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MEASUREMENT OF SMALL VOLUME OCEANIC ^{14}C SAMPLES BY ACCELERATOR MASS SPECTROMETRY

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ABSTRACT. A technique for ^{14}C measurement of small volume (0.5L) oceanic water samples by Accelerator Mass Spectrometry (AMS) is described. Samples were taken from a CTD/rosette system used for standard hydrographic work. After CO_2 extraction and target preparation, the samples were measured at the Zürich tandem accelerator facility. On the basis of ^{14}C data from samples collected on a station in the northern Weddell Sea, the precision of the measurements is estimated to ca ±8‰. The error in the present AMS results is dominated by the statistical error in ^{14}C detection. From results of duplicate targets, it is concluded that a precision of ±5‰ can be reached. The ^{14}C data are discussed in relation to the Weddell Sea hydrography.

INTRODUCTION

During the last decades, ^{14}C measurements have progressed to an important tool in physical oceanography, allowing estimates of large-scale oceanic transport and mixing processes (Stuiver, Quay & Östlund, 1983; Broecker *et al,* 1985; Schlitzer *et al,* 1985). A limiting factor in present oceanographic ^{14}C studies is the fact that the low-level counting technique used so far for ^{14}C measurement requires sampling and processing of 250L of water to obtain a precision of ≤5‰ which is needed in many oceanographic applications to resolve the structures of the ^{14}C distribution. The large volume Gerard bottles used for water sampling requires extra casts for ^{14}C stations and the operation of the CO_2 extraction devices needs additional manpower. Therefore, ^{14}C sampling mainly was restricted to cruises with dedicated geochemical sampling programs as, eg, GEOSECS or TTO.

Recent developments in Accelerator Mass Spectrometry (AMS) allow ^{14}C measurement on samples much smaller than needed for low-level counting. The main question in the application of AMS ^{14}C measurements in oceanographic studies, however, is the precision that can be achieved. A critical limit for oceanographic applications is a precision of ≈10‰, which is sufficient for the treatment of the entry of bomb ^{14}C into the interior of the ocean. The purpose of this paper is to present AMS ^{14}C measurements of small volume water samples collected on a station in the northern Weddell Sea which demonstrate that it is possible to obtain ^{14}C data from samples taken from CTD/rosette systems used for standard hydrographic work with a precision well below 10‰.

SAMPLE COLLECTION AND MEASUREMENT

The first samples were collected during the third cruise of the German Polar Research Vessel *Polarstern* to Antarctica (ANT III, January to March

1985) on station 243 in the northern Weddell Sea. As this station was rather shallow, additional samples of Weddell Sea Bottom Water (WSBW) were taken on station 244 in the central Weddell Sea. (For geographical position of the stations, see Fig 1.)

The samples were drawn from a CTD/rosette system equipped with 12 Niskin bottles (volume: 12L) into pre-evacuated glass bulbs (volume: 1L) sealed with PTFE valves. The glass bulbs had been cleaned with concentrated HCl before they were evacuated. To avoid changes in the CO_2 concentration of the water by microbial activity the water samples were poisoned with $HgCl_2$. In the laboratory the water was acidified with phosphoric acid and the CO_2 was extracted using a technique described by Dörr and Münnich (1980). The AMS targets were prepared by catalytic reduction of the CO_2 to carbon. The experimental setup for the target preparation is similar to that described by Vogel *et al* (1984). Measurement was done at the Zürich AMS facility. The technical details of the measurement are given by Suter *et al* (1984) and Bonani *et al* (1986). The ^{14}C data are reported as $\Delta^{14}C$, *ie,* as the per mil deviations from the 1950 decay-corrected NBS oxalic acid standard (Stuiver & Polach, 1977).

The present 1σ precision of ±8‰ is dominated by the statistical (counting) error of the accelerator sample respective to the standard measurement (5–6‰ each). The corresponding systematic errors are on the

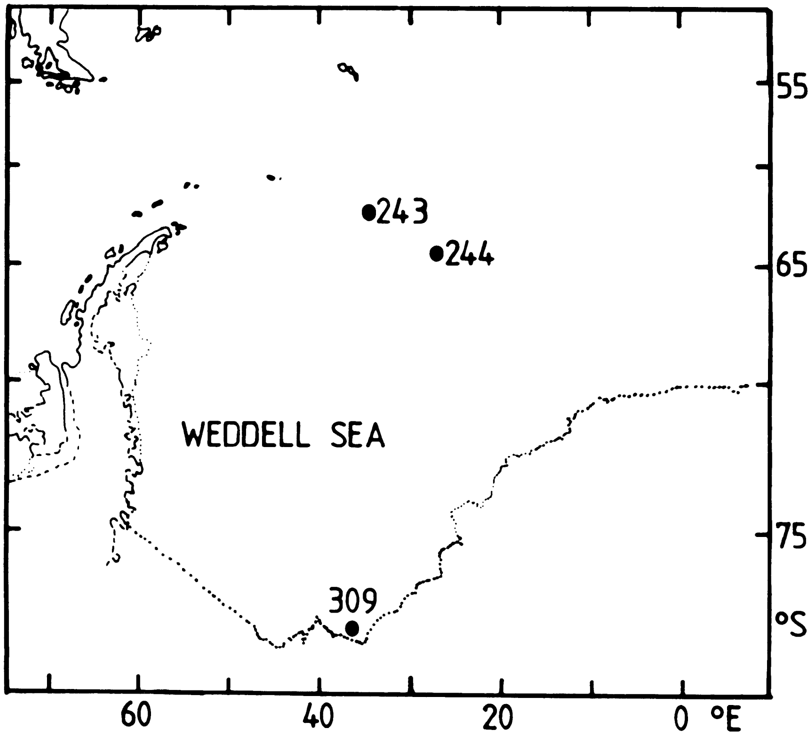

Fig 1. Geographical positions of stations 243 and 244 in the northern Weddell Sea

TABLE 1

^{14}C measurements of water samples taken in the Weddell Sea. Duplicate $\Delta^{14}C$ values are from duplicate targets of the same water sample, which means only target preparation and measurement were independent.

Press (dbar)	θ (°C)	S (‰)	$\Delta^{14}C$** (‰)	$\delta^{13}C$† (‰)	ΣCO_2 (μmol/l)	Water mass
Station 243 (62° 28.6′ S, 34° 38.1′ W) 150185						
10	0.028	33.618	−83.3	1.53	2068	SW
			−94.1			
79	−1.739	34.401	−123.5	0.73	2228	WW
			−120.2			
300	0.096	34.666	−158.8	0.14	2275	WDW
599	0.042	34.669	−146.6	0.14	2318	WDW
			−148.8			
901	−0.042	34.667	−154.0	0.02	2301	DW
			−150.3			
1200	−0.170	34.663	−155.1	0.30	2271	DW
			−149.8*	0.34	2270	
1800	−0.327	34.658	−168.1	0.30	2268	DW
			−165.0			
2701	−0.481	34.656	−155.6	0.51	2241	DW
3300	−0.625	34.650	−157.2	0.52	2247	DW
			−171.8			
			−148.8*	0.49	2267	
3526	−0.680	34.647	−157.2	0.70	2229	DW
			−138.1*	0.50	2242	
Station 244 (64° 33.4′ S, 27° 03.3′ W) 160185						
4798	−0.937	34.634	−133.8	0.64	2233	WSBW
4925	−0.948	34.634	−141.8	0.53	2246	WSBW
			−138.1			
			−132.7*	0.41	2245	

* Numbers are from duplicate samples taken from the same Niskin bottle, and storage, water processing, target preparation and measurement steps were completely independent.

** 1σ error = ±8‰

† ^{13}C was measured using conventional mass spectrometry; 1σ error = ±0.04‰.

order of 2–3‰ only. The observed overall precision derived from the results of duplicate samples (see Table 1) is consistent with the error of the accelerator measurement. Thus, additional errors through sampling, storage, and target preparation seem to be negligible on this level of accuracy. This gives us confidence that by increasing counting time, a ±5‰ precision can be reached.[1] In the discussion of the present data, we assume a total error of ±8‰ for the single measurement, and a $\sigma = 8‰/N^{1/2}$ for each mean value derived from N single measurements.

RESULTS AND DISCUSSION

The hydrography of station 243 (extended by station 244) is typical for the northern Weddell Sea. The potential temperature respective to salinity

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[1] Note added in proof: This precision has been reached meanwhile; see B Kromer *et al* (in press) to appear in the AMS-4 1987 Proceedings volume of *Nuclear Instruments & Methods.*

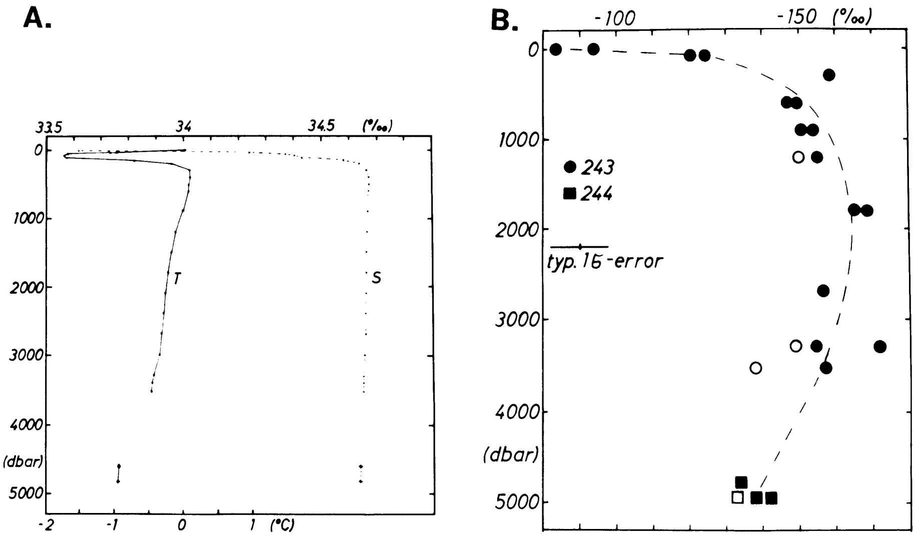

Fig 2A. Depth profiles of potential temperature and salinity for station 243. The lower two data points are taken from station 244 in order to extend the profile into the WSBW.

Fig 2B. ^{14}C profile for station 243/244. The data points marked by open signs are from samples that were run completely independently (see also Table 1).

profiles (Fig 2A) show a thin (≈20m thick) cold layer of Winter Water (WW) directly below the fresher and warmed-up surface layer (SW). The Warm Deep Water (WDW) underlying the WW is relatively cold at this station with a maximum temperature of 0.1°C in its core at ca 300m depth. Below the WDW, the potential temperature decreases steadily with depth to reach a value of −0.94°C in the Weddell Sea Bottom Water (WSBW) found at station 244 at 4930m depth. The salinity increases from the surface to the core of the WDW where a maximum of 34.669‰ is found and slowly decreases again below the center of the WDW to a value of 34.634‰ in the WSBW at station 244. The water mass between the WDW ($\theta \geq 0°C$) and the WSBW ($\theta \geq -0.8°C$) is called the Deep Water (DW).

The ^{14}C data are plotted in Fig 2B and listed in Table 1. The depth profile shows $\Delta^{14}C$ values between −83 and −94‰ in the Surface Water decreasing to −122‰ in the WW (79m). Below the WW the $\Delta^{14}C$ values further decrease to −151 ± 6‰ in the WDW (depth range at station 243: 300–600m; $\Delta^{14}C$ range: −147 to −159‰). In the depth range between 900 and 3500m the mean $\Delta^{14}C$ value is −156 ± 3‰ (range: −138 to −172‰), not significantly different from the WDW value of −151‰. The mean $\Delta^{14}C$ value of the WSBW (4 samples) amounts to −137 ± 4‰, a value significantly higher than the ^{14}C concentration of the overlying water.

Our AMS data can be compared with the existing ^{14}C measurements from the Weddell Sea published by Weiss, Östlund and Craig (1979). These data were obtained by conventional low-level counting with an accuracy of ±4‰. Within the errors the mean surface $\Delta^{14}C$ value of −92‰ given by

Weiss *et al* agrees with our value of $-90‰$ observed at station 243. The same holds for our WDW ^{14}C concentration ($-151‰$ in comparison to $-155‰$ given by Weiss *et al*). As the data from Weiss *et al* are from 1973 it can be concluded that the influence of bomb ^{14}C on the ^{14}C content of the WDW is only of minor importance. The fact that we find a surface concentration not really different from the one in 1973 although the atmospheric ^{14}C concentration has decreased (430‰ in 1973 (Levin *et al,* 1985); 200‰ in 1985 (Levin *et al,* 1987)) may well be due to the different locations of the stations, varying extent of the ice cover, or different gas exchange rates with the atmosphere. In the following, the data are discussed in the context of the Weddell Sea oceanography.

The ^{14}C distribution of the Weddell Sea is controlled by circulation and gas exchange with the atmosphere in this region. The relatively warm and salty WDW is a key water mass transporting heat and salt from the Circumpolar Flow into the Weddell Sea. The fresher and slightly warmed SW, found during summer in the upper 50m of the water column, is formed by atmospheric exchange and water/ice interaction. The WW is the remnant of the winter mixed layer which forms under the sea ice cover with temperatures near the surface freezing point of sea water with a core depth of ca 100m (Gordon & Huber, 1984). The WSBW is a mixture of WDW and shelf water masses.

The low ^{14}C concentrations of the WDW and of the intermediate waters reflect the high ages of the deep Pacific and Atlantic Oceans from which these waters are derived. The higher ^{14}C concentrations in the SW are caused by partial CO_2 re-equilibration of the upper water layers mainly during southern summer (atmospheric $\Delta^{14}C$ values at the time of sampling: 200‰ (Levin *et al,* 1987)). The WW is a mixture between WDW and SW and consequently has a ^{14}C concentration between those of WDW respective to SW. The waters below the WDW core are of the deep Atlantic and deep Pacific origin and show low ^{14}C concentrations comparable to those of the WDW. The WSBW is a mixture of deep waters with low ^{14}C concentrations and shelf-water masses which are partially re-equilibrated with the atmosphere. Under the assumption that WSBW is a mixture of 40% WDW, 19% WW, and 41% Western Shelf Water (WSW), Weiss, Östlund and Craig (1979) calculated a ^{14}C value of $-119‰$ for this water mass. Our measured value of $(-137 \pm 4)‰$ is slightly lower which means that the WSBW is less influenced by atmospheric exchange than assumed so far. It might be that this difference is caused by improper assumptions for the mixing ratios of the water masses involved in the WSBW formation process. The calculation of Weiss *et al* does not take into account that the Ice Shelf Water (ISW)[2] plays an important role in the formation process of WSBW as has been shown in recent work by Foldvik, Gammelsröd and Törresen (1985a,b). For a more detailed understanding of the ^{14}C distribution of the Weddell Sea further work is needed.

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[2] ISW is a water mass formed by cooling and admixture of melt water under the Filchner/Ronne Ice Shelves.

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