# <sup>14</sup>C PROFILES IN THE NORWEGIAN AND GREENLAND SEAS BY CONVENTIONAL AND AMS MEASUREMENTS

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ABSTRACT.  $CO_2$  in the atmosphere is an important climate gas because of its absorption of infrared radiation. More knowledge about  $CO_2$  uptake in the ocean is of critical significance in predicting future climate development. For a period of approximately 30 years, radioactive carbon from nuclear tests has been a very useful tracer in  $CO_2$  exchange studies. Up to now, the measurements have been based mainly on the conventional counting technique with large  $CO_2$  samples (*ca.* 5 liters). Accelerator mass spectrometry (AMS) with small  $CO_2$  samples (1–2 ml) has made sampling much easier, and has especially stimulated the use of <sup>14</sup>C as a tracer in the ocean.

At higher latitudes, the ocean acts as a sink for  $CO_2$ . In addition to  $\Delta^{14}C$  measurements, we are concerned here with dissolved inorganic carbon (DIC) and  $\delta^{13}C$  in the Norwegian and Greenland Seas. During cruises in 1989 and 1990, we obtained several  $\Delta^{14}C$  profiles, and also repeated a few GEOSECS profiles taken in 1972. The shape of these profiles changes with time, and provides information about the mixing rate and the age of the deep water. From changes in the profiles, it appears that the deep water in the Greenland Sea has obtained about 25% of the <sup>14</sup>C concentration in the ocean surface over a period of 25 years. The Norwegian Sea deepwater is estimated to be 50–100 years older than that of the Greenland Sea.

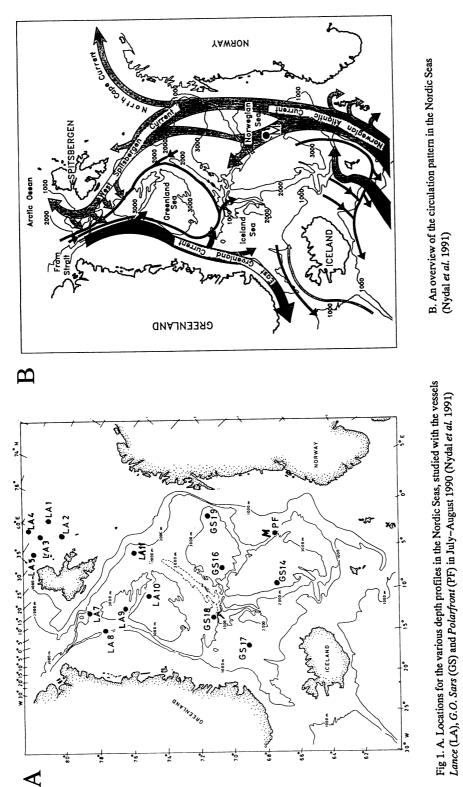
#### INTRODUCTION

Bomb-produced <sup>14</sup>C in the atmosphere has been a main tracer for studying the carbon cycle in nature (Nydal & Løvseth 1983; Nydal *et al.* 1984). This carbon isotope has been applied in the study of the shorter exchange times among various reservoirs, especially between the atmosphere and the ocean. Exchange studies are now highly stimulated by the present interest in climate. Research is focused on various climate or "greenhouse" gases (*e.g.*, CO<sub>2</sub>, CH<sub>4</sub>), which are released into the atmosphere at a gradually increasing rate. CO<sub>2</sub> is regarded as the most important, and its effect on absorption of infrared radiation will contribute to the heating of the Earth. However, permanent temperature change will occur only when a heat balance between the atmosphere and ocean has developed. The ocean, which has a much larger heat capacity than the atmosphere, has, up to now, absorbed about one half of the CO<sub>2</sub> liberated to the atmosphere.

The oceans at higher latitudes act as a sink for  $CO_2$ , and a study of the  $CO_2$  uptake in the northern seas can be successful only when combined with circulation studies. Sampling for  $\Delta^{14}C$  measurements in the ocean has, until recently, suffered from the fact that large samples of seawater (100– 200 liters) were necessary for conventional measurements. For this reason, most laboratories have limited their ocean studies to surface <sup>14</sup>C samples. Earlier, the most important studies of depth profiles using conventional technique were performed during the GEOSECS expeditions in 1972 to 1974 in the Atlantic, Pacific and Indian Oceans. At that time, ocean research was not especially focused on climate or on the special importance of  $CO_2$  uptake at higher latitudes. Nevertheless, GEOSECS includes some important depth profiles from these areas (Östlund, Dorsey & Brecher 1976).

In summer 1990, we collected water samples for dissolved inorganic carbon (DIC),  $\delta^{13}$ C and  $\Delta^{14}$ C measurements with Norwegian research vessels (*Polarfront, Lance* and *G. O. Sars*) at the locations

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given in Figure 1 (Nydal *et al.* 1991). The cruises were planned as a result of some <sup>14</sup>C measurements in these oceans in 1989 (Nydal 1991). Our program is concerned with CO<sub>2</sub> uptake in the Norwegian and Greenland Seas and the further transport to the deepwater in the Atlantic Ocean. It was of particular importance to repeat the GEOSECS  $\Delta^{14}$ C profiles of 1972 for circulation studies. In this paper, we present some of the most interesting  $\Delta^{14}$ C profiles, and discuss the age of the deepwater. We have used both conventional and AMS techniques.

## The Norwegian and Greenland Seas

Previous knowledge about the Norwegian and Greenland Seas is based mainly on hydrographic data, started by Helland Hansen and Nansen (Sverdrup, Johnsen & Fleming 1946). The surface water in this area is mainly supplied from two different sources: the Norwegian Atlantic Current (warm, high salinity) and the East Greenland Current (cold, low salinity). A cyclonic gyre is formed between these two currents in the Greenland Sea (Fig. 1). The classical view of deepwater formation in this sea is that surface and intermediate waters sink down by surface cooling and deep convection during winter. Later research revealed that the mechanism of deepwater formation in the Greenland Sea is more complicated (Schlosser *et al.* 1991). The Norwegian Sea deepwater has a higher salinity than the deepwater in the Greenland Sea, and is thus also regarded as originating from the deepwater in the Eurasian Basin. Intermediate water with high salinity is thought to be formed in this basin and brought down through the Fram Strait. A mixture of deepwater from the Greenland Sea and the Eurasian Basin is certainly formed at the periphery of the Greenland Gyre and brought down through gaps in the ridge, to form the Norwegian Sea deepwater (Smethie, Östlund & Loosli 1986).

The Greenland Sea is assumed to be one of the main source regions for the deepwater in the North Atlantic Ocean. Great uncertainties exist about the origin of the water masses, which appear in the overflow of the Denmark strait and the Iceland-Scotland ridge. According to Heinze *et al.* (1990), the contribution to the overflow should originate mainly in intermediate water. The deepwater should normally be too dense to pass over the ridge, and is forced to circulate in the deep ocean (Aagaard, Swift & Carmack 1985).

## SAMPLING PROCEDURE AND MEASUREMENTS

Our measurements of  $\Delta^{14}$ C profiles in seawater are based on DIC. We have not performed measurements of the much smaller organic fraction, which may have a substantially lower  $\Delta^{14}$ C level (Druffel *et al.* 1989). For conventional  $\Delta^{14}$ C measurements, 100–200 liters of seawater were collected with both 30-liter Niskin bottles and 60-liter Go-Flo bottles (General Oceanics). The seawater was acidified to a pH 2–3 by addition of 85% phosphoric acid. A major part of the CO<sub>2</sub> was then flushed out in a bubbling procedure with a recirculating pump and nitrogen as a carrier gas. Finally, the CO<sub>2</sub> gas was trapped as dissolved sodium carbonate in a 2% NaOH solution. Later, in the laboratory, the CO<sub>2</sub> gas (3–5 liters) was recovered from the solution, and normally counted for 5 to 8 days in CO<sub>2</sub> proportional counters (1–2 liters) at 2 atmospheres pressure (Nydal, Gulliksen & Løvseth 1980). The counting-statistical error (1  $\sigma$ ) of these measurements is 4–5‰. This flushing procedure does not extract the total amount of CO<sub>2</sub> in the sample, with the consequences of extra fractionation between the carbon isotopes. Thus, the  $\delta^{13}$ C value from this gas is not representative of DIC in seawater, and could be applied only as a correction to  $\Delta^{14}$ C. The  $\Delta^{14}$ C values are calculated according to Stuiver and Polach (1977).

The very time-consuming work involved in collecting large samples in deep-sea profiles demonstrates the need for AMS measurements of small samples. In addition to the large seawater samples, small samples were collected with a sampling system in a frame of 12 Niskin bottles,

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each of 2.5-liter volume. The sampling frame was equipped with a cable containing a Neil Brown CTD (conductivity, temperature and depth) probe, where salinity, temperature and pressure were continuously measured. With this system, the sampling time was reduced to about 1/5 in a profile 3000 m deep. We were now able to make a complete extraction of CO<sub>2</sub> from DIC in the small seawater samples, and thus, obtain more information. The measured  $\delta^{13}C$  values will now display the true values in DIC at various depths and different times, and reflect the balance between the carbon isotopes in the water masses. DIC was normally extracted from seawater (0.5 liters) onboard the ship shortly after collection, and therefore, no poison was added. For the extraction of CO<sub>2</sub>, we have developed a flushing procedure (Fig. 2) that differs from that described by Bard et al. (1987). The flushing was carried out with pure nitrogen (99.99%) as a carrier gas, for 45 min (we later found 15 min was sufficient). An advantage of this system is that a limited amount of carrier gas (ca. 2 liters) is recirculated in a closed cycle with no connection to the air.  $CO_2$  is trapped in liquid nitrogen (-196°C) after passing through two dry-ice traps (-70°C), followed by a P<sub>2</sub>O<sub>5</sub> column. The removal of water is a critical part of the purification procedure, and we found it necessary to recirculate the CO2 gas a second time through the drying stage after vacuum was obtained. The exact amount of  $CO_2$  is determined with an oil manometer to a precision of 6‰ (1 σ). The amount of CO<sub>2</sub> (ca. 25 ml) obtained by this procedure is sufficient for both  $\delta^{13}$ C and  $\Delta^{14}$ C (AMS) measurements. The  $\delta^{13}$ C measurements were performed with a precision of 1‰ at the Mass Spectrometry Laboratory, University of Bergen, and are given in permil relative to the PDB standard.

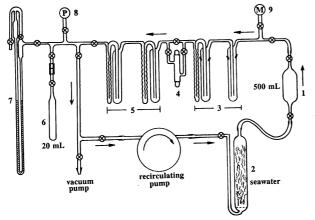


Fig. 2. Schematic description of the  $CO_2$  extraction system. The circulation path in the system is shown by arrows. 1. Measuring volume; 2. Bubbling container; 3. Water traps (-70°C); 4. Drying agent ( $P_2O_5$ ); 5. Traps for collecting  $CO_2$  (-196°C); 6.  $CO_2$ bottle; 7. Oil manometer; 8. Piraniemeter; 9. Mechanical manometer.

The AMS  $\Delta^{14}$ C measurements are performed at the Accelerator Facility for Radioisotope Analysis in Tucson, Arizona. Samples of 1–2 ml CO<sub>2</sub> are converted to CO over hot Zn, and the CO is further reduced to graphite over an iron catalyst at 625°C (Slota *et al.* 1987). The graphite powder is pressed into an aluminum target holder for the AMS analysis. Eight graphite samples are loaded into the ion source along with two standards (NBS OX I and OX II). The <sup>14</sup>C/<sup>13</sup>C isotope ratio of the graphite samples is measured and compared to the known standards. A typical measurement consists of five repeat cycles of measurement of the isotopic ratios of the samples and standards. The final precision in the isotope ratio measurement is about 6‰ for a measurement time of 50 min per sample. This includes the counting-statistical error in the ratio, plus other sources of random error (4‰). Precision of 3‰ can be achieved using four accelerator targets. Complete details of the measurements are given by Linick *et al.* (1986), and of the calculations by Donahue, Linick and Jull (1990).

## **RESULTS AND INTERPRETATION**

The following measurements of profiles from the Norwegian and Greenland Seas are presented in graphs. Each profile is given by a station number, which also identify the operating research vessel (*Lance* as LA and *G. O. Sars* as GS). The DIC and  $\delta^{13}$ C profiles, which are presented in Figures 3 and 4, show a general trend. The most important change in DIC with depth occurs in the upper few hundred meters, where primary plankton production occurs. For this reason, DIC has a minimum value at the surface and increases downward with decreasing light intensity. The further slow change with depth is dependent on exchange of water masses and combustion and dissolution of falling particles. The DIC profiles decrease slightly with greater depth in the Greenland Sea, whereas the profiles in the Norwegian Sea are either constant or increase slightly with depth. Minor laboratory accidents sometimes disturb the results. This may be the case for two DIC samples in Figure 3C (at 785 m and 2940 m). A study of the influence of the storage time of water samples on the DIC results was also performed at Station GS19 (Fig. 4G). One series of samples was treated immediately after collection onboard the ship, and a parallel series of water was stored 4 months at 2–4°C before treatment. The generally higher DIC values for the stored samples probably are the result of bacterial action.

The  $\delta^{13}$ C profiles show a quite opposite trend compared to DIC. Planktonic organisms in the surface layer have a preference for the lighter isotope, <sup>12</sup>C, and leave behind a <sup>13</sup>C-enriched DIC fraction during the blooming season.  $\delta^{13}$ C in the deep water is also determined by respiration and dissolution of particles, and by the exchange of water masses. Special care has to be taken to avoid extra fractionation during the sample treatment. There may still be errors in two samples in Figures 4A and 4C (at 500 m). Most  $\Delta^{14}$ C profiles include both AMS and conventional measurements. Measurements of complete parallel samples with the two methods were not performed systematically, but may be compared in adjacent surface samples and in samples deeper in the profiles. For three samples (Nydal *et al.* 1991), however, we have observed  $\Delta^{14}$ C values far higher than any normal value in this ocean, and which show contamination from atmospheric carbon. It was possible to make a control measurement of only one of these samples, which now gives a normal value at the present depth.

# $\Delta^{14}$ C in the Greenland Sea

Figure 3 shows measurements from two stations, LA7 and LA10, from the Greenland Sea. These AMS measurements have a precision of 6‰. Figure 3B shows a  $\Delta^{14}$ C range between +50‰ in the ocean surface to about -40‰ at the bottom. The relatively small  $\Delta^{14}$ C gradient in the upper *ca.* 500 m is due to a mixed layer of the Atlantic surface water, carried by the West Spitsbergen Current (Fig. 1). Unfortunately, there are no  $\Delta^{14}$ C measurements between 500 m and 1000 m, which could give more details about the transition to deeper layers.

Station LA10, in the center of the Greenland Gyre, has nearly the same location as the earlier GEOSECS Station 17 (74°56.0'N, 01°07.3'W) from 1972. The shape of the upper part of the  $\Delta^{14}$ C profile (Fig. 3D) indicates a more continuous exchange with the deepwater than in the case of LA7. The lowest part of the profile has a vertical shape, which may indicate a well-mixed deep reservoir with internal rapid circulation. This deepwater is further in exchange with the deepwater in the Norwegian Sea and the Arctic Ocean (Östlund, Possnert & Swift 1987).

According to Östlund *et al.* (1976), the Greenland Sea deepwater was influenced by bomb tritium in 1972, and consequently, also by bomb <sup>14</sup>C. A calculation from the GEOSECS data below 2000 m (10 samples) gave a mean  $\Delta^{14}$ C result of  $-51.0 \pm 1.5\%$ , a value that has changed to  $-33.0 \pm 1.5\%$  in 1990 (5 samples). According to the change of  $18.0 \pm 2.0\%$  over a period of 18 years, a

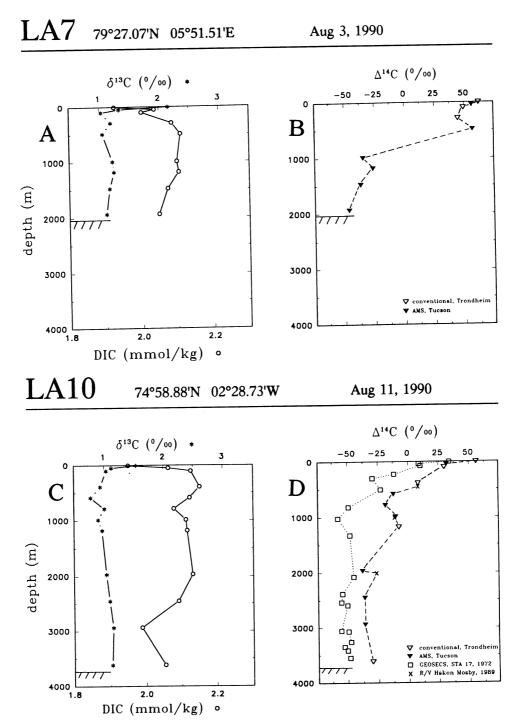


Fig. 3. Carbon profiles in the Greenland Sea

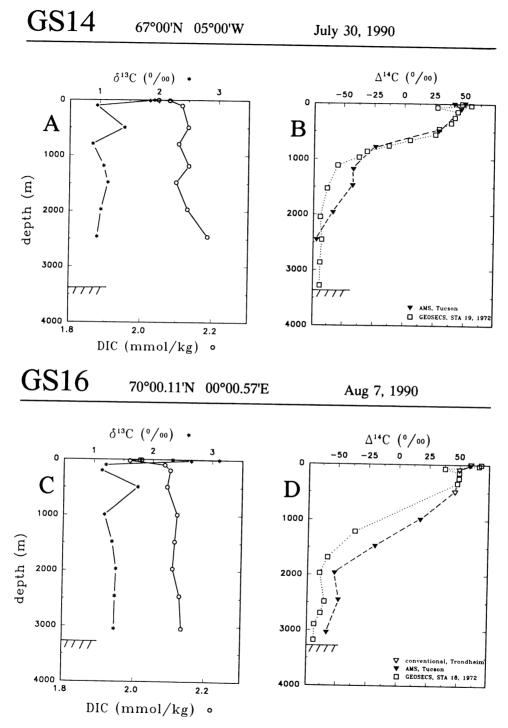


Fig. 4. Carbon profiles in the Norwegian Sea

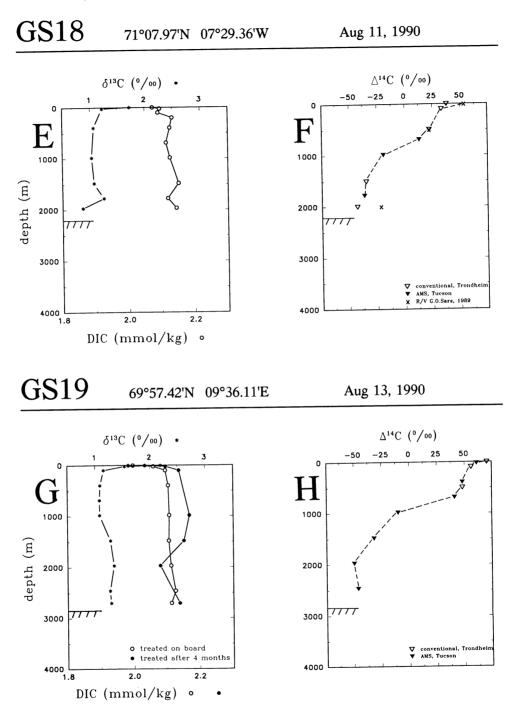


Fig. 4. (continued)

tentative extrapolation to a pre-bomb  $\Delta^{14}$ C level of  $-60.0 \pm 2.0\%$  (about 1965) should be a reasonable figure. This calculation is based on a regular formation of deepwater, which is not always the case (Schlosser *et al.* 1991).

# $\Delta^{14}$ C in the Norwegian Sea

As shown in Figure 4, a common feature of the  $\Delta^{14}$ C profiles in the Norwegian Sea is a relatively small gradient in the upper few hundred meters. This is also caused by an upper mixed layer of the Atlantic surface water. The course down to the deeper layers shows some variations, dependent on the location. All  $\Delta^{14}$ C values at GS18 were measured with a precision of 4–5‰, and this profile demonstrates, to some extent, the agreement between conventional and AMS techniques. The shape of the  $\Delta^{14}$ C profile at GS19 (Fig. 4H) in the Lofoten Basin is close to the profile at LA7 (Fig. 3B) in the West Spitsbergen Current. These AMS samples (Fig. 4H) were measured with a precision of 6‰, and are in satisfactory agreement with the conventional result (precision 4‰) in the surface layer.

 $\Delta^{14}$ C measurements at the two stations, GS14 and GS16, in the Norwegian Sea are compared with the corresponding GEOSECS measurements from 1972. GS14 (Fig. 4B) is located 3° north of GEOSECS Station 19 (64°12.0'N, 05°34.2'W) in the Norwegian Basin, whereas GS16 (Fig. 4D) is located close to GEOSECS Station 18 (70°00.0'N, 00°00.5'W) in the Lofoten Basin. The AMS samples at GS14 were measured with a precision of 4‰ (GS16 with 6‰), but for more details, the profile has to be completed with additional samples. A single measurement below 2000 m is not enough to decide whether or not the bomb carbon has reached the bottom layer in the Norwegian Basin. According to Östlund (1976), both GEOSECS profiles are free of bomb tritium in the deep layers, and the  $\Delta^{14}$ C values from 1972 should thus approach a pre-bomb level. However, this is most convincing for GS14 (Fig. 4B), which shows a  $\Delta^{14}$ C result of -68.0 ± 2.0‰ below 2000 m (4 samples). Compared to the estimated pre-bomb level for the deepwater in the Greenland Sea (-60.0 ± 2.0‰), the Norwegian Sea deepwater is 50 to 100 years older.

## SUMMARY AND CONCLUSION

The present study is concerned with CO<sub>2</sub> uptake and carbon cycling in the Norwegian and Greenland Seas and a transfer to the deepwater in the Atlantic Ocean. The Greenland Sea is a central region for deepwater formation in this area. The deepwater in the Norwegian Sea is fed from the deepwater in the Greenland Sea and the Eurasian Basin. Several deep-sea profiles of DIC,  $\delta^{13}$ C and  $\Delta^{14}$ C have been performed during cruises in summer 1990, and we have focused particularly on the application of <sup>14</sup>C as a tracer. <sup>14</sup>C samples are measured with both conventional and AMS techniques, and the results seems to be in satisfactory agreement. In deep-sea profiles, the small samples have several advantages. From 0.5 liters of seawater, we obtain DIC,  $\Delta^{14}$ C (AMS) and the true  $\delta^{13}$ C value. The obtained carbon profile in the central Greenland Sea (Fig. 3D) indicates a relatively rapid downwelling. Compared to the GEOSECS result from 1972, the  $\Delta^{14}$ C level in the deepwater has increased from -60 to -33‰ over a period of 25 years. This means that about 25% of the deepwater is replaced by surface water during this period.

The main conclusion from the profiles in the Norwegian Sea (Fig.4) is that important variations in  $\Delta^{14}$ C occur among different basins of this ocean. Two GEOSECS profiles from 1972 and our measurements from 1990 (Fig. 4B, D) show that the deepwater in the Norwegian Sea is 50 to 100 years older than that of the Greenland Sea. According to the GEOSECS measurements, the deepwater in the Norwegian Basin in 1972 had a  $\Delta^{14}$ C value of  $-68.0 \pm 2.0\%$ , which may represent the pre-bomb level. Our measurements from 1990 are not well documented below 2000 m, but may indicate very little influence of bomb carbon, even in 1990. This is also in agreement with the assumption that the deepwater is too heavy to take part in the overflow over the Scotland-

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Greenland ridge (Aagaard, Swift & Carmack 1985). The overflow must then consist mainly of surface and intermediate water. The transfer of water over this ridge to the deep Atlantic Ocean is a very important research field, which is also a main project for Nordic WOCE (World Ocean Circulation Experiment). This program, which is scheduled to start in 1993, is a cooperative effort of the Scandinavian countries and is a link to the International WOCE, which is not concerned with the formation of deep water in the Nordic Seas.

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