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The Contrasting Behaviour of Arsenic and Germanium Species in Seawater

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The vertical profiles of inorganic arsenic [As(III) + As(V)], monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), inorganic germanium and monomethylgermanium (MMGe) were investigated at three sampling stations in the Pacific Ocean. In addition, the concentrations of these species in various surface waters have also been determined.

The vertical profile of both inorganic arsenic and germanium displayed low concentrations, 1100 to 1450 ng dm^{-3} for inorganic arsenic and $<$0.7 to 2 ng dm^{-3} for inorganic germanium, in the surface zone. The concentrations of inorganic arsenic increased with depth to maximum concentrations that varied from 1500 to 2200 ng dm^{-3} at a depth of 2000 m and then slowly decreased to concentrations that varied from 1300 to 1900 ng dm^{-3} at a depth of 5000 m. On the other hand, the vertical profiles of inorganic germanium displayed a relatively constant concentration (4 to 8 ng dm^{-3}) from a depth of 2000 m to 5000 m. These vertical profiles of inorganic germanium were linearly correlated with those of silicate with a Ge/Si molar ratio of 0.715×10^{-6}.

Both MMAA and DMAA displayed maximum concentrations in surface water and abruptly dropped with depth from 0 to 200 m. The concentration in surface water was 12 ng dm^{-3} for MMAA and varied from 48 to 185 ng dm^{-3} for DMAA. At depths $>$200 m, MMAA and DMAA were generally at comparable concentrations of about 3 ng dm^{-3}. In the case of MMGe, it was uniformly distributed throughout the water column at a concentration of approximately 16 ng dm^{-3}, indicating that MMGe was not involved in the biogeochemical cycling of inorganic germanium.

In deep waters ($>$200 m), the concentrations of both inorganic arsenic and germanium increased from the southern Tasman Sea to the north. The increase in inorganic arsenic concentration was linearly correlated with that of phosphate and the increase in inorganic germanium concentration was linearly correlated with that of silicate, with apparent ΔAs/ΔP and ΔGe/ΔSi molar ratios of 4.53×10^{-3} and 0.73×10^{-6}, respectively. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

In nature, both arsenic and germanium are found in the form of inorganic compounds associated with igneous rock. Their distributions throughout all environmental compartments are the result of both natural processes such as weathering of igneous rocks and geothermal activity, and anthropogenic processes such as coal combustion.[1, 2]

Due to the presence or organism-mediated transformations, the existence of organic forms of arsenic in natural water is well documented. These transformations are mainly mediated by primary producers in both freshwater[3, 4] and seawater.[5–10] Although biotransformation can result in a number of structurally complex organic forms, monomethylarsonic acid

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(MMAA) and dimethylarsinic acid (DMAA) are the only organic forms of arsenic found in seawater.

As has been found for arsenic, the simple organic forms of germanium, monomethylgermanium (MMGe) and dimethylgermanium (DMGe) species, are also ubiquitous in seawater. They make up more than 70% of the total known germanium compounds present in seawater.[11, 12] However, the process that leads to their formation is still unclear. Attempts to locate natural marine and freshwater sources for them have been unsuccessful. Their formation may be a microbially mediated process in anoxic sediments.[12]

The difference in the formation processes for organic arsenic and germanium leads to their different distributions in seawater. Previous studies showed the presence of surface water enrichment for both MMAA[13, 14] and DMAA[13–16] but low concentrations for As(V)[13, 17] or inorganic arsenic.[14–16, 18] In the case of germanium species, although a decrease in the concentration of the inorganic form in surface water was observed,[2, 19, 20] MMGe and DMGe were not enriched in the surface zone but uniformly distributed throughout the water column.[11, 12] This uniform distribution for MMGe and DMGe is consistent with the fact that they are neither produced nor removed by marine algae.

In this study, we present vertical profiles of MMAA, DMAA, inorganic arsenic, MMGe and inorganic germanium species in the Pacific Ocean. Increases in inorganic arsenic and germanium concentrations from the southern Tasman Sea to the northwest Pacific Ocean that correlate linearly with those of phosphate and silicate, respectively, are observed in deep water. In addition, the behaviour of these species in surface waters of the Pacific Ocean and other oceanic regions is discussed.

EXPERIMENTAL

Sampling sites

Surface water samples were collected at various locations in the Pacific Ocean using Niskin bottles (R/V *Hakuho-Maru*) (Fig. 1). The collection of surface water samples in the other locations such as the Indian and Antarctic Oceans, the Indonesian Archipelago, the Tasman Sea and the East and South China Seas has been

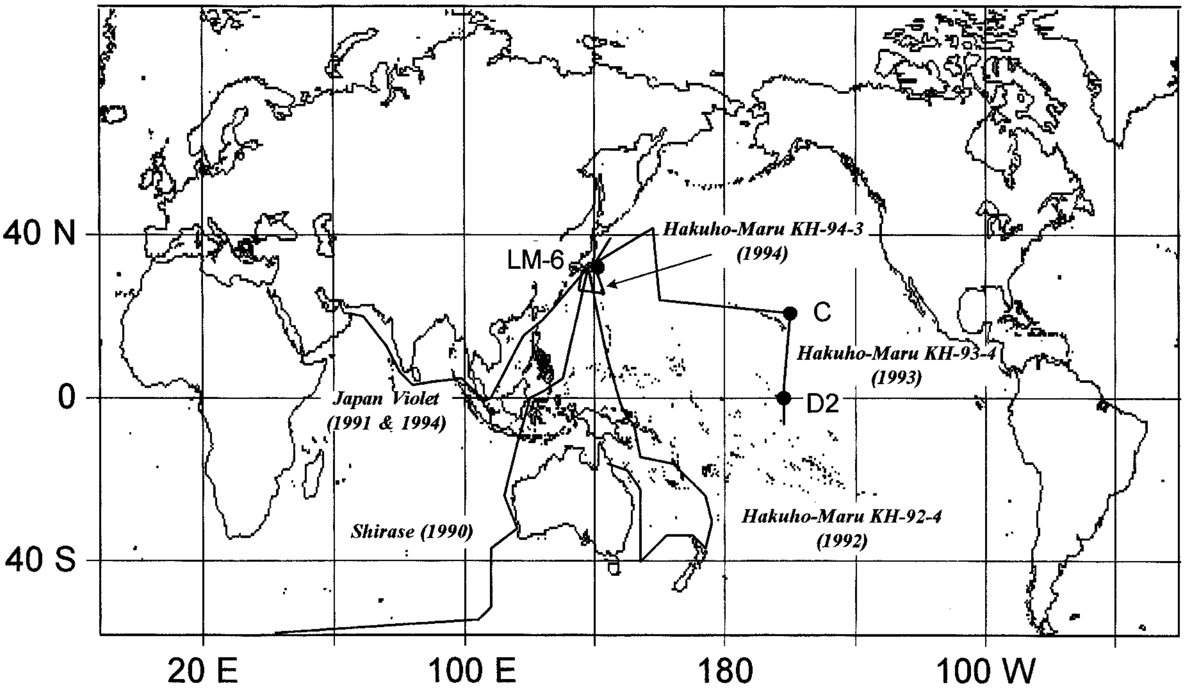

Figure 1 Sampling locations. Full lines depict the route of six separate cruises; solid circles depict vertical profile stations.

in part described in our previous papers.[14–16] In addition, vertical profile samples down to the bottom were also collected at sampling stations C(22°45.83′N, 158°06.60′W) in the central north Pacific gyre, D2 (0°, 159°W) in the equatorial region of the central Pacific Ocean, and those down to a depth of 5000 m were collected at station LM-6 (34°10.25′N, 141°56.54′E) in the north-west Pacific Ocean on 31 October 1993, 31 October 1993 and 11 October 1994, respectively. The water samples were filtered on board through a Millipore filter (pore size, 0.45 μm) and stored in polypropylene bottles at 0 °C in darkness. Analysis was performed at our laboratory within three months of sampling. During storage, it was confirmed that no change in the arsenic and germanium species occurred.

Method of analysis

Analysis of the arsenic and germanium species was performed by inductively coupled plasma mass spectrometry (ICP–MS) model PMS 2000 (Yokogawa Analytical System) after generating their hydrides from samples using $NaBH_4$. The hydrides were trapped in a U-tube packed with OV-3 15% Chromosorb WAW DMCS 60/80-mesh and cooled with liquid nitrogen, then the arsines and germanes were successively volatilized by heating and transferred to ICP–MS using helium as a carrier gas. The method was originally adapted for the determination of arsenic species.[15] The analytical condition for generating both arsines and germanes, along with the operating conditions for ICP–MS, are shown in Table 1. Detection limits were 9.2 ng dm^{-3} for As(V) + As(III), 0.2 ng dm^{-3} for MMAA, 0.7 ng dm^{-3} for DMAA, and 0.7 and 0.2 ng dm^{-3} for inorganic germanium and MMGe, respectively. Precision was estimated to be 4% for both As(III) + As(V) and MMAA, 6% for DMAA and 4 and 3% for inorganic germanium and MMGe, respectively.

RESULTS AND DISCUSSION

Vertical distribution of arsenic and germanium species

The vertical profiles of dissolved arsenic and germanium species, along with those of dissolved oxygen and nutrients, at two sampling stations (C and D2) are given in Figs 2 and 3, respectively.

A consistently low concentration in the surface zone was observed for inorganic arsenic. This low concentration was more severe at sampling station C in the oligotrophic area of the central north Pacific gyre (Fig. 2) than at sampling station D2 in the eutrophic area of the equatorial region (Fig. 3). The low concentrations of inorganic arsenic in the surface water of stations C and D2 are 1100 and 1450 ng dm^{-3}, respectively. As has been suggested in our previous paper,[14] the lower concentration in the surface zone of station C must be associated with the lower phosphate concentration. Compared with the other sampling stations, the concentration of phosphate in the surface zone (< 100 m) of station C was the lowest (Table 2). Because the biological uptake pathway for As(V) (the dominant inorganic arsenic compound in oxygenated water) by marine algae is believed to be via the phosphate-active transport system,[21–23] the

Table 1 Analytical conditions for generating arsines and germanes from the various arsenic and germanium species, and operating conditions for their determination by ICP–MS

Analytical conditions for generation of arsines and germanes		Operating conditions for ICP–MS	
Sample volume	5 cm^3	Forward RF power	1.3 kW
HCl	6 M, 0.5 cm^3	Argon gas flow rate	
$NaBH_4$ (reducing agent)	5%, 1 cm^3	Coolant	14 dm^3 min^{-1}
Reaction time	3 min	Auxiliary	1.3 dm^3 min^{-1}
Masking agent	Tartaric acid (3 g) + EDTA (0.19 g) added to 50 cm^3 of sample	Carrier	0.7 dm^3 min^{-1}
		Counting conditions	
Carrier gas (He)	300 cm^3 min^{-1}	Dwell time	20 ms
		Number of scans	2
		Monitoring ion (m/z)	^{72}Ge, ^{75}As

lower phosphate concentration in the surface water of station C must increase the probability of As(V) entering the transport pathway of phosphate and hence result in a higher intake and subsequent reduction and methylation. Therefore, the concentration of methylated arsenic species was higher in the surface water of station C than that of stations D2 and LM-6 (Table 2).

Both MMAA and DMAA were detected throughout the water column of stations D2 and LM-6. Their average concentrations in the surface zone (<100 m) were 12.4 and 53.3 ng dm^{-3}, respectively, for MMAA and DMAA at station D2 and 11.8 and 47.7 ng dm^{-3}, respectively, for those at station LM-6 (Table 2). The concentrations in the deeper waters were relatively constant at a value of about 3 ng dm^{-3} for both stations.

MMAA and DMAA in the surface zone were suggested to result primarily from the direct excretion from marine algal cells and their abundances may be associated with the composition of the phytoplankton community.[14] That suggestion is now also confirmed for stations C, D2 and LM-6. According to the nutrient data as given in Table 2, it can be seen clearly that the nutrient composition in the surface zone of station C is very different from that at stations D2 and LM-6. With the extremely limited phosphate, nitrate and nitrite concentrations in the surface zone of station C, the dominant phytoplankton species that lives successfully is

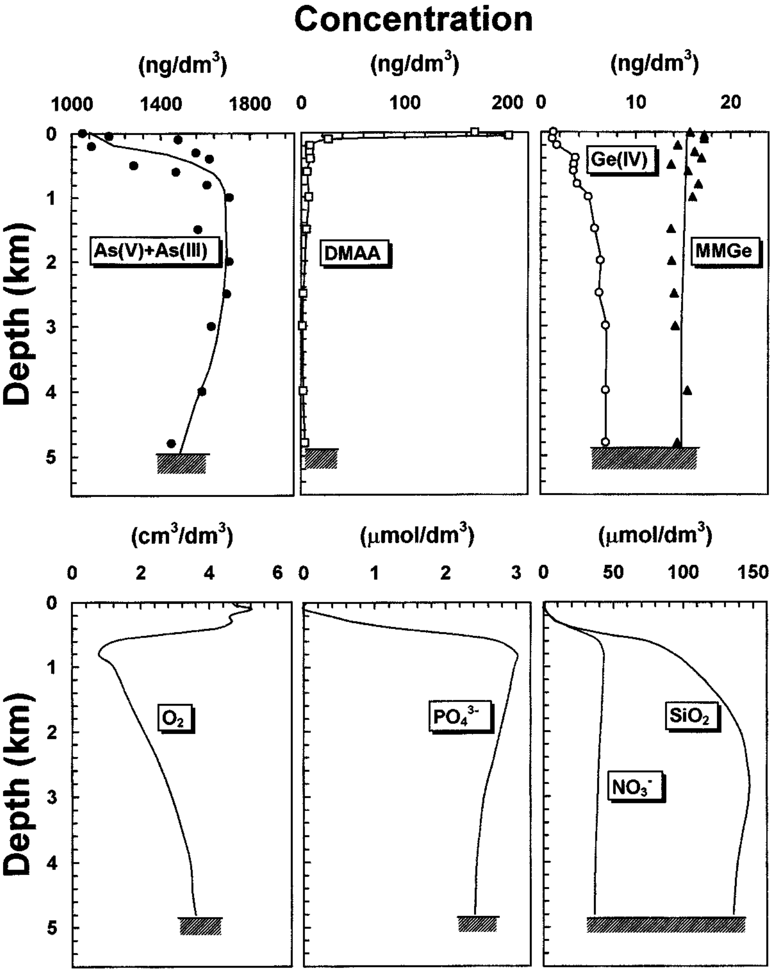

Figure 2 Vertical profiles of dissolved inorganic arsenic [As(V(+As(III)], DMAA, inorganic germanium [Ge(IV)], MMGe, oxygen, phosphate, nitrate and silicate at station C (22° 45.83′ N, 158° 06.60′ W; 31 October 1993)

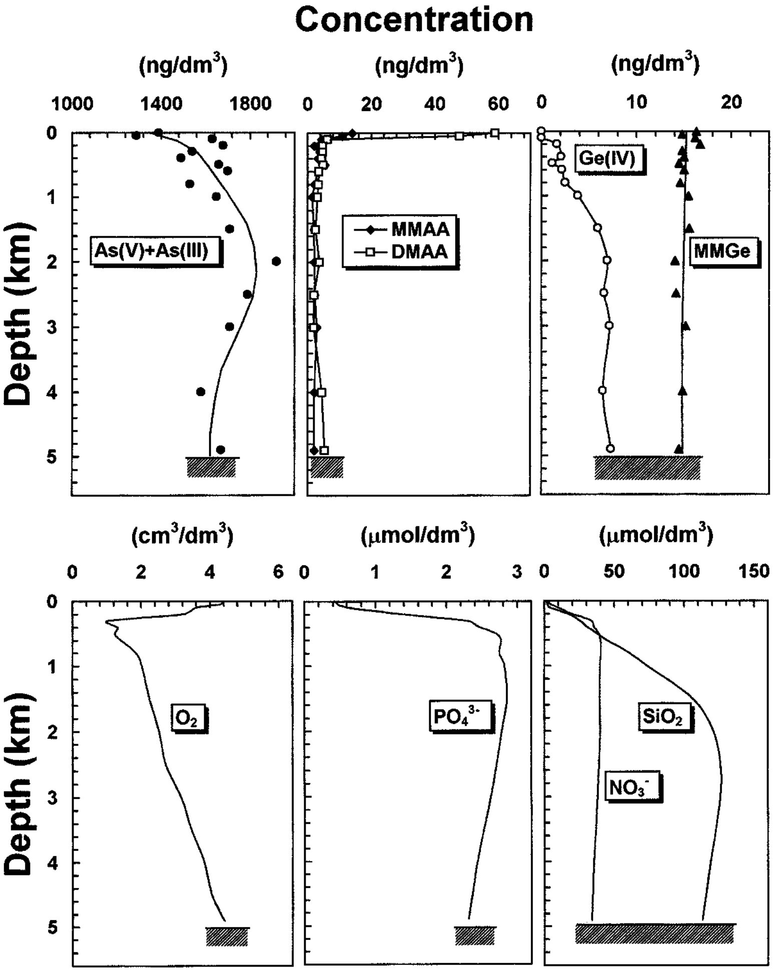

Figure 3 Vertical profiles of dissolved inorganic arsenic [As(V)+As(III)], MMAA, DMAA, inorganic germanium [Ge(IV)], MMGe, oxygen, phosphate, nitrate and silicate at station D2 (0°N, 159°W; 31 October 1993).

Table 2 Average concentrations of arsenic and germanium species, nutrients and temperature in the surface zone (<100 m) of three sampling stations (LM-6, C and D2) in the Pacific Ocean

		Nutrient (μmol dm^{-3})			Arsenic species (ng dm^{-3})			Germanium species (ng dm^{-3})	
Sampling station	Seawater temp. (°C)	Phosphate	Nitrite+nitrate	Silicate	Inorg. As	MMAA	DMAA	Inorg. Ge	MMGe
LM-6 (north-west Pacific)	23.9	0.06	0.25	0.43	1483	11.8	47.7	2.5	15.9
C (central north Pacific gyre)	25.7	<0.02	<0.09	1.20	1110	15.9	184.5	2.0	16.5
D2 (central Pacific equatorial region)	27.2	0.51	3.42	2.19	1450	12.4	53.3	<0.7	15.8

likely to be different compared with those surviving with more abundant phosphate, nitrate and nitrite concentrations in the surface zones of stations D2 and LM-6. The successful phytoplankton in station C mainly excretes DMAA rather than MMAA. In the case of stations D2 and LM-6, the concentrations of DMAA and MMAA are nearly equal.

As shown for inorganic arsenic, the low concentration in the surface zone was also observed for inorganic germanium. The average concentrations of inorganic germanium in the surface zone were 2.0, <0.7 and 2.5 ng dm^{-3} for stations C, D2 and LM-6, respectively (Table 2). These concentrations increased with depth to values of about 7.0 ng dm^{-3} at a depth of 2000 m for all of the sampling stations. Below 2000 m, the concentration was relatively constant (Figs 2 and 3).

Compared with the surface zones of stations C and LM-6, the surface zone of station D2 contained more silicate. However, the most depleted concentration of inorganic germanium occurred in the surface zone of station D2 (Table 2). It is commonly known that due to the similar atomic radii and electronic configuration (both atoms belong to Group IV in the Periodic Table), the chemical properties of germanium and silicon are closely similar. The similarity of these chemical properties may result in a competitive uptake and incorporation between germanium and silicon into the marine algal cell. However, the fact that the most depleted inorganic germanium occurred in the surface zone of station D2, that contained more silicate than that of stations C and LM-6, was in contradiction with the expectation.

The concentration of inorganic germanium in the ocean is much lower than that of As(V). Once As(V) is taken up by phytoplankton, As(V) undergoes considerable restructuring of its chemical form. This process occurs in order to avoid the toxicity of As(V), that can replace phosphate in many physiological pathways. In the case of germanium, due to its presence in significantly low concentrations (Ge/Si atomic ratio $\sim 0.7 \times 10^{-6}$),[2] the detoxification process is unlikely to occur. The siliceous organisms take up inorganic germanium as a trace analogue of silicon and incorporate it into their cells without restructuring its chemical form. Therefore, the formation of structurally complex arsenic compounds such as arsenosugars and the rejection of MMAA and DMAA from the algal cell, which is believed to be a detoxification process for As(V), are not likely to occur for inorganic germanium. Indeed, alkali digestions of plankton and opal samples did not reveal the presence of methylgermanium.[11]

As has been mentioned above, the vertical profile of inorganic germanium showed a relatively constant concentration from the deep to the bottom zones. For inorganic arsenic, however, this trend was not observed. Instead of being relatively constant, the concentration of inorganic arsenic decreased from the mid-depth to the deep zone. The maximum concentrations of 1700, 2150 and 1850 ng dm^{-3} were found at a depth of 2000 m at all the sampling stations. The decrease in arsenic concentration from the mid-depth to the deep-zone is not caused by simple physical mixing among the different water masses but is suggested to be a result of arsenic being scavenged by iron- and manganese-oxide-rich particulate matter.[14] On the other hand, scavenging of inorganic germanium by iron- and manganese-oxide-rich particulate matter is unlikely. Indeed, the concentration of inorganic germanium is significantly low in metalliferous sediments near the crest of the East Pacific Rise, which emanates hydrothermal fluid enriched in germanium.[24] Ge/Fe and Ge/Mn ratios in metalliferous sediments near the crest are much lower than ratios measured in the vent solution, suggesting that germanium is not scavenged from seawater by iron and manganese oxides.[24, 25]

In contrast to MMAA and DMAA, the maximum concentration of MMGe was not observed in the surface zone. MMGe was uniformly distributed from the surface to the bottom at a concentration of about 16 ng dm^{-3}. The concentration of MMGe reported here is slightly lower than that reported in the literature for other oceanic areas.[11, 12, 20] The absence of the maximum concentration in the surface zone is consistent with the fact that MMGe is not produced by marine phytoplankton.[20]

Attempts to locate sources of methylgermanium other than marine phytoplankton have been unsuccessful. Methylation of in organic germanium by means of purely chemical processes has been attempted. The highest result (6% MMGe) was obtained from the reaction of Ge(II) with methyl iodide (CH_3I) in artificial seawater at pH 7.6.[26] No DMGe was produced in this reaction. CH_3I is certainly present in the ocean and its concentration is related to the level of marine primary production.[27] However, inorganic germanium in the ocean is present as Ge(IV) rather than Ge(II). Therefore, the formation of methylgermanium as a result of the reaction between Ge(II) and CH_3I in common seawater is unlikely. There is the possibility that Ge(II) might be found in anoxic marine sediments; however, the presence of CH_3I in these same sediments is questionable.

As has been pointed out by Mortlock and Froelich,[25] inorganic germanium may be present in hydrothermal solutions as soluble Ge(II), perhaps as GeS. Hydrothermal vent areas are suitable habitats for microorganisms. The presence of much denser bacterioplankton and higher bacterial production inside the hot and warm fluids of hydrothermal vents compared with populations outside the vents has been confirmed.[28] However, the production of CH_3I by microorganisms in the hot and warm fluids of hydrothermal vents has not been reported. If the presence of Ge(II) and CH_3I in hydrothermal solutions is confirmed, in addition to the continental supply via rivers, the natural source of methylgermanium in the ocean may be hydrothermal vents. Direct analysis of MMGe and DMGe in hydrothermal fluids is needed to prove this prediction.

Inorganic arsenic and germanium versus nutrients

The similar chemical and biochemical properties of inorganic germanium and silicon result in their having vertical profiles (Figs 2 and 3). In the case of inorganic arsenic, although its vertical profile from the mid-depth to the deep zone resembled that of phosphate (both of them consistently displayed a small decrease in their concentration from the mid-depth to the deep zone), the decrease in inorganic arsenic concentration from the mid-depth to the surface zone was much lower than that of phosphate. As a result, the relationship between inorganic arsenic and phosphate (Fig. 4) shows that only in a phosphate concentration range higher than 2 μmol dm^{-3} does the concentration of inorganic arsenic appear to increase with increasing phosphate concentration. On the other hand, the concentration of inorganic germanium clearly increases with increasing silicate concentration from 0 to 170 μmol dm^{-3}. The vertical profiles of inorganic arsenic and phosphate for the southern Tasman Sea (station SA-16), south-west Pacific (station 12) and north-west Pacific (stations LM-2 and LM-9) have been reported in our previous papers,[14–16] although the inorganic ger-

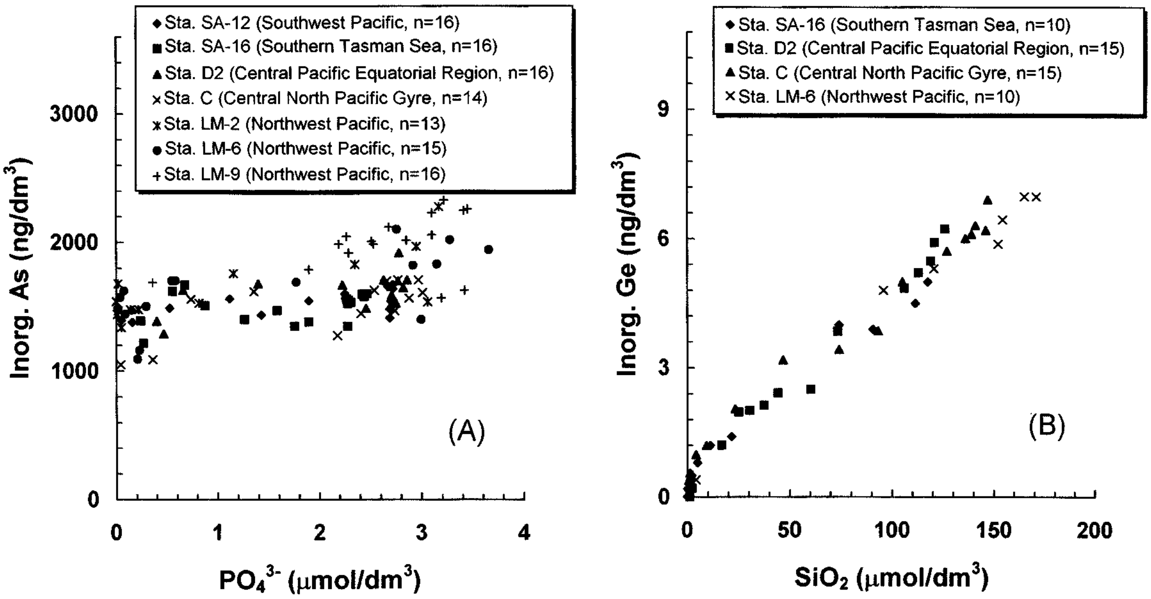

Figure 4 Comparison between the relationship of (A) dissolved inorganic arsenic [As(V + As(III)] and phosphate and (B) dissolved inorganic germanium [Ge(IV)] and silicate at various sampling stations.

manium data for station SA-16 have not been published yet. The regression analyses for the relationship between inorganic arsenic and phosphate and that between inorganic germanium and silicate are given in Eqns [1] and [2].

$$\text{As (nmol dm}^{-3}) = 1.06\ \text{PO}_4^{3-}\ (\mu\text{mol dm}^{-3}) + 20.15$$

$$(r = 0.354,\ n = 106) \qquad [1]$$

$$\text{As/P} = 1.06 \times 10^{-3}\ \text{(molar ratio)}$$

$$\text{Ge (pmol dm}^{-3}) = 0.72\ \text{SiO}_2\ (\mu\text{mol dm}^{-3}) + 8.07$$

$$(r = 0.987,\ n = 50) \qquad [2]$$

$$\text{Ge/Si} = 0.72 \times 10^{-6}\ \text{(molar ratio)}$$

As shown in Eqns [1] and [2], a much higher correlation coefficient for the relationship between inorganic germanium and silicate than that between inorganic arsenic and phosphate was confirmed. As/P and Ge/Si molar ratios were 1.06×10^{-3} and 0.72×10^{-6}, respectively. The Ge/Si molar ratio obtained in this study was very close to that reported by Froelich *et al.*[2] This ratio reflected the Ge/Si molar ratio recycled by algal activity. As has been mentioned before, the nonlinear relationship between inorganic arsenic and phosphate that mainly occurred in the surface zone could be caused by the ability of marine phytoplankton to discriminate As(V) from phosphate. Moreover, the maximum concentration of inorganic arsenic also generally occurred in a deeper region than that of phosphate. This evidence suggests that the regeneration of arsenic from structurally complex arsenic compounds released from the sinking biogenic material to inorganic arsenic, especially As(V), was relatively slower than that of phosphate, so that more time was needed to convert it completely.

Horizontal segregation of inorganic arsenic and germanium in the deep zone

If we carefully examine Figs 2 and 3, the concentrations of both inorganic arsenic and germanium in the deep zone showed an increase from the Pacific equatorial region to the north. It is commonly known that most biogenic particles produced by phytoplankton in the surface waters sink to the deep zone and are remineralized. Considering that the deep-water flow in the Pacific Ocean from the south to the north and the input of biogenic particles continuously occurs along its path, an increase in concentration in the deep zone of the Pacific Ocean from the south to the north is common for the nutrients, and elements displayed a nutrient-type vertical profile. The increase in the average concentrations of inorganic arsenic and germanium at a depth below 200 m from the sampling station in the southern Tasman Sea to the sampling stations in the central north Pacific gyre and north-west Pacific Ocean is shown in Fig. 5. The data on inorganic germanium and silicate from other oceanic areas[29] are also given for comparison. Depths up to 200 m were excluded in order to avoid the local variability of the algal activity, and hence depths greater than 200 m are representative for the regeneration zone. As can be seen (Fig. 5), the increase in average concentrations of inorganic arsenic was linearly correlated with that of phosphate and that of inorganic germanium was linearly correlated with that of silicate. The regression analyses as shown in Eqns [3] and [4] resulted in a good correlation between both the increase in inorganic arsenic and that in phosphate and the increase in inorganic germanium and that in silicate, with apparent ΔAs/ΔP and ΔGe/ΔSi molar ratios of 4.53×10^{-3} and 0.73×10^{-6}, respectively.

$$\text{As (nmol dm}^{-3}) = 4.532\ \text{PO}_4^{3-}\ (\mu\text{mol dm}^{-3}) + 10.47$$

$$(r = 0.970,\ n = 94) \qquad [3]$$

$$\Delta\text{As}/\Delta\text{P} = 4.53 \times 10^{-3}\ \text{(molar ratio)}$$

$$\text{Ge (pmol dm}^{-3}) = 0.726\ \text{SiO}_2\ (\mu\text{mol dm}^{-3}) + 2.96$$

$$(r = 0.999,\ n = 39) \qquad [4]$$

$$\Delta\text{Ge}/\Delta\text{Si} = 0.73 \times 10^{-6}\ \text{(molar ratio)}$$

The apparent ΔGe/ΔSi molar ratio (0.73×10^{-6}) from the regeneration zone (>200 m) of the southern Tasman Sea to that of the north-west Pacific Ocean (Eqn [4]) was relatively similar to the Ge/Si molar ratio (0.72×10^{-6}) in the whole water column (Eqn [2]). Considering that the Ge/Si ratio in Eqn [2] is composed of the Ge/Si ratio taken up by phytoplankton in the surface waters and the Ge/Si ratio regenerated in the deep zone, the relatively similar Ge/Si molar ratio between the whole water column and the regeneration zone implied that the Ge/Si ratio taken up by algal activity in the surface zone was not significantly different from that regenerated in deeper waters. This evidence was consistent with the suggestion that inorganic germanium is a trace analogue of silicon and is indiscriminately incorporated into the algal cell without restructuring its chemical

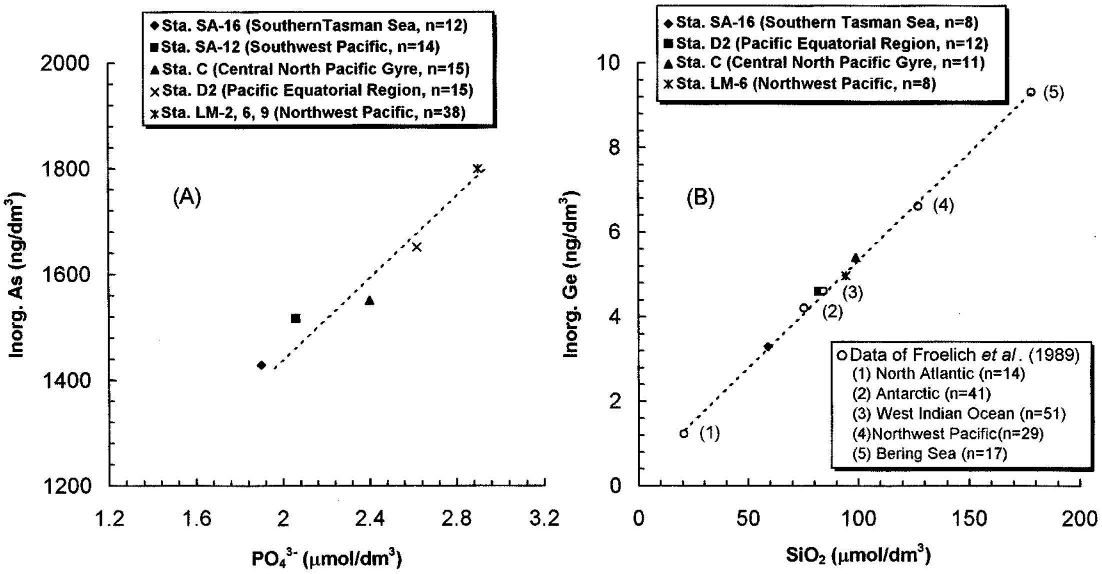

Figure 5 Comparison between the relationship of deep-water (>200 m) average concentrations of (A) dissolved inorganic arsenic [As(V)+As(III)] and those of phosphate, and (B) dissolved inorganic germanium [Ge(IV)] and those of silicate at various stations.

form, with subsequent rejection from the cell.

In contrast to inorganic germanium, the apparent ΔAs/ΔP molar ratio in the regeneration zone (Eqn [3]) was more than four times as much as the As/P molar ratio in the whole water column (Eqn [1]). As has been suggested before, this difference may be caused by the slower transformation from structurally complex arsenic compounds that are released from sinking biogenic material to inorganic arsenic, especially As(V). As phosphate reaches its maximum concentration, the transformation from structurally complex arsenic compounds to As(V) is still in progress. Therefore, the increase in the As/P ratio occurred within the deep zone and contributed to the significantly higher ΔAs/ΔP ratio in the regeneration zone.

Arsenic and germanium species in surface waters

In Pacific surface waters, the ratio of organic arsenic to total arsenic (org. As/tot. As) has been found to be dependent on temperature.[14] The organic arsenic is the sum of MMAA and DMAA and the total arsenic is the sum of As(V), As(III), MMAA and DMAA. In other reports, we also presented the temperature dependence of the distribution of arsenic species, especially methylated arsenic, in the Indian Antarctic Oceanic surface waters.[15, 16] After combining the two results in those previous reports and the results for the north Indian Ocean, the East and South China Seas and the Indonesian Archipelago, the temperature dependence on the ratio of organic arsenic to total arsenic is shown in Fig. 6.

As can be seen clearly in eastern and northeastern parts of the North Pacific gyre as well as in Antarctic surface waters with the water temperature of about 4 °C, organic arsenic comprised only about 2% of the total arsenic. The portion of organic arsenic then increased with increasing water temperature to an average value of 18% in the tropical seawaters (in the equatorial upwelling region of the central Pacific Ocean, the north Indian Ocean and the Indonesian Archipelago). This evidence indicated that cycling of arsenic species between As(V) and the biologically produced species (MMAA and DMAA) was more effective in tropical seawaters rather than in temperate and cold seawaters.

In contrast to arsenic species, germanium species displayed no temperature dependence on their distributions. As shown in Fig. 7, inorganic germanium displayed high concentrations (~8 ng dm^{-3}) in surface waters that are relatively close to land, such as the East and South China Seas and the Tasman Sea. From these seas to the open ocean, the concentration of inorganic germanium gradually decreased and became undetectable ($<0.7\ \mathrm{ng\ dm^{-3}}$) in the equatorial upwelling region of the central Pacific Ocean. Therefore both natural processes, such as weathering of igneous rocks and geothermal activity on land, and anthropogenic processes, such as coal combustion, must be responsible for the relatively high concentration of inorganic germanium in surface waters near land.

Although MMGe has been postulated to be a continentally derived species and transported to the ocean via rivers,[12, 20] the higher concentration in surface waters of seas near land than in the surface water of the open ocean was not confirmed (Fig. 7). Unlike inorganic germanium, MMGe is unreactive in the ocean with no apparent production and removal. Once MMGe enters the ocean, it is physically mixed and does not enter the biogeochemical cycle of inorganic germanium.

CONCLUSIONS

The nutrient compositions in the surface waters of the ocean are likely to affect the cycle of arsenic species between inorganic arsenic and the methylated arsenic species MMAA and DMAA. The presence of elevated methylated arsenic levels and lower concentrations of inorganic arsenic in the surface water that contain less phosphate implies that the probability of

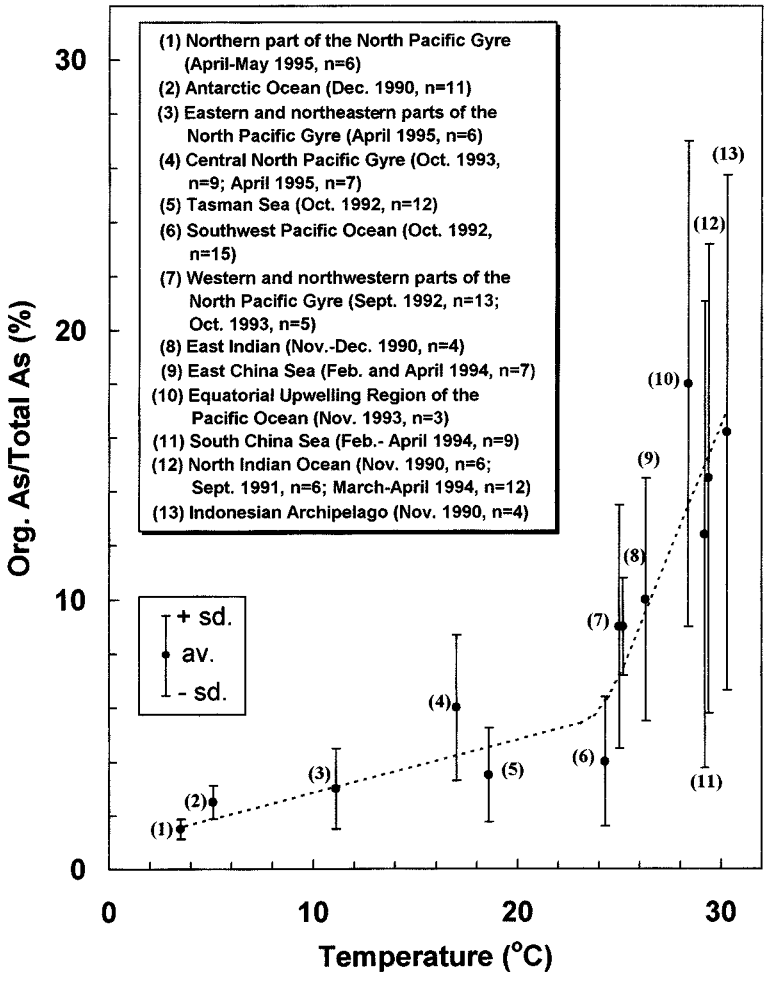

Figure 6 The variation of the (MMAA+DMAA)/[As(V)+As(III)+MMAA+DMAA] ratio relative to temperature of various sea and ocean surface waters.

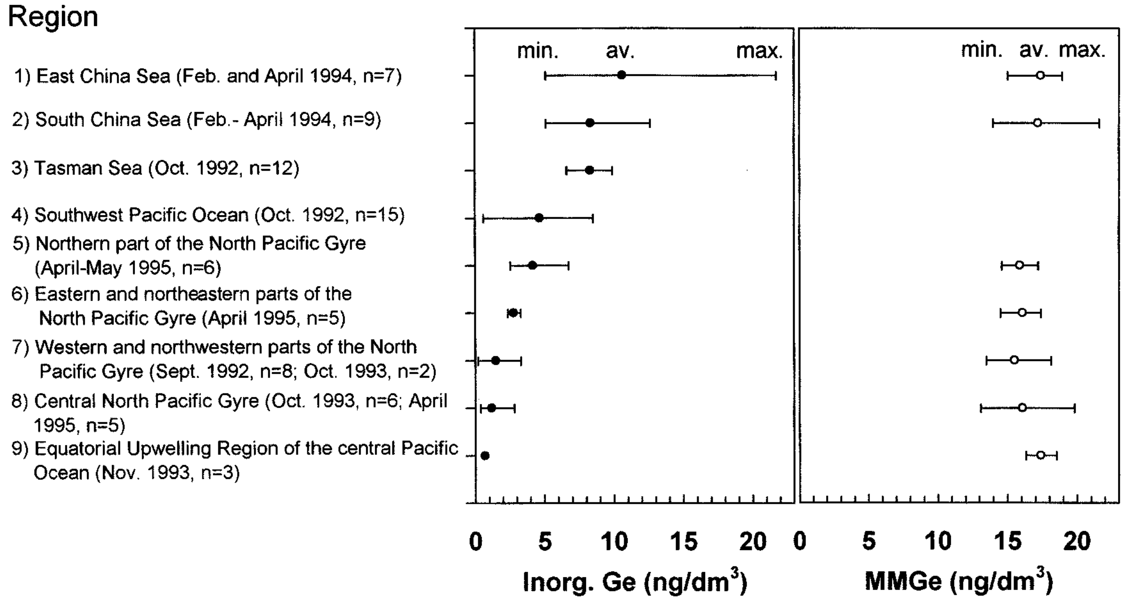

Figure 7 Dissolved inorganic germanium [Ge(IV)] and MMGe in various sea and ocean surface waters.

As(V) entering the biological uptake pathway of phosphate is higher when the concentration of phosphate is lower.

In the case of inorganic germanium, the most depleted concentration occurred in surface water that contained a high concentration of silicate. Therefore, a competitive mechanism between inorganic germanium and the chemically similar silicon during uptake and incorporation into the marine algal cell is unlikely.

In contrast to MMAA and DMAA, the surface zone maximum was not observed for MMGe. MMGe was uniformly distributed throughout the water column. The absence of the surface zone maximum is consistent with the fact that MMGe is not produced by marine phytoplankton.

The concentrations of both inorganic arsenic and germanium in the regeneration zone (>200 m) of the Pacific Ocean showed an increase from the south to the north. The apparent ΔGe/Si molar ratio in the regeneration zone was relatively similar to the Ge/Si molar ratio in the whole water column. This evidence suggests that the Ge/Si ratio taken up by algal activity is not significantly different from that regenerated in the deep zone.

In contrast to inorganic germanium, the apparent ΔAs/ΔP molar ratio in the regeneration zone is more than four times as much as the As/P molar ratio in the whole water column. This difference may be caused by a slow transformation from structurally complex arsenic compounds that are released from the sinking biogenic material to As(V).

In the surface water, the ratio of org.As/tot.As increased with increasing water temperature. Higher water temperature leads to higher biological activity so that higher concentrations of organic arsenic (MMAA and DMAA) are observed. For inorganic germanium, instead of the temperature dependence, its concentration in surface waters appeared to be affected by local input from the nearest land.

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