	94375	44642	0.5	84533	45815	0.5	91141	51655	0.6

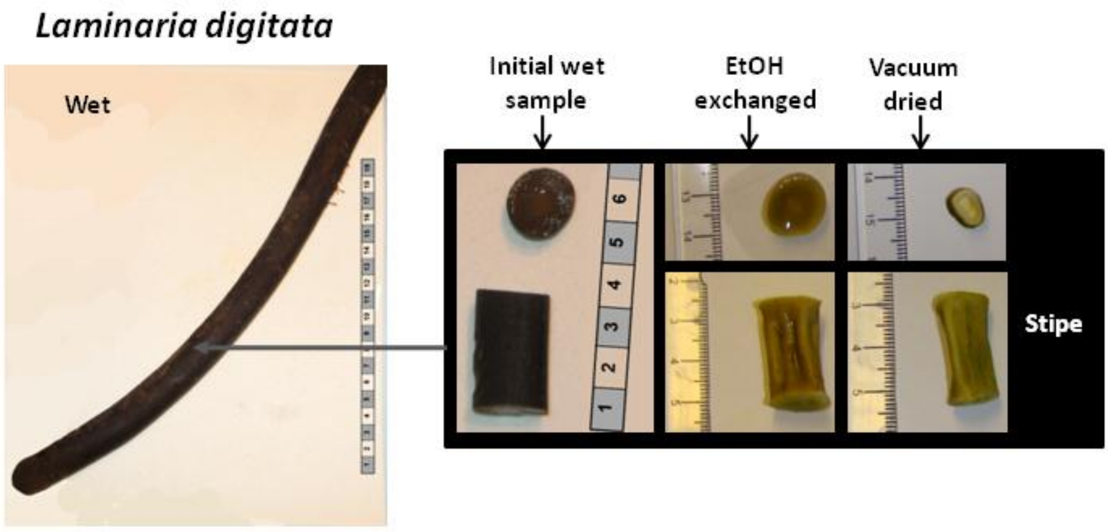


Figure S6: Shaped sections of *Laminaria digitata* material during processing

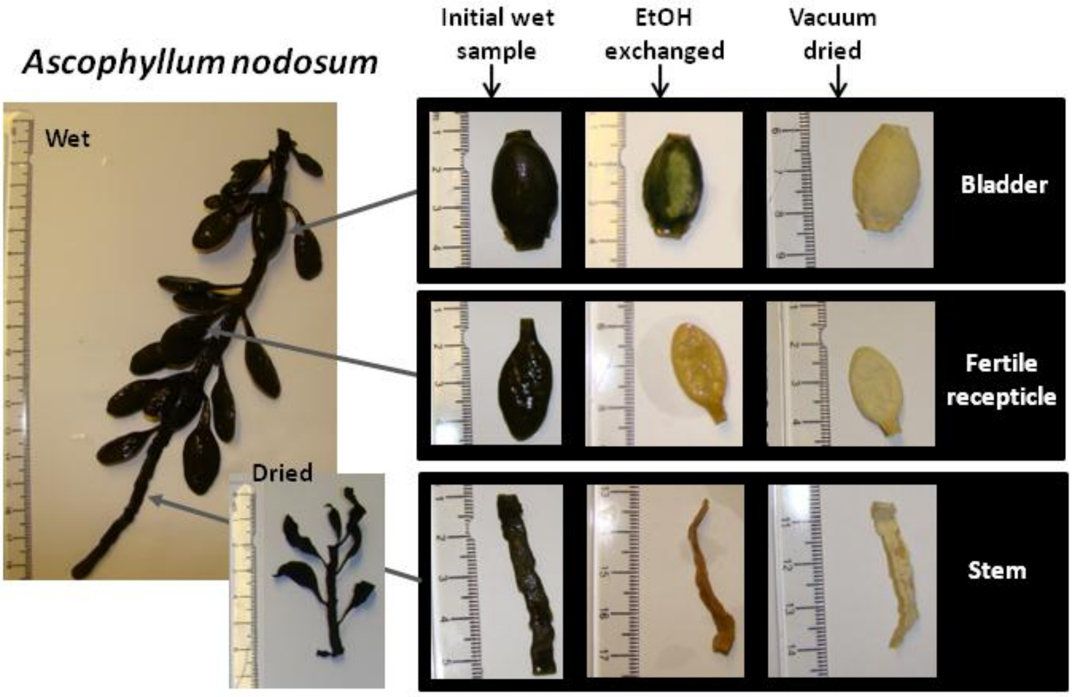


Figure S7: Shaped sections of *Ascophyllum nodosum* material during processing

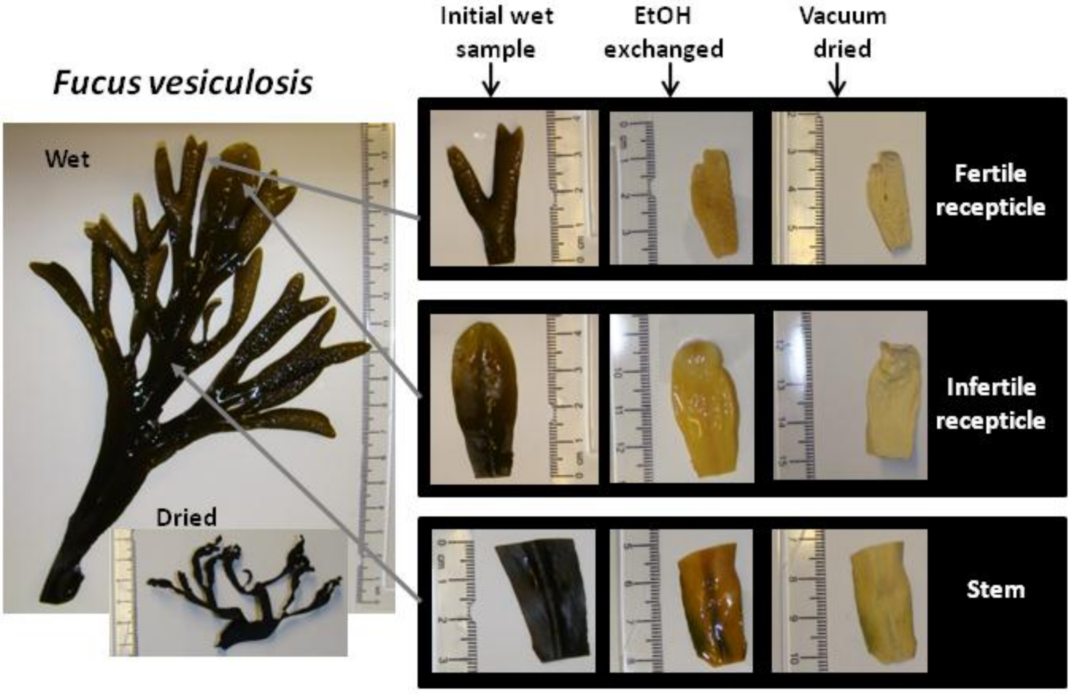


Figure S8: Shaped sections of *Fucus vesiculosus* during processing

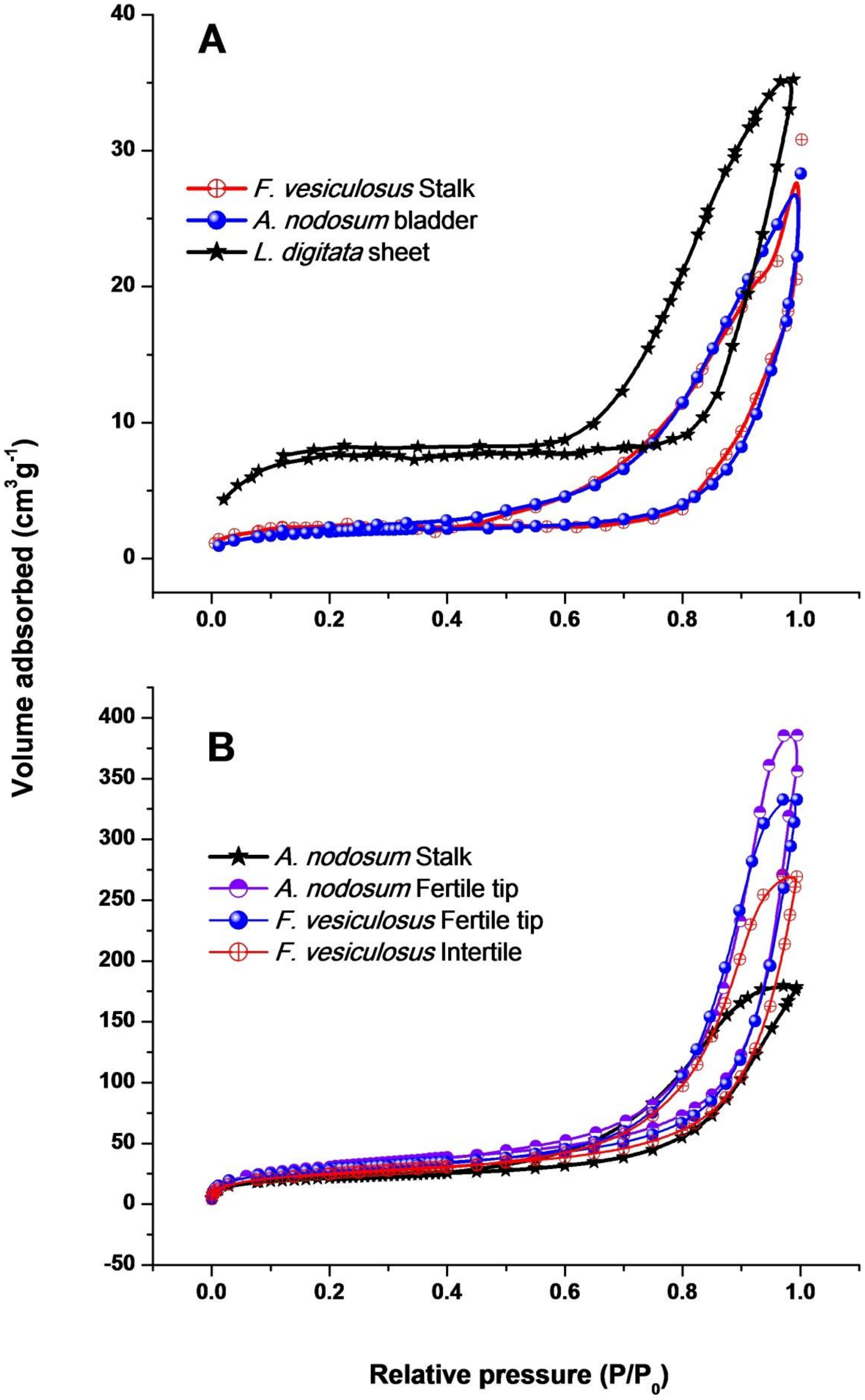


Figure S9: Nitrogen adsorption isotherms of macroalgae components following expansion and vacuum oven drying