scopic coupling to the global structure coordinate.

REFERENCES AND NOTES

1. M. F. Perutz, G. Fermi, B. Luisi, B. Shannan, R. C. Liddington, *Acc. Chem. Res.* **20**, 309 (1987).
2. A. E. Siegman, *J. Opt. Soc. Am.* **67**, 545 (1977); H. J. Eichler, P. Gunter, D. W. Pohl, *Laser-Induced Dynamic Gratings* (Springer-Verlag, Berlin, 1986).
3. K. A. Nelson, R. Casalegno, R. J. D. Miller, M. D. Fayer, *J. Chem. Phys.* **77**, 1144 (1982); H. Kogelnik, *Bell Syst. Tech. J.* **48**, 2909 (1969).
4. R. J. D. Miller, in *Time-Resolved Spectroscopy*, R. J. H. Clark and R. E. Hester, Eds. (Wiley, Chichester, England, 1989), vol. 18, pp. 1–54, and references therein.
5. L. Genberg, Q. Bao, S. Gracewski, R. J. D. Miller, *Chem. Phys.* **131**, 81 (1989); L. Genberg, F. Heisel, G. McLendon, R. J. D. Miller, *J. Phys. Chem.* **91**, 5521 (1987).
6. M. B. Zimmt, *Chem. Phys. Lett.* **160**, 564 (1989).
7. J. W. Petrich, C. Poyart, J. L. Martin, *Biochemistry* **27**, 4049 (1988).
8. P. A. Anfinrud, C. Han, R. M. Hochstrasser, *Proc. Natl. Acad. Sci. U.S.A.* **86**, 8387 (1989).
9. L. P. Murray, J. Hofrichter, E. R. Henry, W. A. Eaton, *Biophys. Chem.* **29**, 63 (1988).
10. W. P. Leung, K. C. Cho, S. K. Chau, C. L. Choy, *Chem. Phys. Lett.* **141**, 220 (1987).
11. J. A. Westrick, K. S. Peters, J. D. Ropp, S. G. Sligar, *Biochemistry* **29**, 6741 (1990).
12. E. R. Henry, W. A. Eaton, R. M. Hochstrasser, *Proc. Natl. Acad. Sci. U.S.A.* **83**, 8982 (1986).
13. A. H. Reynolds, S. D. Rand, P. M. Rentzepis, *ibid.* **78**, 2292 (1981).
14. J. W. Petrich, J. L. Martin, D. Houde, C. Poyart, A. Orszag, *Biochemistry* **26**, 7914 (1987); S. Dasgupta and T. G. Spiro, *ibid.* **25**, 5941 (1986).
15. D. A. Chernoff, R. M. Hochstrasser, A. W. Steele, *Proc. Natl. Acad. Sci. U.S.A.* **77**, 5606 (1980); J. M. Friedman *et al.*, *Science* **229**, 187 (1985).
16. E. W. Findsen, J. M. Friedman, M. R. Ondrias, S. R. Simon, *Science* **229**, 661 (1985); S. M. Janes, G. A. Dalickas, W. A. Eaton, R. M. Hochstrasser, *Biophys. J.* **54**, 545 (1988).
17. A. Ansari *et al.*, *Biochemistry* **25**, 3139 (1986).
18. S. Cusack and W. Doster, *Biophys. J.* **58**, 243 (1990).

19. Supported by NIH grant 1 R01 GM41909-01A1 and an NSF Presidential Young Investigator Award (R.J.D.M.). R.J.D.M. is the recipient of an A. P. Sloan and a Camille and Henry Dreyfus Teacher-Scholar Award.

20 August 1990; accepted 15 November 1990

Reduction of Deepwater Formation in the Greenland Sea During the 1980s: Evidence from Tracer Data

PETER SCHLOSSER, GERHARD BÖNISCH, MONIKA RHEIN, REINHOLD BAYER

Hydrographic observations and measurements of the concentrations of chlorofluorocarbons (CFCs) have suggested that the formation of Greenland Sea Deep Water (GSDW) slowed down considerably during the 1980s. Such a decrease is related to weakened convection in the Greenland Sea and thus could have significant impact on the properties of the waters flowing over the Scotland-Iceland-Greenland ridge system into the deep Atlantic. Study of the variability of GSDW formation is relevant for understanding the impact of the circulation in the European Polar seas on regional and global deep water characteristics. New long-term multitracer observations from the Greenland Sea show that GSDW formation indeed was greatly reduced during the 1980s. A box model of deepwater formation and exchange in the European Polar seas tuned by the tracer data indicates that the reduction rate of GSDW formation was about 80 percent and that the start date of the reduction was between 1978 and 1982.

THE NORTHERN SOURCE OF DEEP water in the world ocean is fed by water flowing over the sills separating the European Polar seas from the Atlantic Ocean. The overflowing waters are produced in the European Polar seas through a complex circulation system that links the Greenland-Iceland-Norwegian seas to the Arctic Ocean (*1, 2*). Deep water formation in the central Greenland Sea plays a key role in this system. Direct contact in this region between the cold water domain and the atmosphere forms the densest part of the potential temperature-salinity sequence observed in the deep waters of the European Polar seas. Recent investigations (*3–5*) indicate that the formation of GSDW was considerably changed during the 1980s. Quantification of the reduction rate has been difficult because of the small signals in temperature and salinity data. Tracer measurements provide a better tool for estimation of the reduction rate of GSDW formation and the time when the GSDW formation rate changed.

Tracer data [concentrations of tritium, ^3He, and the CFCs F11 (CCl_3F) and F12 (CCl_2F_2)] have been collected on several cruises to the European Polar seas between 1972 and 1989 (Fig. 1). These data provide sufficient time resolution to study trends in the formation rate of GSDW (*6–12*). For each cruise, we averaged all data below a depth of 1500 m from stations located in the central Greenland Sea. As the hydrographic parameters and the tracer concentrations are homogeneous below this depth (*5, 7, 12, 13*), such a procedure yields a good estimate of the mean tracer concentration of GSDW even in cases where data are available only from single stations. The most remarkable features in the data (Fig. 2) are the increase of the tritium-^3He age with time which, for the period between 1979 and 1988, was not significantly different from the one expected for a stagnant water body (indicated by the line in Fig. 2C), and the constant F11 level between 1982 and 1989. Both the linear increase of the tritium-^3He age and the constant level of F11 directly indicate that renewal of GSDW slowed considerably during this period. This conclusion is in agreement with the tritium observations between 1979 and 1988, which follow more or less directly the radioactive decay curve calculated for a stagnant water body (Fig. 2A). However, addition of near-surface water is not the only process renewing the deep waters in the Greenland Sea. Exchange with the Arctic Ocean and the Norwegian Sea also contributes to GSDW renewal (*1, 13*). Therefore, we simulated the tracer data with a model designed to estimate the rates of

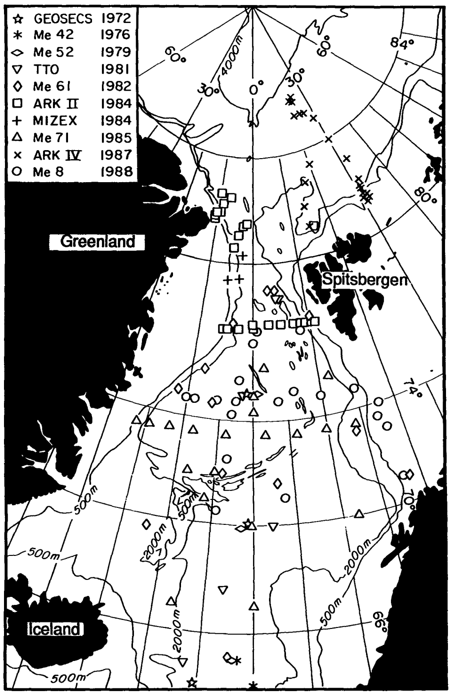


Fig. 1. Locations of tritium and ^3He stations occupied on several cruises (*6*) between 1972 and 1988. The Greenland Sea data used in this study are from cruises GEOSECS, Me42, Me52, TTO, Me62, Me71, and Me8. Only some of the available samples have been measured from Me71 and Me8. Station maps for the CFC stations are in (*5, 11, 12*).

P. Schlosser, Lamont-Doherty Geological Observatory of Columbia University and Department of Geological Sciences, Palisades, NY 10964.
G. Bönisch and R. Bayer, Institut für Umweltphysik der Universität Heidelberg, Im Neuenheimer Feld 366, D-6900 Heidelberg, Germany.
M. Rhein, Institut für Meereskunde an der Universität Kiel, Düsternbrooker Weg 20, D-2300 Kiel, Germany.

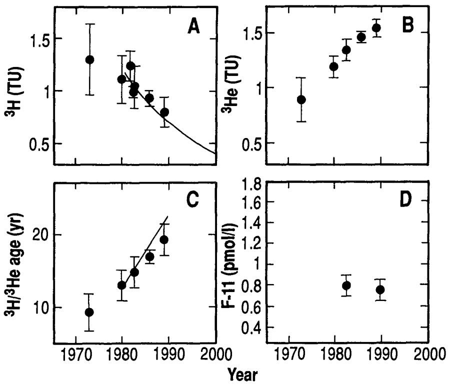


Fig. 2. Mean tracer concentrations in GSDW as a function of time. (**A**) tritium; (**B**) ^{3}He; (**C**) ^{3}H/^{3}He-age; (**D**) F11. The line in (A) is the radioactive decay curve for a stagnant water body, the line in (C) is the corresponding theoretical increase of the ^{3}H/^{3}He age. The error bars indicate 1 SD of the mean value of all data from stations in the central Greenland Sea (depths ≥1500 m).

deepwater formation and exchange in the European Polar seas.

The model is based on the kinematic box model described by Heinze *et al.* (*13*). It consists of boxes for each of the deepwater reservoirs (Fig. 3). Deepwater formation was allowed in the Greenland Sea and in the Eurasian Basin. The pattern of deepwater exchange was implemented on the basis of hydrographic and tracer observations (*1, 13*) (Fig. 3). The model was tuned by a set of stable and radioactive tracers (temperature, salinity, and ^{39}Ar levels). Additionally, the concentrations of transient tracers were used to tune the model (tritium, tritiogenic ^{3}He, CFCs F11 and F12, and ^{85}Kr). In contrast to the Heinze *et al.* model, our version is sensitive to the deepwater exchange pattern. The boundary conditions for the surface boxes of the model were reconstructed following the procedures described by Heinze *et al.* (*13*). The GSDW is thought to be renewed by a mixture of surface and subsurface waters involving free convection, cabbeling, and double diffusion (*14–16*). To take these processes into account, we adapted the tritium boundary condition for the surface waters of the North Atlantic established by Dreisigacker and Roether (*17*) to the Greenland Sea surface waters by fitting it to observations (multiplication by ~0.7). The GSDW box was renewed by a four-to-one mixture of surface water and intermediate water. The tritium concentration of the intermediate water was simulated by a 5-year-old Atlantic component. The age of the Atlantic component was derived from the tritium/^{3}He ratio measured in the Atlantic core in the central Greenland Sea. A similar procedure was applied for the Barents Sea shelf waters that are renewing the Eurasian Basin deep and bottom waters. In this case a small runoff component (about 0.75%) was added to 3-year-old Atlantic water. The CFC surface concentrations were established following the procedure described by Bullister and Weiss (*12*) and Smethie *et al.* (*18*). All the reconstructed surface concentrations were fitted to available surface tracer data. This procedure ensured that the boundary conditions used for the transient tracers are reasonably well constrained (*19*).

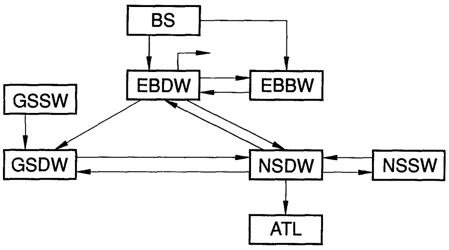
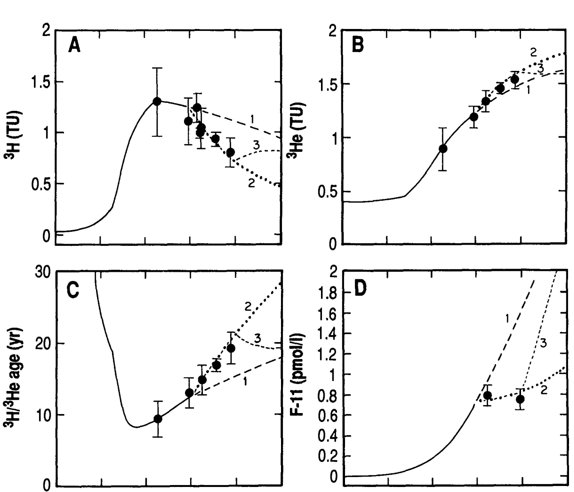


Fig. 3. Schematic view of the box model used for the simulation of the tracer concentrations in GSDW. Surface water boxes: GSSW, Greenland Sea Surface Water; NSSW, Norwegian Sea Surface Water; BS, Barents Sea Shelf Water. Deep water boxes: GSDW, Greenland Sea Deep Water; NSDW, Norwegian Sea Deep Water; EBDW, Eurasian Basin Deep Water; EBBW, Eurasian Basin Bottom Water. EBDW and EBBW are distinguished on the basis of the criteria given by Aagaard (*23*) and Smethie *et al.* (*18*). The overflow of deep water into the Atlantic Ocean is indicated by the loss of NSDW into the box denoted ATL.

The tracer observations in the deep waters of the European Polar seas can only be reconstructed by the model if the deepwater formation rate in the Greenland Sea decreased in the 1980s (Fig. 4). We obtained the results for ^{3}He and the tritium/^{3}He ages (Fig. 4, B and C) in the model by adding a ^{3}He flux to the deepwater boxes to match the observed ^{3}He values (Fig. 4B; without this additional flux the model reproduces the shape of the ^{3}He versus time curve perfectly, but has a small offset to lower ^{3}He values compared to the observations). The ^{3}He flux needed to adapt the model curves to the observed ^{3}He concentrations is ~1 atom cm^{-2} s^{-1}. This value is consistent with the global average oceanic ^{3}He flux estimated by Craig *et al.* (*20*) to be about 4 atoms cm^{-2} s^{-1}. The reason that the estimated ^{3}He flux in the European Polar seas is significantly lower than the global average is most likely related to the low spreading rates of the mid-ocean ridges in this region.

We estimate that the formation of GSDW slowed down some time between 1978 and 1982. The reduced rate of deepwater formation has persisted to the time of the last sampling campaign in 1989. The best estimate for the decrease of the deepwater formation rate is about 80% (± ~10%). The model yielded a GSDW formation rate of about 0.47 Sv in the 1960s and 1970s, which decreased to about 0.1 Sv during the 1980s. Using CFC data with sparse time resolution (observations from 1982 and 1989) and a model that was not sensitive to the deepwater flow pattern, Rhein (*5*) derived a similar reduction rate of the formation of GSDW in the 1980s. Our model results correspond to an increase of the mean turnover time of GSDW due to renewal from surface waters from 34 to 170 years. In contrast, the effective turnover time (renewal from the surface plus deepwater exchange with the Norwegian Sea and the Eurasian Basin) increased more moderately from 17 to 28 years in the model. We extrapolated the model curves to the year 2000 for three different scenarios: (i) GSDW renewal at a constant rate, (ii) decreased GSDW formation between 1980 and 2000 and (iii) decreased GSDW formation between 1980 and 1990 followed by increase to pre-1980 levels after 1990. Comparison of the three curves clearly shows that significantly different tracer concentrations are expected for the three scenarios. Moni-

Fig. 4. Tracer concentrations in GSDW as a function of time as simulated by the model sketched in Fig. 3. (**A**) tritium; (**B**) ^{3}He, (**C**) ^{3}H/^{3}He-age; (**D**) F11. The tracer concentrations are simulated for three scenarios: (i) continuous GSDW formation, (ii) cessation of GSDW formation during the 1980s, (iii) cessation of GSDW formation during the 1980s followed by restored deepwater renewal after 1990.



toring of the transient tracer concentrations of GSDW will be valuable in studying the variability of deepwater formation in the Greenland Sea.

In our model calculations we assumed that the deepwater formation in the Greenland Sea operates in two modes (deepwater formation at full intensity before 1980 and slowed down deepwater formation during the 1980s). Such a simplistic view is certainly not correct. Instead, deepwater formation is a highly variable process in time and space. Whether formation of GSDW occurred continuously or sporadically in the period before 1980 cannot be derived from the tracer data because of a lack of time resolution. However, the observed tracer concentrations in GSDW between 1972 and 1979 clearly demonstrate that intensive deepwater renewal must have taken place between the appearance of the tritium bomb peak in the mid-1960s and the early 1970s. The observed tracer concentrations can be reconstructed by the model for the case of a constant deepwater renewal rate before 1980. The results demonstrate that on average formation of GSDW stopped almost completely during the 1980s. The model calculations have to be seen as a first-order approximation. Tracers are the only tool to monitor the average deepwater formation rate in the Greenland Sea on the basis of a station grid that can be realized in practical terms.

The model yields no information on the reason for the reduction of GSDW formation in the 1980s. Reduction could be connected to the appearance of the salinity anomaly observed in the northern Atlantic and the Greenland-Norwegian seas in the 1970s (*21*). This anomaly reached the Norwegian Current and Fram Strait in 1978 and the East Greenland Current between 1981 and 1982. This period coincides with the estimate of the start date of the cessation (1978 to 1982). A decrease in the salinity of the upper water column in the Greenland Sea can lead to the situation that the waters sinking from near-surface layers to deeper layers are, even after winter cooling, not sufficiently dense to reach the deep and bottom waters of the Greenland Sea. Such a scenario is also consistent with the observation that the temperature of GSDW increased during the 1980s (*3*). The deep and bottom waters would be affected first by a weakened convection. However, a further decrease of the salinity of the surface waters leading to even shallower convection depths would influence the formation of Arctic Intermediate Water. This water contributes significantly to the Denmark Strait overflow. In this way the properties of the newly formed North Atlantic Deep Water (NADW) can be changed. Another possible process for reduction of GSDW formation could be an increase in the influence of the East Greenland Current on the surface waters of the Greenland Sea leading to a freshening of the upper water column (*22*). To obtain a clear link between the processes in the European Polar seas and variability in NADW requires a long-term monitoring program at key positions north and south of the Scotland-Iceland-Greenland ridges.

REFERENCES AND NOTES

1. K. Aagaard, J. H. Swift, E. C. Carmack, *J. Geophys. Res.* **90**, 4833 (1985).
2. J. H. Swift, K. Aagaard, S.-A. Malmberg, *Deep-Sea Res.* **27**, 29 (1980).
3. R. A. Clarke, J. H. Swift, L. J. Reid, K. P. Koltermann, *ibid.* **37**, 1385 (1990).
4. Greenland Sea Project Group, *Eos* **71**, 750 (1990).
5. M. Rhein, *Deep-Sea Res.*, in press.
6. The tritium data were obtained on cruises of R.V. *Meteor* (Me42, 1976; Me52, 1979; Me61, 1982; Me71, 1985; Me8, 1988) and of R.V. *Knorr* (GEOSECS, 1972; TTO/NAS, 1982). The *Meteor* tritium samples were measured in the Heidelberg tritium laboratory and the data (except those from Me71 and Me8) are reported by Schlosser (*7*). The *Knorr* tritium data were produced in the Miami tritium laboratory and reported by Östlund and Brescher (*8*) and Östlund and Grall (*9*). The ^{3}He data were collected on cruises Me52, Me61, Me71, and Me8 and on the *Knorr* GEOSECS cruise. The *Meteor* samples were measured in the Heidelberg helium isotope laboratory and are partially reported by Schlosser (*7*) (Me42 and Me52). The GEOSECS ^{3}He data were measured at the Scripps Oceanographic Institution (*10*). The concentrations of CFCs were measured on cruises of R.V. *Hudson* (1982) and R.V. *Valdivia* (1989). The data are reported by Bullister and Weiss (*11,12*) and Rhein (*5*).
7. P. Schlosser, thesis (in German), University of Heidelberg, Heidelberg, Germany (1985).
8. H. G. Östlund and R. Brescher, *Tritium Lab. Data Rep. 12* (Rosenstiel School of Marine and Atmospheric Science, University of Miami, *Miami*, 1982).
9. H. G. Östlund and C. Grall, *ibid. 16*, (1987).
10. GEOSECS Atlantic, Pacific, and Indian Ocean Expeditions, Shore-based data and graphics, vol. 7 (National Science Foundation, Washington, DC, 1987).
11. J. L. Bullister, thesis, University of California, San Diego (1984).
12. ——— and R. F. Weiss, *Science* **221**, 265 (1983).
13. C. Heinze *et al.*, *Deep-Sea Res.* **37**, 1425 (1990).
14. B. Rudels, *ibid.*, p. 1491.
15. T. J. McDougall, *ibid.* **30**, 1109 (1983).
16. E. C. Carmack and K. Aagaard, *ibid.* **20**, 687 (1973).
17. E. Dreisigacker and W. Roether, *Earth Planet Sci. Lett.* **38**, 301 (1978).
18. W. M. Smethie, Jr., D. W. Chipman, J. H. Swift, K. P. Koltermann, *Deep-Sea Res.* **35**, 347 (1988).
19. G. Bönisch and P. Schlosser, in preparation.
20. H. Craig, W. B. Clarke, M. A. Beg, *Earth Planet Sci. Lett.* **26**, 125 (1975).
21. R. P. Dickson *et al.*, *Progr. Oceanogr.* **20**, 103 (1988).
22. K. Aagaard and E. C. Carmack, *J. Geophys. Res.* **94**, 14485 (1989).
23. K. Aagaard, *Deep-Sea Res.* **28**, 251 (1981).
24. The officers and crews of the research vessels *Meteor*, *Knorr*, and *Valdivia* provided logistical support during sample collection. G. Fuchs, K. P. Koltermann, J. Meincke, A. Suckow, and W. Weiss collected part of the tracer samples. G. Bader and G. Zimmek performed most of the tritium and ^{3}He measurements. We profited from discussions with K. Aagaard, K. P. Koltermann, W. Smethie, J. Swift, and D. Wallace. This work was supported by the Deutsche Forschungsgemeinschaft and the Office of Naval Research through contract N00014-90-J-1362. L-DGO contribution no. 4749.

24 September 1990; accepted 18 December 1990

Evidence for a Phytotoxic Hydroxy-Aluminum Polymer in Organic Soil Horizons

DOUGLAS HUNTER* AND DONALD S. ROSS

The toxicity of Al that has been mobilized in soil, streams, and lakes through acid deposition primarily has been attributed to mononuclear Al species. Polynuclear Al species are more toxic than mononuclear species, but they have not been considered to be significant in the environment. Aluminum-27 nuclear magnetic resonance (NMR) spectra of forested spodosol soil horizon samples show the presence of polynuclear $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$. The $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ species accounted for 30 percent of the aqueous Al observable by NMR, and this could make a significant contribution to the toxicity of the Al in these soils.

ALUMINUM IS A FUNDAMENTAL component of clay minerals in soils (*1*) that can be solubilized by acid deposition. The toxicity of Al to plants in acid soils and to fish in acid lakes has been observed to increase from pH 3 to pH 5.4 (*2, 3*). This phenomenon has been attributed to mononuclear hydroxy-aluminum species on the basis of equilibrium thermodynamic models. Aluminum can also polymerize to form polynuclear species at these higher pHs. Recently, a soluble polymer of Al, $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (hereafter referred to as Al_{13}), has been shown to inhibit the growth of several plant species at one-tenth the concentration of Al^{3+} (*4*). Solutions containing polynuclear

---

D. Hunter, Department of Botany, University of Vermont, Burlington, VT 05405.
D. S. Ross, Department of Plant and Soil Science, University of Vermont, Burlington, VT 05405.

*Present address: Division of Biogeochemistry, The University of Georgia, Savannah River Ecology Laboratory, Drawer E, Aiken, SC 29802.