

FACTORS AFFECTING THE DISTRIBUTION OF SILICATE IN THE NORTH ATLANTIC OCEAN AND THE FORMATION OF NORTH ATLANTIC DEEP WATER

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(Text-figs. 1-2)

In the deep water of the eastern North Atlantic below 2000 m. the variations with depth of salinity, temperature, density, oxygen, phosphorus compounds and nitrate are quite small. By contrast the silicate content is doubled in a descent from 2000 to 4000 m.

The distinctive behaviour of silicate is revealed by diagrams (Fig. 1) relating it to salinity, temperature, density and total phosphorus at station 2659 worked by R.R.S. *Discovery II* on 12 May 1950 (Armstrong, 1951; Cooper 1952, Table IV). The temperature-salinity diagram (Cooper, 1952, fig. 15, to 1500 m. only) suggests that between 1200 and 2000 m. we have to deal with simple mixing of the mean Gulf of Gibraltar and North Atlantic Deep waters. If silicate concentration were subject only to mixing processes the curves in Fig. 1 between these depths would be straight lines. They are not—consequently it would seem that solution of either particulate silica or of aluminosilicates may be occurring. As yet, clear interpretation is not possible. At least five hypotheses may be erected to explain, in whole or in part, the observed distribution: (i) solution of bottom deposits; (ii) solution of 'clay' and of silica in suspension; (iii) concentration by vertical partitioning; (iv) tundra drainage; (v) sinking of surface water. These are examined in turn.

SOLUTION OF BOTTOM DEPOSITS

Discovery station 2659 was near the continental slope, solution from which could have occurred. The results of Wattenberg (1937) and Koczy (1950), however, suggest that the converse process occurs, adsorption or chemical combination of silicate from the water into the material of the bottom or into hexactinellid sponges.

SOLUTION OF 'CLAY' AND OF SILICA IN SUSPENSION

The distribution may have come about by solution of minerals of terrigenous origin. If this were so the content of aluminium should increase with depth in much the same way as does silicate, and a diagram relating silica in solution to aluminium in solution should approach a straight line.

The distribution may also have come about by re-resolution of the skeletons of diatoms and radiolarians and the faeces of herbivores feeding on these.

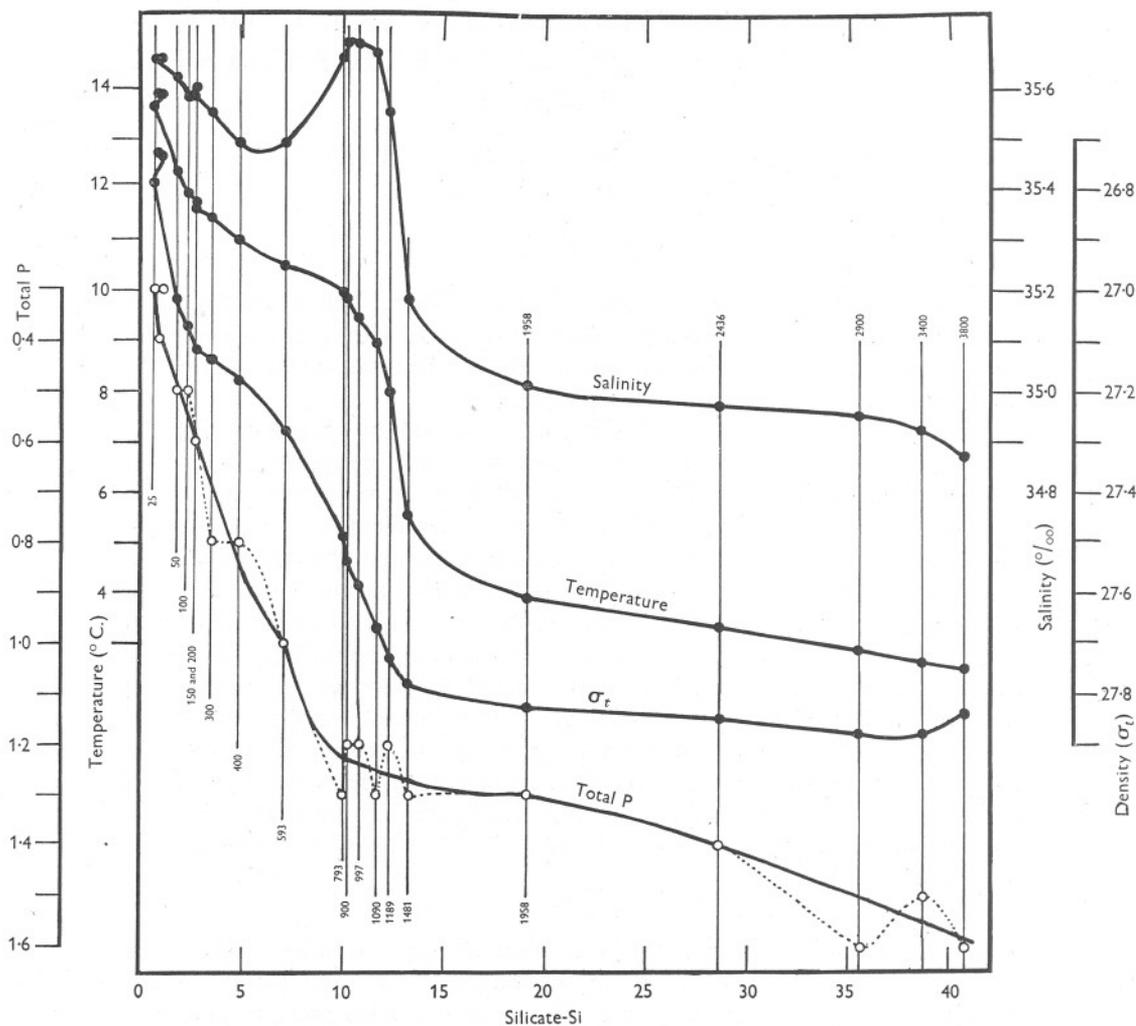


Fig. 1. Diagrams relating the vertical distribution of silicate to salinity, temperature, density, and total phosphorus at *Discovery II* station 2659 on 12 May 1950. Since the results for total phosphorus are less accurate than the rest, its curve has been smoothed. Silicate-silicon (Si) and total phosphorus (P) in $\mu\text{g.-atom/l.}$ The figures against the thin vertical lines represent depths (in metres).

As the particles dissolve, whether they be of mineral or biological origin, they become smaller, sink more slowly, and expose to the action of the water a greater surface area relative to volume, which favours solution. Wattenberg (1937), who found a similar distribution of silicate in the neighbourhood of

the Cape Verde Islands, explained it in this way, whilst Clowes (1938) has produced cogent evidence for the process in the Antarctic. King (1938) stated that most of the reported figures for the solubility of silica in water vary between 700 and 2300 $\mu\text{g.}-\text{atom/l.}$ Correns (1940) measured the variation with pH of the solubility of silica in terms of the fraction able to pass a membrane filter (Fig. 2). By interpolation at pH 8.15, the content of silica in solution was about 5 mg.-atom/l. Si. Natural sea water should never be saturated with silica.

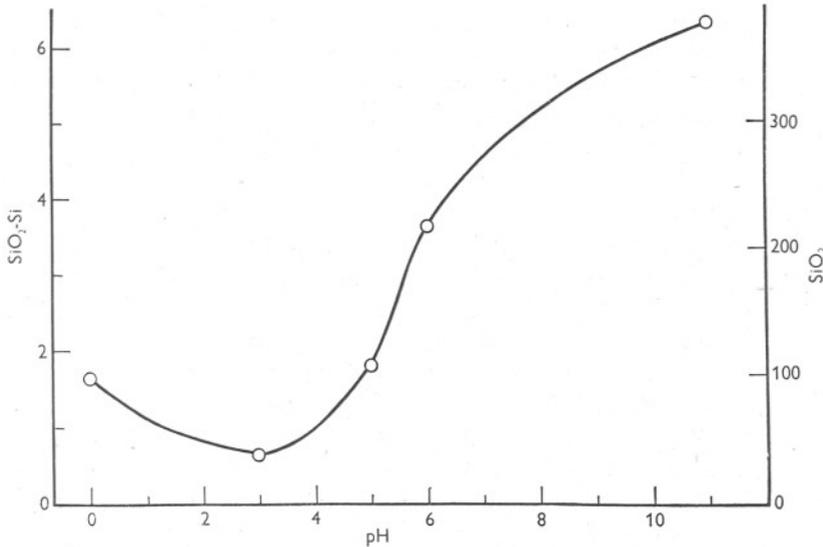


Fig. 2. Dependence of the solubility of silica (SiO_2) in water on pH (after Correns, 1940). Silica expressed as mg.-atom/l. silicon (left) and as mg./l. silica (right).

Hart (1934, pp. 11 and 185-6; 1942, pp. 322-39) has marshalled much evidence, circumstantial but strongly supporting the view that re-solution of diatomaceous silica is a speedy process in the sea. He examined (1942, p. 327 and private communication) the stomach contents of *Euphausia superba* and other planktonic animals, and found that the diatom species identifiable were those most strongly silicified, the same that remain recognizable in bottom deposits and in bird guano, such as *Fragilariopsis*, Discoidea (including *Thalassiosira* and also *Coscinodiscus* and *Actinocyclus* spp.), spines of the most robust of all chaetocerids, *Chaetoceros criophilum*, terminal spines of *Rhizosolenia* spp., etc. The more typically oceanic, exceedingly numerous but less strongly silicified forms, including most *Chaetoceros* species, are probably quite as important as food for the planktonic herbivores but are digested too thoroughly to be identified in the stomach contents. These less strongly silicified forms (p. 338) are also very rarely recognizable in the bottom deposits. It is therefore of interest that Wailes (1929) found that the silica

content of a collection consisting mostly of small species of *Chaetoceros* was only 40 %, whereas a collection mostly composed of large *Coscinodiscus* contained 75 % on the dry weight.

Again Hart (1942, p. 334) has discussed the removal of phosphate and silicate from Antarctic water by phytoplankton, largely diatoms. He considers that the same process of rapid re-solution of silica is going on there as was proposed for the English Channel (Cooper, 1933, p. 744). There the much lower production of phytoplankton computed from fall in silicate was attributed by the writer to the rapid return and immediate re-use of silica from the previous crop. It is suggestive that the shorter the time interval between sampling and re-sampling at the Antarctic stations the more nearly the crop of phytoplankton calculated from decrease in silicate approached that calculated from decrease in phosphate. Hart also pointed out (pp. 324-6) that in the northern zone of the Antarctic (i.e. immediately south of the Antarctic Convergence) as the silicate content of the upper waters decreases with the advance of spring so does the solenoid diatom *Corethron criophilum* change from a large strongly silicified spinose phase to a less strongly silicified, usually spineless, *inermis* phase.

There is evidence for the insolubility of the silica in diatoms, the result of direct experiment. Diatomaceous ooze is found on the floor of the oceans where the skeletons of strongly silicified species retain through geological ages the delicate markings of the living cell. According to Rogall (1939), the skeletons of marine and fresh-water diatoms consist of pure silicic acid (Kieselsäure) shown by chemical analysis and X-ray crystallography. The preparation of most of the samples would have removed any organic material which would protect silica against solution. None the less, the recent, chemically untreated sample of the marine diatom *Coscinodiscus concinnus* gave X-ray photographs by the technique of Debye and Scherrer which showed no diffraction rings but only some scattering of X-radiation around the point of penetration of the main beam. This suggests that in geologically recent diatoms no 'crystallites' of significant size are present. In geologically older material annular scattering is to be seen, becoming fairly strong in Miocene diatomaceous earth. As diatomaceous earths age part of the 'sub-colloidal' silica becomes transformed by inner metamorphosis to a micro-crystalline crystal lattice which indicates progressive formation of an opal structure. Such a change would affect solubility.

Atkins and Miss F. A. Stanbury (Atkins, 1945) found evidence for the insolubility of diatom skeletons in sea water even at pH 8 and up to 10.6. Miss Stanbury's earlier observations to the contrary (1931) were based on an error of observation due to the difficulty of seeing nearly transparent diatom skeletons in sea water. Addition of safranin to the water allowed the uncoloured skeletons to be seen. Conger (1941) stated that although diatom shells present a great amount of thin surface to possible solution, the purity

of the hydrated silica (also Rogall, 1939) appears to render them resistant to such solution. Diatom shells, once formed, are said to be practically a permanent deposition or fixation of silica. Coupin (1922) studied the fresh-water diatom, *Nitzschia linearis*, cultured in Knop agar medium with various sources of silica. Washed sand, gelatinous silica, and alkaline silicates led to no increased growth, whereas in presence of kaolin, feldspar and pure clay the cultures flourished. Atkins (1927) has shown the readiness with which soils and disintegrating rocks part with silicate to water; he concludes that solution of silicate most likely takes place from dispersed clay and that the rate of solution of diatom skeletons is too slow to matter. Consequently, he (1945) interprets Cooper's calculation of an apparently low phytoplankton crop from silicate consumption as due not to re-use of silica but to the production of autotrophic flagellates which require no silica and are more abundant than had been previously realized.

There is thus a direct conflict of much well-attested evidence. Is there an unrecognized factor which would allow this apparent conflict to be resolved? In this paper by 'dissolved silicate' we have meant no more than that form of dissolved hydrated silica sufficiently dispersed in sea water to react quantitatively with the standard reagents to form molybdosilicate. This presumably—but only presumably—is identical with the material which diatoms are able to withdraw from the sea to build their skeletons. Much has been written on the nature of 'dissolved silicate', but few clear unassailable conclusions have been drawn. One of the clearest expositions is that of Carman (1940). The metasilicate ion, SiO_3^{2-} , almost certainly does not exist. The simplest silicate ion is probably orthosilicate, SiO_4^{4-} , or more often $\text{H}_n\text{SiO}_4^{(4-n)-}$. In all silica compounds the central building bricks are SiO_4 tetrahedra linked through oxygen bonds. In vitreous silica, such as exists in colloidal silicates and in diatom skeletons, the tetrahedra are linked to produce a random three-dimensional network.

When sodium silicate is acidified, monosilicic acid is first formed. Molecular weight determinations by several workers have given values between 60 and 150. The lower figure would require that (mono)orthosilicic acid should be 60% dissociated. The low-molecular silicic acid is believed to condense to long chains of polysilicic acid. The structure which results is heavily hydrated and holds fluid by capillarity and, no doubt, foreign ions also. Treadwell (1935) found that the molecular weight between 149 and 1015 increased at the rate of 22.2 per hour. Tourky (1939, 1942) found that the rate of increase depended upon pH; at pH 11.7 there is no polymerization, but this occurs at pH 10.85 and the rate of polymerization reaches a maximum between pH 6 and 7. The rate and extent fall to a minimum at pH 2.3 in a region much used for the development of yellow molybdosilicate for analytical purposes. In more strongly acid solutions polymerization again becomes more rapid and extensive. At pH 8.32, near that of sea water, 28% of newly

formed silicic acid becomes in 1 hr. unable to pass an ultrafine membrane filter having a time constant of 200–300 min. Hurd & Merz (1946) found that the amount of silica capable of diffusing from a hydrosol through a membrane appears to approach a constant value. They explain this unexpected result as follows. The process of setting a silicic acid gel, whatever it may be, does not run entirely to completion but comprises a series of equilibria very much displaced towards the more complex side. Dialysis removes the simpler particles with a shift in the equilibrium towards the simpler materials. If correct this conclusion has great significance in oceanography if, instead of 'dialysis', we read 'removal of silica by diatoms'. A similar displacement of equilibrium would be achieved under the analytical conditions of determination of silicate in sea water (Hurd, 1938; Correns, 1940).

Tourky & Bangham (1936) recorded that nearly all the silica in Nile and Egyptian well waters and in dilute (20 $\mu\text{g.}$ -atom/l. silicate-Si) Graham sols was held back by ultra-filters, but that sea water appears to exert a 'peptizing' action akin to that of alkali. Thus, known volumes of a dilute Graham sol of known silica content were added to silica-poor sea water, the quantities being such as to correspond to a silica-rich sea water. After addition of alkali, colorimetric determination returned the correct silicate content. Without addition of alkali 25–100 % of this was found, depending on the age of the solution when the molybdate reagent was added.

Kargin & Rabinovitch (1935) prepared a very pure SiO_2 sol by oxidizing silane, SiH_4 , by ozone in water. This sol was electrochemically neutral, had a pH near to 7, no acidic properties and only a small quantity of compensating ions (*Gegenionen*) in the outer component of the double layer. Thus very pure hydrated silica dispersed in water is not an acid in the sense that hydrochloric acid, boric acid, or even phenol are acids.

Sols prepared by methods employing electrolytes—and these have been the subject of most investigations and correspond better to the process of solution of silica in sea water—seem always to retain ions of strong electrolytes either tightly bound as part of an electrical double layer or as components of interstitial fluids. The dissociation constants of so-called silicic acid derived from such systems are functions rather of these associated ions of strong electrolytes and vary much from experiment to experiment. Indeed it needs to be proved that orthosilicate ions can persist at the pH of natural sea water.

Carman (1940) described a method of hydration of colloidal silica which would set free hydrogen ions giving the surface of the colloid a negative charge, i.e. converting it into a large anion. The anionic character of such a colloid will depend on size, i.e. on the ratio of surface to volume. A solution of hydrated silica may contain aggregates or particles of every size ranging from an odd orthosilicate ion through $\text{Si}_3\text{O}_8^{4-}$ to a large diatom skeleton. Viewed in this way attempts to classify silicate in sea water, either in terms of ions all alike, or as all crystalloidal or all colloidal, become meaningless.

The practical problems are: (1) to establish what ranges of colloid particle size down to orthosilicate ion allow 'dissolved silicate' to react quickly to form molybdosilicate under analytical conditions; (2) what ranges are suitable for use by diatoms, radiolarians and sponges; and (3) how the solution or dispersion of large particles to smaller takes place.

Observations by Briscoe, Holt, Matthews & Sanderson (1937) and Kitto & Patterson (1942) are relevant. They established that freshly fractured surfaces of quartz and some mineral silicates are in a highly reactive state and readily yield 'soluble silica' on contact with water. In the sea much the commonest way of exposing fresh silica surfaces by fracturing will occur in the guts of herbivores which grind or triturate their food. During grinding the structure of the surface is disturbed and a layer of more irregular structure, possibly a Beilby layer, is formed. Such a Beilby layer, if formed, would increase with the amount of grinding to become many ångströms thick and would be likely to have a higher solubility than the underlying material. One may visualize the process of solution in the herbivore gut not as like the solution of sugar or common salt, but as one of mechanical attrition by which ever more reactive surfaces may become exposed and by which smaller pieces of colloidal silica, necessarily further hydrated by the process, may be torn from larger ones.

Dr T. J. Hart has made the following comment: 'At depths more than a few hundred metres below the photic zone herbivores cannot be feeding as such. Yet the bathypelagic fauna is very considerable. Obviously it cannot consist entirely of carnivores and their parasites. Detritus feeders ultimately dependent on the rain from above must here be the "key industry" forms. Hence my emphasis on the probability that most diatom skeletons pass through several stomachs on their way down.'

To sum up, the following assertions seem valid. (i) The phrase 'sea water saturated with silica or silicate' has little meaning. (ii) More silica or silicate could be 'dissolved' or held in sea water than is ever present in nature. (iii) Aluminium silicates or 'clay' are concerned in the silica system in sea water. (iv) Hydrated silica in equilibrium in sea water consists of particles of very varying size some of which can penetrate membrane filters and some of which cannot. (v) Aggregated hydrated silica is in the main electrochemically neutral and the acidic properties attributed to it are due to anions held in interstitial fluid, or to electrochemical charges on the surface, or to an electrical double layer arising from the distribution in space of SiO_4 tetrahedra and of unsatisfied valencies produced as the result of the process of hydration. Thus the term 'silicate' which suggests the anion of an acid or salt, whilst appropriate at $\text{pH} > 12$, is of doubtful validity at the pH of natural sea water: 'dispersed hydrated silica' or 'dispersed silica' may be more fitting terms than 'dissolved silicate'. (vi) If the equilibrium system is disturbed by removal of the simpler particles by dialysis in the laboratory

or by diatoms in the sea, more complex particles will slowly yield simpler ones in order to restore the equilibrium. (vii) Polymerization is least in the range of pH commonly used for the development of the yellow molybdo-silicate complex in analytical practice. (viii) The chemical constitution of the silica in diatom skeletons is similar to that of hydrated silica dispersed in water. (ix) In spite of this, the skeletons of many but not all species of diatoms are resistant to solution and for all practical purposes are insoluble whilst intact. (x) This insolubility is difficult to understand unless the surfaces of the skeletons are in some way protected against solution by an organic skin. Such a skin has never been demonstrated by chemical or X-ray analysis. Since it would be sufficient to satisfy the residual valencies of the SiO_4 tetrahedra in the boundary surface more strongly than does water, a protective layer only a few molecules thick and undetectable

chemically would suffice. Postulation of a siloxane bond $\begin{array}{c} | \qquad | \\ \text{—Si—O—C—} \\ | \qquad | \end{array}$,

never yet found in nature,¹ would assist the formulation of such a protective coating. (xi) Freshly fractured surfaces of silica are highly reactive and soluble. (xii) The skeletons of diatoms, particularly thin fragile ones, are likely to be so fractured in the guts of herbivores browsing on them. Herbivores and detritus feeders are likely to be responsible for the greater part of the redispersion of hydrated silica frequently reported in the upper layers of sea. (xiii) In surface waters in which diatoms and radiolarians grow and are eaten a true equilibrium involving dissolved or dispersed hydrated silica may never be reached. (xiv) Sea water containing dispersed silica completely in equilibrium is likely to be found only in the ocean abyss. Only abyssal water may be suitable for a study of silica equilibria.

Confronted with the same body of evidence Atkins and the author have on some issues drawn opposed conclusions. The author's opinion is that the conflict is apparent and not real and arises from some condition of the intact diatom skeleton which is not understood. The conflicting lines of argument are presented to stimulate further study of the process of solution of siliceous matter in deep waters, especially in North Polar waters, the Norwegian Sea and the north-western North Atlantic.

¹ The following information has since been received by the Department of Scientific and Industrial Research in answer to their *Unanswered Question* 67: 'Is there any authentic case of organic silicon compounds having been isolated or detected in living organisms?' (1) T. Takeuchi (*Bull. Coll. Agric., Tokyo*, Vol. 7, pp. 929-31; *Chem. Abs.*, 1907, Vol. 1, p. 2620) reported detecting an organic silicon compound in hay. (2) E. Drechsel (*Chem. Zentralblatt*, 1897, Vol. 2, p. 666) reported a substance $\text{Si}(\text{OC}_{34}\text{H}_{59}\text{O})_4$ which appears to have been an ester of silicic acid. This compound was, it is understood, isolated from duck feathers and may originate in the oily gland at the base of the tail and be transferred to the feathers during preening. Thus the possible presence of Si—O—C linkages in diatoms may not be without precedent in other living organisms.

It remains for the future to show how great is the effect of solution of silica from siliceous matter compared with the processes to be described.

CONCENTRATION BY VERTICAL PARTITION

The enormous concentration of silicate in Antarctic waters is much assisted by the vertical circulation (Clowes, 1938). The Antarctic surface water flows towards the north. The water goes on to sink at the Antarctic Convergence but much of the silicate remains behind. It has been removed by diatoms which get eaten by herbivores who need no silica. Siliceous faeces and dead broken frustules sink into the Intermediate Water beneath which, enriched in the writer's view by re-solution, returns to the Antarctic. In the North Atlantic there is a similar Intermediate Water (Wüst, 1936, p. 176). Comparatively it is rudimentary and its progress difficult to follow. The Polar front associated with it makes a seasonal migration of 500-1000 km. None the less, this Intermediate Water working against the Irminger Current above would seem capable of some degree of concentration of silicate. It needs to be shown whether this happens on a scale that matters, and whether the enriched water moves into the region where Nansen (1912) believed the North Atlantic bottom water may be formed in winter.

TUNDRA DRAINAGE

The North Polar Sea receives much drainage from the tundra areas of Siberia, northern Canada and Alaska. Under a tundra climate the subsoil is permanently frozen. In summer this stops the normal downward percolation of subsurface water derived from thawing of the soil above and from precipitation (Flint, 1947, p. 459). As a result the thawed mantle becomes saturated with water and flows bodily downhill, a process known as 'solifluction'. Such a climate with hard freezing, shallow thawing, bad drainage, and much solifluction is likely to lead to rapid weathering and comminution of rock particles. Moreover, poor development of humus will hinder the development of a stable soil. Conditions should be very favourable for solution of silica and its transport by summer drainage into the surface waters of the North Polar Sea from which it may escape in the East Greenland Current. This in turn contributes to the mixing areas south-east and south-west of Greenland in which the North Atlantic deep water may be formed. Although the pure Polar water which escapes as the East Greenland Current is, according to Küllerich (1945, p. 56), poor in nutrients, no silicate analyses have to the writer's knowledge ever been made on it. There is a strong probability that the silicate content will prove to be very high (at least $50 \mu\text{g.}-\text{atom/l. SiO}_2\text{-Si}$). Thus it would seem that a full knowledge of the distribution of silicate in the North Polar Sea, in the East Greenland Current, the north-western Atlantic generally, and in the deeper water of the Norwegian Sea, will be needed for interpretation of deep-water results elsewhere.

Dr H. U. Sverdrup (private communication) has suggested that Antarctic waters should also receive much dispersed silica formed by comminution of rock beneath the very large glaciers of the Antarctic continent.

SINKING OF SURFACE WATER

Though Nansen's view (1912) that much of the bottom water of the North Atlantic is formed in an area south-east of Greenland around $59-62^{\circ}$ N., $38-48^{\circ}$ W., has gained wide currency, it has never been finally proved. The observations which he used were not his own and some of them may be suspect. In March 1933 and March 1935, the German research ship *Meteor* ran sections across the area (Defant, Böhnecke & Wattenberg, 1936). The densest surface water (temp. 4.07° C.; sal. 34.96‰ ; σ_t , 27.76) was found at station 79 ($59^{\circ} 38' \text{N.}$, $4^{\circ} 42.5' \text{W.}$), but water at least 1° colder and $0.10 \sigma_t$ -unit heavier was needed to provide satisfactory proof of Nansen's hypothesis. Defant (1936) had stated that a main objective of the *Meteor* cruises was to test Nansen's hypothesis but in the end he has nothing to say on the matter. He would seem to feel that the hypothesis remains unproven. Von Schubert (1935, pp. 35-7) examined the stability at *Meteor* station 76 (29 March 1933; $60^{\circ} 56' \text{N.}$, $41^{\circ} 28' \text{W.}$). Down to 800 m. there was no obstacle to vertical mixing, but he also considers that the formation of bottom water there remains an open question.

The extent of formation of bottom water will depend upon the coldness of the winter. Smed (1947, 1948) has recently published monthly anomalies of the surface temperatures in areas of the North Atlantic from 1876 to 1939 (i.e. departures from Ryder's area monthly means for the years 1876-1915). Nansen's postulated region of formation of bottom water lies close to the point of union of Smed's areas B, C and D and mostly within areas B and D. The observations used by Nansen (1912, p. 25) were mostly collected in April 1906, which Smed's tables show to have been very cold (Table I), whereas the *Meteor* worked in years (March 1933 and March 1935) when the water temperatures were 0.5° above the long-term mean. It is therefore probable that temperatures in the late winter and early spring of 1906 were between 1 and 2° lower than in 1933 and 1935. In Table II the densities found by the *Meteor* have been adjusted for conditions 1 and 2° colder than in 1933. Thus, in 1906, the surface water may well have been heavy enough to sink right to the bottom of the Atlantic, and Nansen's conclusion for that year was correct, whereas in 1933 and also 1935 it could not have sunk much below 800 m. Only in 1907, 1918 and 1921 have comparable cold conditions recurred so that formation of North Atlantic bottom water south-east of Greenland may now have become a rare event.

Nansen (1912) showed quite clearly that in the years 1903 and 1910 cold heavy water from the Norwegian Sea flowed into the Eastern Basin of the North Atlantic over the sill of the Faeroe-Iceland ridge at about 64° N.,

13° W., a result substantiated in 1938 by the *Dana* (Cons. Perm. Int. Explor. Mer, 1944, p. 119, stations 5954-5957). He also definitely established a similar outflow over the Iceland-Greenland ridge into the Western Basin. Although he considered neither of these outflows adequate to account for the great volume of the cold bottom water of the Atlantic, that over the Faeroe-Iceland Ridge may be locally important for the hydrography of the waters bathing western Europe. The *Meteor*, on 21 March 1933, also found a small area of heavy water (temp. 3.66° C.; sal. 34.99‰; σ_t , 27.82) on the

TABLE I. MONTHLY ANOMALIES OF TEMPERATURE OF PART OF NORTH ATLANTIC

Departures from Ryder's 'area monthly means' for the years 1876-1915 of the sea surface temperature (° C.) in three areas south-east of Greenland in March and April in years studied by Nansen and by the *Meteor* expeditions; n is the number of observations averaged; from Smed (1947, 1948).

Latitude range...	Area B 55° N. to coast of Greenland		Area C 60-66° N.		Area D 55-60° N.		Mean of area means ° C.	Arithmetic mean of all observations	
	40-50° W.		30-40° W.		30-40° W.			Σn	° C.
Longitude range...	n	° C.	n	° C.	n	° C.			
Mean anomalies									
March 1906	4	-0.7	6	+0.5	13	0.0	-0.1	23	0.0
April 1906	64	-1.1	2	-2.2	34	-1.3	-1.5	100	-1.2
March 1933	13	-0.1	5	+1.4	25	+0.7	+0.7	43	+0.5
April 1933	82	0.0	22	+1.0	53	+0.7	+0.6	157	+0.4
March 1935	19	+0.3	3	+0.9	15	+0.2	+0.5	37	+0.3
April 1935	76	+1.0	21	+0.1	29	+0.5	+0.5	126	+0.5

TABLE II. COMPUTED DENSITIES FOR APRIL 1906

Probable densities of the waters south-east of Greenland in April 1906 computed from *Meteor* observations in March 1933 and assuming that surface water temperatures were 1 or 2° C. colder.

Station no.	Latitude N.	Longitude W.	Observed temperature	Observed salinity	Actual σ_t	σ_t if temperature lowered by	
						1°	2°
76	60° 56'	41° 28'	4.67	35.00	27.72	27.85	27.94
78	60° 12.5'	41° 52.5'	4.21	34.91	27.69	27.82	27.91
79	59° 38'	40° 42.5'	4.07	34.96	27.77	27.86	27.95

West Icelandic island shelf at 65° 17' N., 25° 30' W. heavy enough to cascade to a great depth. Jacobsen (1943), in his account of the water movements through the Faeroe-Shetland Channel, makes no mention of any outflow over that sill into the Atlantic, and no evidence for it was found by the *Explorer* in 1933 and 1935 (Cons. Perm. Int. Explor. Mer, 1934, p. 67; 1935, p. 69).

Smith, Soule & Olav Mosby (1937; see also Dunbar, 1951) suspect that the bottom water of the Labrador Sea is formed in winter in a restricted area of that sea centred on 60° N., 55° W., and discuss its rather complex

origin in so far as this can be surmised from summer observations. They point out that 'our deep water which evidently drains out of the Labrador Basin into the North Atlantic embraces what Wüst (1936) has designated as North Atlantic deep water'. Wüst himself (1936) also leaves the origin of the North Atlantic bottom water as unsolved. It would seem that only in one year in ten are temperatures low enough to produce water heavy enough to sink to the bottom of the Atlantic, and that attention would be better focused on the Labrador Sea rather than on the waters south-east of Greenland.

Since direct winter observations in these uncharitable waters are hard to come by, an alternative means of search for the origin of the North Atlantic bottom water should be welcome. This may well be provided by determinations of silicate by the quick and accurate method now available (Armstrong, 1951). For reasons already given, the postulated high silicate content of the fresh waters draining from the tundras should mark in turn the East Greenland Current, the Labrador Current and the waters of the Labrador Sea with distinctive contents of silicate. The deeper water of the Norwegian Sea may also acquire a high and characteristic content of silicate. In all these, except in surface water above the thermocline, content of silicate may be reasonably assessed in summer.

To enter the basin of the Eastern North Atlantic directly, heavy water from either south-east of Greenland or from the Labrador Sea would need to cross the mid-Atlantic Ridge in a region where its depth is about 3000 m. According to Wüst's charts (1936, Beilage LVI, LVII, LXXI and LXXII) the temperature there exceeds 2.9° (potential temperature 2.64°) and the salinity exceeds 34.96‰ , whereas the water abreast of the English Channel between 3000 and 4000 m. has a lower temperature, $2.5\text{--}2.7^{\circ}$ (potential temperature $2.15\text{--}2.45^{\circ}$) and a lower salinity of $34.90\text{--}34.92\text{‰}$. There is no obvious passage north of 24° N. for bottom water from the north-western Atlantic to cross the Ridge into the Eastern Basin so that such water must needs approach Europe from the south. The water which the *Dana* observed entering the Atlantic from the Norwegian Sea across the Faeroe-Iceland Ridge in 1938 was cold enough but was 0.08‰ too saline. Consequently, the origin of the bottom water west of Europe is still uncertain.

The Antarctic bottom water extends well north of the Equator. Wüst (1936, Abl. 16) pictures it as extending to 40° N. in the Western Basin and to 25° N. in the Eastern. His conclusion is based largely on an apparent density inversion widely recorded below 4500 m. Since a true inversion is very unlikely, he attributes the phenomenon to a breakdown in Knudsen's equation, $S = 0.030 \times 1.8050 \text{ Cl}$, when applied to the bottom water of the Atlantic.

Sverdrup (1929, p. 129) had shown that the brine which becomes enclosed in sea-ice when it freezes retains relatively more chloride than other salts leaving the unfrozen water relatively deficient by about 0.02‰ Cl. The true

density of this water measured directly is about 0.03σ -unit heavier than that computed from salinity and temperature by Knudsen's tables. When such water becomes admixed with Atlantic water to form North Atlantic deep water this anomalous property will become incorporated. The Antarctic bottom water arising more directly by a similar freezing-out process in the Weddell Sea (Deacon, 1937) would seem, according to Wüst, to have acquired an even greater chlorinity-density anomaly. The result is that in the deep water of large areas of the Atlantic, water of slightly greater computed density overlies lighter. When this occurs Wüst suggests that North Atlantic deep water overlies Antarctic bottom water.

There is abundant evidence that the Northern Hemisphere is warming up (*inter alia*, Helland-Hansen, 1949; Defant & Helland-Hansen, 1939; Cooper, 1952, p. 501), a state of affairs which in the area south-east and south-west of Greenland in winter should slow down the rate of formation of the North Atlantic deep water. Less should be sinking to the ocean abyss than in years past. Much less is known about any similar warming up in the Antarctic and Southern Oceans, but the huge reserves of ice there should slow down the process. Consequently, in a struggle between North Atlantic and Antarctic bottom waters, victory would be expected to go to the Antarctic water. There should to-day be a marked tendency for Antarctic bottom water to spread northwards in the Atlantic and to fill the Eastern basin to a greater depth. At *Discovery II* station 2659 the water at 3800 m. (salinity 35.87‰, computed density σ_t 27.84, computed potential density σ 27.87) is apparently lighter than the water at 3400 m. by $0.03 \sigma_t$ -unit. Error in any single result is always likely but, at least, the need is indicated for fresh deep observations in the Eastern North Atlantic. Since the presence of Antarctic water is in question, determinations of silicate may be of much value.

Locally down to 1200 m. near the continental slope of the eastern North Atlantic the distribution of silicate will be affected by cascading in winter and by capsizing of water masses, processes which are under investigation.

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SUMMARY

The distribution of silicate at the deep *Discovery II* station No. 2659 west of Ushant between 1200 and 2000 m. cannot be attributed to simple mixing of 'Gulf of Gibraltar' water and North Atlantic Deep water as can the distribution of some other constituents. Moreover, between 2000 and 4000 m. the concentration of silicate is doubled. Five hypotheses have been examined which may bear on the distribution of silicate.

The chemistry of silicate dispersed in water has been examined with respect to the possible solution of aluminosilicates and of intact and fractured diatom skeletons in sea water. Conclusions have been summarized.

Solution of silicate from, and removal by, the sea bottom and concentration within the sea by vertical partition are severally discussed.

Reasons are presented for believing that drainage from the tundras of the Northern Hemisphere should yield very large amounts of silicate to the North Polar Sea. From this initial hypothesis further oceanographical deductions have been drawn.

The evidence for the formation of North Atlantic Bottom Water at the sea surface south-east of Greenland, first proposed by Nansen, has been re-examined in relation to the movement of dissolved silicate. It is suggested that in the cold spring of 1906, from which year Nansen drew most of his data, his conclusion was probably sound, but that in most years sufficiently cold surface conditions are not attained.

The probable effect of the warming up of the Northern Hemisphere in recent years on the deep circulation of the Atlantic is reviewed.

It is suggested that the great variations which occur in the concentration of silicate in the sea should be of use in interpreting the nature and movements of the major ocean water masses.

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