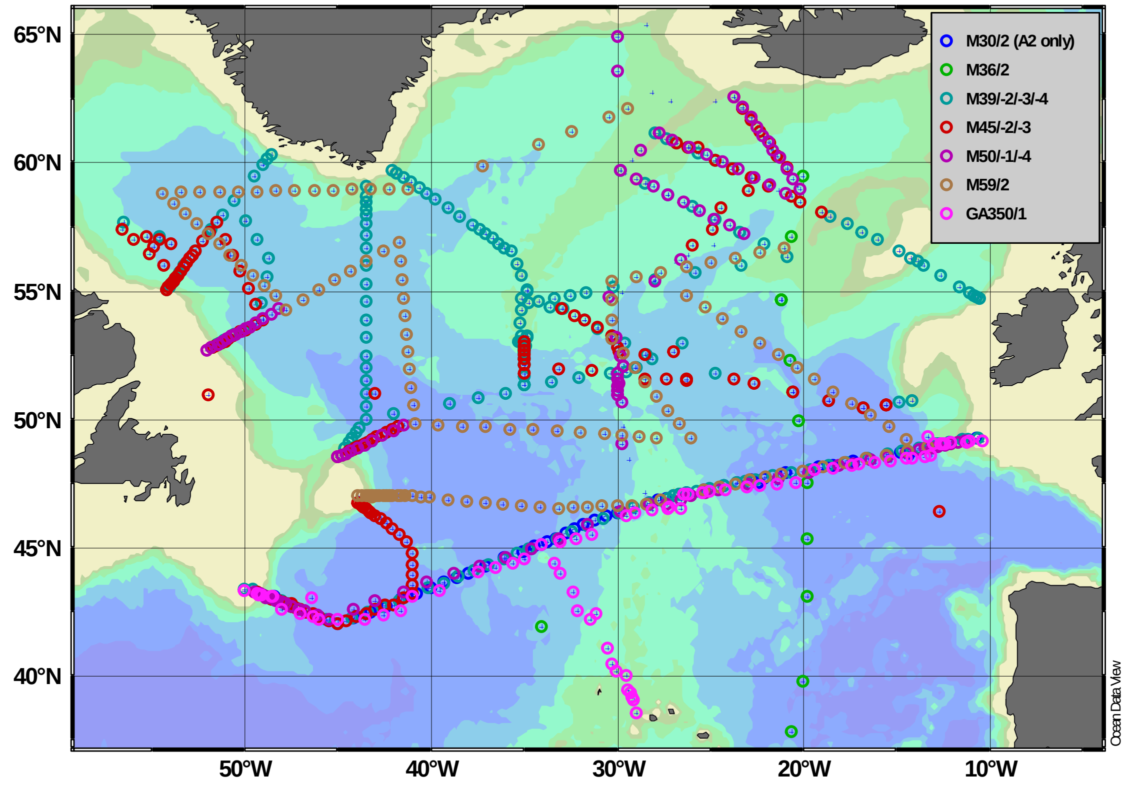
Overview of the hydrographic NA data of the carbon dioxide research group at the IfM/SFB 460

Relevant data sets are from the following cruise legs:

M30/2	1994	WOCE A2 section	
		(C_T, A_T, O_2, nutrients, CFCs)	52 Stations
		PI Körtzinger	
M36/2	1996	quasi meridional section through the Eastern Basin 30-60°N	
		(C_T, A_T, O_2, nutrients)	16 Stations
		PI Mintrop	
M39/2/3/4	1997	WOCE A2 section and subpolar gyre up to 61.2 °N central sampling	
		(C_T, A_T, O_2, nutrients, CFCs)	230 Stations
		PI Körtzinger (/2); PI Kö/Min [Neill/Lewis] (/3); PI Mintrop	
M45/2/3	1999	/2 focus subpolar gyre in the Easten Basin up to 62.5 °N	
		/3 focus Western Basin deep west boundary currents along the shelf	
		(C_T, pH_T, O_2, nutrients, CFCs)	155 Stations
		PI Friis [Johnson]	
G350/1	2000	WOCE A2 section and quasi meridional section to the Azores	
		(C_T, A_T, O_2, nutrients)	75 Stations
		PI Wallace [Neill/Lueger]	
M50/1/4	2001	/1 focus subpolar gyre in the Easten Basin up to 62.5 °N	
		/3 focus Western Basin especially Deep West Boundary Curr. 42°-57°N	
		(C_T, A_T, pH_T, O_2, nutrients, CFCs)	126 Stations
		PI Friis	
M59/2	2003	"quasi WOCE A2 section", whole subpolar gyre 46.7° - 62.1°N	
		(C_T, A_T, pH_T, $sfcpCO_2/C_T$, O_2, nutrients, CFCs)	140 Stations
		PI Friis	

Figure 1. Cruise map



Data quality assessment

Certified reference materials and duplicate analyses

The quality control of all data was usually performed by the use of certified reference materials provided by A.G. Dickson (Scripps, La Jolla, CA, USA), if available (see table). The controls are not well documented or in my reach prior to 1999. An exception from this is the M39/3 cruise in 1997, that was performed by Craig Neill and Ernie Lewis. They have reported their controls and measurements in the corresponding Meteor cruise report. After 1999 all controls are described in the cruise reports in detail, in these the last stations are often not considered, due to a lack of time in data work at the end of a cruise. Even though not reported I can state that the qualities haven't changed significantly with the last stations. Since 1997 all METEOR cruise reports are available from the internet http://www.marum.de/Meteor-Berichte.html. The Gauss cruise report was available from K. P. Koltermann. And can be downloaded from this site.

Cruise to cruise intercomparison

A second control is done by cruise to cruise intercomparision to assure the consistency between different data sets. The cruise intercomparison has two figures for each parameter:

(1) an overall profile comparison;
(2) a comparision of deep water values of Vema Fracture Zone Water (VFZW) the Eastern Basin.

With step (2) it is taken advantage of the stable bottom water conditions in the Eastern Basin of the subpolar North Atlantic. The bottom waters should show nearly no changes in CO_2-Parameters, oxygen, nutrients, and CFCs.

Table. Cruise quality control: CRM and duplicate analyses

Cruise	C_T [μmol/kg]		A_T [μmol/kg]		pH_T	
	CRM (accuracy)	Duplicates (precision)	CRM (accuracy)	Duplicates (precision)	CRM (accuracy)	Duplicates (precision)
M30/2 (1994)	± 1.5 * (#20, #22)	0.68 ± 0.58 (n= 26)	No crm control	Unknown	Not measured	Not measured
M36/2 (1996)	± 1.5 ++	± 0.5 +	± 2.0 ++	± 0.5 +	Not measured	Not measured
M39/2 (1997)	+ 1.09 ± 1.4 (#34, #35, #36, n?)	± 0.5 – 1.0 +	± 5.0 +	± 3.0 +	Not measured	Not measured
M39/3 (1997)	+ 0.69 ± 1.08 (#34, #36, n=59)	0.85 (n= 61)	+3.17 ± 3.6 (#34, #36, n=59)	2.9 (n=61)	Not measured	Not measured
M39/4 (1997)	± 2 +	± 0.5 +	± 2.0 +	± 0.5 +	Not measured	Not measured
M45/2 (1999)	-0.32 ± 1.55 (#45, n= 36)	0.80 ± 0.64 (n= 50)	Not measured	Not measured	± 0.0015 (#45, n=20)	
M45/3 (1999)	-0.67 ± 1.52 (#45, n= 49)	1.06 ± 0.97 (n= 69)	Not measured	Not measured	± 0.0015 (#45, n=24)	± 0.002 (n=20)
G350 (2000)	+ 1.5 ± 1.4 (#3, n=53)	0.63 (n= 55)	+3.1 ± 4.0 (#, n=53)	Measured but not available	Not measured	Not measured
M50/1 (2001)	+ 0.20 ± 1.28 (#41, #47, #52 n=26)	1.3 ± 1.4 (n=38)	- 0.89 ± 1.58 (#41, #47, #52 n=52)	2.1 ± 1.45 (n=58)	± 0.0017 (#52, n=40)	0.0016 ± 0.0016 (n=66)
M50/4 (2003)	- 0.37 ± 1.14 (#35, #36, #48, #52, n=50)	1.1 ± 1.0 (n=81)	+ 0.34 ± 2.41 (#35, #52, n=80)	2.9 ± 2.6 (n=82)	± 0.0023 (#52, n=37)	0.0009 ± 0.0009 (n=83)
M59/2 (2003)	+ 0.02 ± 1.48 (#56, #58, #60, n=129)	1.2 ± 1.4 (n=120)	+ 0.02 ± 1.93 (#56, #58, #60, n=116)	2.3 ± 2.8 (n=119)	Needs work	Needs work

*CRM values were used for calibrations; + from available cruise report information, CRM use; ++ cruise report information, CRM use likely, but not sure

Total dissolved inorganic carbon, C_T (Fig. 3)

The cruise intercomparison shows overall a good profile agreement between the different cruises; lowest C_T values in the surface waters, a relative maximum between 900-1100 m and finally two branches in the deep waters that are linked to the Western and the Eastern Basin (the latter with highest C_T values). The higher C_T variability in the deep waters of the Western Basin is associated with the highly variable hydrography in this region and also with differing sampling locations from cruise to cruise.

In the Western Basin the deep water C_T variability has a counterpart in AOU and silicate.

In the Eastern Basin the VFZW C_T values do not vary much more than the C_T accuracy of 2-3 µmol/kg. The C_T variability is here about 5 µmol/kg. The comparably low M36/2 values are due to the most southerly sampling locations associated with lower AOU and a younger 'water mass age'.

Total alkalinity, A_T (Fig. 4)

The overall alkalinity plot shows highest varability of A_T in the upper waters and two A_T branches in the deep waters (like the C_T measurements). The high A_T values in the deep waters are again linked to the Eastern Basin.

The cruise intercomparison shows significantly higher values of the A_T measurements on the M30/2 cruise by about 20-30 µmol/kg. The reference materials from the Scripps were not certified at that time (1994) for A_T. It is likely that the acid concentration was not correct, i.e. thought to be too low. If so the M30 A_T values could be corrected with a acid factor adjustment, which is equal to an A_T adjustment. A correlation of the the well quality controlled M59/2 data with silicate leads to an inverse A_T-silicate model in the bottom waters that allow a factor determination for the M30/2 A_T data of *0.9877*. (Fig. 2). It is proposed to use this factor for the correction of all A_T values of the M30/2 cruises.

Compared to most A_T measurements in the VFZW the M39/3 leg seems to have a problem with some measurements in the Eastern Basin. These problems are linked to a few stations only that are namely the stations 283, 285, 288 and possibly 293. All other cruises and stations show A_T measurements which are close by in the VFZW within ~10 µmol/kg. Only the Gauss cruise measurements have a tendency to have a little bit too high A_T values by 2-3 µmol/kg. This is about the offset that Craig Neill has found in comparision to the CRM controls as described in the Gauss cruise report. It is unclear if the present Gauss data were corrected already for this offset or not.

A small surprise are the A_T values from the M45 cruises which fit with the profiles of most other cruises. These A_T values are calculated from pH_T and C_T using the constants of Mehrbach et al. (Dickson and Millero, 1987) and the pH_T correction by (DelValls et al., 1998).

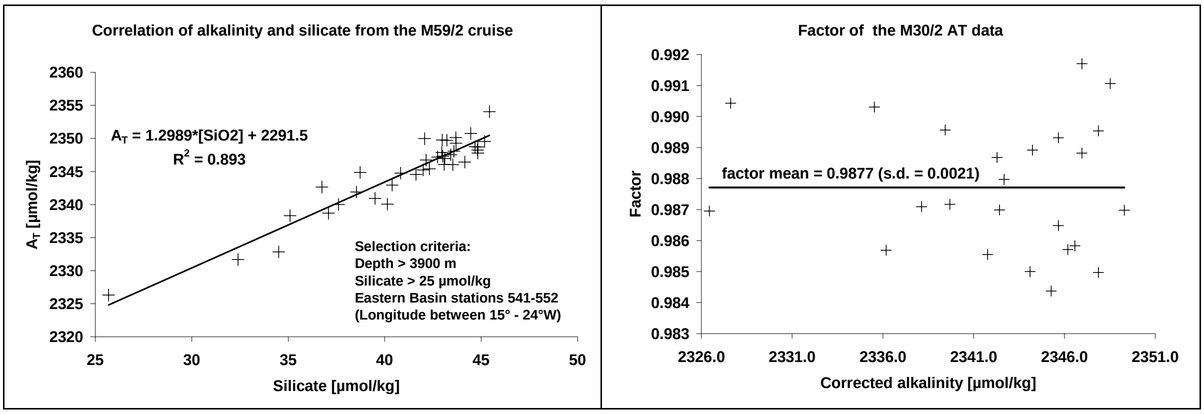


Figure 2. Proposed steps to the M30/2 A_T correction. **(A)** Derivation of the A_T-silicate relation (A_T^{pred}) in the VFZW. **(B)** Mean factor determination using $f = A_T^{meas}/A_T^{pred}$

O_2 and Apparent Oxygen Utilization (AOU) (Fig. 5 & Fig. 6)
The quality control of the O_2 measurements is easier to do from the AOU profiles. Temperature and salinity effects are so removed for a profile comparision. In the VFZW there can't be seen any AOU concentration change for the expeditions from 1996 on. The excecption is the earliest expedition from 1994. Here one can find too low AOU (too high O_2) concentations of about 6 µmol/kg. This somehow too high O_2 concentrations does not correspond with a nitrate or silicate variability (see below) and have been identified by K. P. Koltermann already. These data were flagged as not realistic in his analysis. O_2 measurements shouldn't be used from the M30/2 cruise, as far as these have not been not corrected.
The partly low AOU (high O_2) concentrations of the M36/2 cruise are in aggreement with the southern most sampling positions.
The deep waters of the Western Basin show a high variability which indicates the high ventilation activity. Oxygen concentrations increase from 1997 to 2001 continously and seem to be kind of stable from 2001 to 2003.

Nitrate (Fig. 7)
The nitrate measurements of all data sets look consistent in case of the high-concentration-deep-water-branch, which is once again the VFZW. There is small concentration variability in the VFZW of about 0.5 µmol/kg only. The nitrate measurements from the M45 cruises are bit too high maybe, because the AOU profiles do not indicate highest concentrations in the deep waters of the Western Basin, but this remains unclear. If one takes out the M45 data the nitrate values in the Western Basin show nearly the same ventilation patterns as AOU; a decrease from 1997to 2001/2003.

Phosphate (Fig. 8)
The phosphate profiles have the highest 'relative variability' from expedition to expedition. The deep water of Eastern Basin (VFZW) has concentrations of about 1.5 µmol/kg and the deep water of the Western Basin has concentrations of about 1.1 µmol/kg. If one assumes nearly Redfield ratio between nitrate, phosphate and AOU the higher variability in the Eastern Basin can be interpreted as analytical imprecision from on cruise to another. In fact the M50 data are about 0.2 µmol/kg lower than the phosphate measurements of all other data sets. The M50 data have to be flagged as invalid for use so. If the M50 data are excluded, the phospate variability is still more than 0.1 µmol/kg in the VFZW. The phosphate variability is about 2-3 times higher relative to the nitrate measurements and hides informations about the ventilation activities in the Western Basin.

Silicate (Fig. 9)
The silicate profiles do not indicate inconsistent measurements between the different expeditions. The maximum deviation in the VFZW is about 3 µmol/kg, i.e. from 42 to 45 µmol/kg from the Gauss cruise data and the M39/M59 data. Even though such deviation can not be suggested from the AOU or C_T data (that do not show corresponding deviations), it is unclear if this deviation is correct or not. The overall silicate profiles do not show a constant underestimation of Gauss data especially between 1200 and 1300 m.

Figure 3. Total dissolved inorganic carbon

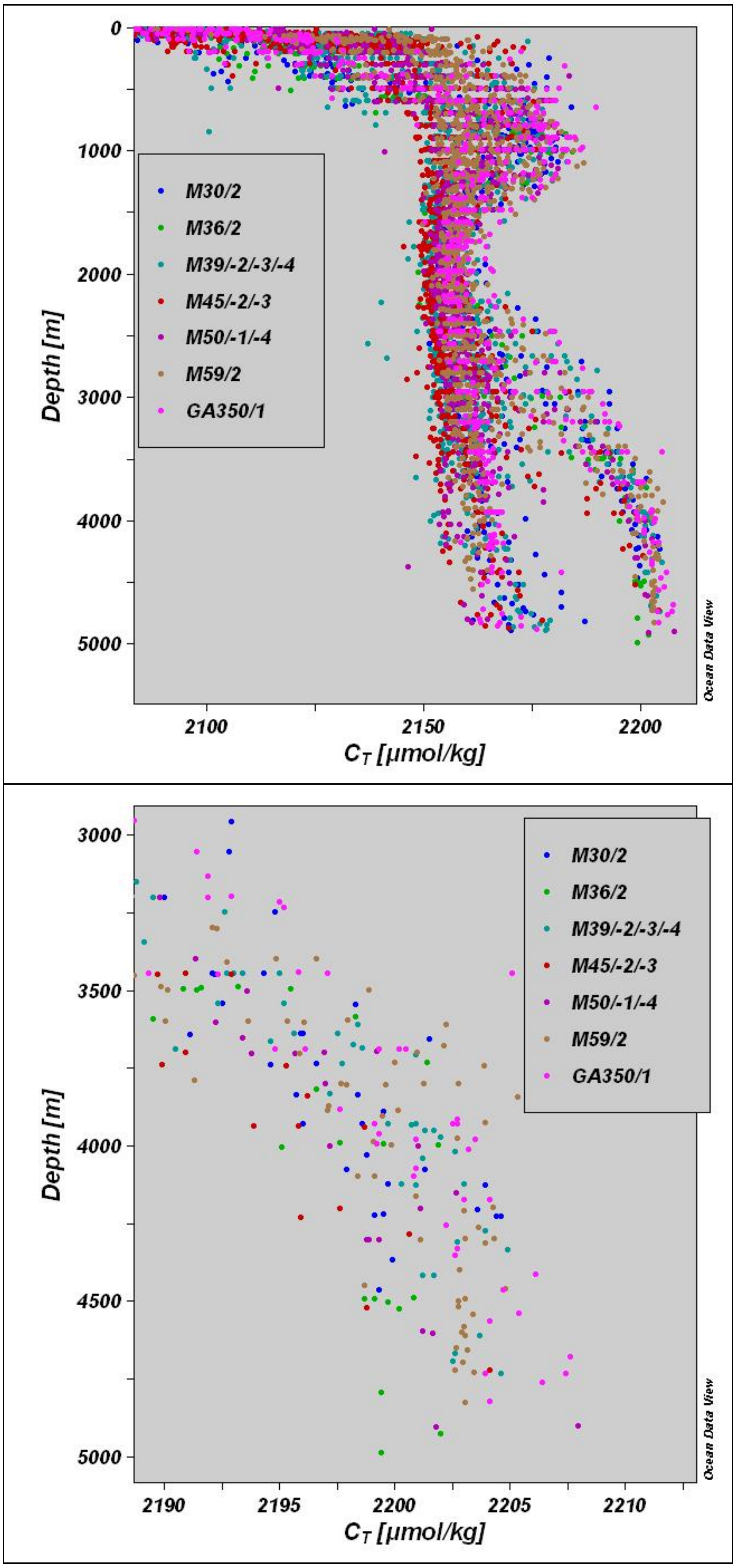


Figure 4. Total alkalinity

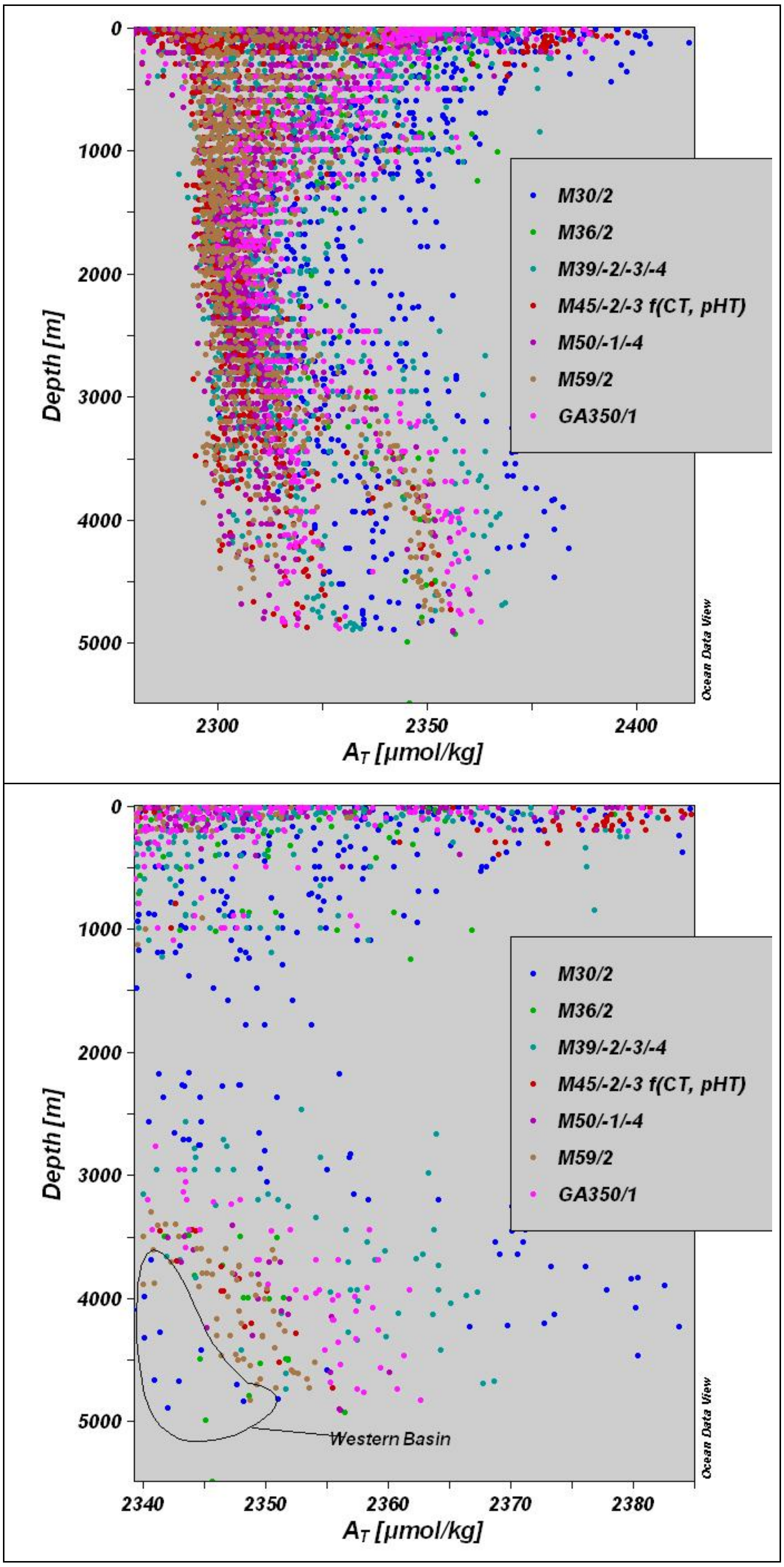
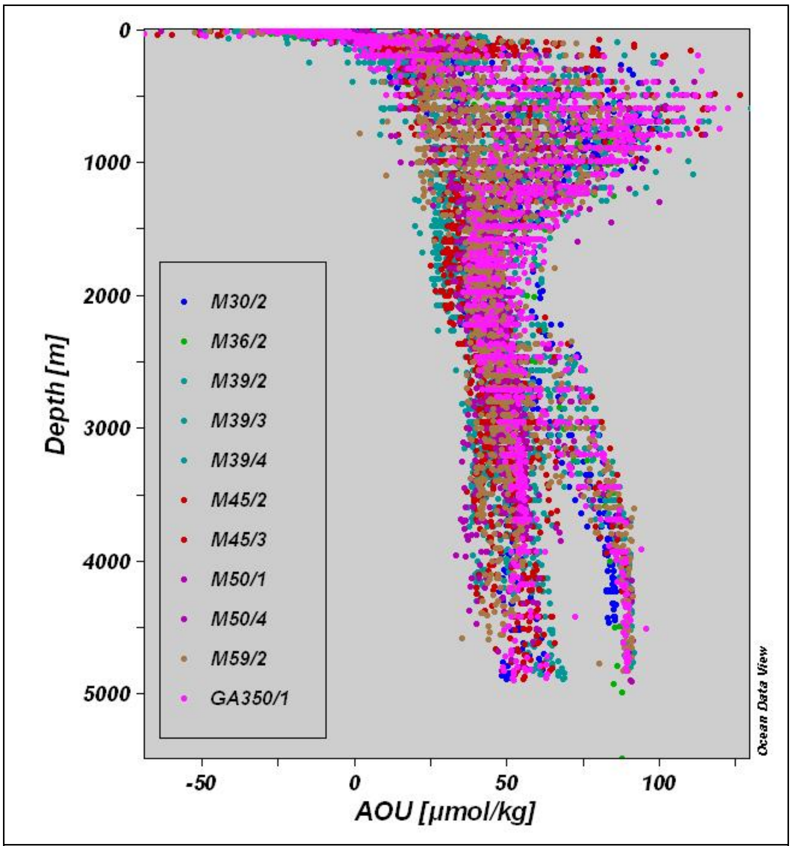


Figure 5. Apparent Oxygen Utilization



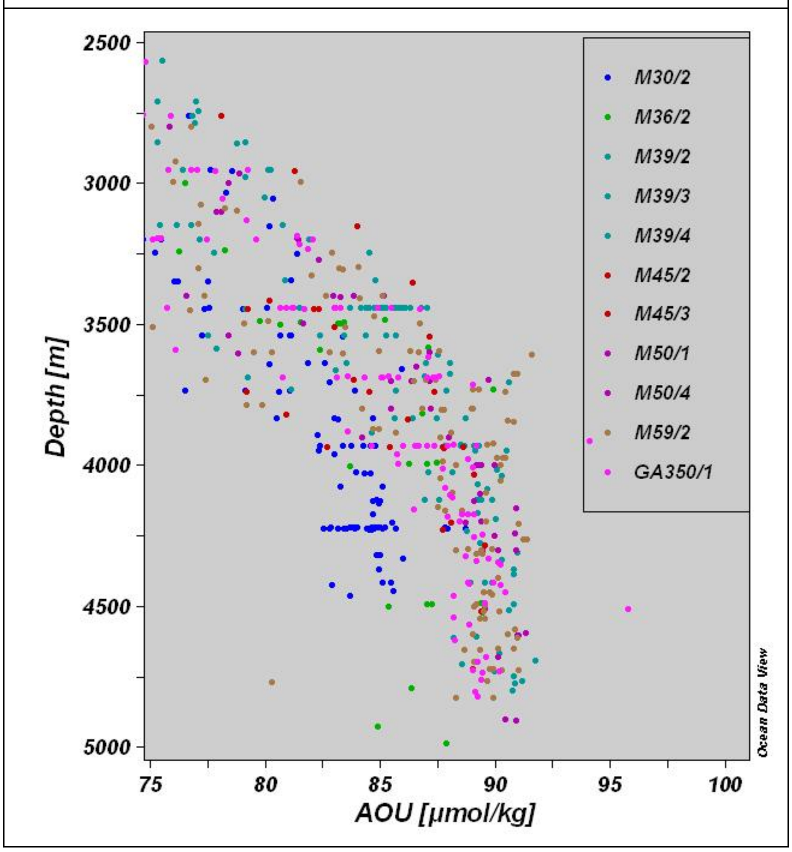


Figure 6. Oxygen

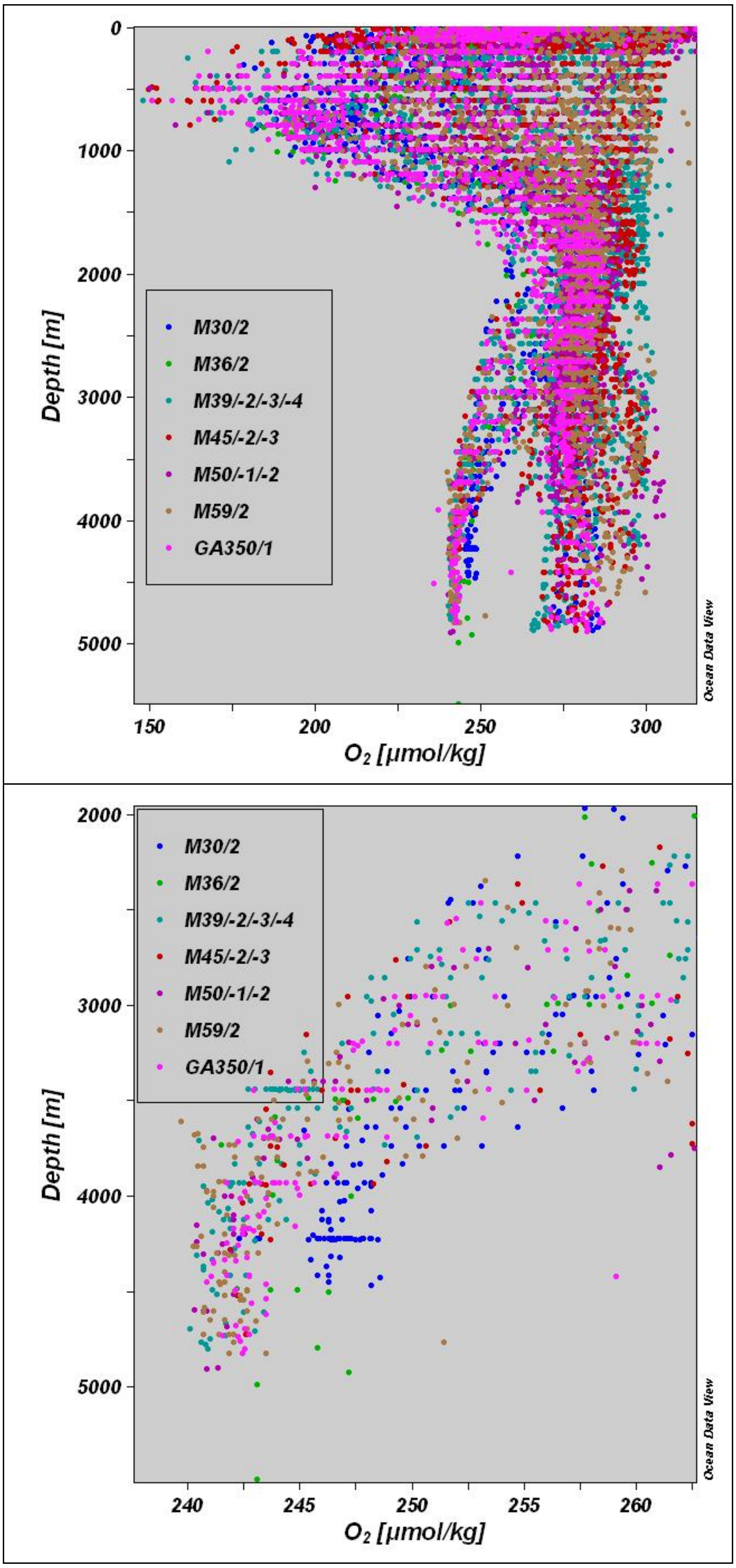


Figure 7. Nitrate

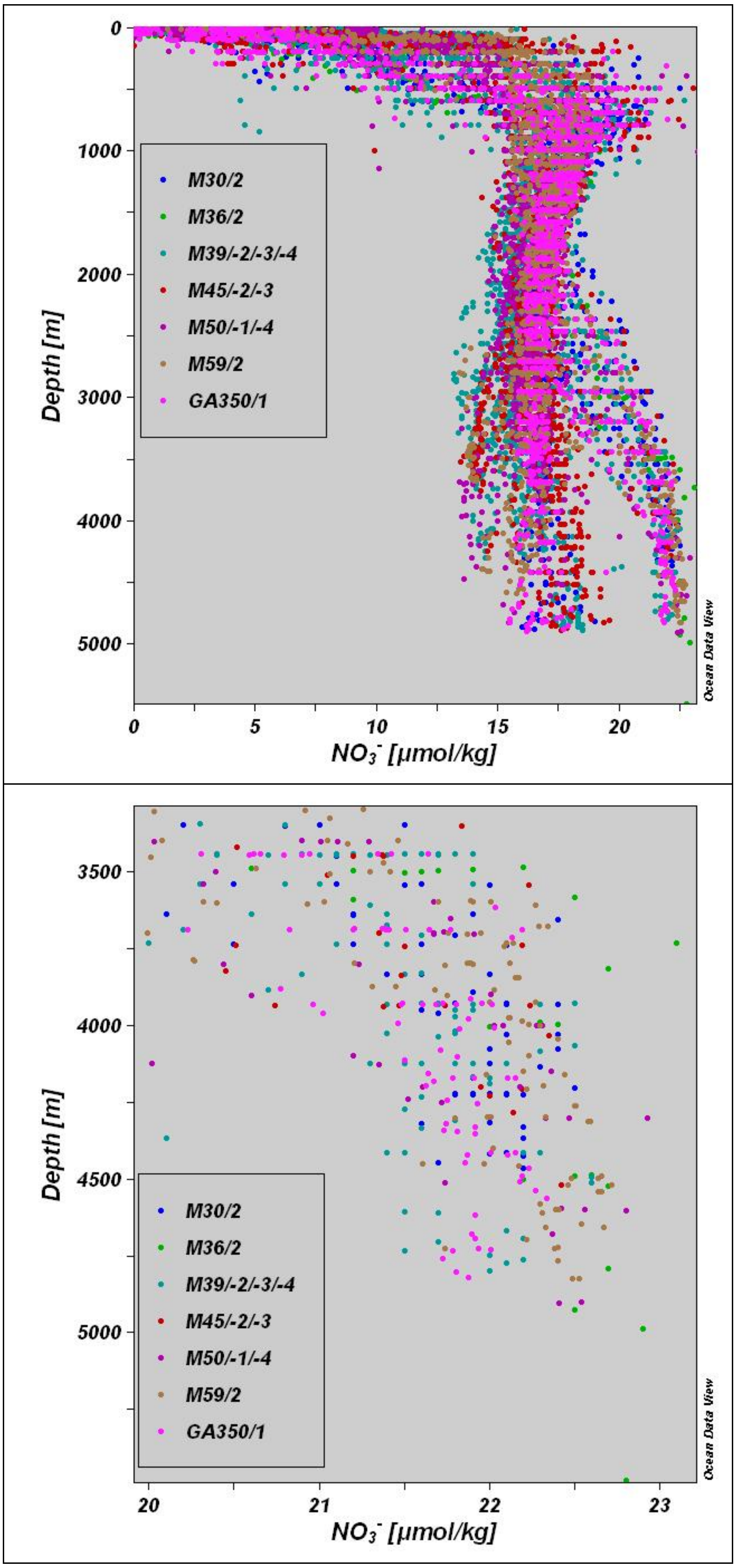


Figure 8. Phosphate

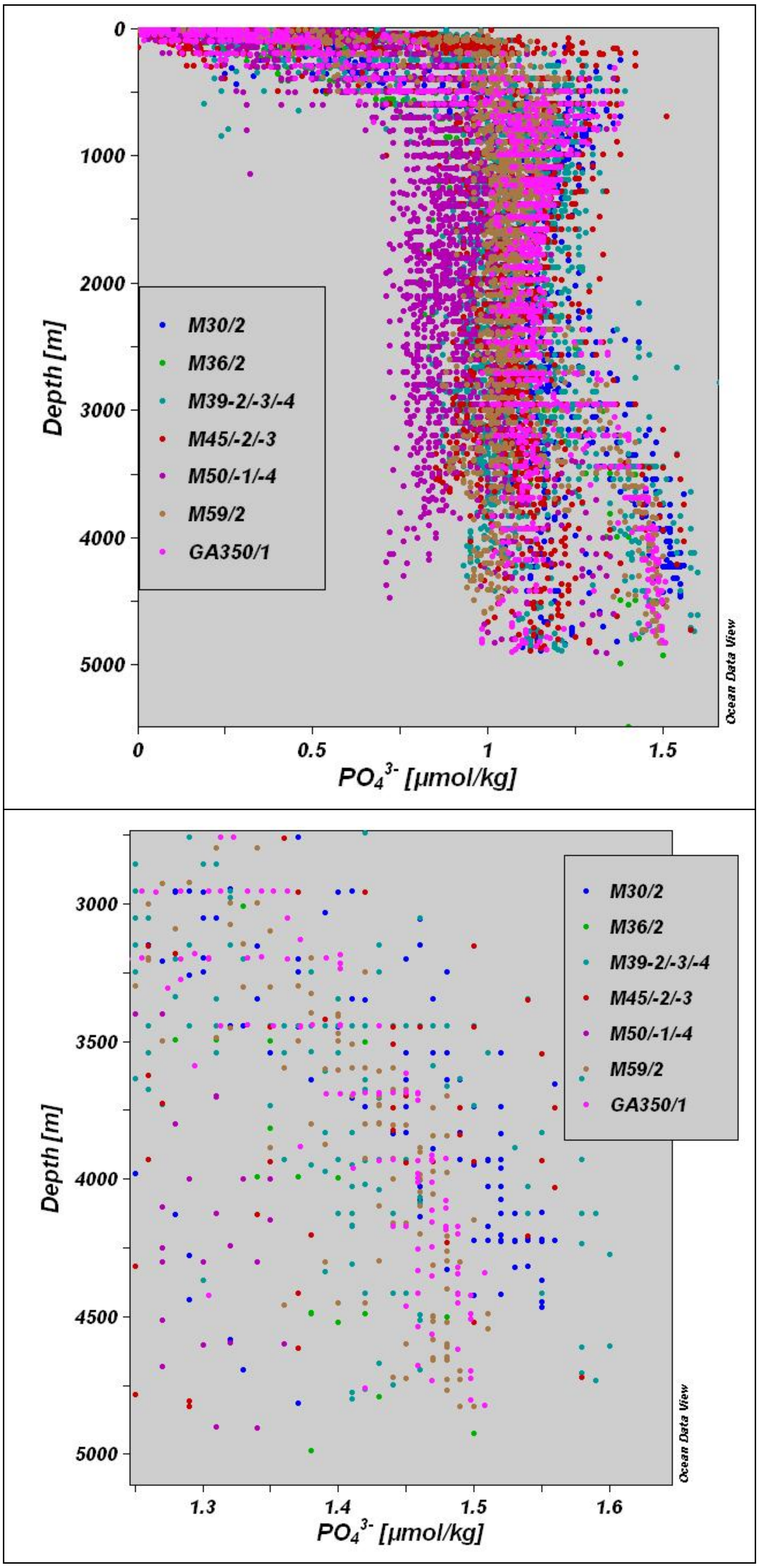


Figure 9. Silicate