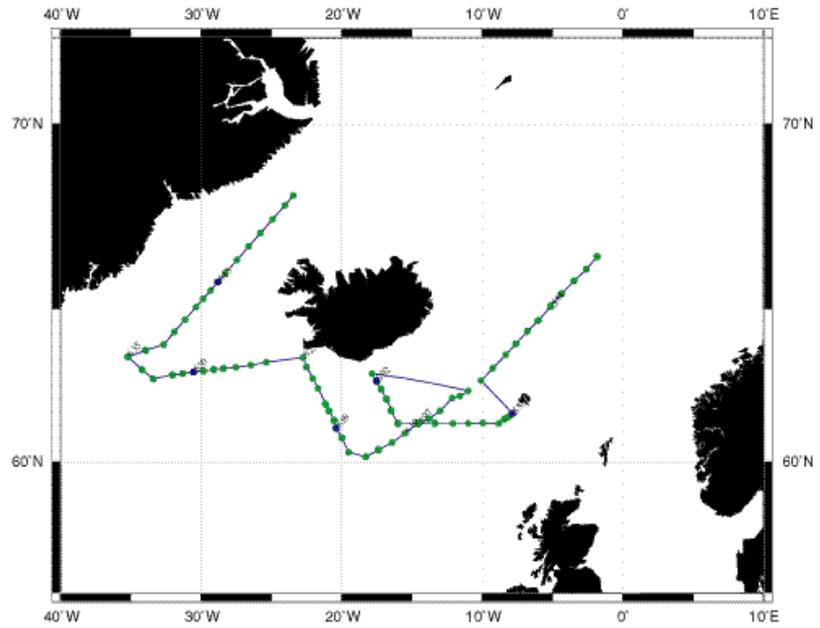


WOCE LINE **AR18**  
EXPOCODE:58JH0894\_1

Cruise Report  
NORDIC WOCE



## 1. HIGHLIGHTS

Chief Scientist: Johan Blindheim Institute of Marine Research, Bergen.  
Co-chief Scientist: Erik Buch Royal Danish Administration of Navigation and Hydrography  
Ship: R/V JOHAN HJORT  
Port of call: Reykjavik  
Cruise dates: July 23, 1994 to August 16, 1994.

## 1.2. CRUISE SUMMARY.

The cruise track and station locations are shown in Fig. A.1

### SAMPLING ACCOMPLISHED.

74 CTD/rosette stations were occupied using a 12 bottle rosette equipped with 10 l Niskin bottles. Water sampling on the cruise included measurements of CFCs (CFC-11, CFC-12, CFC-113 and carbon tetrachloride), salinity, dissolved oxygen, nitrate, nitrite, phosphate, silicate, partial pressure of carbon dioxide, total dissolved inorganic carbon. Additional samples were drawn and returned to shore laboratories for analysis of tritium, helium, carbon-13 and carbon-14.

Depths were measured with a SIMRAD echosounder set with the sound velocity set to 1500 m/sec.

### 1.3. LIST OF PRINCIPAL INVESTIGATORS.

Table 1.1. List of principal investigators, measurement responsibility and institution.

Principal Investigator	Measurement responsibility	Institute
Erik Buch	CTD/Rosette	RDANH, Copenhagen
F. Rey	O <sub>2</sub> ,NO <sub>3</sub> ,NO <sub>2</sub> ,PO <sub>4</sub> ,SiO <sub>3</sub>	IMR, Bergen
E. Fogelqvist	CFCs	Univ. Gothenburg
R. Bayer	Helium/Tritium	Univ. Heidelberg
J. Olafsson	CO <sub>2</sub>	MRI, Reykjavik
R. Nydal	Carbon isotopes	RLD, Trondheim

### 1.4. PRELIMINARY RESULTS

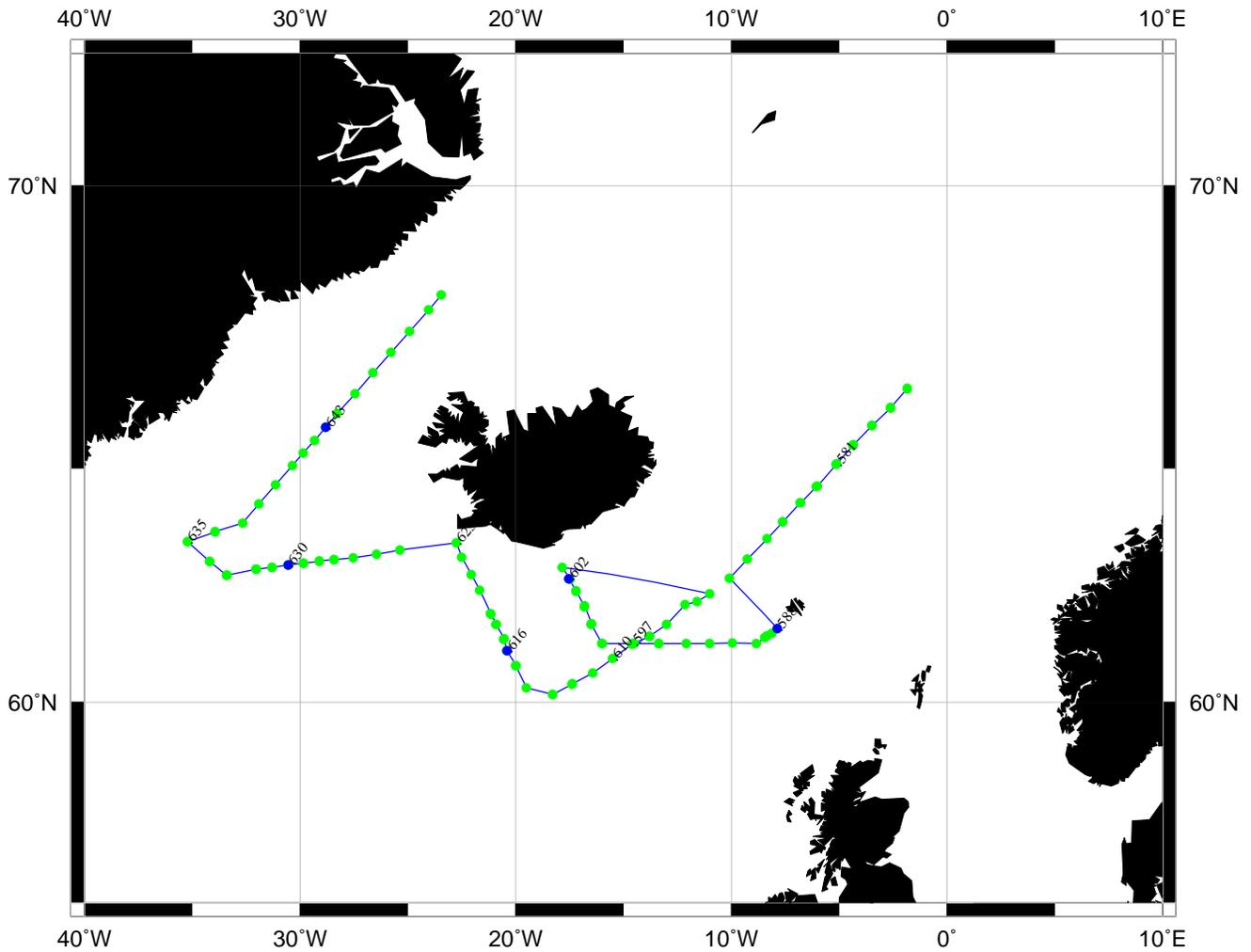
R/V "JOHAN HJORT" departed Bergen July 23, 1994, and made 17 stations on the Norwegian Svinoy standard section on which instruments, working and measuring procedures were tested and optimized. On July 26 the work on the WOCE sections, shown in Fig.A.1., began. A change of crew took place at Reykjavik on 5 August and the last WOCE station was occupied on August 10. Before ending the cruise, four stations which are part of a Nordic Carbon Cycle Program, were worked north of Iceland.

At each station CTD profiling was done with a Sea-Bird 911 Plus CTD equipped with a 12-place SBE Carousel sampler. This CTD system functioned satisfactorily during the whole cruise.

### 1.5. PROBLEMS.

On 2-3 stations single bottles did not trip.

# Station locations for AR18 JUL 1994: BLINDHEIM



Produced from .sum file by WHPO-SIO

## 1.6. LIST OF PARTICIPANTS.

Participant	Responsibility	Affiliation
Johan Blindheim	Chief Scientist	IMR, Bergen
Erik Buch	Co-chief scientist, CTD	RDANH, Copenhagen
Volker Buerkel	Helium/tritium	Univ. Heidelberg
Britt-Marie Dahlberg	Salinity	UNIV, Gothenburg
Magnus Danielsen	Carbon dioxide	MRI, Reykjavik
Elisabet Fogelqvist	CFCs	Univ. Gothenburg
John Goddard	Carbon dioxide	LDEO, Palisades, NY
Merete Fonn	Nutrients/oxygen	IMR, Bergen
Magnar Mjanger	Instrument tech.	IMR, Bergen
Jon Mortensen	CTD	Univ. Copenhagen
Kjell Arne Mork	CTD	Univ. Bergen
Reidar Nydal	C-13, C-14	Univ. Trondheim
Jon Olafsson	Carbon dioxide	MRI, Reykjavik
Marek Ostrowski	Data processing	IMR, Bergen
Francisco Rey	Nutrients/oxygen	IMR, Bergen
Jane Stromstad	Nutrients/oxygen	IMR, Bergen
Toste Tanhua	CFCs	Univ. Gothenburg
Hedinn Waldimarsson	Data processing	Mri, Reykjavik
Christoph Wagner	CTD	RDANH, Copenhagen

## 2. DESCRIPTION OF MEASUREMENT TECHNIQUES AND CALIBRATION.

### 2.1. CTD MEASUREMENTS.

(Erik Buch)

The CTD measurements were carried out using a SeaBird 911 Plus CTD equipped with dual temperature and conductivity sensors. The CTD was mounted together with a 12-place SeaBird Carousel Sampler and 10 l Niskin bottles.

The temperature and conductivity sensors were calibrated at the SeaBird calibration facility before and after the cruise. In addition, conductivity was calibrated at sea using data from the analyses of the salinity samples.

The CTD pressure sensor is Paroscientific Digiquarts model 410K-015 having a resolution of 0.001% of full scale i.e. 0.07dbar and a accuracy of 0.015% of full scale i.e. 1 dbar.

The temperature sensors used were SeaBird SBE 3 having a resolution of 0.0002°C and an accuracy of 0.002°C. Pre- and post cruise calibrations (23 Apr 94 and 01 Sep 94) at SeaBird calibration facility showed a drift of 0.0022 °C/year for the primary thermometer and 0.0011°C/year for the secondary. Both thermometers were accurate within 0.0001°C in both calibrations.

The conductivity sensors used were Seabird SBE 4 having a resolution of 0.00004 S/m and an accuracy of 0.0003 S/m. Pre- and post cruise calibrations at the Seabird calibration facility (23 Apr 94 and 01 Sep 94) showed a drift of 0.00005 S/m/month for the primary sensor and 0.000025 S/m/month for the secondary sensor, both at a conductivity of 3.0 S/m.

The CTD data were collected and processed using the Seasoft version 4.032 software provided by Seabird, installed on a TCI personal computer (486, 66MHz).

## **2.2. SALINITY MEASUREMENTS.**

(Johan Blindheim)

Water samples for salinity analysis were collected from almost all sampling depths, normally 12 or 24 samples on every station. After temperature stabilization, the samples were analyzed on board using a Guildline 8400 Autosol salinometer within a day or two after collection. Salinometer readings were controlled against IAPSO Standard Sea Water, Batch P124, after each 24th sample bottle.

The salinometer was placed in a temperature stabilized laboratory where the temperature was kept between 22°C and 24 °C throughout the cruise. Each sample was determined at least 3 times and the standard deviation between the multiple determinations throughout the cruise was 0.00048 (double conductivity ratio). The standard deviation between 45 multiple samples during the cruise, drawn from the same Niskin bottle, was 0.0009 in salinity.

Data from the salinity samples at pressures of 1000 dbar or greater were used for in situ calibration of the CTD. The relation between primary CTD conductivities and conductivity of the samples at the same pressure and temperature is given by:

$$\text{DEL C} = -1.5194 \text{ E-2} + 4.6145 \text{ E-4} * \text{C}$$

Here C is the CTD conductivity reading and DELC is the correction which has to be added to the CTD conductivity reading. We are of the opinion that this gives a more correct calibration than a fit with a slope and no offset which is recommended by the manufacturer.

## **2.3. OXYGEN MEASUREMENTS.**

(Francisco Rey)

Oxygen concentrations were measured with the Winkler method with visual determination of the titration endpoint. Samples were collected into 120 ml volume calibrated bottles, added pickling reagents, shaken and left for about two hours after which it were shaken again. After adding acid the whole sample was carefully poured into a 200 ml Erlenmeyer flask and titrated using a 20 ml automatic burette ( Schott-Geräte T90/20) with a dispensing precision of 0.01 ml.

All reagents were prepared with p.a. quality chemicals closely following WOCE recommendations (Culberson, 1991). Standardization of the 0.01N thiosulphate solution was done with potassium biiodate (0.0100 N).

The precision of the method was determined several times for each of the two analysts during the cruise by analyzing 10 replicates collected from a single 10 liter Niskin bottle. The lowest precision obtained by the less trained analyst was of 0.23 % (standard deviation 0.55  $\mu\text{mol kg}^{-1}$  at a concentration of about 237  $\mu\text{mol kg}^{-1}$ ). The lowest precision for the other analyst was 0.13 % (0.39  $\mu\text{mol kg}^{-1}$  at a concentration of 301  $\mu\text{mol kg}^{-1}$ ).

Oxygen concentrations were calculated in ml l<sup>-1</sup> and converted to weight concentrations by using the equation recommended by WOCE (Culberson, 1991). The density of the seawater was also calculated by the equation recommended by Culberson (1991) using salinity and potential temperature values recorded by the Seabird CTD probe at the depth where the Niskin bottles were triggered.

## REFERENCES.

Culberson, C.H.(1991). Dissolved oxygen. WOCE Operations Manual. Vol.3, Section 3.1, Part 3.1.3: WHP Operations and methods. WHP Office Report WHPO 91-1, WOCE Report No. 68/91, Woods Hole, Mass, .USA.

## 2.4. NUTRIENT MEASUREMENTS

(Francisco Rey and Jane Stromstad)

Seawater samples were collected into polyethylene test tubes with pressure caps and kept refrigerated at 4°C in the dark. Analysis of nitrate, nitrite, phosphate and silicate were carried out within 12 hours after collection with an AutoAnalyzer that comprised the following units:

- Pumping system from ChemLab, England.
- Reaction units of own fabrication
- Autosampling, detection and computing units from SANplus Segmented Flow Analyzer, Skalar Analytic B.V., the Netherlands.

The methods used were adaptations of standard methods (Strickland and Parsons, 1981) slightly modified to the AutoAnalyzer system (Foynt et al.,1981). A new modification was applied during the cruise for the analysis of nitrate. The Cd-reduction column used this time was a Cd- tube manufactured by Alpkem Inc. and the segmentation of the flow was achieved by pumping nitrogen gas instead of air as in the previous version of the method.

The precision of the analyses was monitored by running ten replicates samples from a single Niskin bottle several times during the cruise. The precision obtained for the different analyses at full scale was better than 0.1% for nitrite, 0.25% for nitrate, 1.5% for phosphate and 0.2% for silicate. The precision of the phosphate analysis it seems to have been affected by the use of

new polyethylene tubes at the start of the cruise. After soaking the tubes in seawater and rinsing them with distilled water before use the precision improved to about 1% at full scale.

The reproducibility of the analysis was assessed by running a set of control samples which were newly made every day from stock solutions prepared ashore. The control samples were prepared in low nutrient seawater and were run in the same way as the other samples. The obtained reproducibility ( one standard deviation) during 14 days for the different analysis were:

• Nitrite:	0.39 % at a level of about 0.50 $\mu\text{mol l}^{-1}$
• Nitrate:	1.14 % at a level of about 8.10 $\mu\text{mol l}^{-1}$ 0.50 % at a level of about 18.00 $\mu\text{mol l}^{-1}$
• Phosphate:	1.16 % at a level of about 0.66 $\mu\text{mol l}^{-1}$ 0.52 % at a level of about 1.250 $\mu\text{mol l}^{-1}$
• Silicate:	0.36 % at a level of about 4.50 $\mu\text{mol l}^{-1}$ 0.10 % at a level of about 11.00 $\mu\text{mol l}^{-1}$

## REFERENCES:

- Foyn, L., M. Magnussen and K. Seglem (1981). Automatic analysis of nutrients with an online data processing. A presentation of construction and functioning of the system used at the Institute of Marine Research. Fiskerihavet, Serie B, 1981(4): 1-9. In Norwegian.
- Strickland, J.D.H. and T.R. Parsons(1972). A practical handbook of seawater analysis, 2nd. ed. Bull.Fish.Res.Bd.Can. No.167.

## 2.5. MEASUREMENTS OF TOTAL DISSOLVED CO<sub>2</sub>, DELC14 AND DELC13. (Reidar Nydal)

### SAMPLING STRATEGY AND PROCEDURE.

The main goal for the cruise was to get some basic carbon profiles north and south of the Denmark Strait Ridge, as a contribution to the study of water overflow. It was especially important to repeat one GEOSECS profile from 1972. Fairly complete carbon profiles were performed at 4 stations. The changes in the profiles during a period of 20 years could give valuable information about the water exchange with depth.

The samples were collected in 500 ml glass bottles, which first were rinsed with some of the sampling water, and then filled up.. The samples were stored in a refrigerator and analyzed within a few days.

### EQUIPMENT AND TECHNIQUE.

The extraction of total dissolved CO<sub>2</sub> from 500 ml seawater was carried out onboard shortly after collection. A bubbling procedure with nitrogen (99.99%) as a carrier gas, in a closed cycle, was applied for this purpose. The sample was acidified in advance with phosphoric acid

to a pH value of 1.5. The bubbling lasted for 15 minutes. The water was removed from the CO<sub>2</sub>-gas using vapor traps (-80oC) and a drying agent (P<sub>2</sub>O<sub>5</sub>). CO<sub>2</sub> was continuously trapped with liquid nitrogen (-196oC) during the cycle. After the flushing was finished nitrogen was removed and the CO<sub>2</sub>-gas was trapped in 25 ml glass ampoules for later measurements in the laboratory after return.

The quantitative measurements of the CO<sub>2</sub>-gas are performed with an oil manometer. The obtained precision (standard error) in a single measurement, derived from several measurements of identical samples, has been found to be less than 3 permill. The present procedure for CO<sub>2</sub>-extraction is developed at the Radiological Dating Laboratory.

The obtained CO<sub>2</sub>-gas (ca 25 ml.) is applied for both <sup>13</sup>C/<sup>12</sup>C (ca.5 ml) and <sup>14</sup>C/<sup>12</sup>C AMS measurements (ca 2 ml). The measurements of DELC13 will be carried out in a mass spectrometer at the geological Institute, Univ. of Bergen. The precision in each measurement is about 0.1 permill. <sup>14</sup>C measurements will be performed with the AMS (accelerator mass spectrometry) facility in Tucson, Univ. of Arizona with a precision of about 4 permill.

## **2.6. TOTAL DISSOLVED INORGANIC CARBON (TCO<sub>2</sub>), PARTIAL PRESSURE OF CO<sub>2</sub> IN SEAWATER (pCO<sub>2</sub>).**

(Jon Olafsson and John Goddard)

### **TOTAL DISSOLVED INORGANIC CARBON.**

Total CO<sub>2</sub> measurements are made ashore on discrete seawater samples collected at various depths. An approximately 20 ml subsample is injected by positive displacement syringe into a stripping column. Acidification converts all inorganic carbonate species in the sample into CO<sub>2</sub> gas which is then swept into a electrochemical titration cell. The titration results are measured using a Utopia Instruments Corp. (UIC) model 5011 Coulometer. The performance of the instrument is monitored several times daily using a gas loop calibration system. Overall analytical quality control is evaluated daily with reference material for oceanic CO<sub>2</sub> measurements. This reference material is kindly supplied by Dr. A. Dickson of Scripps Institution of Oceanography, USA. After final processing, results are reported as TCO<sub>2</sub> 10<sup>-6</sup> moles /kg.

### **PARTIAL PRESSURE OF CO<sub>2</sub> IN SEAWATER (pCO<sub>2</sub>).**

The pCO<sub>2</sub> analysis system uses a closed system seawater equilibrators to bring the partial pressure of CO<sub>2</sub> of discrete seawater samples into equilibrium with a small quantity of air, and a gas chromatograph to analyze the concentration of CO<sub>2</sub> in the equilibrated air. The gas chromatograph uses a flame ionization detector (FID), which is insensitive to CO<sub>2</sub>, but which has a highly linear response to hydrocarbons. Using hydrogen as a carrier gas and a ruthenium catalyst, the CO<sub>2</sub> is converted completely to methane prior to reaching the FID. The highly sensitive and linear FID is thus used to quantify the CO<sub>2</sub> content of the equalibrated air. The discrete seawater samples are collected in 500 ml flasks and are equilibrated a constant

temperature bath at 40°C. After corrections and final processing, results are reported as pCO<sub>2</sub> 10<sup>-6</sup> atm at 20°C.

## **2.7. CHLOROFLUOROCARBON TRACER MEASUREMENTS.** (Elisabet Fogelqvist)

The chlorofluorocarbons provide a powerful tool for studying time scales and magnitudes of large-scale oceanic subsurface mixing and deep water renewal processes. Four chlorofluorocarbon tracer compounds, namely CFC-11, CFC-12, CFC-113 and carbon tetrachloride (also classified as CFC-10), were measured. Carbon tetrachloride has been present in the atmosphere since the beginning of this century, the two CFCs 11 and 12 since the forties and CFC-113 since the beginning of the seventies, all at increasing concentration levels. Equilibration with seawater at the sea surface gives a time dependent signature of the surface waters that can be traced.

Seawater samples were analyzed for the CFCs at 70 stations, i.e. all but four of the stations and at most of the depths sampled for chemical measurements. Water samples, drawn directly from the sampling bottles into 100 ml ground glass syringes, were analyzed using a purge-and-trap sample work-up technique followed by gas chromatographic separation on a 75 meters long megabore open tubular column and electron capture detection. The entire analytical set-up was built with two identical channels, whereby two water samples were analyzed simultaneously utilizing a gas chromatograph holding two separation columns and two detectors. The standardization was made with a standard gas mixture, which was calibrated against a standard supplied by Dr. Andrew Watson, Plymouth Marine Laboratory, England. The two detectors of the analytical set-up, standardized separately, showed standard curves that were best fit to a polynomial function of the second order.

The reproducibility of the analytical method was measured from replicate samples of a deep water (800 m) with moderate CFC concentration levels. The relative standard deviations (RSD) in the first channel of the analytical system were 0.8%, 1.0%, 6.0%, and 1.1% for CFC-11, CFC-12, CFC-113 and CFC-10, respectively. In the second channel, the corresponding RSDs were 1.0%, 1.5%, 2.4% and 1.1%. The detection limits of CFC-11, CFC-12 and CFC-10 are estimated to 0.01 pmol/kg and somewhat higher, 0.02 pmol/kg, for CFC-113.

## **2.8. HELIUM/TRITIUM SAMPLING.**

(Volker Buerckel)

### **GENERAL ASPECTS.**

Tritium is the radioactive isotope of hydrogen. It decays with an half-life of 12.43 years to the helium isotope He-3. The major source for tritium was the nuclear weapon testing in the atmosphere mainly in the 1960s.

At the sea surface He-3 concentrations usually are close to solubility equilibrium with the atmosphere. Water isolated from the surface due to convection will be enriched in tritiogenic He-3 while spreading along the isopycnals. The tritiogenic He-3 is detectable as a deviation of the He-3/He-4 ratio of the water sample from that of an air standard. Measurements of both He-3 excess and tritium concentration allow calculation of a formal tritium/He-3 age, which is a tool for estimation of mean transfer times, current speeds and renewal times.

### **SAMPLING.**

During the cruise 143 samples for measurement of both helium and tritium were taken. The helium samples (volume about 40 cc) were stored in copper tubes closed tightly at both ends by means of special stainless steel pinch-off clamps.

For tritium analysis 250cc of water was stored in a glass bottle sealed by a polyethylene cap.

### **MEASUREMENT.**

The analyses will be performed at Univ. of Heidelberg. For measurements of He-3/He-4 ratio a special helium isotope mass spectrometer with an accuracy of about + 0.2% is used. Tritium measurements in Heidelberg are either done by low level counting (with an accuracy of +5%) or by mass spectrometry (He-3 ingrowth method with an accuracy of about +2% and a detection limit of 0.05 TU). Data will be available during 1995.