Table S1. Isotopically-labelled internal standard mixture used in metabolomics analysis. POS: positive iron mode; NEG: Negative ion mode ; CAS: Chemical Abstracts Service Registry Number.

Num.	Name	POS	NEG	CAS
1	[RING-2H5]-L-Phenylalanine	N/A	m/z = 169.1030857	56253-90-8
2	Decanoic Acid-d19	N/A	m/z = 190.2583114	88170-22-3
3	L-Leucine-5,5,5-d3	N/A	m/z = 133.1061822	87828-86-2
4	[RING-2H5]-L-Phenylalanine	m/z = 171.1176389	N/A	56253-90-8
5	2-Chloro-L-phenylalanine	m/z = 200.0472828	N/A	103616-89-3
6	DiisobutylPhthalate-3,4,5,6-D4	m/z = 283.1841927	N/A	358730-88-8

Table S2. X-ray photoelectron spectroscopy (XPS) spectral parameters of the cell surface of diatom *P. tricornutum* under different treatment of Si-Al and CO_2.

Element	Core-level	Assignment[a]	400 ppm CO_2						1200 ppm CO_2					
			-Si-Al			+Si+Al			-Si-Al			+Si+Al		
			AP[b] (%)	BE[c] (eV)	CD[d] (%)	AP (%)	BE (eV)	CD (%)	AP[b] (%)	BE[c] (eV)	CD[d] (%)	AP[b] (%)	BE[c] (eV)	CD[d] (%)
C	1s	**C**-(C, H),[1]	57.32	284.7	81.50	48.30	284.7	85.50	66.88	284.7	69.88	62.08	284.8	75.30
		C-(O, N),[2, 3]		286.1	12.35		286.1	10.96		286.4	22.52		286.4	16.48
		O-**C**-O, **C**=O,[1, 3]		288.4	6.15		288.2	3.54		288.3	7.60		288.1	8.22
O	1s	**O**=C,[1, 3]	38.59	531.5	78.54	43.95	531.5	77.34	28.98	531.8	42.45	29.49	531.8	38.49
		C-**O**H, C-**O**-C, **O**-Si,[3]		532.8	21.46		533.0	22.66		533.1	57.55		533.0	61.51
N	1s	C-**N**H_2,[1,3]	2.44	399.8	96.60	2.24	399.7	90.14	2.19	399.9	82.34	2.11	399.9	87.60
		N$(CH3)_3^+$,[1,3]		401.7	3.40		401.8	9.86		401.7	17.66		401.6	12.40
Si	2p	**Si**-OH,[1, 3]	0.49	102.1	49.19	4.04	102.1	79.35	0.36	102.1	42.19	3.91	102.3	88.56
		SiO_2, [1, 3]		103.1	50.81		103.1	20.65		103.2	57.81		103.3	11.44
P	2p	–	0.78	–	–	1.25	–	–	1.13	–	–	1.97	–	–
S	2p	–	0.38	–	–	0.22	–	–	0.47	–	–	0.43	–	–

a: The references for the assignment of binding energy are shown in the supporting information. b: AP: atomic percentage; c: BE: binding energy; d: CD: component distribution, that is, the proportion of each component peak.

Corresponding references in assignment column:

1. Cicco, S., Vona, D., Gristina, R., Sardella, E., Ragni, R., Lo Presti, M., & Farinola, G., 2016. Biosilica from living diatoms: investigations on biocompatibility of bare and chemically modified Thalassiosira weissflogii silica shells. Bioengineering 3 (4), 35.;

2. Dufrêne, Y.F., Van der Wal, A., Norde, W., & Rouxhet, P.G., 1997. X-ray photoelectron spectroscopy analysis of whole cells and isolated cell walls of gram-positive bacteria: comparison with biochemical analysis. Journal of Bacteriology, 179(4), 1023-1028.;

3. Tesson, B., Genet, M.J., Fernandez, V., Degand, S., Rouxhet, P.G., & Martin-Jézéquel, V., 2009. Surface chemical composition of diatoms. ChemBioChem, 10(12), 2011-2024.

Table S3. Annotation of the top ten up- and down-regulated metabolites in comparative analysis between treatments

Metabolite name	KEGG ID	Super class	Sub class	Comparison between the treatments					
				+Si+Al-1200 / +Si+Al-400	+Si+Al-1200 / −Si−Al-400	+Si+Al-1200 / −Si−Al-1200	−Si−Al-1200 / +Si+Al-400	−Si−Al-1200 / −Si−Al-400	+Si+Al-400 / −Si−Al-400
Phosphatidylcholine (PC)	C00157	Lipids and lipid-like molecules	Glycerophosphocholines	↑	–	–	↑	–	↑ ↓
Masticadienediol	–	Lipids and lipid-like molecules	Triterpenoids	↑	–	↑	↑	↓	↑
9-cis-retinoic acid	C15493	Lipids and lipid-like molecules	Retinoids	↑	–	–	↑	↓	↑
5-Heptadecyl-1,3-benzenediol		Benzenoids	Benzenediols	↑	↑	↑	–	↑	–
Lysophosphatidylcholine (LPC)	C04230	Lipids and lipid-like molecules	Glycerophosphocholines	↑	↓ ↓	–	↑	↓ ↓	↑
2-(2-Methylpropoxy)naphthalene	–	Benzenoids	–	↑	–	↑	–	–	↑
Phosphatidylmethanol (PMeOH)	–	Lipids and lipid-like molecules	–	↑	↑	↑ ↑			
5-Hydroxy-14,16-hentriacontanedione	–	Lipids and lipid-like molecules	Fatty alcohols	↑	↓	–	↑	↓	↑
Pyrophaeophorbide a	–	–	–	↑	–	–	↑	–	↑
Progesterone	C00410	Lipids and lipid-like molecules	Pregnane steroids	↑	–	–	–	–	–
Nevskin	–	Phenylpropanoids and polyketides	–	↓	–	–	–	–	–
Avocadene 1-acetate	–	Lipids and lipid-like molecules	Fatty alcohols	↓	–	–	–	–	–
Lysophosphatidylethanolamine (LPE)	–	Lipids and lipid-like molecules	Glycerophosphoethanolamines	↓	–	↓ ↓	↓	–	–
(4E)-1,7-bis(4-hydroxyphenyl)hept-4-en-3-one	–	Phenylpropanoids and polyketides	Linear diarylheptanoids	↓	–	–	↓	–	–
Parakmerin A	–	Phenylpropanoids and polyketides	–	↓	–	–	↓	–	–
2,2-Bis[4-(2,3-epoxypropoxy)phenyl]propane	C14348	Benzenoids	Diphenylmethanes	↓	–	–	↓	–	–
Cochliophilin A	–	Phenylpropanoids and polyketides	Flavones	↓	–	–	↓	–	–
Tetradecanoylcarnitine	–	Lipids and lipid-like molecules	Fatty acid esters	↓	–	–	–	–	–
Taurocholic acid	C05122	Lipids and lipid-like molecules	Bile acids, alcohols and derivatives	↓	–	–	↓	–	–
Petasinoside	–	Hydrocarbons	Alkanes	↓	–	–	↓	–	↓
21-Hydroxypregnenolone	C05485	Lipids and lipid-like molecules	Hydroxysteroids	–	↑	↑	–	–	–
5',5''',8,8''-Tetrahydroxy-3',3''',4',4''',7',7''-hexamethoxy-5,5''-biflavan	–	Phenylpropanoids and polyketides	O-methylated flavonoids	–	↑	–	–	↑	–
Desglucocheirotoxin	–	Lipids and lipid-like molecules	Steroid lactones	–	↑	–	–	↑	↓

Metabolite name	KEGG ID	Super class	Sub class	Comparison between the treatments					
				+Si+Al-1200 / +Si+Al-400	+Si+Al-1200 / −Si−Al-400	+Si+Al-1200 / −Si−Al-1200	−Si−Al-1200 / +Si+Al-400	−Si−Al-1200 / −Si−Al-400	+Si+Al-400 / −Si−Al-400
3-(2-Heptenyloxy)-2-hydroxypropyl undecanoate	–	Lipids and lipid-like molecules	Diradylglycerols	–	↑	–	–	–	↓
3'-Sialyllactosamine	–	Organic oxygen compounds	Carbohydrates and carbohydrate conjugates	–	↑	–	–	↑	–
Harderoporphyrin	–	–	–	–	↑	–	–	↑	–
5',8,8"-Trihydroxy-3',3"',4',4"',5"',7',7"-heptamethoxy-5,5"-biflavan	–	Phenylpropanoids and polyketides	O-methylated flavonoids	–	↑	–	–	↑	–
Arachidonic acid	C00219	Lipids and lipid-like molecules	Fatty acids and conjugates	–	↑	–	–	↑	–
Lysophosphatidic acid (LPA)	C15646	Lipids and lipid-like molecules	Glycerophosphates	–	↓	–	–	–	–
AFN911	–	Organoheterocyclic compounds	Pyrimidines and pyrimidine derivatives	–	↓	↓	–	–	–
Cucurbitacin B	C08794	Lipids and lipid-like molecules	Cucurbitacins	–	↓	–	–	–	–
(3beta,22E,24R)-Ergosta-4,6,8(14),22-tetraen-3-ol	–	–	–	–	↓	–	↑	↓	↑
Ercalcitriol	–	Lipids and lipid-like molecules	Vitamin D and derivatives	–	↓	↓	↑	↓	↑
Ergosterol peroxide	–	Lipids and lipid-like molecules	Ergostane steroids	–	↓	–	–	↓	↑
1-Heptadecene-4,6-diyne-3,9-diol	–	Lipids and lipid-like molecules	Fatty alcohols	–	–	↑	–	–	–
2,3-Butanediol glucoside	–	Organic oxygen compounds	Carbohydrates and carbohydrate conjugates	–	–	↑	↓	–	–
Stearidonic acid	C16300	Lipids and lipid-like molecules	Lineolic acids and derivatives	–	–	↑	–	–	–
Costunolide	–	Lipids and lipid-like molecules	Terpene lactones	–	–	↑	–	–	–
D-Proline	C00763	Organic acids and derivatives	Amino acids, peptides, and analogues	–	–	↓	–	–	–
Ethyl (Z,Z)-5,8-tetradecadienoate	–	Lipids and lipid-like molecules	Fatty acid esters	–	–	↓	–	–	–
2,6-Di-tert-butyl-4-ethylphenol	–	Benzenoids	Phenylpropanes	–	–	↓	–	–	–
Trigonelline	C01004	Alkaloids and derivatives	–	–	–	↓	–	–	–
Eugenitol	–	Organoheterocyclic compounds	1-benzopyrans	–	–	↓	↑	↑	–
7,8-Dihydrovomifoliol 9-[rhamnosyl-(1->6)-glucoside]	–	Lipids and lipid-like molecules	Fatty acyl glycosides	–	–	–	↑	–	–
(4E)-1,7-bis(4-hydroxyphenyl)hept-4-en-3-one	–	Phenylpropanoids and polyketides	Linear diarylheptanoids	–	–	–	↓	–	–
Phosphatidylglyceride (PG)	–	Lipids and lipid-like molecules	Glycerophosphoglycerols	–	–	–	↓	–	↓
Diglycerol (DG)	–	Lipids and lipid-like molecules	Lineolic acids and derivatives	–	–	–	↓	–	↓
Aurasperone B	–	Organoheterocyclic compounds	Naphthopyranones	–	–	–	–	↑	–

Metabolite name	**KEGG ID**	**Super class**	**Sub class**	**Comparison between the treatments**					
				+Si+Al-1200 / +Si+Al-400	**+Si+Al-1200 / −Si−Al-400**	**+Si+Al-1200 / −Si−Al-1200**	**−Si−Al-1200 / +Si+Al-400**	**−Si−Al-1200 / −Si−Al-400**	**+Si+Al-400 / −Si−Al-400**
O-Methylsomniferine	–	–	–	–	–	–	–	↑	↓
Allopregnanolone	C13712	Lipids and lipid-like molecules	Pregnane steroids	–	–	–	–	↓	–
Monoacylglycerol (MG)	–	Lipids and lipid-like molecules	Monoradylglycerols	–	–	–	–	↓	↓
5-(10,13-Nonadecadienyl)-1,3-benzenediol	–	Benzenoids	Benzenediols	–	–	–	–	–	↓
(R)-2-Hydroxysterculic acid	–	Lipids and lipid-like molecules	Fatty alcohols	–	–	–	–	–	↓

Table S4. Summary of the number (Num.) of identified (Ident.) metabolites. Significant (Sig.) threshold was set for *p* value (< 0.05) and log 2 fold change (< −1 or >1).

Compared Groups	Num. of Ident.	Num. of Sig.	Num. of Sig. Up	Num. of Sig. Down
+Si+Al-1200 ppm CO_2 / +Si+Al-400 ppm CO_2	199	97	89	8
+Si+Al-1200 ppm CO_2 / -Si-Al-400 ppm CO_2	240	93	73	20
-Si-Al-1200 ppm CO_2 / +Si+Al-400 ppm CO_2	233	119	113	6
-Si-Al-1200 ppm CO_2 / -Si-Al-400 ppm CO_2	252	121	103	18
+Si+Al-1200 ppm CO_2 / -Si-Al-1200 ppm CO_2	145	33	11	22
+Si+Al-400 ppm CO_2 / -Si-Al-400 ppm CO_2	176	75	53	22

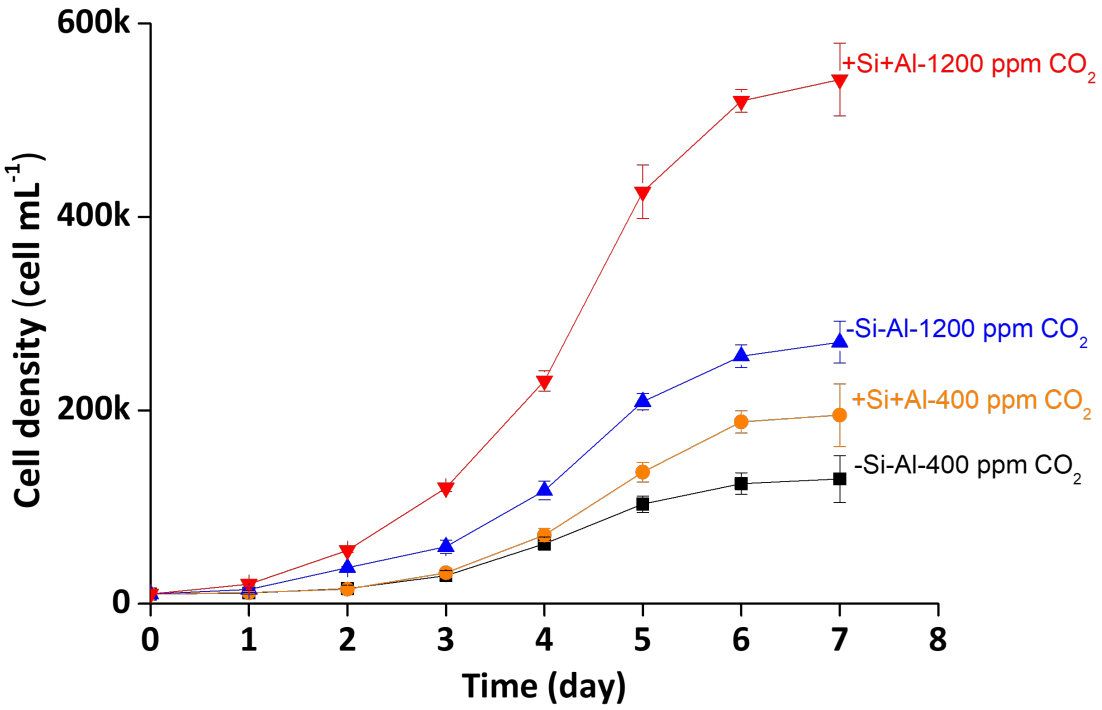

Fig. S1 Increase in the cell density under different CO_2 (400 or 1200 ppm) and Si-Al (−Si−Al or +Si+Al) conditions. The initial cell density was at 1×10^4 cells mL^{-1}.

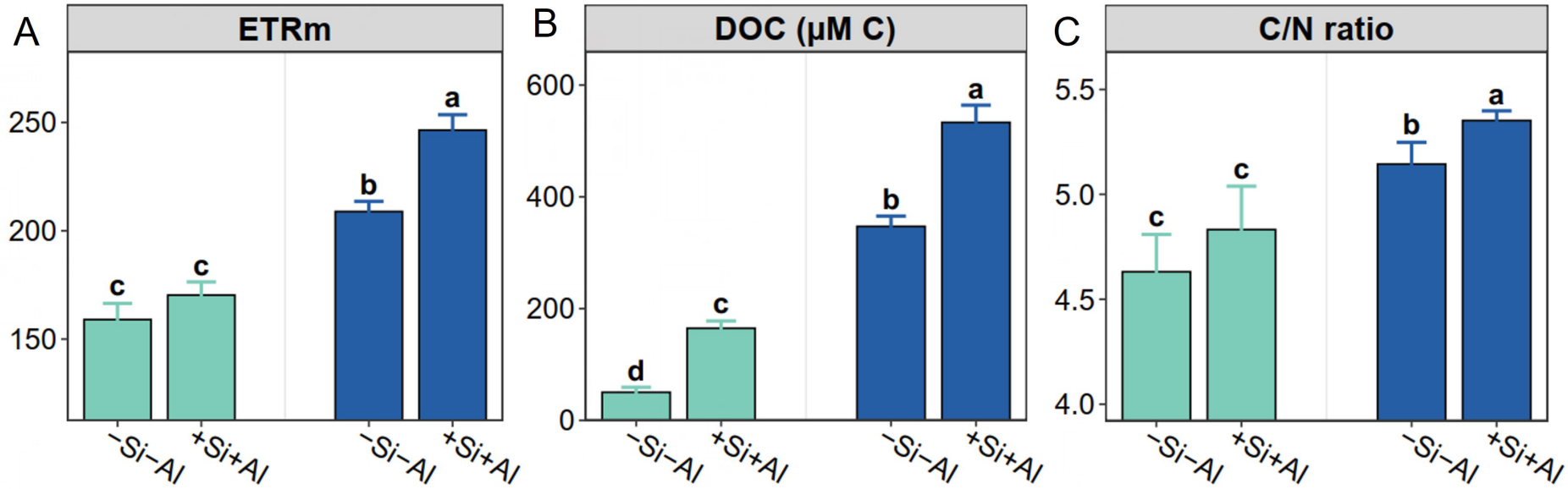

Fig. S2 Influence of CO_2 (400 or 1200 ppm) and Si-Al (−Si−Al or +Si+Al) on the physiology parameters of *P. tricornutum*. (A) The photosynthetic parameters of maximum electron transport rate (ETRm). (B) The dissolved organic carbon (DOC) content in cultural seawater. (C) The total C/N ratio for the cells. Data are presented as mean ± SD (n = 3), and different lower cases indicate statistical difference at $p < 0.05$.

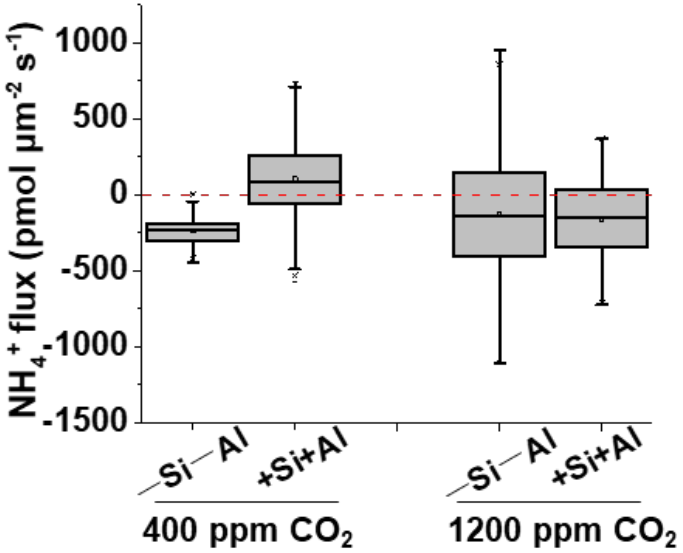

Fig. S3 Influence of CO_2 (400 or 1200 ppm) and Si-Al (−Si−Al or +Si+Al) on the NH_4^+ flux on the cell surface.

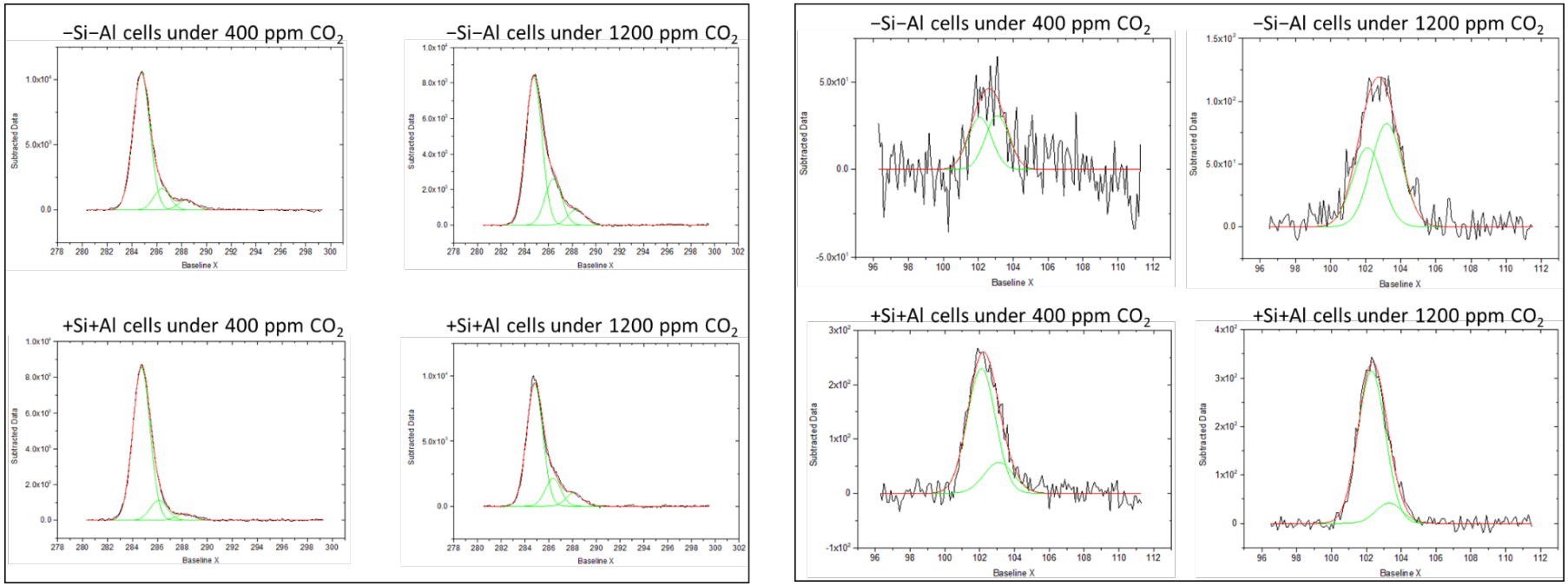

Fig. S4 The raw fitting curves of X-ray photoelectron spectroscopy (XPS) analysis of C and Si chemical states in the frustule of the diatom *P. tricornutum.* (left) The variation of C-related functional groups, and (right) the variation of Si-related functional groups in varying CO_2 and Si-Al treatments.

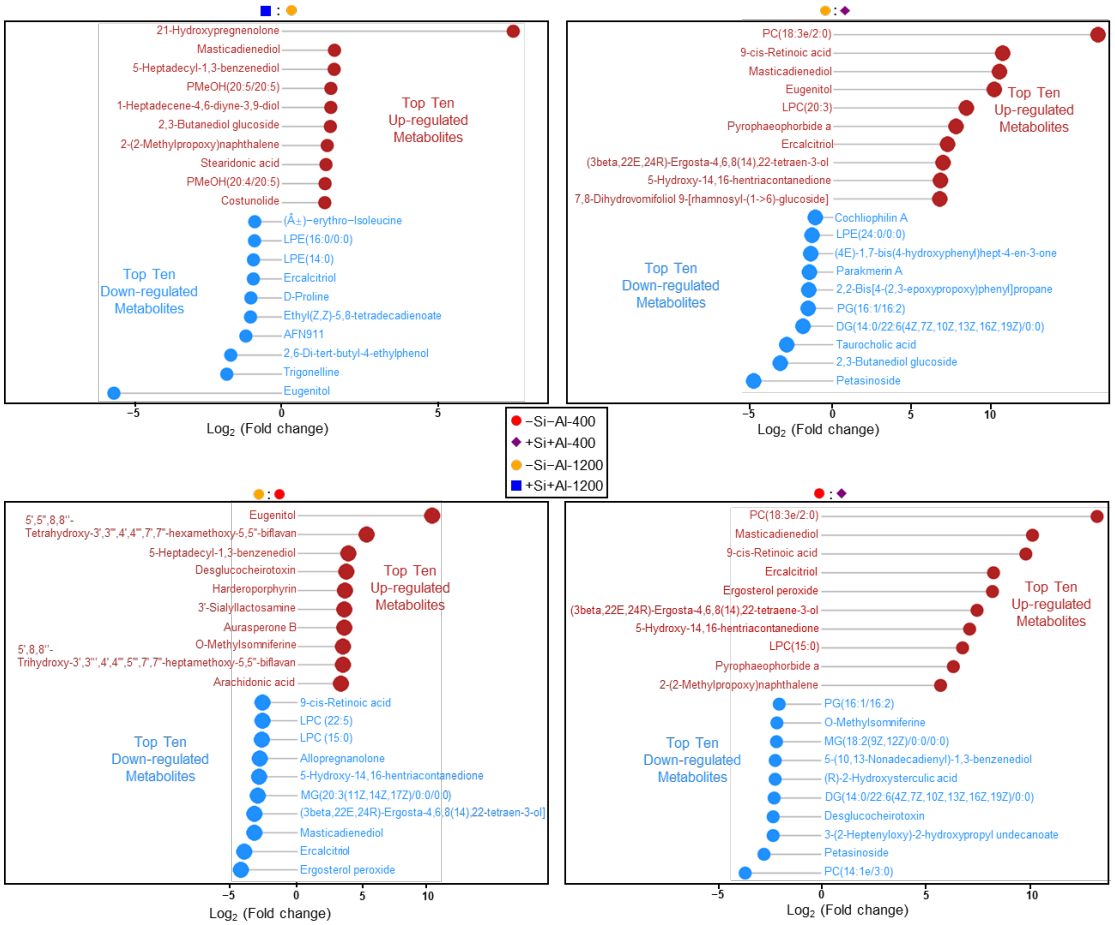

Fig. S5 The top ten up- and down-regulated metabolites in the compared treatments.

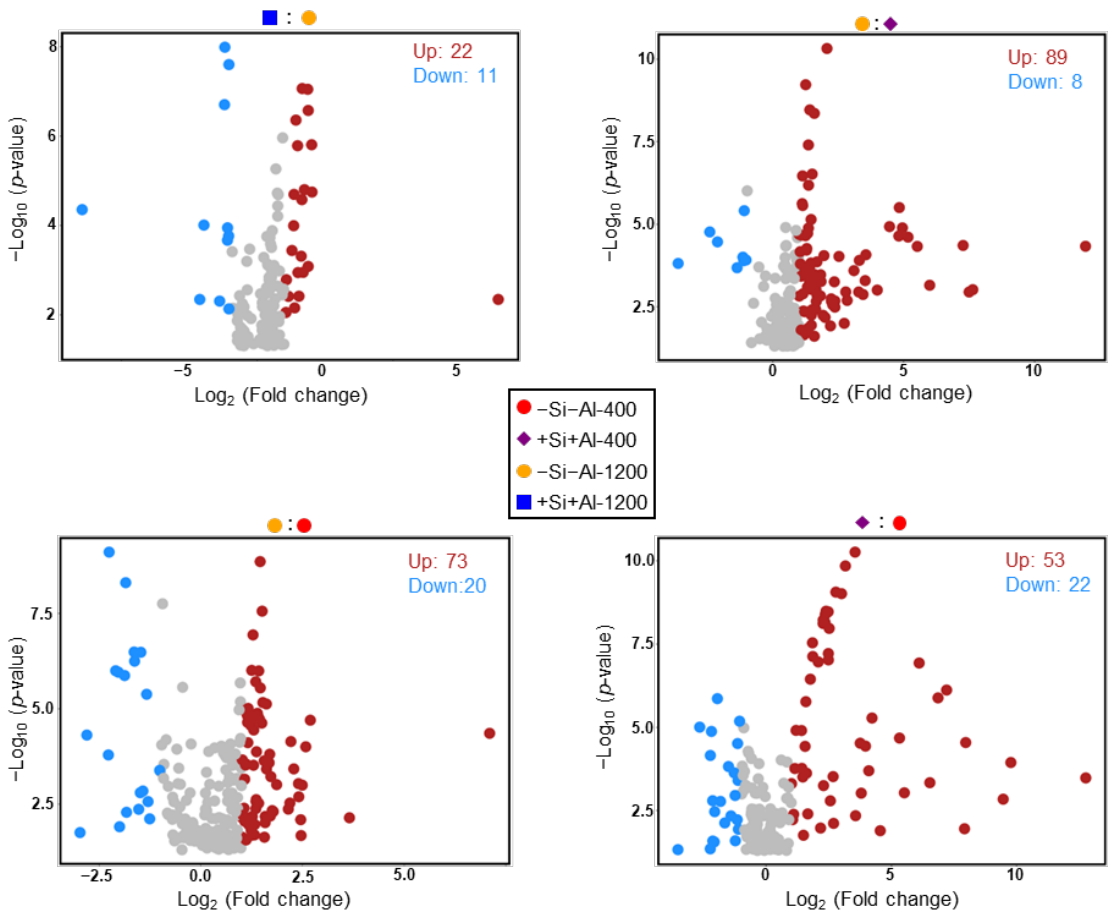

Fig. S6 Volcano plots for comparing the differentially expressed metabolites between the selected treatments. The significant threshold was set for p-value (< 0.05) and fold change (> 2-fold).

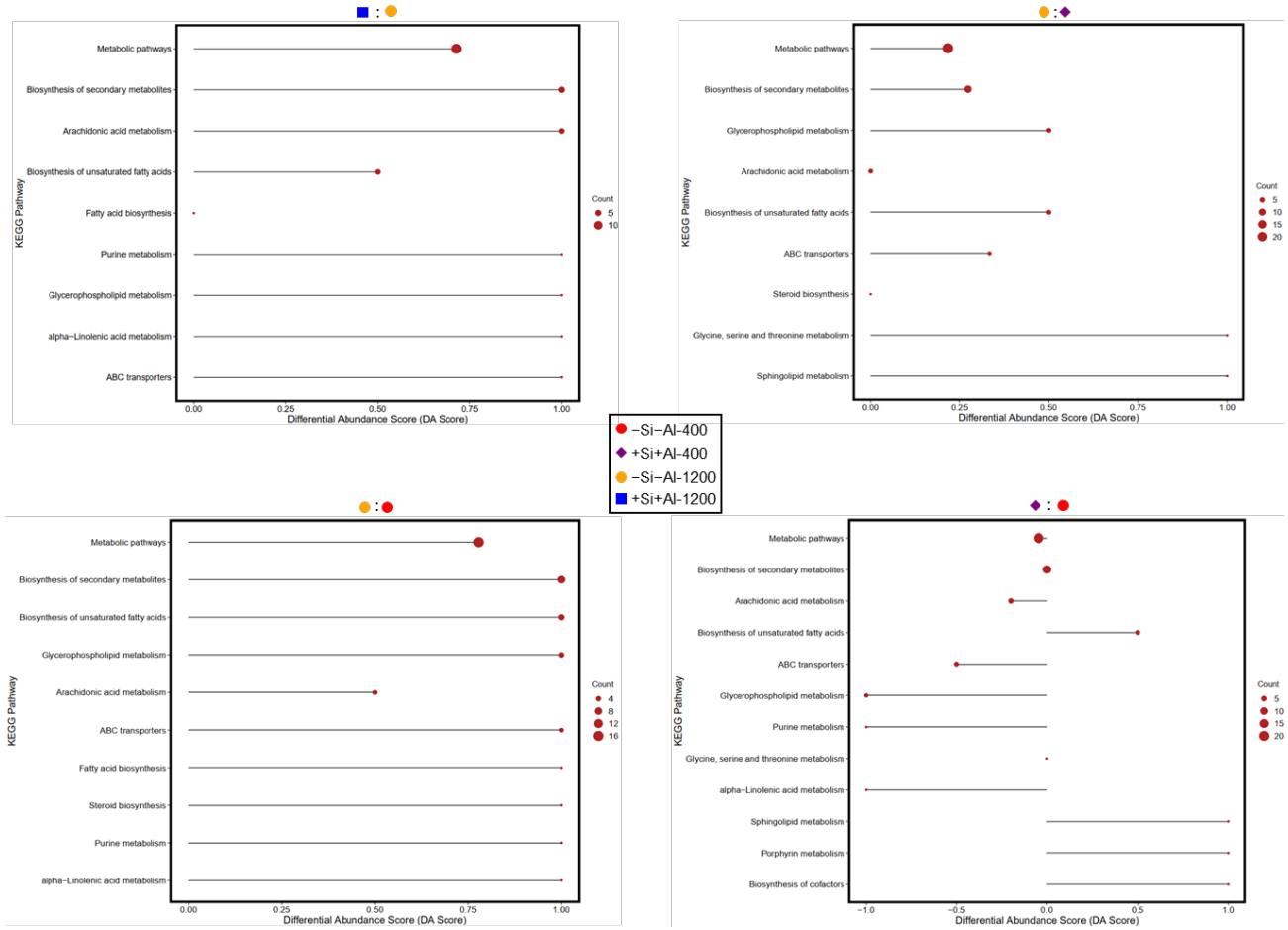

Fig. S7 The differential abundance (DA) score for each pathway, this score explores the overall metabolite changes in these pathways, as positive values mean up-regulation of overall metabolite expression. The length of the line represents the absolute value of the DA score, and the size of the dot represents the number of annotated differential metabolites in that pathway.