Cobalt in the Western Philippine Sea

George T. F. WONG [a], Su-Cheng PAI [b] and Shi-Wei CHUNG [b]

[a] Department of Oceanography, Old Dominion University, Norfolk, VA 23529-0276 U.S.A.

[b] Institute of Oceanography, National Taiwan University, Taipei, Taiwan, Republic of China.

ABSTRACT

The distribution of cobalt was determined at one station in the oligotrophic western Philippine Sea that is far removed from the direct influence of any major land mass. Concentrations of cobalt (> 95 pM) in the top 150 m of water in and above the thermocline were much higher than those (about 25 pM) in the deep waters below 1000 m. Since no major river drained directly into the study area, these elevated concentrations in the surface waters could not have been sustained by a riverine input. A more likely source of cobalt to these waters might have been atmospheric deposition. Below 150 m, as a first approximation, the relationship between cobalt and salinity mimicked that between potential temperature and salinity with inflection points occurring at about the same depths. Thus, the distribution of cobalt in these deeper waters was governed primarily by mixing processes. Within the top 150 m, a subsurface maximum, centered around 48 m, was found in the shallow halocline. This maximum might have resulted from the preferential trapping and re-mineralization of particles in a strong pycnocline.

RÉSUMÉ

Cobalt dans l'ouest de la mer des Philippines.

La répartition du cobalt a été déterminée dans la partie occidentale oligotrophe de la mer des Philippines, en une station très éloignée de toute influence directe des principales masses continentales. Dans la couche d'eau superficielle de 150 m, c'est-à-dire dans et au-dessus de la thermocline, les concentrations de cobalt (> 95 pM) sont bien supérieures à celles (environ 25 pM) des eaux profondes au-dessous de 1 000 m.
Comme aucun fleuve important ne se déverse dans la région étudiée, ces concentrations élevées ne peuvent pas être attribuées à des apports fluviaux. Il est plus probable que le cobalt trouvé dans ces eaux provienne de l'atmosphère. Au-dessous de 150 m de profondeur, la relation entre le cobalt et la salinité est, en première approximation, similaire à la relation entre la température potentielle et la salinité, avec des points d'inflexion presque aux mêmes profondeurs. Ainsi la répartition du cobalt dans ces eaux plus profondes est déterminée principalement par des phénomènes de mélange. Dans la couche superficielle, vers 48 m de profondeur, un maximum se trouve dans l'halocline ; il pourrait résulter du piégeage des particules par une forte pynocline et de leur minéralisation.

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INTRODUCTION

Cobalt is a transition metal in the first transition series in Group VIII of the periodic table. Many of these transition metals are known to be rather reactive (Cotton and Wilkinson, 1980). In the oceans, it is widely suspected that cobalt may participate in biological and abiological processes since it is considered a necessary trace nutrient, it is the central atom of vitamin B_{12} and it is enriched in manganese nodules (Bruland, 1983). Nonetheless, the detailed chemistry of cobalt in the oceans at the molecular level is poorly known. In fact, even data on its distribution in the oceans are still quite limited.

One of the major reasons for the paucity of data on the distribution of cobalt in the oceans is its low concentrations, usually less than 100 pM, in sea water. Reliable data, and especially vertical profiles, were not available until the early part of the last decade (Knauer et al., 1982). Previously, the concentrations of cobalt in sea water had been reported as mostly undetectable in some studies (Bewers et al., 1976; Danielsson, 1980) and as unrealistically high and/or widely scattered values in other cases (Fukai, 1968; Robertson, 1970). It is now generally recognized that cobalt exists in sea water at concentrations of less than 0.2 nM. The concentration is higher in the surface waters and decreases with depth (Knauer et al., 1982; Martin, 1985; Ngoc and Whitehead, 1986; Sakamoto-Arnold and Johnson, 1987; Johnson et al., 1988; Martin et al., 1989, 1990; Westerlund and Öhman, 1991). Cobalt may be added to the surface oceans from anthropogenic and natural sources via riverine input and atmospheric deposition (Pacyna, 1984; Arimoto et al., 1989; Donat and Bruland, 1995). The relative importance of these sources is probably spatially and temporally variable. Since most of the presently available vertical profiles were obtained in close proximity to major land-masses and the concentration of cobalt increases towards the coast, reaching concentrations as high as nM levels in the rivers, the source of cobalt in the surface waters has frequently been suggested to be direct runoff from land (Knauer et al., 1982; Tappin et al., 1993). The importance of atmospheric input, even when this was suspected, was not well quantified

(Ngoc and Whitehead, 1986). At greater depths, presumably, cobalt is scavenged on to the particulate phases. As a result, the concentration decreases with depth. In the bottom waters, the concentration of cobalt has been observed to increase with depth towards the water-sediment interface in oxygen-poor basins. It was suggested that under reducing conditions, as manganese oxide is reduced, cobalt is released from the solid phases and subsequently migrates into the bottom water (Johnson et al., 1988). Thus, the geochemistries of cobalt and manganese may be intertwined (Knauer et al., 1982).

Few reliable profiles of cobalt in the oligotrophic ocean-interior have been reported. Almost all of them were from the northeastern Pacific. Bruland (1983), Martin and Gordon (1988) and Martin et al. (1989) reported that the concentration of cobalt does not always decrease monotonically with depth. A sub-surface maximum was found within the nutricline in some profiles. The origin of this maximum is at present unknown. Reliable profiles of cobalt in the western Pacific have not been reported in the literature. We have measured the distribution of cobalt in the oligotrophic Western Philippine Sea in a location that is rather isolated from the influence of major land masses and major rivers. The results are reported here.

MATERIALS AND METHODS

Sampling

Stations were occupied at about 30' intervals in a transect along 21° 45' from about 119° E in the South China Sea to about 130° E in the Philippine Sea during cruise ORI-316A of the R/V Ocean Researcher I between May 5 and 15, 1992, as a part of WOCE (World Ocean Circulation Experiment) line PR-20 (Fig. 1). The distribution of temperature and salinity at each station was measured down to about 2000 m with a Seabird CTD (conductivity-temperature-depth) recorder. Discrete water samples were collected with 2.5-l GoFlo bottles (Type #1080, General Oceanics,
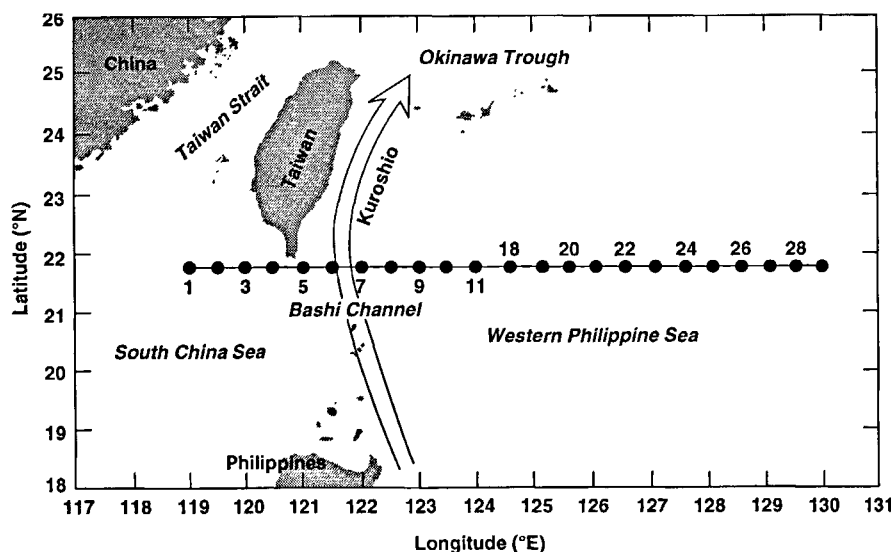

Figure 1

Cruise track and station locations.

Miami, FL) mounted on a rosette sampler for the determination of salinity, oxygen, phosphate, silicate, nitrite and nitrate at all stations except Station 11. At this station (124°00' E, 21°45' N), sub-samples, about 1.3 l each, were drawn for the determination of cobalt.

Instruments and methods

Salinity in discrete water samples was measured with an AUTOSAL salinometer that had been calibrated with certified IAPSO standard sea water. The precision of the method was better than ± 0.003 (Fang et al., 1990).

Oxygen was determined on board ship spectrophotometrically by measuring the absorbance of the tri-iodide ions formed in the classical Winkler method (Carpenter, 1965; Pai et al., 1993). The precision of the method was about ± 0.2%.

Phosphate and nitrite were determined manually on board ship by the standard methods: the molybdenum blue method for phosphate (Murphy and Riley, 1962) and the pink azo-dye method for nitrite (Pai et al., 1990a). Silicate and nitrate were also determined on board by the standard methods: the heteropoly blue method for silicate and the cadmium-copper reduction/pink azo-dye method for nitrate (Strickland and Parsons, 1972), modified for use with a flow injection analyzer (Pai et al., 1990a, 1990b). The precision was about ± 3% and ± 1% for the determination of silicate and nitrate respectively.

Cobalt in sea water was determined by graphite furnace atomic absorption spectrometry by the method of Pai and Chung (1995), a modification of the method of Knauer et al. (1982). Briefly, cobalt was quantitatively preconcentrated from sea water (1.3 l) at its natural pH onto a Chelex-100 chelating ion-exchange column on board ship with a low-contamination technique (Pai et al., 1990c, 1990d). The column was returned to a shore-based laboratory where it was recovered by eluting the column with 2M nitric acid. The volume of the eluate was reduced to 2 ml and its matrix was converted to a 0.5 M nitric acid solution. Then, cobalt in this concentrate was determined with a graphite furnace atomic absorption spectrometer, Hitachi Model Z-8100 with Zeeman effect background correction, using a repetitive deposition-technique, which involved the transfer, drying and charring of up to five 20 μl aliquots in the graphite tube prior to atomization, to give a concentration factor of about 3200 for the entire analytical scheme. The detection limit of the method was about 1 pM. The precision was ± 3% at 50 pM. Sub-boiling distilled water prepared from double distilled water was used for the preparation of all reagents. Sample manipulation was minimal on board ship and was carried out in a Class 100 environment in the shore-based laboratory. The reagent blank of the method was only about 1 pM. The accuracy and precision of the method was checked by measuring repeatedly the concentration of cobalt in NASS-4 Referenced Seawater (Institute for Environmental Chemistry, Ottawa, Canada) (Pai and Chung, 1995). The duplicated results were 0.0095 and 0.0093 μg/l and these values are in good agreement with the certified value of 0.009 ± 0.001 μg/l for this referenced sea water.

RESULTS AND DISCUSSION

Hydrography of the study area

The transect along 21°45' extended from the South China Sea, across the Bashi Channel and the Kuroshio into the western Philippine Sea. The distribution of potential temperature and salinity along the transect is shown in Figure 2. Stations 1 to 4 were located within the South China Sea and were characterized by warmer (> 28 °C) and fresher (< 34.3) surface waters. The western and eastern boundaries of the Kuroshio were marked by the dipping isotherms and isohalines in the top 300 m between Stations 4 and 7 in the Bashi Channel and between Stations 7 and 9 in the western edge of the western Philippine Sea (Fig. 2a and 2b). In the surface waters, there was an abrupt increase in salinity and temperature between Stations 5 and 6 which was followed by an equally abrupt decrease in temperature between Stations 6 and 9 (Fig. 2c). The core of the Kuroshio was located probably at around Station 6 and 7. Stations further east of Station 9 were located outside of the Kuroshio proper. Thus, Station 11, the station where the distribution of cobalt was measured, was separated from the nearest significant land mass, Taiwan, by the Kuroshio. However, while Stations 11 was not part of the Kuroshio, it could have been influenced by the countercurrents associated with the warm eddies that originated from the Kuroshio (Nitani, 1972). Indeed, dipping isotherms and isohalines with temperatures and salinities similar to those found in the Kuroshio were again found between Stations 10 and 19 (Fig. 2a and 2b). In the surface waters, there were temperature maxima of similar magnitude at Station 6 and at Stations 10 and 11 (Fig. 2c).

In the western North Pacific north of the North Equatorial Current, the major water masses that can be found are the surface water, the North Pacific Tropical Water (NPTW), the North Pacific Intermediate Water (NPIW) and the Pacific Deep Water (PDW) (Nitani, 1972). In the study area, NPTW and NPIW were represented, respectively, by the salinity-maximum (S > 34.8) centered around 150 m at the stations east of Station 2 and the salinity-minimum centered around 600 m (S < 34.4) at the stations east of Station 6 (Fig. 2b) (Masuzawa, 1972; Nitani, 1972). These four major water masses can be readily identified at Station 11 from the distribution of potential temperature and salinity, and, the relationship between them (Fig. 3). Above 40 m, there was the relatively well-mixed surface water with rather uniform salinity. Below 40 m, salinity increased while temperature decreased sharply with depth until the salinity-maximum was reached at 170 m resulting in a strong halocline and thermocline. Both salinity and temperature decreased sharply with depth from 170 m down to the salinity minimum at 610 m. At greater depths, salinity increased while temperature continued to decrease gradually with depth. Although samples were collected only down to 2000 m, the properties of the water at this depth were already close to those reported for the PDW (Nitani, 1972; Moriyasu, 1972). The T-S diagram (Fig. 3b) may be represented approximately by four consecutive linear line segments from a salinity and temperature of 34.61 and 27.3 °C at the surface to 34.64 and 23.2 °C at 40 m, to 34.93 and 20.2 °C at 170 m, to 34.15 and 7.2 °C
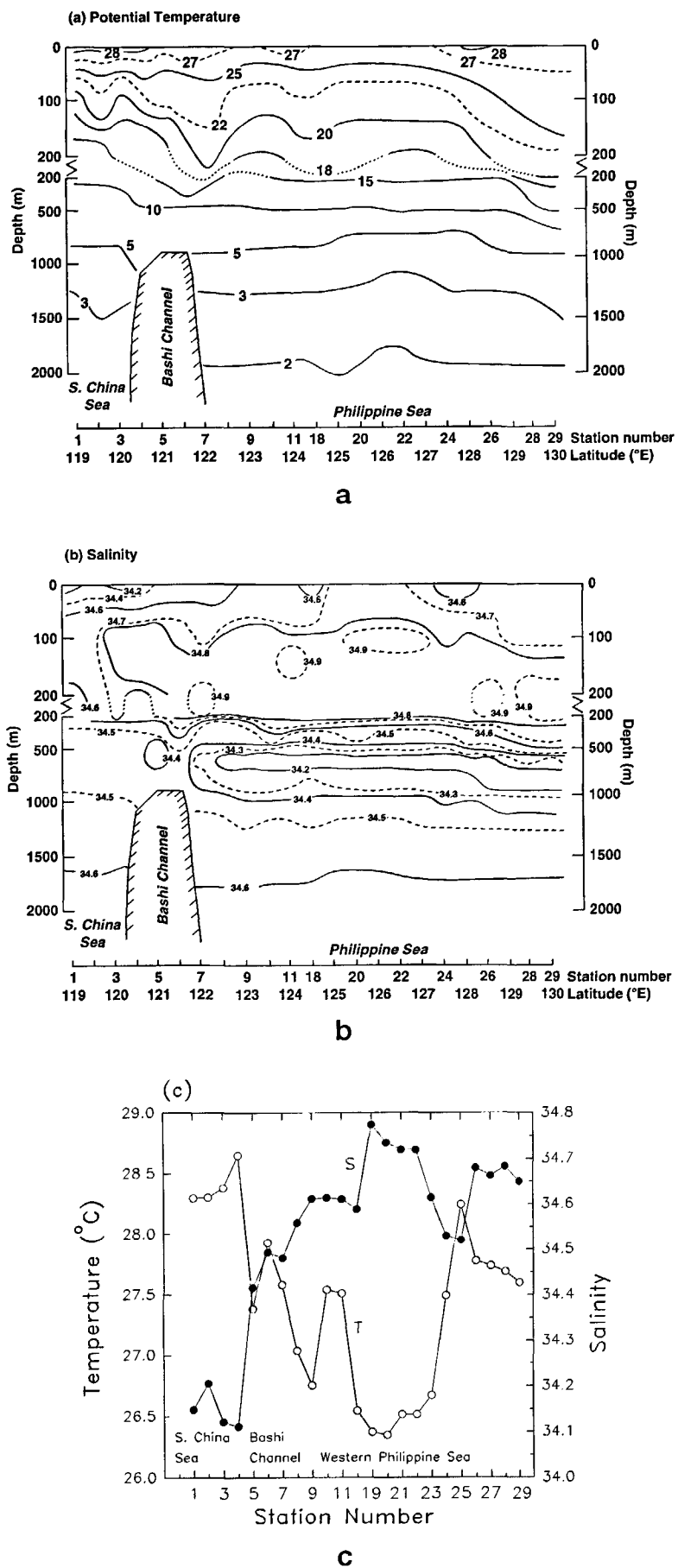
(a) Potential Temperature

(b) Salinity

(c)

Figure 2

The distribution of (a) potential temperature and (b) salinity along the transect. (c) The distribution of temperature (open circle) and salinity (filled circle) in the surface waters along the transect.
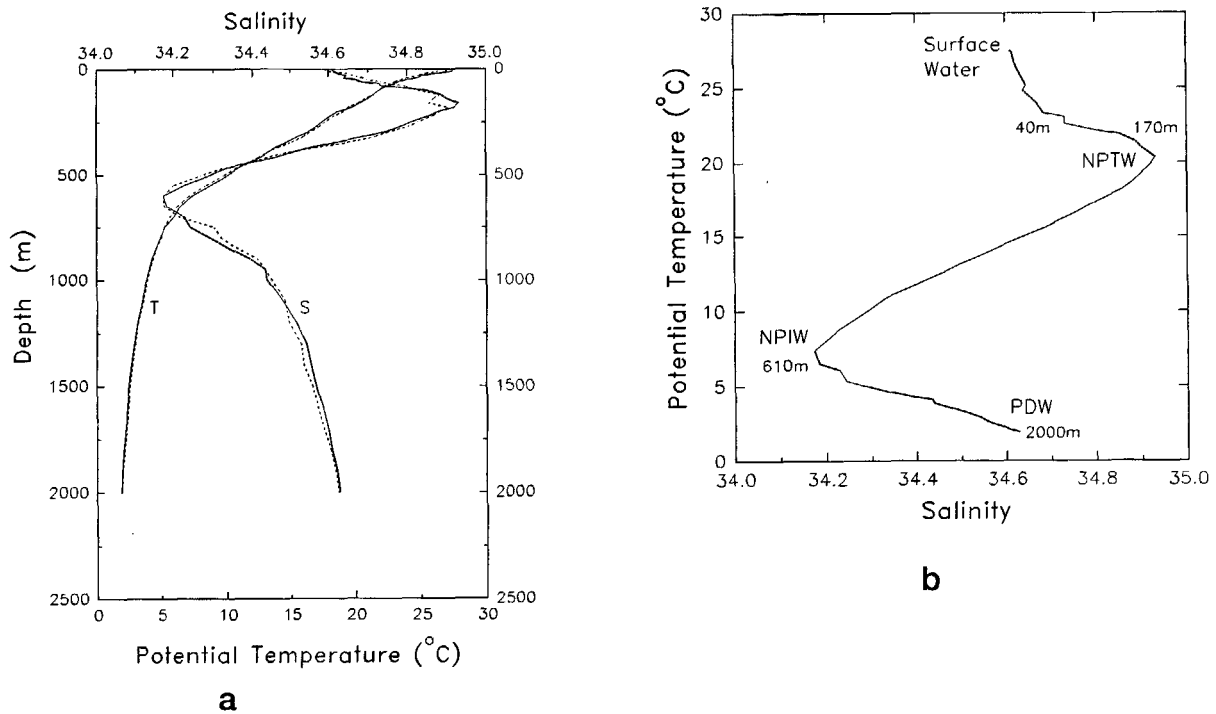
Figure 3

(a) The distribution of potential temperature and salinity at Station 11 (solid lines) and Station 18 (dashed lines). (b) The relationship between potential temperature and salinity at Station 11. NPTW - North Pacific Tropical Water. NPIW - North Pacific Intermediate Water. PDW - Pacific Deep Water. Numbers denote depths at various inflection points in the graph.

at 610 m, and to 34.63 and 2.0 °C at 2 000 m. The inflection points at 20.2 and 7.2 °C represented the core of NPTW and the NPIW at this location and the line segments represented the relatively well mixed surface water, mixing between the surface water and the NPTW, between the NPTW and the NPIW and between the NPIW and the PDW respectively.

Although the distribution of oxygen, phosphate, nitrate and silicate were not determined at Station 11, their distributions at Station 18 (Fig. 4) were probably also representative of those at Station 11 since the distribution of salinity and temperature at these two stations were almost identical (Fig. 3a). The water in the top 200 m was almost devoid of all nutrients and should be considered to be characteristic of oligotrophic water. The nutricline for nitrate and phosphate was located between 200 and 800 m. The phosphate- and nitrate-maximum and the oxygen- minimum were located at about 1000 m. The silicate maximum might not have been reached at 2000 m.

The distribution of cobalt at Station 11

The distribution of cobalt at Station 11 is shown in Figure 5. Higher concentrations of cobalt (> 95 pM) were found in the top 150 m in the surface waters above the salinity maximum. Below 150 m, the concentration decreased systematically with depth to about 700 m. There was a suggestion of a slight secondary maximum between 700 and 1000 m. Below 1000 m, the concentration remained approximately constant with depth between 22 and 30 pM with an average of

25 ± 2 pM. Both the shape of the profile and the concentrations in the deep water are similar to those found in the northeastern Pacific (Knauer et al., 1982; Martin and Gordon, 1988; Martin et al., 1989; Bruland, 1983).

Knauer et al. (1982) suggested that the geochemistry of cobalt may be similar to that of manganese and that, if this were true, the concentration of cobalt in the oligotrophic surface oceans should be low, less than 20 pM. Our data do not support this hypothesis as the concentrations of cobalt found in the surface waters above 150 m (> 95 pM) were considerably higher than this value. Furthermore, an external source of cobalt is needed to sustain these elevated concentrations. The two most likely sources are riverine input and atmospheric deposition (Donat and Bruland, 1995). However, since Station 11 was located in a part of the oligotrophic ocean that was quite remote from any major land mass and there was no major river that drained into the study area, the higher concentrations of cobalt in the surface waters cannot be explained by a direct input from land as invoked in previous studies in more coastal waters (Knauer et al., 1982). Thus, the more likely source of cobalt to the surface waters is probably atmospheric deposition as suggested in explanation of the high concentrations observed in the surface waters of the Mediterranean Sea (Hgoc and Whitehead, 1986). This input may include both anthropogenic and naturally occurring material. However, their relative importance at the sampling site is not known.

Within the top 150 m of water, a sharp and prominent shallow sub-surface maximum, centered around 48 m at a concentration of cobalt of 168 pM, was found. This is
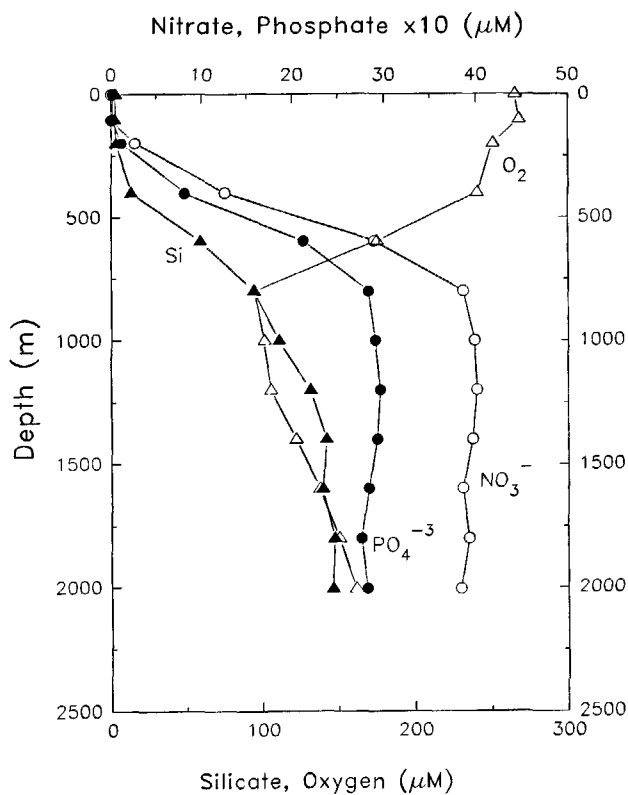
Figure 4

The distribution of nitrate (open circle), phosphate (filled circle, in concentration × 10), oxygen (open triangle) and silicate (filled triangle) at Station 18.
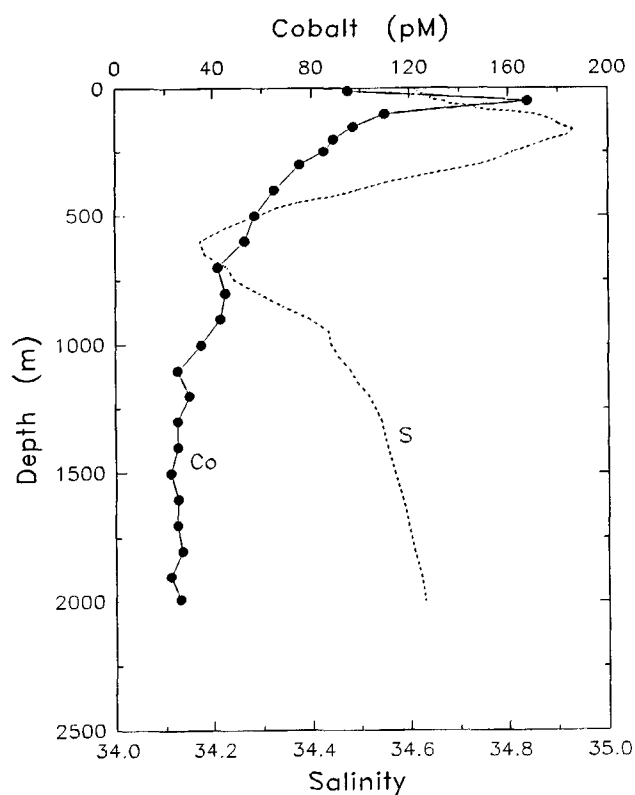

Figure 5

The distribution of dissolved cobalt (filled circle) and salinity

admittedly a rather high concentration found at only one depth. However, even if this datum point is disregarded, the presence of a sub-surface maximum within the top 150 m can still be seen readily. A re-examination of the reported

Figure 6

The relationship between cobalt and salinity (filled circle and solid line), and, potential temperature and salinity (dashed line) at Station 11. Numbers denote the depths of selected data points in cobalt-salinity plot.

cobalt data to date reveals that a sub-surface maximum within the pycnocline in the top 200 m of water can be found quite frequently (Bruland, 1983; Knauer *et al.*, 1982; Ngoc and Whitehead, 1986; Martin *et al.*, 1989) although its presence has seldom been stated explicitly and its origin has yet to be explained. The maximum found in these earlier data sets was less prominent than that observed in this study although Bruland (1983) did report the presence of a shallow maximum, whose exact depth was not given, with a concentration of 100 pM. Since none of the profiles reported to date were sampled at a sampling interval as close as that reported here, it is possible that higher concentrations were not found because the depth at which the maximum concentration occurred might not have been sampled. In this study, the maximum at 48 m was located within the strong shallow halocline. Since cobalt may be associated with bio-molecules such as vitamin-12, a plausible explanation for the occurrence of this shallow maximum may be the preferential trapping and re-mineralization of organic particles within a strong density gradient. This mechanism would imply that cobalt undergoes a very shallow recycling process. There was no evidence of a corresponding nutrient-maximum. Although the sampling intervals for the nutrients were probably too far apart to detect fine-scale features, it seems that the surface waters were almost devoid of nutrients at least down to 100 m. If the observed maximum in cobalt were real, it would suggest that the cobalt and nutrient cycles may not be tightly coupled to each other. If nutrients were regenerated together with
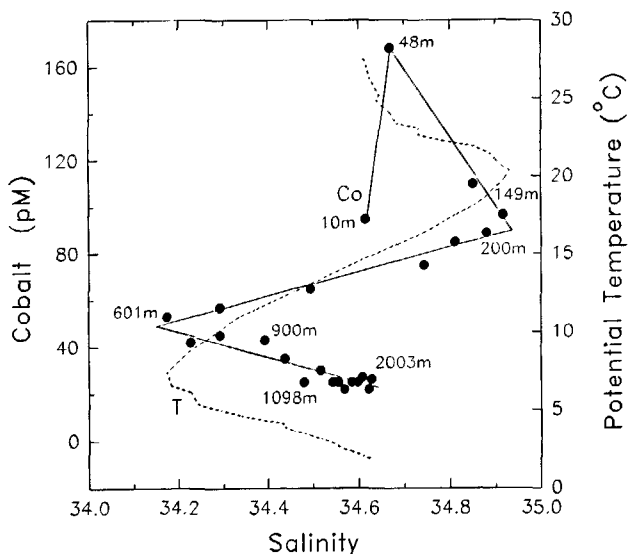
cobalt, they were used up rapidly enough for there to be no accumulation of nutrients at the depth where the cobalt-maximum was found. The present data base is insufficient for more definitive conclusions. Additional observations are needed to verify the general presence of this shallow maximum and the mechanism for sustaining it.

The relationship between cobalt and salinity is shown in Figure 6. Below the shallow cobalt maximum at 48 m, its correspondence to the T-S relationship is clearly evident. The cobalt-salinity relationship can also be represented, as a first approximation, by consecutive linear line segments with inflection points occurring at about the same salinities and corresponding depths as in the T-S relationship. Thus, the NPTW and the NPIW were characterized by concentrations of cobalt of about 97 pM at 149 m and 53 pM at 601 m respectively. The correspondence between the cobalt-salinity and temperature-salinity relationship in these waters suggests that the distribution of cobalt below the maximum at 48 m was governed primarily by physical mixing processes.

Although the relationship between cobalt and salinity from 600 m at the salinity minimum to 2000 m was linear as a first approximation, there was a suggestion that there may be a slight inflection or convexity at about 900 m where the oxygen minimum, nutrient maximum and a slight cobalt maximum were found. The origin of this slight cobalt maximum is uncertain. If it were real, it could have been sustained conceivably by *in situ* regeneration of particulate material or by an advective transport. Martin *et al.* (1985) found a maximum in the concentration of manganese that associates with the oxygen minimum in the northeast Pacific and suggested that it might have an advective origin. Whether a similar explanation may be used for explaining this cobalt maximum remains to be shown.

CONCLUSION

The distribution of cobalt in the oligotrophic western Philippine Sea indicates that, even in the absence of any direct input from land, the concentration of cobalt was elevated significantly in the surface waters in the top 150 m relative to the deep water. Thus, other processes, such as atmospheric deposition, may also be important in controlling the geochemical cycling of cobalt in the surface waters. Below 150 m, the relationship between cobalt and salinity corresponds to the relationship between potential temperature and salinity. Both relationships can be represented, as a first approximation, by successive linear line segments with inflection points at about the same depth. This suggests that the distribution of cobalt in the deep waters was driven primarily by mixing processes. Furthermore, different water masses may have characteristic concentrations of cobalt. Within the euphotic zone, there may be a shallow cycling of cobalt which results in a cobalt-maximum in the shallow pycnocline at 48 m.

Acknowledgments

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