GEOTRACES

An International Study of the Marine Biogeochemical
Cycles of Trace Elements and their Isotopes

Distribution of Trace Elements in the Pacific: Known knowns and known unknowns

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UC Santa Cruz

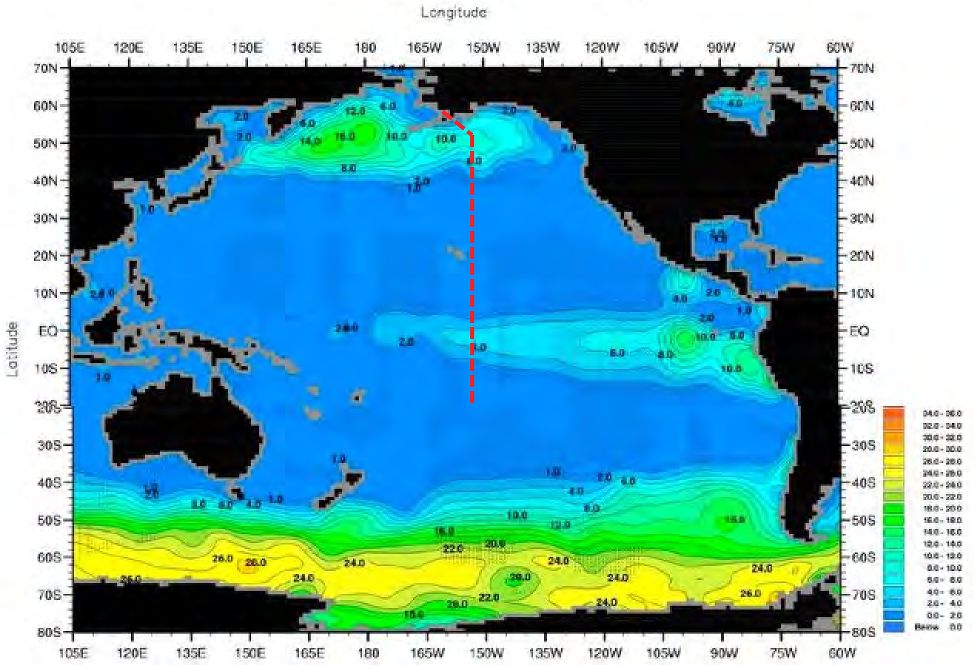
Planning Meeting for US GEOTRACES Pacific
Meridional Transect – October 2016

International Council for Science
SCOR
Scientific Committee on Oceanic Research

NSF

HNLC regions of the Pacific Ocean

Summer-time mean nitrate (μM) at 10 meters depth



Modelled Export Production

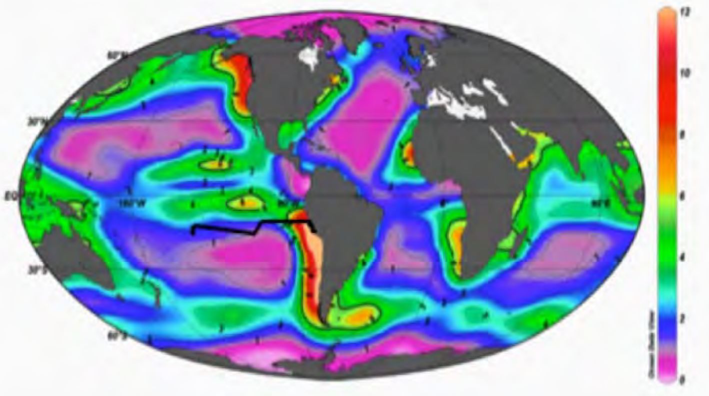
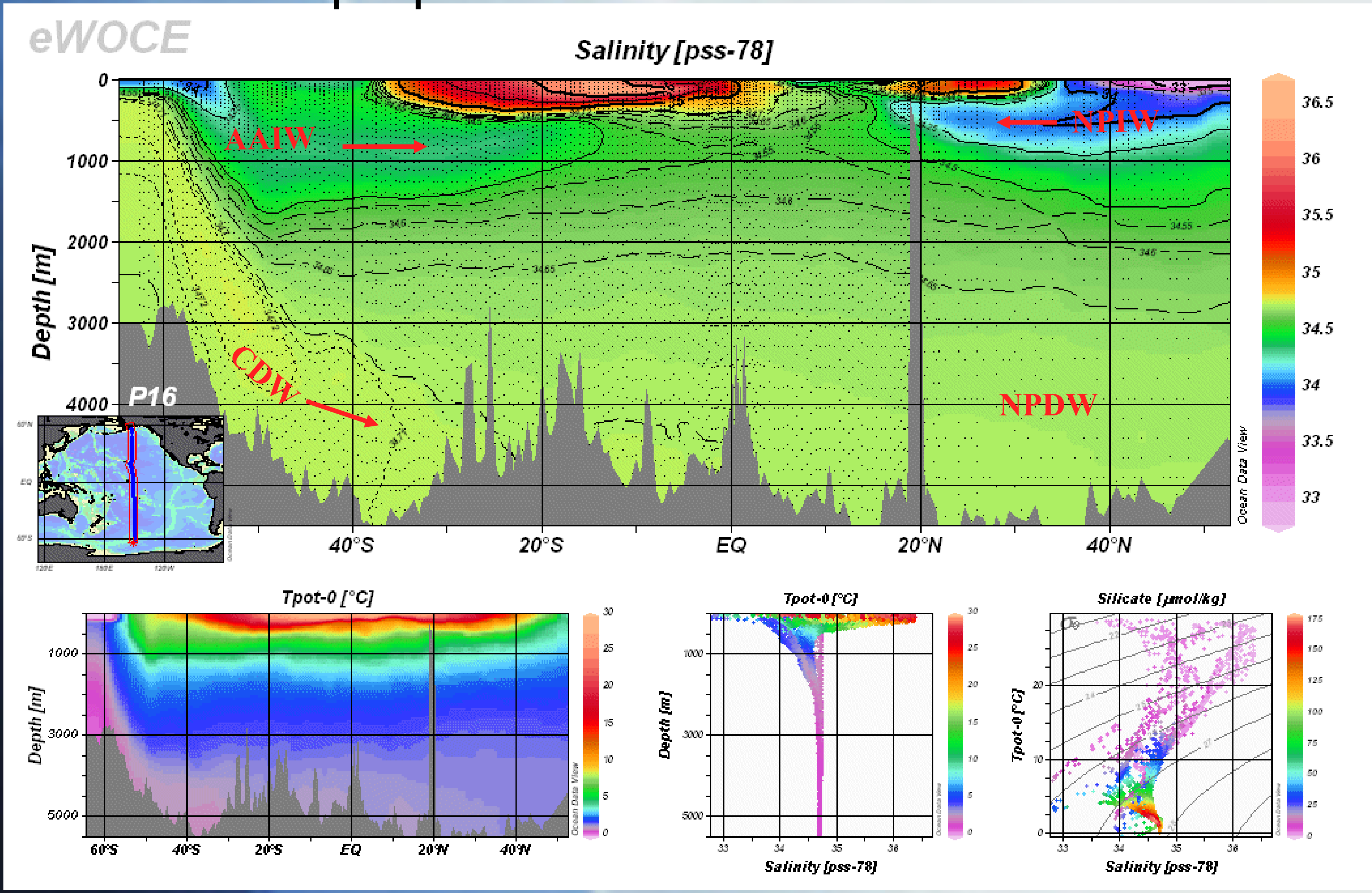
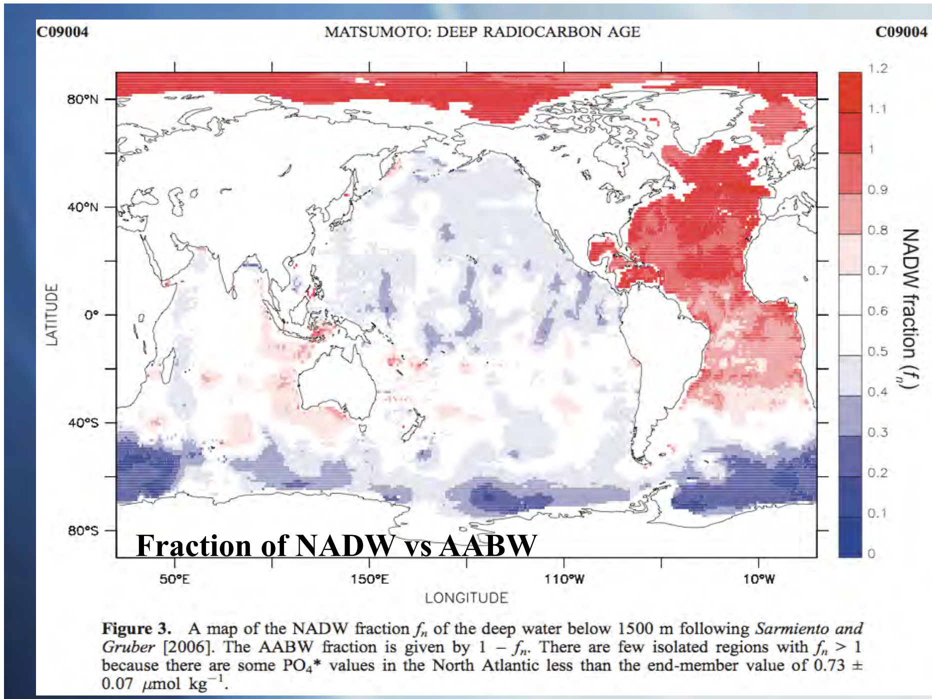


Figure 28: Export production of particulate organic carbon POC (mol C m^{-2} yr^{-1}) in the world ocean determined by an inverse model from water column oxygen, nutrient and carbon distributions. From R. Schlitzer, Applying the adjoint method for global biogeochemical modelling. In: P. Rayner (Editor), *Inverse Methods in Global Biogeochemical Cycles*. AGU Geophys. Monograph Series, Vol. 114, pp. 107-124, 2000. Copyright (2000) American Geophysical Union. Reproduced by permission of American Geophysical Union.

P16 Meridional section of salinity – near the proposed GEOTRACES transect



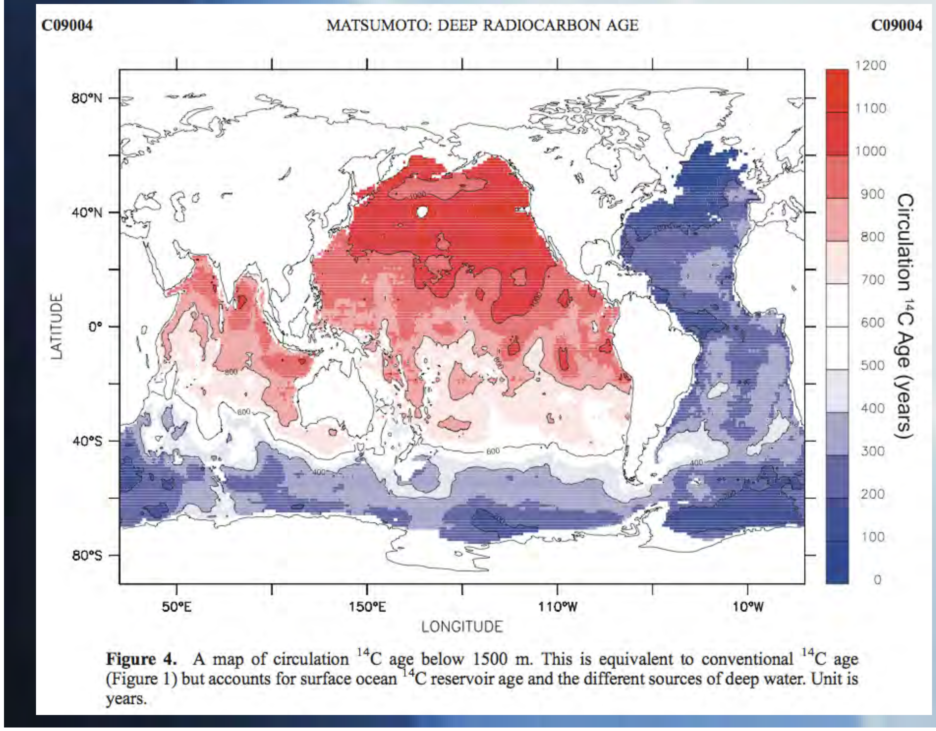


C09004 MATSUMOTO: DEEP RADIOCARBON AGE **C09004**

Fraction of NADW vs AABW

Figure 3. A map of the NADW fraction f_n of the deep water below 1500 m following *Sarmiento and Gruber* [2006]. The AABW fraction is given by $1 - f_n$. There are few isolated regions with $f_n > 1$ because there are some PO_4^* values in the North Atlantic less than the end-member value of 0.73 ± 0.07 μmol kg^{-1}.

View of the circulation age of deep waters based upon Matsumoto's argument that AABW has a "zero age" and the fraction of AABW vs NADW that contributes to North Pacific Deep Water (NPDW).



C09004 MATSUMOTO: DEEP RADIOCARBON AGE **C09004**

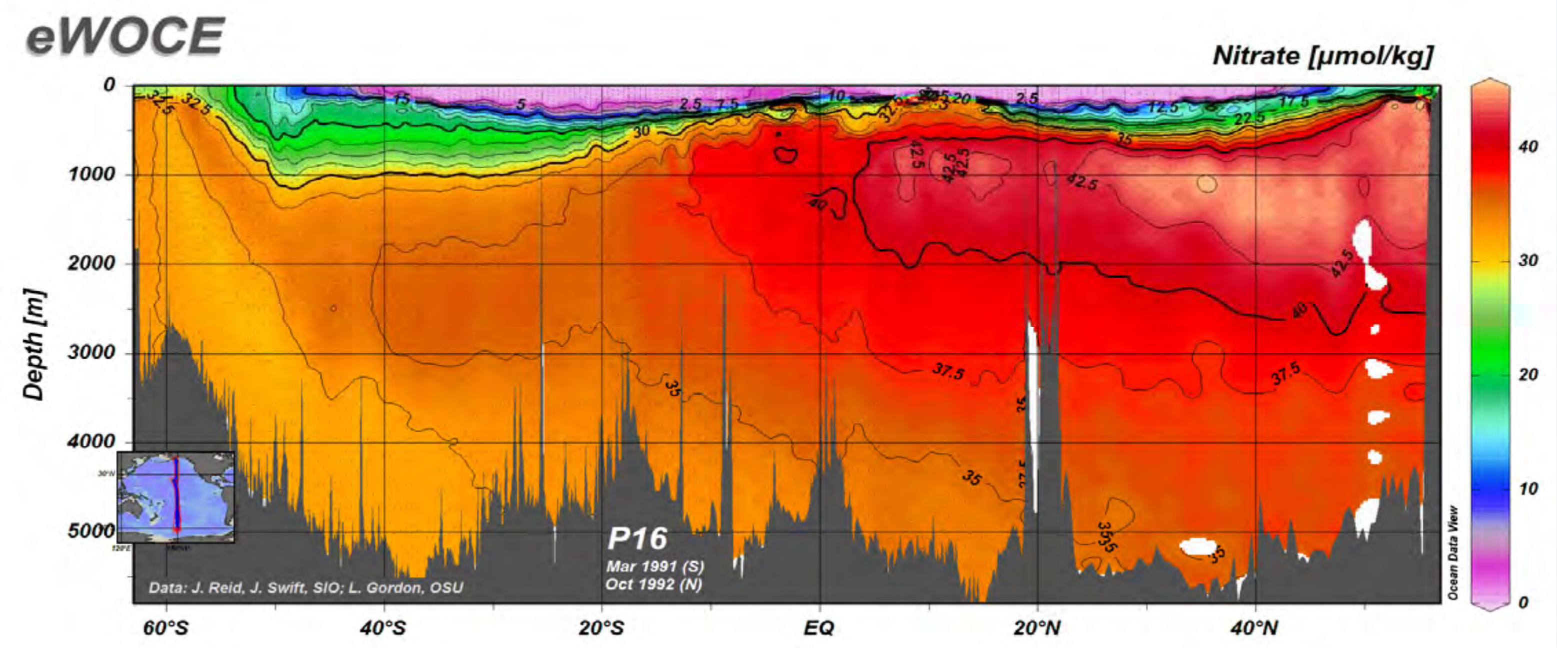
Figure 4. A map of circulation ^{14}C age below 1500 m. This is equivalent to conventional ^{14}C age (Figure 1) but accounts for surface ocean ^{14}C reservoir age and the different sources of deep water. Unit is years.

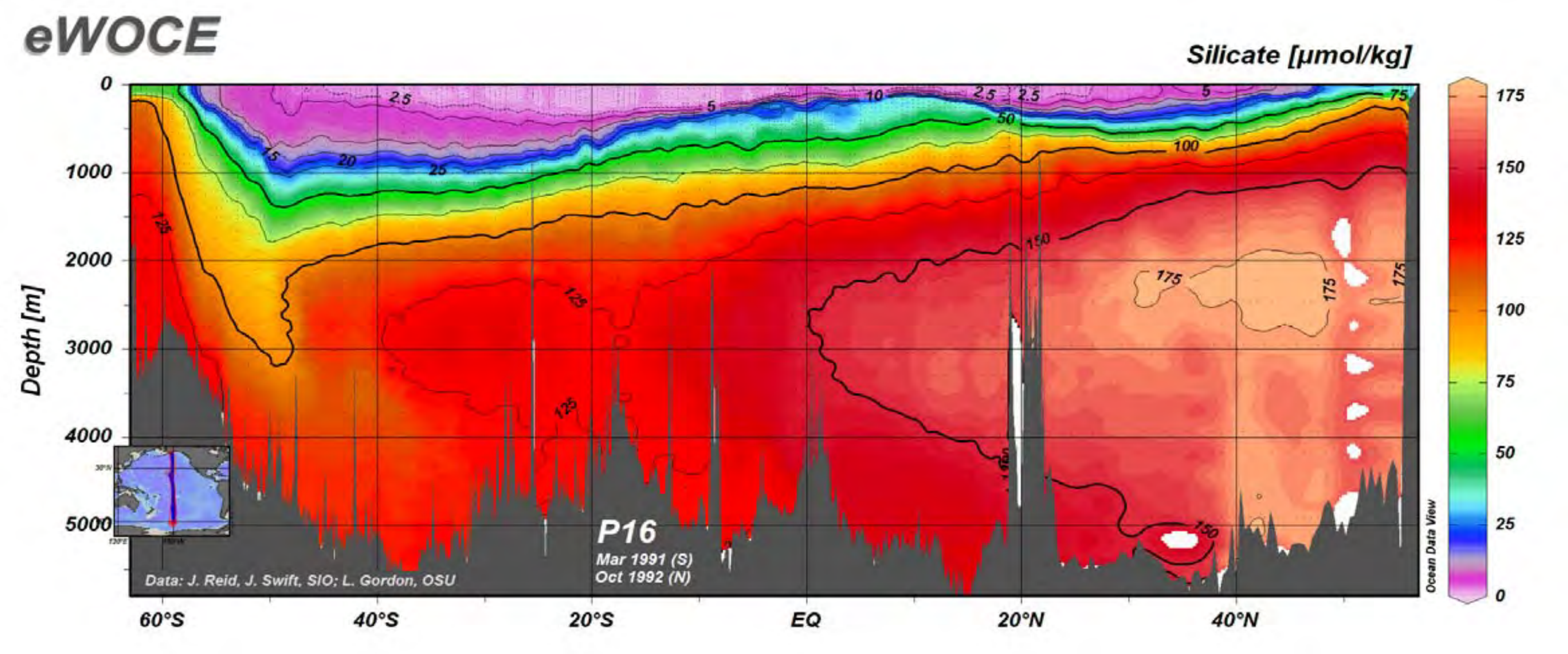
NPDW in the eastern North Pacific is the oldest in the world oceans.

Citation: Matsumoto, K. (2007), Radiocarbon-based circulation age of the world oceans, *J. Geophys. Res.*, *112*, C09004, doi:10.1029/2007JC004095.

Nitrate and Silicic Acid on the WOCE P16 Section

Examples of nutrients for the Pacific meridional section. Imagine such ‘textbook’ images for all the TEI’s.

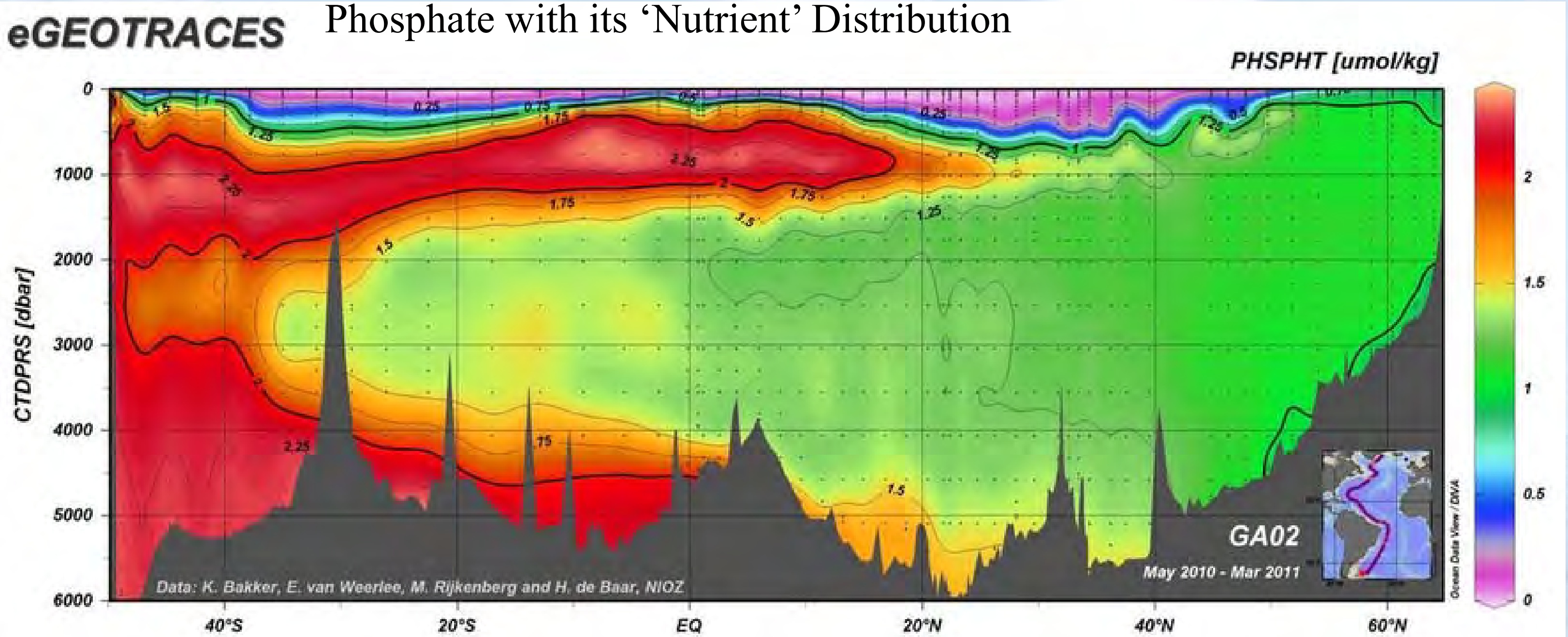




GEOTRACES Western Atlantic Section carried out by the Netherlands

We can look forward to obtaining meridional sections for TEI's such as we have for Cd in the western Atlantic.

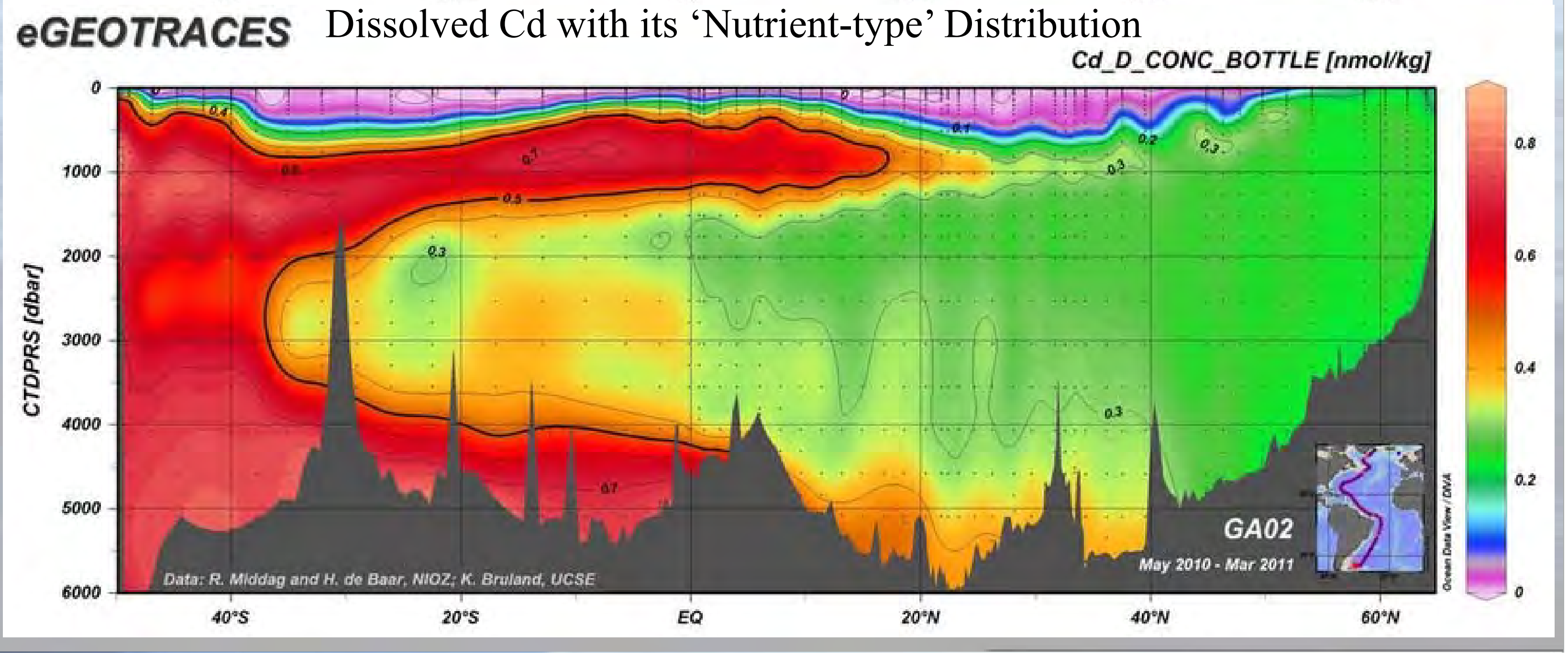
From Rob Middag, Hein de Baar, and Bruland on samples analyzed at UCSC. Middag et al (in prep)


Phosphate with its 'Nutrient' Distribution

Data: K. Bakker, E. van Weerlee, M. Rijkenberg and H. de Baar, NIOZ

GA02

May 2010 - Mar 2011


Dissolved Cd with its 'Nutrient-type' Distribution

Data: R. Middag and H. de Baar, NIOZ; K. Bruland, UCSE

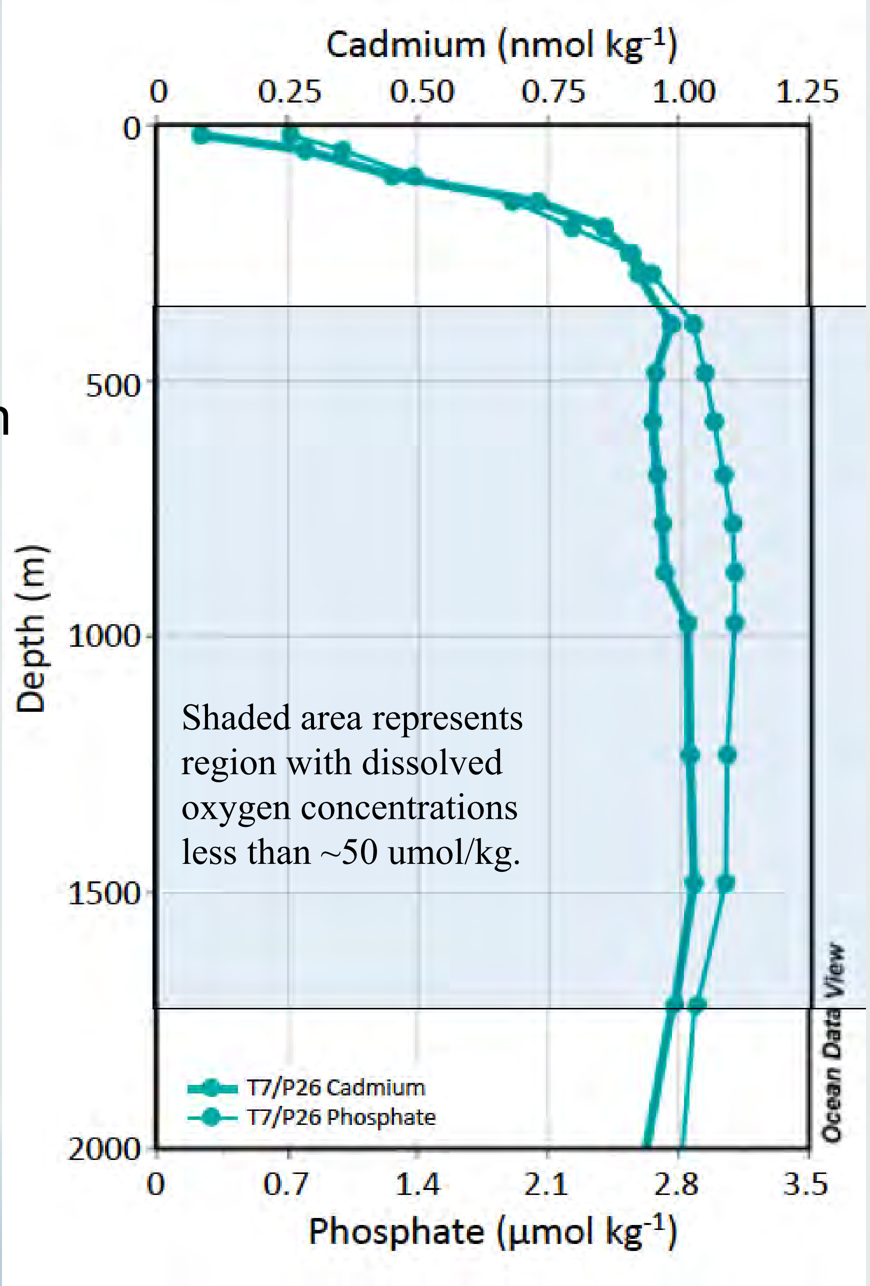
GA02

May 2010 - Mar 2011

Recent insight into the distribution of Cd in the North Pacific

Janssen et al. (2014) ‘Undocumented water column sink for Cd in open ocean oxygen-deficient zones.’

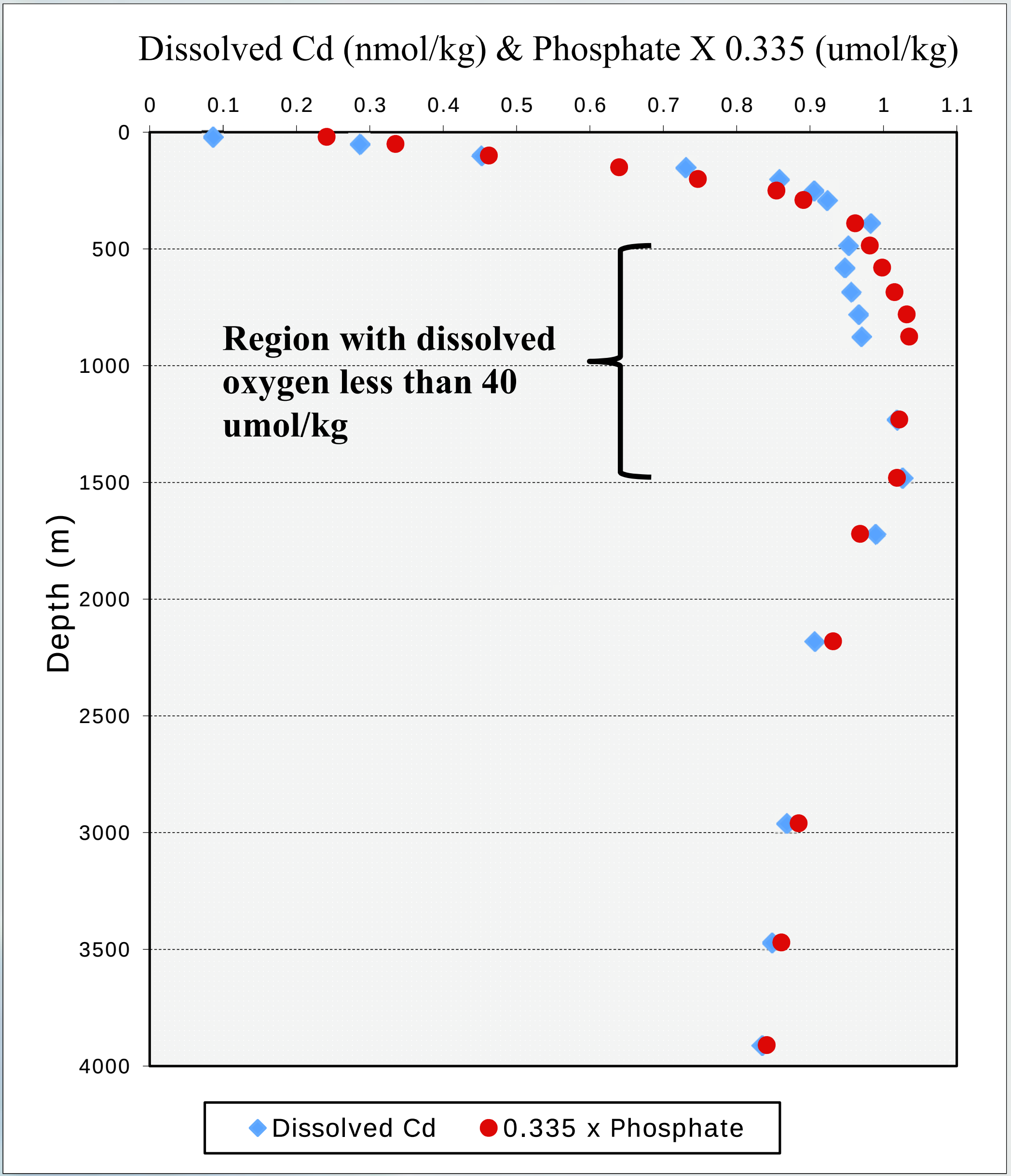
Presented is a profile from Stn P in the subarctic North Pacific. The authors attribute this uncoupling in oxygen-deficient zones ‘to Cd sulfide (CdS) precipitation in euxinic micro-environments around sinking biological particles.’



Shaded area represents region with dissolved oxygen concentrations less than ~50 umol/kg.

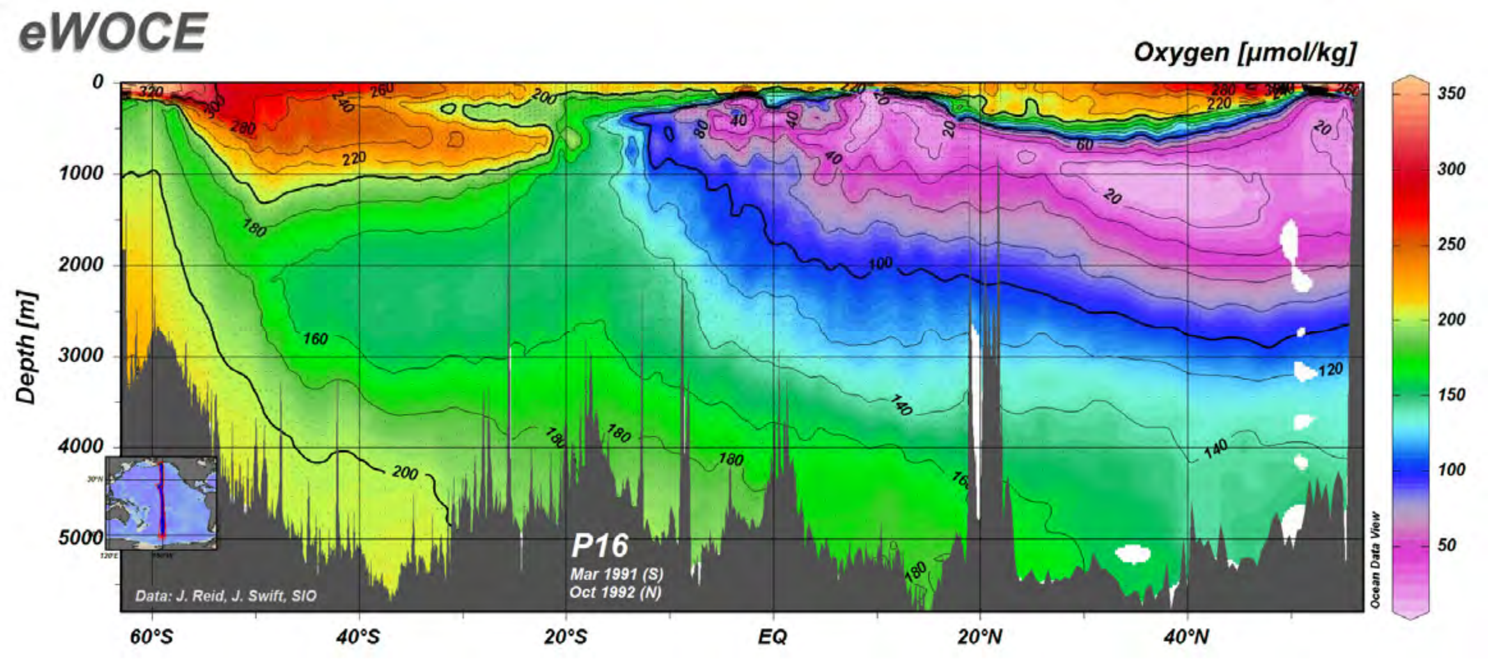
I plotted the historical VERTEX data of John Martin and Mike Gordon from Ocean Stn P (Martin et al. 1989) and used a value of 0.335 x Phosphate to make the deep water Cd and phosphate data similar. The dissolved Cd depletion relative to phosphate within the oxygen minimum zone is similar to that observed by Janssen et al. (2014).

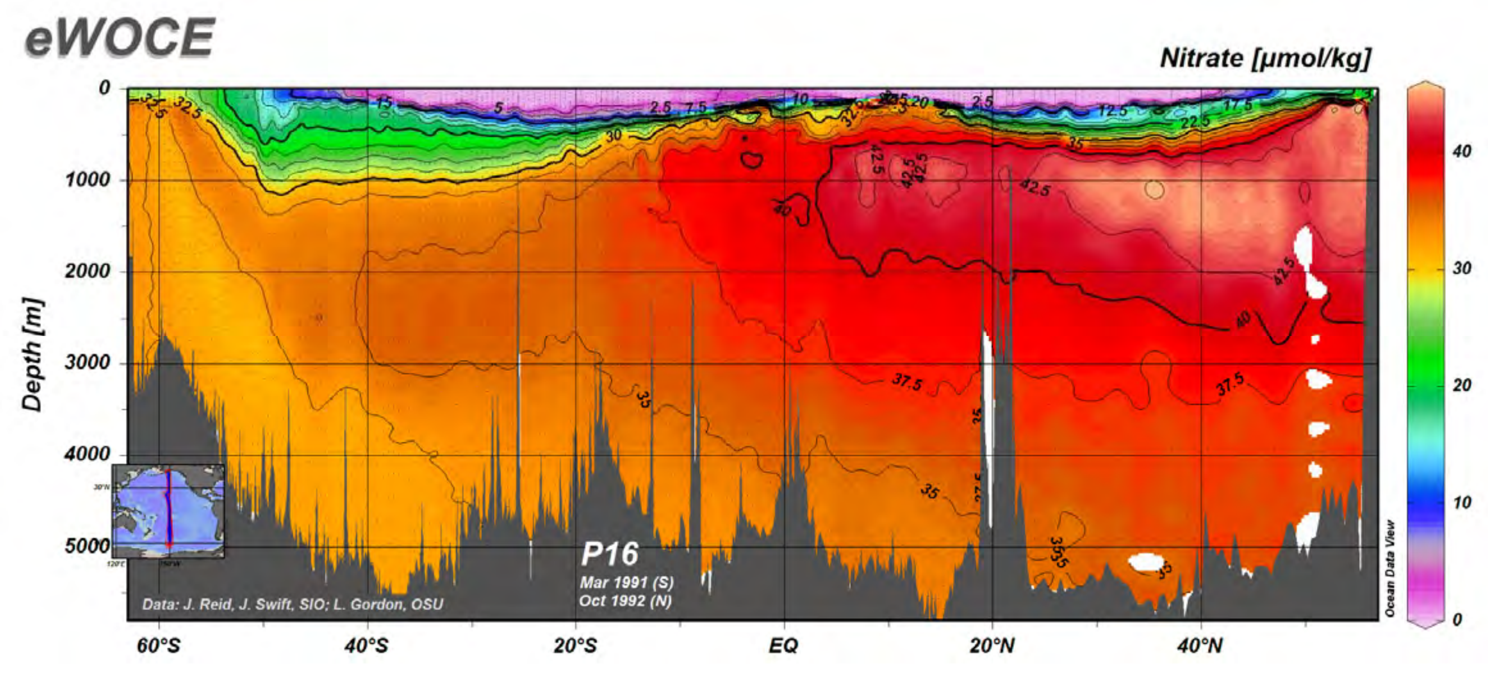
A ‘known unknown?’



Dissolved oxygen and nitrate on the P16 meridional section.

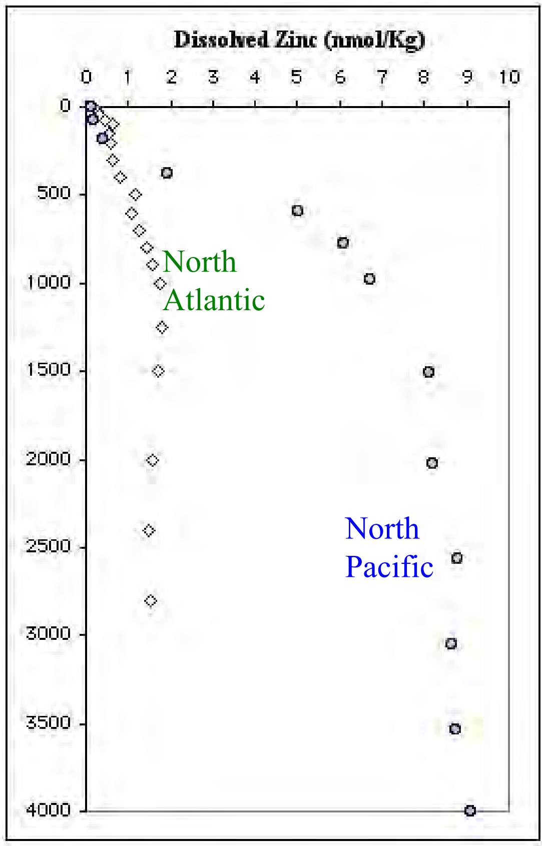
The GEOTRACES section will be able to check this idea of a substantial water column sink in low oxygen waters (Janssen et al., 2014). There is a widespread region with dissolved oxygen less than 40 umol/kg. It may, however, also require it to be in a region of high particle flux/export production. Studies of Particulate Cd and Cd isotopes should compliment this.

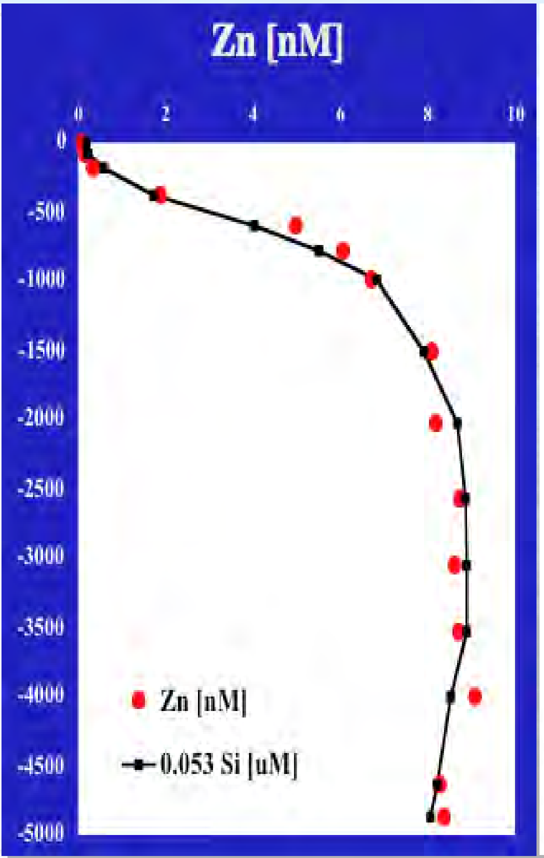




Distribution of another nutrient-type TEI, dissolved Zn, in a few existing profiles prior to GEOTRACES

In addition, much of the dissolved Zn data prior to GEOTRACES was of questionable quality.





Profiles from Bruland (1980) and
Bruland and Franks (1983)

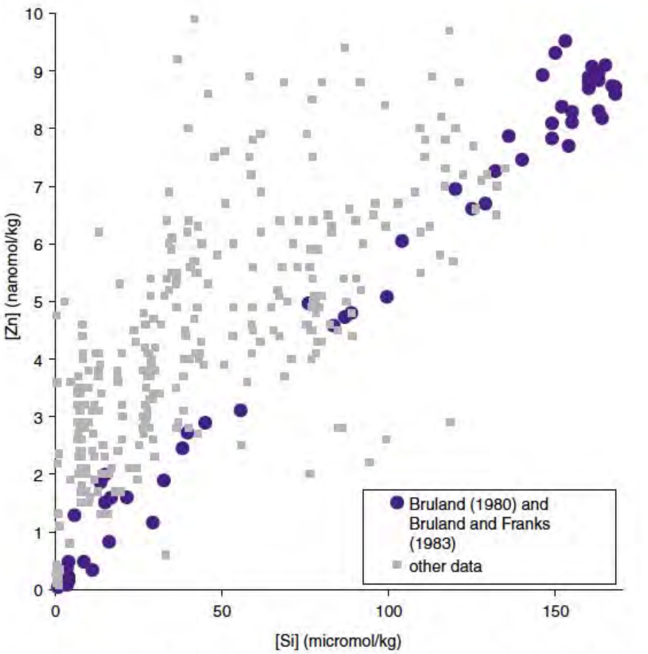
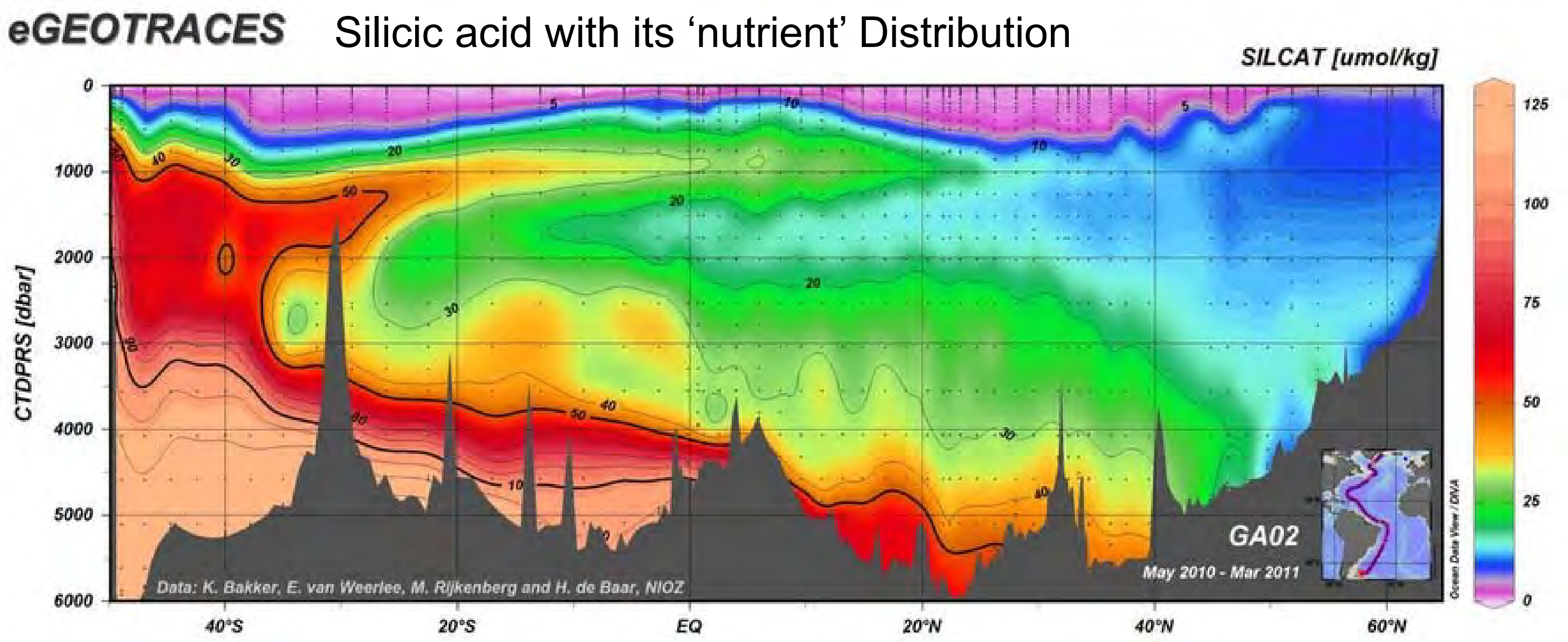


Figure 25. Zn versus Si concentrations reported from ocean water samples. The early data (blue circles) of Bruland (1980) from the North Pacific and Bruland and Franks (1983) from the North Atlantic indicated that there was a strong relationship between Zn and Si. Other data published subsequently (grey squares) do not follow that simple relationship. We cannot determine whether this scatter is due to real variations between different regions of the ocean, or to unresolved problems with contamination or analytical quality control. GEOTRACES is needed to answer this puzzle, with clear implications for the use of Zn as a proxy to reconstruct dissolved Si distributions in the past. Figure provided by Ros Rickaby and Ed Boyle.

From the GEOTRACES Planning document

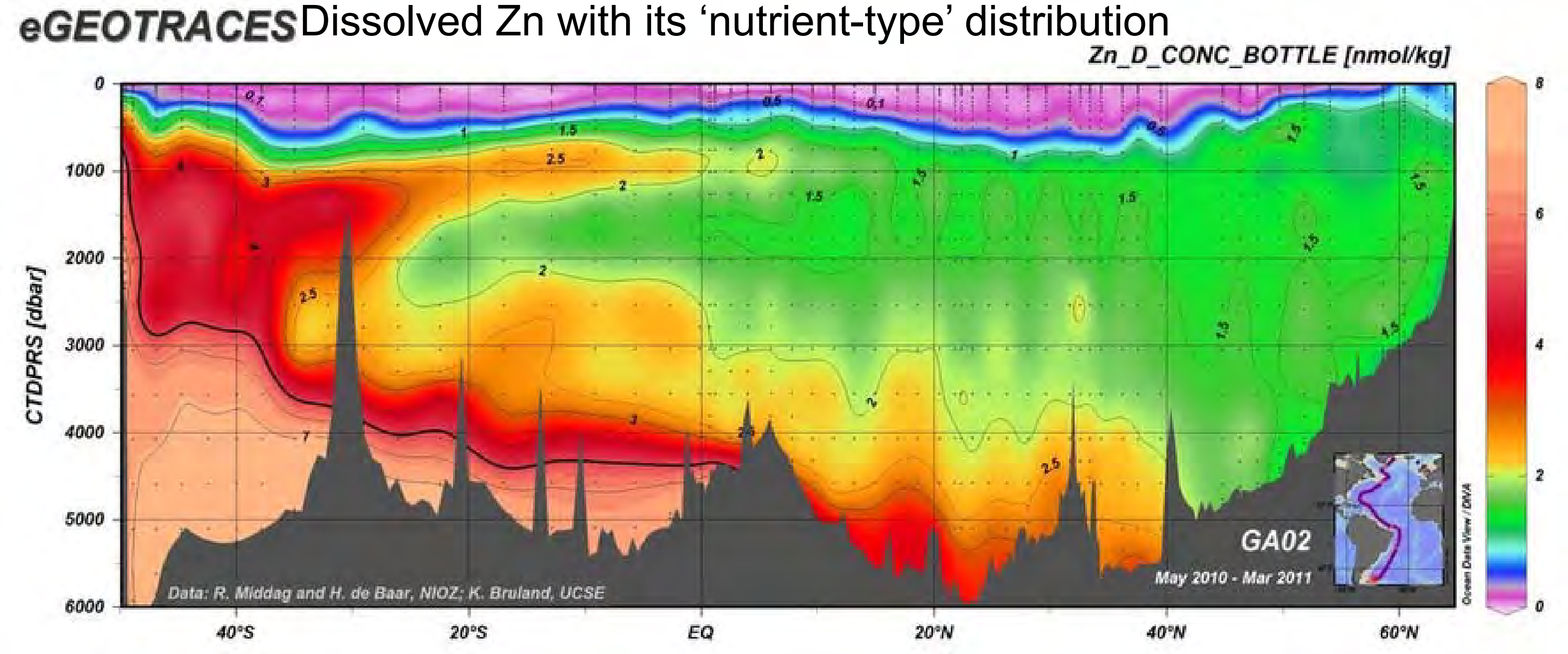
GEOTRACES Atlantic Section carried out by the Netherlands

Dissolved Zn - another example of a meridional section for a nutrient-type trace metal from the western Atlantic.



Silicic acid with its ‘nutrient’ Distribution

Data: K. Bakker, E. van Weerlee, M. Rijkenberg and H. de Baar, NIOZ

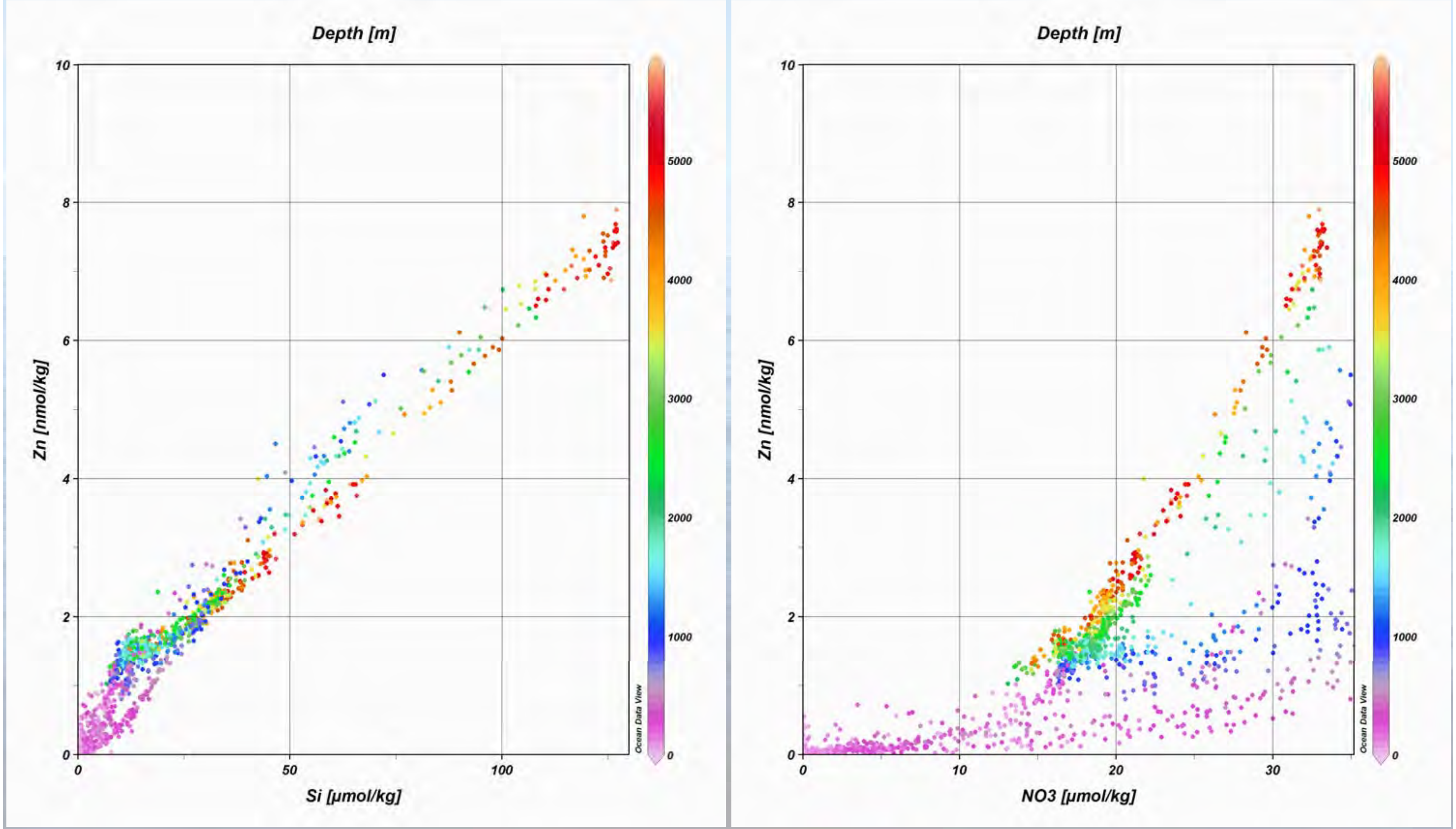


Dissolved Zn with its ‘nutrient-type’ distribution

Data: R. Middag and H. de Baar, NIOZ; K. Bruland, UCSE

From Rob Middag, Hein de Baar and Bruland on samples analyzed at UCSC. Middag et al (in prep)

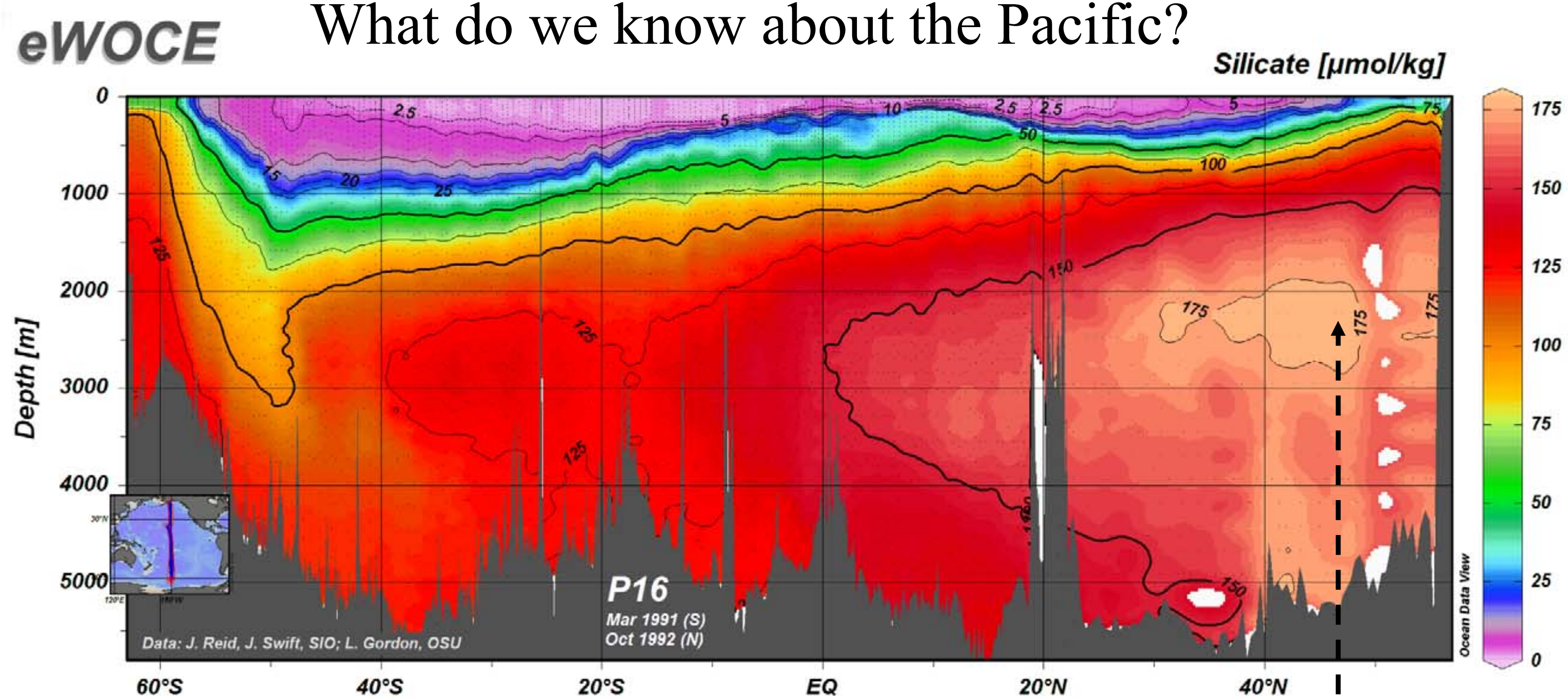
Dissolved Zn vs silicic acid and nitrate in the Western Atlantic meridional section. The deep water values exhibit a strong correlation with respect to both nutrients.

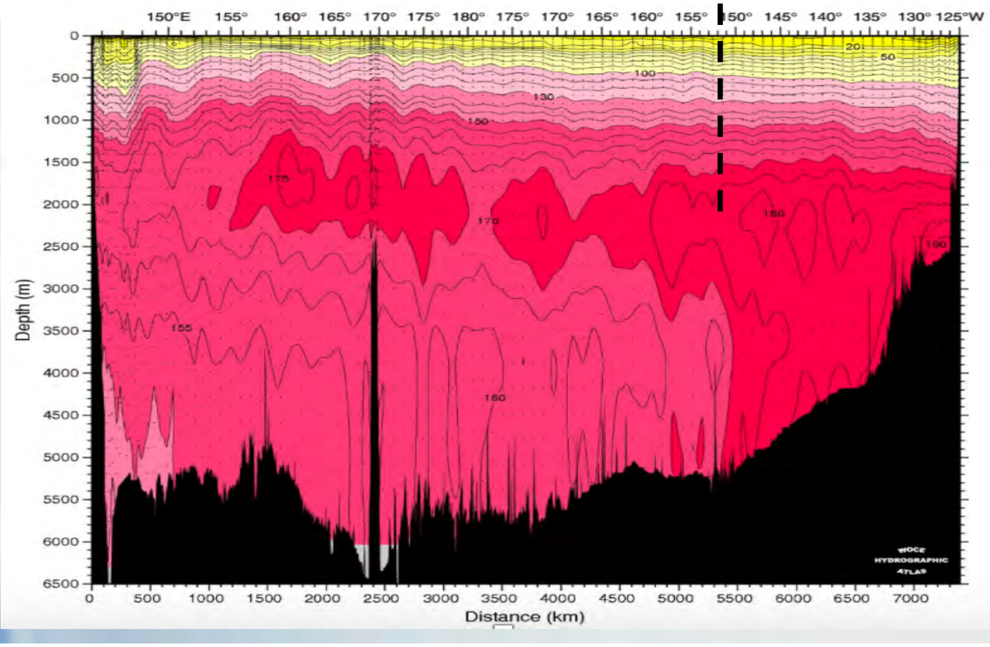


GEOTRACES

From Rob Middag, Bruland and Hein de Baar on samples analyzed at UCSC. Middag et al (in prep)

What do we know about the Pacific?





Above is silicic acid along the meridional section of P16 showing a maxima of >175 umol/kg at 45° N at depths of 2000 to 3000 m. On the right is the zonal silicic acid section at 47^0 N showing a maxima of 190 umol/kg at these depths off the North American slope.

Interesting new data from the GEOTRACES zonal section of the South Pacific showing the influence of hydrothermal inputs providing a major source of ’excess Zn’ at depths of ~2500 meters (Roshan et al. 2016).

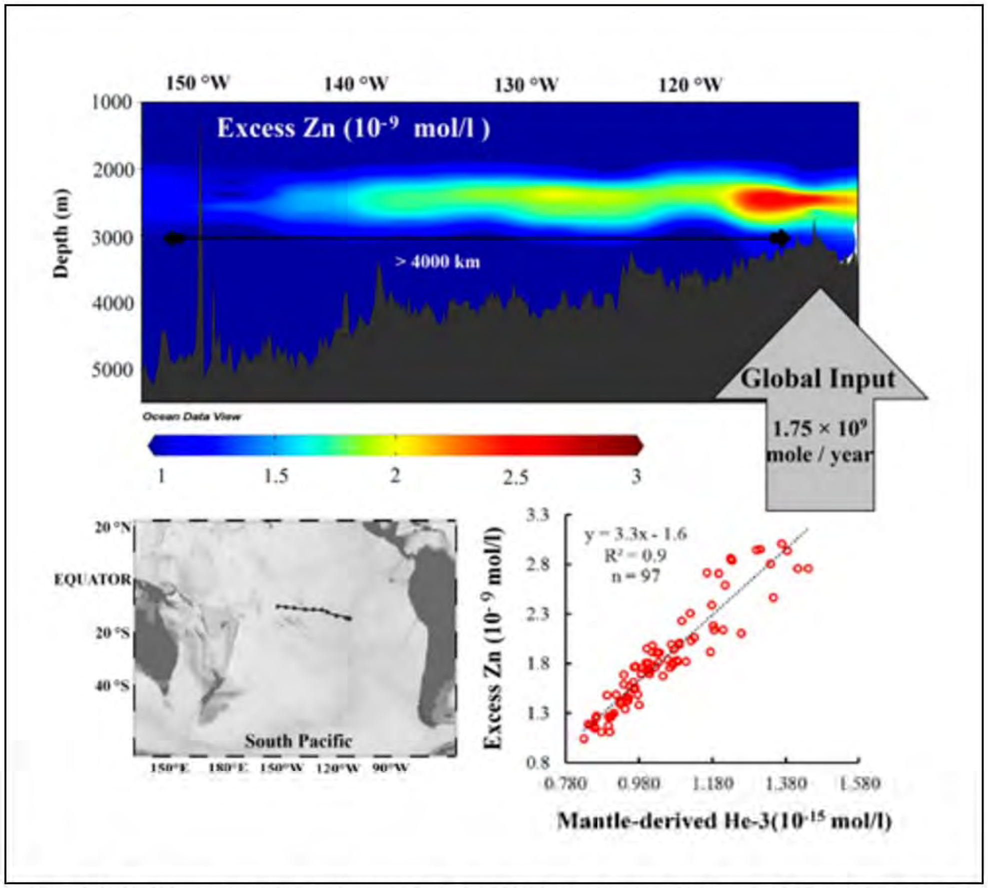
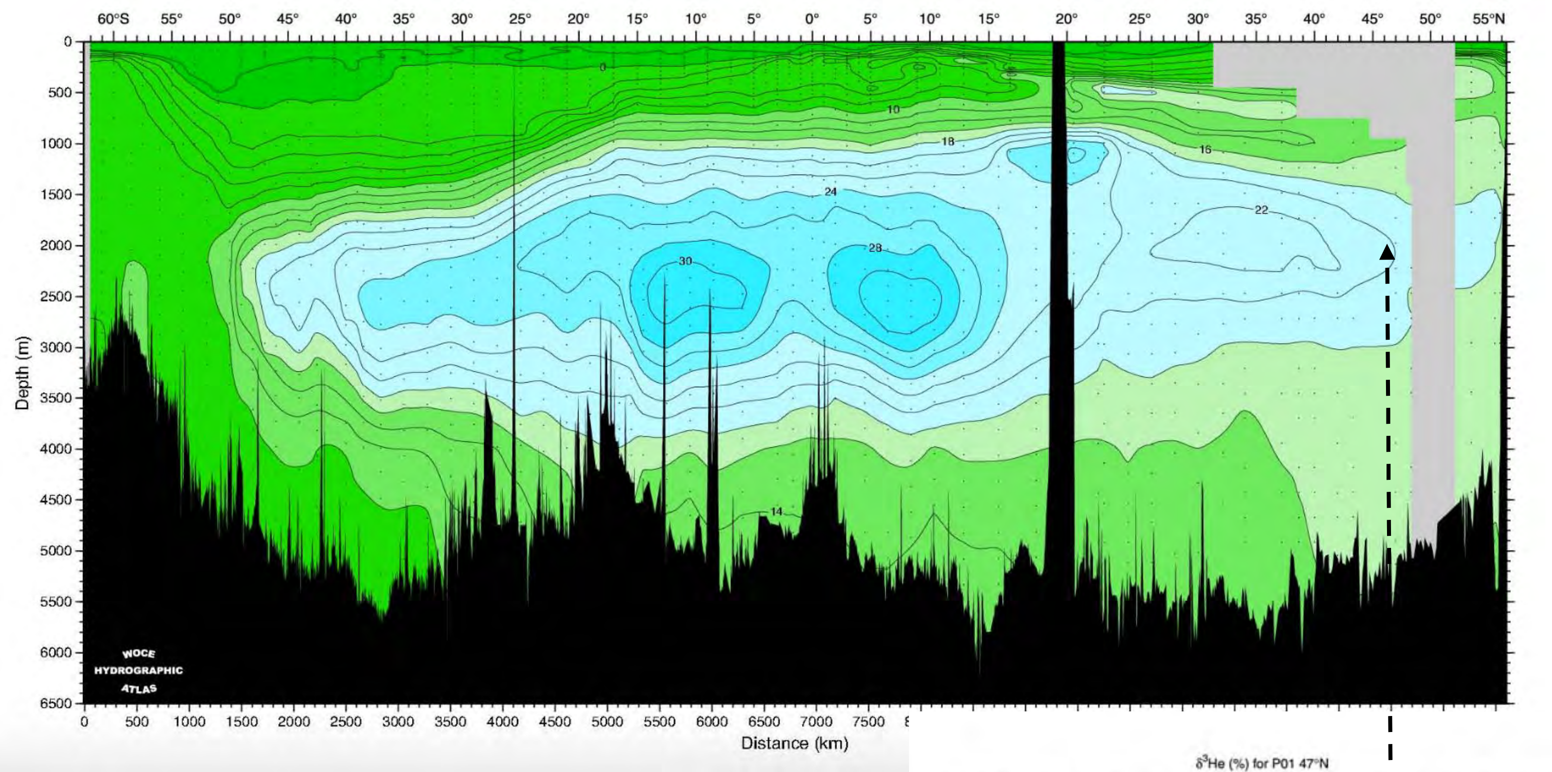


Figure: The top panel shows the dispersion of hydrothermal-controlled component of dissolved Zn (Excess Zn) from the East Pacific Rise (elevated topography at the east of the transect and shown in the bottom left panel) to the west of the transect (>4000 km). Excess Zn shows a strong correlation with hydrothermal tracer, ^{3}He which allows for the accurate estimation of hydrothermal dissolved Zn input rate of 1.75 G mole/year.

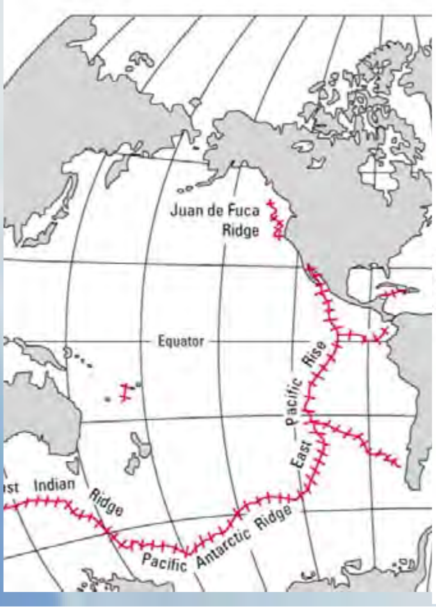
Reference:

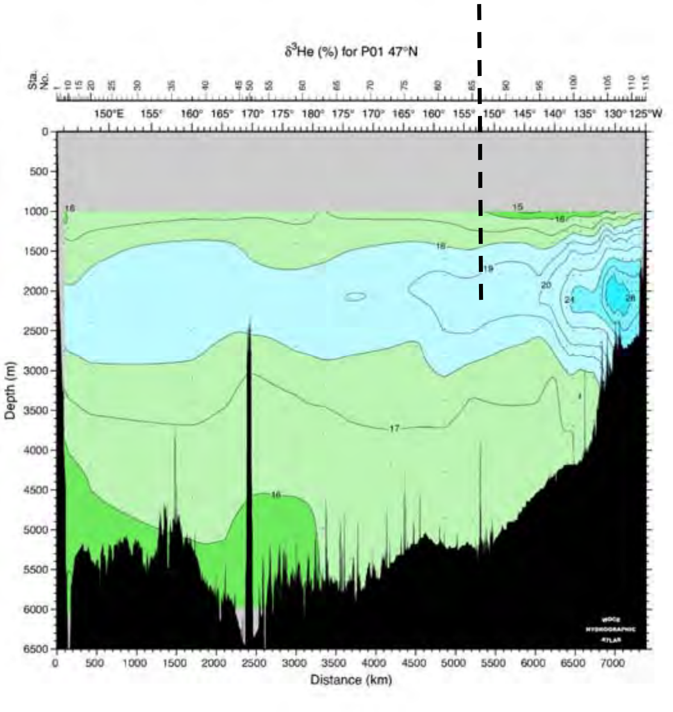
Roshan, S., Wu, J., & Jenkins, W. J. (2016). Long-range transport of hydrothermal dissolved Zn in the tropical South Pacific. Marine Chemistry, 183, 25–32. doi:10.1016/j.marchem.2016.05.005

del ^{3}He for the P16 section in the Pacific showing hydrothermal inputs extending off axis out to the P16 meridional section.



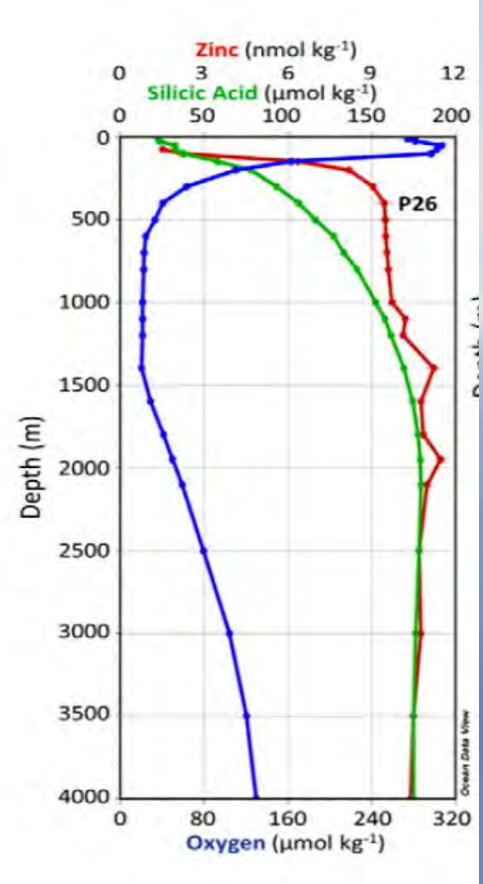
However, the proposed GEOTRACES meridional section may be too far West to clearly detect the hydrothermal component of ‘excess Zn’ in the dissolved Zn distribution. A high degree of precision and accuracy will be required.





Another recent idea concerning Zn

Janssen & Cullen (2015) ‘Decoupling of zinc and silicic acid in the subarctic northeast Pacific interior’



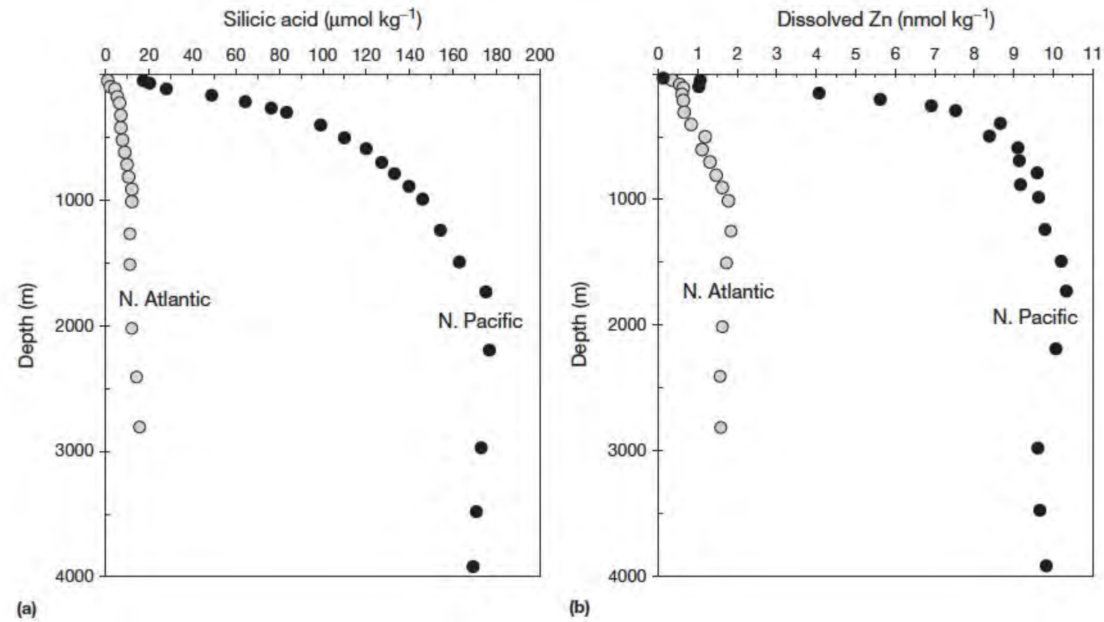
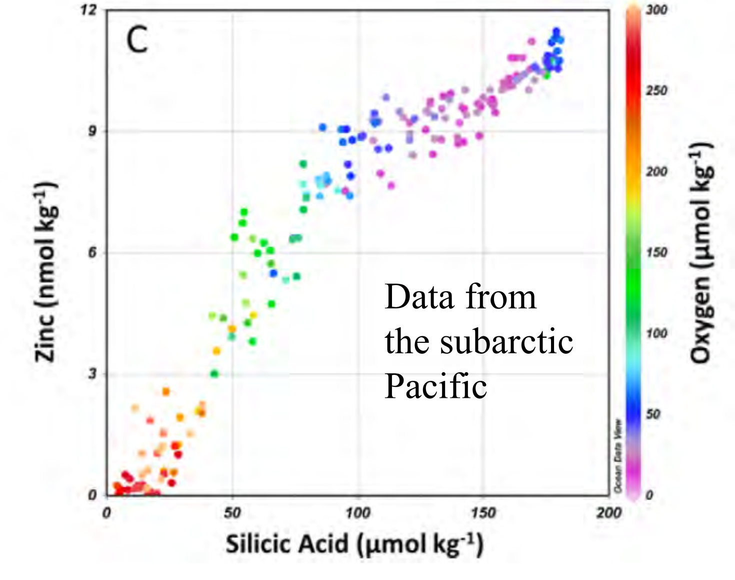


Figure 2 Vertical profiles of (a) silicic acid and (b) dissolved zinc observed at high latitudes of the North Atlantic (○) (59° 30′ N, 20° 45′ W; reproduced from Martin JH, Fitzwater SE, Gordon RM, Hunter CN, and Tanner SJ (1993) Iron, primary production and carbon–nitrogen flux studies during the JGOFS North Atlantic bloom experiment. *Deep Sea Research Part II: Topical Studies in Oceanography* 40: 115–134) and the North Pacific (●) (50° N, 145′ W; reproduced from Martin JH, Gordon RM, Fitzwater S, and Broenkow WW (1989) VERTEX: Phytoplankton/iron studies in the Gulf of Alaska. *Deep Sea Research Part A. Oceanographic Research Papers* 36: 649–680).

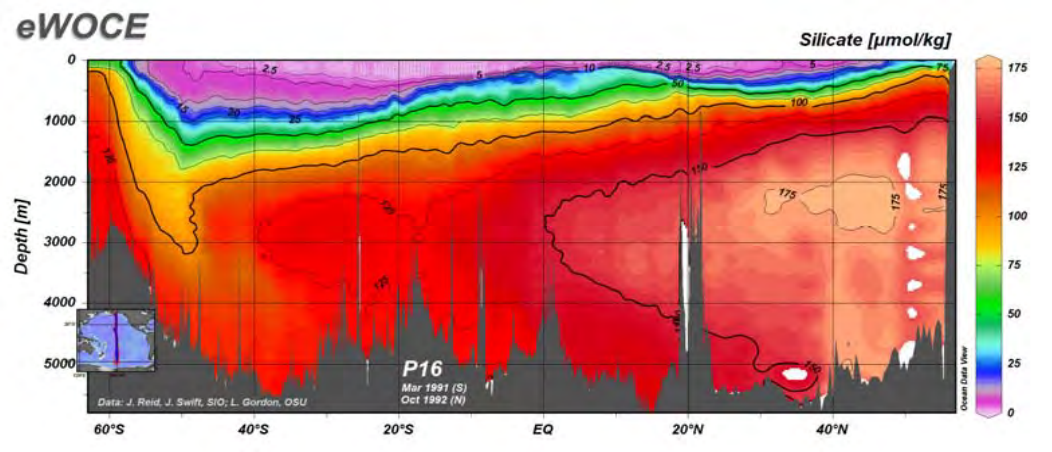
Janssen and Cullen (2015) propose that this data is evidence implicating the formation of solid Zn sulfides in low oxygen, particle-associated micro-environments as an important loss term in the oceanic Zn budget.

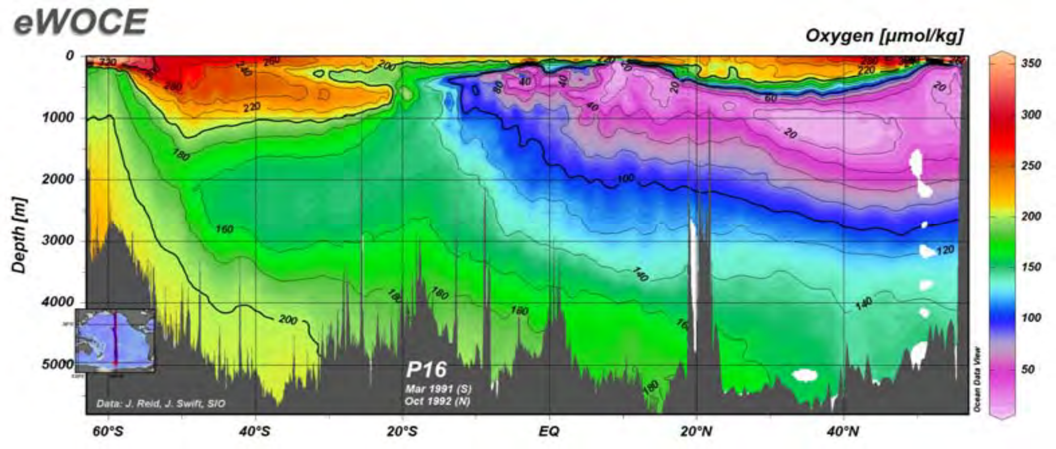


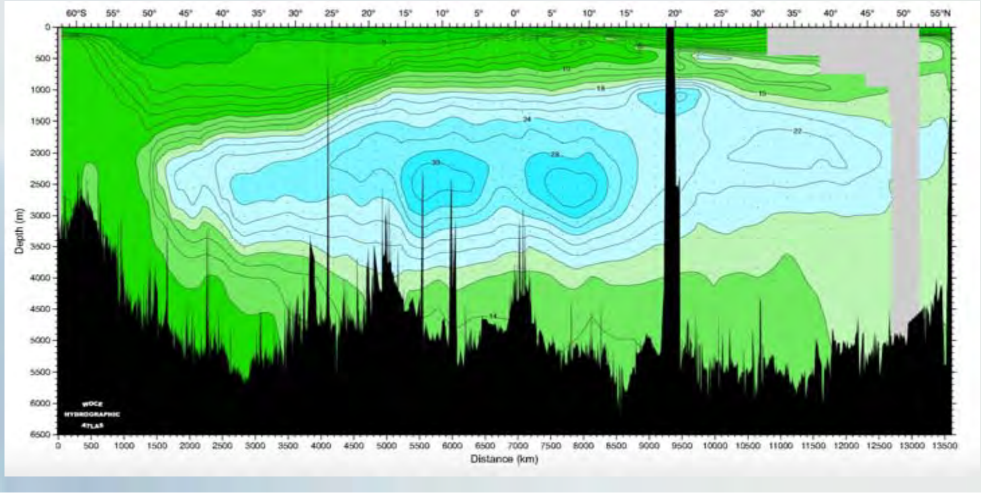
Data from the subarctic Pacific

The proposed GEOTRACES meridional section with silicic acid-rich deep water, low oxygen intermediate depth waters, and off-axis hydrothermal influence should allow these various inputs and sinks for dissolved Zn to be evaluated.

Non-contaminated samples analyzed with a high degree of accuracy and precision will be required. Particulate Zn and isotopes should also compliment this effort.







What about particle reactive, scavenged-type, TEI’s?

Dissolved Al: We knew Al had a scavenged-type distribution based upon the limited profiles available prior to GEOTRACES.

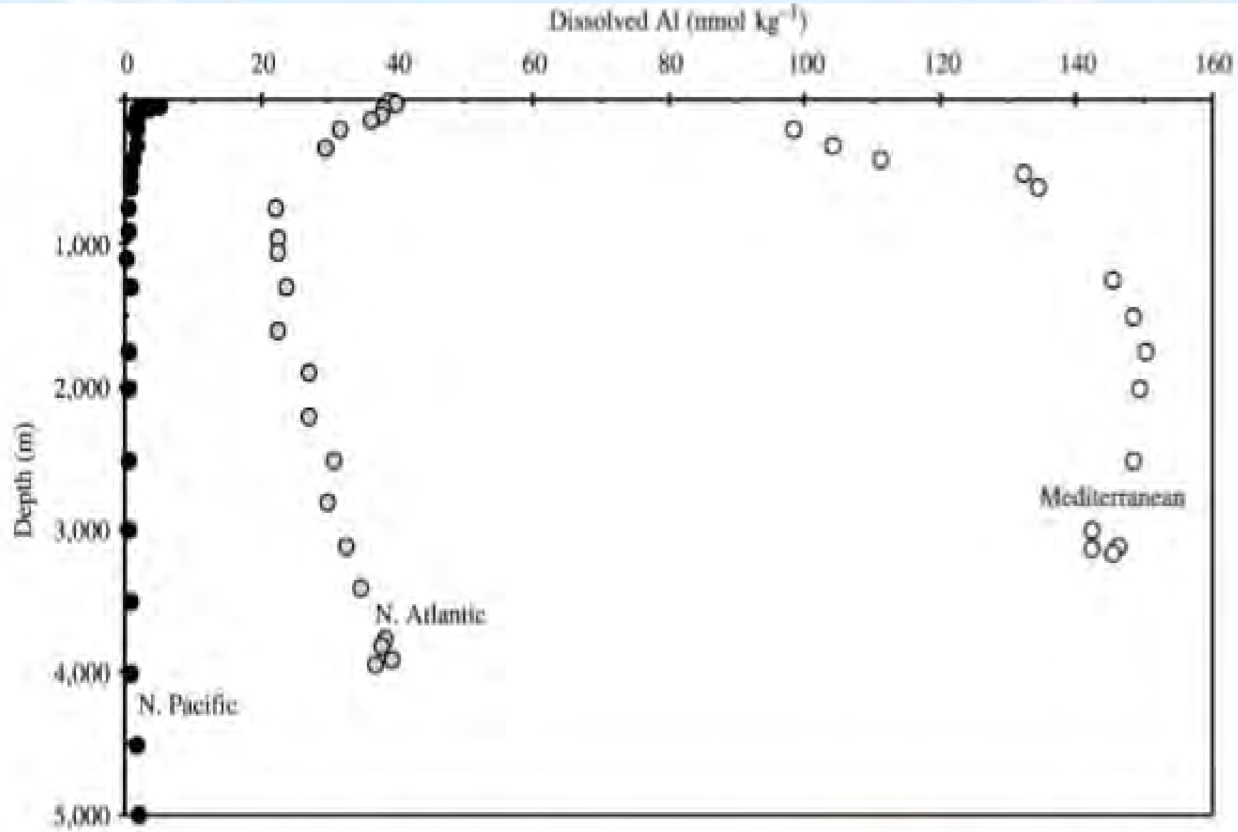


Figure 4 Vertical profiles of dissolved aluminum in the Mediterranean Sea (○) (34° 18′ N, 20° 02′ W; data from Hydes *et al.*, 1988), the North Atlantic (◎) (40° 51′ N, 64° 10′ W; data from Hydes, 1979), and the North Pacific (●) (28° 15′ N, 155° 07′ W; data from Orians and Bruland, 1986).

From Bruland, Middag and Lohan (2014)

This North Pacific meridional section will be particularly interesting for aluminum

Central
North Pacific
VERTEX T4

Central
North Atlantic

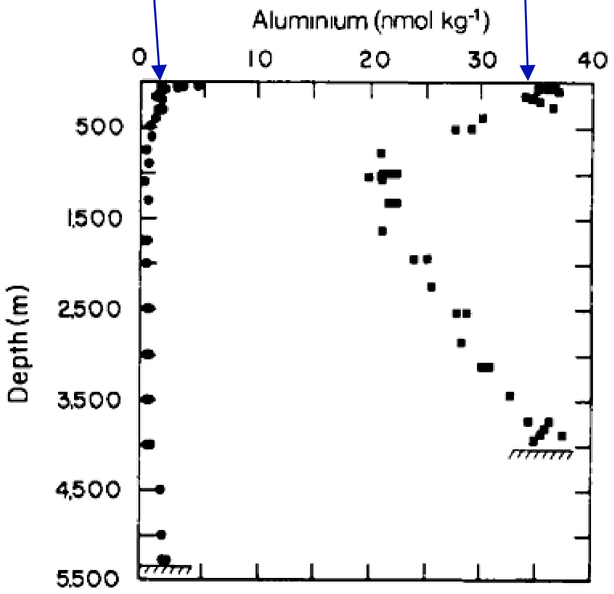


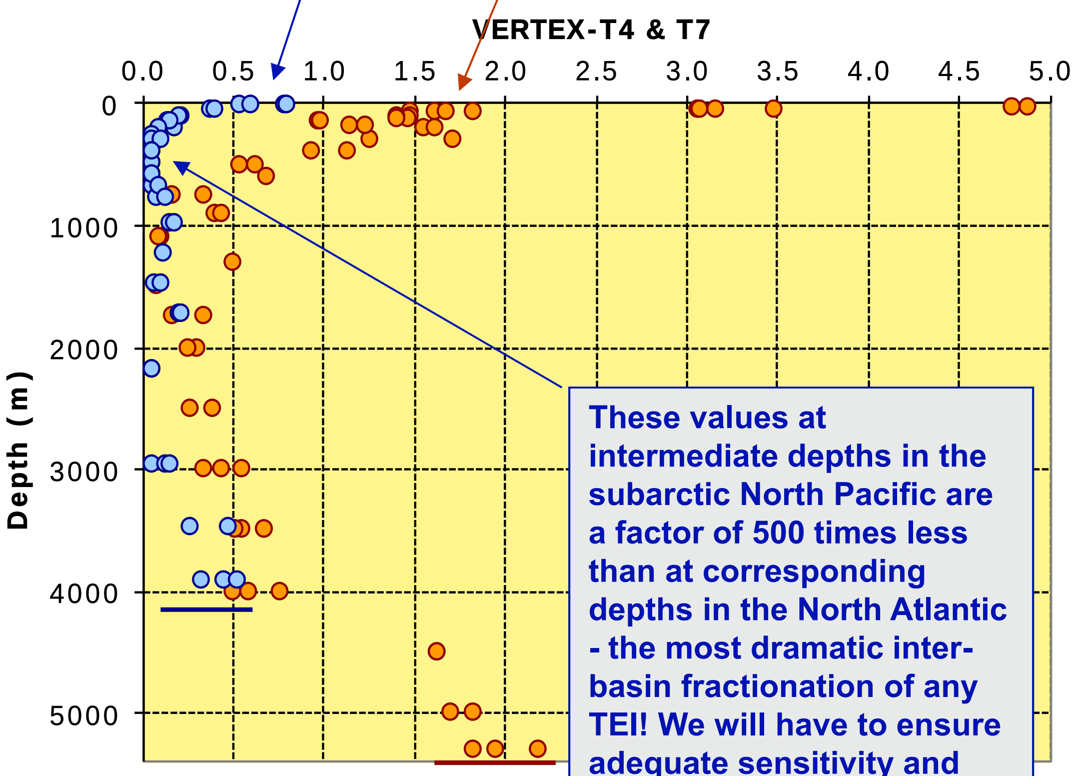
Fig. 2 Variation of dissolved aluminium with depth at 28° N, 155° W in the North Pacific (●) and at 41° N, 64° W in the North Atlantic (■). The Pacific data are from VERTEX IV and the Atlantic data are from K69/10, by Hydes[3]. Copyright 1979 by the AAAS. A deep western North Atlantic seawater reference sample (NASS-1) was analysed by our technique and found to have a dissolved aluminium concentration comparable with that Hydes[3] found at the same depth at his western North Atlantic station.

Orians and Bruland (1985)

Subarctic
Pacific, Stn P

Central
North Pacific

Dissolved Al (nmol/kg)



These values at intermediate depths in the subarctic North Pacific are a factor of 500 times less than at corresponding depths in the North Atlantic - the most dramatic inter-basin fractionation of any TEI! We will have to ensure adequate sensitivity and detection limits for these pmol/kg concentrations of dissolved Al.

Orians and Bruland (1986)

The net scavenging rate constant of ^{234}Th from the surface mixed layer (Bruland et al., 2014). Note the intense scavenging of dissolved ^{234}Th in the subarctic Pacific that is consistent with the low dissolved Al concentrations we have observed in this region. Other particle reactive TEI's such as scandium (Parker et al. 2016) will also be of interest).

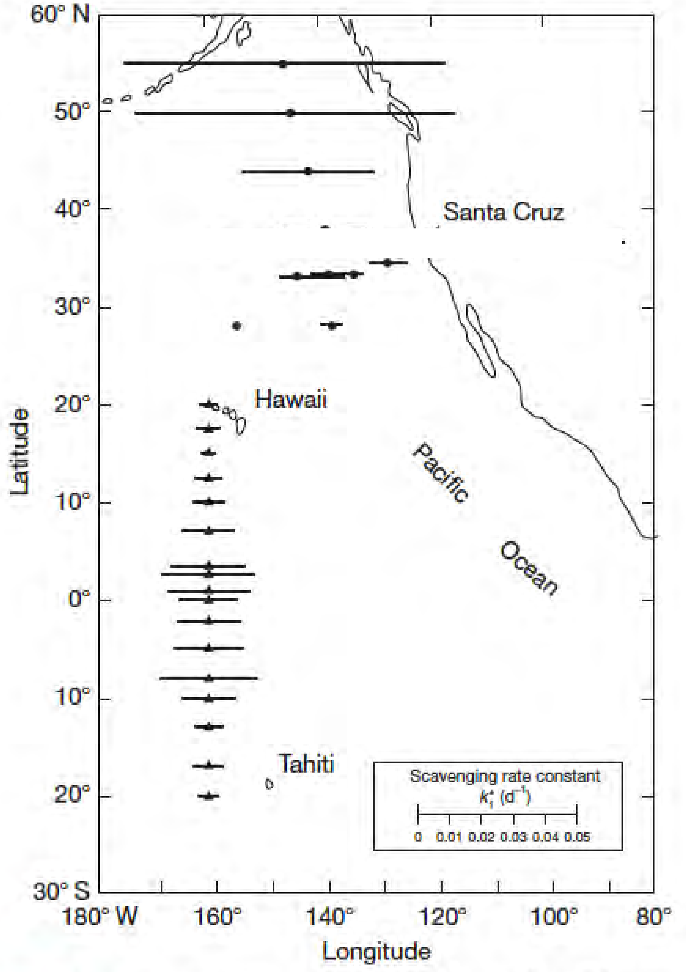


Figure 13 The net scavenging rate constant, k^*_1 (day^{-1}), of ^{234}Th from the surface mixed layer of the Pacific Ocean (reproduced from Bruland and Coale, 1986; Bruland and Beals, unpublished).

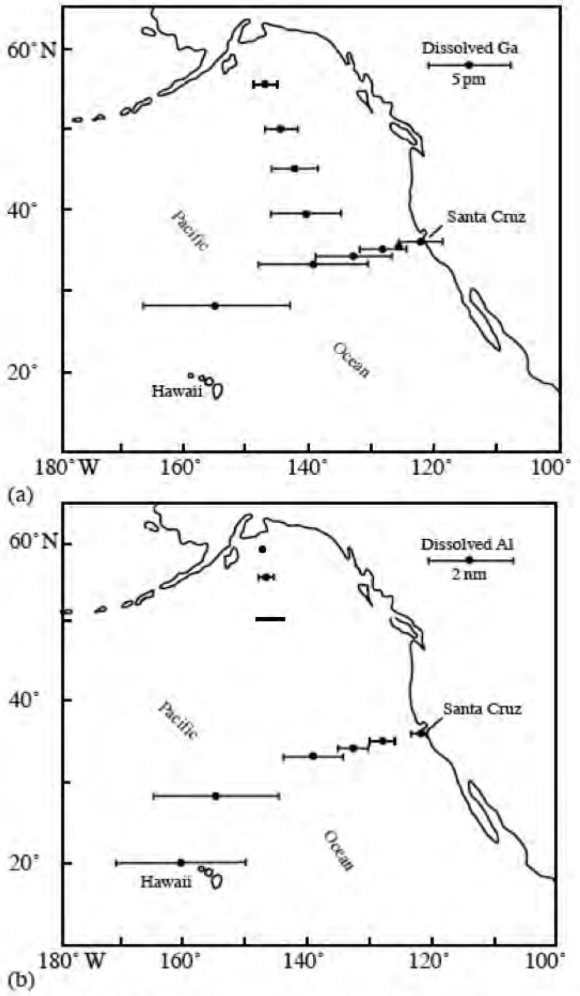
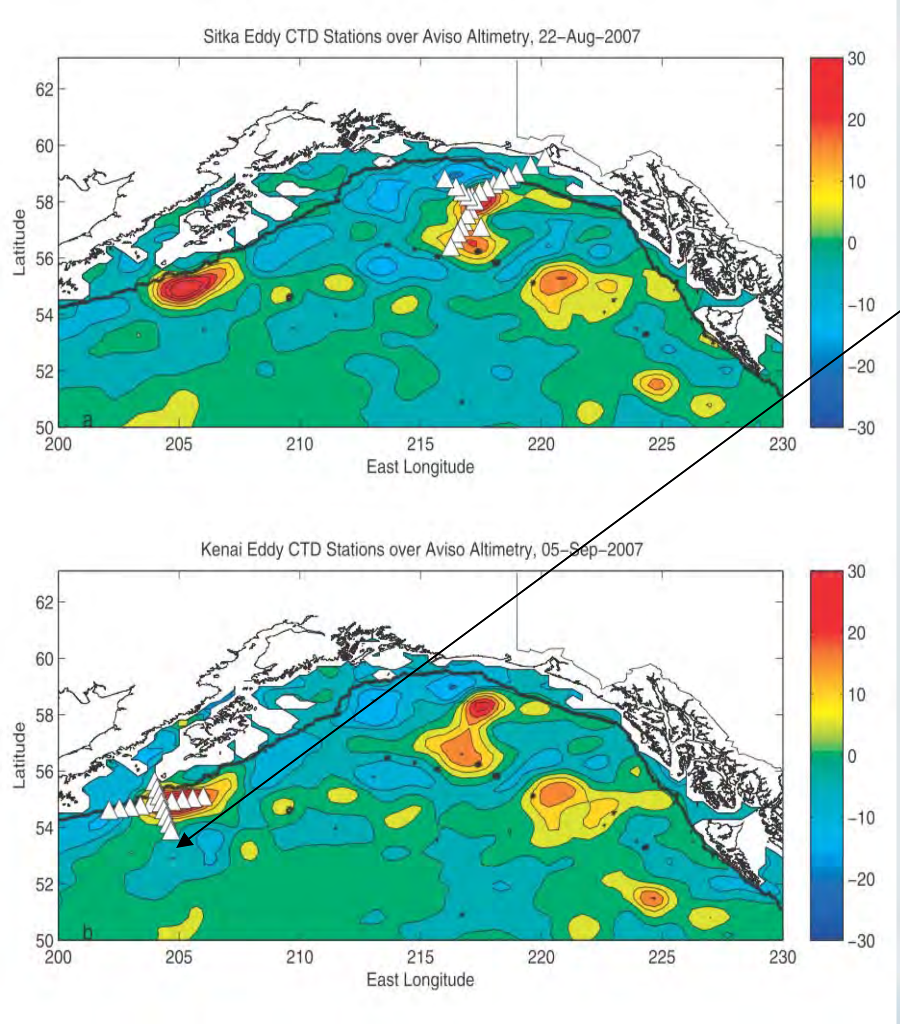


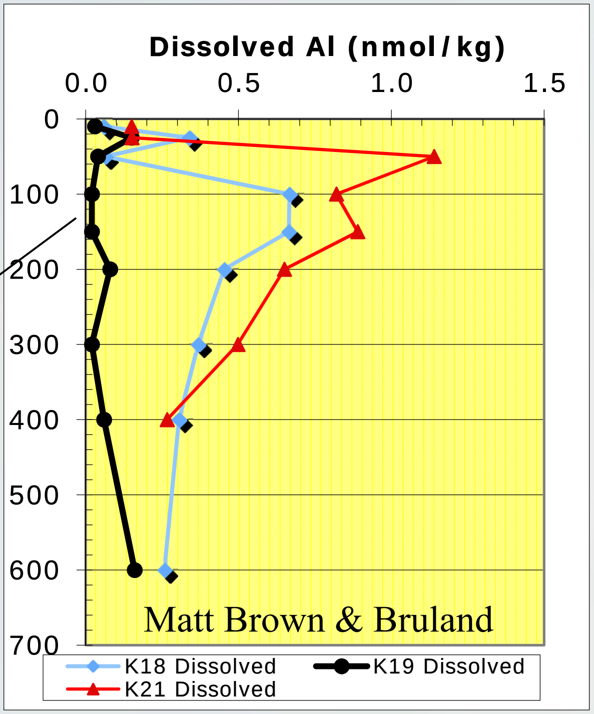
Figure 13 Concentrations of (a) dissolved gallium (data from Orians and Bruland, 1988) and (b) dissolved aluminum (data from Orians and Bruland, 1986) in the surface waters of the eastern North Pacific at stations for which ^{234}Th net scavenging rate data exist (see Figure 12).

Figures from Bruland and Lohan (2003) and Bruland, Middag and Lohan (2014)

In the Gulf of Alaska region of the Sub-Arctic Pacific with intense scavenging we have observed exceptionally low dissolved Al values.

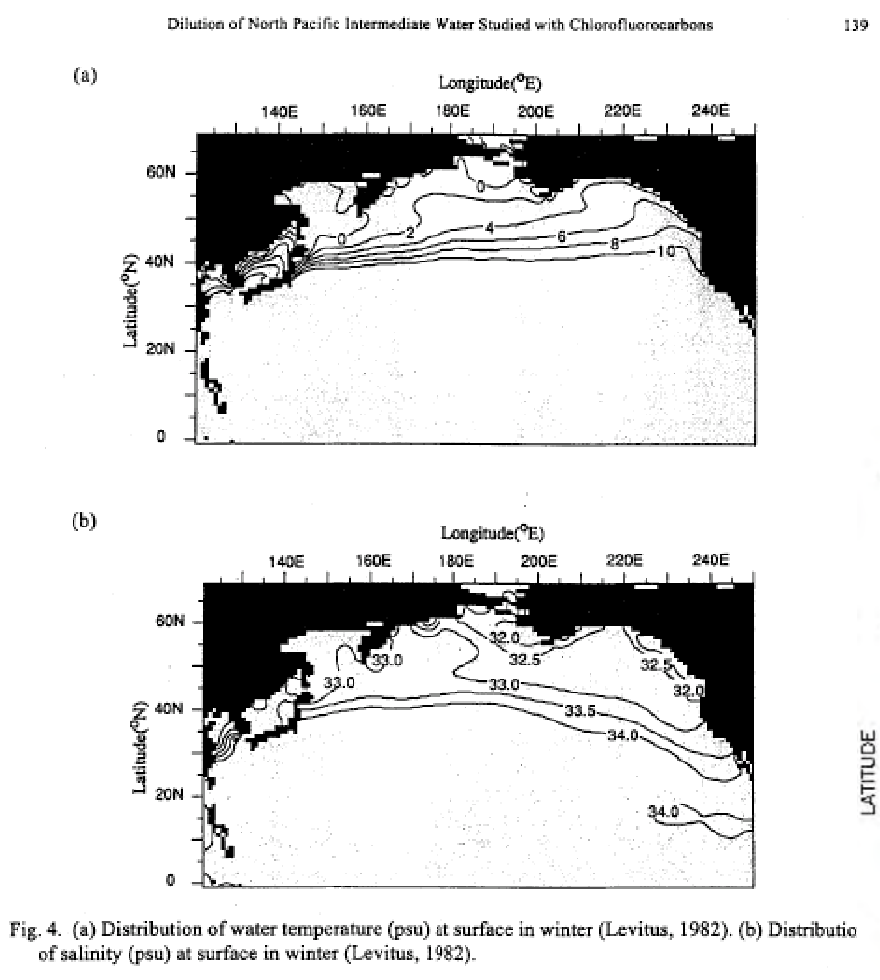
Sub-Arctic Pacific





Inside and outside anti-cyclonic eddies in the Gulf of Alaska, Subarctic North Pacific (Brown et al., 2014). Note the extremely low concentrations of dissolved Al outside of the anti-cyclonic eddies. Background concentrations are on the order of 20 pmol/kg in the Gulf of Alaska outside of the influence of the anti-cyclonic eddies. A factor of 1000 fold lower than in the North Atlantic. This will be an analytical challenge that needs to be met.

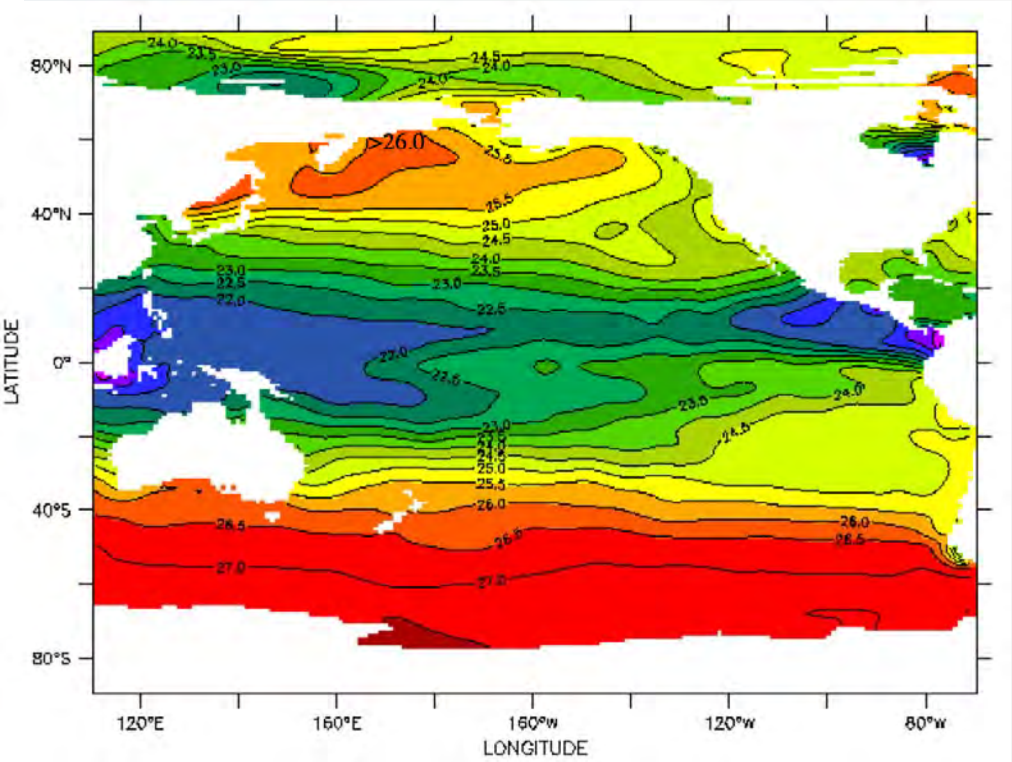
North Pacific Intermediate Water (NPIW) is formed at the northwestern corner of the subarctic Pacific where the surface water in winter is cold and relatively salty - but only enough to sink to depths of ~500 meters.



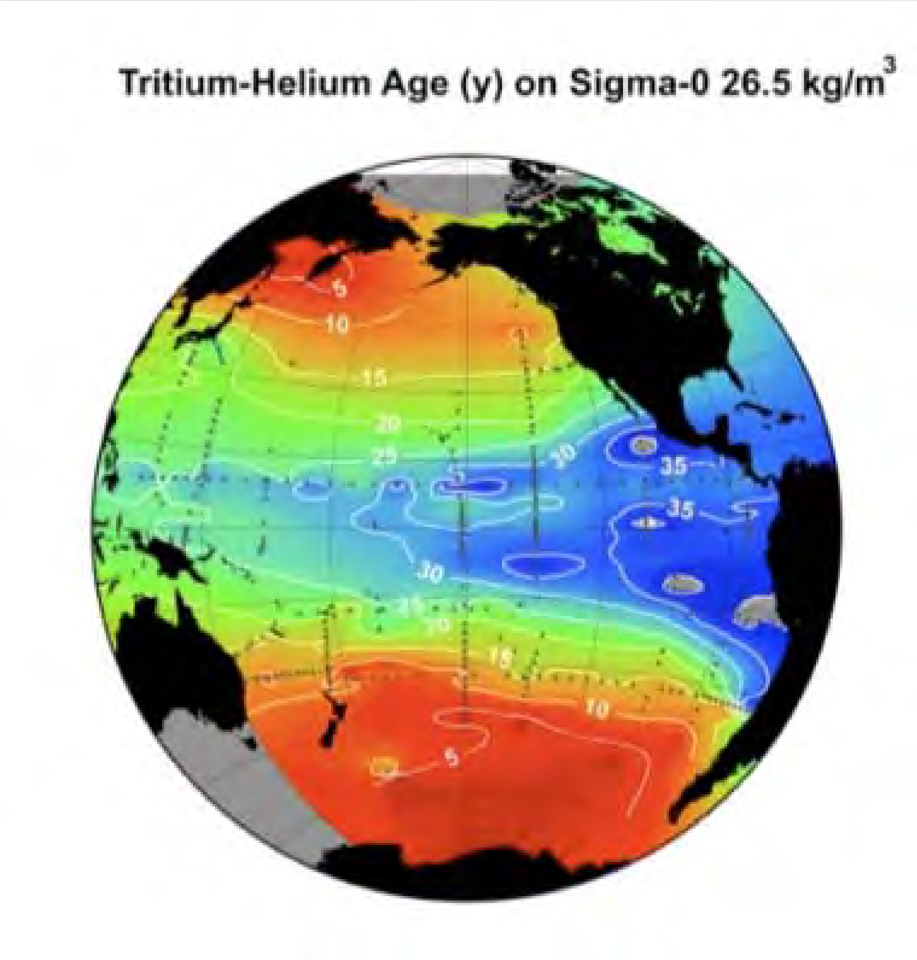
Dilution of North Pacific Intermediate Water Studied with Chlorofluorocarbons 139

Fig. 4. (a) Distribution of water temperature (psu) at surface in winter (Levitus, 1982). (b) Distributio of salinity (psu) at surface in winter (Levitus, 1982).

This surface water with a temperature of 0 to 2^{0}C and a salinity of between 33.0 and 33.5 can yield relatively dense water with a sigma-t or σ_t of ~ 26.5 kg/m^3

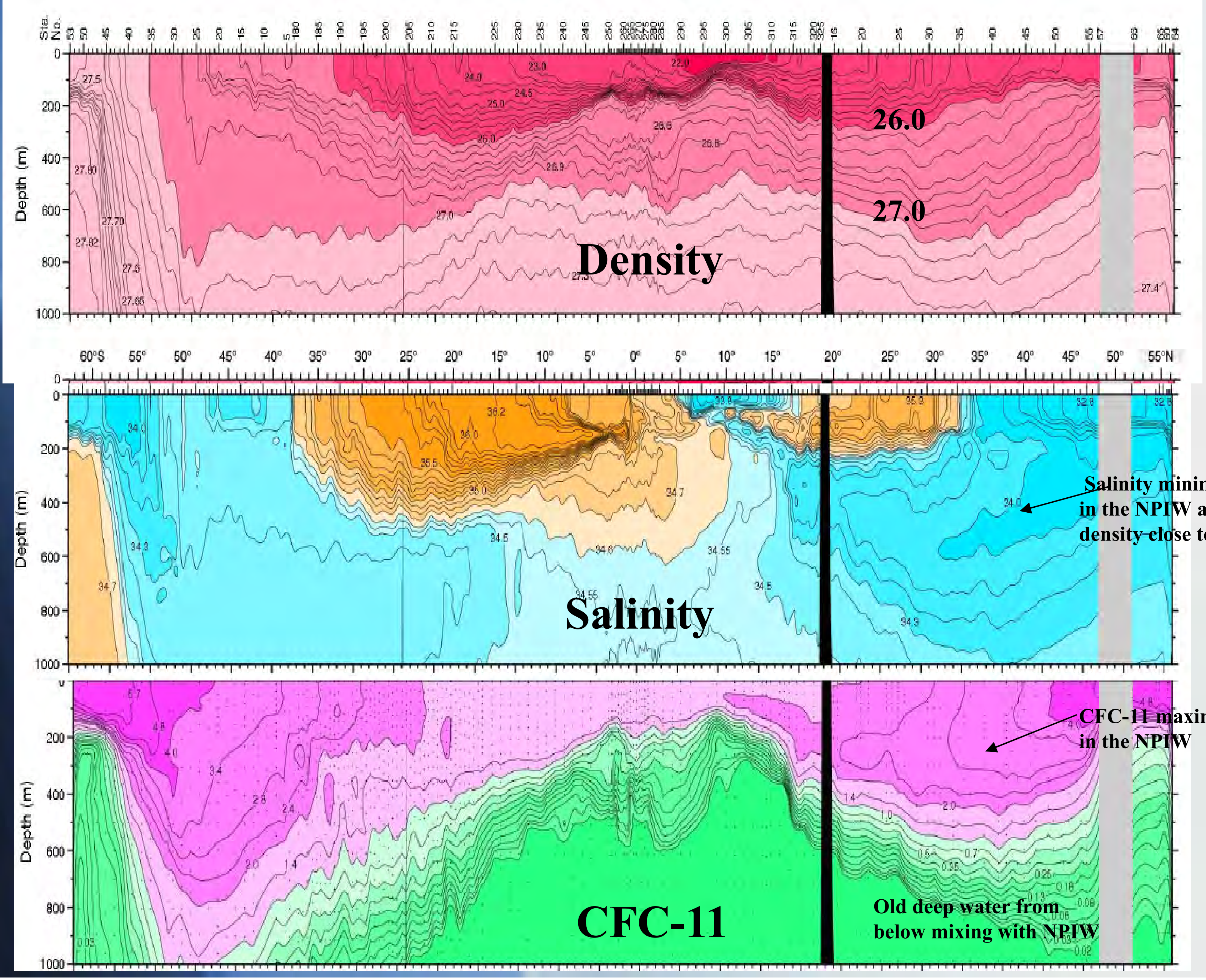


Bill Jenkin’s tritium-helium ages along the 26.5 isopycnal. In the North Pacific, this density layer outcrops in the western North Pacific in winter and then forms NPIW water that mixes eastward at intermediate depths and ages - but at a very different time scale than the deep waters.



Tritium-Helium Age (y) on Sigma-0 26.5 kg/m^3

Upper 1000 m of P16 highlighting Intermediate Waters



Density

26.0

27.0

Salinity

Salinity minimum in the NPIW at a density close to 26.5

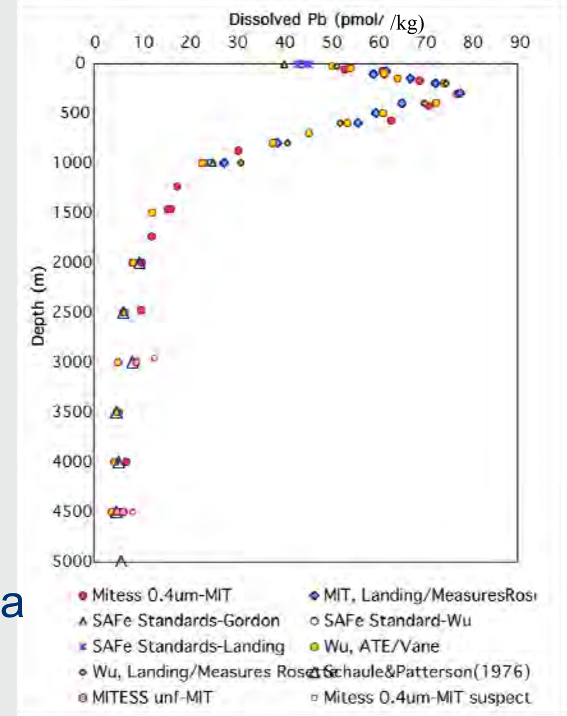
CFC-11

CFC-11 maximum in the NPIW

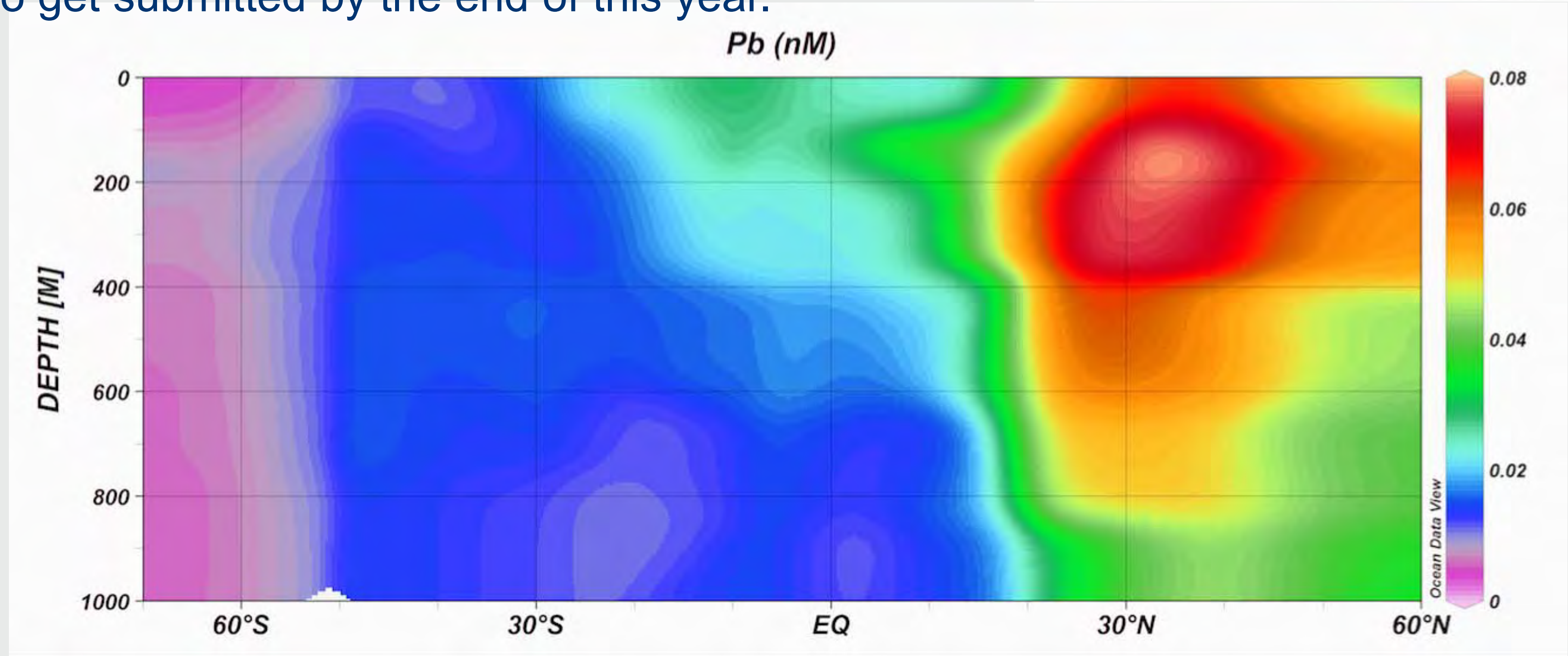
Old deep water from below mixing with NPIW

Lead: a TEI influenced by anthropogenic sources

Vertical profile of dissolved Pb at the SAFe station obtained by a variety of GEOTRACES scientists. A maximum close to the 26.5 isopycnal similar to CFC-11.

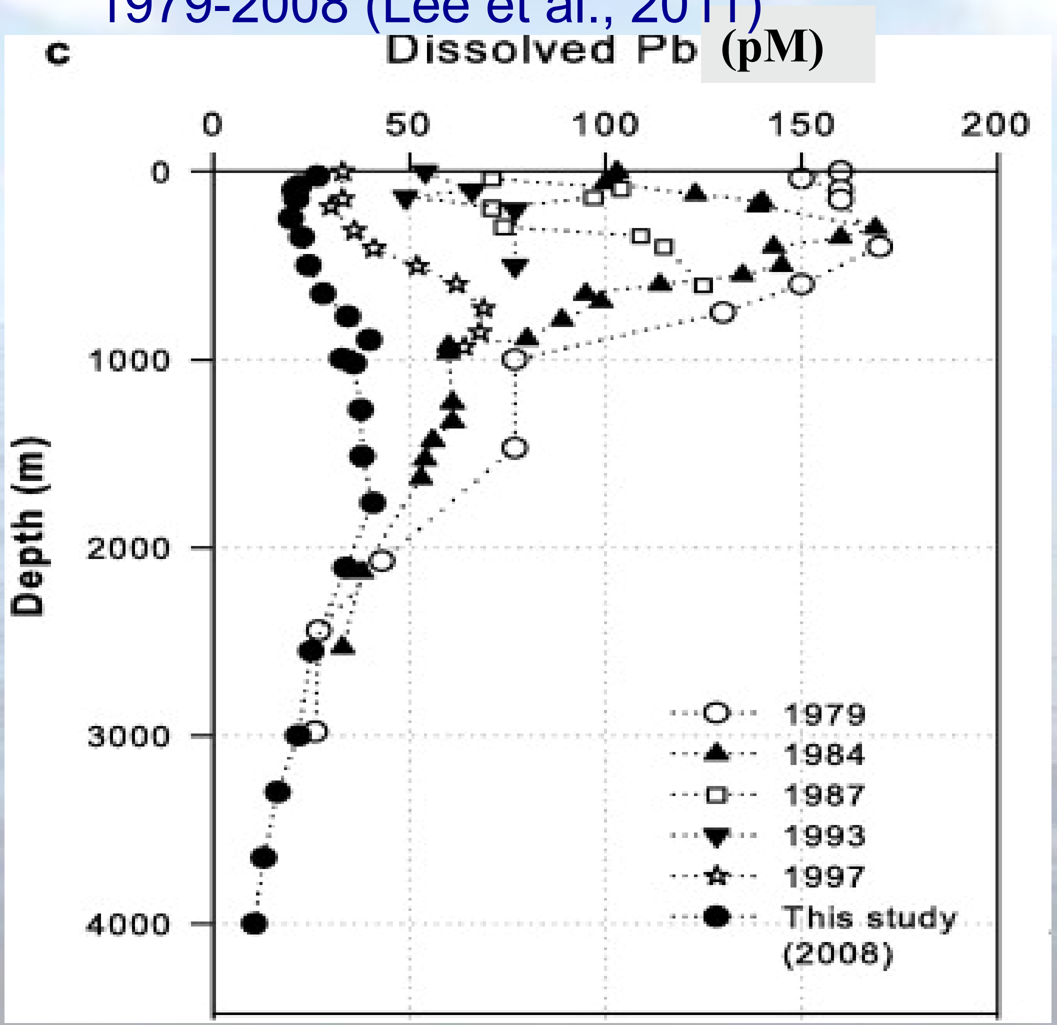


Dissolved Pb in the upper 1000 m on the P16 section (Bill Landing and Angie Milne unpublished). They also have data on other trace metals in the upper 1000 m that Bill Landing hopes to get submitted by the end of this year.



Dissolved Pb – an anthropogenic tracer with a transient input

Data from the NW Atlantic BATS
1979-2008 (Lee et al., 2011)



Time series of vertical profiles of lead showing a decrease from 1979 to 2008 corresponding to decreasing atmospheric inputs. The data from 1984 to 2008 was from Ed Boyle's lab, while the 1979 data was from Schaule and Patterson (1983).

GEOTRACES in the Atlantic has continued this time series.

A time series in the North Pacific may soon be possible.

Pb isotopes compliment this effort.

With the proposed cruise being in September, there is another interesting aspect to examine. A seasonal thermocline develops with a shallow summer-time surface mixed layer and a photic zone deeper than the mixed layer with export from within the seasonal thermocline that is part of the photic zone.

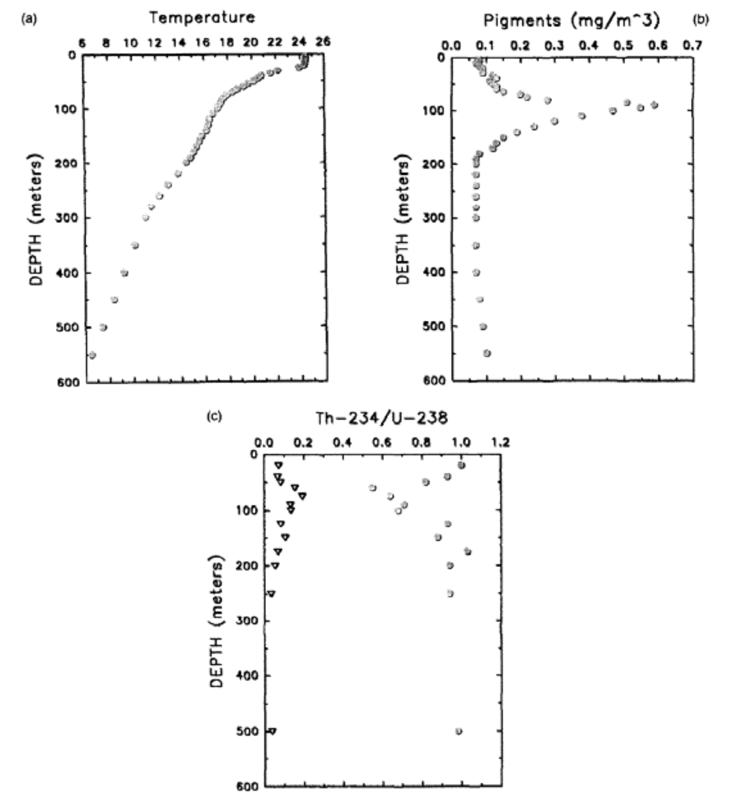


FIG. 7. Vertical profiles of (a) temperature (°C), (b) phytoplankton pigments, and (c) activity ratio of ^{234}Th:^{238}U in dissolved and particulate fractions at VERTEX-IV (COALE and BRULAND, 1987).

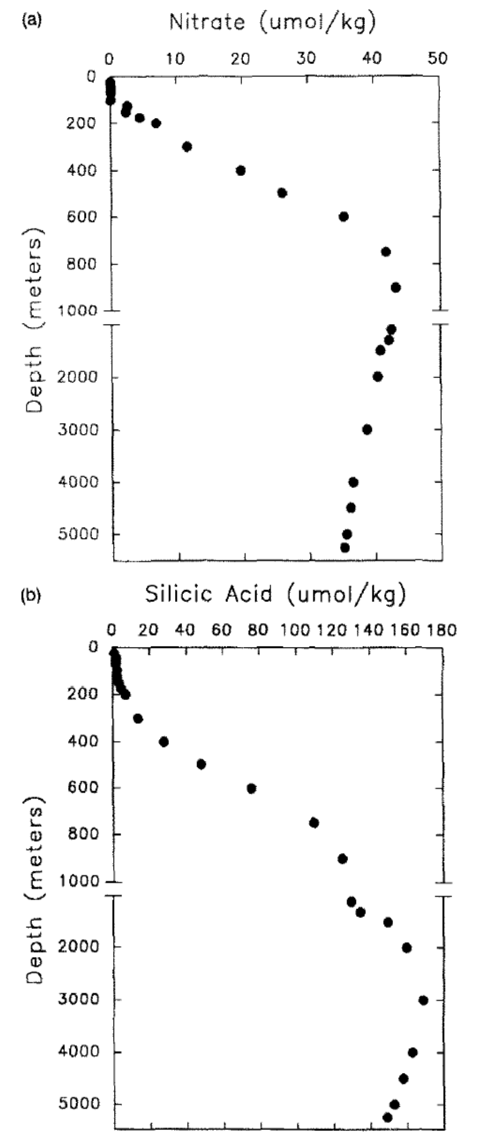
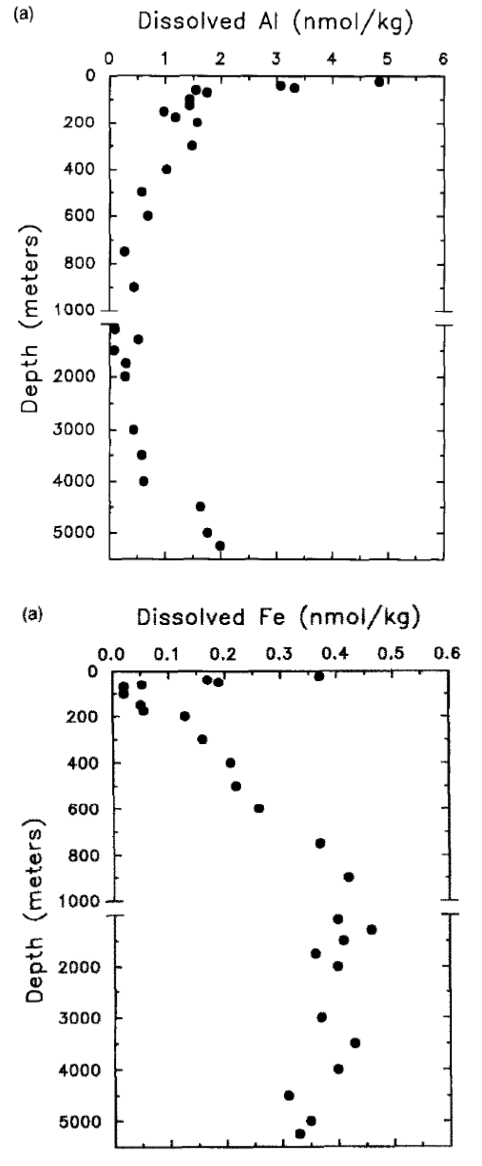


FIG. 1. Vertical profiles of (a) nitrate (μmol · kg^{-1}), and (b) silicic acid (μmol · kg^{-1}) at VERTEX-IV.



Bruland et al. (1984)

John Martin and Mike Gordon’s VERTEX dissolved Fe data for a meridional transect in the North Pacific (Martin et al., 1989)

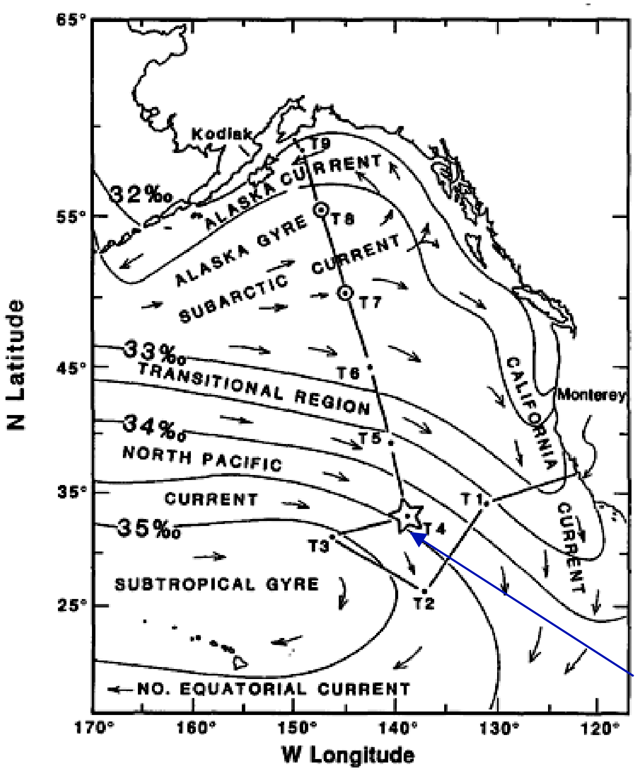


Fig. 1. Northeast Pacific surface current systems and surface isohalines. VERTEX Stas T-1 to T-5 were occupied in September 1986. Stations T-4 to T-9 were occupied on the July–August 1987 VERTEX Alaska cruise (CTD Stas 1–16 were interspersed along this transect; Appendix Table A1). The VERTEX seasonal station is located at T-4 (star); floating particle traps were set at Stas T-7 and T-8 (open circles).

SAFe stn, VERTEX T4

GEOTRACES Pacific Intercalibration

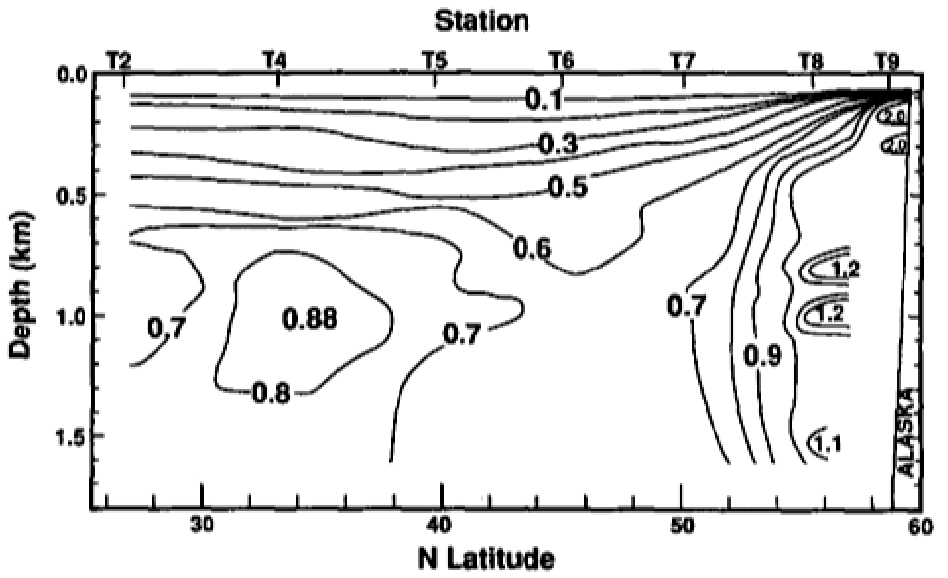


Fig. 7. A dissolved Fe section; station locations are shown in Fig. 1.

John purposely left out details of the near surface mixed layer data and essentially started this section at a depth close to 100 m. A September sampling will provide interesting data as the shallow surface mixed layer and seasonal thermocline will have existed all summer. The aerosol studies will compliment this detailed surface mixed layer sampling.

No more time left to continue with ‘knowns and unknowns’ of the suite of other TEI’s, or aspects of chemical speciation and organic ligands

You are fortunate to be participants in this grand GEOTRACES adventure.

I consider myself to be extremely fortunate to have been a colleague of this bio-geochemistry community for my 40-year career (1974-2014) at UC Santa Cruz and being involved in helping GEOTRACES get started. I will follow your progress with great interest.

Finally, I’d like to acknowledge Geoffrey Smith and all the graduate students and post docs that have been involved in my research group – a number of whom are currently active in GEOTRACES.