

## Arsenic, antimony and vanadium in the North Atlantic Ocean

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**Abstract**—New measurements of arsenic, antimony and vanadium in samples from vertical profiles at nine stations between 50° and 70°N in the Atlantic Ocean are presented. Antimonate concentrations exhibit little variation with depth and location, the average concentration being 1.16 nmol l<sup>-1</sup>. The vertical distribution of arsenate is similar to that reported for the South Atlantic and Pacific Ocean, with somewhat lower surface concentrations (14 to 18 nmol l<sup>-1</sup>) and uniform deep water concentrations (mean, 19 nmol l<sup>-1</sup>). Uniform vertical profiles for vanadium with a mean concentration of 32.6 nmol l<sup>-1</sup> are in agreement with data for the Central Atlantic, but differ from profiles in the Pacific which exhibit surface water depletion.

The presented data for As and V have extended the limited basis for comparison, so that inter-ocean fractionation processes can now be recognized. The concentrations of both As and V show regular increases in the ocean deep water as it passes from the North Atlantic (As 19.0; V 32.6 nmol l<sup>-1</sup>) via the South Atlantic (As 21.1 nmol l<sup>-1</sup>) and Indian Ocean (As 22.5; V 35.6 nmol l<sup>-1</sup>) to the Pacific Ocean (As 24.0; V 36.4 nmol l<sup>-1</sup>). The magnitude of biological recycling for V and As, as deduced from interoceanic fractionation, is consistent with estimates based on particle or algal compositions.

### INTRODUCTION

RECENT INVESTIGATIONS HAVE revealed the major processes controlling the oceanographic distribution of various elements. On the basis of their oceanographic distributions and estimated oceanic residence times, the elements can be subdivided into three categories: conservative, recycled and scavenged elements (WHITFIELD and TURNER, 1987).

Oxyanions, which are fully hydrolysed elements, are largely restricted to Groups III to VII of the Periodic Table. In sea water most oxyanions interact weakly with the major dissolved cations and with solid phases (TURNER *et al.*, 1981). As a result of their low reactivity, oxyanions are expected to show conservative or recycled profiles. Conservative profiles are indeed found for oxyanions such as sulphate and borate, which have concentrations that greatly exceed biological requirements. On the other hand, oxyanions such as phosphate and nitrate are the essential or classical nutrients, and the recycled-type profiles are in fact exemplified by profiles of these oxyanions (WHITFIELD and TURNER, 1987).

Molybdenum and tungsten are among the trace elements that form oxyanions (COLLIER, 1985; SOHRIN *et al.*, 1987; MORRIS, 1975) and that show conservative profiles, whereas profiles for chromium (CAMPBELL and YEATS, 1981; MURRAY *et al.*, 1983), iodine (ELDERFIELD and TRUESDALE, 1980), selenium (MEASURES and BURTON, 1980; CUTTER and BRULAND, 1985), arsenic (ANDREAE, 1979; STATHAM *et al.*, 1987; VAN DER WEIJDEN *et al.*, 1988) and vanadium (COLLIER, 1984) show slight surface depletion. In general, the surface depletions that are related to biological cycling are minor in the Atlantic, but more significant in the Pacific due to the large contrast in age between the surface and deep water in that ocean (WHITFIELD and TURNER, 1987). In addition, the progressive increase in age of the deep water as it passes from the North Atlantic via the Indian Ocean to the Pacific is accompanied by a progressive increase in the concentration of recycled elements (BROECKER and PENG, 1983).

Here we report the first complete vertical profiles of antimony in oceanic waters. In addition, we present new measurements of dissolved arsenic and vanadium in the North Atlantic, which provide new information concerning the distribution of these elements in the open ocean. These new observations may help to elucidate the processes controlling the oceanographic distribution of trace oxyanions.

### GENERAL OCEANOGRAPHY OF THE NORTH ATLANTIC

We will consider the Northeastern and Northwestern Atlantic separately. The Northeastern Atlantic basically represents a topographically enclosed deep-water basin. It is separated from the West Atlantic by the Mid-Atlantic Ridge. Deep water enters from the Western Atlantic mainly through the Romanche Fracture Zone (0°N, 18°W) and Vema Passage (11°N, 43°W) (SCHLITZER *et al.*, 1985). There is no evidence of significant ventilation from the north (BROECKER *et al.*, 1985). The Northeastern Atlantic has a net northward flow, fed at equatorial latitudes, and is closed by upwelling. Compared to the Northwestern Atlantic, the Northeastern waters are enriched in nutrients and depleted in oxygen and <sup>14</sup>C.

At higher latitudes in the western North Atlantic, one is closer to the formational areas of North Atlantic Deep Water (NADW). In these areas, the three major contributing sources, Iceland-Scotland Overflow Waters (ISOW), Denmark Strait Waters (DSW), and Labrador Sea Water (LSW), merge to form the northern component of NADW (BROECKER and TAKAHASHI, 1980; SWIFT, 1984). This proto-NADW complex is nutrient poor and is marked by relatively constant nutrient concentrations vs. depth profiles (VAN BENNEKOM, 1985; BROECKER and TAKAHASHI, 1980).

### SAMPLING AND ANALYTICAL METHODS

Samples were collected at the stations shown in Fig. 1 during a R.V. *Tyro* cruise in the summer of 1983, using 30-l Niskin or Go-



FIG. 1. Map of the North Atlantic Ocean showing sampling locations.

Flo bottles fitted to a rosette-CTD assembly. At some stations, surface samples were also collected from a rubber inflatable boat some distance upwind of the drifting research vessel. The agreement between surface and shallow hydrocast trace element data demonstrates the adequacy of the sampling procedures (BRULAND *et al.*, 1979). Temperature, salinity and nutrients were measured at each site to identify the various water masses (VAN BENNEKOM, 1985). After removal of subsamples for routine hydrographic measurements, large aliquots of sea water were poured into thoroughly acid-cleaned and sample rinsed large volume polyethylene containers. Samples were analysed for V, Sb and As using methods based on neutron activation analysis after preconcentration on activated carbon (VAN DER SLOOT, 1976) or by hydride generation (HOEDE and VAN DER SLOOT, 1979; VAN DER SLOOT *et al.*, 1982). The omission of a filtering step, which obviates the risk of contamination during the handling involved in filtering, can be justified since, for the elements under consideration, particulate concentrations are negligible compared to dissolved concentrations (ANDREAE, 1979; COLLIER, 1984; JEANDEL *et al.*, 1987; our unpublished results). The analytical procedures described below were designed to permit the initial stage of separation and concentration to be carried out on board ship as rapidly as possible after sample collection. The adequacy of our analytical and sample handling procedures is demonstrated by the internal "oceanographic consistency" of our data and by the fact that they agree with other data sets, as will be discussed later (BRULAND, 1983).

The method of analysing dissolved vanadium has been reported in detail by VAN DER SLOOT (1976) and will be summarized briefly below. The pH of 1 litre of sea water is adjusted to and maintained at a pH of about 3.6. Then 2 ml APDC (ammonium-pyrrolidinedithio-carbamate) solution (50 mg APDC/ml), 2 ml cupferron solution (30 mg cupferron per ml of acetone/water (1:1) solution) and 2 ml carbon suspension (50 mg activated carbon per ml of isopropanol) are added. The resulting solution is stirred for 15 minutes. The activated carbon powder is ultra pure, prepared in the laboratory from PVDC (polyvinylidene chloride) after activation by CO<sub>2</sub>. Vanadium and APDC combine to form a water-insoluble complex, which is absorbed well on activated carbon. A 8 µm membrane filter fitted in a radiochemical filter-holder is covered with a layer of activated carbon by pipetting 0.5 ml carbon suspension onto the filter. After 15 minutes of stirring, the sample is filtered through the carbon covered filter. Sea salts are removed by washing with distilled water, which is adjusted to pH = 3.6 and contains 50 mg APDC/l. The filter is stored in a polyethylene capsule until needed for analysis. The optimum conditions for quantitative and reproducible preconcentration were investigated extensively using <sup>48</sup>V as a carrier-free radiotracer (VAN DER SLOOT, 1976). On the basis of tracer experiments and after improvements made to the procedure, the chemical yield of the preconcentration procedure was found to be 96 ± 2%.

The preconcentration of As and Sb is based on the generation of the hydrides and subsequent collection on activated carbon. The hydride generation method employed has been reported in detail by HOEDE and VAN DER SLOOT (1979) and VAN DER SLOOT *et al.* (1982) and will be summarized briefly below. The pH of 400 ml of

sea water is adjusted to pH 1.5–2 by the addition of ultrapure HCl. The system is flushed with He at 1 l/min for three minutes and a solution containing 10% sodiumborohydride is added. The generated hydrides are collected on the carbon adsorber of the hydride generation apparatus, which is filled with 250 mg activated carbon grains (see above) having a diameter of 0.8–1.2 mm. Then the carbon cartridge is changed and 200 ml 37% HCl and 5 ml 0.2 M KI/10% ascorbic acid are added to the closed hydride generation system. After ten minutes another 5 ml of 0.2 M KI/10% ascorbic acid is added. During this procedure, which takes 20 minutes, He is continuously purged. The two carbon cartridges, one containing trivalent and methylated species and the other containing pentavalent species, are stored in polyethylene capsules until required. It should be realized that the arsenite and antimonite values reported here represent the total of trivalent and methylated species. The concentrations of methylated forms in the surface waters normally appear to be less than 1.5 nmol l<sup>-1</sup> for arsenic (ANDREAE, 1979) and 0.03 nmol l<sup>-1</sup> for antimony (BERTINE and LEE, 1983) respectively, while those in deeper water are insignificant (ANDREAE, 1983). Moreover, our sampling strategy was focussed on deep rather than surface waters. The optimum conditions for quantitative and reproducible preconcentration and speciation were investigated extensively; some of the tests have been presented by HOEDE and VAN DER SLOOT (1979) and VAN DER SLOOT *et al.* (1982). The recoveries were calculated to be 90 ± 2% for As and 100 ± 2% for Sb.

Thermal neutron activation analysis was performed in the High Flux Reactor at Petten (VAN DER SLOOT, 1976; VAN DER SLOOT and ZONDERHUIS, 1979). The carbon-covered filters containing V were irradiated for five seconds using a fast pneumatic rabbit system (FASY) at 5 × 10<sup>11</sup> neutrons/cm<sup>2</sup> s. Starting two minutes after the end of irradiation, the sample was counted for <sup>52</sup>V for four minutes with a Ge(Li) detector connected to a multichannel analyser. The carbon cartridges containing the hydrides were irradiated for three hours using the poolside rotating facility (PROF) at 5 × 10<sup>12</sup> neutrons/cm<sup>2</sup> s. Starting 24 hours after the end of irradiation, samples were counted for <sup>122</sup>Sb and <sup>76</sup>As for 3000 seconds using a Ge(Li) detector.

For V, precision is estimated to be 3% with a detection limit of 0.5 nmol l<sup>-1</sup>. The reproducibility of the analytical results for As and Sb is estimated to be ± 5%. The detection limits for As(III), As(V), Sb(III) and Sb(V) were 0.01, 0.05, 0.03 and 0.05 nmol l<sup>-1</sup>, respectively. The results of our measurements are given in the Appendix.

## RESULTS AND DISCUSSION

### Vanadium

In oxygenated sea water vanadium is predicted to occur in the +5 oxidation state, primarily as HVO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>VO<sub>4</sub><sup>-</sup> and as the complex NaHVO<sub>4</sub><sup>-</sup> (TURNER *et al.*, 1981; WEHRLI, 1987; SADIQ, 1988). As a consequence, the vanadium species involved in adsorption processes appear to be anionic, resulting in a relatively low affinity for natural particles (WHITFIELD and TURNER, 1987; SHILLER and BOYLE, 1987). Laboratory experiments by VAN DER SLOOT (1976), JEANDEL *et al.* (1987) and SHILLER and BOYLE (1987) have shown that complexation with organic matter is not a major factor in determining the aquatic behaviour of vanadate.

Appendix 1 lists the results of our measurements for dissolved vanadium in the North Atlantic. The corresponding profiles are plotted in Fig. 2. Variations in concentrations of vanadium with location and depth are relatively small and there are no indications of a pronounced surface depletion. Similar observations were made by MORRIS (1975) and JEANDEL *et al.* (1987) for the Atlantic Ocean. However, COLLIER (1984) and ZHOU *et al.* (1982) have reported pronounced surface depletions in the Pacific Ocean, whereas HUIZINGA and KESTER (1982) have reported a slight surface water enrichment in the Sargasso Sea.

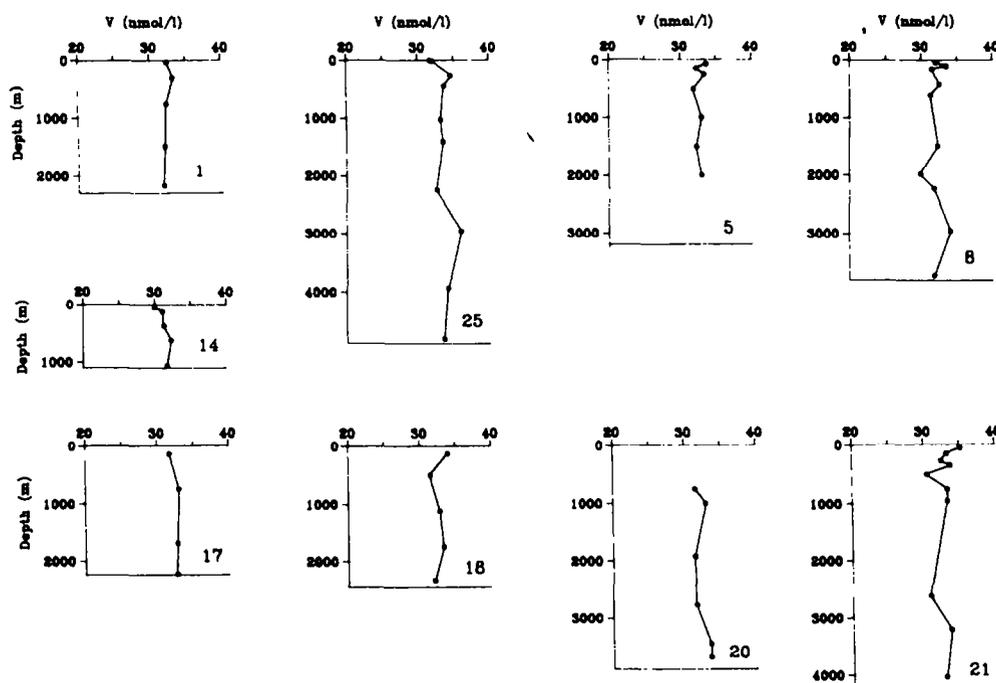


FIG. 2. Vanadium concentrations versus depth profiles.

The average concentration of V varies between 31.8 and 33.9 nmol l<sup>-1</sup>. These data are consistent with, although slightly lower than, recent information on dissolved vanadium in the Atlantic Ocean (HUIZINGA and KESTER, 1982; JEANDEL *et al.*, 1987). Regarding the recently reported interlaboratory bias (JEANDEL *et al.*, 1987), it is not yet clear to what extent these differences reflect inaccuracies in the measurements or real regional variations. For instance, the average V concentration of NEADW (st. 25; 33.9 nmol l<sup>-1</sup>) is higher than that of NADW (31.8–32.8 nmol l<sup>-1</sup>), but similar to adjacent Atlantic Waters immediately west of the Strait of Gibraltar (33.7 nmol l<sup>-1</sup>) (SHERREL and BOYLE, 1988).

The vertical profiles of vanadium for various basins (this study; MORRIS, 1975; HUIZINGA and KESTER, 1982; COLLIER, 1984; ZHOU *et al.*, 1982; JEANDEL *et al.*, 1987; SHERREL and BOYLE, 1988) suggest that the flux of vanadium by transport from the euphotic zone into deeper water is small relative to the concentration of vanadium in the oceanic reservoir. This should be reflected in a relatively small increase of vanadium in the deep water as it passes from the North Atlantic *via* the Indian Ocean to the Pacific. Inter-oceanic fractionation of dissolved V is difficult to assess because of the above mentioned interlaboratory bias (JEANDEL *et al.*, 1987). JEANDEL *et al.* (1987), using data based on one single method and from one laboratory, reported an increase of about 10 to 15 nmol l<sup>-1</sup> from the Atlantic to Pacific. Assuming that there is no interlaboratory bias between the Pacific data of COLLIER (1984) and our data for the North Atlantic, we obtain an increase in the mean V concentration of 4 nmol l<sup>-1</sup> between the deep North Atlantic and the deep Pacific Ocean (Table 1). This relatively small increase in mean V concentration is supported by our data for the Northeast Indian Ocean (Table 1).

Various researchers have reported similarity in the behaviour of vanadium and phosphate in marine systems (COLLIER, 1984; JEANDEL *et al.*, 1987; SHILLER and BOYLE, 1987). This is probably related to their chemical similarity in terms of molecular size and hydrolysis. There is a good correlation between the mean concentrations of vanadium and phosphate for the North Atlantic, Northeast Indian and Pacific Ocean, with an apparent  $\Delta V/\Delta P$  molar ratio of  $2.4 \cdot 10^{-3}$  (Fig. 3a). This  $\Delta V/\Delta P$  molar ratio is intermediate between the estimated oceanic V/P particle flux ratios of  $0.5 \cdot 10^{-3}$  and  $4 \cdot 10^{-3}$  for high and low primary productivity areas respectively and is very close to the apparent  $\Delta V/\Delta P$  estuarine removal ratio ( $5 \cdot 10^{-3}$ ) (SHILLER and BOYLE, 1987). Considering the complex estuarine behaviour of phosphorus and the differences in time and space scales of estuarine and oceanic cycling processes, some caution is needed in comparing the estuarine removal ratio with the ratio deduced from Fig. 3a. Nevertheless, all these data support the active involvement of vanadium in biogeochemical cycles. This is consistent with the role of vanadium enzymes in biological processes (SHECHTER

TABLE 1 INTER-OCEANIC FRACTIONATION (Values are averaged for all samples below 200 m; if no phosphate data were given, values are based on appropriate GEOSECS data).

	V	As	PO <sub>4</sub>
North Atlantic <sup>1</sup>	32.6	19.0	1.0
South Atlantic <sup>2</sup>	--	21.1	1.8
Northeast Indian Ocean <sup>3</sup>	35.6	22.5	2.3
Pacific <sup>4</sup>	36.4	--	2.6
Pacific <sup>5</sup>	--	24.0	3.0

<sup>1</sup> this study<sup>4</sup> COLLIER (1984)<sup>2</sup> STATHAM *et al.* (1987)<sup>5</sup> ANDREAE (1979)<sup>3</sup> HOEDE, WIJKSTRA, VAN DER SLOOT, unpublished data.

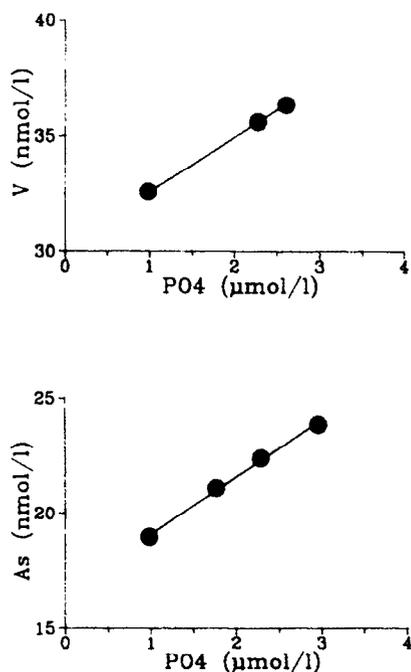


FIG. 3. a) Relationship between the vanadium and phosphate content of open ocean deep water. b) Relationship between the arsenate and phosphate content of open ocean deep water. Only average deep-water data for selected regions of the ocean are considered (see Table 1).

and KARLISH, 1980; KUSTIN and MCLEOD, 1983; ROBSON *et al.*, 1986).

Let us now consider the surface depletion in dissolved V due to biological uptake of V. This surface depletion can be estimated by using a simple vertical two-box model (BROECKER, 1971; COLLIER and EDMOND, 1984). The amount of available data on the fluxes of V does not warrant any further complexity at this time. Depletion of vanadium from surface waters must be balanced by primary inputs, including riverine and atmospheric inputs as well as physical exchange with deeper water (BROECKER and PENG, 1983). Actual surface depletions ( $\Delta V$ ) are calculated according to BROECKER (1971):

$$\Delta V = (P - R - A)/V_m$$

where  $P$  is the particulate V flux out of the surface ocean.  $R$  and  $A$  are the riverine and atmospheric inputs respectively and  $V_m$  is the volume mixing rate between surface and deep reservoirs. Based on a dissolved vanadium concentration for the world average river water of  $15 \text{ nmol l}^{-1}$  (SHILLER and BOYLE, 1987) and a flux of river water to the ocean of  $11.5 \text{ cm yr}^{-1}$  (COLLIER and EDMOND, 1984), we estimate a riverine input of  $1.7 \cdot 10^{-6} \text{ mol m}^{-2} \text{ yr}^{-1}$ . Atmospheric inputs vary in time and space in response to meteorological processes. For instance, WALSH and DUCE (1976) estimate a global atmospheric input of  $1.1 \cdot 10^{-7} \text{ mol m}^{-2} \text{ yr}^{-1}$ , whereas JICKELLS *et al.* (1987) propose an atmospheric flux of  $4.3 \cdot 10^{-6} \text{ mol m}^{-2} \text{ yr}^{-1}$  to the Sargasso Sea. The latter value is assumed to

be representative for the North Atlantic. The particulate V flux from the surface to the deep water reservoir can be estimated from the known V/P molar ratio ( $2.4 \cdot 10^{-3}$ ) and the average particulate  $P$  flux. COLLIER and EDMOND (1984) propose a global average  $P$  flux of  $8.7 \cdot 10^{-3} \text{ mol m}^{-2} \text{ yr}^{-1}$ , whereas JICKELLS *et al.* (1987) deduce a much lower flux of  $6.5 \cdot 10^{-4} \text{ mol P m}^{-2} \text{ yr}^{-1}$  for the Sargasso Sea. At an average volume exchange rate of  $3.5 \text{ m yr}^{-1}$  distributed over the ocean surface (COLLIER and EDMOND, 1984), the global surface water reservoir should be depleted in vanadium by about  $4.2 \text{ nmol l}^{-1}$  relative to the deep water reservoir. However, if we use the atmospheric input data of WALSH and DUCE (1976) instead of those of JICKELLS *et al.* (1987), then the surface depletion would be about  $5.4 \text{ nmol l}^{-1}$ . These values are in reasonable agreement with the  $4 \text{ nmol l}^{-1}$  observed by COLLIER (1984) in surface Pacific waters. A similar calculation for the Sargasso Sea yields a surface water reservoir enrichment of  $1.3 \text{ nmol l}^{-1}$ . This estimated enrichment is consistent, although slightly lower than, recent information on dissolved vanadium in the Sargasso Sea (HUIZINGA and KESTER, 1982). If we assume that the average North Atlantic particulate V flux is intermediate between the global average and particulate V flux in the Sargasso Sea, then the average surface water depletion in the North Atlantic should be  $1.4 \text{ nmol l}^{-1}$ . Such a slight decrease is within the present precision and consistent with the data in Fig. 2. These model calculations show the potential importance of atmospheric input as well as the importance and spatial variability of biological cycling.

#### Arsenic

Arsenic forms oxyanions based on a tetrahedral coordination of As by oxygen. In oxygenated sea water, arsenic primarily exists as the  $\text{HAsO}_4^{2-}$  anion, which chemically closely resembles the corresponding species formed by phosphorus, *i.e.*  $\text{HPO}_4^{2-}$ . In the euphotic zone, arsenic occurs not only in the form of arsenate but also as the species arsenite ( $\text{HAsO}_2$ ), methylarsonate ( $\text{CH}_3\text{AsO}(\text{OH})\text{OH}$ ) and dimethylarsinate ( $(\text{CH}_3)_2\text{AsOOH}$ ) (ANDREAE, 1978). The latter species are positively correlated with indicators of primary production (ANDREAE, 1978) and are believed to be formed by biochemical interactions (ANDREAE, 1978, 1979; IRGOLIC and STOCKTON, 1987).

The vertical profiles of arsenate and arsenite are shown in Fig. 4. The methylated forms of arsenic are analysed together with arsenite under the conditions used. Variations in concentrations of arsenate with location and depth are relatively small and there are no indications of clearly defined maxima in the water column. The rather constant concentrations of arsenate are consistent with the limited degree of nutrient fractionation in the North Atlantic (BROECKER and PENG, 1983). Some of the profiles for arsenate exhibit slight nutrient-type surface depletion. Surface depletions for arsenate have already been reported for borderland basins (PETERSON and CARPENTER, 1983; VAN DER WEIJDEN *et al.*, 1988), the South Atlantic (STATHAM *et al.*, 1987) and the Pacific (ANDREAE, 1979). This depletion of arsenate in surface waters is a function both of biological arsenate uptake and release, and of the rate of upward mixing.

The oceanographic distribution of arsenite is less regular than that of arsenate (Fig. 4) in that both variations with

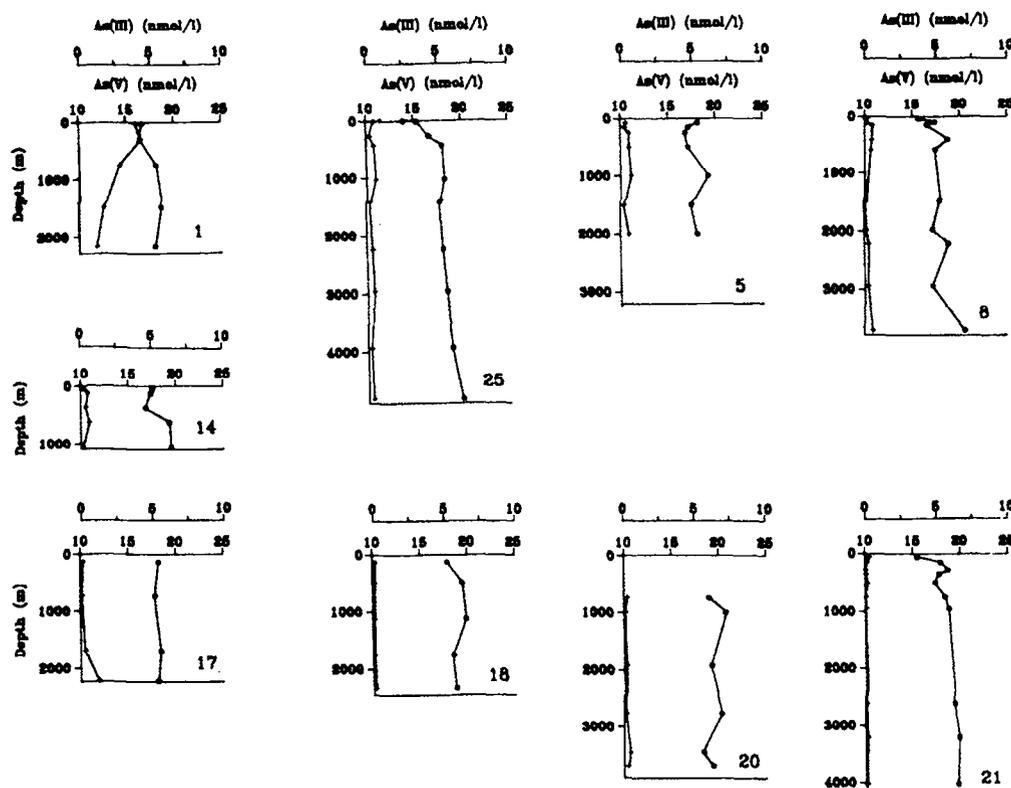


FIG. 4. Arsenate (dots) and arsenite (crosses) concentrations versus depth profiles.

depth and with location are observed. The variation in concentration of arsenite is probably related to the characteristics of the different water masses. Stations 17, 18, 20 and 21 have a relatively large component of Labrador Sea Water (VAN BENNEKOM, 1985) and arsenite levels are very low. At stations 5, 8 and 14, being characteristic for ISOW and DSW, arsenite concentrations are intermediate and similar to those in NEADW (St. 25). However, a detailed interpretation of the data for arsenite is not warranted since the concentrations found are close to the detection limit. The range of arsenite concentrations for the North Atlantic surface waters ( $0.05\text{--}4.3\text{ nmol l}^{-1}$ ) compares well with the range reported for the Pacific surface waters ( $0.1\text{--}11.6\text{ nmol l}^{-1}$ ; ANDREAE, 1978;  $0.1\text{--}10.6\text{ nmol l}^{-1}$ ; ANDREAE, 1979).

The average concentration of total arsenic for North Atlantic deep waters varies between  $18.3$  and  $20.3\text{ nmol l}^{-1}$ . These data are consistent with, although slightly lower than, recent information concerning dissolved total arsenic in the South Atlantic ( $21.1\text{ nmol l}^{-1}$ ) (STATHAM *et al.*, 1987). The significant difference in deep water total arsenic concentrations between the South and North Atlantic and the nutrient-type surface depletions indicate that arsenic has a relatively large recycled component. In order to quantify the involvement of arsenic in biogeochemical processes, we will assess again the interoceanic fractionation. Assuming that there is no interlaboratory bias between the data for the Pacific of ANDREAE (1978, 1979), the data for the South Atlantic of STATHAM *et al.* (1987) and our data for the North Atlantic and Northeast Indian Ocean, we find an increase in the mean total arsenic concentrations of  $5\text{ nmol l}^{-1}$  between the deep waters of the North Atlantic and the Pacific (Table 1). This

increase of arsenic concurs with an increase of phosphate in the ocean deep waters as it passes from the North Atlantic via the South Atlantic and Indian Ocean to the Pacific. There is a good correlation between the increase of total dissolved arsenic and the increase of phosphate with an apparent  $\Delta\text{As}/\Delta\text{P}$  molar ratio of  $2.5 \cdot 10^{-3}$  (Fig. 3b). This  $\Delta\text{As}/\Delta\text{P}$  molar ratio is very close to the As/P ratio found for marine algae ( $2.9 \cdot 10^{-3}$ ) (ANDREAE, 1979).

#### Antimony

Oceanographically consistent profiles for antimony in the open ocean are not available. In oxygenated waters the antimonate ion ( $\text{Sb}(\text{OH})_6^-$ ) should be the thermodynamical stable form of Sb (TURNER *et al.*, 1981). Thermodynamic predictions suggest that antimonate is subject to scavenging (WHITFIELD and TURNER, 1987), although experiments have shown that this element has a relatively weak affinity for natural particles (LI *et al.*, 1984). Measurements in natural waters, however, revealed the presence of four species, namely antimonate ( $\text{Sb}(\text{OH})_6^-$ ), antimonite ( $\text{HSbO}_2$ ), methylstibonic acid ( $\text{CH}_3\text{SbO}(\text{OH})\text{OH}$ ) and dimethylstibonic acid ( $(\text{CH}_3)_2\text{SbOOH}$ ) (ANDREAE *et al.*, 1981; ANDREAE, 1983; BERTINE and LEE, 1983). The presence of the thermodynamically non-equilibrium species antimonite and the methylantimony acids is probably due to biological activity (ANDREAE, 1983).

The vertical profiles of antimonate and antimonite are shown in Fig. 5. In our analytical procedure the methylated forms of antimony are analysed together with antimonite.

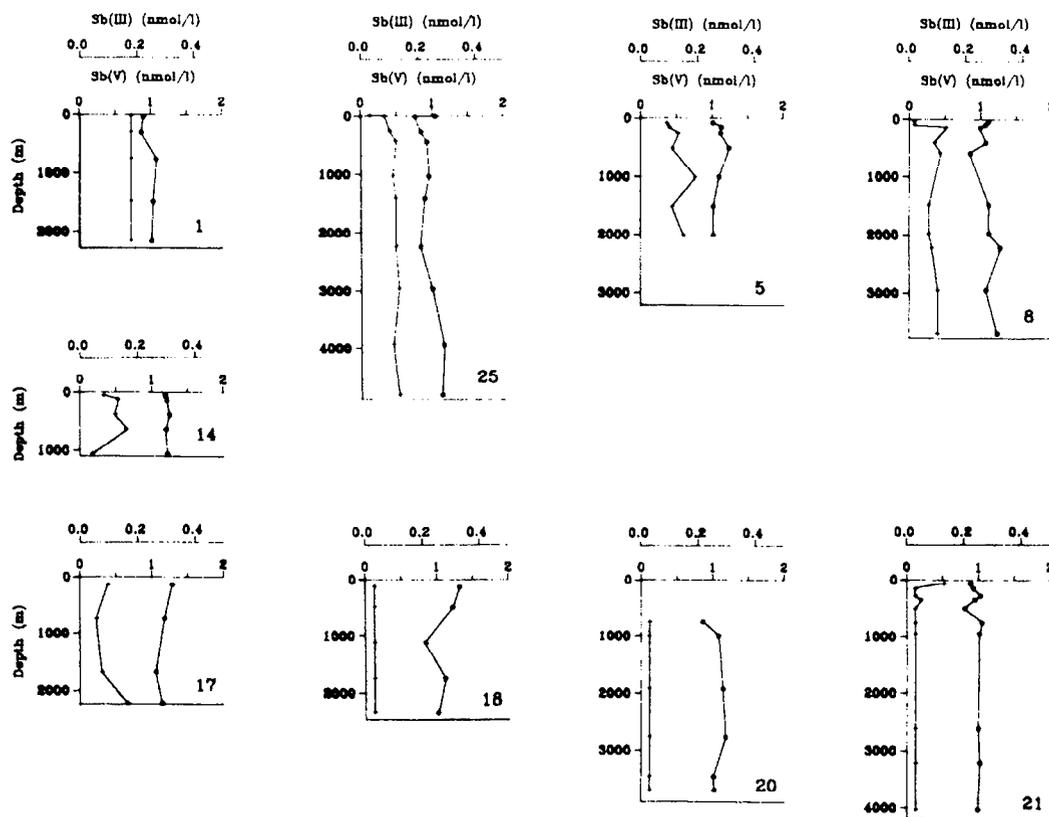


FIG. 5. Antimonate (dots) and antimonite (crosses) concentrations versus depth profiles.

Variations in concentrations of antimonate with location and depth are relatively small. Vertical profiles for dissolved antimonate were hitherto available only for borderland basins such as Kau Bay (VAN DER WEIJDEN *et al.*, 1988) and Saanich Inlet (BERTINE and LEE, 1983); these profiles also exhibit constant concentrations of antimonate from surface to bottom. The average concentrations of dissolved antimonate found in this study (0.99–1.22 nmol l<sup>-1</sup>) are closely similar to values reported in the literature, namely 1.02–1.28 nmol l<sup>-1</sup> for Saanich Inlet (BERTINE and LEE, 1983), 1.17–1.36 nmol l<sup>-1</sup> for Kau Bay (VAN DER WEIJDEN *et al.*, 1988), 1.28 nmol l<sup>-1</sup> for Loch Ewe (APTE *et al.*, 1986), 0.74–1.13 nmol l<sup>-1</sup> for the North Pacific Ocean (ANDREAEE, 1983) and 1.20 nmol l<sup>-1</sup> for the surface waters of the Gulf of Mexico (ANDREAEE *et al.*, 1981).

The distribution of antimonite is less regular than that of antimonate in that there is a clear variation with location. However, a very detailed interpretation of the data for antimonite is not warranted since the concentrations found at some stations are close to the detection limit. The variation of antimonite concentrations with location is related to the characteristics of the different water masses and resembles the general pattern observed for arsenite (Figs. 4, 5; Appendix 1). The range of antimonite concentrations for the North Atlantic (0.03–0.19 nmol l<sup>-1</sup>) compares well with the range reported for oxic waters of Saanich Inlet (0.02–0.14 nmol l<sup>-1</sup>) (BERTINE and LEE, 1983). On the basis of the present data we can neither prove nor rule out a significant recycling component for Sb.

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APPENDIX 1. Concentrations of V, As and Sb in samples collected in the North Atlantic.

Depth	V	As (3)	As(5)	Sb(3)	Sb(5)
Station 1 (61°N, 20°30'W; 7-23-1983)					
30	32.40	3.97	16.61	0.18	0.89
300	33.20	4.28	16.43	0.18	0.86
750	32.30	2.85	18.07	0.18	1.07
1480	32.00	1.74	18.70	0.18	1.03
2170	31.80	1.23	18.00	0.18	1.01
Station 5 (64°50'N, 3°36'W; 7-26-1983)					
75	33.70	0.37	18.16	0.09	1.01
148	32.30	0.28	17.16	0.10	1.13
250	33.40	0.59	16.80	0.13	1.12
500	31.90	0.59	17.13	0.11	1.24
1000	33.00	0.73	19.21	0.19	1.10
1500	32.30	0.27	17.51	0.11	1.02
2000	33.00	0.59	18.12	0.15	1.02

## Station 8 (68°N, 3°W; 7-29-1983)

41	32.00	0.10	15.62	0.02	1.11
100	33.50	0.10	17.38	0.02	1.07
150	31.50	0.53	16.57	0.13	0.99
405	32.50	0.48	18.73	0.09	1.07
590	31.30	0.40	17.41	0.11	0.85
1490	32.30	0.11	17.95	0.07	1.11
1980	29.90	0.15	17.20	0.07	1.11
2230	31.80	0.30	18.82	0.08	1.27
2950	34.10	0.24	17.16	0.10	1.07
3718	31.80	0.58	20.59	0.10	1.23

## Station 14 (67°48'N, 23°25'W; 8-2-1983)

52	30.00	0.17	17.55	0.08	1.19
125	31.10	0.49	17.36	0.13	1.21
375	31.30	0.36	16.83	0.12	1.25
624	32.30	0.59	19.33	0.16	1.20
1058	31.70	0.14	19.48	0.04	1.22

## Station 17 (61°15'N, 31°50'W; 8-4-1983)

135	31.70	0.20	18.22	0.10	1.29
740	33.00	0.10	17.82	0.06	1.18
1690	32.80	0.33	18.40	0.08	1.06
2217	32.70	1.27	18.10	0.17	1.15

## Station 18 (56°47'N, 30°43'W; 8-5-1983)

130	34.00	0.21	17.90	0.03	1.32
495	31.50	0.18	19.47	0.03	1.22
1122	32.80	0.14	19.83	0.03	0.84
1750	33.30	0.13	18.44	0.03	1.11
2326	32.00	0.17	18.71	0.03	1.01

## Station 20 (52°45'N, 34°28'W; 8-7-1983)

750	31.50	0.21	18.97	0.03	0.86
1000	33.00	0.10	20.75	0.03	1.08
1920	31.50	0.16	19.18	0.03	1.14
2765	31.70	0.16	20.30	0.03	1.18
3450	33.60	0.42	18.37	0.03	1.01
3690	33.60	0.29	19.39	0.03	1.02

## Station 21 (49°16'N, 36°09'W; 8-8-1983)

60	35.20	0.31	15.47	0.13	0.89
150	33.30	0.13	17.94	0.03	0.93
276	32.50	0.05	18.73	0.03	1.03
350	33.80	0.09	17.77	0.05	0.95
500	30.50	0.16	17.37	0.03	0.81
750	33.30	0.05	18.40	0.03	1.05
950	33.30	0.07	18.78	0.03	1.01
2612	30.90	0.10	19.40	0.03	0.99
3200	33.70	0.14	19.86	0.03	1.01
4027	32.90	0.07	19.64	0.03	0.98

## Station 25 (50°N, 16°55'W; 8-11-1983)

0	31.70	1.00	13.95	0.03	1.04
10	32.00	0.55	15.32	0.08	0.76
265	34.60	0.26	16.62	0.10	0.84
432	33.70	0.54	17.98	0.12	0.92
1025	33.20	0.64	18.20	0.11	0.95
1405	33.50	0.28	17.74	0.12	0.89
2245	32.60	0.38	18.00	0.12	0.83
2960	36.00	0.47	18.37	0.13	0.99
3930	34.20	0.26	18.93	0.11	1.15
4820	33.60	0.35	19.95	0.13	1.12

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