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Supplementary material

Importance of refractory ligands and their photodegradation for iron oceanic inventories and cycling

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Table S1. Average trace element content for labile and refractory dissolved organic carbon (lDOC and rDOC) measured by inductively coupled plasma–mass spectrometry (ICP–MS) in duplicate

Average recoveries for seawater spiked with DOC (SW-DOC) and to biological reference materials are shown. Bivalve digestion product (SW-Bivalve) and DORM-4 fish protein reference material (SW-Fish) were used (n = 1–3)

	Iron	Zinc	Cobalt	Valium	Chromium	Manganese	Nickel	Copper	Arsenic	Selenium
Parameter										
lDOC (pmol µmol^{-1} C)	37.7	191	2.13	9.48	3.59	67.1	19.3	85.9	20.6	5.18
rDOC (pmol µmol^{-1} C)	75.2	41.9	1.53	8.24	5.52	5.91	12.6	28.1	26.8	3.30
Recovery level (%)										
SW-DOC	108	69	107	103	100	100	101	103	94	98
SW-Bivalve	97	114	100	108	103	105	99	100	99	100
SW-Fish	98	100	100	100	96	97	94	97	94	95

Table S2. Raw titration data and humic-substance data

CLE–AdCSV, competitive ligand exchange–adsorptive cathodic stripping voltammetry. DOM, dissolved organic carbon. SRFA, Suwannee River fulvic acid; Ip, peak height of the voltammograms determined with ECDSoft. Each measurement was realised in triplicate (n = 3)

Labile DOC (30 µmol C L^{-1})		Refractory DOC (30 µmol C L^{-1})	
Iron organic titration (CLE–AdCSV)			
[Fe] added (nM)	Ip (4th derivative)	[Fe] added (nM)	Ip (4th derivative)
0	89 700	0	251 300
1	344 733	1	1 014 400
1.5	975 233	1.5	1 570 000
2	1 094 333	2	2 379 000
2.5	1 976 333	2.5	2 879 333
5	4 239 667	3	4 446 667
7.5	8 284 667	5	6 103 333
10	9 251 333	7.5	10 046 667
Humic substances (CSV)			
[SRFA] added (µg L^{-1})	Ip (nA)	[SRFA] added (µg L^{-1})	Ip (nA)
0	1.98	0	2.37
100	4.375	100	5.63
200	7.63	200	11.15
400	13.4	400	20.95
Refractory DOC (30 µmol C L^{-1} after exposition to full sun spectra)			
Iron organic titration (CLE–AdCSV)		Humic substances (CSV)	
[Fe] added (nM)	Ip (4th derivative)	[SRFA] added (µg L^{-1})	Ip (nA)
0.8	457 100	0	0
1	500 500	100	3.8
1.2	899 000	200	8.4
1.6	1 347 000	400	14.8
2	2 003 000		
2.8	3 084 000		
3.4	4 024 000		
4	4 937 000		
5	6 630 000		
6	773 6000		

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Table S3. Iron bioavailability measured using *Phaeocystis antarctica* and *Pseudo-nitzschia subcurvata* in synthetic seawater

In addition to inorganic iron, bioavailability associated with refractory (rDOC) and labile (lDOC) dissolved organic molecules (at concentration of 7 and 14 μM C respectively), mono- and poly-saccharides (glucuronic acid, GLU, and carrageenan, CAR, 0.2 mg L^{-1}), bacterial exopolymeric substances (EPS, 0.2 mg L^{-1}), bacterial siderophores (enterobactin, ENTERO, and desferrioxamine B, DFB, 15 nM), and Suwannee River fulvic acid (SRFA std 1, 0.1 mg L^{-1}) were determined. Average relative bioavailability with respect to equimolar inorganic iron is given with standard deviations (n = 3)

Organic ligand	Relative bioavailability	
	P. antarctica	*P. subcurvata*
EPS	1.00 ± 0.26	1.24 ± 0.14
CAR	1.52 ± 0.04	1.88 ± 0.09
GLU	1.71 ± 0.03	2.27 ± 0.26
SRFA	1.12 ± 0.06	0.41 ± 0.03
lDOC	0.83 ± 0.02	0.80 ± 0.08
rDOC	0.24 ± 0.06	0.18 ± 0.07
ENTERO	0.06 ± 0.01	0.08 ± 0.004
DFB	0.03 ± 0.002	0.05 ± 0.01

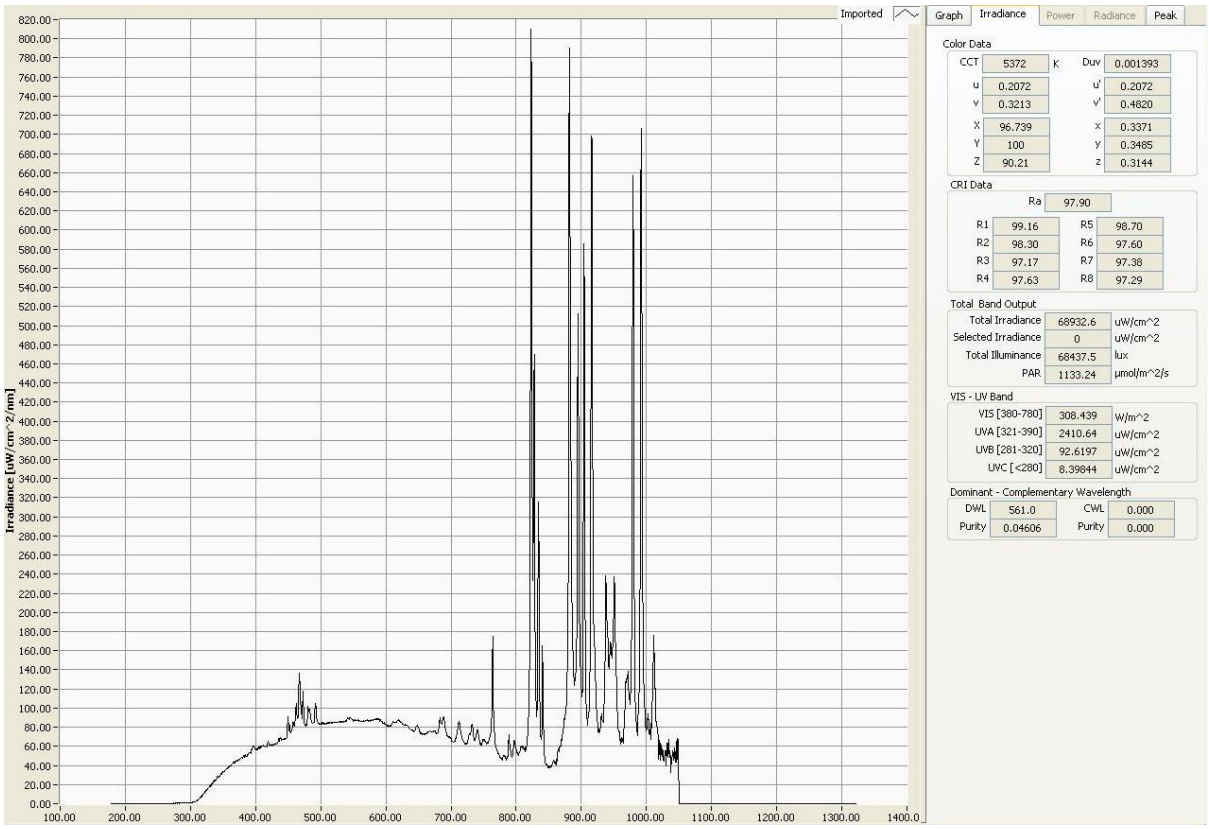

Fig. S1. Spectra light of solar simulator (ABET Technologies Sun 2000, Milford, CT, USA).

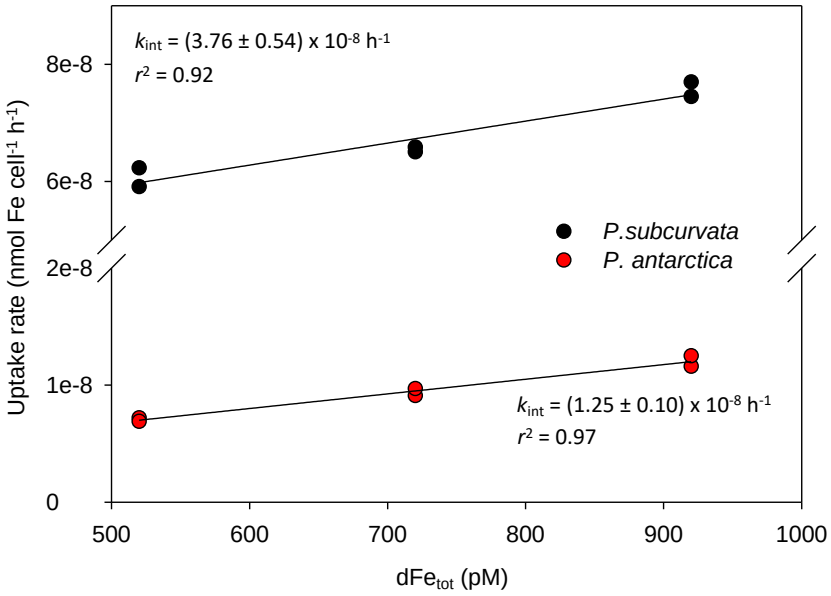

Fig. S2. Internalisation rate constants (k_{int}). k_{int} was determined for two iron-limited phytoplankton isolates from the Southern Ocean (*Pseudo-nitzschia subcurvata* and *Phaeocystis antarctica*) in synthetic seawater (AQUIL major-salt only) with incremental additions of $^{55}FeCl_3$ at 4°C.