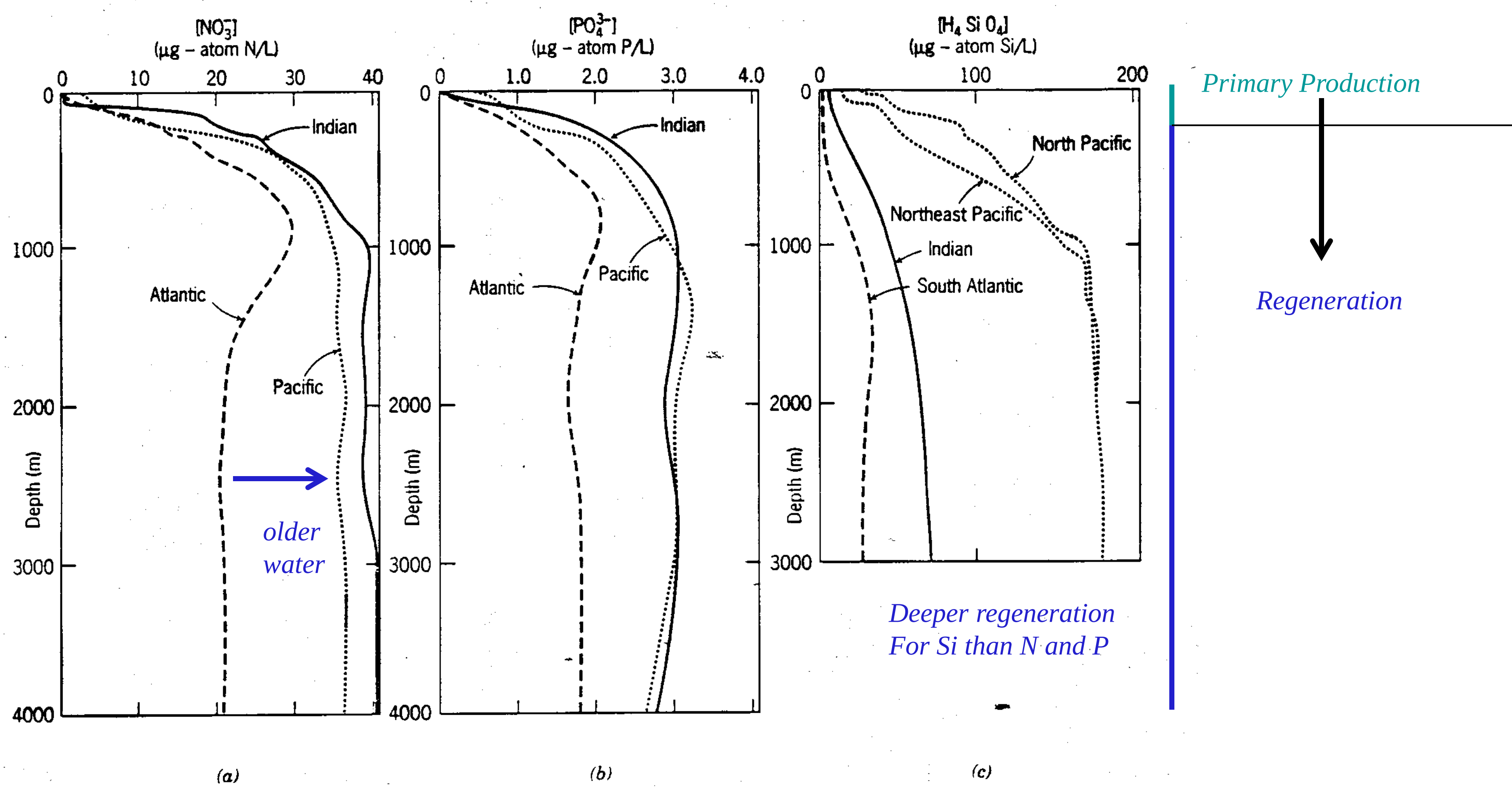


FIGURE 10.1. Vertical distribution of (*a*) nitrate, (*b*) phosphate, and (*c*) dissolved silicon in the Atlantic, Pacific, and Indian oceans. Note that 1 μg-atom/L is equivalent to 1 μ*M*. Thus 1 μg-atom NO_3-N/L is equivalent to 1 μmol of dissolved nitrogen (in the form of NO_3^-) per liter of seawater. *Source:* From *The Oceans*, H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, copyright © 1941 by Prentice Hall, Inc., Englewood Cliffs, New Jersey, p. 242. Reprinted by permission. See Sverdrup et al. (1942) for data sources.

BASIC PRODUCTION/RESPIRATION EQUATIONS:::REDFIELD RATIO

I. ORGANIC MATTER ---SOFT TISSUE

$$CH_2O + O_2 \underset{\text{PHOTO.}}{\overset{\text{RESPIR}}{\rightleftharpoons}} CO_2 + H_2O$$

R $\longrightarrow$

$$(CH_2O)_{105}(NH_3)_{15}H_3PO_4 + 135O_2 = 105CO_2 + 120H_2O + 15HNO_3 + H_3PO_4$$

$\longleftarrow$ *P*

REDFIELD RATIO = 105:15:1 = C:N:P (ATOM RATIO)

C:N= 7

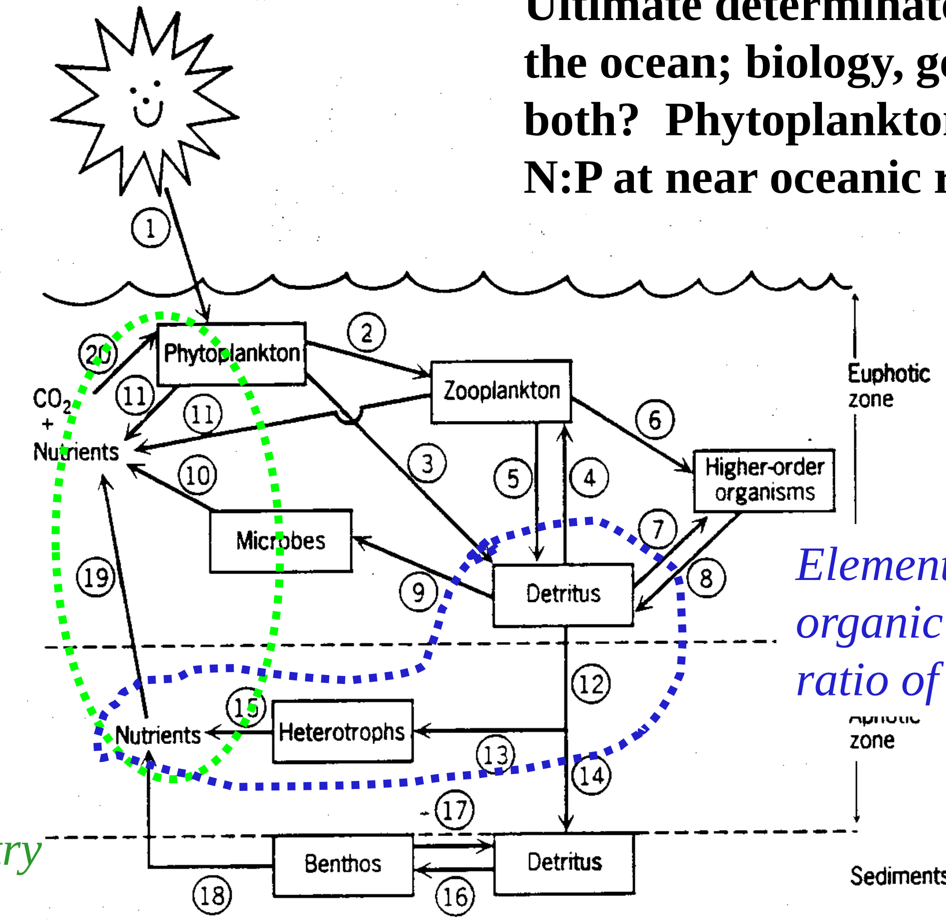
$C:O_2 = 0.78$

or $C:O = 1.56$

Ultimate determinate of C:N:P etc in the ocean; biology, geochemistry, or both? Phytoplankton happen to use N:P at near oceanic ratio!

Uptake ratio of CO_2, NO_3, PO_4^{-3}, etc major control on elemental ratio of organic matter.

Where nutrients limit organic matter production, stoichiometry determines strength of biological pump.



Elemental ratio of sinking organic matter sets regeneration ratio of inorganic species

FIGURE 8.1. Biogeochemical cycle of POM illustrating the following processes: (1) Photosynthesis, (2) consumption, (3) death, (4) consumption of detritus, (5) excretion of POM and death, (6) consumption, (7) consumption of detritus, (8) excretion of POM and death, (9) bacterial degradation, (10) nutrient regeneration, (11) excretion of nutrients, (12) sinking POM, (13) consumption, (14) sedimentation, (15) nutrient regeneration, (16) consumption, (17) excretion of POM and death, (18) nutrient regeneration, (19) nutrient transport via vertical advection and eddy diffusion, (20) nutrient assimilation.

Change elemental stoichiometry - change ΔCO_2, etc.!

TABLE 7.6

Changes in the CO_2 System Due to the Oxidation of Plant Material

	Initial[a]	ΔAOU (mM) 0.13	ΔAOU (mM) 0.26	% Change
ΔCO_2	0	0.10	0.20	—
TCO_2	2.200	2.300	2.400	9.1 ± 0.1
CA	2.487	2.487	2.487	0
pCO_2	350	610	1.160	231 ± 1.0
pH	8.200	8.001	7.753	–5.5 ± 0.04
$[CO_2]$	0.012	0.021	0.040	233
$[HCO_3^-]$	1.889	2.072	2.234	18
$[CO_3^{2-}]$	0.299	0.208	0.126	–58

[a] All the concentrations are mM.

TABLE 8.1
Distribution of Elements in Organisms (N) and Seawater (A) — A Measure of Availability to Need

Element	N (g/100 g)	A (g/m³)	A/N
H	7		
Na	3	10,750	3,600
K	1	390	390
Mg	0.4	1,300	300
Ca	0.5	416	830
C	30	28	1
Si[a]	0.5	0.50	1
Si[b]	10	0.50	0.05
N	5	0.30	0.06
P	0.6	0.030	0.05
O ($O_2 + CO_2$)	47	90	2
S	1	900	900
Cl	4	19,300	4,800
Cu	0.005	0.010	2
Zn	0.020	0.005	4
B	0.002	0.005	2,500
V	0.003	0.0003	0.1
As	0.0001	0.015	150
Mn	0.002	0.005	2.5
F	1	1.4	1,400
Br	0.0025	66	26,000
Fe[a]	0.001	0.05	0.05
Fe[b]	0.000	0.050	1.3
Co	0.00005	0.0001	2
Al	1	0.120	120
Ti	0.100	—	—

[a] Phytoplankton.
[b] Diatoms.

TABLE 7.6
Carbon and Nitrogen Fixation Reactions

Carbon fixation[a]

$\frac{1}{4}CO_2(g) + \frac{1}{4}H_2O = \frac{1}{4}\text{“}CH_2O\text{”} + \frac{1}{4}O_2(g);\ \Delta G^0_w = +29.9$ kcal/mol

$\frac{1}{4}CO_2(g) + \frac{1}{2}H_2S(g) = \frac{1}{4}\text{“}CH_2O\text{”} + \frac{1}{16}S_8(col)^b + \frac{1}{4}H_2O;\ \Delta G^0_w = +4.7$ kcal/mol

$\frac{1}{4}CO_2(g) + \frac{1}{6}NH_4^+ + \frac{1}{12}H_2O = \frac{1}{4}\text{“}CH_2O\text{”} + \frac{1}{6}NO_2^- + \frac{1}{3}H^+;\ \Delta G^0_w = +17.8$ kcal/mol

Nitrogen fixation[c]

$\frac{1}{6}N_2(g) + \frac{1}{3}H^+ + \frac{1}{4}\text{“}CH_2O\text{”} + \frac{1}{4}H_2O = \frac{1}{3}NH_4^+ + \frac{1}{4}CO_2(g);\ \Delta G^0_w = -4.8$ kcal/mol

TABLE 7.5
Oxidation of Organic Compounds Represented Generically as “CH_2O”[a]

Aerobic respiration

$\frac{1}{4}\text{“}CH_2O\text{”} + \frac{1}{4}O_2(g) = \frac{1}{4}CO_2(g) + \frac{1}{4}H_2O;\ \Delta G^0_w = -29.9$ kcal/mol

Denitrification

$\frac{1}{4}\text{“}CH_2O\text{”} + \frac{1}{5}NO_3^- + \frac{1}{5}H^+ = \frac{1}{4}CO_2(g) + \frac{1}{10}N_2(g) + \frac{7}{20}H_2O;\ \Delta G^0_w = -28.4$ kcal/mol

Sulfate reduction

$\frac{1}{4}\text{“}CH_2O\text{”} + \frac{1}{8}SO_4^{2-} + \frac{1}{8}H^+ = \frac{1}{4}CO_2(g) + \frac{1}{8}HS^- + \frac{1}{4}H_2O;\ \Delta G^0_w = -6.1$ kcal/mol

Methane fermentation

$\frac{1}{4}\text{“}CH_2O\text{”} = \frac{1}{8}CO_2(g) + \frac{1}{8}CH_4(g);\ \Delta G^0_w = -5.6$ kcal/mol

Hydrogen fermentation

$\frac{1}{4}\text{“}CH_2O\text{”} + \frac{1}{4}H_2O = \frac{1}{4}CO_2(g) + \frac{1}{2}H_2(g);\ \Delta G^0_w = -1.6$ kcal/mol

Source: After *Principles of Aquatic Chemistry*, F. M. M. Morel, copyright © 1983 by John Wiley & Sons, Inc., New York, p. 330. Reprinted by permission.
[a] Accomplished by chemoorganotrophs, all heterotrophs.

1934 On the proportions of organic derivatives in sea water and their relation to the composition of plankton. In *James Johnstone Memorial Volume* , pp. 176-92. Liverpool: University of Liverpool.
1942 The processes determining the concentration of oxygen, phosphate and other organic derivatives within the depths of the Atlantic Ocean. *Pap. Phys. Oceanogr. Meteorol.* 9(2):1-22.
1948 The exchange of oxygen across the sea surface. *J. Mar. Res.* 7(3):347-61.
1958 The biological control of chemical factors in the environment. *Am. Sci.* 46(3):205-21.

Alfred C. Redfield *November 15, 1890 — March 17, 1983*

www.nap.edu/readingroom/books/biomems/aredfield.html

1934 In *James Johnstone Memorial Volume* , pp. 176-92.

ON THE PROPORTIONS OF ORGANIC DERIVATIVES IN SEA WATER AND THEIR RELATION TO THE COMPOSITION OF PLANKTON[1]

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(*Received September* 5, 1933)

"Chemical analysis shows that the animal and plant body is mainly built up from the four elements, nitrogen, carbon, hydrogen, and oxygen. Added to these are the metals, sodium, potassium and iron, and the non-metals, chlorine, sulphur and phosphorus. Calcium or silicon are also invariably present as the bases of calcareous or siliceous skeletons. All these, with some others, are indispensable constituents of the organic body, and in an exhaustive study of the cycle of matter from the living to the non-living phases, and *vice versa*, we should have to trace the course of each." JAMES JOHNSTONE, "Conditions of Life in the Sea," p. 273. 1908.

It is now well recognized that the growth of plankton in the surface layers of the sea is limited in part by the quantities of phosphate and nitrate available for their use and that the changes in the relative quantities of certain substances in sea water are determined in their relative proportions by biological activity. When it is considered that the synthetic processes leading to the development of organic matter are limited to the surface layers of the sea in which photosynthesis can take place, it becomes evident that the chemical changes which occur in the water below this zone must arise chiefly from the disintegration of organic matter. In so far as this disintegration goes to completion, the changes in the derived inorganic constituents of sea water must depend strictly upon the quantity and composition of the organic matter which is being decomposed. This is true quite irrespective of the agencies of decomposition, be they bacterial action,

1. Contribution No. 30, from the Woods Hole Oceanographic Institution.

various plankton, and on the whole the latter differ among themselves much more than their average differs from the calculated ratios.

TABLE II

Proportions of carbon, nitrogen, and phosphorus in various samples of plankton.

Sample	Parts by Weight		
	Carbon	Nitrogen	Phosphorus
Mixed copepods from Buzzards Bay ..	100	21	1·98
Centropages typicus, Gulf of Maine ..	100	25·6	1·06
Calanus finmarchicus, Gulf of Maine ..	100	13·4	2·04
Calanus finmarchicus, Gulf of Maine ..	100	15·8	2·26
Diatoms—Bay of Fundy, almost entirely *Thalassiosira nordenskiöldi*.	100	18·2	1·36
Diatoms—Off Nova Scotia coast—17 species of somewhat the same abundance.	100	15·6	2·26
Peridinians—Meyer (1914)	100	13·2	2·2
Chiefly peridinians—average of samples No. 1, 2, 3, 4, of Brandt (1898).	100	8·1	—
Chiefly diatoms—average of samples No. 6 and 7, Brandt (1898).	100	12·4	—
Chiefly copepods—average of samples No. 8 and 9, Brandt (1898).	100	15·3	—
Mixed plankton—sample no. 10, Brandt (1898). ..	100	11·3	—
Average all samples	100	15·4	1·88
Estimated from analyses of sea water ..	100	16·7	1·85

In this connection it is of interest to note that Braarud and Føyn (1930) have observed that each cell of *Chlamydomonas* removes 2·98 × 10[-12] gr. NO_3 nitrogen and 0·98 × 10[-12] gr. P_2O_5 from the sea water in which it grows. Here we see in a laboratory experiment an organism modifying the concentration of nitrate and phosphate in the medium in a ratio ($\Delta N : \Delta P = 15 : 1$) not very different from that observed in the oceans as a whole.

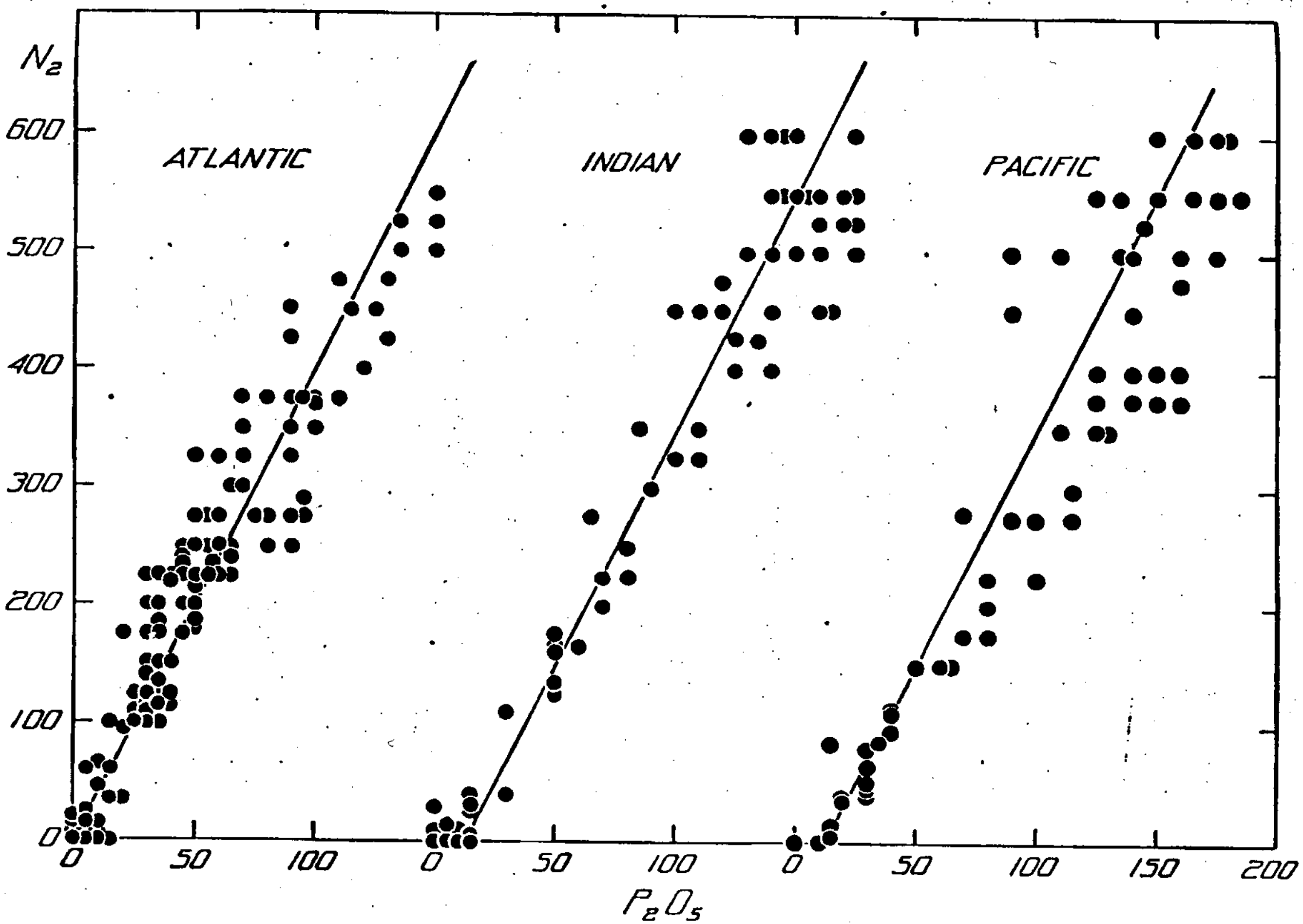


FIG. 4. Correlation between concentration of nitrate and phosphate in waters of the Atlantic, Indian, and Pacific Oceans. Data of Thomsen. Ordinate, concentration of nitrate nitrogen, units milligrams of nitrogen per cubic meter; abscissa, concentration of phosphate, units milligrams P_2O_5 per cubic meter. The lines correspond to a ratio of $\triangle N : \triangle P = 20 : 1$ milligram atoms.

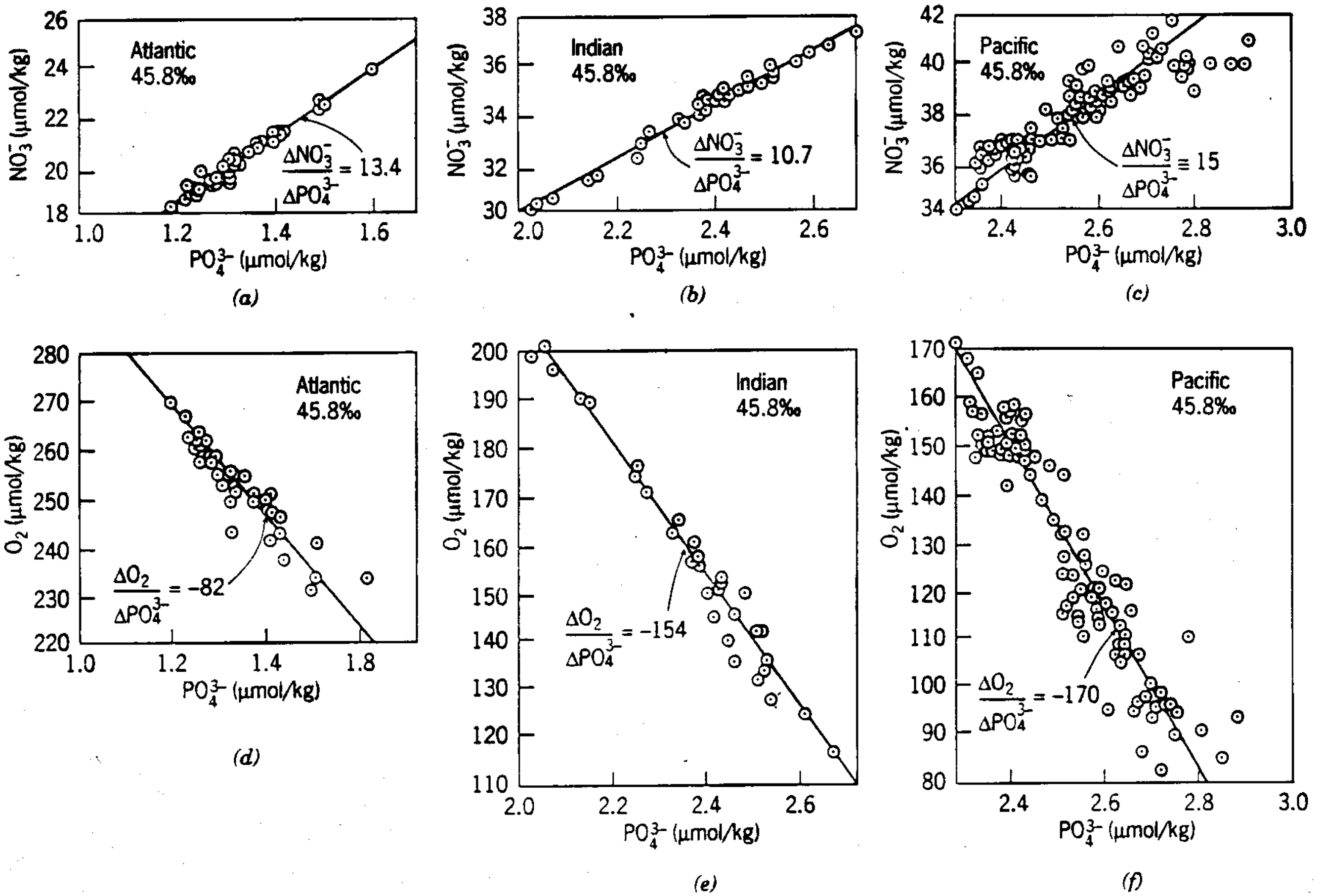


FIGURE 10.8. Nitrate versus phosphate concentrations along the 45.8‰ σ_t isopycnal surface (~2500 m depth) in the (*a*) Atlantic, (*b*) Indian, and (*c*) Pacific Oceans. Dissolved oxygen versus phosphate concentrations along the 45.8‰ σ_t isopycnal surface (~2500 m depth) in the (*d*) Atlantic, (*e*) Indian, and (*f*) Pacific Oceans. The slopes of these lines represent the proportions by which these constituent concentrations are altered by the remineralization of POM in the deep sea. *Source:* From *Tracers in the Sea*, W. S. Broecker and T.-H. Peng, copyright © 1982 by the Lamont-Doherty Geological Observatory, Palisades, New York, p. 141. Reprinted by permission. See Broecker and Peng (1982) for data sources.

$$AOU = [O_2]_{sat} - [O_2]_{obs}$$

TABLE 8.9
Molecular Ratios of P, N, C, O_2, and $CaCO_3$ Changes in the Atlantic and Indian Oceans

Location	Surface	P	N	CO_2	(O_2-2N)	O_2	$CaCO_3$
N. Atl.	27	1	17.6 ± 0.6	97 ± 9	130 ± 6	165 ± 7	15 ± 4
	27.2	1	16.8 ± 0.5	88 ± 6	139 ± 6	173 ± 6	8 ± 3
S. Atl.	27	1	16.7 ± 0.7	102 ± 7	131 ± 6	165 ± 6	8 ± 2
	27.2	1	16.7 ± 1.2	95 ± 10	150 ± 2	182 ± 9	8 ± 4
Mean Atl.		1	17 ± 0.4	96 ± 6	138 ± 9	171 ± 8	10 ± 4
S. Ind.	27	1	15.2 ± 0.6	112 ± 6	138 ± 7	169 ± 8	15 ± 4
	27.2	1	14.5 ± 0.5	125 ± 7	145 ± 5	174 ± 6	19 ± 6
Mean Ind.		1	14.9 ± 0.4	119 ± 5	142 ± 5	172 ± 5	17 ± 4
Overall Mean		1	16.3 ± 1.1	103 ± 14	140 ± 8	172 ± 7	12 ± 5

Seasonal variations in the Ross Sea Antarctica as another way to calculate elemental stoichiometery

Sweeney et al., 1998

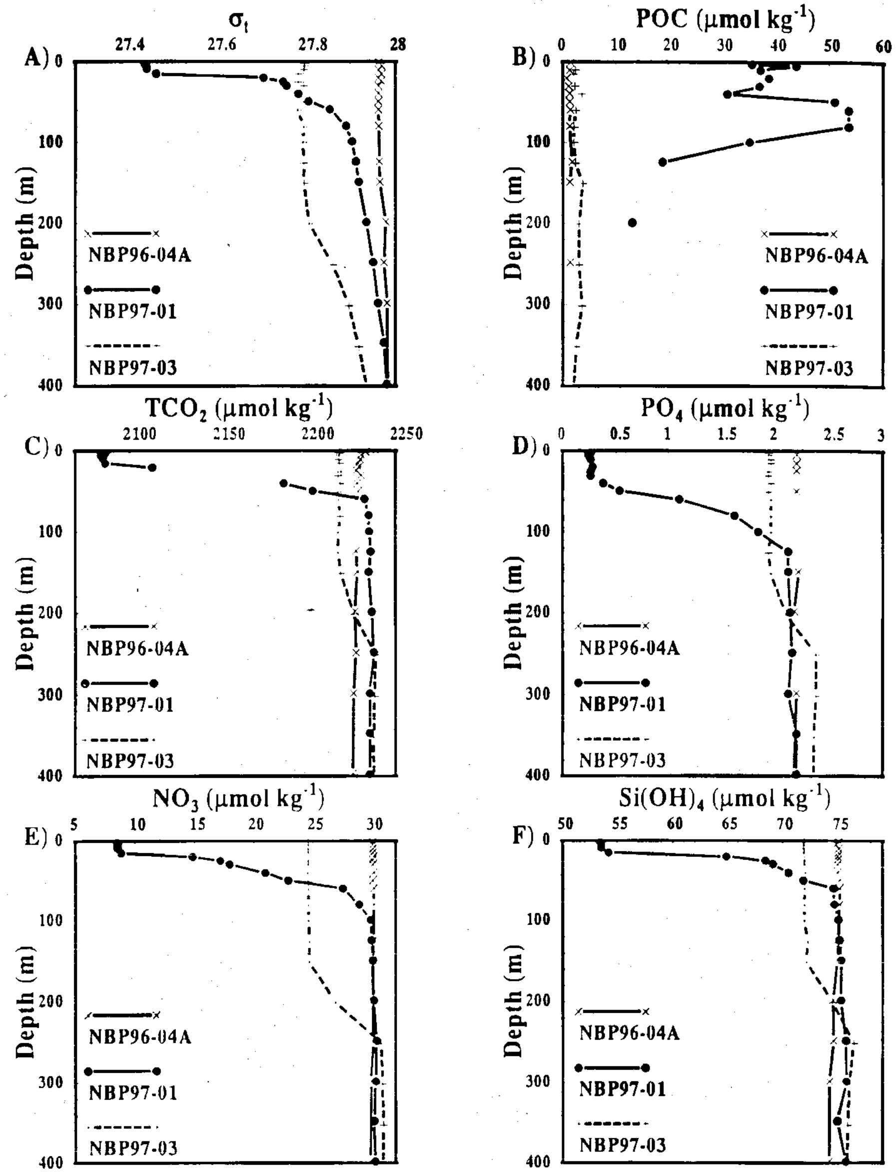
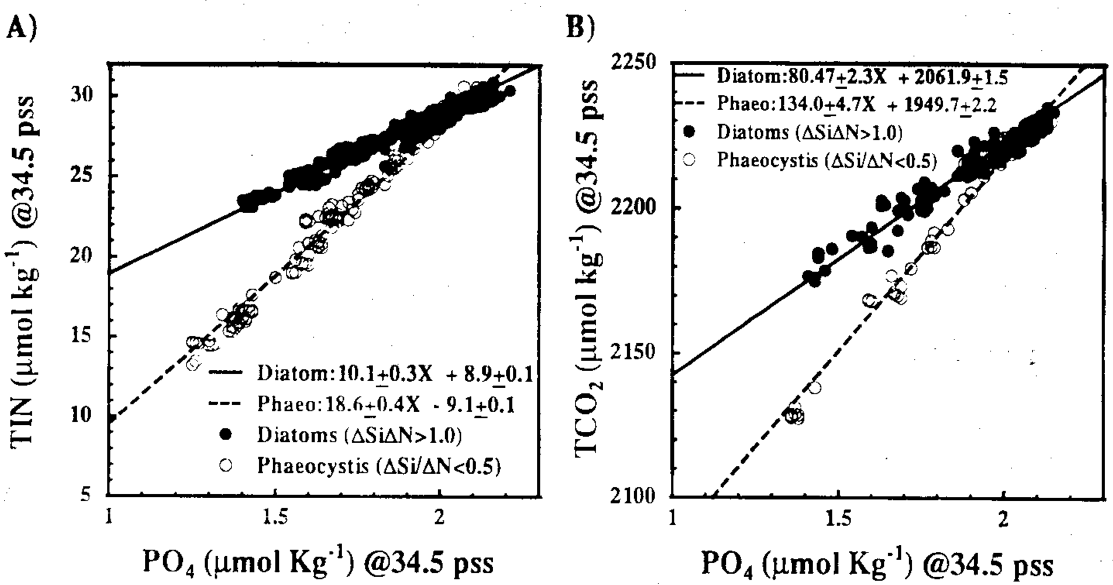


Fig. 2. Vertical profiles of (A) σ_T, (B) POC, (C) salinity-normalized TCO_2, (D) salinity-normalized PO_4, (E) salinity-normalized NO_3, and (F) salinity-normalized $Si(OH)_4$ observed during early spring [NBP96-04A, Station. 10, October 10, 1996; ×], summer [NBP97-01, Station 1, January 13, 1997; •] and autumn [NBP97-03, Station 13, April 13, 1997; +)] at 76 30′S and 169 00′E. All concentrations normalized to 34.5 (PSS) salinity.

Example of departures from Redfield stoichiometry as function of phytoplankton species



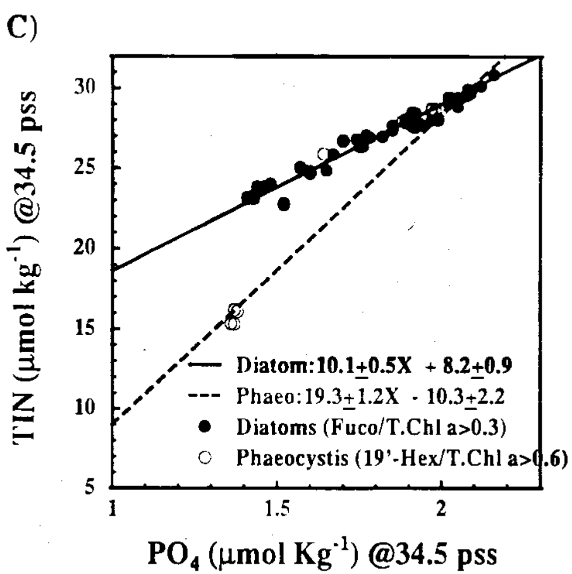
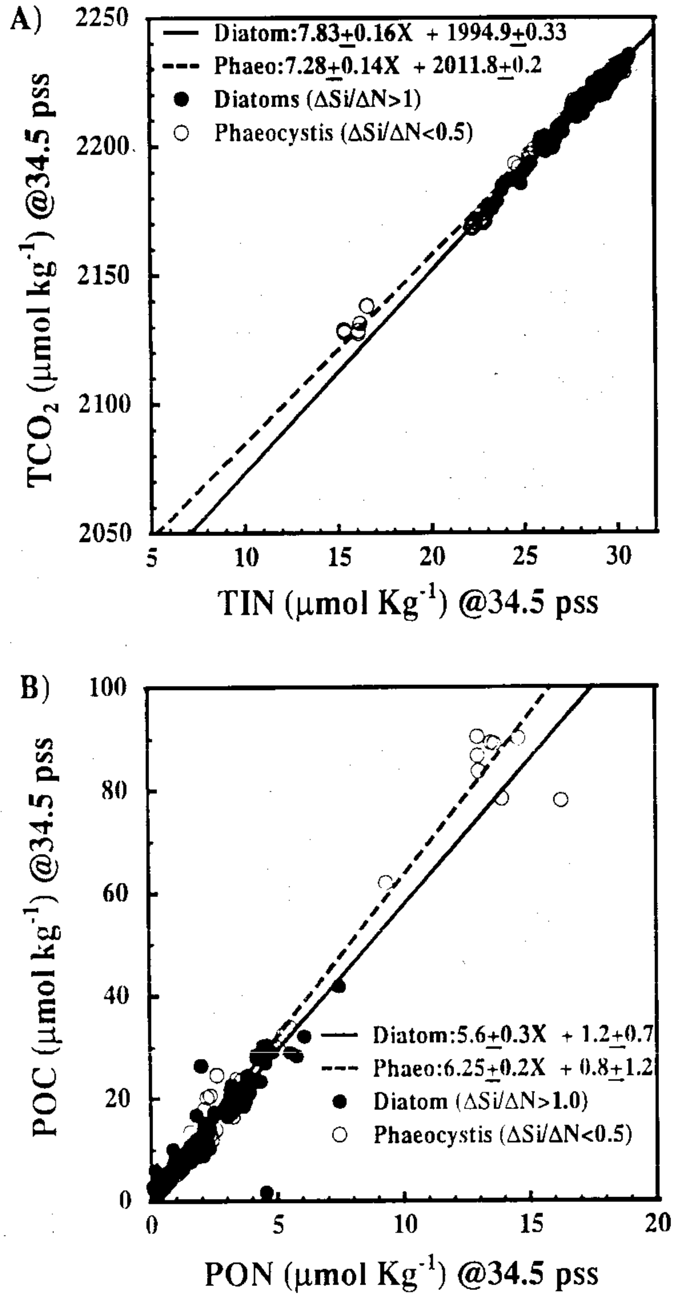


Fig. 4. (A) Relationship between total inorganic nitrogen (TIN) (nitrate + nitrite + ammonium) and phosphate concentrations scaled to a salinity of 34.5 during the late spring cruise (NBP97-08). Solid line represents all points with $\Delta Si/\Delta N > 1.0$ and $\Delta N > 0.12\,\mu mol\,kg^{-1}$ and dashed line represents all points with $\Delta Si/\Delta N < 0.5$ and $\Delta N > 0.12\,\mu mol\,kg^{-1}$. Each linear regression was forced through an early spring value ($PO_4 = 2.14\,\mu mol\,kg^{-1}$ and $TIN = 30.4\,\mu mol\,kg^{-1}$). (B) Relationship between total carbon dioxide and phosphate concentrations. Solid line represents all points with $\Delta Si/\Delta N > 1.0$ and $\Delta N > 0.12\,\mu mol\,kg^{-1}$ and dashed line represents all points with $\Delta Si/\Delta N < 0.5$ and $\Delta N > 0.12\,\mu mol\,kg^{-1}$. Each linear regression was forced through an early spring value ($TCO_2 = 2234\,\mu mol\,kg^{-1}$ and $PO_4 = 2.14\,\mu mol\,kg^{-1}$). (C) Relationship between total inorganic nitrogen and phosphate concentrations. Solid line is a linear regression using all samples with fucoxanthin: total chlorophyll ratio > 0.3 and $\Delta N > 0.12\,\mu mol\,kg^{-1}$, and dashed line is a linear regression of all points with 19′-hexanoyloxyfucoxanthin: total chlorophyll ratio > 0.6 and $\Delta N > 0.12\,\mu mol\,kg^{-1}$. Each regression has been forced through an early spring value ($PO_4 = 2.14\,\mu mol\,kg^{-1}$ and $TIN = 30.4\,\mu mol\,kg^{-1}$).



Elemental ratio of C or N with P more variable than between C and N

Fig. 5. (A) Relationship between total inorganic nitrogen (TIN) (nitrate + nitrite + ammonium) and total CO_2 concentrations scaled to a salinity of 34.5 during the late spring cruise (NBP97-08). Solid line represents all points with $\Delta Si/\Delta N > 1.0$ and $\Delta N > 0.12\ \mu mol\ kg^{-1}$. Dashed line represents all points with $\Delta Si/\Delta N < 0.5$ and $\Delta N > 0.12\ \mu mol\ kg^{-1}$. Each linear regression was forced through an early spring value ($TCO_2 = 2234\ \mu mol\ kg^{-1}$ and $TIN = 30.4\ \mu mol\ kg^{-1}$). (B) Relationship between particulate organic nitrogen (PON) and particulate organic carbon (POC) concentrations during late spring. Solid line represents all points with $\Delta Si/\Delta N > 1.0$ and $\Delta N > 0.12\ \mu mol\ kg^{-1}$, and dashed line represents all points with $\Delta Si/\Delta N < 0.5$ and $\Delta N > 0.12\ \mu mol\ kg^{-1}$. Each linear regression was forced through an early spring value ($POC = 3.1\ \mu mol\ kg^{-1}$ and $PON = 0.31\ \mu mol\ kg^{-1}$).

The Modern Mediterranean – A non-Redfield mini-ocean? (Krom et al., 1991 L&O)

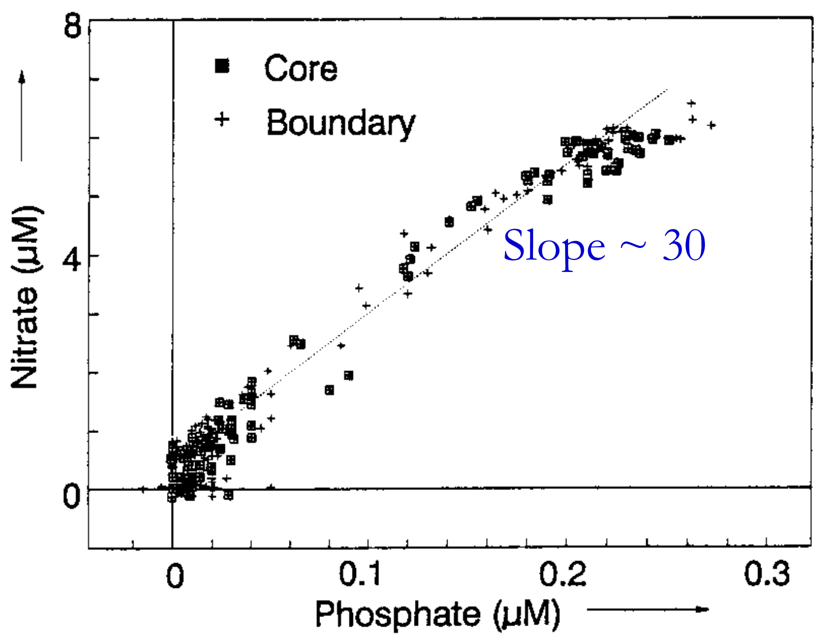


Fig. 5. NO_3^- vs. PO_4^{3-} in combined data from both the core and boundary stations of the Cyprus eddy. Data from February, May, September, and November 1989. Of the 272 data points included, 15 are from depths >1,000 m.

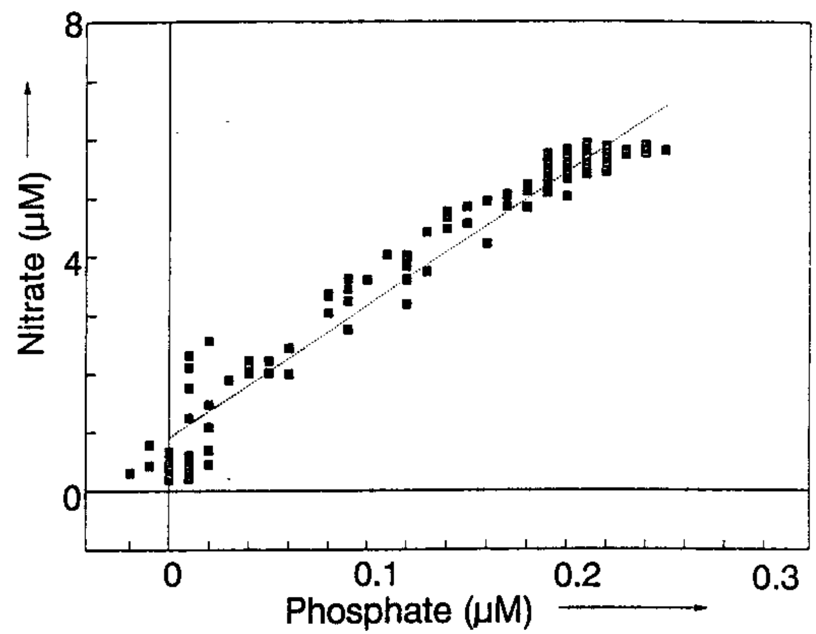
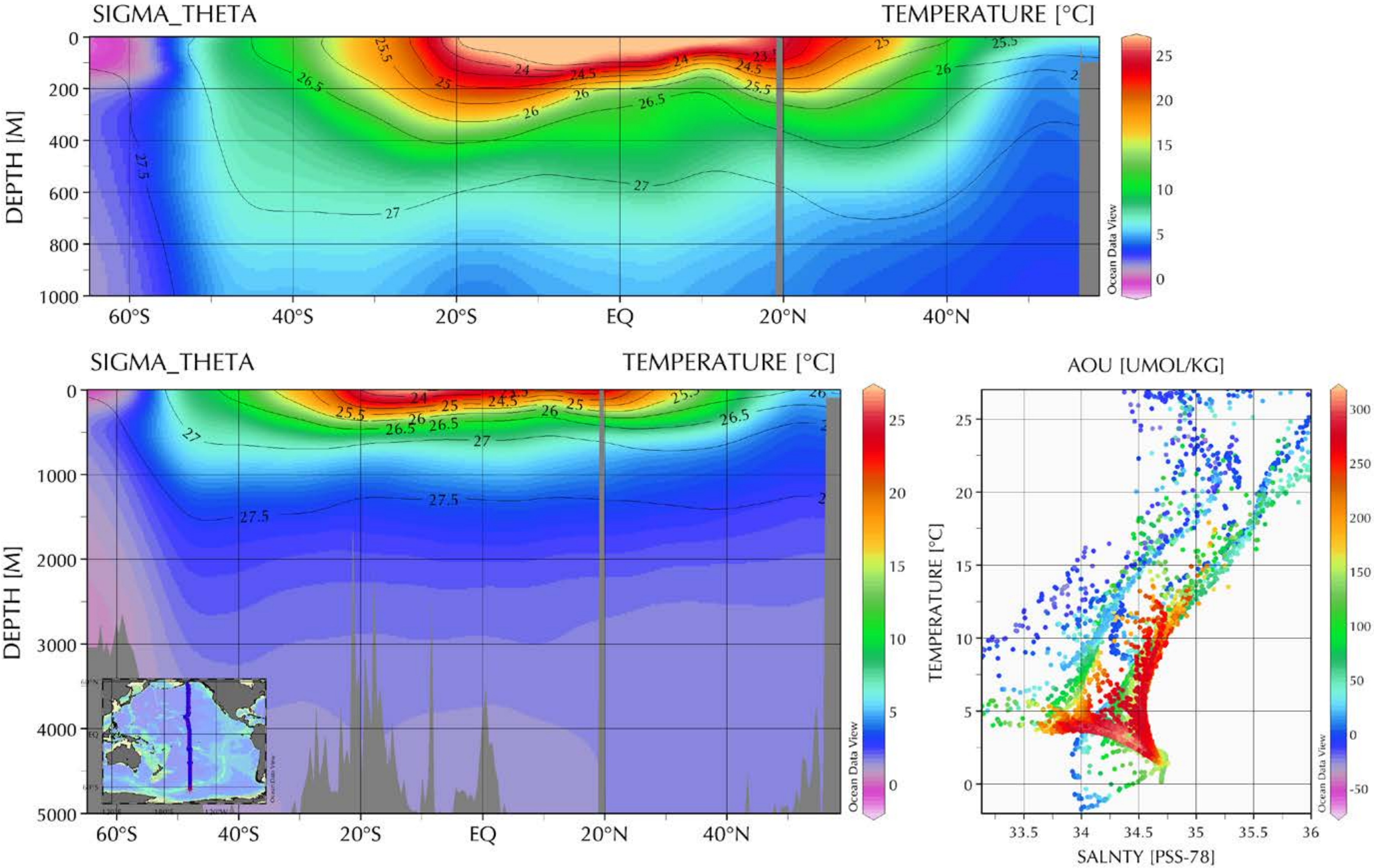


Fig. 6. NO_3^- vs. PO_4^{3-} from stations sampled across the southeastern Levantine basin at 33°30′N collected at 0.5° spacing from 34°30′E to 27°30′E. Of the 150 data points included, 10 are from depths >1,000 m.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DEPTH [M]
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400
600
800
1000
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40°S
20°S
EQ
20°N
40°N
25
20
15
10
5
0
Ocean Data View
SIGMA_THETA
TEMPERATURE [°C]
DEPTH [M]
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1000
2000
3000
4000
5000
60°S
40°S
20°S
EQ
20°N
40°N
Ocean Data View
AOU [UMOL/KG]
TEMPERATURE [°C]
SALNTY [PSS-78]
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34.5
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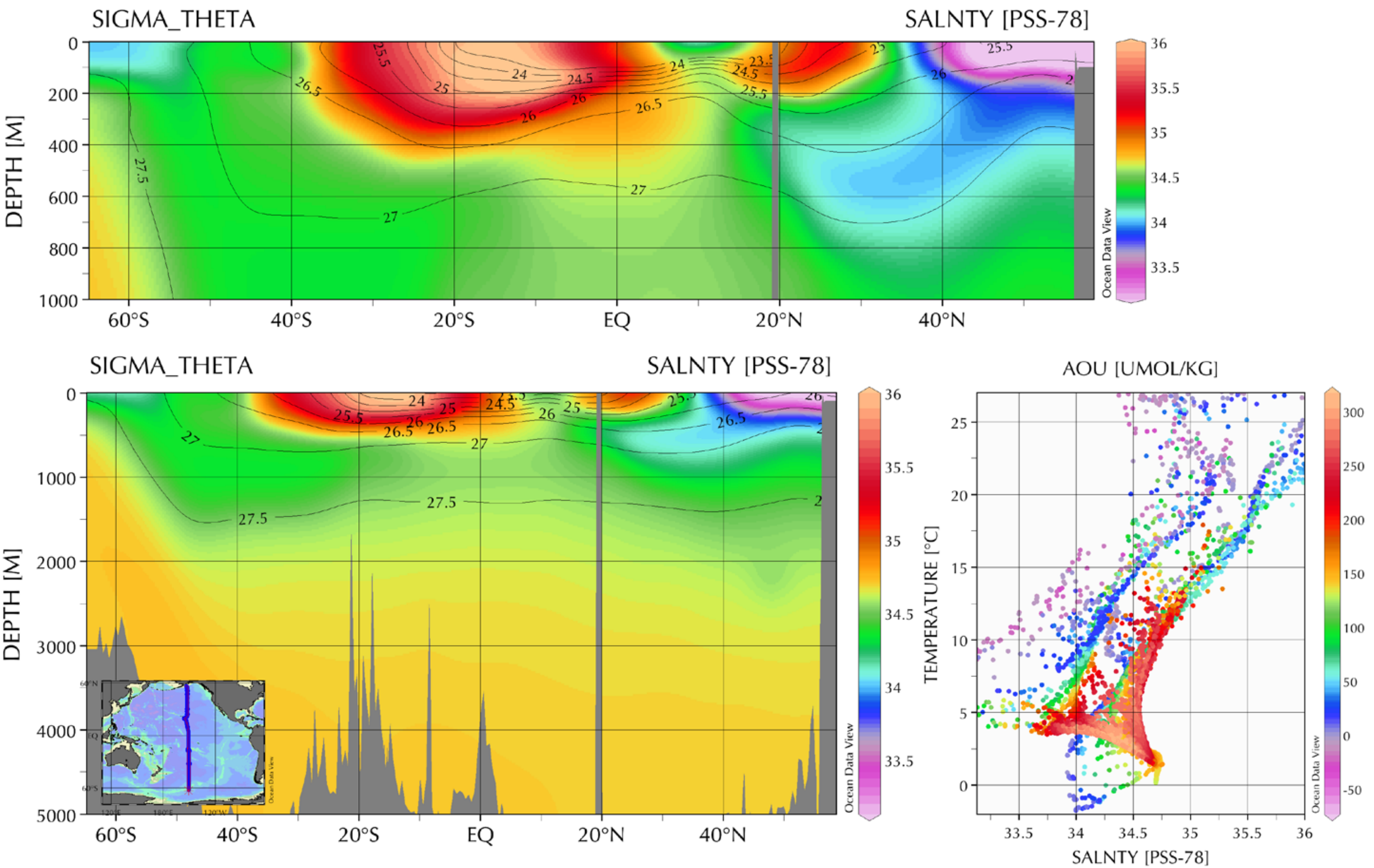

SIGMA_THETA
SALNTY [PSS-78]
DEPTH [M]
60°S
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EQ
20°N
40°N
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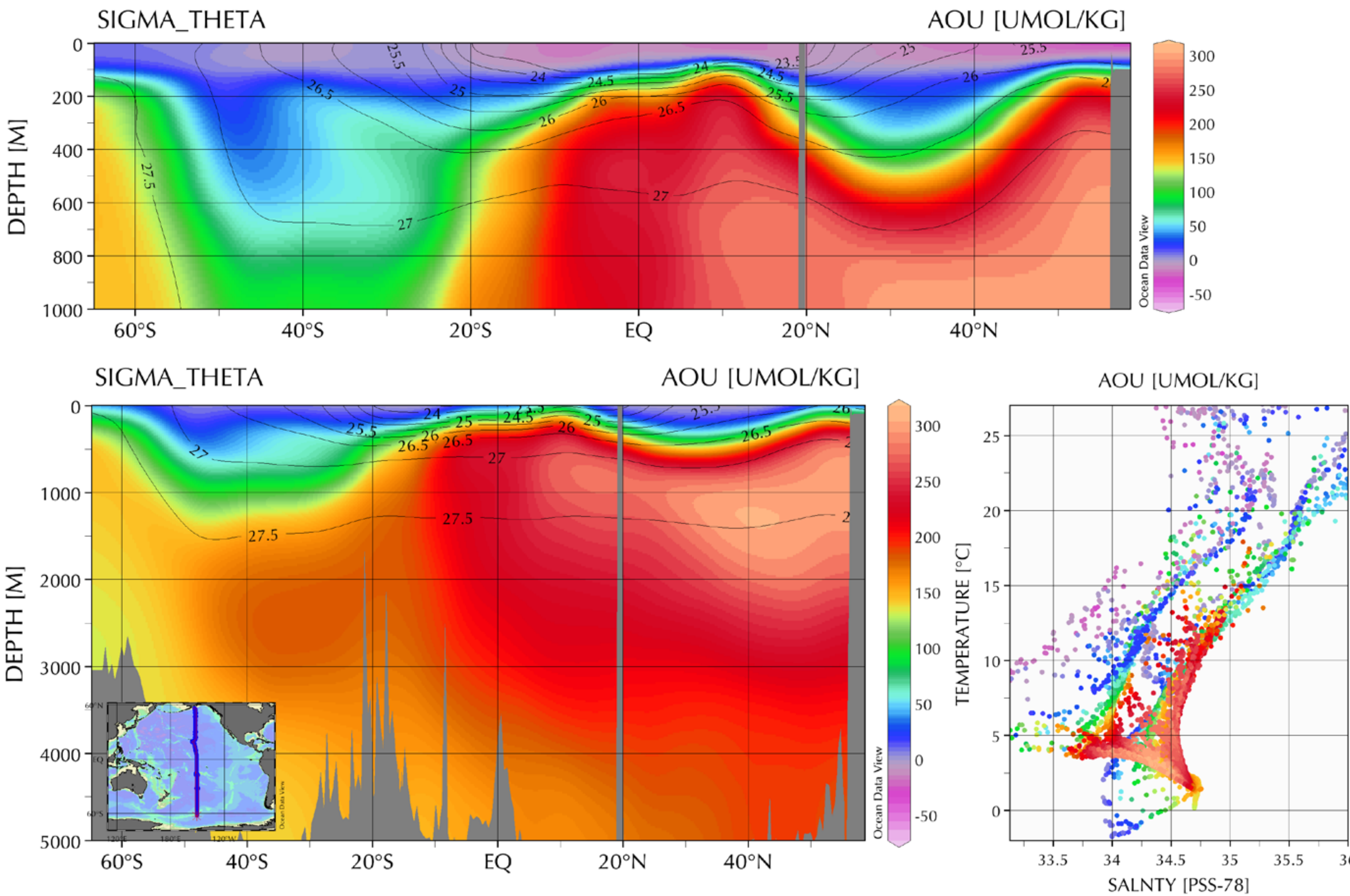
AOU [UMOL/KG]
TEMPERATURE [°C]
SALNTY [PSS-78]



SIGMA_THETA
AOU [UMOL/KG]
DEPTH [M]
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40°S
20°S
EQ
20°N
40°N
Ocean Data View
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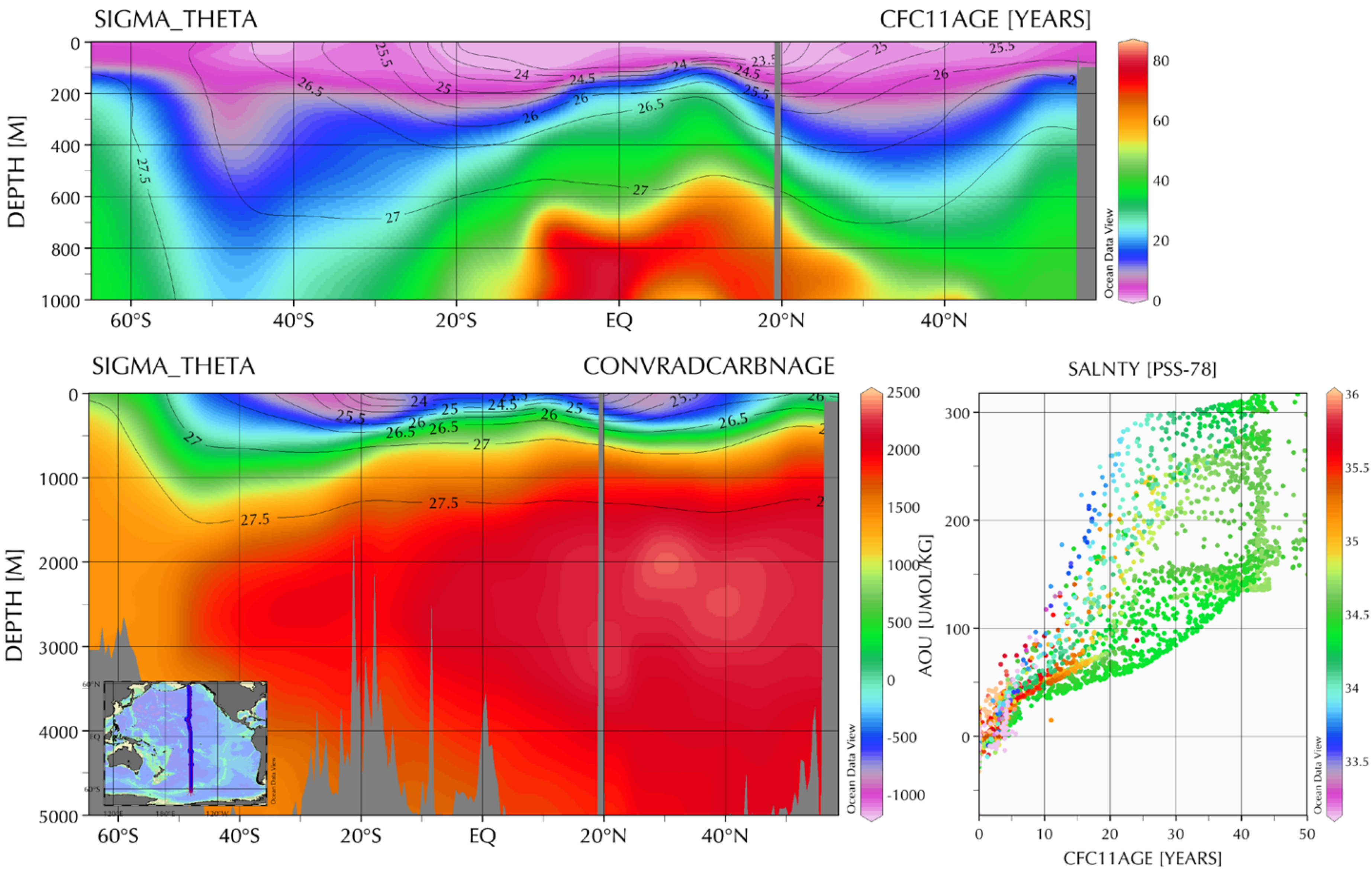
DEPTH [M]
AOU [UMOL/KG]
TEMPERATURE [°C]
SALNTY [PSS-78]



SIGMA_THETA
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DEPTH [M]
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20°S
EQ
20°N
40°N
Ocean Data View
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DEPTH [M]
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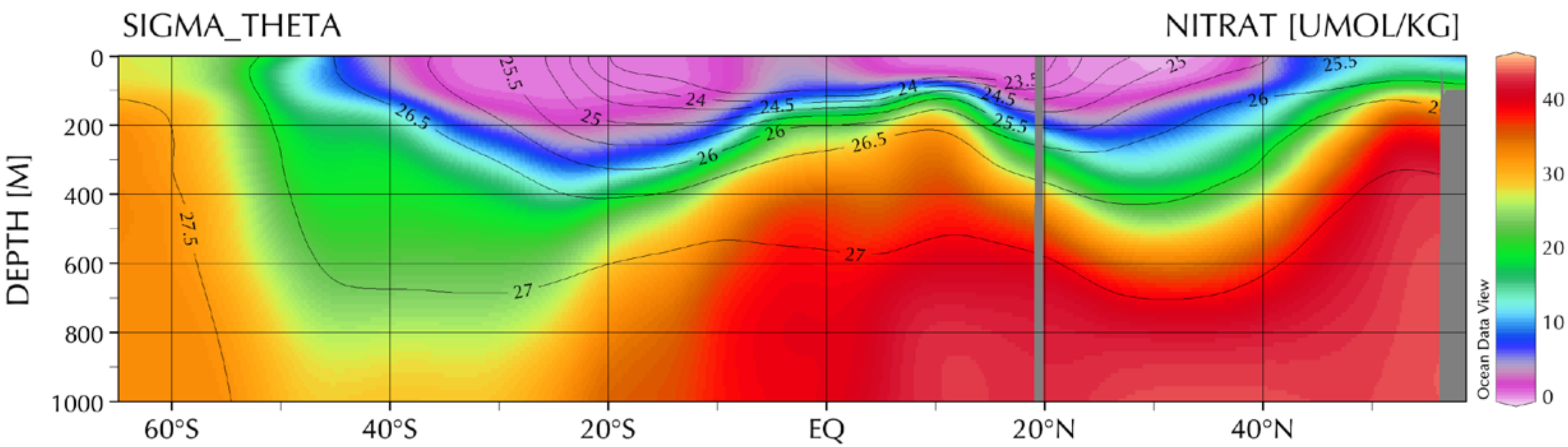
AOU [UMOL/KG]
CFC11AGE [YEARS]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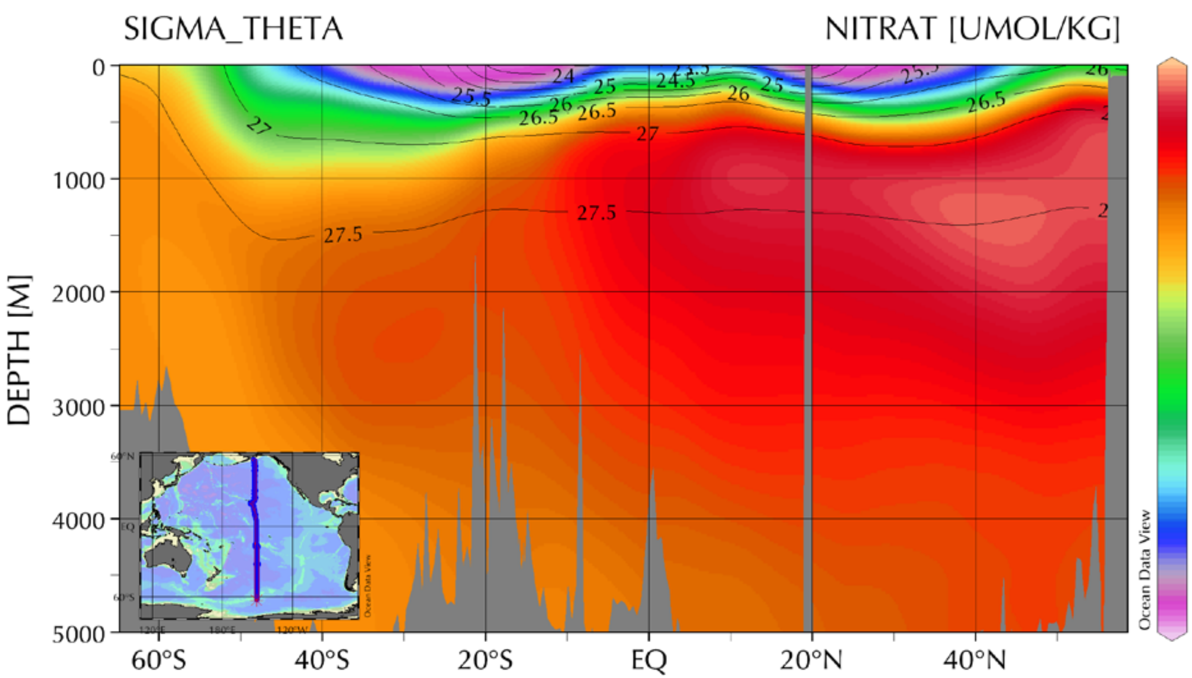
Ocean Data View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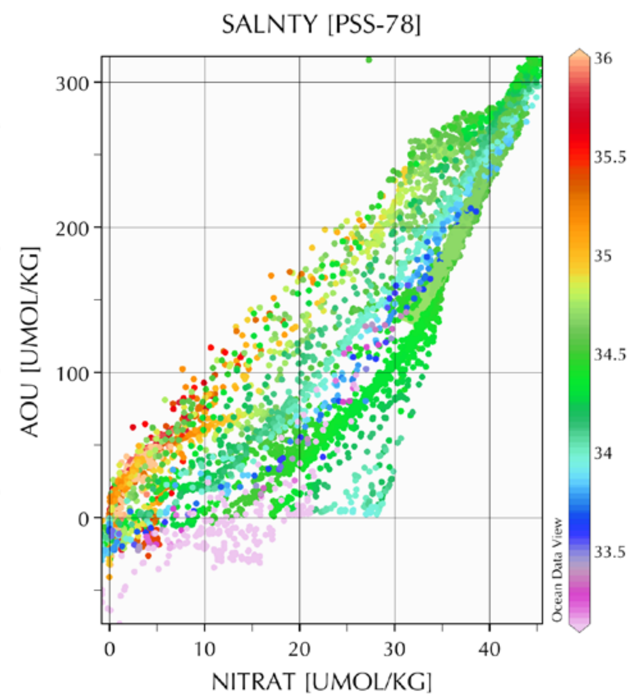
Ocean Data View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NITRAT [UMOL/KG]
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35.5
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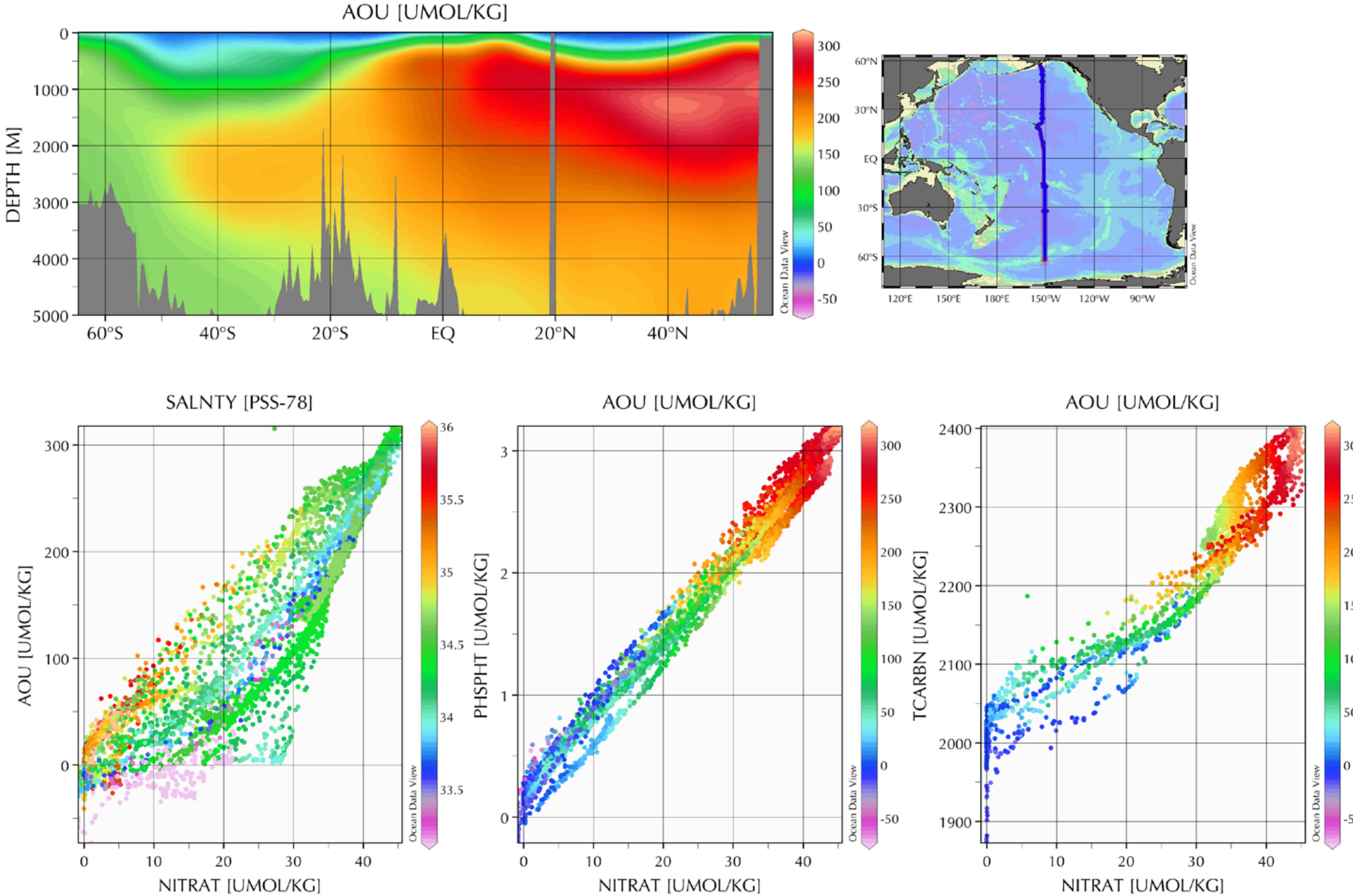
Ocean Data View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DEPTH [M]
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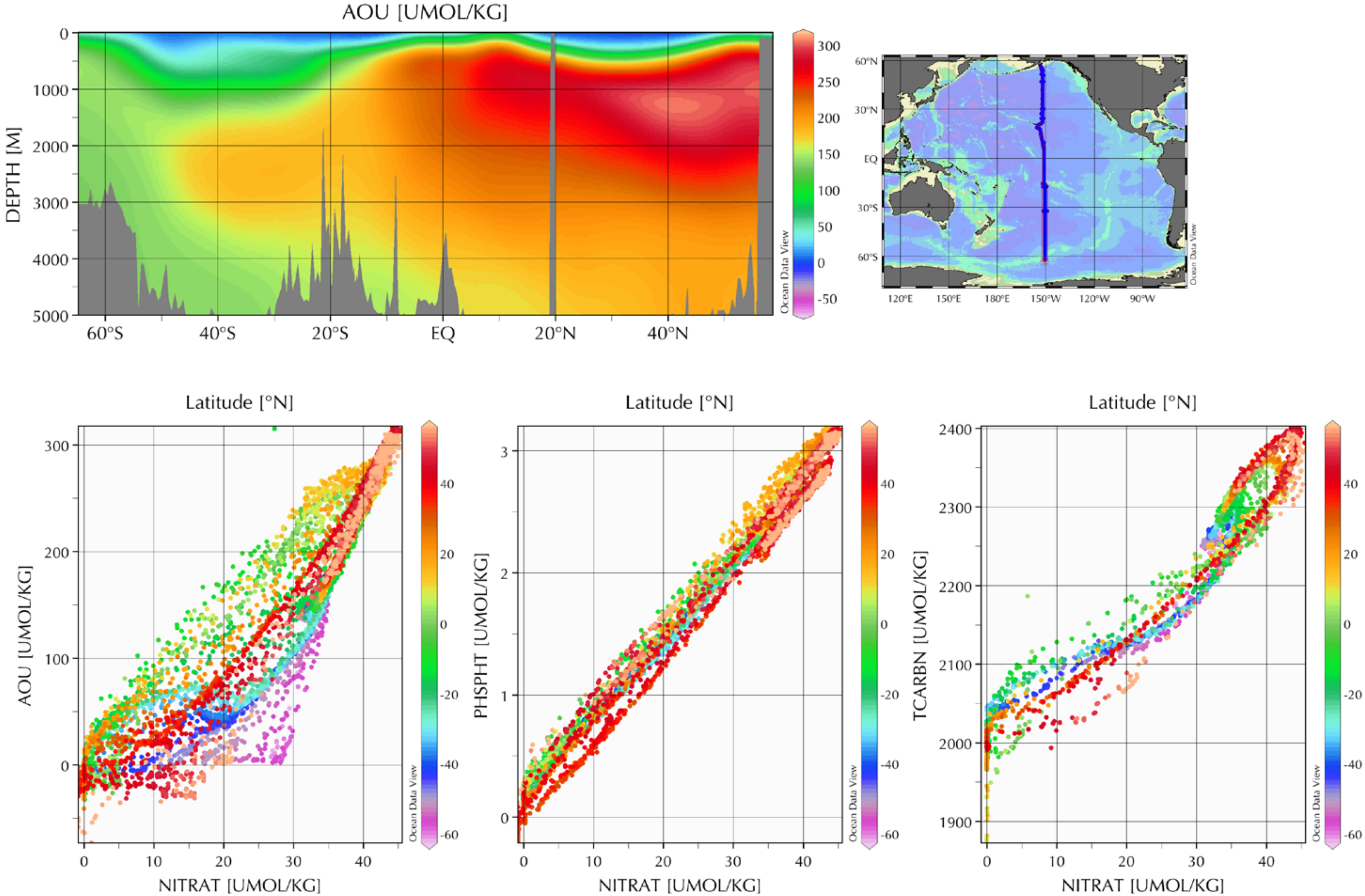
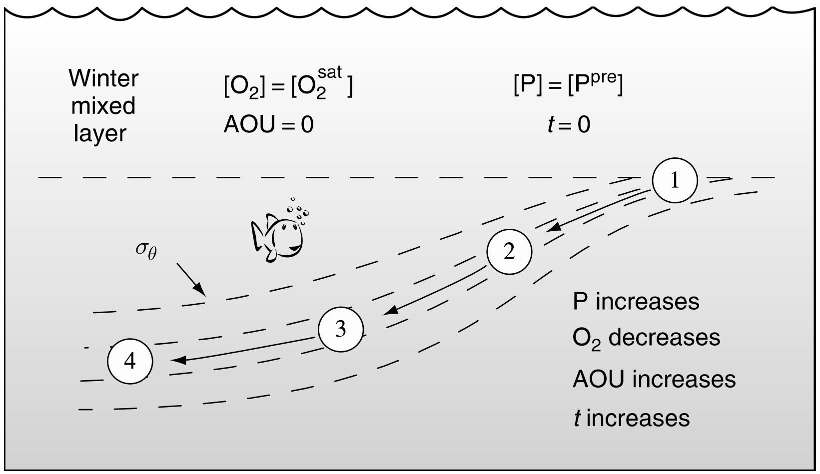
5000
60°S
40°S
20°S
EQ
20°N
40°N
300
250
200
150
100
50
0
-50
Ocean Data View
60°N
30°N
EQ
30°S
60°S
120°E
150°E
180°E
150°W
120°W
90°W
Ocean Data View
SALNTY [PSS-78]
AOU [UMOL/KG]
NITRAT [UMOL/KG]
36
35.5
35
34.5
34
33.5
Ocean Data View
AOU [UMOL/KG]
PHSPHT [UMOL/KG]
NITRAT [UMOL/KG]
Ocean Data View
AOU [UMOL/KG]
TCARBN [UMOL/KG]
NITRAT [UMOL/KG]
2400
2300
2200
2100
2000
1900
Ocean Data View



AOU [UMOL/KG]
DEPTH [M]
60°S
40°S
20°S
EQ
20°N
40°N
Ocean Data View
60°N
30°N
EQ
30°S
60°S
120°E
150°E
180°E
150°W
120°W
90°W
Latitude [°N]
AOU [UMOL/KG]
NITRAT [UMOL/KG]
Latitude [°N]
PHSPHT [UMOL/KG]
NITRAT [UMOL/KG]
Latitude [°N]
TCARBN [UMOL/KG]
NITRAT [UMOL/KG]

(A)



nd time since the water mass was at the surface, t. (B) Schematic plots of O_2, P, AOU and t versus locations 1, 2, 3 and 4 in (A); and a plot of AOU versus t used to derive oxygen utilization rates (OUR).

(B)

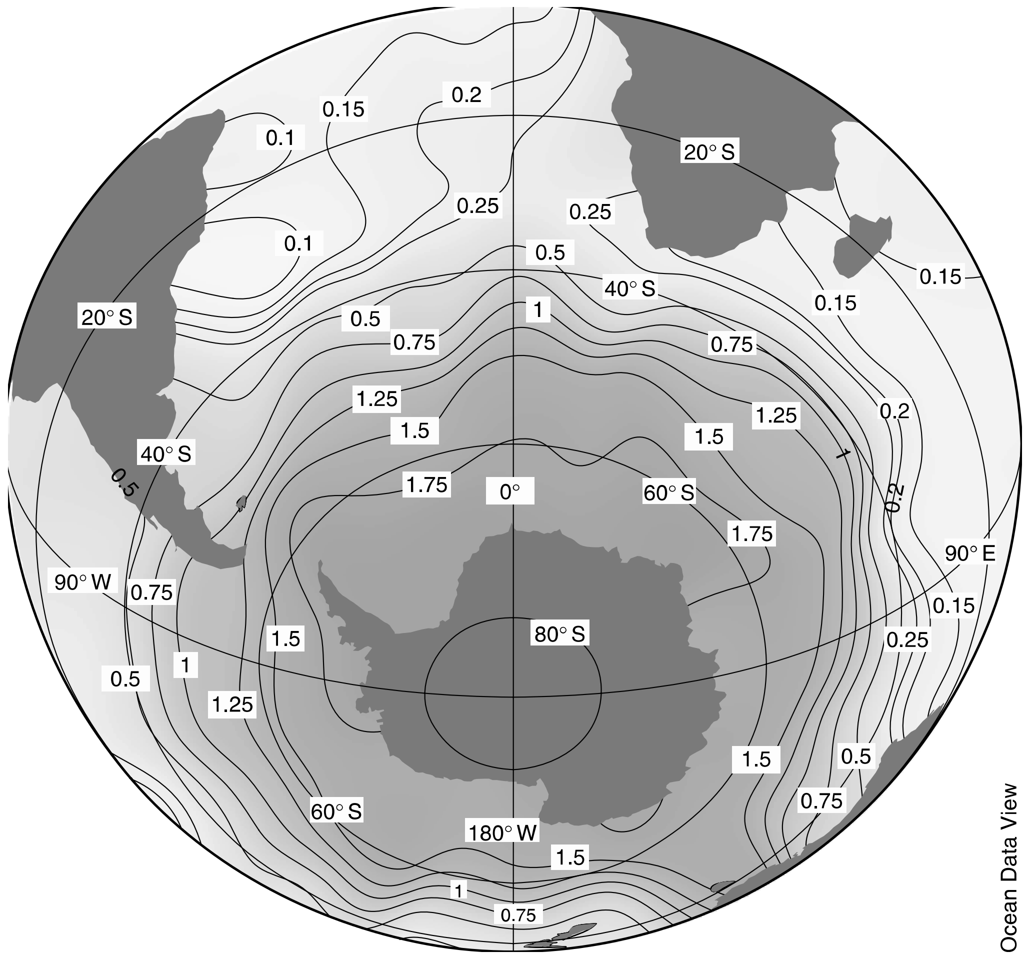
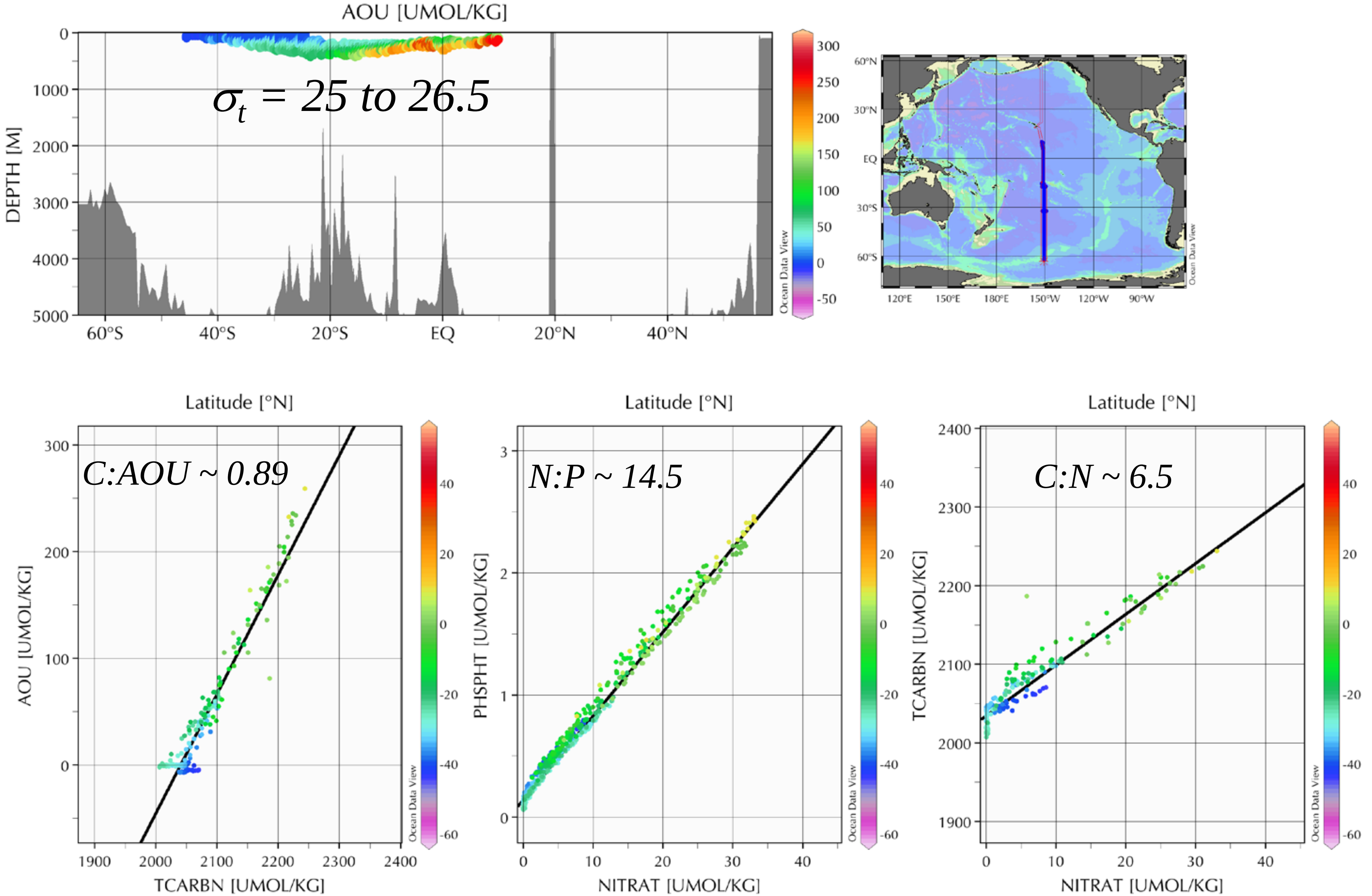
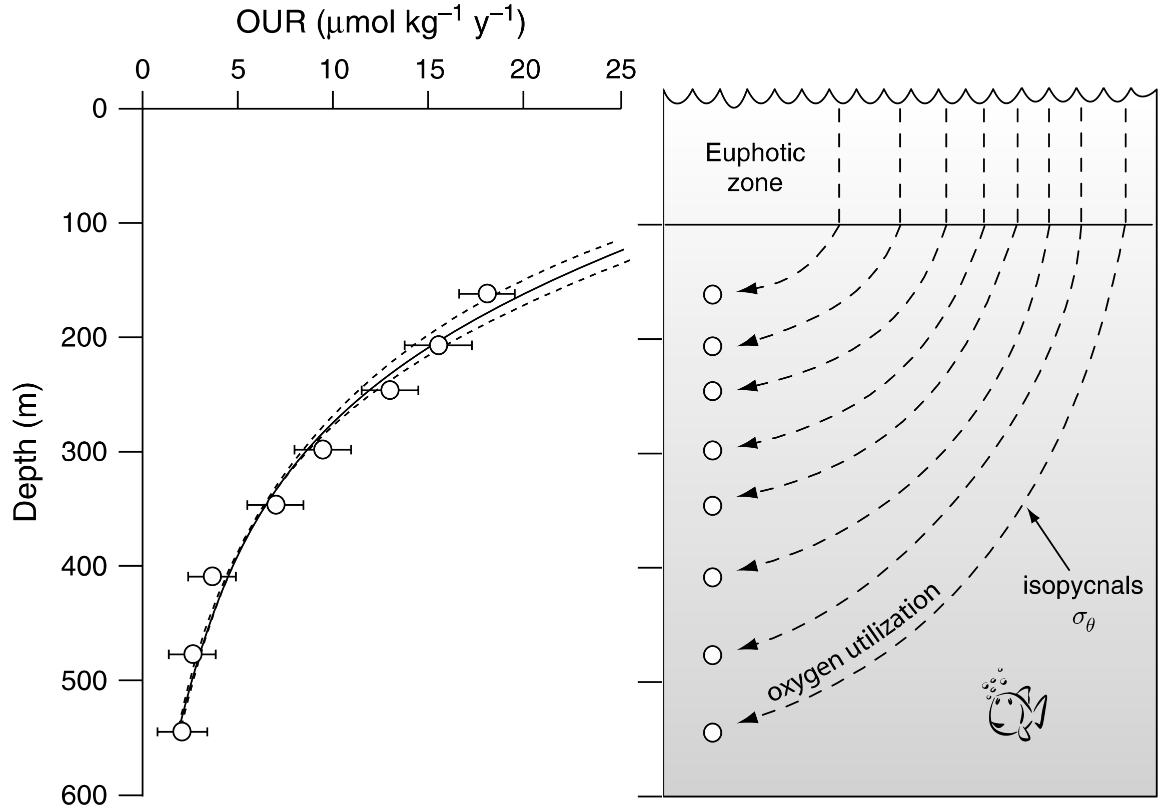


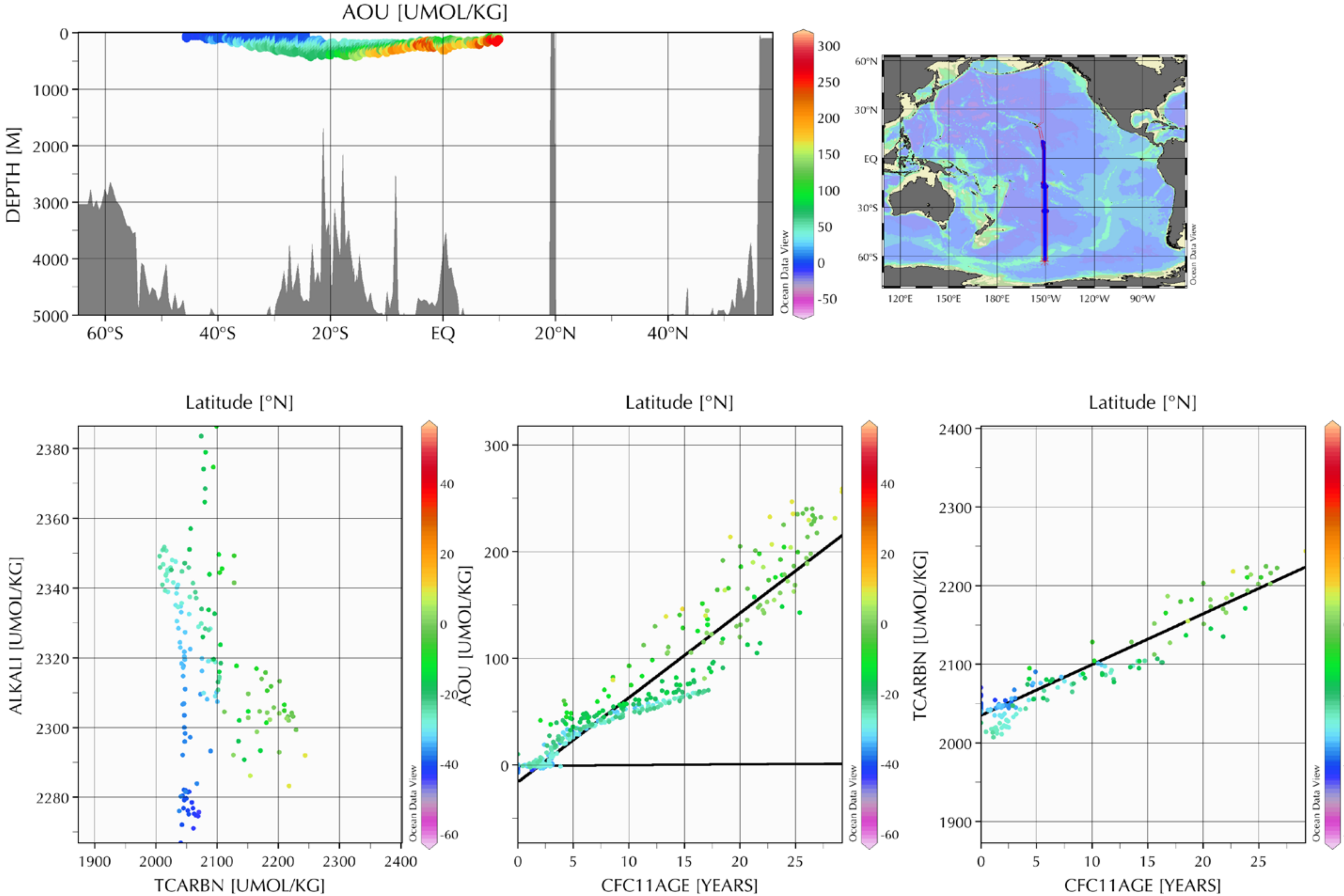
Figure 6.15. Surface-water dissolved phosphate distribution, illustrating the relatively high concentrations (in µmol kg^{-1}) in the Southern Ocean. From Ocean Data View (Schlitzer, 2002).



AOU [UMOL/KG]
σ_t = 25 to 26.5
DEPTH [M]
0
1000
2000
3000
4000
5000
60°S
40°S
20°S
EQ
20°N
40°N
300
250
200
150
100
50
0
-50
Ocean Data View
60°N
30°N
EQ
30°S
60°S
120°E
150°E
180°E
150°W
120°W
90°W
Latitude [°N]
C:AOU ~ 0.89
AOU [UMOL/KG]
TCARBN [UMOL/KG]
N:P ~ 14.5
PHSPHT [UMOL/KG]
NITRAT [UMOL/KG]
C:N ~ 6.5
TCARBN [UMOL/KG]
NITRAT [UMOL/KG]


OUR (μmol kg⁻¹ y⁻¹)
0
5
10
15
20
25
0
100
200
300
400
500
600
Depth (m)
Euphotic zone
isopycnals
σ_θ
oxygen utilization

s.


AOU [UMOL/KG]
DEPTH [M]
0
1000
2000
3000
4000
5000
60°S
40°S
20°S
EQ
20°N
40°N
300
250
200
150
100
50
0
-50
Ocean Data View
60°N
30°N
EQ
30°S
60°S
120°E
150°E
180°E
150°W
120°W
90°W
Latitude [°N]
ALKALI [UMOL/KG]
2380
2360
2340
2320
2300
2280
1900
2000
2100
2200
2300
2400
TCARBN [UMOL/KG]
40
20
0
-20
-40
-60
Latitude [°N]
AOU [UMOL/KG]
300
200
100
0
0
5
10
15
20
25
CFC11AGE [YEARS]
Latitude [°N]
TCARBN [UMOL/KG]
2400
2300
2200
2100
2000
1900
CFC11AGE [YEARS]