Supplementary Information

Structure and Function of Stony Coral Intra-Skeletal Polysaccharides

Annamaria Naggi, Giangiacomo Torri, Marcello Iacomini, Gabriele Colombo, Michela Reggi, Simona Fermani, Zvy Dubinsky, Stefano Goffredo and Giuseppe Falini*

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Table S1: Assignment of organic compounds to bands on the FTIR spectra of *psc*OM; ν-stretching vibration, δ-bending vibrations, s-symmetric and as-asymmetric.

Wave number (cm^{-1})	Assignment
3422	ν(O–H): water molecules
2924	$\nu_{as}(CH_2)$:
2854	$\nu_{s}(CH_2)$:
1735	ν (C=O):
1649-1634	Amide I: GAGs
1620	: uronic acid
1558	$\nu_{as}(C=O)$: COO^-
1540	$\nu_{s}(C=O)$: COO^-
1470-1400	$\delta(CH_2)$: sugars
1384	$\delta(CH_3)$: O-acetyls
1255-1235	ν(S=O): esterified sulphate
1163	ν(C-O-C): glycosidic linkage
1078	ν(C-O-C): ether bonds
1036	ν(C-C): sugars

The broad band detected around 3422 cm^{-1} was assigned to ν(O–H) of water molecules. The bands assigned to asymmetric and symmetric stretching vibrations of the methyl and methylene groups were observed from 3050 to 2750 cm^{-1}. At 1735 cm^{-1} is located the band associated with stretching vibrations of the carbonyl group ν(C=O) that could be associated to the presence of acidic polysaccharides. Subsequent bands 1649-1634 cm^{-1} were associated to amide vibration modes of glycosaminoglycans.[1] The band at 1620 cm^{-1} indicated the presence of uronic acid. The doublet at 1558 cm^{-1} and 1540 cm^{-1} corresponds to the asymmetric stretching vibration of carboxyl functional group. The bands between 1470 and 1384 cm^{-1} could be attributable to scissoring vibration of CH_2 (galactose, mannose) and asymmetric bending vibration of CH_3 (fucose, O-acetyls).[2,3] The bands assigned to stretching vibrations of sulphate groups were observed from 1255 to 1225 cm^{-1} and indicate the presence of esterifies sulphate. The bands from 1120 to 1030 cm^{-1} can be assigned to a stretching vibration of the C–O group and are dominated by glycosidic linkage and at lower frequencies (around 1036 cm^{-1}) were polysaccharides with mannose, arabinose and rhamnose constituents.[4]

Table S2: Proton and carbon NMR chemical shifts values of principal and minor components of *psc*OM from *S. pistillata*. Reference carbon chemical shifts data of oxidized curdlan are also reported.

atom	Principal component		Minor components			Polyglucuronic acid[5]
	H (C) chem shifts (ppm)	^{3}J coupling (Hz)		H (C) chem shifts (ppm)		
1	4.86 (104.8)	7.9	5.02 (104.2)	5.06 (103.9)	5.51 (101.8)	101.87
2	3.59 (76.3)	8.7	4.12 (72.1*)	4.09 (nd*)	4.10 (78-80*)	73.27
3	3.82 (85.7)	9.1		3.59* (nd)		82.80
4	3.62 (73.2)	9.1	n.d.	3.56 (88)	n.d.	70.05
5	3.77 (78.7)	9.5		3.82 (72.2)		75.63
6	- (178.5)			1.21*		175.47

* Indicative assignment

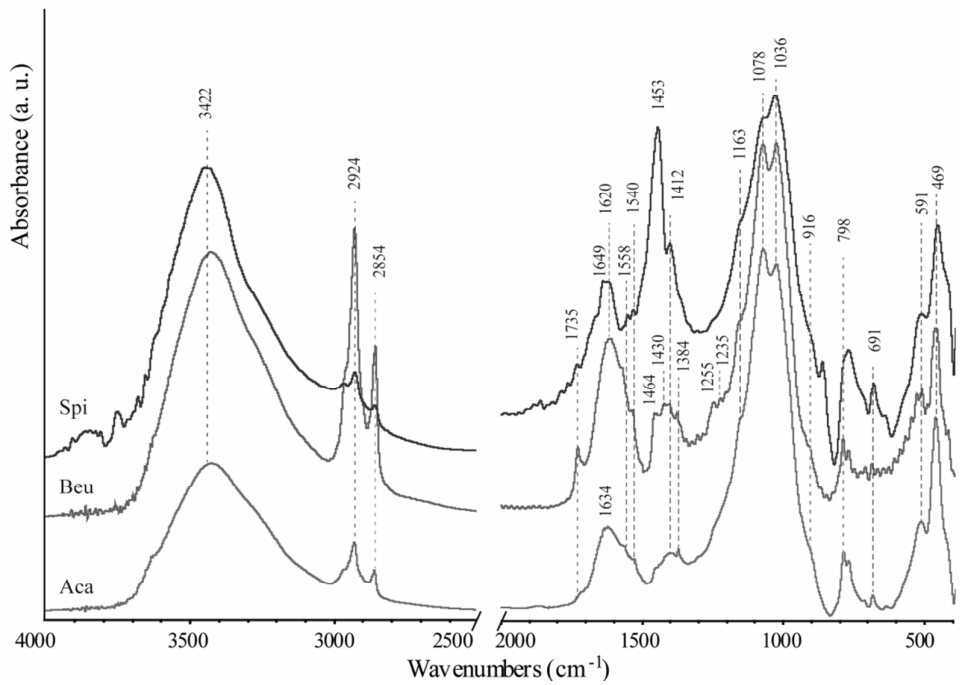

Figure S1: FTIR spectra of intra-skeletal polysaccharidic components of the organic matrix extracted from skeleton of *A. calycularis* (Aca), *B. europaea* (Beu), and *S. pistillata* (Spi).

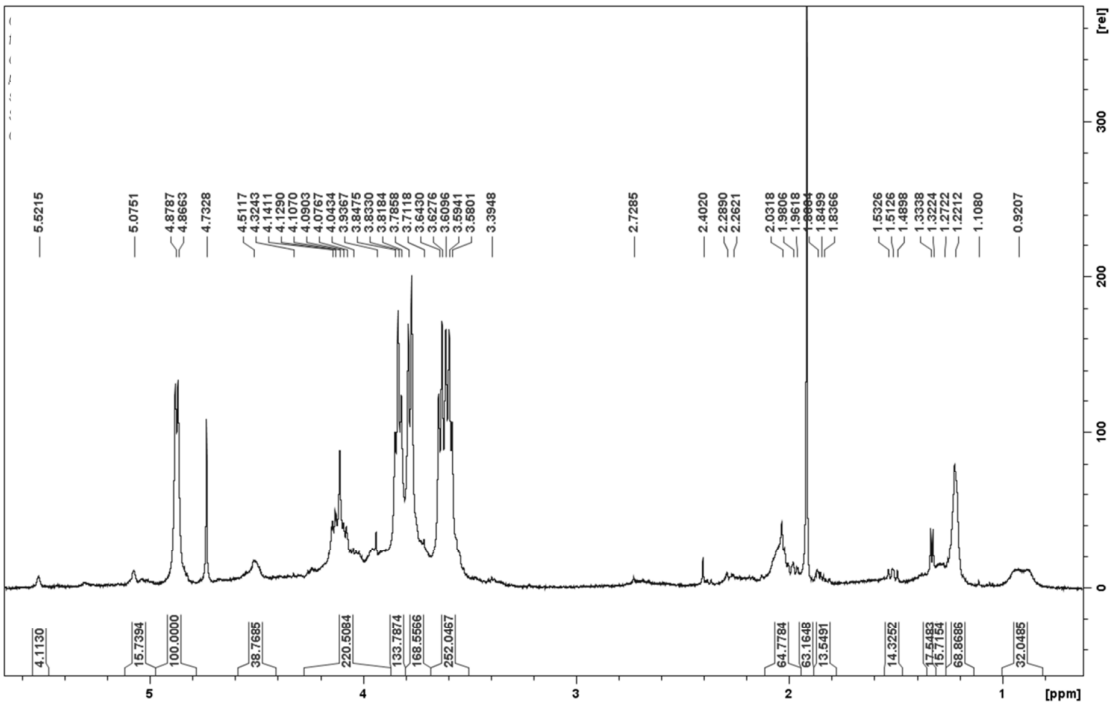

Figure S2. ^{1}H NMR spectrum of the *psc*OM of *S. pistillata.*

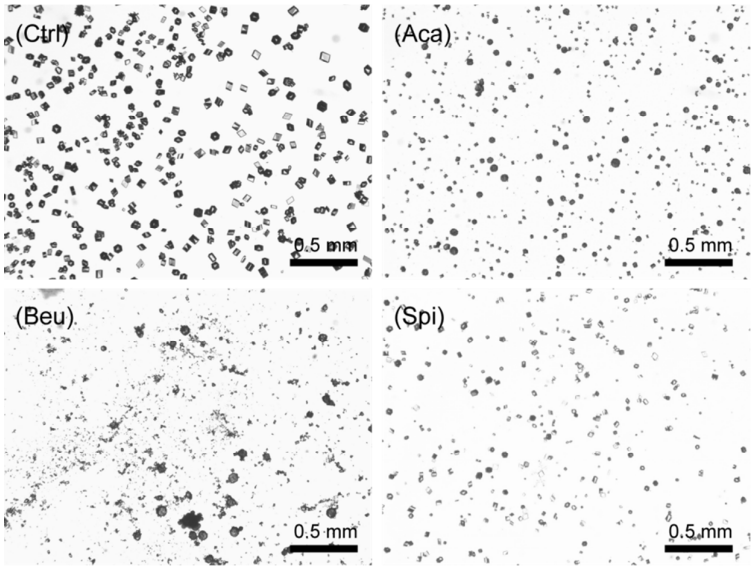

Figure S3. Optical microscope images of calcium carbonate particles precipitated in the absence of additives (Ctrl), in the presence of the *psc*OM extracted from *A. calycularis* (Aca), *B. europaea* (Beu) or *S. pistillata* (Spi).

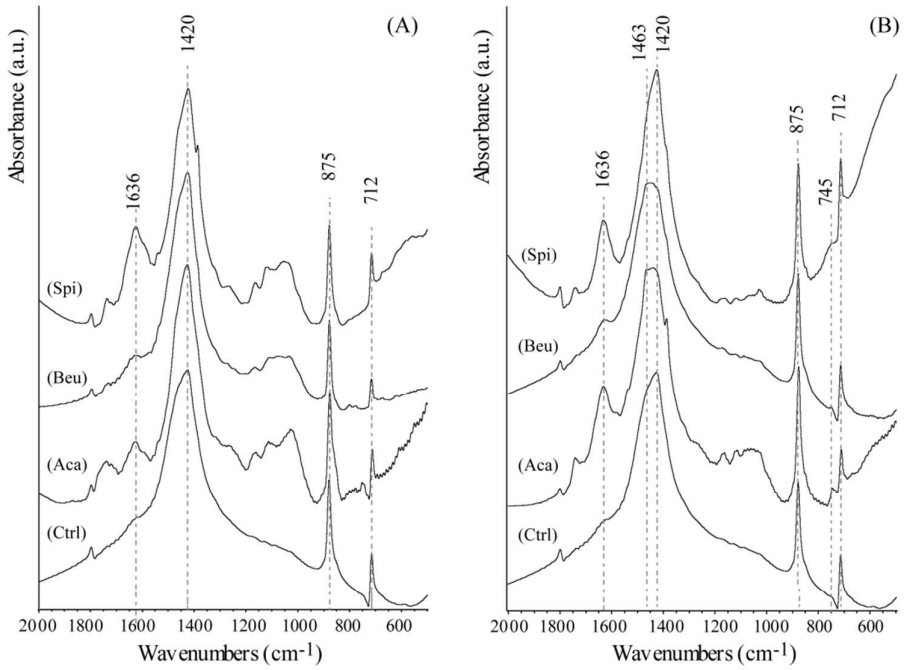

Figure S4. FTIR spectra of calcium carbonate precipitated from 10 mM $CaCl_2$ solutions in the presence of *w*OMs (A) and *psc*OM (B) which were extracted from the skeletons of *A. calycularis* (Aca), *B. europaea* (Beu), *S. pistillata* (Spi). FTIR spectrum of calcium carbonate precipitated from 10 mM $CaCl_2$ solution without additives is also reported (Ctrl). The wavenumbers of the main absorption bands are indicated. The bands at 1420 cm^{-1}, 875 cm^{-1} and 712 cm^{-1} are from calcite, the one at 745 cm^{-1} is from vaterite and that at 1636 cm^{-1} could be assigned to polysaccharide and water.

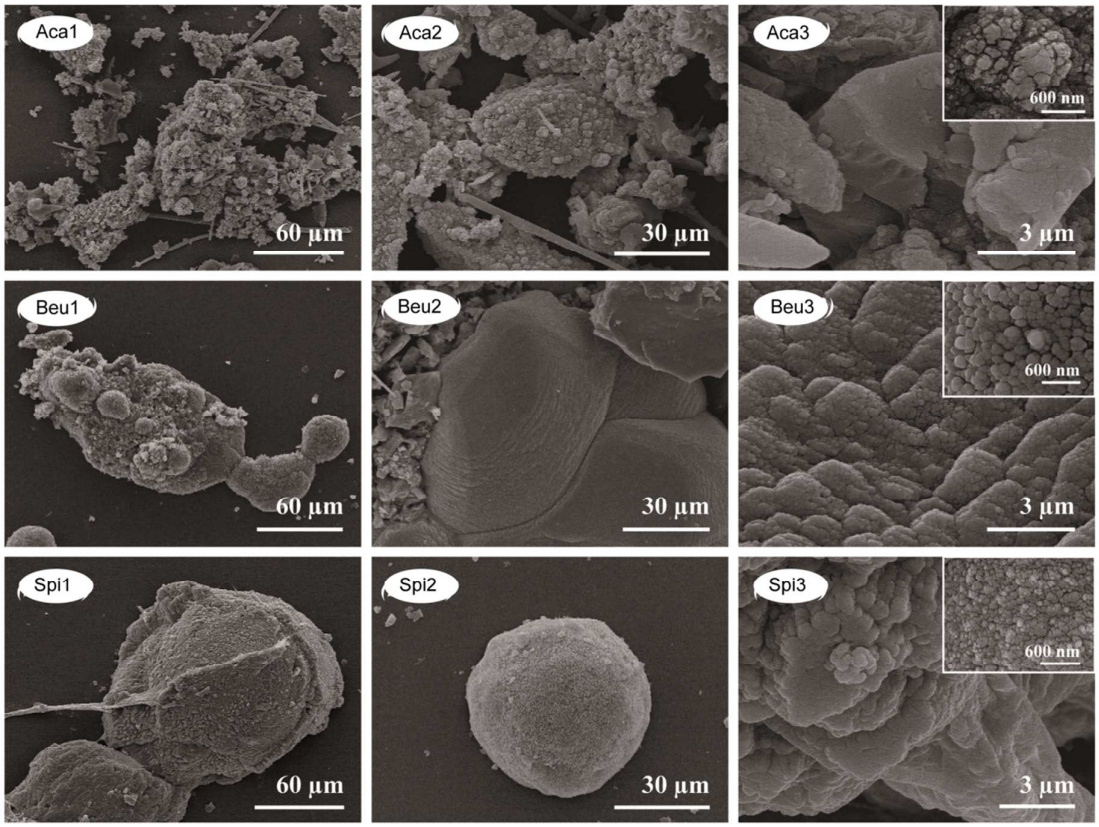

Figure S5. Scanning electron microscopy pictures at increasing magnification (1-3) of particles obtained from *in vitro* $CaCO_3$ crystallization experiments from 10 mM $CaCl_2$ solution in presence of *w*OM extracted from *A. calycularis* (Aca), *B. europaea* (Beu) and *S. pistillata* (Spi). In the column 3 particles that covered *w*OMs surface are showed. In the insets high magnification images are reported with the granular submicrometer particles from crystals surface. These pictures show most representative particles of each population.

References

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