

# **$^{39}\text{Ar}$ Measurements from the High Latitude Oceans**

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**TANGR Workshop, Argonne national Laboratory, June 21-22, 2012**

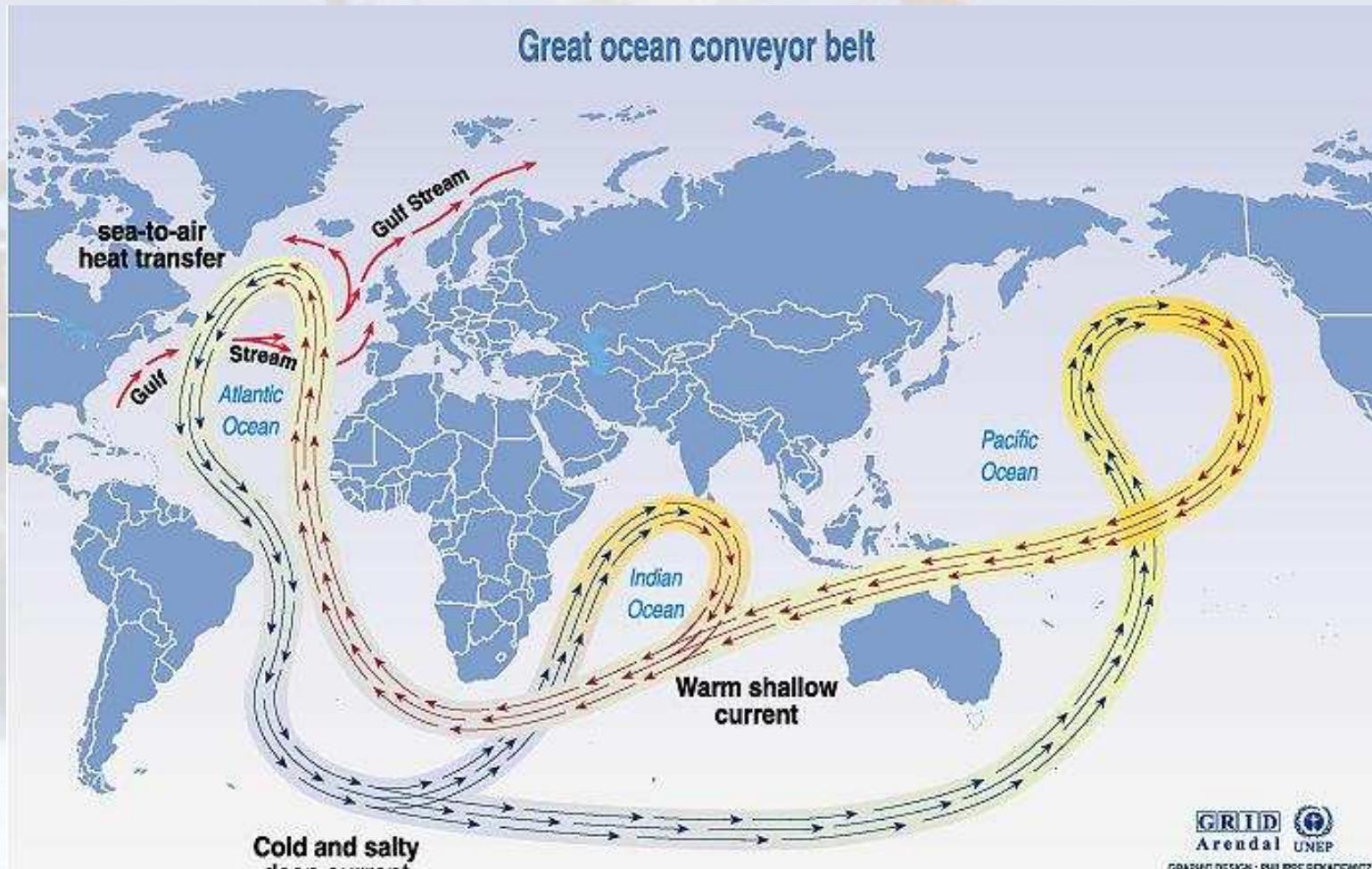
# Outline

- **Introduction**
- **$^{39}\text{Ar}$  in the Ocean**
  - General Considerations
  - Southern Ocean (Weddell Sea)
  - Arctic Ocean (Nansen Basin)
  - Arctic Ocean (Eurasian Basin and Makarov Basin)
- **Perspectives**

# Can a good case be made for Ar and Kr isotope measurements?

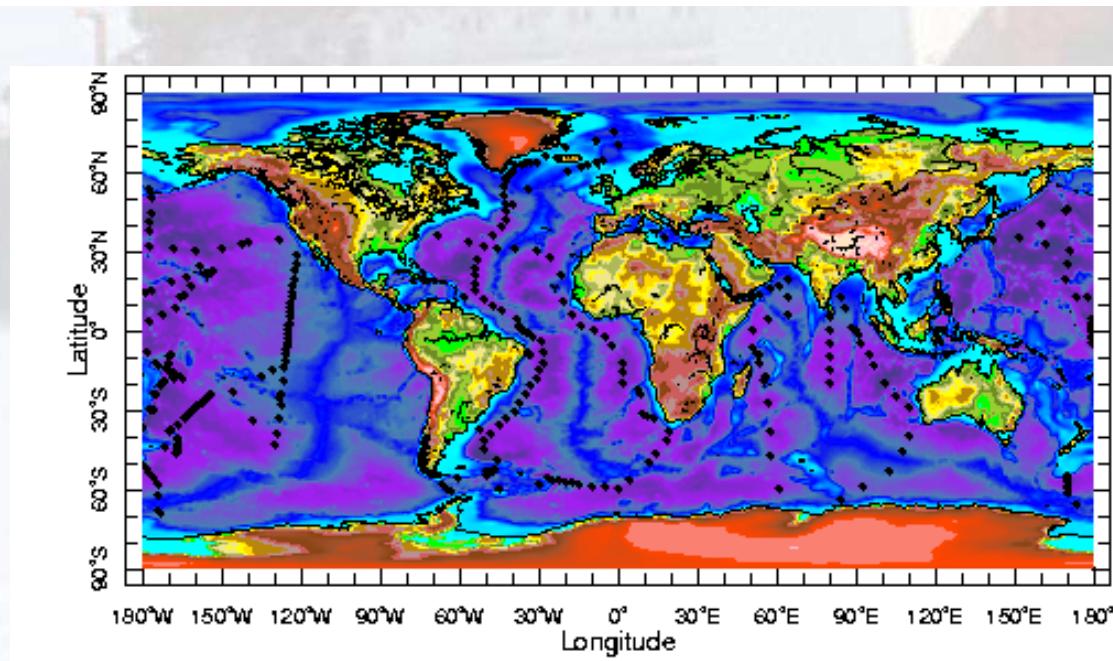
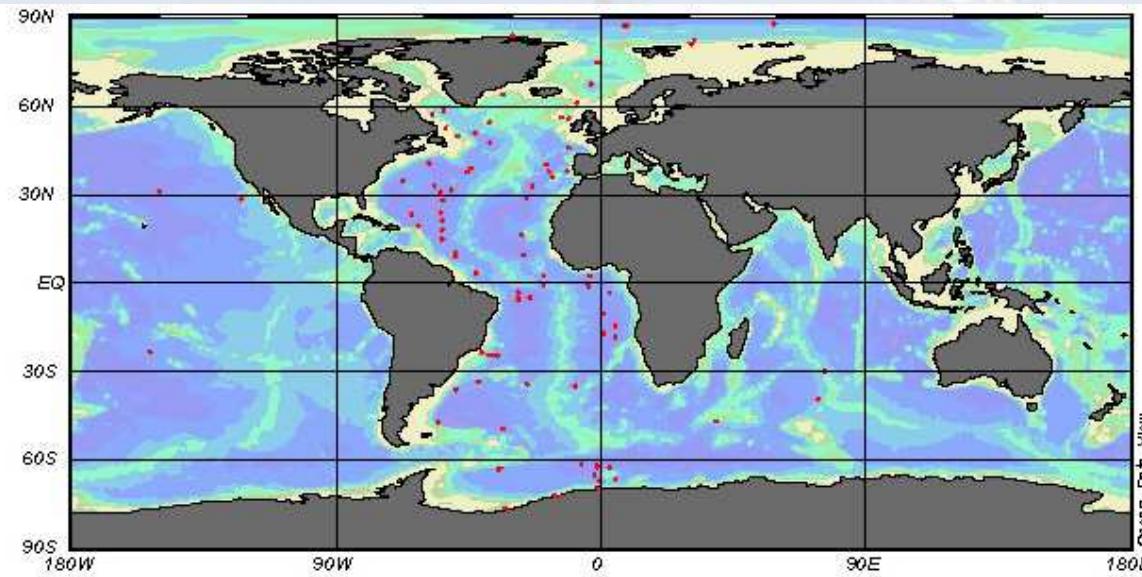
- In principle there is considerable support for Kr and Ar isotope measurements.
  - However, skepticism concerning the feasibility, as well the costs/benefit ratio.
  - These concerns have to be addressed before new resources can be secured.
  
  - In groundwater,  $^{39}\text{Ar}$  faces significant problems due to the in situ production.
  - There is a clear niche for  $^{85}\text{Kr}$  due to the complications of CFC dating.
  - Large amounts of water is not a real problem (small sample numbers).
  - Oceanic measurements typically were used to test the  $^{14}\text{C}$  data. Strong evidence for added value of oceanic  $^{39}\text{Ar}$  measurements needed.
  - There seems to be valuable information in  $^{39}\text{Ar}$  measurements for studies of the age spectra of water.
- 
- Noticeable lack in efforts on sophisticated interpretation of the existing  $^{39}\text{Ar}$  data.
  - New resources will not come from the presently largest hydrographic program that is just being started (CLIVAR/ $\text{CO}_2$  repeat sections).
  - It is critical to summarize the available data to form a solid foundation for proposals.
  - Best strategy to sell the development of Ar and Kr isotope measurement as a package.
  - Convene a mtg. to discuss these issues

# Ocean: $^{39}\text{Ar}$

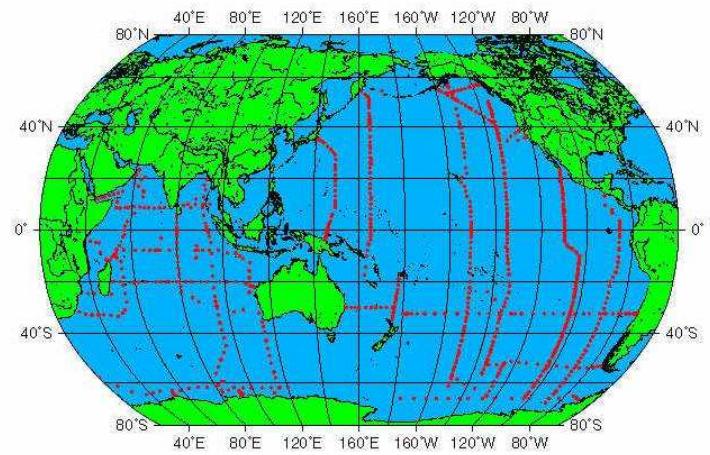


Source: Broecker, 1991, in Climate change 1995, Impacts, adaptations and mitigation of climate change: scientific-technical analyses, contribution of working group 2 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge press university, 1996.

# Ocean: $^{39}\text{Ar}$



U.S. WOCE  $\Delta^{14}\text{C}$  Station Locations



# Ocean: $^{39}\text{Ar}$

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P. Fritz and J.Ch. Fontes (Editors), *Handbook of Environmental  
Isotope Geochemistry*, Vol. 3. *The Marine Environment*, A.

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Chapter 11

386

## ARGON-39: A TOOL TO INVESTIGATE OCEAN WATER CIRCULATION AND MIXING

HEINZ HUGO LOOSLI

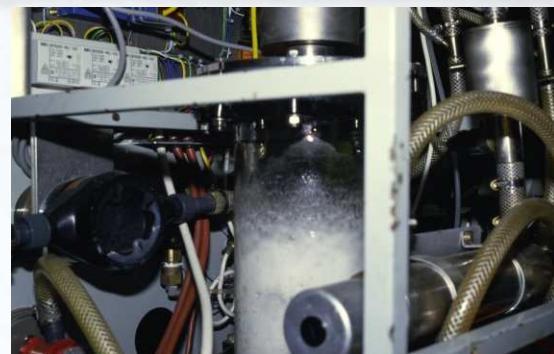


TABLE 11-1

Summarized characteristics of the radionuclide  $^{39}\text{Ar}$  and of the  $^{39}\text{Ar}$  dating method

<i>Decay</i>	
Half-life	269 years
$\beta$ energy	560 keV, no $\gamma$
<i>Production</i>	
Natural	by cosmic rays, mainly $^{40}\text{Ar}$ ( $n,2n$ ) reaction
Specific activity in air	$0.107 \pm 0.004$ dpm/l Ar
Concentration in air	$^{39}\text{Ar}/^{40}\text{Ar} = 1:1.2 \times 10^{15}$
Estimated variations of natural production	< 7% (in the last $10^3$ years)
Man-made contribution	< 5% (up to 1983)
<i>Sample collection from ocean water</i>	
Minimum amount of argon needed for activity measurement	250 ml Ar (STP)
Minimum amount of water to be degassed	1000 l
<i>Activity measurements</i>	
Volume of proportional counter	16 ml
Gas pressure in counter	10 – 30 atm
Background of counter	0.02 – 0.03 cpm
Modern net effect for 10 – 30 atm	0.012 – 0.036
Counting time of one sample	6 weeks
Dating range	20 – 1000 years
Relative statistical errors of $^{39}\text{Ar}$ results, 1 $\sigma$	examples: $50 \pm 20$ years $250 \pm 30$ years $600 \pm 80$ years

# Ocean: $^{39}\text{Ar}$

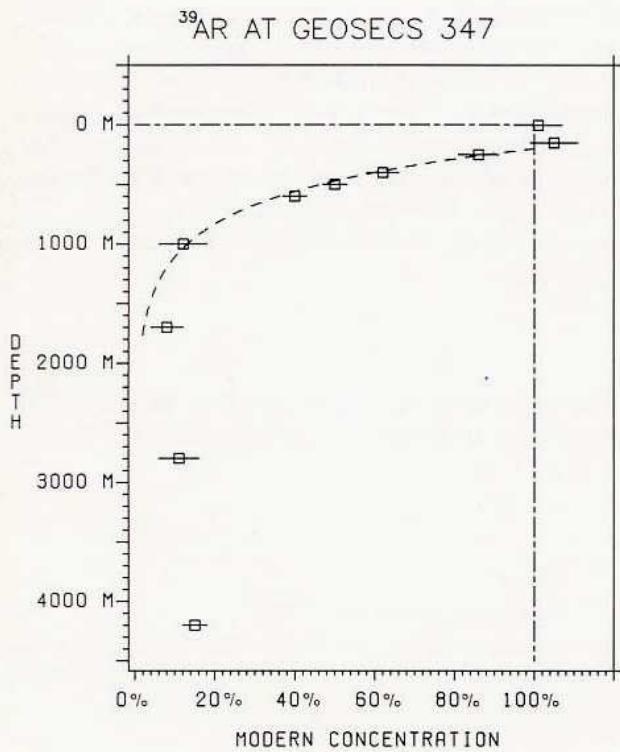


Fig. 11-2. Measured  $^{39}\text{Ar}$  depth profile in GEOSECS station 347 in the northeast Pacific (revisited in 1979). The sharply decreasing  $^{39}\text{Ar}$  activity from the mixed layer to about 1500 m can be approximated by an exponential function, which corresponds to a one-dimensional advection-diffusion approach. The dotted line represents the best fit yielding a penetration depth of 500 m. The  $^{39}\text{Ar}$  activity in the deep samples developed mainly from the activity of circumpolar deep water, which decreased during the flow from south to north.

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Chapter 11

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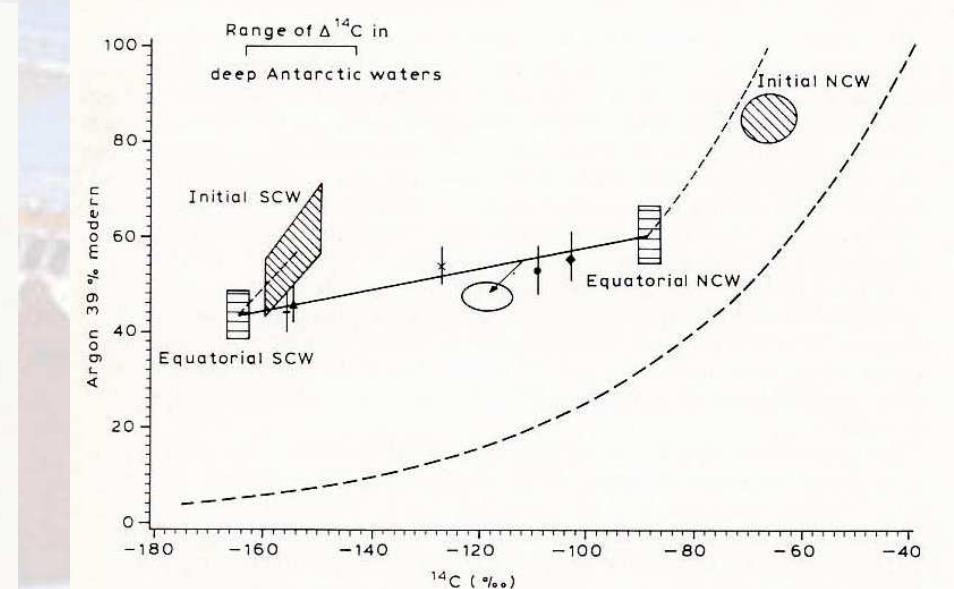


Fig. 11-1.  $^{39}\text{Ar}$  versus  $\Delta^{14}\text{C}$  plot for Atlantic water masses. In the center of the figure, a mixing line between equatorial Southern Component Water (SCW) and equatorial Northern Component Water (NCW) is given. The activity of these two water masses decreases during the flow from their *initial* source areas to the equator; dotted lines represent parallel  $^{14}\text{C}$  and  $^{39}\text{Ar}$  decay without mixing. Northeast Atlantic deep waters are marked by an open circle; they developed by ageing from equatorial mixed water (arrow). For details see Schlitzer et al. (1985).



# Ocean: $^{39}\text{Ar}$



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Nuclear Instruments and Methods in Physics Research B 172 (2000) 473-478

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## Comparison of $^{39}\text{Ar}$ and $^{14}\text{C}$ ages for waters in the deep ocean

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### Abstract

$^{39}\text{Ar}$  ages on ocean water samples are consistently younger than  $^{14}\text{C}$  ages. The difference is the result of diffusive mixing in the sea which has a greater impact on ages based on short-lived than those based on long-lived radiotracers. It is clear that a more dense survey of  $^{39}\text{Ar}$  with higher accuracy measurements would prove of great value in constraining ocean general circulation models. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 92.10.M

Keywords: Oceans; Thermohaline structure and circulation

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# Ocean: $^{39}\text{Ar}$

478

W.S. Broecker, T.-H. Peng / Nucl. Instr. and Meth. in Phys. Res. B 172 (2000) 473–478

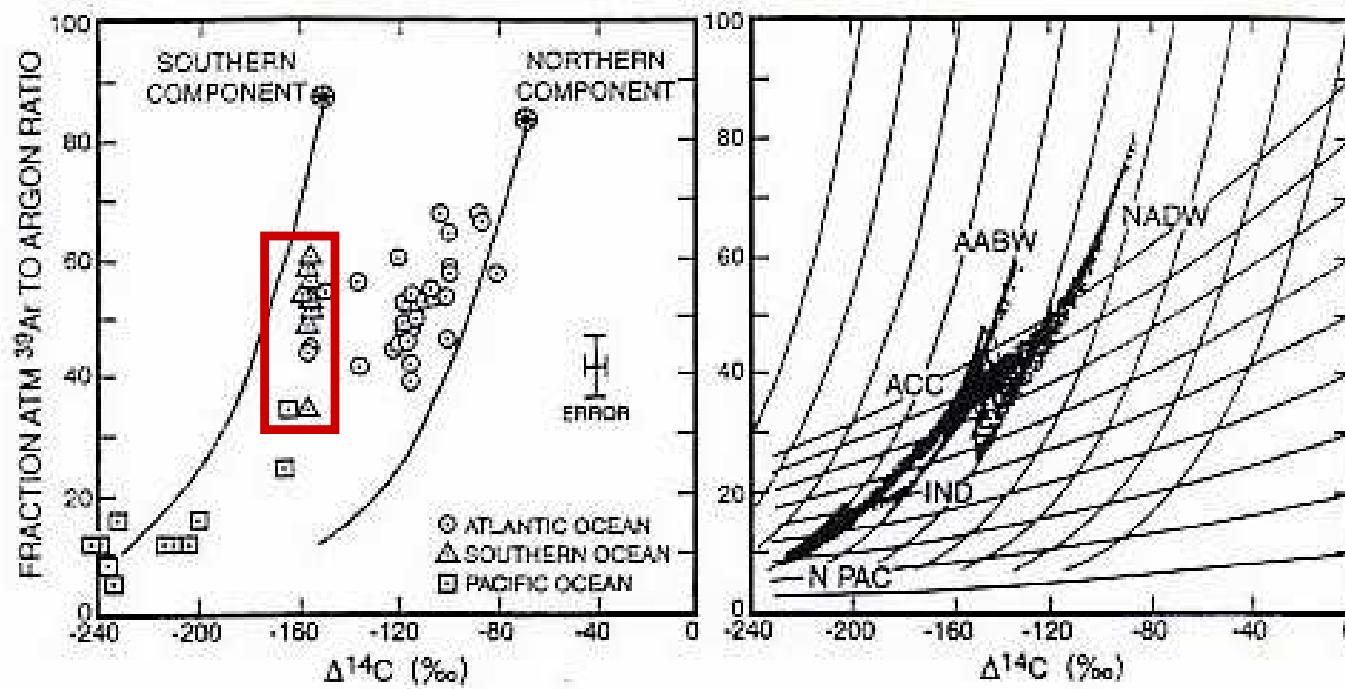


Fig. 3. Comparison between the measurements (left) and the output of the Hamburg ocean model (right). In both, the trends expected for radiodecay alone are shown. For the Hamburg ocean model [12], the set of lines with the lower slope reflect the impact of diffusion. The two trend lines shown in the left-hand panel portray the influence of radiodecay on deep water formed in the northern Atlantic and Southern Ocean, respectively.

# Ocean: $^{39}\text{Ar}$ in the Weddell Sea

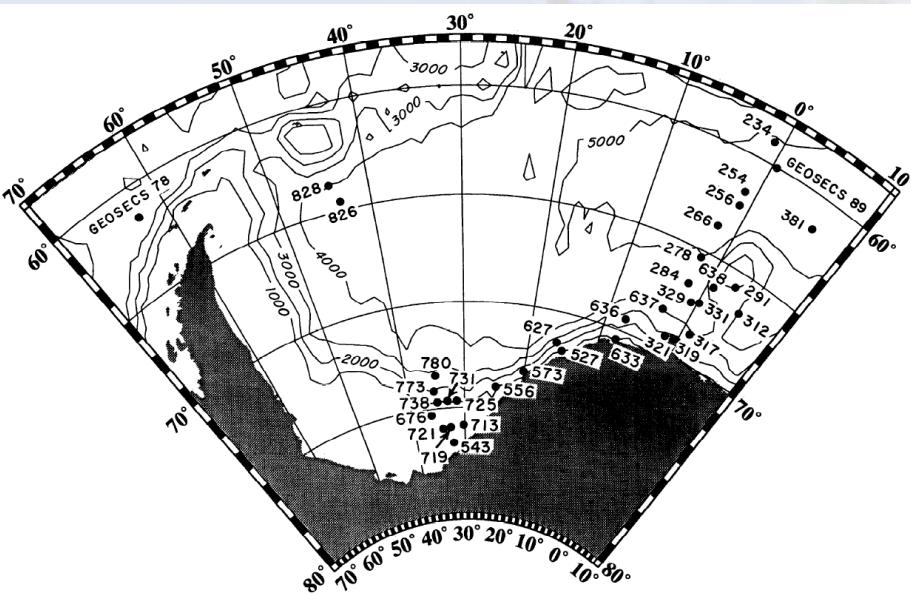


Figure 1. Geographical positions of the stations occupied during WWSP 86 and ANT V/4 (stations 773, 780, 826, 828).

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 99, NO. C5, PAGES 10,275–10,287, MAY 15, 1994

## The distribution of $^{14}\text{C}$ and $^{39}\text{Ar}$ in the Weddell Sea

P. Schlosser,<sup>1,2</sup> B. Kromer,<sup>3</sup> R. Weppernig,<sup>1,4</sup> H.H. Loosli,<sup>4</sup> R. Bayer,<sup>3</sup> G. Bonani,<sup>5</sup> and M. Suter<sup>5</sup>

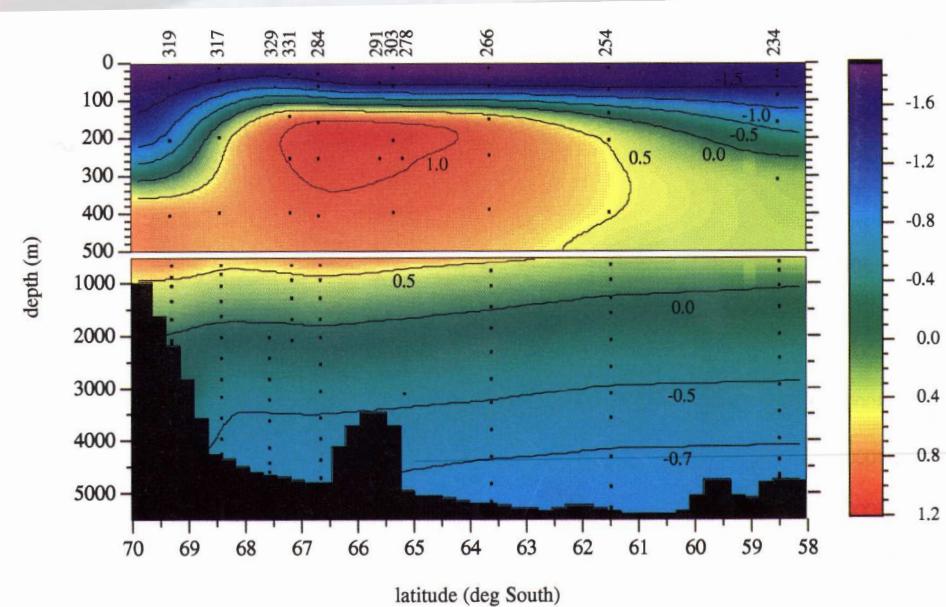
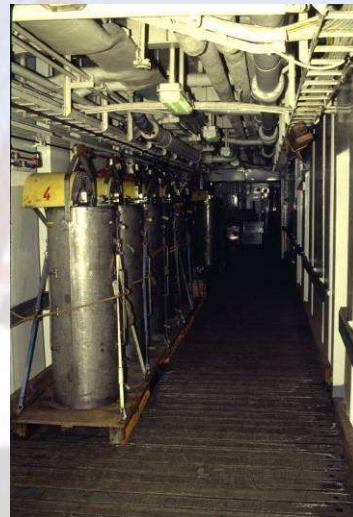


Plate 1. Potential temperature section along the 0° longitude section (data from reversing thermometers attached to the Gerard-Ewing water samplers).

# Ocean: $^{39}\text{Ar}$ in the Weddell Sea

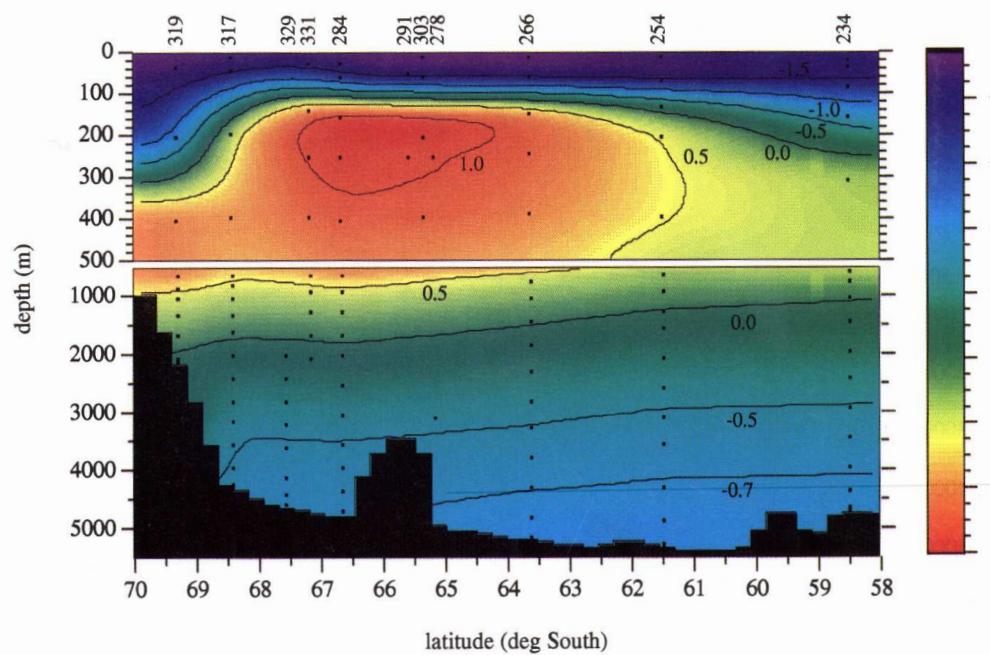


Plate 1. Potential temperature section along the  $0^{\circ}$  longitude section (data from reversing thermometers attached to the Gerard-Ewing water samplers).

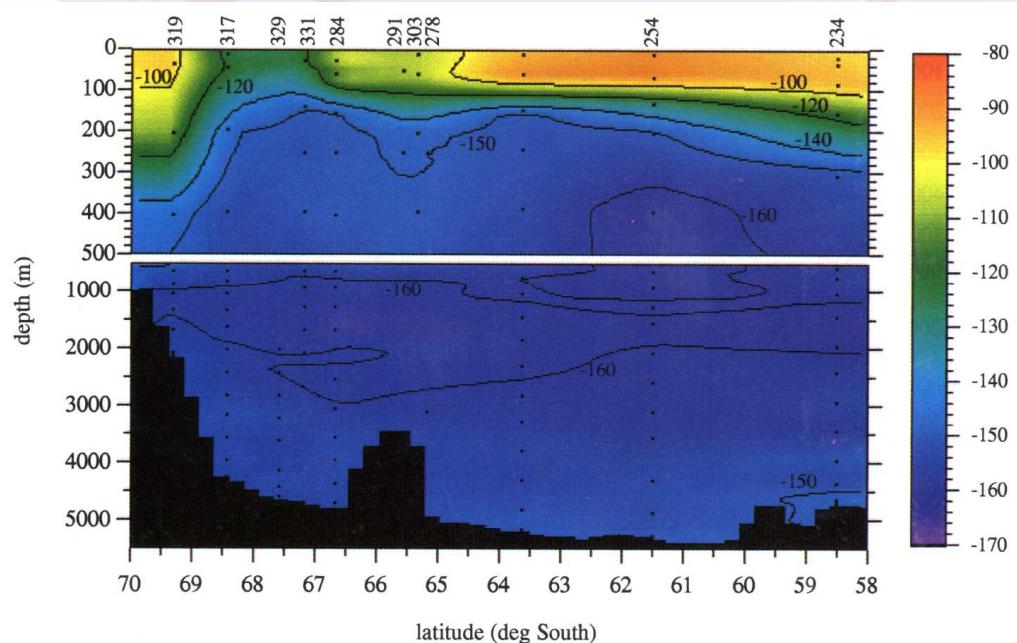


Plate 2. The  $\Delta^{14}\text{C}$  section along  $0^{\circ}$  longitude.

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 99, NO. C5, PAGES 10,275–10,287, MAY 15, 1994

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# Ocean: $^{39}\text{Ar}$ in the Weddell Sea

10,280

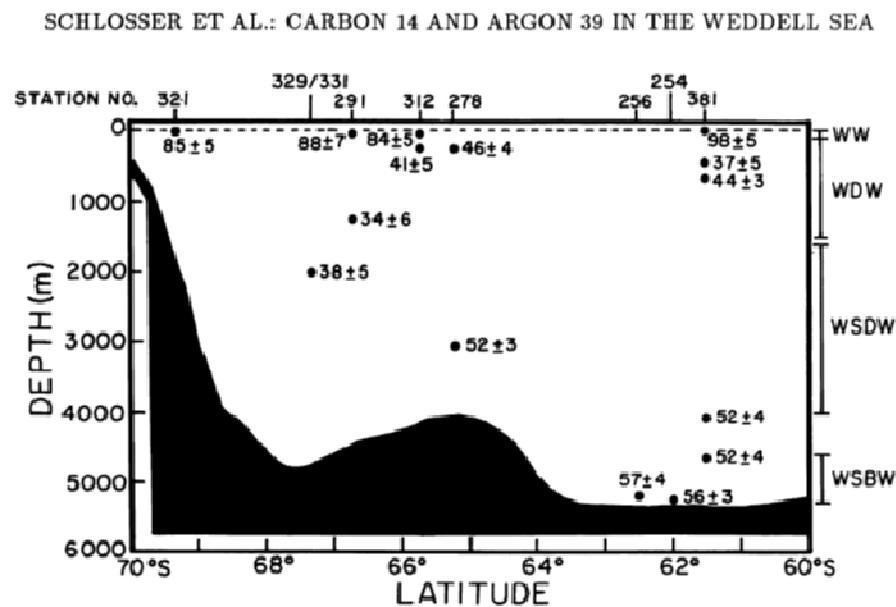


Figure 4. The  $^{39}\text{Ar}$  results plotted on a section across the Weddell Sea along  $0^\circ$  longitude.

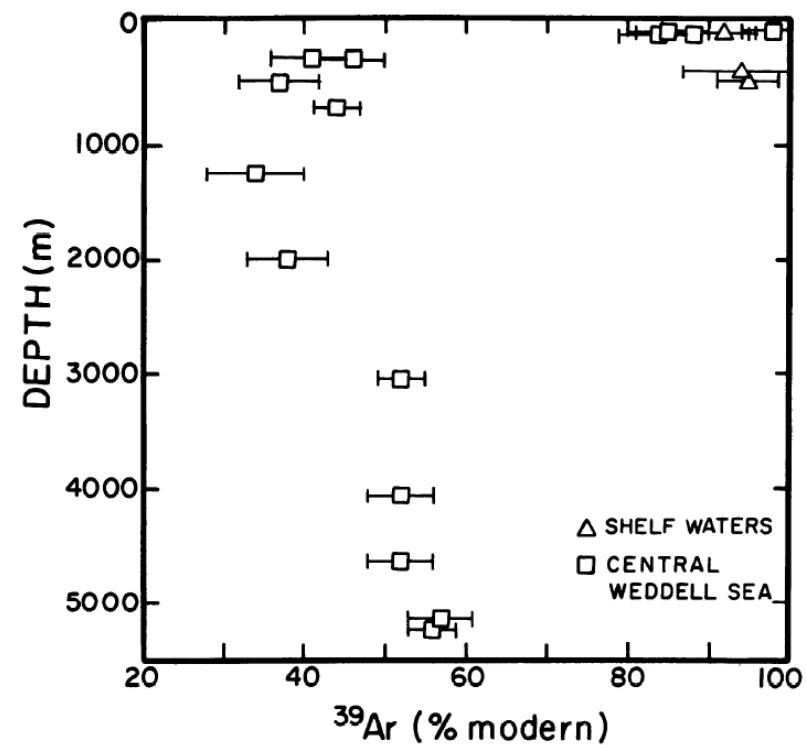


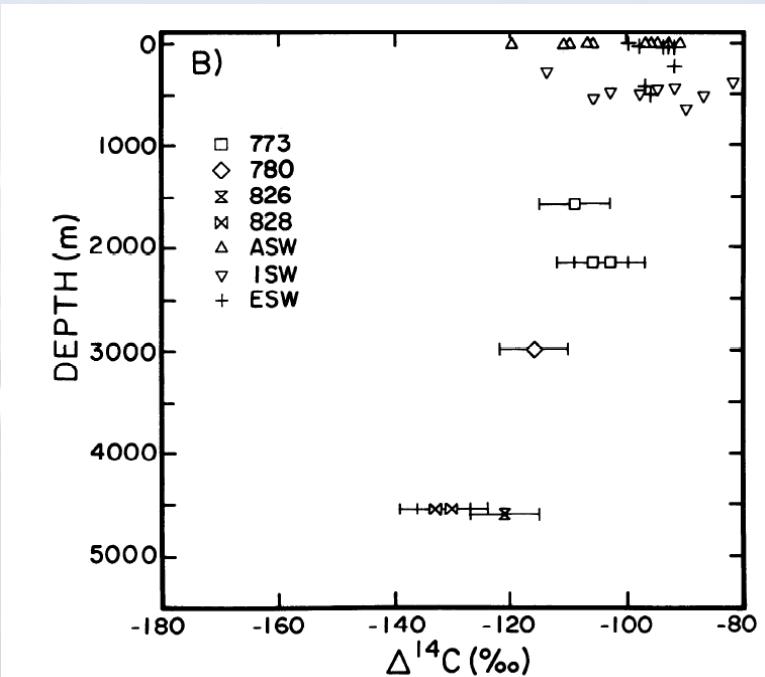
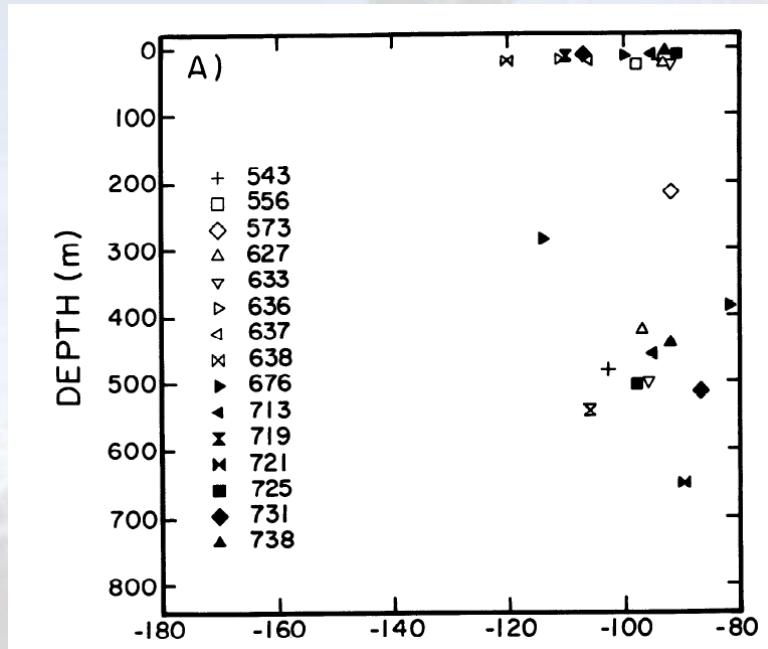
Figure 5. The  $^{39}\text{Ar}$  data summarized in a composite depth profile.

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 99, NO. C5, PAGES 10,275–10,287, MAY 15, 1994

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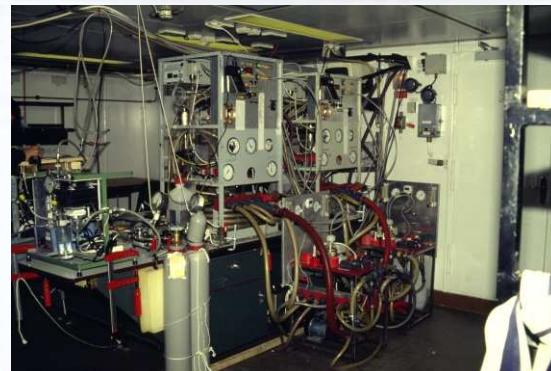


**Figure 3.** (a) Depth profiles of  $\Delta^{14}\text{C}$  for stations located on the shelf (for geographic position, see Figure 1). (b) Same as Figure 3a for stations located on the continental slope (stations 773, 780, 826, 828). The  $\Delta^{14}\text{C}$  values of the shelf samples are categorized by water mass.

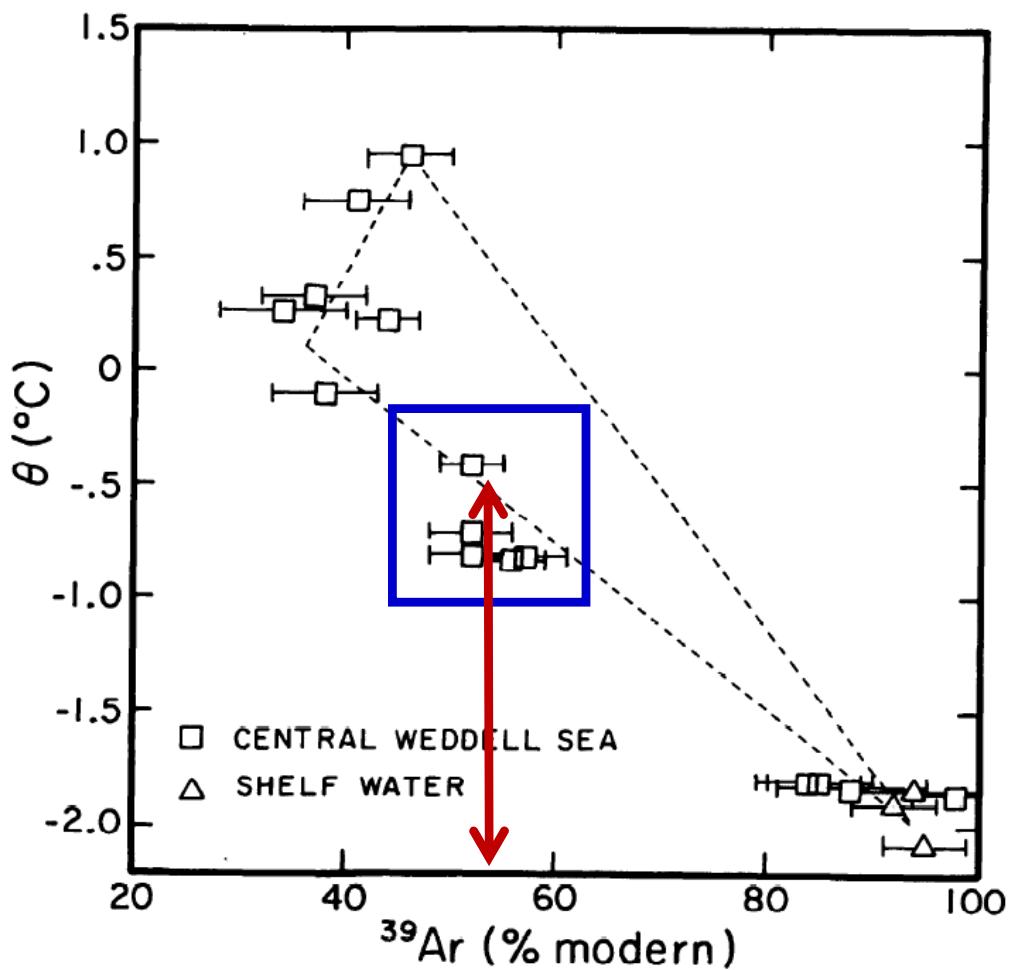
JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 99, NO. C5, PAGES 10,275–10,287, MAY 15, 1994

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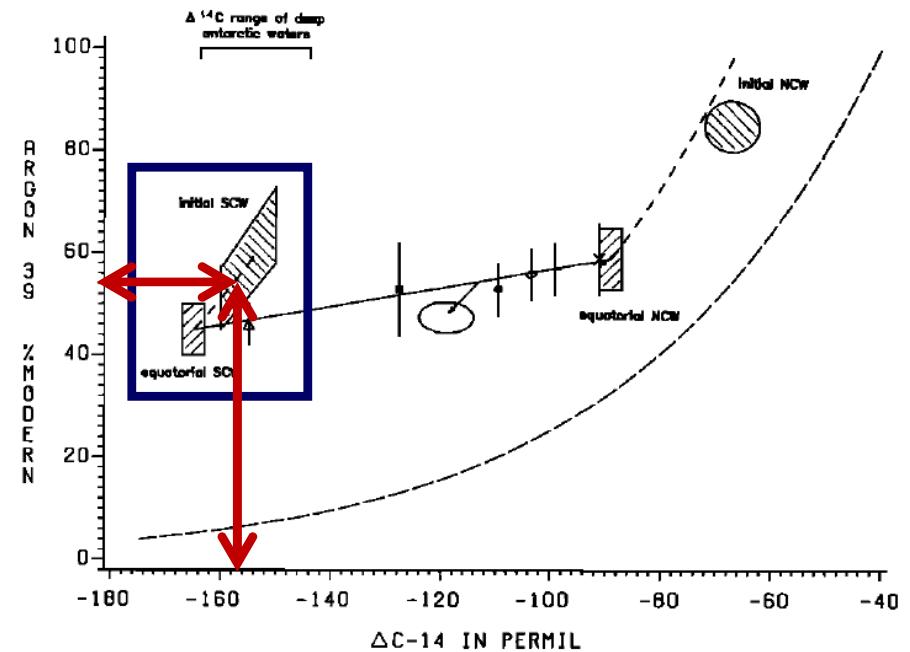


**Figure 11.** Potential temperature versus  $^{39}\text{Ar}$  plot for all WWSP 86 samples.

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 99, NO. C5, PAGES 10,275–10,287, MAY 15, 1994

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**Fig. 9.** Extended  $^{39}\text{Ar}$  versus  $^{14}\text{C}$  plot. Hatched areas represent the data of Table 4. Dashed lines represent lines of parallel  $^{14}\text{C}$  and  $^{39}\text{Ar}$  decay without mixing. For explanation, see text. The  $\Delta^{14}\text{C}$  range of deep Antarctic waters [Weiss et al., 1979] is shown for comparison.

55 %; -156 per mil

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 90, NO. C4, PAGES 6945–6952, JULY 20, 1985

## A Meridional $^{14}\text{C}$ and $^{39}\text{Ar}$ Section in Northeast Atlantic Deep Water

REINER SCHLITZER AND WOLFGANG ROETHER

Institut für Umweltphysik, Universität Heidelberg, Federal Republic of Germany

URS WEIDMANN, PETER KALT, AND HEINZ HUGO LOOSLI

Physikalisches Institut, Universität Bern, Switzerland

# Ocean: $^{39}\text{Ar}$ in the Arctic Ocean (NB)

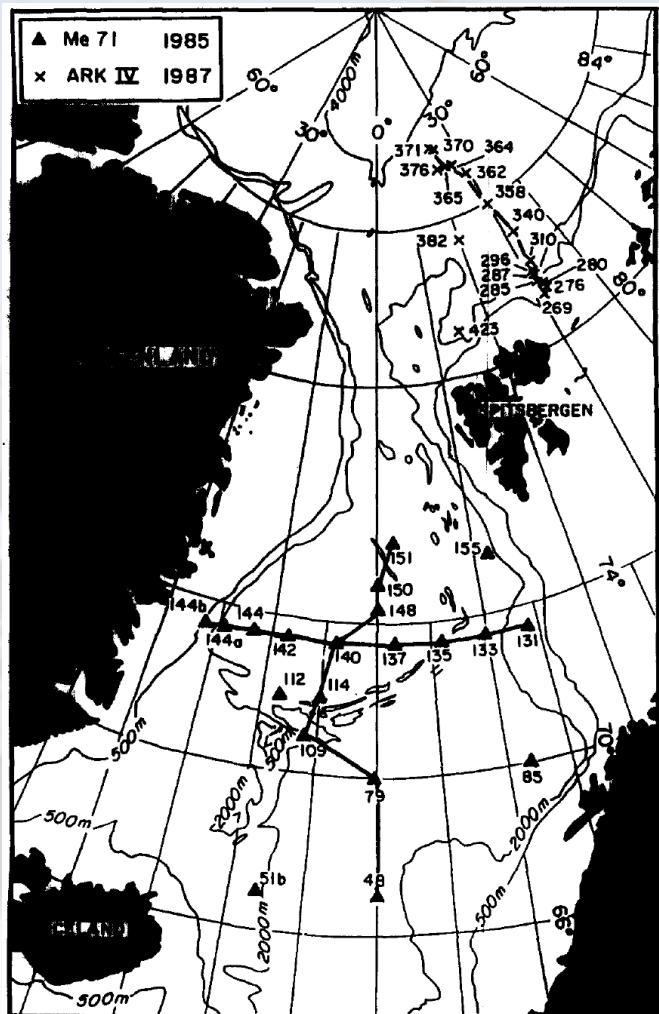


FIG.1. Geographic positions of the *Meteor 71* and *ARK IV/3* stations.



Pergamon

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0079-6611(95)00003-00

Mid-1980s distribution of tritium,  $^3\text{He}$ ,  $^{14}\text{C}$  and  $^{39}\text{Ar}$  in the Greenland/Norwegian Seas and the Nansen Basin of the Arctic Ocean

PETER SCHLOSSER<sup>1,2</sup>, GERALD BENIGH<sup>1</sup>, BERND KOMER<sup>1</sup>, H. HEIKO LÖSSL<sup>1</sup>, RENÉDKI BÖHLER<sup>4</sup>,  
RINHOLD BAYER<sup>1</sup>, GEORGES BOUAN<sup>1</sup> and KLAUS PETER KOTTERMANN<sup>3</sup>

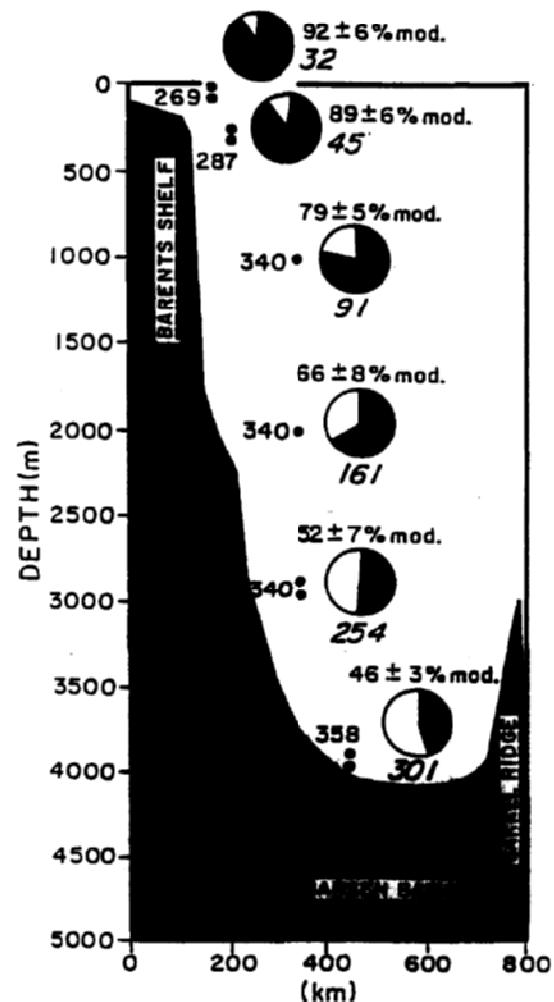
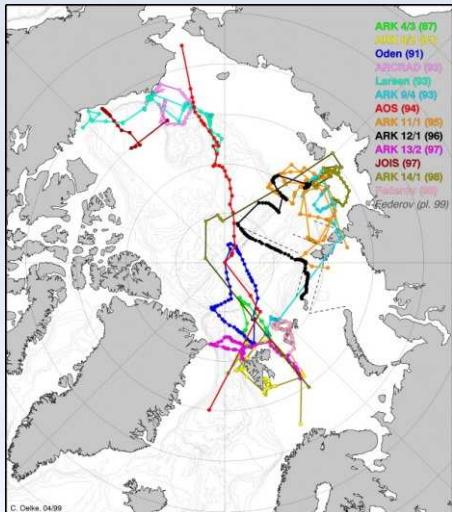


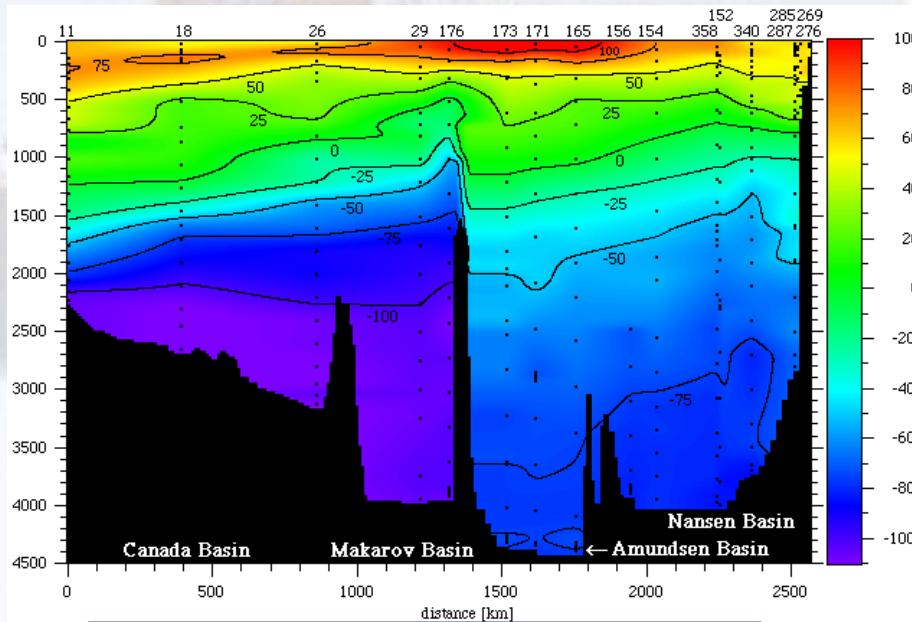
FIG.5.  $^{39}\text{Ar}$  distribution in the main water masses of the Nansen Basin. The symbols display the  $^{39}\text{Ar}$  concentration in % modern. Full symbols would mean 100% modern, open circles would indicate 0% modern.

$\Delta^{39}\text{Ar} \approx 46$  per cent; ca. 270 ys

# Ocean: $^{39}\text{Ar}$ in the Arctic Ocean (NAM B)

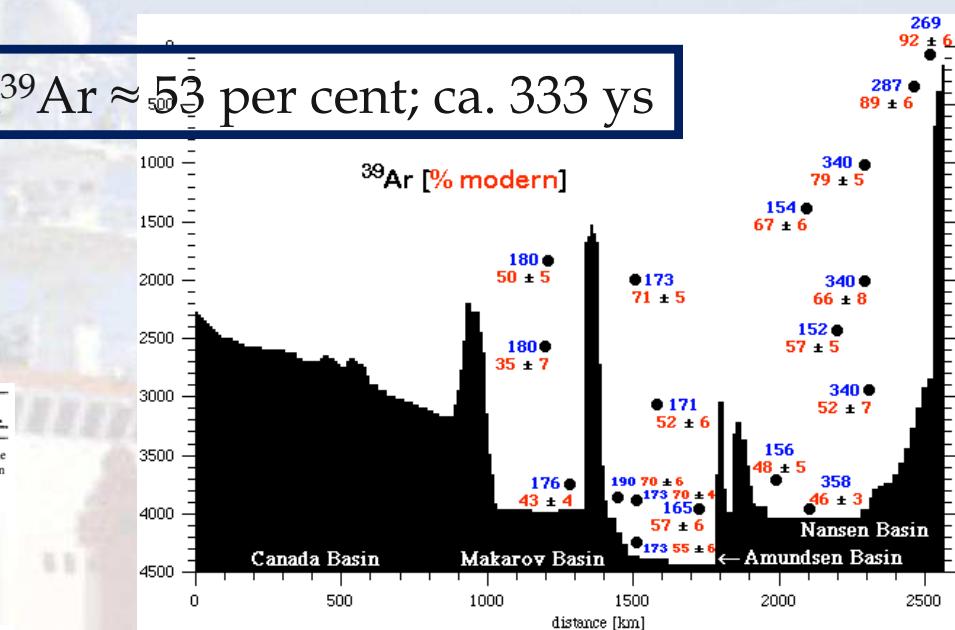


Nucl. Instruments and Methods in Physics Research B 121 (1997) 411-417  
NH  
ELSEVIER  
The first trans-Arctic  $^{14}\text{C}$  section: comparison of the mean ages of the deep waters in the Eurasian and Canadian basins of the Arctic Ocean  
Peter Schlosser <sup>a,b</sup>, Bernd Kramer <sup>c</sup>, Brenda Ekwaruz <sup>b</sup>, Gerhard Reimach <sup>c</sup>,  
Ann McNicol <sup>d</sup>, Robert Schneider <sup>e</sup>, Karl von Reden <sup>f</sup>, H.G. Ostlund <sup>f</sup>, J.H. Swift <sup>f</sup>

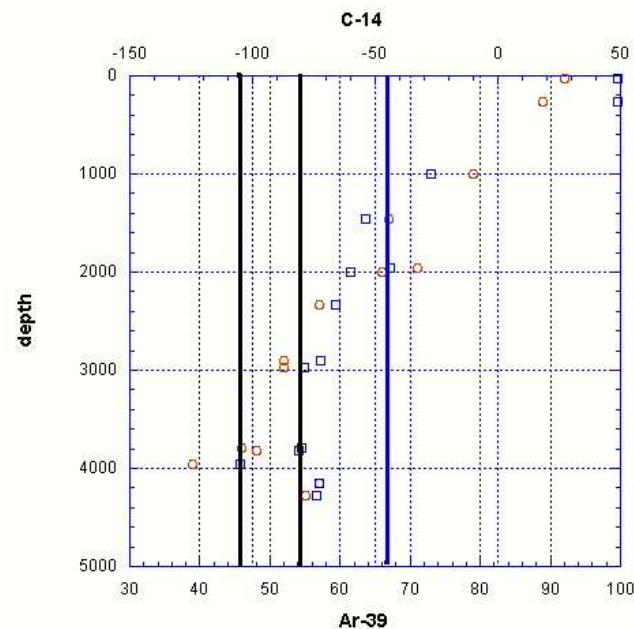


$\Delta\Delta^{14}\text{C} \approx 25/20/50$  per mil;  
ca. 200/160/400 ys

$\Delta^{39}\text{Ar} \approx 53$  per cent; ca. 333 ys



$\Delta^{39}\text{Ar} \approx 46(36)$  per cent; ca. 270(193) ys



# Mean Residence Times

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P. Schlosser et al. / The Science of the Total Environment 237 / 238 (1999) 15–30

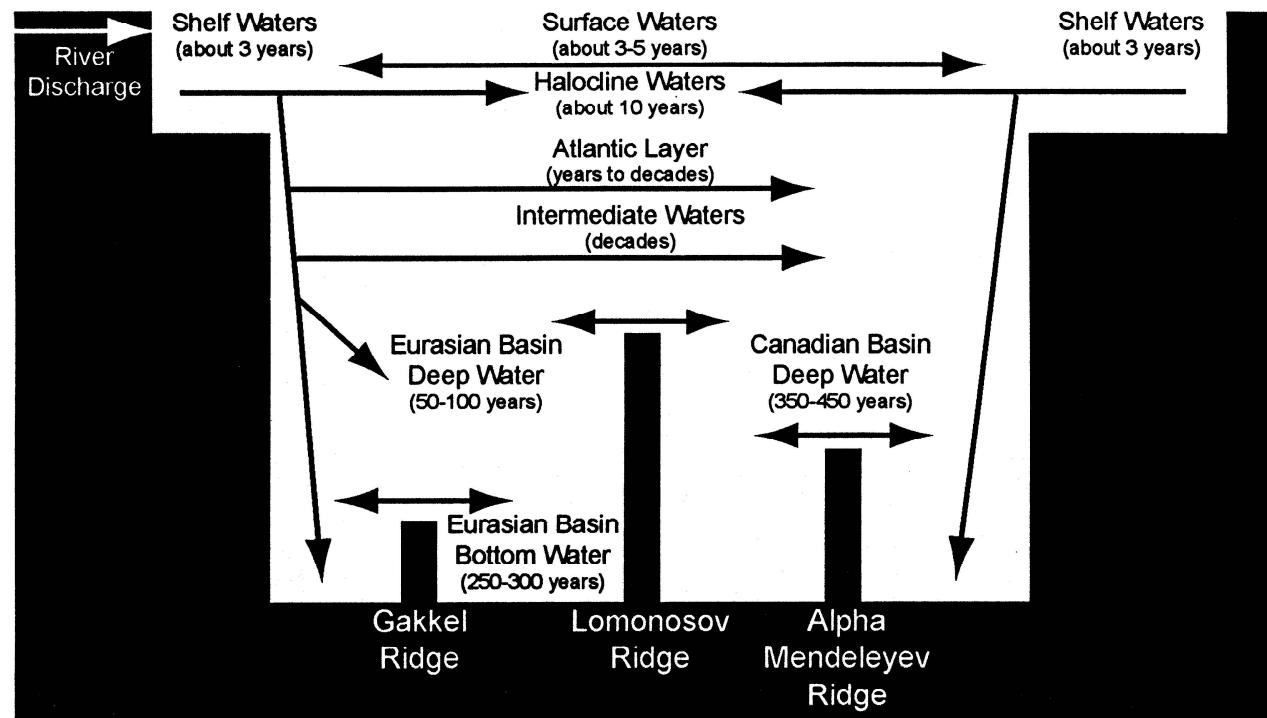
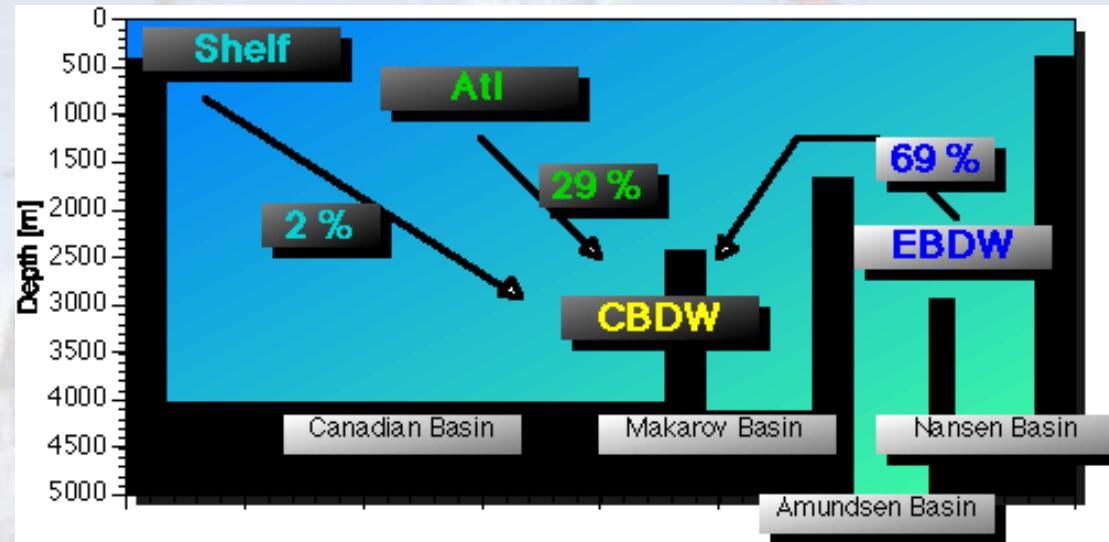
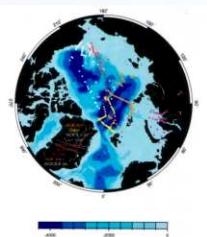


Fig. 9. Schematic diagram of the mean residence times of the waters in the Arctic Ocean derived in this and previous studies.

# Water mass composition



	pot.Temp [C]	Salinity	$^{14}\text{C}$ [%o]	$^{39}\text{Ar}$ [%]
Atl	0.8 (0.05)	34.9 (0.05)	-65 (5)	90 (5)
Shelf	-1.8 (0.1)	36.5 (1)	-51.5 (3.5)	100 (5)
EBDW	-0.872 (0.005)	34.927 (0.005)	-73.5 (3.5)	66 (4)
CBDW	-0.4 (0.05)	34.95 (0.01)	-105 (5)	42 (4)



# Mean Residence Times: ‘Model’

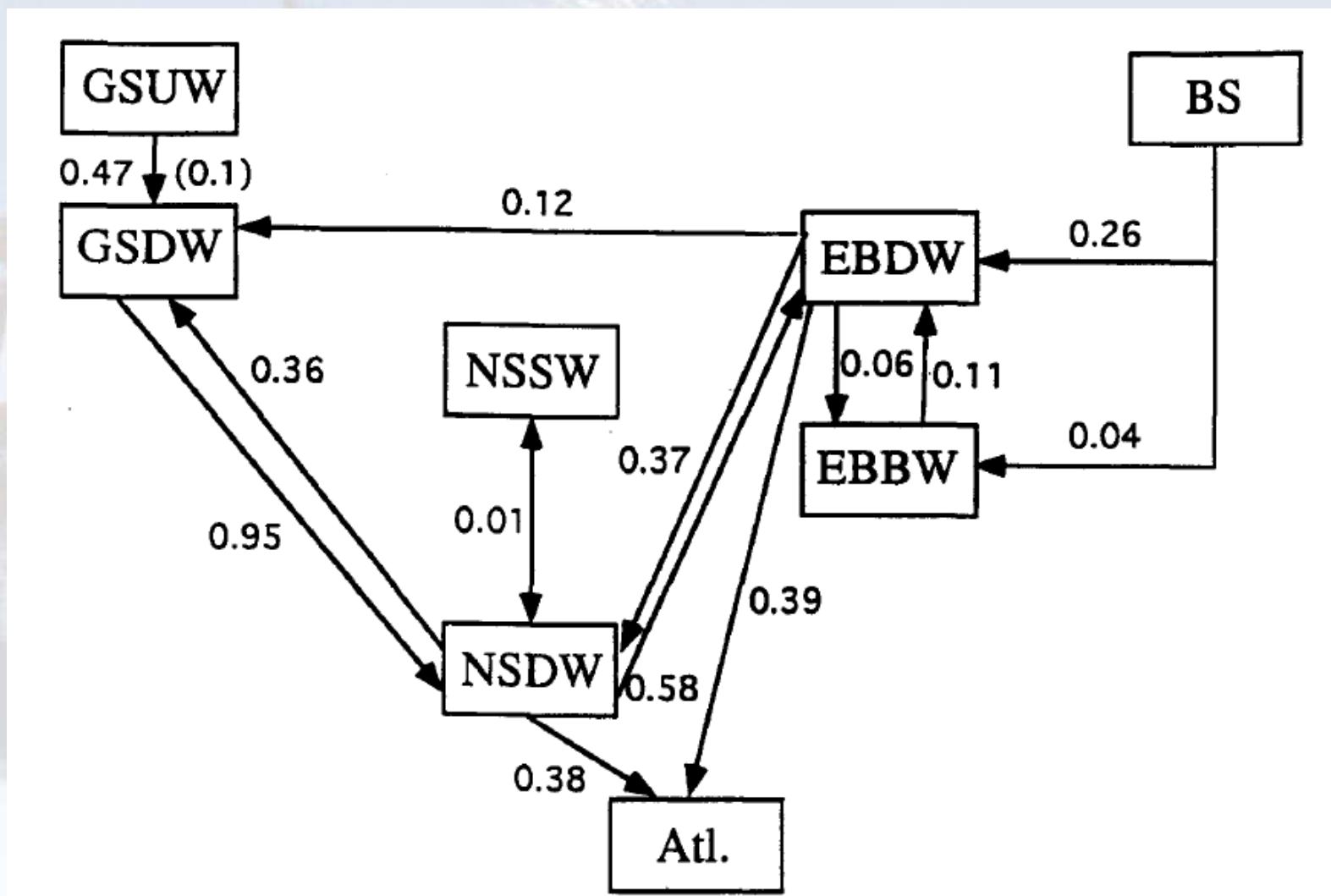


FIG.8. Schematic view of the box model. Fluxes between individual boxes are indicated in Sv (rounded to 0.01Sv).

$\Delta^{39}\text{Ar} \approx 60$  per cent; ca. 350 ys

# Ocean: $^{39}\text{Ar}$

## 6. Conclusions

The bottom line is that  $^{39}\text{Ar}$  ages are by no means redundant to  $^{14}\text{C}$  ages. Rather, they offer two pieces of additional information:

1. as the ratio of the two ages is strongly influenced by diffusive mixing,  $^{39}\text{Ar}$  offers a means to constrain the model parameters for this sub-grid scale process;
2. as  $^{39}\text{Ar}$  has a half life (270 years) shorter than the ocean mixing time (i.e.,  $\sim 800$  years), its distribution might carry hints regarding changes in the ventilation of the deep sea during the course of the last mixing cycle.

# Volume considerations



POLARSTERN  
RV POLARSTERN  
Cruise: ARCTIC VIII/3 1991  
Present Position of the Ship:  
90° 0.00'N 36° 17.88'E  
7-SEP-1991 10:35:18.96

# CLIVAR repeat lines

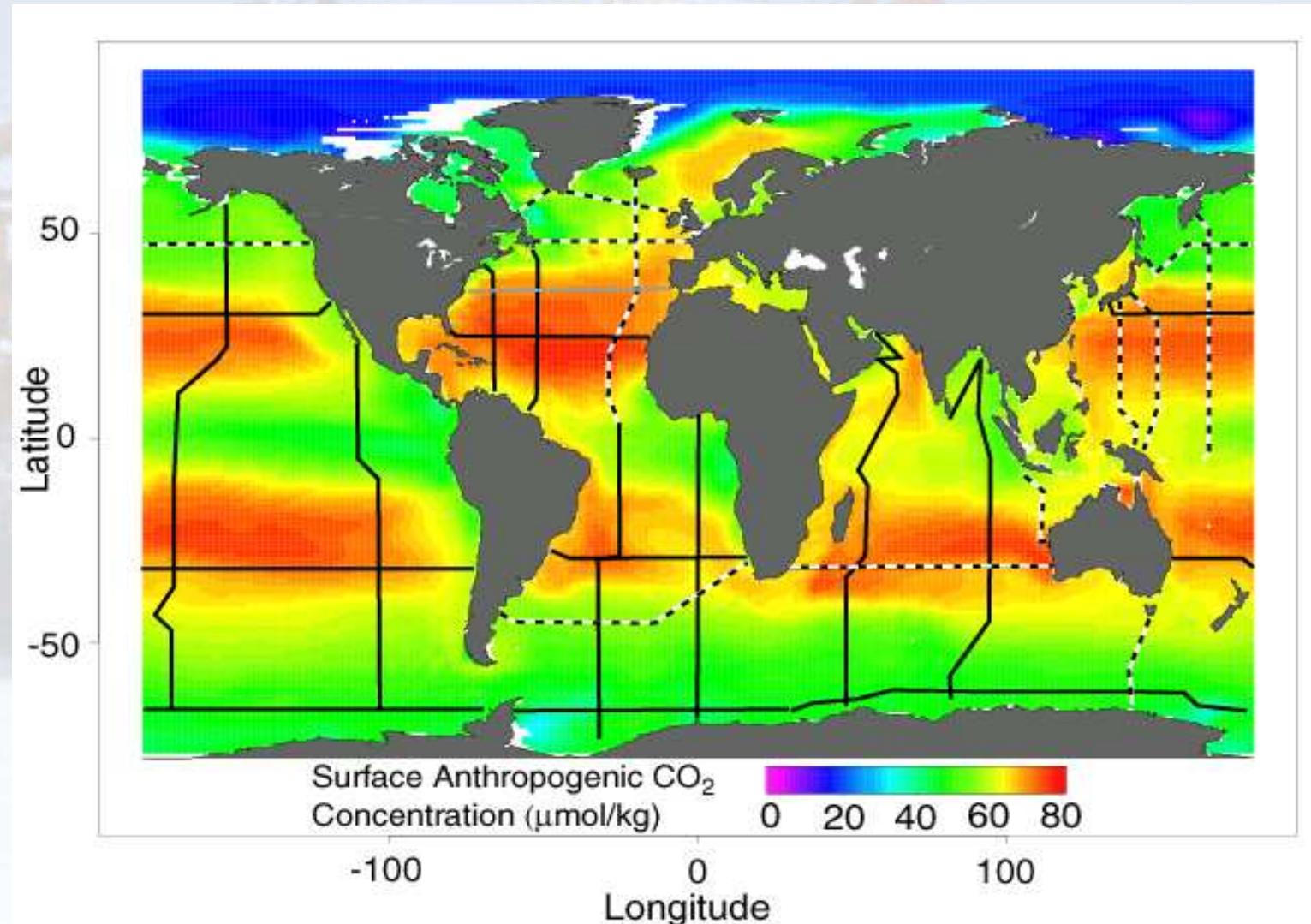
## Priority 1 Measurements

- CTD pressure, temperature, conductivity (salinity)
- CTD oxygen (sensor)
- Bottle salinity
- Nutrients by standard auto analyzer ( $\text{NO}_3/\text{NO}_2$ ,  $\text{PO}_4$ ,  $\text{SiO}_3$ )
- Dissolved oxygen ( $\text{O}_2$ )
- Chlorofluorocarbon tracers CFC-11, -12, -113
- Tritium- ${}^3\text{He}$
- Surface underway system: T, S, pCO<sub>2</sub>
- ADCP shipboard
- ADCP lowered

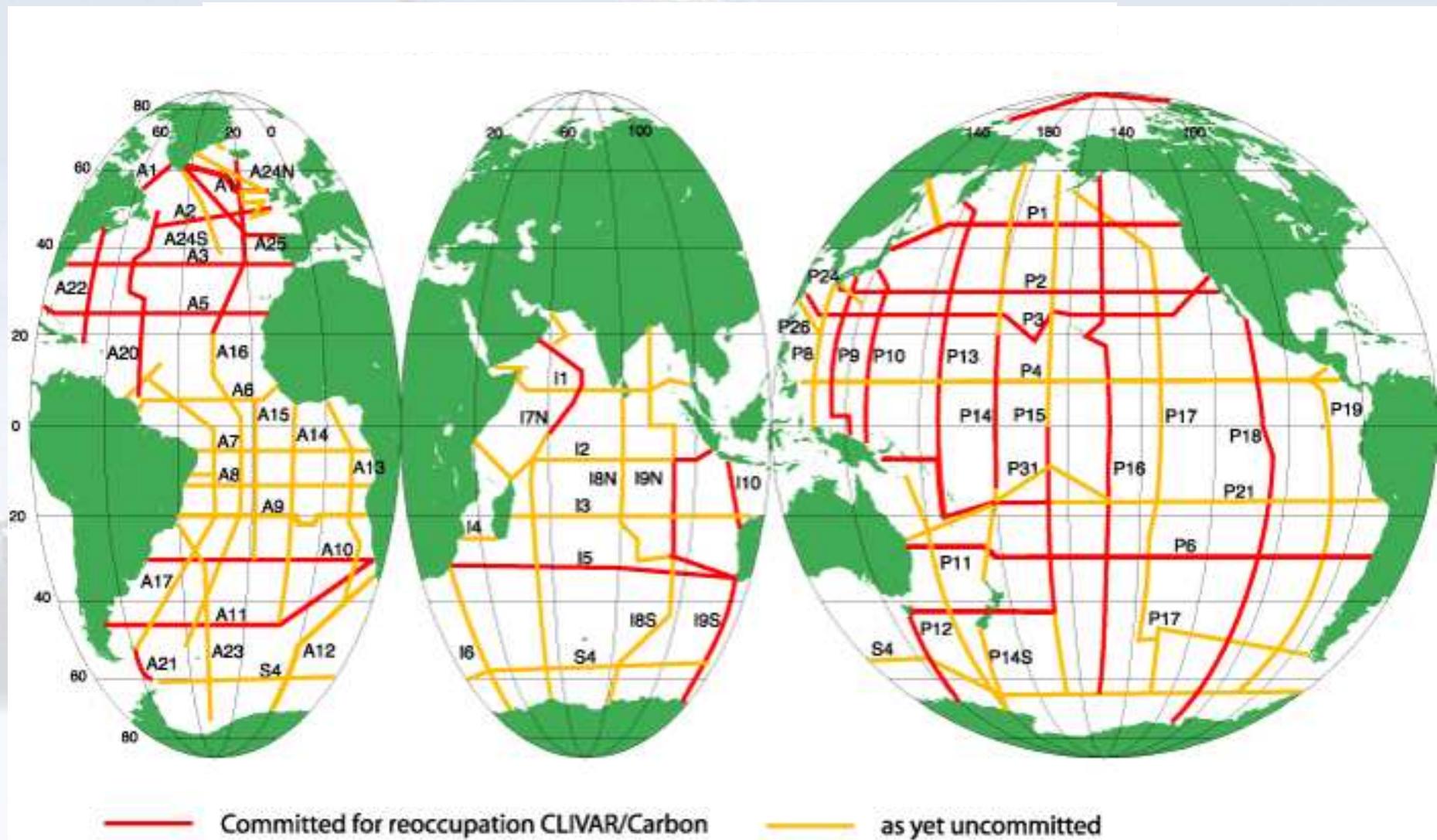
# International CLIVAR/CO<sub>2</sub> Lines (including US)

[Tentative!!!!]

Black = proposed US lines; Black&White = committed international lines;  
Gray = additional lines proposed for CLIVAR



# The WOCE/JGOFS Survey 1990-98 and Future Commitments



International efforts are summarized at:

From: <http://clivar-search.cms.udel.edu/oceanobs/>

## Objectives of the Repeat Hydrography Effort

- Data for Model Calibration and Validation
- Heat and freshwater storage and flux studies:
  - \* Divergence of transport-surface fluxes
  - \* Transport of heat and salt
  - \* Storage of heat and freshwater
  - \* Globally changing inventories of heat and fresh water
- Deep and shallow water mass and ventilation studies:
  - \* Changes in subduction and formation rates
  - \* Water mass ages
  - \* Pathways of ventilation
  - \* Rates of dilution
- Calibration of autonomous sensors:
  - \* ARGO salinity sensors
  - \* Biogeochemical moorings and floats
  - \* Relationships between sensors and other properties
- Carbon system studies:
  - \* Changes in anthropogenic carbon inventory
  - \* Transport of carbon, oxygen and nutrients
  - \* Large scale natural and anthropogenic variability of biogeochemical properties

# Prioritization of Observations

## **Level I, core measurements:**

Mandatory on all cruises; suggested standard for international collaborators; measured at highest spatial resolution practical; funded through the omnibus proposal across all cruises.

## **Level II, recommended measurements:**

Highly desirable on subset of US cruises; may be collected on coarser station spacing; coordinated with the core effort but funded by separate proposals either on a cruise by cruise basis or by specific measurement.

## **Level III, ancillary measurements:**

On opportunity and space available basis; not to significantly interfere with Level I or II effort; may be regional or specific to individual cruise; extramural funding.

## Level I: Core Measurements

Rationale based on measurements required to directly quantify change in ocean carbon inventory, estimate anthropogenic CO<sub>2</sub> empirically, characterize large-scale water mass ventilation rates, constrain horizontal heat, freshwater, C, N, and O<sub>2</sub> transports and/or net divergence, and provide on-going basis for model evaluation.

### *Measurements*

Dissolved inorganic carbon (DIC) \*\*\*

Total Alkalinity (TALK) \*\*\*

CTD pressure, temperature, conductivity (salinity) \*\*\*

CTD oxygen (sensor)

Bottle salinity \*\*\*

Nutrients by standard auto analyzer (NO<sub>3</sub>/NO<sub>2</sub>, PO<sub>4</sub>, SiO<sub>3</sub>)\*\*\*

Dissolved oxygen (O<sub>2</sub>)\*\*\*

Chlorofluorocarbon tracers CFC-11, -12, -113 \*\*\*

Tritium-<sup>3</sup>He

Total organic carbon

Total organic nitrogen

Surface underway system: T, S, pCO<sub>2</sub>

ADCP shipboard\*\*\*

ADCP lowered

\*\*\*: unanimous agreement amongst working group members

\* Level II: related to large-scale carbon cycle and/or ventilation  
specific rationale listed after measurement; possibly on coarser  
spatial resolution than Level I but on all cruises

pH	(internal carbonate system consistency)
Discrete pCO <sub>2</sub>	(internal carbonate system consistency)
<sup>14</sup> C by AMS	(bomb penetration; southern ocean circulation changes; may need to repeat only on 20 year time-scale) (to extend range of age tracers further back in time (CCl <sub>4</sub> ) and into the future (SF <sub>6</sub> ))
CCl <sub>4</sub> and SF <sub>6</sub>	
del <sup>13</sup> C of DIC	(independent measure of anthropogenic CO <sub>2</sub> uptake and inventory changes)
Fe/trace metals	(others? Zn? Al for dust? There are three sampling approaches <ul style="list-style-type: none"><li>-on "regular" rosette</li><li>-Teflon/plastic water sampler hanging below CTD</li><li>-Separate Kevlar wire; separate casts)</li></ul>
Transmissometer	(POC distribution; ambiguity as to calibration; regional?)
More complete surface underway system:	<i>nutrients, O<sub>2</sub>, Chl, DIC, surface skin temperature</i>

## \* Level III: Upper ocean biogeochemistry and cycling

Chlorophyll

Primary production

HPLC pigments

Experimental continuous analyzers (*as they develop and go full depth*)

del  $^{15}\text{N}$  NO<sub>3</sub>

$^{32}\text{Si}$

$^{18}\text{O}$  of H<sub>2</sub>O

NH<sub>4</sub>

Low level nutrients

Total organic phosphorus

Upper ocean optical profile

(*on deck incubations*)

(*phytoplankton community comp.*)

(*as they develop and go full depth*)

(*nutrient utilization*)

(*difficult to measure??*)

(*similar to AMT line; algorithm development/validation; short cast; needs to be coherent with biological sampling*)

(*gross primary production*)

(*linkages to SOLAS*)

(*linkages to SOLAS*)

(*(biological) particle enumeration*)

$\delta^{17}\text{O}$  of O<sub>2</sub>

methyl halides

DMS

ADCP (multibeam)

## Contact Persons for Measurements

The working group will focus their planning of measurements on suites of related parameters listed below. The working group members listed after the measurements will serve as contact persons for information exchange:

### Level 1 Measurements

CTD and Hydrography including Oxygen and nutrients:

*Greg Johnson and Jim Swift*

Inorganic and Organic Carbon parameters (DIC, TALK, pCO<sub>2</sub>, pH and organic C):

*Richard Feely and Rik Wanninkhof*

Chloro-Fluorocarbons and tritium/<sup>3</sup>He:

*Rana Fine and Peter Schlosser*

### Level 2 Measurements

Other ventilation tracers:

*Rana Fine and Peter Schlosser*

Other CTD and ADCP:

*Greg Johnson and Jim Swift*

Other CO<sub>2</sub> & biogeochemical measurements:

*Niki Gruber and Scott Doney*

# Conclusions and perspectives

- **$^{39}\text{Ar}$  still difficult to measure and it is not clear which precision can be obtained.**
- **For use in oceanic studies  $^{39}\text{Ar}$  has to be measured on water samples with volumes of the order of 10 liters with precision of ca. 2 %.**
- **Not yet clear what is offered beyond  $^{14}\text{C}$  although there seems to be potential.**
- **Hope rests on ATTA**