Trace Metals as Tracers in the Ocean [and Discussion]

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Trace metals as tracers in the ocean

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The trace metals that have the greatest potential value as tracers for circulation and mixing in the ocean are markedly non-conservative, with short oceanic residence times. Their distributions strongly reflect the influence of sources either at boundaries or within the water column itself. The signals arising from these inputs can act as indicators for sources and transport pathways. These characteristics are well exemplified by dissolved manganese, which shows variations in concentration within the ocean that reflect the advection and mixing of waters that have acquired enhanced concentrations as a result of three principal processes. First, injection at the sea floor in hydrothermal fluids leads to anomalies in deep-water concentrations that are detectable over about 1000 km in parts of the Pacific Ocean. At the Mid-Atlantic Ridge, the advection of hydrothermal inputs is largely restricted by the topography of the axial rift valley, but the signals have proved valuable in exploration for hydrothermal sites. Secondly, pronounced maxima are associated with the highly oxygen-deficient waters of the oxygen minimum in parts of the eastern North Pacific Ocean. They are accounted for by *in situ* remobilization from particulate forms of manganese and by lateral advection from sources at the ocean margins. Interpretation of the data for the manganese maximum layer with two-dimensional box models has illustrated the potential to estimate lateral advective velocities on the basis of fluxes of manganese. Thirdly, the occurrence of maxima in the surface mixed layer of the ocean, which is particularly marked in areas where aeolian inputs appear to be an important source for dissolved manganese, suggests its potential use as a tracer for mixing and transport in the upper ocean. In all three cases, a more detailed and quantitative knowledge of the geochemical processes that determine the observed features will be needed if the potential for tracer applications is to be fully realized.

Dissolved aluminium varies in concentration in deep-ocean waters by about two orders of magnitude, suggesting that it may be useful as a tracer for the movement and mixing of water masses. Systematic differences in concentration occur in water masses in the northwest Atlantic Ocean, but the origins of the differences remain to be clarified. Beryllium may also serve to identify water masses in the Atlantic Ocean. The few data available for cobalt suggest that this metal also may find applications as a tracer.

INTRODUCTION

Trace metals would probably have received little attention in any discussion of tracers in the sea before the late 1970s. The major advances that began a few years earlier, in clean sampling and in the handling and analysis of samples under clean conditions, have led to a much improved knowledge of the distributions of trace metals (Burton & Statham 1982; Bruland 1983). Some aspects of the processes of input and removal and of the mechanisms of internal cycling within the ocean have now begun to be investigated more fully.

These studies have established that a number of trace metals behave conservatively in the ocean, or show only minor divergences from such behaviour. Examples include the alkali metals, lithium and caesium. Molybdenum, which forms a relatively stable oxy-anion, appears to behave essentially conservatively in most marine environments. Methylated germanium species have recently provided an unexpected addition to the group of conservative constituents (Lewis *et al.* 1984). The conservative behaviour of uranium leads to important applications because it gives rise to uniform generation of radioactive daughter products in the uranium and actino-uranium series and these nuclides provide valuable means of estimating geochemical parameters such as scavenging rates.

A second group of trace metals contains those that show more or less strong positive correlations with micronutrients such as phosphate and dissolved silicon, and accordingly tend to increase in concentration along the direction of the main advective flow of deep water through the ocean basins. These correlations reflect involvement of the metals with the major vertical flux of particulates from the euphotic zone into deeper waters and their release during the decomposition of organic material or the dissolution of skeletal carrier phases, such as opal and calcium carbonate. Cadmium, zinc, and the inorganic forms of germanium show such behaviour to a very marked degree.

Of greater potential interest as tracers for transport and mixing are those metals that have distributions that strongly reflect the presence of sources, either at boundaries or within the water column itself, leading to distinctive signatures that can act as indicators of sources and transport pathways. These metals are markedly non-conservative, with short oceanic residence times, so that the concentrations in waters distant from sources become depleted in concentration relative to those close to inputs.

The difficulty in using these constituents quantitatively as tracers for physical processes can be summarized in terms of the one-dimensional advection–diffusion–scavenging model of Craig (1974) for trace elements in the deep sea. This model shows the distribution of a dissolved constituent to be dependent upon the ratio of the advective velocity to the scavenging rate constant; scavenging is assumed here to be a first-order reaction. In geochemical interpretations with this model (see also, for example, Weiss 1977) the advective velocity is constrained through other measurements to estimate the scavenging rate constant. To make the inverse calculation would require quantitative information on the scavenging rate that is at present essentially lacking. Nevertheless, the qualitative value of certain trace metals as tracers for inputs and as labels on water masses is apparent. It is the purpose of this paper to review, in this context, the geochemical behaviour of two principal examples, namely manganese and aluminium, and to consider data that indicate their potential for more quantitative applications; brief comments are included on two other metals, beryllium and cobalt, which may find some uses as tracers.

MANGANESE

The dominant factor influencing the aquatic geochemistry of manganese is the change of oxidation state of the element between reducing and oxidizing environments, coupled with the marked difference between the oxidation states in terms of their forms and reactivity.

For the reaction:

$$\mathrm{MnO_2(s)} + 4\mathrm{H^+} + 2\mathrm{e^-} \rightleftharpoons \mathrm{Mn^{2+}} + 2\mathrm{H_2O}, \tag{1}$$

it may be calculated (Stumm & Morgan 1981) that in seawater of pH 8.1, at 25 °C, the pE† at which the activities of the oxidized and reduced species are equal is 5.3. Seawater containing free oxygen at the concentrations that characterize most oceanic waters has a considerably

† In this paper, $\mathrm{pE} = -\lg a_{\mathrm{e^-}}$, where a is activity.

higher pE and on thermodynamic grounds manganese should be present as Mn^{IV}, in which oxidation state the element has a very low solubility. Under reducing conditions, Mn^{II} is the stable oxidation state, and the element is then much more soluble and geochemically mobile.

The oxidation of Mn^{II} in the environment produces a solid phase in which the average oxidation number of the metal is less than (IV) (see, for example, Grill 1982). It has been argued that the solid phase in equilibrium with Mn^{II} in seawater may be Mn_3O_4 (hausmannite) (Klinkhammer & Bender 1980) or γ-MnOOH (Grill 1982). The initially formed phase becomes more highly oxidized following deposition. The oxidation rate of Mn^{II} is sufficiently slow for the reduced form to persist in natural waters for significant periods. In oceanic deep waters the scavenging rate, which appears to reflect both removal to particles by oxidation at the particle surface and adsorption, particularly onto calcium carbonate (Martin & Knauer 1983), may be of the order of 0.01 a^{-1} (Landing & Bruland 1980). A similar value of 0.02 a^{-1} was derived by Weiss (1977) for the scavenging rate constant, assumed to be first order, in a plume of hydrothermal manganese above the Galapagos Spreading Centre. Where the scavenging rate is low relative to the rate of input or release of Mn^{II}, enhanced concentrations of the metal are observed; these can provide distinctive signatures for certain water bodies.

In studies of manganese in ocean waters a number of operationally defined parameters have been used in addition to dissolved and particulate fractions resolved by conventional filtration methods. These other parameters, total dissolved manganese and reactive manganese, are nearly equivalent to dissolved manganese in most of the situations discussed here and in such cases are referred to in the text as dissolved manganese without further qualification.

The distribution of dissolved manganese is shown in figure 1 for a vertical oceanic profile

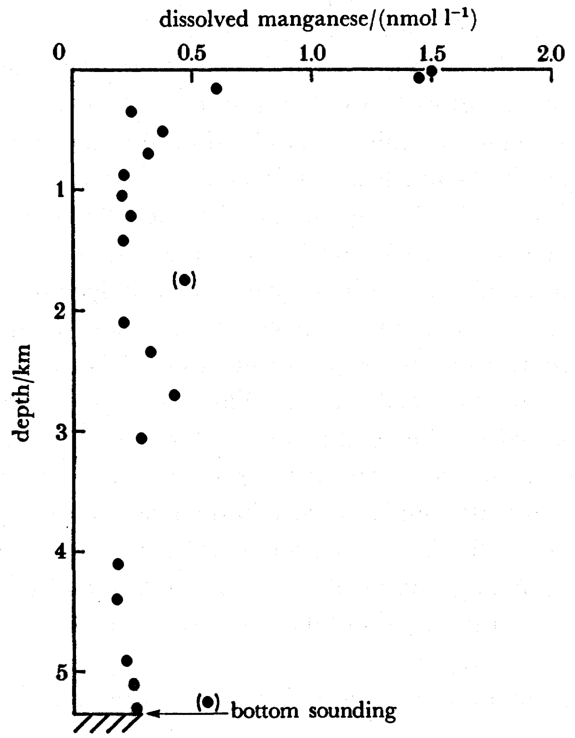

Figure 1. Vertical profile of concentration of dissolved manganese in the eastern North Atlantic Ocean (19° 22′ N, 12° 51′ W). Points in parentheses are considered analytically suspect. (From Statham *et al.* (1985).)

typical of areas where there are no significant inputs to intermediate and deep waters. The characteristic features of such areas are a maximum or several maxima in the mixed layer, sometimes occurring at the surface, a marked decrease within the upper few hundred metres, leading in some profiles to a minimum around the top of the thermocline, and relatively uniform and low values in the deep waters. This general pattern has been observed in many regions (Bender *et al.* 1977; Klinkhammer & Bender 1980; Martin & Knauer 1980; Landing & Bruland 1980, 1987; Bruland & Franks 1983; Burton *et al.* 1983; Yeats & Bewers 1985; Statham *et al.* 1985; Statham & Burton 1986).

The concentrations in deep waters are towards the lower end of the range of analytical methods and often close to the detection limits. Thus, there are uncertainties about the comparability of results reported by different workers for different oceanic regions. Nevertheless, some data have been reported indicative of regional variations in deep-water concentrations. Yeats & Bewers (1985) report regional differences in concentration of dissolved manganese in deep waters of the northwestern Atlantic Ocean. For example, concentrations in waters deeper than 2000 m at about 50° N averaged 0.56 nmol l^{-1}, whereas at 32° N concentrations averaging about 0.3 nmol l^{-1} were found at 1100–1450 m, which were the greatest depths sampled there. These workers suggest that differences between these two regions reflect the increased effects of scavenging during the southward transport of deep water that originally has a relatively high concentration of manganese as a result of its recent formation by sinking from the surface. Bruland & Franks (1983), however, report a concentration of 0.56 nmol kg^{-1} at 2962 m in the Sargasso Sea at 34° N, and Jickells (1986) has reported similar values for this region.† For the northeastern Atlantic Ocean, concentrations averaging about 0.25 nmol l^{-1} have been reported for waters below about 1000 m (Statham *et al.* 1985; Statham & Burton 1986); the results from these studies suggest no significant differences between deep Mediterranean and northeastern Atlantic Ocean waters.

Consideration of data for the Pacific Ocean is complicated not only by analytical uncertainties but also by the effects of hydrothermal inputs on the deep-water concentrations at some locations, as discussed below. Landing & Bruland (1980) gave a value of approximately 0.2 nmol kg^{-1} for deep waters in the northeastern Pacific Ocean; at an open-ocean station their results are in the range of 0.10–0.15 nmol kg^{-1} for depths below 3000 m. Further measurements on profiles in the central and eastern Pacific Ocean between 37° N and 20° S (Landing & Bruland 1987) have yielded notably smooth and correspondingly convincing profiles in which some features in deeper water are apparent. At the VERTEX II station, in the eastern tropical North Pacific Ocean, and at a central oceanic station southwest of Hawaii, concentrations in the depth range corresponding to the Pacific Deep Water averaged about 0.2–0.3 nmol kg^{-1}, values similar to those reported for the northeastern Atlantic Ocean. At the remaining open-ocean station, southwest of Tahiti, a broad maximum was apparent within the Pacific Deep Water that was provisionally attributed to advection from flank sediments of islands or seamounts of the region. For all offshore stations examined in this work, the lowest concentrations of dissolved manganese, typically less than 0.2 nmol kg^{-1}, occurred in bottom waters. Higher average concentrations, about 0.5 nmol kg^{-1}, characterized deep waters at two stations in the California Current.

Overall, these data suggest that there are significant, although small, variations in the

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† We have chosen to quote measured concentrations in the units reported by the workers concerned.

concentrations of dissolved manganese in deep waters within the major ocean basins. Although in some cases variability may reflect the differences in age between waters that have sunk very recently from the surface and waters that are older in relation to this process, it is clear that variations of comparable magnitude can arise in other ways. Some differences may reflect local sources, as in the example of the possible influence of seamount or island flank sediments, quoted above. Accurate measurements on sections carefully chosen in relation to the patterns of deep-water flow are needed to evaluate and interpret the variations. It is clear that any systematic difference along the direction of the major global deep water circulation is small, although the lowest concentrations found in Pacific Ocean waters deeper than about 3000 m are less than any reported so far for the Atlantic Ocean. This is probably attributable to the rapid scavenging of manganese that leads to depletion even in recently formed deep waters. It may be that over much of the deep ocean the concentrations of dissolved manganese are close to a background value determined by a quasi-equilibrium between manganese in solution and the solid phase intially formed by its oxidation, as suggested by Klinkhammer & Bender (1980).

Much more clearly defined variations in concentrations of dissolved manganese are associated with the advection and mixing of waters that have received localized inputs of mobilized Mn^{II}. These phenomena are associated with three principal processes that mobilize manganese.

(1) Injection at the sea bed in hydrothermal fluids.

(2) Release from either bottom sediments or suspended particulate material under suboxic or anoxic conditions.

(3) Input to surface ocean waters, which at least in central areas appears to arise mainly by release from particulate material introduced by aeolian transport.

Hydrothermal inputs of manganese

The penetration of seawater through oceanic crustal material at ocean-ridge spreading centres can lead to high-temperature water–basalt interactions, producing hydrothermal fluids that are returned to the ocean through vents at the sea floor. The chemical processes that occur have been extensively described by, among others, Edmond *et al.* (1979, 1982), Von Damm *et al.* (1985*a*, *b*) and Bowers *et al.* (1985). Concentrations of manganese in the high-temperature hydrothermal fluids have been reported to range from 0.13 to 1.5 mmol kg^{-1} (Von Damm *et al.* 1985*a*, *b*; Klinkhammer & Hudson 1986), about a million times higher than those in ocean-bottom waters.

The hot buoyant water emanating from vents rises to some few hundred metres above the sea bed before attaining density stability and spreading laterally, large amounts of water from deeper in the water column becoming entrained in the process (Lupton *et al.* 1985). These processes were observed to produce large anomalies in the concentrations of dissolved and particulate manganese in the waters above the Galapagos Spreading Centre (Klinkhammer *et al.* 1977; Weiss 1977; Bolger *et al.* 1978). Corresponding features have been observed in other areas of hydrothermal activity in the Pacific Ocean, namely on the East Pacific Rise at 21° N (Lupton *et al.* 1980), over the Juan de Fuca Ridge (Jones *et al.* 1981), and in the Guaymas Basin (Campbell & Gieskes 1984). Lateral spreading leads to anomalies in the concentrations of dissolved manganese in deep waters over extensive areas, the concentrations reflecting the dilution of the water enriched in manganese and the scavenging of the metal. Klinkhammer *et al.* (1977) and Weiss (1977) estimated from a one-dimensional dispersion model that the horizontal propagation distance for the inputs in the Galapagos Spreading Centre region was of the order of 1000 km. This has been confirmed by observation of anomalies probably attributable to distant hydrothermal sources, in the Guatemala Basin (Klinkhammer 1980) and the detection, in the data set of Klinkhammer & Bender (1980), of a slight anomaly at a station (GEOSECS 317) about 2000 km west of the ridge axis (Klinkhammer & Hudson 1986).

A detailed examination of the dispersal patterns in the region of the East Pacific Rise between about 10° S and 40° S has been made by Klinkhammer & Hudson (1986). A profile for a station on the ridge axis, with a pronounced maximum above the sea floor, is shown in figure 2*a*. In this region the flow of deep water at depths corresponding to those of plume injection is dominantly westward but at 30° S the flow is eastward. An approximately north–south section east of the East Pacific Rise, at 91°–94° W, shows a core of manganese-rich water centred on about 30° S at a level corresponding to that of plume injection at the ridge axis (figure 3). West of the Rise, at about 12°–19° S, the westward flow of deep water is reflected in anomalies, generally with several maxima, arising from the effects of several plumes arising from vents at different depths.

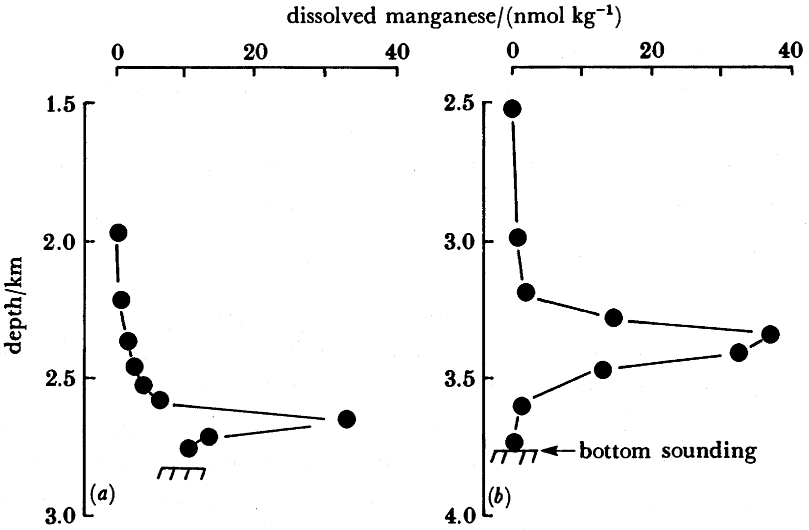

FIGURE 2. Vertical profiles, showing anomalies in concentration of dissolved manganese associated with advection from hydrothermal sources, at (*a*) the East Pacific Rise at 20° S (Klinkhammer & Hudson 1986) and (*b*) the Mid-Atlantic Ridge at 26° N (Klinkhammer *et al.* 1986). See text for explanation of use of the term dissolved manganese.

Studies on the Pacific Ocean have demonstrated that anomalies in the concentration of manganese, like those in the conservative tracer helium-3 (see, for example, Weiss (1977), Lupton *et al.* (1977, 1980) and Lupton & Craig (1981)), can provide information about the patterns of deep-water circulation in regions influenced by hydrothermal inputs. They have also shown the potential for the use of manganese as a geochemical indicator in exploring for hydrothermal vents. This approach is particularly valuable because measurements of manganese can be carried out fairly readily on board ship.

The value of measurements of manganese in detecting hydrothermal inputs has been effectively realized in recent work in the Atlantic Ocean. Evidence of hydrothermal activity on the Mid-Atlantic Ridge, where spreading rates are considerably lower than those on the East-

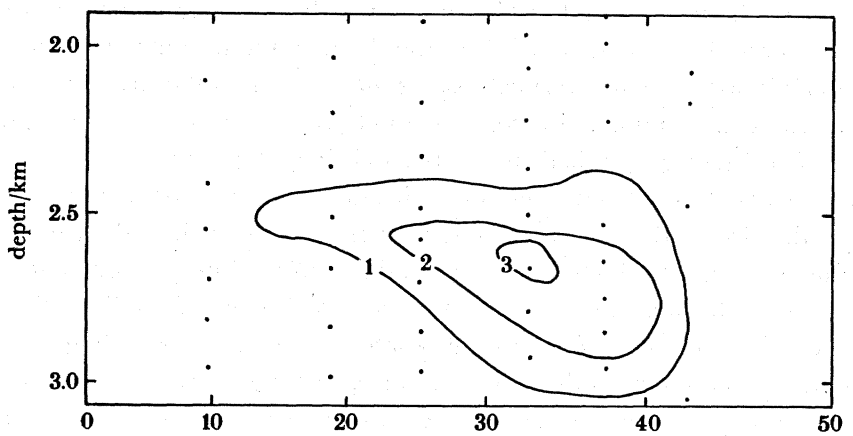

FIGURE 3. Concentrations of total dissolvable manganese (nanomoles per kilogram) along a section in the Galapagos Basin at about 93° W (Klinkhammer & Hudson 1986).

Pacific Rise, has been obtained from findings of metalliferous deposits and sediments with anomalously high concentrations of trace metals such as iron and manganese, from observations of suspended particulate material enriched in manganese and iron, and from anomalies of temperature and helium-3 in the water column, as well as from magnetic measurements on crustal material. These discoveries, which have been summarized by Rona (1980) and Rona *et al.* (1984), have focused on the Trans-Atlantic Geotraverse (TAG) hydrothermal field at 26° N, on the east wall of the rift valley. Rona *et al.* (1984) concluded that the observed features were consistent with alternating periods of low-temperature and high-temperature venting.

The first observations of anomalies in manganese were those of Klinkhammer *et al.* (1985) at stations above the rift valley of the Ridge, extending from the TAG area at 26° N to the Vema Fracture Zone (11° N). These observations showed anomalies of dissolved manganese up to about 2 nmol $\mathrm{kg^{-1}}$, in maxima above the sea bed. The amounts of acid-soluble particulate manganese present varied considerably between stations, probably reflecting differences in the degree of scavenging of dissolved manganese on to particulate phases and thus in the age of the manganese relative to its time of injection, i.e. differences in distance from the vent. From such differences, together with variations in the depth of the maxima, and the extent and shape of the anomalous section of the profile, it was concluded that there were at least five sources within this section of the rift valley.

An anomaly in concentration of manganese was also found in the median valley of the Mid-Atlantic Ridge at 43° N (Hydes *et al.* 1986). In the section of the ridge between 42°–47° N, there occurs a series of major segments of the valley, each of which contains, below 3000 m, water of uniform potential temperature (Saunders & Francis 1985). The properties of the water that enters the valley are determined by the shallowest depth at which exchange with an exterior source can occur, in effect a sill depth analogous to that of a fjord. The observations on manganese were made in the valley designated by Saunders & Francis (1985) as valley A with a sill depth of 2450 m. The water within the valley was found to be very well mixed, as described by Saunders & Francis (1985) for valleys to the north. Concentrations of manganese, like those of copper, nickel and cadmium, were uniform below 2400 m but unlike these other elements, manganese was significantly enriched relative to typical Atlantic Ocean deep waters, with a concentration of about 1.7 nmol l^{-1}. The anomaly in dissolved manganese was attributed to a hydrothermal source. It was concluded from the shape of the profile above the sill depth, and a consideration of horizontal and vertical dispersion rates, that other hydrothermal inputs occurred along the ridge and that a major component of deep-water flow was along the axis of the ridge, which is consistent with other observations (Keller *et al.* 1975).

Further measurements of manganese were made in the TAG area as part of an investigation (Rona *et al.* 1986) that led to the discovery of active vents on the wall of the rift valley, with a range of associated phenomena, including active and inactive chimneys, and vent biota. The data for manganese have been given by Klinkhammer *et al.* (1986). They show the existence of advective plumes with concentrations of total reactive manganese exceeding 30 nmol kg^{-1} in maxima in the water column, both the concentrations, and the shapes of the maxima (figure 2*b*), resembling those observed on the East Pacific Rise. The dominant contrast between the Atlantic and Pacific Oceans is that in the former there is an effective topographic restriction on the dispersal of the manganese introduced from vents. Thus, observations of anomalous concentrations of manganese, associated with hydrothermal inputs, have so far been restricted to the rift valley. Klinkhammer *et al.* (1985) point out the possibility that leakage of manganese could occur through fracture zones. Labelling of deep water in this way could potentially provide a useful tracer for deep-water movements but the present indications are that any signals would be small.

Inputs resulting from depletion of oxygen in the water column or in sediments at the ocean margin

In regions of the Pacific Ocean where the oxygen concentration at depths near the oxygen minimum falls below about 100 μmol l^{-1}, a significant increase in the concentration of dissolved manganese was reported by Klinkhammer & Bender (1980). This phenomenon has been extensively studied only in the eastern Pacific Ocean where substantial anomalies in dissolved manganese are generally associated with the suboxic conditions that occur in the oxygen minima over extensive areas (Murray *et al.* 1983; Martin & Knauer 1984, 1985; Martin *et al.* 1985; Jones & Murray 1985). A few examples of small anomalies associated with much less intense oxygen minima have been reported for the Atlantic Ocean (Statham & Burton 1986).

The occurrence of enhanced concentrations of dissolved manganese at intermediate depths in parts of the North Pacific Ocean is illustrated by the results for VERTEX stations on a section approximately normal to the western coastline of the U.S.A., between 28° N and 36° N (Martin *et al.* 1985). The variations with distance offshore are shown in figure 4; the enhanced concentrations in the surface waters are discussed subsequently. The section shows a core of water with enhanced concentrations of dissolved manganese (0.5–1.4 nmol l^{-1}) centred on about 600–700 m, with decreasing concentrations in the offshore direction. Similar features were described by Jones & Murray (1985) for a section at about 47° N, with concentrations of dissolved manganese in the oxygen minimum decreasing from 4.7 nmol kg^{-1} close to the continental slope to about 0.7 nmol kg^{-1} offshore.

Two principal processes may contribute to the increase in dissolved manganese in the dissolved oxygen minimum: the diffusion and advection of manganese from the continental slope region and the release of manganese from particles sinking from the surface waters. Such release is probably primarily caused by the dissolution of an oxidized phase under the conditions of lowered pE, by the decomposition of organic material, or by a combination of

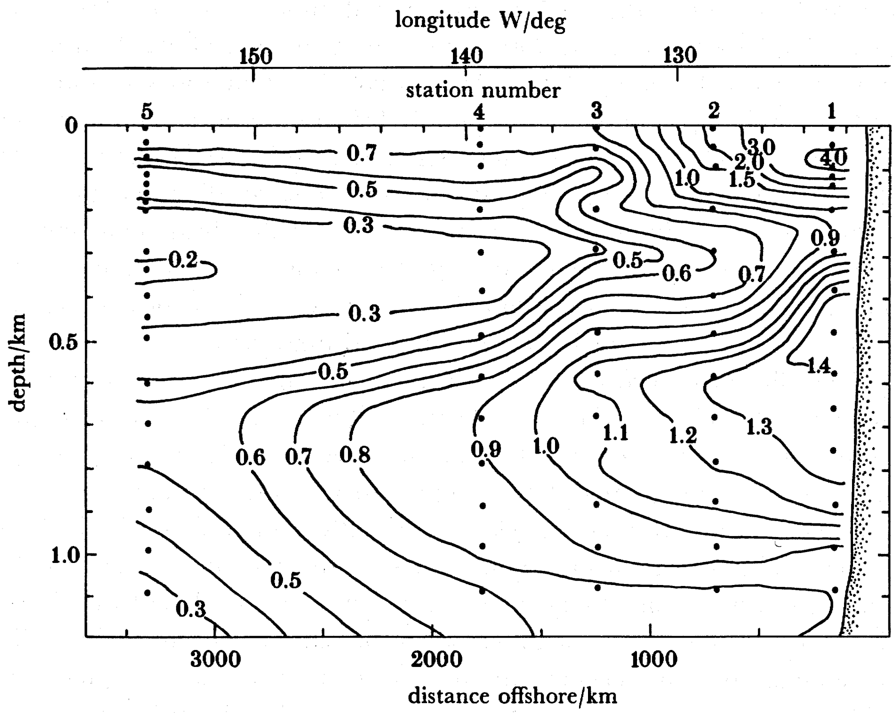

Figure 4. Concentrations of dissolved manganese (nanomoles per kilogram) along a section (VERTEX V) from Monterey Bay to the VERTEX IV station north of Hawaii (Martin *et al.* 1985).

these processes. The occurrence of such processes is indicated by the fact that particulate material in the oxygen minimum is markedly depleted in leachable manganese (Martin & Knauer 1984).

The clearest evidence concerning the relative importance of these processes has come from interpretations by box models of measurements made during VERTEX cruises. Martin & Knauer (1984) determined manganese in the material collected by sediment traps at various depths at the VERTEX station at 18° N, 108° W, and the concentrations of dissolved and particulate manganese in the water column. The data were interpreted by using a box model with eight compartments representing sections of the water column in the vertical, with depth limits defined by the depths of deployment of the sediment traps. Vertical fluxes of particulate manganese were determined from the measurements on material collected in the sediment traps; these values excluded the refractory fraction of particulate manganese, that held in mineral lattice structures, which forms only a small and rather uniform component of the total particulate manganese throughout the water column. Vertical fluxes of dissolved manganese were calculated by using estimated values of the eddy diffusivity coefficient and the vertical advection velocity. Mass-balance calculations with the box model indicated that in the depth range containing the core of the maximum in dissolved manganese (200–400 m), with oxygen concentrations below 10 μmol kg^{-1}, the net release from particles was inadequate to sustain the observed concentrations of dissolved manganese and it was necessary to invoke a balancing flux due to horizontal diffusion and advection, amounting to about twice that due to net release from particles.

Calculations made by Landing & Bruland (1987) for the same station led to a very similar conclusion. These workers applied the vertical advection–diffusion model of Craig (1974) to a region of linear mixing between 150 and 750 m, to estimate the loss of dissolved manganese from the maximum by vertical mixing. Release from particulate material accounted for only about half of the loss, implying a compensating supply by offshore horizontal advection.

The patterns of distribution of dissolved manganese observed by Martin *et al.* (1985) (see figure 4) and Jones & Murray (1985) suggest that the concentration maximum that is associated with the oxygen minimum arises from a source of dissolved manganese at the interface with slope sediments. Jones & Murray (1985) have discussed the processes that can supply dissolved manganese to the water column. They conclude that for the continental slope off Washington, in the northeast United States, diffusive fluxes across the sediment–water interface, arising from diagenetic processes in the sediments, provide the major input.

The box-modelling approach developed by Martin & Knauer (1984) was also applied to data from four of the five stations on the section shown in figure 4 (Martin *et al.* 1985). The results for the fluxes of manganese at different depths in the water column indicated that scavenging by, and release from, particulates were not usually a major factor in the formation of either the subsurface minimum in dissolved manganese or the maximum associated with the oxygen minimum. At station 5, increasing fluxes with depth indicated that manganese was being scavenged within the manganese maximum even though the concentration of dissolved oxygen at the oxygen minimum that occurred in the same box was less than 30 μmol kg^{-1}. Use of the box-modelling approach, as summarized above, indicated that the subsurface manganese minimum must be maintained by horizontal advection shoreward of water containing low concentrations of dissolved manganese, whereas maintenance of the maximum requires the offshore advection of water with a high concentration of dissolved manganese. The approach also allowed calculation of the net horizontal advective velocities necessary to balance the net vertical fluxes of dissolved and particulate manganese. With the data for stations 1–4 offshore velocities in the manganese maximum layer were estimated as about 0.4 cm s^{-1}, whereas estimates of onshore velocities in the manganese minimum layer ranged from 0.9 cm s^{-1} at station 4 to 4.4 cm s^{-1} at station 1.

Similar calculations were made by Martin & Knauer (1985) for the whole section shown in figure 4, including station 5. A plot of dissolved manganese against σ_t for station 5 and a location close to station 1 (figure 5) shows a clear similarity in shape between the depths of 500 and 1100 m, which interval includes the oxygen minimum layer. Assuming that station 1 is representative of the marginal regions that supply manganese to the gyre circulation, the net advective velocity over the 3150 km dividing the stations was estimated as 0.9 cm s^{-1}, within the depth intervals considered.

These calculations are essentially illustrative. They involve a number of simplifying assumptions, one of the most important being implied by the use of two-dimensional models. The importance of longshore horizontal mixing in the eastern tropical North Atlantic Ocean is emphasized by Landing & Bruland (1987). Sampling grids extending alongshore as well as offshore will be needed to realize the very considerable potential for the use of manganese as a tracer for large-scale circulation processes in this area.

Manganese in the surface ocean

A surface or near-surface maximum in dissolved manganese is a ubiquitous feature in the ocean, although the concentrations found vary considerably. The results shown in figure 4

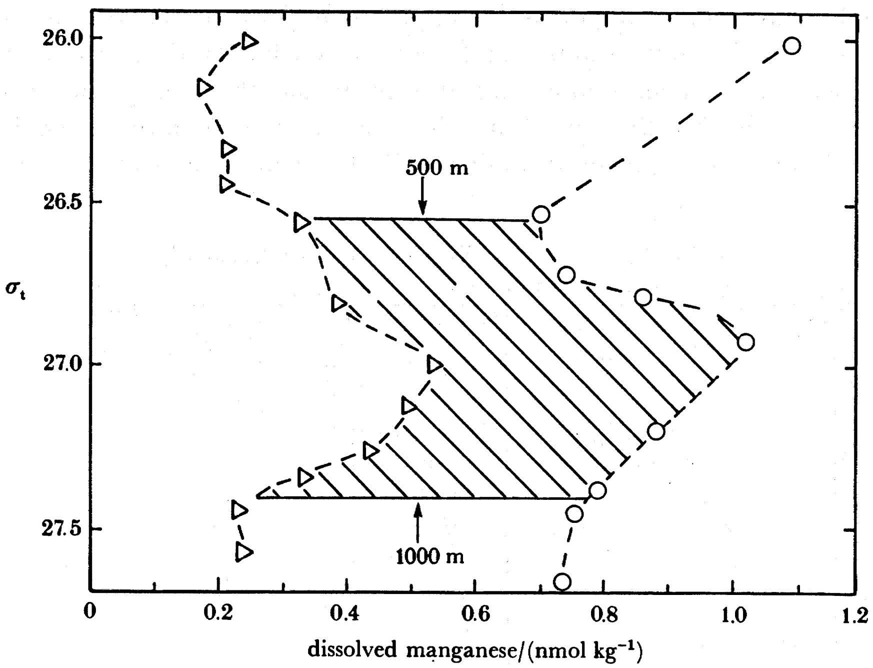

FIGURE 5. Relation between concentration of dissolved manganese and σ_t at station 5 (△) and a station close to station 1 (○) in figure 4. The hatched area was used in the box-model calculations summarized in the text. (From Martin & Knauer (1985).)

suggest the existence of a source of manganese at the ocean margin supplying the element to surface waters. Such a source was invoked by Landing & Bruland (1980) to explain the marked increase in concentrations between the California Current and the adjacent coastal waters. Similar features to those shown in figure 4 were found by Jones & Murray (1985) off the Washington coast. The features in both cases are consistent with inputs from shelf waters where the metal can be enhanced by river inputs and diffusion from, and resuspension of, reducing sediments. Upwelling of deeper water, which is rich in manganese in these environments, is another possible mechanism of supply (Jones & Murray 1985).

Transport of manganese from shelf waters may influence areas at considerable distance from the sources. Thus, Landing & Bruland (1987) found evidence for transport of manganese from the eastern boundary region of the North Pacific Ocean by the Equatorial Current. There is substantial evidence, however, for a role of aeolian input as a source of manganese for surface waters in many regions. Klinkhammer & Bender (1980) considered this source to be important at the stations they studied in the Pacific Ocean, a view that is supported by an increase in the concentrations of dissolved manganese in the surface mixed layer between the western boundary of the California Current and central gyre waters. Data for the shelf break off northwestern Europe (Kremling 1985) do not indicate any major advection of dissolved manganese to the adjacent ocean, and the distribution of dissolved manganese over extensive areas of the northeastern Atlantic Ocean is consistent with the influence of aeolian inputs (Kremling 1985; Statham & Burton 1986), high concentrations occurring in the latitudes most affected by the Saharan dust plume.

In areas where inputs of aeolian dust imprint signatures of enhanced concentrations of dissolved manganese on surface waters there may be considerable potential for using these signatures to study mixing and transport in the upper ocean. In figure 6, vertical profiles for dissolved manganese are shown for a station in the eastern North Atlantic Ocean, occupied on two separate occasions. Data for salinity are also given and these show the pronounced deepening of the mixed layer at the time of the winter occupation. With the deepening of the mixed layer, the dissolved manganese maximum is displaced to about 150 m. The complex distribution of dissolved manganese shown under the conditions of shallower stratification prevailing on re-occupation, with subsidiary maxima below 100 m, may reflect the decay by scavenging of signals that had been produced at these depths by the downward mixing of water from the surface, where high concentrations of dissolved manganese had been produced by *in situ* processes.

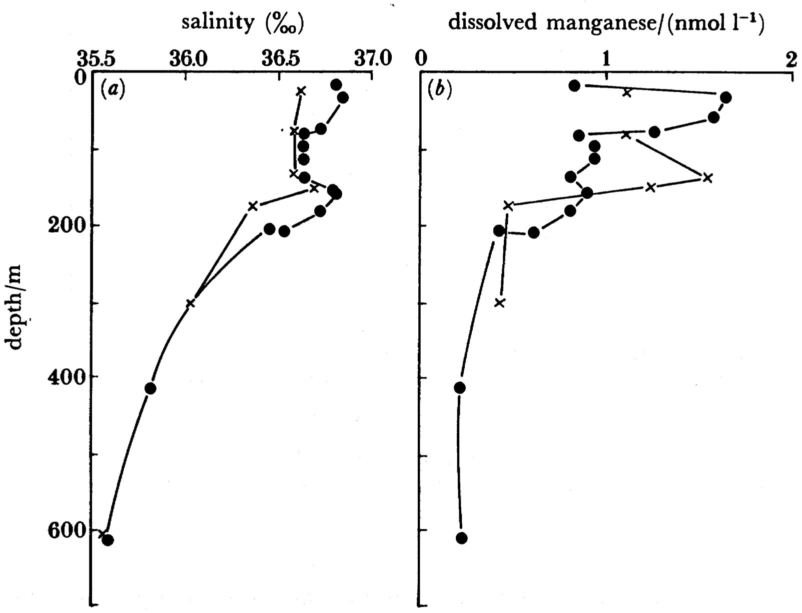

FIGURE 6. Temporal variations in the near-surface distribution of (*a*) salinity and (*b*) dissolved manganese at a station in the eastern Atlantic Ocean (31° 28′ N, 24° 30′ W). Crosses indicate data for February 1982 and circles those for June 1982. (From Statham & Burton (1986).)

Although cycling involving organisms may play a part in the chemistry of manganese in the surface waters, the most probable hypothesis concerning the formation of near-surface maxima is that the manganese is released from particles by desorption and dissolution under the conditions prevailing in the surface ocean. Laboratory experiments with an artificially prepared manganese oxide phase have demonstrated a release of manganese to solution, the rate being enhanced by light and organic matter (Sunda *et al.* 1983). The mechanism of photoreduction of manganese oxide phases is not understood. One possibility is that it occurs through the presence of hydrogen peroxide, the pE for the O_2–H_2O_2 couple being lower than that for the O_2–H_2O couple (Breck 1974). The presence of significant concentrations of hydrogen peroxide in precipitation and in surface seawater has been established (see, for example, Cooper & Zika (1983) and Zika *et al.* (1982, 1985)). Its distribution, with surface maxima and a rapid decrease in concentration with depth, parallels somewhat that of dissolved manganese. Irrespective of the mode of formation of Mn^{II} its relatively slow oxidation is a likely factor contributing to its often complex distributions in the mixed layer. It seems probable that these reflect, in addition to the effects of mixing and convection, the balance between release of Mn^{II} from particles, by desorption and by dissolution under the direct and indirect influences of photochemical reactions, and scavenging onto particle surfaces. Unravelling and quantifying these processes are prerequisites for exploitation of the potential of manganese as a tracer in the upper ocean.

ALUMINIUM

The measurements of aluminium discussed here have been made on both filtered and unfiltered samples. As pointed out by Orians & Bruland (1986), analyses on unfiltered samples that have been acidified to low pH can for some environments lead to substantial differences between the results thus obtained and those for filtered samples. In most studies where unfiltered samples have been analysed, however, storage under acidic conditions has not been employed and contributions of particulate fractions to the reactive aluminium have been small. For the purposes of this discussion it therefore seems permissible to regard the aluminium measured on either filtered or unfiltered samples as being dissolved.

Aluminium is a particle-reactive element with a short residence time in oceanic waters; for example, the residence time of dissolved aluminium in deep Pacific Ocean waters has been estimated as 50–150 years (Orians & Bruland 1986). Concentrations are markedly lower in the older deep waters of the Pacific Ocean than in deep Atlantic waters. The latter typically contain some 10–30 nmol kg^{-1}, whereas concentrations in the deep and bottom waters of the Panama Basin are 1–6 nmol kg^{-1} (Measures *et al.* 1984) and the deep waters of the central gyres of the Pacific Ocean contain 0.5–2.0 nmol kg^{-1} (Orians & Bruland 1985, 1986).

With the low concentrations in Pacific Ocean waters, effects of inputs at the atmospheric and benthic boundaries are more readily seen; they are strikingly apparent in the data of Orians & Bruland (1986) for the VERTEX IV station, north of Hawaii (figure 7). The enhanced

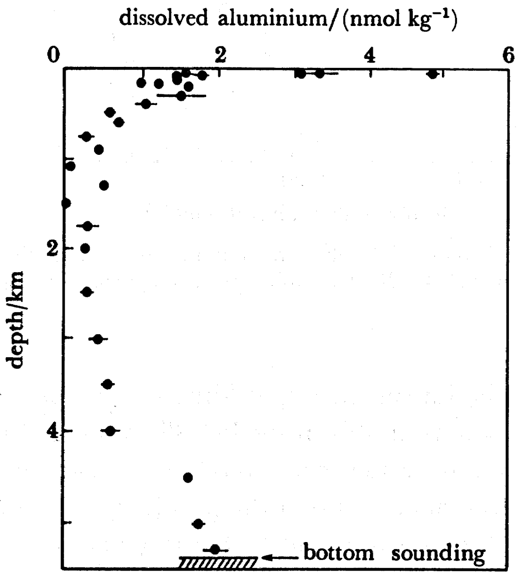

FIGURE 7. Vertical profile of concentration of dissolved aluminium in the central North Pacific gyre (28° 15′ N, 155° 07′ W). (From Orians & Bruland (1986).)

concentrations in deep waters may be attributable to dissolution in the benthic boundary layer or to diffusion from sediments. The fact that the surface water concentrations increase from the California Current region to the central gyre indicates that aeolian input is a major source for aluminium in the latter waters. The importance of this source in the Atlantic Ocean is suggested by the data of Hydes (1983) for dissolved aluminium in surface waters of the eastern Atlantic Ocean, showing an association of higher concentrations with the region most influenced by the Saharan dust plume.

As observed by Orians & Bruland (1986) the range of the concentration of dissolved aluminium in the deep waters of various ocean regions is greater than that shown by any other metal that has been investigated. There is a difference by two orders of magnitude between the concentrations in the deep waters of the North Pacific gyre and those reported by Caschetto & Wollast (1979) for the Mediterranean Sea. Such differences suggest that aluminium should be a useful element in the study of the movement and mixing of water masses. At present, the scope for the interpretation of measurements of the element in terms of circulation models is restricted by limited knowledge of the geochemical factors that initially determine and subsequently modify the signatures on water masses.

Measures *et al.* (1986) determined dissolved aluminium in samples from four profiles in the Sargasso Sea. Their data for subsurface waters are shown in figure 8 in the form of a plot of concentration of dissolved aluminium against σ_θ. Additional data on temporal variations in the upper waters at one of the stations are given by Jickells (1986). Certain general trends are apparent from these studies. Surface waters contain relatively high but variable concentrations of dissolved aluminium (18–45 nmol l^{-1}). From the profiles given by Measures *et al.* (1986) a decrease in concentration with depth to about 200 m is generally apparent. The time series data of Jickells (1986) show this to be a seasonal feature. Concentrations tend to increase in the Eighteen Degree Water, centred on about 300 m, and then decrease to a broad minimum, with concentrations of about 10 nmol l^{-1}, centred on about 1400 m. Below this zone concentrations

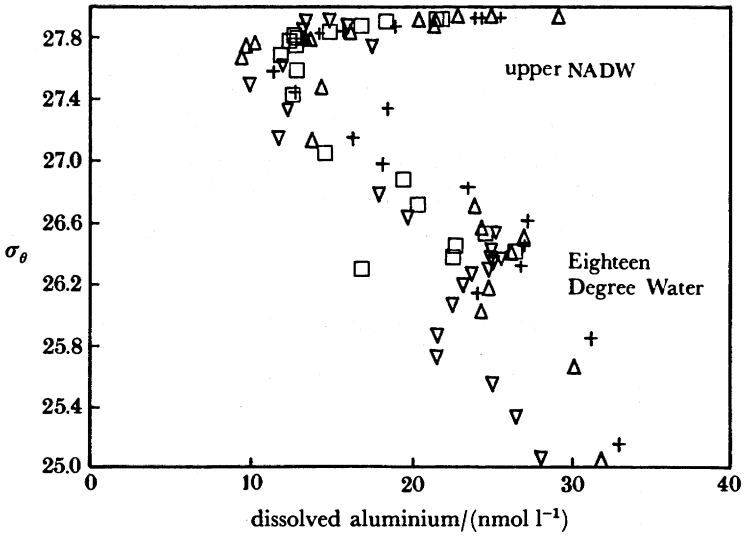

FIGURE 8. Relation between concentration of dissolved aluminium and σ_θ for subsurface waters in the western Atlantic Ocean between about 32°–38° N. The different symbols correspond to different stations. (From Measures *et al.* (1986).)

increase with depth, typically to about 25 nmol l^{-1}. Features that are consistent with these were reported earlier for the northwestern Atlantic Ocean by Hydes (1979) and Moore & Millward (1984).

In this region the North Atlantic Deep Water (NADW) with an upper boundary at about 1200 m can be considered as consisting of Upper NADW to about 2000 m, overlying the Iceland–Scotland overflow and Denmark Strait overflow waters that have their origins in the upper waters north of Iceland. The Upper NADW has contributions of Labrador Sea Water and Mediterranean Outflow Water, the latter being weakly represented so far west. Measures *et al.* (1986) have suggested that the increased concentrations of dissolved aluminium in the Lower NADW reflect rapid transport of aluminium-rich waters from the northwestern European shelf region into the Norwegian Sea and the relatively short transit time between the formation of the deep water and its appearance in the Sargasso Sea. Data for a station south of Iceland at about 60° N (Ólafsson 1983) show deep-water concentrations of dissolved aluminium very similar to those in the Sargasso Sea. The rapidity of transfer of material from northern regions of the Greenland Sea to deep water south of Denmark Strait is shown by measurements of caesium -137, which is introduced anthropogenically from British shelf waters (Livingston *et al.* 1985). These suggest that the transit time may be only a few years.

The Labrador Sea Water, which is a major component of the Upper NADW, also has a short transit time between formation and appearance in the Sargasso Sea. Measurements of chlorofluoromethanes in the Atlantic Ocean (Weiss *et al.* 1985) have demonstrated the rapid transport of these substances along a western boundary undercurrent of Upper NADW. Interpretation of the results using a mixing model suggests a mean velocity of about 450 km a^{-1}. On this basis the transit time to the Sargasso Sea for the Labrador Sea Water is of the order of 10 years. The low concentration of dissolved aluminium in the Upper NADW is attributed by Measures *et al.* (1986) to the fact that this water has a major source in Arctic surface water transported in the East Greenland Current; surface waters in the Arctic Ocean have been shown by Moore (1981, 1983) to be low in dissolved aluminium (less than 5 nmol l^{-1}).

The hypothesis of Measures *et al.* (1986) raises questions regarding the role of shelf waters as a source of aluminium for the Norwegian and Greenland Seas. Measurements of dissolved aluminium in northwestern European shelf waters have shown high concentrations, averaging over 150 nmol kg^{-1}, in the Western Approaches, English Channel and southern North Sea in early Spring 1982 (Kremling 1985). Values averaging only 28 nmol kg^{-1} have been reported, however, by Kremling & Hydes (1988) for the Celtic Sea and English Channel in November 1985, and concentrations lower by a factor of about three were found under summer conditions. Oceanic surface waters close to the shelf-break in the section examined by Kremling (1985) were not enriched in dissolved aluminium relative to surface Atlantic Ocean waters generally, although there was no clear depletion in the boundary current region as has been observed for the California Current (Orians & Bruland 1986) and the Gulf Stream (Moore & Millward 1984; Measures *et al.* 1984). A role for the shelf waters in supplying high concentrations of aluminium to the Norwegian Sea has thus not been established.

A further uncertainty arises from the absence, in the findings of Moore (1981), of a signal of increased concentration of aluminium in Arctic Sea waters originating in the Atlantic Ocean. Much more detailed studies will be needed to clarify the ways in which the distribution of aluminium in the North Atlantic Ocean and Arctic Sea arises by the interaction of source functions, scavenging, and the formation and circulation of water masses. Concomitant studies of aluminium and conservative and time-dependent tracers are particularly required.

OTHER METALS

Beryllium

Recent measurements suggest that beryllium may provide a label for water masses in the Atlantic Ocean, although relatively few data are so far available. Measures & Edmond (1982, 1983) have shown that this metal has a mean oceanic residence time of the order of a thousand years, longer than those of aluminium and manganese, and that the concentrations in deep water of the Pacific Ocean are slightly higher than those in the Atlantic Ocean. Different water masses in the Atlantic Ocean appear to carry somewhat different signatures of dissolved beryllium (Measures *et al.* 1984), presumably reflecting differences in supply in the source regions. The NADW has a high concentration relative to water masses of Antarctic origin. In the western basin, at 8° S the concentration in the NADW is 31 pmol kg^{-1}, compared with 19 pmol kg^{-1} in the Antarctic Intermediate Water and 26 pmol kg^{-1} in the Antarctic Bottom Water. These differences are not large but the potential of the metal as a label for waters of different origins may be worth investigating further in regions where deep waters are formed.

Cobalt

Information on cobalt in the ocean is very limited, because it has been difficult to achieve analytical detection limits that are adequate in relation to the concentrations of the element in seawater, which are usually below 0.1 nmol l^{-1}. The distribution of this metal is thus poorly known, but there are preliminary indications that it may be of potential interest as a tracer. Results for the northeastern Pacific Ocean (Knauer *et al.* 1982; Martin 1985) suggest overall that concentrations in surface waters decrease from nearshore (60–120 pmol kg^{-1}) to offshore (*ca.* 20 pmol kg^{-1}) waters. In the former, the concentrations are highest in surface waters, and thus the distributions resemble those of manganese, but offshore they increase with depth. Similar deep-water concentrations of less than 20–30 pmol kg^{-1} have been reported for both nearshore and offshore stations (Knauer *et al.* 1982; Martin 1985). The offshore data also show a mid-depth maximum for cobalt associated with the oxygen-minimum layer; as with manganese, this is contributed to by lateral transport as well as by release from particles sinking in the water column. It thus appears that cobalt may resemble manganese in that the concentrations in oceanic surface water nearshore are enhanced by marginal inputs, probably dominated by fluvial sources (Knauer *et al.* 1982), and that mobilization occurs in intense oxygen minima. Enhancement in open oceanic surface waters is not, however, apparent in the few profiles examined in the Pacific Ocean.

Measurements made on northeastern Pacific Ocean waters by Bruland & Landing, summarized by Bruland (1983), generally tend to confirm these features. They found, however, a shallow maximum, with a concentration of about 100 pmol kg^{-1}, in a profile in the California Current, and deep-water concentrations as low as about 10 pmol kg^{-1} in an open ocean profile.

Surface maxima have been reported for the Atlantic Ocean (Jickells 1986) and also for the Mediterranean Sea, where concentrations higher than those in the Pacific Ocean, by a factor of about two, have been found (Huyng Ngoc & Whitehead 1986). Jickells (1986) gives two profiles for the Sargasso Sea that indicate a rapid decrease in concentration below the surface waters, containing 18–44 pmol l^{-1}, to values of less than 15–20 pmol l^{-1} from 200–600 m, followed by a slow increase in concentration with depth to values comparable with or higher than those in surface waters. The concentrations were too close to the analytical detection limit to sustain a detailed interpretation but it was suggested that the increase in the concentrations in the deep waters of this area might reflect the advection of waters that had recently sunk from the surface at higher latitudes, carrying initially enhanced concentrations of the metal, as has been suggested for manganese and aluminium.

Concluding comments

The foregoing sections by no means exhaust the list of metals with potential tracer applications. The distribution of lead, which has a low scavenging residence time, is strongly influenced by anthropogenic aeolian inputs (Schaule & Patterson 1981, 1983; Flegal & Patterson 1983) making it a potentially useful time-dependent tracer. Investigations have been limited because of the great difficulties of avoiding contamination, particularly in sampling. Measurements by Boyle *et al.* (1986) of stable lead and ^{210}Pb in the mixed layer of the water column near Bermuda have shown the response of surface-water concentration to the decreasing anthropogenic input of stable lead and also a considerable seasonal variability in the concentrations of both constituents. The supply of stable lead and ^{210}Pb to the thermocline was shown to be mainly by lateral transfer along isopycnals. Iron and tin may be useful elements from the standpoint of tracer applications but contamination is a major problem and so far the data are very restricted. The use of rare-earth elements is discussed by Elderfield (this symposium). The present account has concentrated on non-conservative metals. Metals that show conservative or quasi-conservative behaviour may, however, be very useful in following the mixing history of water bodies that become labelled with distinctively high concentrations as a result of localized inputs.

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Discussion

H. **Elderfield** (*Department of Earth Sciences, University of Cambridge, U.K.*). It is interesting that the shape of the seawater Mn profile from the Mid-Atlantic Ridge at 43° N, which Dr Burton ascribes to hydrothermal activity, is unlike the shapes of all the hydrothermal manganese plumes previously observed. Geophysical models of plumes from magma chambers imply that the top of the buoyant hydrothermal plumes in seawaters can act as a lid so that the median valley can be thought of as a 'leaky box' where, elsewhere in the Atlantic, there is significant lateral leakage at fracture zones. This suggests two possible explanations for the profile at 43° N. (1) There is a very large hydrothermal flux and (2) the ridge topography is such that there is nowhere for the manganese to escape. Has Dr Burton any comments?

J. D. **Burton**. The shape of the profile is certainly different. The profile given by Klinkhammer *et al.* (1985) for their station 8LI (16° 47.7′ N, 46° 26.6 W′) resembles it more closely than do any others reported, but that profile still shows a significant advective maximum within the depth range of elevated concentrations. There is no evidence concerning the possible magnitude of a hydrothermal flux in the region of 43° N. The anomaly of dissolved manganese in excess of background concentrations in deep water is relatively small (*ca.* 1.5 nmol l^{-1}) but if the profile is typical of the whole valley the total amount of dissolved manganese attributable to hydrothermal input would be of the order of 10^5 moles. The fact that the valley contains an isolated and well-mixed body of water is clear from the vertical and horizontal uniformity of potential temperatures observed by Saunders & Francis (1985); the vertical uniformity was confirmed at the time the measurements of manganese were made. If the source of manganese is within the valley then it is possible either that the flux from an active vent or vents is small enough for the vertical concentration gradient at this station to be rendered undetectable by mixing or that venting is episodic with sufficient time having elapsed since input occurred to have allowed the injected material to become well mixed.