An implication of the above mechanism is the tendency for longer molecules to orient to a greater degree than smaller molecules, so that there is more chance of longer molecules reacting with other long molecules, leading to a wider molecular weight distribution. The polydispersity index (p, a measure of the width of this distribution) for poly(p-phenylene terephthalamide) (PPTA) was obtained by gel permeation chromatography of samples which were made soluble in tetrahydrofuran after n-alkylation by n-octadecyl bromide[7,8]. For 19 min of reaction and $\dot{\gamma} = 30\ s^{-1}$, the polydispersity index ($p = 2.45$) was significantly lower than that for $\dot{\gamma} = 413\ s^{-1}$ ($p = 3.25$), in agreement with the proposed mechanism.

Previous studies of polymerization of rod-like polymers have shown the necessity of high shear rates for obtaining high molecular weights[4,9]. The type of mixer used also affects the limiting molecular weight[10]. Such results can be explained if the shearing causes an increase in the rate of polymerization relative to the rate of reactive end-group terminating side reactions.

The above results have relevance for systems with rotational constraints for reaction, in which slow rotational diffusion of the molecules severely reduces the reaction rate. Flow fields as well as other orienting fields can significantly enhance such reaction rates, as well as alter the molecular weight distribution. Besides the obvious benefit of increasing production rates, the above mechanism could also be used to advantage in systems in which side reactions with small impurity molecules occur. In these cases, a better (higher-molecular-weight) product would be obtained by increasing the polymerization rate relative to the side reactions, which would be unaffected by shearing. □

Received 12 March; accepted 30 September 1992.

1. Kwolek, S. L., Morgan, P. W. & Schaefgen, J. R. in *Encyclopedia of Polymer Science and Technology* (eds Mark, H. F., Bikales, N. M., Overberger, C. G. & Menges, G.) Vol. 9, 1–61 (Wiley, New York, 1987).
2. Cotts, D. B. & Berry, G. C. *Macromolecules* **14,** 930–934 (1981).
3. Chella, R. & Ottino, J. M. *Arch. Ration. Mech. Anal.* **90,** 15–42 (1985).
4. Arpin, M. & Strazielle, C. *Polymer* **18,** 591–598 (1977).
5. Doi, M. & Edwards, S. F. *The Theory of Polymer Dynamics*, 324–349 (Clarendon, Oxford, 1986).
6. Agarwal, U. S. & Khakhar, D. V. *J. chem. Phys.* **96,** 7125–7134 (1992).
7. Ogata, N., Sanui, K. & Kitayama, S. *J. Polym. Sci. Polym. Chem.* edn **22,** 865–867 (1984).
8. Takayanagi, M. & Katayose, T. *J. Polym. Sci. Polym. Chem.* edn, **19,** 1138–1145 (1981).
9. Morgan, P. W. *Macromolecules* **10,** 1381–1390 (1977).
10. Vollbracht, L. in *Comprehensive Polymer Science* (eds Allen, G. & Bevington, J. C.) Vol. 5, 375–386 (Pergamon, Oxford, 1989).
11. Asada, T., Muramatsu, H., Watanabe, R. & Onogi, S. *Macromolecules* **13,** 867–871 (1980).

Cooling and freshening of the subpolar North Atlantic Ocean since the 1960s

J. F. Read & W. J. Gould

Institute of Oceanographic Sciences Deacon Laboratory, Brook Road, Wormley, Surrey GU8 5UB, UK

LITTLE is known of the interdecadal variability in the thermohaline circulation of the world's oceans, yet such knowledge is essential as a background to studies of the effects of natural and anthropogenic climate change. The subpolar North Atlantic is an area of extensive water mass modification by heat loss to the atmosphere. Lying as it does at the northern limit of the global thermohaline "conveyor belt"[12], changes in this region may ultimately have global consequences. Here we report that in August 1991 the waters between Greenland and the United Kingdom were on average 0.08 °C and 0.15 °C colder than in 1962 and 1981, respectively, and slightly less saline than in 1962. The cause appears to be renewed formation of intermediate water in the Labrador Sea from cooler and fresher source waters, and the spreading of this water mass from the west. Variations in the source characteristics of Labrador Sea Water can be traced across the North Atlantic, with a circulation time of 18–19 years between the Labrador Sea and Rockall Trough. More recently formed Labrador Sea Water, with even lower temperature and salinity, should cool and freshen the North Atlantic still further as it circulates around the ocean in the coming decade.

A survey of the subpolar North Atlantic was made in August 1991 as a contribution to the World Ocean Circulation Experiment. The survey (CONVEX-91) was designed to resolve the features of the gyre-scale circulation. The conductivity-temperature-depth (CTD) stations discussed here were along two roughly zonal tracks at ~58° N (north section) and 53° N (south section), linked by a section near 40° W (west section)[1] (Fig. 1). One of the most striking features of the data was the abundance and extreme characteristics of Labrador Sea Water (LSW) in the western part of the survey. LSW is one of the main water masses of the North Atlantic. It is believed to form in the central Labrador Sea by deep convection[2] and spreads out at intermediate depths throughout most of the area north of 40° N[3]. It is characterized by a marked salinity minimum and has been defined[3] as having potential temperature and salinity characteristics between 3.3–3.4 °C and 34.84–34.87, respectively. The potential temperature and salinity minimum seen during CONVEX-91 was pronounced, reaching 2.83 °C, 34.84. Another distinguishing feature of LSW is its weak vertical density gradient[3], and during CONVEX-91 this was found between depths of 500 and 2,000 m within the density range of $\sigma_{1.5} =$ 34.64–34.68 kg m^{-3} (where $\sigma_{1.5}$ is potential density referenced to a depth of 1,500 db).

Changes in LSW and other water masses of the subpolar North Atlantic have already been observed over the past few years[4–8]. The characteristics of LSW near the source show considerable variation within tens of years[2–4,9]. The variability is believed to be caused by a combination of changes in the rate of renewal and changes in the properties of the water from which LSW is formed[9]. Monitoring over the past 50 years[9] has shown that during the 1960s deep convection did not occur and the temperature and salinity of LSW gradually increased. Deep convection was renewed in 1971–72[9] and resulted in an abrupt drop in temperature. (J. R. N. Lazier, manuscript in preparation) has updated the time series of ref. 3 of temperature on the density surface $\sigma_{1.5} = 34.64$ kg m^{-3} from which we have inferred salinity (Fig. 2a). This shows that after a freshening in the early 1970s, the salinity (and temperature) began to increase in the early 1980s, although not to the same level as in 1970. Since then there has been a further, more extreme freshening (and cooling) on this density surface. Thus there have been two

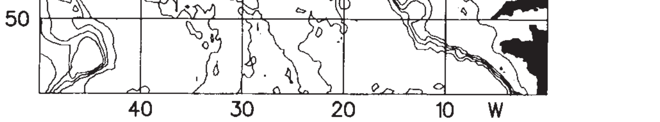

FIG. 1 Location of the CONVEX-91 sections, with Erika Dan (1962), TTO (1981), and Knorr (1983) stations, showing the topography of the region.

© 1992 Nature Publishing Group

periods of renewal and change; during 1971–76 and again between 1984–90.

Salinity on density surfaces close to the temperature and salinity minimum of LSW from the CONVEX-91 northern section shows two main features (Fig. 2*b*): first, an increase in salinity from west to east (high salinity values over the Mid-Atlantic Ridge and Rockall plateau are probably the result of enhanced mixing over the topography); second, a change in the density surface of the salinity minimum.

LSW seems to be advected around the North Atlantic with modification by mixing and by time changes at the LSW source[3]. Salinity on the $\sigma_{1.5} = 34.64$ kg m^{-3} density surface at the eastern end of the north section (Fig. 2*b*) are higher than anything seen at the LSW source (Fig. 2*a*) implying that mixing has taken place. Here we will not examine the mixing processes, but accept their role in modifying the water mass as we seek to relate the time-series (Fig. 2*a*) to the spatial distribution (Fig. 2*b*). Salinity on the $\sigma_{1.5} = 34.64$ kg m^{-3} density surface in the Rockall Trough is ~34.925, and we will start by associating this with the highest values in the Labrador Sea, ~34.915, seen in 1970–71. Salinity on the same density surface in the Iceland Basin is fresher, between 34.89–34.90, so it could be older than that in the Rockall Trough, that is before 1970, or it could have originated more recently, when salinity increased between 1981 and 1985. If the circulation scheme proposed in ref. 3 is adopted, namely cyclonic flow out of the Labrador Sea eastwards across the North Atlantic, with northward branches into the Irminger Basin and into the Iceland Basin and Rockall Trough, then the water in the Iceland Basin should be of more recent origin than that of the Rockall Trough because it is closer to the source. Therefore we suggest that the LSW in the Iceland Basin formed during the period 1981–85 in the Labrador Sea.

We can corroborate our timescale of the circulation by looking at the changes in density surface of the salinity minimum. The density of LSW was about $\sigma_{1.5} = 34.66$ kg m^{-3} during the 1960s[3], decreasing to $\sigma_{1.5} = 34.64$ kg m^{-3} in the early 1970s[3,6], and has since increased again reaching $\sigma_{1.5} = 34.66$ kg m^{-3} in 1986[4] and $\sigma_{1.5} = 34.67$ kg m^{-3} in 1992 (J. R. N. Lazier, manuscript in preparation). The CONVEX-91 north section (Fig. 2*b*) shows the salinity in the Iceland Basin to be least on the $\sigma_{1.5} = 34.64$ kg m^{-3} isopycnal surface. This suggests that this water must have formed before 1986, but later than the 1960s. The salinity minimum in the Irminger Basin lies between $\sigma_{1.5} = 34.66$ and 34.67 kg m^{-3}, indicating its recent origin, and is markedly fresher than the rest of the section. The difference in both salinity and density of the salinity minimum west and east of the Mid-Atlantic Ridge suggests that more recent, denser LSW has not yet spread to the east.

The density surface of the salinity minimum in the Rockall Trough is poorly defined. Long-term monitoring of a section across the northern end of the Trough has shown little change in the properties of LSW since 1975 (D. J. Ellett, manuscript in preparation). The variation in salinity at a depth of 1,600 m has been less than ±2 standard deviations from the 1975–78 mean. In 1990, however, there was an unprecedented freshening and cooling of up to 7 standard deviations (Ellett, manuscript in preparation). If we relate this to the changes in the Labrador Sea we see (Fig. 2*a*) that the only time there has been such a long period with little or no change in salinity, followed by a sudden marked freshening, was the period leading up to the renewal in 1972. This suggests that the effects of the renewal of LSW in the early 1970s have just reached the Rockall Trough, and from this we can deduce that there is a circulation time of 18–19 years between the Labrador Sea and the Rockall Trough.

To expand the discussion to cover the changes in water properties over the entire water column, we have made comparisons with previous data sets. The CONVEX-91 north and south sections lay close to the Transient Tracers in the Ocean (TTO) 55° N (1981) and Erika Dan 53.5° N (1962) sections respectively (Fig. 1). We have linearly interpolated each pair of sections onto a common grid with points 40 m apart vertically

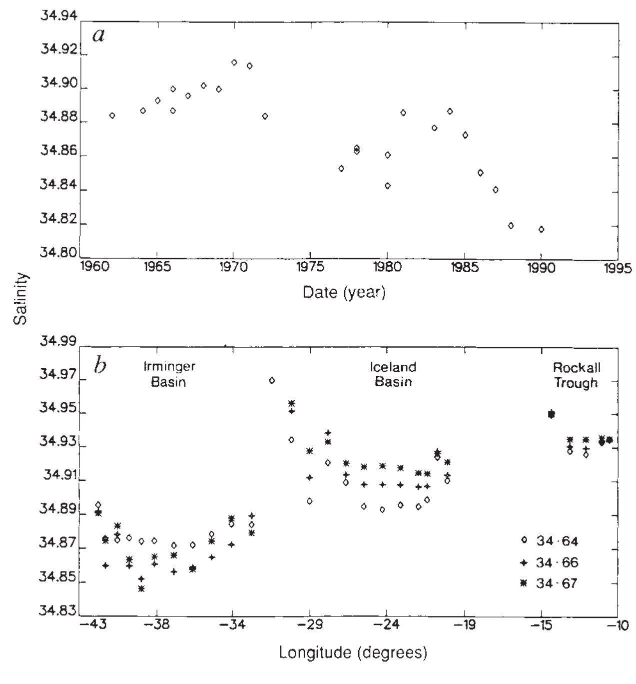

FIG. 2 *a*, Salinity on the density surface $\sigma_{1.5} = 34.64$ kg m^{-3} in the central Labrador Sea from Lazier (personal communication). *b*, Salinity on the density surfaces $\sigma_{1.5} = 34.64$ kg m^{-3}, $\sigma_{1.5} = 34.66$ kg m^{-3}, $\sigma_{1.5} = 34.67$ kg m^{-3} from the CONVEX-91 northern section.

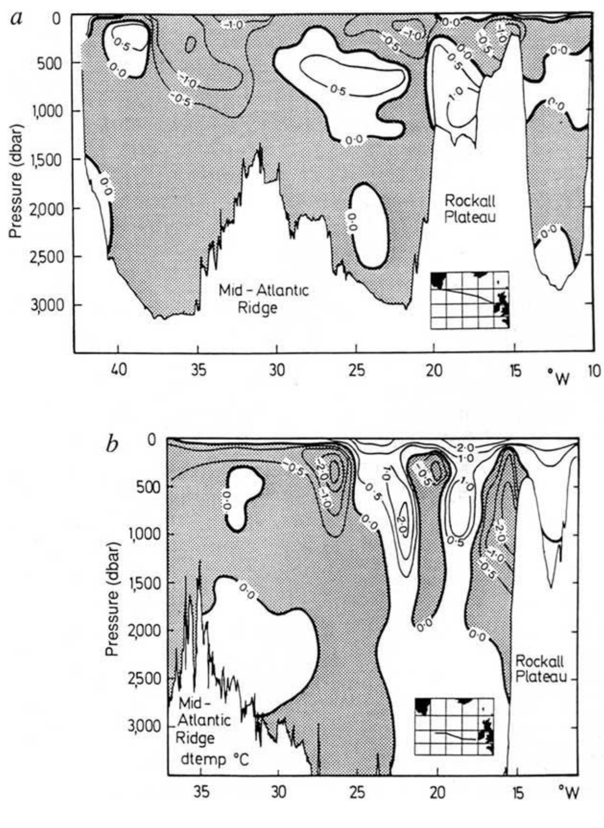

FIG. 3 Smoothed temperature difference (°C) between (*a*) CONVEX-91 north section and the TTO 55° N section from 1981, and (*b*) CONVEX-91 south section and the Erika Dan 53.5° N data from 1962. Shaded areas indicate negative temperature difference.

© 1992 Nature Publishing Group

and 0.25° of longitude apart horizontally, and we have subtracted the earlier temperatures from CONVEX-91 temperatures (Fig. 3) (the west sections are not shown). Care must be taken in interpreting Fig. 3*b* because the CTD stations at the eastern end were not worked in the same location (Fig. 1), and some effect from the different topography might account for the eddy-like structure seen between 15–28° W. Nevertheless the general trend indicated is of a decrease in temperature. Cooling seems to be more pronounced and more extensive in the west than the east; for example, since 1981 (Fig. 3*a*) there has been a decrease of more than −1 °C in the upper layers to the west, compared with warming in the intermediate water to the east of the Mid-Atlantic Ridge. Ignoring measurements above 50 m (the mixed layer depth) the mean temperature difference of −0.15 °C between 1991 and 1981 shows that cooling has been much greater than since 1962 (−0.08 °C). Previous results showed[10,11] that the subpolar North Atlantic had warmed between the early 1950s and early 1970s, whereas since then there has been cooling[6–8]. It would now appear that cooling has continued to temperatures lower than those of 1962. Comparison of the CONVEX-91 west section (Fig. 1) with data from Erika Dan (1962) and Knorr (1983) in a similar fashion (but on a 0.25° latitudinal grid) shows that there has been marked cooling since 1962, averaging −0.42 °C, whereas since 1983 there has been no change, presumably because the effects of the first renewal of LSW had already reached the Irminger Basin.

The renewal of LSW during 1972 now seems to have reached the Rockall Trough, with a consequent cooling and freshening across the subpolar North Atlantic. More recently formed LSW, however, is considerably colder and fresher than previously formed LSW and has not yet spread beyond the Irminger Basin. Given that this was formed in the late 1980s and that our estimated time for previous changes to reach the Rockall Trough was ~18–19 years, we predict that the next decade will see continued cooling and freshening of the subpolar gyre as the latest form of LSW circulates around the North Atlantic. Coupled ocean-atmosphere models[13–15] show surface cooling and freshening of the subpolar North Atlantic in response to greenhouse warming. The freshening dominates in such a way as to suppress convective water mass formation. Our measurements show that cooling is predominant, resulting in renewed convection, and is therefore somewhat at odds with the model results. □

Received 27 April; accepted 25 September 1992.

1. Gould, W. J. *Cruise Report* No. 230 (Institute of Oceanographic Sciences Deacon Laboratory, 1992).
2. Clarke, R. A. & Gascard, J. C. *J. phys. Oceanogr.* **13**, 1764–1778 (1983).
3. Talley, L. D. & McCartney, M. S. *J. phys. Oceanogr.* **12**, 1189–1205 (1982).
4. Wallace, D. W. R. & Lazier, J. R. N. *Nature* **332**, 61–63 (1988).
5. Lazier, J. R. N. & Gershey, R. M. *WOCE News* **11**, 5–7 (1991).
6. Brewer, P. G. *et al. Science* **222**, 1237–1239 (1983).
7. Swift, J. H. in *Climate Processes and Climate Sensitivity* (eds Hansen, J. E. & Takahasi, T.) 39–47 (AGU, Washington DC, 1984).
8. Swift, J. H. in *Glaciers, Ice-Sheets, and Sea-Level Effect of a CO_2-induced Climate Change* (ed. Lingle, C. S.) 129–138 (Department of Energy, Washington DC, 1985).
9. Lazier, J. R. N. *Atmos. Ocean* **18**, 227–238 (1980).
10. Levitus, S. *J. geophys. Res.* **94**, 6091–6131 (1989).
11. Levitus, S. *J. geophys. Res.* **94**, 16125–16131 (1989).
12. Broecker, W. S., Peteet, D. M. & Rind, D. *Nature* **315**, 21–26 (1985).
13. Stouffer, R. J., Manabe, S. & Bryan, K. *Nature* **342**, 660–662 (1989).
14. Manabe, S., Bryan, K. & Stouffer, R. J. *J. phys. Oceanogr.* **20**, 722–749 (1990).
15. Mikolajewicz, U., Santer, B. D. & Maier-Reimer, E. *Nature* **345**, 589–593 (1990).

ACKNOWLEDGEMENTS. The measurements were made on RRS *Charles Darwin* and we thank the Master and crew for their assistance. The quality of the CTD data was assured by Peter Saunders, Mark Brandon, Sheldon Bacon, Pat Gwilliam and Chris Paulson. We also thank John Lazier for additional information on the properties of LSW, and Raymond Pollard for constructive criticism of our manuscript.

A refractory HIMU component in the sources of island-arc magma

Rosemary Hickey-Vargas

Department of Geology, Florida International University, Miami, Florida 33156, USA

THE strontium, neodymium and lead isotopic compositions of most island-arc magmas seem to require a component in the source region with the characteristics of ocean-island basalts (OIB)[1–5]. In contrast, however, the trace-element compositions of arc magmas and OIB do not match: OIB sources are highly enriched in incompatible elements, whereas island-arc basalts are depleted in high-field-strength and light rare-earth elements. Peridotite that has undergone an episode of melting, and hence depletion of incompatible elements, is an appropriate source for island-arc basalts[6,7]. I have previously proposed that an OIB component with the characteristics of the mantle endmember HIMU[8] (notably, high U/Pb ratio) is present in arc magmas of the Mariana Island region (Philippine Sea). Here I show, using isotopic comparisons of Philippine Sea arc and basin magmas, including the highly magnesian lavas known as boninites, that this HIMU component is refractory and is selectively incorporated into the depleted mantle lithosphere during extraction of mid-ocean-ridge basalt and back-arc-basin basalt. This process creates the mixture of depleted and OIB-source mantle required for island-arc basalt.

The Philippine Sea region was formed by three successive arc building and back-arc spreading phases, and is therefore ideal for studying the nature and relationship of arc and basin magma sources. Back-arc-basin basalts were erupted 65–40 million years before present (Myr BP) (West Philippine basin), 32-17 Myr BP (Parece Vela and Shikoku basins) and 6-0 Myr BP (Mariana Trough)[9], and are beginning to be erupted at the Sumisu Rift. Isotope characteristics of these basin magmas are remarkably uniform (Fig. 1*a*). On lead isotope diagrams they plot along single linear trends and they share the anomalous Dupal isotope characteristics of mid-ocean-ridge basalts (MORB) from the Indian Ocean, such as elevated $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$. In contrast, island-arc magmas erupted 45-30 Myr BP (Palau-Kyushu arc), 9-13 Myr BP (West Mariana arc) and 3-0 Myr BP (Mariana arc)[9] have the Pb-isotope characteristics of the Northern Hemisphere (Fig. 1*b*), similar to Pacific Ocean mid-ocean-ridge basalt (MORB). Lavas of the Palau-Kyushu arc, in particular, lack evidence of sediment involvement and therefore may reflect the composition of the subarc mantle wedge. Lead isotope ratios in these arc lavas extend from values typical of normal Pacific Ocean MORB (NMORB) towards HIMU[8], the OIB source component characterized by highest $^{206}Pb/^{204}Pb$ (Fig. 1*b*).

In terms of plate tectonics, the Indian Ocean character of the Philippine Sea basins is not surprising. Adjacent spreading centres in the Japan Sea and South China basin also show Dupal characteristics[10–12], and palaeomagnetic data indicate the Philippine plate originated in the Southern Hemisphere[13]. The alternation of two different mantle signatures in the basin and island arc lavas is, however, difficult to explain within the context of existing arc models, because such models call on either a common asthenospheric source for basin and arc magma[1–3], or the derivation of arc magmas from the mantle residue of MORB or back-arc-basin basalt (BABB) generation[6,7,14]. One possible explanation is that the arc magmas include lead derived from subducted Pacific Ocean crust, including both MORB sea floor and OIB seamounts[15–19], but excluding pelagic sediments[17–19]. Detailed consideration of Palau-Kyushu arc magmatism shows, however, that this model is implausible for several reasons. Palau-Kyushu arc lavas with both high and low $^{206}Pb/^{204}Pb$ were erupted concurrently at the same sites[17–19], requiring that distinct fluids derived from subducted normal MORB sea floor and OIB seamounts be present at the same location. The higher $^{206}Pb/^{204}Pb$ values are found in boninites compared with

© 1992 Nature Publishing Group