

# Selenium Speciation in the Eastern Tropical and Subtropical South Pacific Ocean

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## Abstract

Three selenium species, selenite, selenate, and organic selenide, were determined simultaneously in the eastern tropical, and subtropical South Pacific Ocean. Selenite shows a typical nutrient-like profile. Selenate also shows a nutrient-type profile. The highest correlation between selenite and silicate ( $r=0.98\sim 1.00$ ,  $p<0.00001$ ) indicates that selenite is supplied from decomposition of selenite-silicate compounds in the hard tissue of phytoplankton. On the other hand, the correlation coefficient between selenite and nitrite + nitrate (phosphate) is higher than that between selenite and silicate in the subtropical South Pacific Ocean. These results indicate that selenite is supplied from the decomposition of not only the hard tissue of plankton body but also the soft tissue. The organic selenide was detected in deep waters. This might be due to the presence of refractory selenium compounds such as selenium-humic acid complex. The selenite/selenate ratio in deep water is not necessarily decreased with increasing total selenium concentrations. This might be due to the irregular addition of selenium to deep waters via sinking particulate matter.

**Keywords:** Selenium, speciation, nutrient, South Pacific Ocean

## 1. Introduction

A new international programme in marine geochemistry, "GEOTRACES," was started in 2005. The GEOTRACES mission includes determining the full water column distribution of selected trace elements and evaluating the sources and sinks and internal cycling of these species of the elements.

It is well known that selenium is a trace element that has three chemical forms and limiting nutrients for aquatic organisms (Cutter and Bruland, 1984). Selenite and selenate exhibit nutrient-like ocean profiles that indicate the utilization

of inorganic selenium by phytoplankton in the surface water (Measures *et al.*, 1983). The preferential uptake of selenite over selenate by phytoplankton has been documented in laboratory culture studies and field study (Vandermeulen and Foda, 1988; Hu *et al.*, 1996; Wrench and Measures, 1982). The chemical speciation of selenium species has been described for various oceans: the Pacific Ocean (Measures *et al.*, 1980, 1983; Cutter and Bruland, 1984, Sherrard *et al.*, 2004), the Atlantic Ocean (Measures and Burton, 1980; Measures *et al.*, 1983; Cutter and Cutter, 1995, 1998, 2001), the

Indian Ocean (Measures *et al.*, 1983; Hattori *et al.*, 2001a), and the Southeast Asian Basin (Nakaguchi *et al.*, 2004). However, the speciation and recycling of selenium in the eastern Pacific Ocean are still not well known. The eastern tropical and subtropical Pacific exhibits a complex ocean circulation system. The eastern tropical Pacific is distinguished by wind forcing that is strongly influenced by the topography of the American continent, and its properties and circulation are nearly independent of longitude (Kessler, 2006). The tropical thermocline dome, “The Costa Rica Dome,” has been observed at the eastern Pacific Ocean. The surface winds and currents in the region of the Costa Rica Dome change seasonally as the intertropical convergence zone (Fiedler, 2002a). Variability in the equatorial Pacific, particularly in the central and western Pacific, is dominated by the El Nino Southern Oscillation (ENSO) with periods of 2 to 7 yr (Fiedler, 2002b).

The present paper describes the vertical profiles of dissolved selenium species in the eastern tropical, and subtropical Pacific Ocean.

## 2. Material and Methods

### 2.1 Sea water sampling

Sea water samples were collected from the eastern Pacific during the KH-03-1 “Hydra” Expedition (June-August, 2003) cruise of the R/V *Hakuho-Maru* (Japan Agency for Marine-Earth Science and Technology); their sampling locations are shown in Fig. 1, and the depth, latitude, and longitude are shown in Table 1. For sampling, we used 12-L lever-action type Niskin bottles mounted on a 36-position Sea-Bird’s 911 plus CTD-rosette, hung from a titanium-armored cable. The Niskin

bottles were pre-cleaned successively with distilled HCl and deionized water. After collection, the water samples for selenium speciation were filtered through a 0.45- $\mu\text{m}$  membrane filter (ADVANTEC Tokyo Co., Ltd.). Following filtration, all samples were acidified with hydrochloric acid to pH=1.6 and refrigerated in the dark until analysis. All samples were analyzed within 2 months of collection.

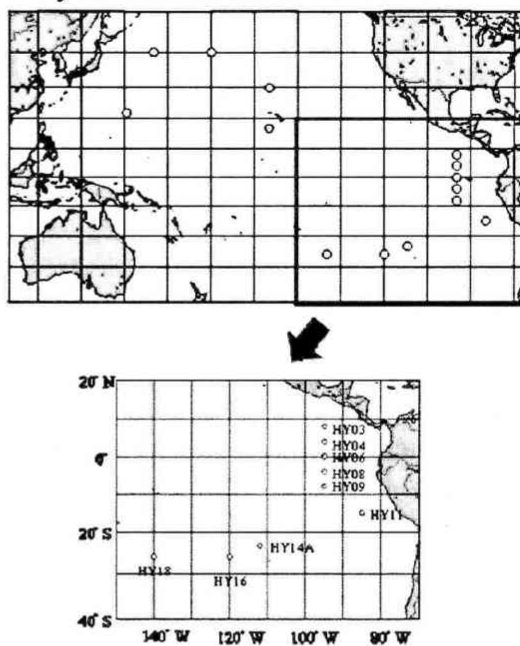


Fig. 1 Sampling locations

Table 1 Sampling depth and locations

| Sampling station                                      | Depth(m) | Latitude | Longitude |
|---|----------|----------|-----------|
| <i>eastern Tropical and Subtropical Pacific Ocean</i> |          |          |           |
| HY03  | 3671     | 8° 02'N  | 94° 57'W  |
| HY04  | 3578     | 4° 02'N  | 95° 03'W  |
| HY06  | 3247     | 0° 02'N  | 95° 26'W  |
| HY08  | 3622     | 3° 58'S  | 95° 00'W  |
| HY09  | 3870     | 7° 59'S  | 95° 01'W  |
| HY11  | 4635     | 15° 08'S | 85° 50'W  |
| HY14A   | 3148     | 23° 30'S | 112° 03'W |
| HY16  | 2917     | 26° 00'S | 120° 00'W |
| HY18  | 4347     | 26° 00'S | 140° 00'W |

### 2.2 Selenium speciation

The analytical procedures for the determination of selenite, selenate, and organic selenide in sea water have been described elsewhere (Hattori *et al.*, 2001b). Only brief descriptions are given here.

Determination of selenite: A 30-ml sample of filtered water was placed into a 100-ml glass beaker, and 5 ml of 0.1% 2,3-diaminonaphthalene (DAN, Nacalai Tesque Co. Ltd.) -0.1M hydrochloric acid solution and 0.5 ml of 0.1 M ethylenediaminetetraacetic acid-sodium fluoride (EDTA-NaF, Kishida Kagaku Co. Ltd.) solution were added to ask any interfering metal ions. The sample solution was adjusted to pH 1 with 6 M hydrochloric acid, and was warmed at 50°C for 20 min. After cooling, the solution was transferred to a separating funnel and was mechanically shaken with 5 ml of cyclohexane for 10 min. The piaselelol in the cyclohexane was determined by HPLC (high performance liquid chromatography) with a fluorescence detector at Ex. 375nm / Em. 520nm. The detection limit (S/N=2) of the DAN-HPLC method was 1 pM.

Determination of selenate: The selenate amount was calculated by subtracting the selenite amount from the summed selenite and selenate amount, which was obtained by the following reduction procedure. A 20-ml filtered water sample was placed into a 100 ml Erlenmeyer flask, and the acidity of the sample solution was adjusted to 1.2 M hydrochloric acid solution. After 2.0 g of potassium bromide was added, the flask was placed in a water bath and the solution was warmed at 85~90°C for 25 min. After cooling, the amount of reduced selenate and selenite in the solution was determined by HPLC.

Determination of organic selenide: The amount of organic selenide was estimated by subtracting both the selenite and selenate from the total amount of selenium, which was determined after wet-ashing decomposition with conc. nitric and 60% perchloric acid (analytical grade), followed by HPLC.

### 3. Results and Discussion

#### 3.1 *The characteristics of the sampling stations*

The T-S diagram of HY stations is shown in Fig. 2. Sampling stations HY03, 04, 06, 08, and 09 were located in the eastern tropical Pacific. The T-S diagram shows different features at the surface. The intrusion of low saline water show was recognized at the surface at HY 03 and 04. The sampling stations of HY03 and 04 were influenced by the California Current. The low saline water at HY 03 and 04 might be due to the inflow of land water with the California Current. The salinity minimum was observed at 800 m at HY14A, 16, and 18. It can be seen in the intrusion of Antarctic Intermediate Water (AAIW). The influence of AAIW for HY14A, 16, and 18 is stronger than that for other HY stations. The tropical thermocline dome (the Costa Rica Dome) was observed several times. The mean position of the dome is near 9° N 90° W, at the end of a thermocline ridge that shoals from west to east across the Pacific between the westward North Equatorial Current and the Eastward North Equatorial Counter-current (Fiedler, 2002a). Sampling stations HY06, 08, 09, and 11 were influenced by the Peru (Humboldt) Current and the South Equatorial Current. Sampling locations HY14A, 16, and 18 were located at the subtropical South Pacific. These stations were influenced by the South Equatorial Current.

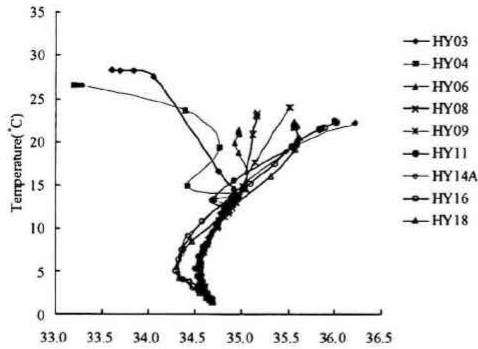


Fig.2 T-S diagram

### 3.2 Vertical profiles of selenite, selenate, and organic selenide in the eastern tropical and subtropical South Pacific Ocean

Vertical profiles of selenite, selenate, organic selenide, and total selenium in the eastern tropical and subtropical South Pacific Ocean are shown in Fig. 3 (HY03, 04, 06, 08, and 09) and Fig. 4 (HY11, 14A, 16, and 18), respectively. The concentrations of selenite at the surface in the eastern tropical Pacific stations from HY03 to 11 are one order magnitude higher than other sampling stations. The concentrations of nutrients were also found to be higher than those of other sampling stations. There are significant thermocline ridge and upwelling regions in the Pacific Ocean. There are the Countercurrent Thermocline Ridge with the Costa Rica Dome near HY03 and 4 and the Equatorial Thermocline Ridge near HY06 and the Peru Upwelling near HY 11. The selenite at the surface might be derived from deep water by upwelling. The vertical profile patterns of selenite show a nutrient-like profile at HY03, 04, 06, 08, and 09. The concentrations of selenite in the deep water below 1000 m of HY08 were slightly higher than those at HY03, 04, 06 and 09. The concentrations of

organic selenide in shallow water at HY08 and 11 were  $0.43 \pm 0.18$  and  $0.41 \pm 0.16$  nM, respectively.

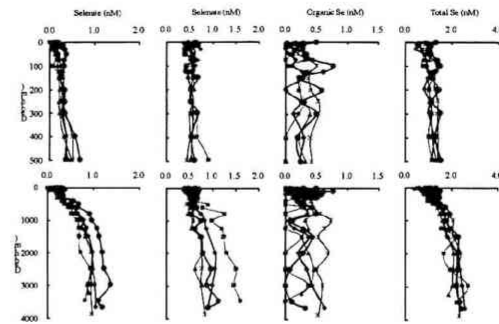


Fig. 3 Vertical profiles of selenite, selenate and organic selenium at HY03(◆), HY04(■), HY06(▲), HY08(●) and HY09(×).

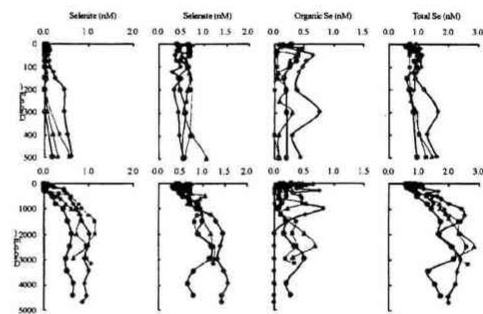


Fig. 4 Vertical profiles of selenite, selenate and organic selenium at HY11(◆), HY14A(■), HY16(▲) and HY18(●).

The concentrations of organic selenide in deep water below 2000 m at HY13 and 16 were  $0.70 \pm 0.33$  and  $0.50 \pm 0.18$  nM, respectively. Cutter and Bruland have reported that organic selenide is not detected below 2000 m at the VERTEX II site ( $18^\circ$  N,  $108^\circ$  W) in the eastern tropical North Pacific Ocean (Cutter and Bruland, 1984). However, organic selenide was detected in deep water of  $\sim 3700$  m at the IOC station ( $54^\circ$  N,  $48^\circ$  W) in the high latitude North Atlantic Ocean (Cutter and Cutter, 1998). They explained the existence of organic selenide in deep water by calculation of the residence time of organic selenide. They calculated the oxidation/loss rate of organic selenide by assuming a pseudo first-order loss and using Freon-11 ages. As a result, the residence time of organic selenide was estimated to be 10.3 yr. This

value allows organic selenide to be widely distributed in surface waters and also to exist in newly formed deep waters. The deep water mass age of the North Pacific is approximately 1900 yr. (Broecker, 1982) According to the residence time of organic selenide estimated by Cutter, organic selenide is not able to exist in North Pacific deep water. In addition, the multistep regeneration process of selenium in seawater was suggested by Cutter and Bruland (1984). They pointed out that organic selenide is a regeneration intermediate, and that it would not be expected to be present at significant levels in oxic waters due to its thermodynamic instability. However, organic selenium might be found if its production rate is fast, or if its removal rate is slow. In deeper waters, particulate fluxes and oxygen consumption rates are quite low in comparison to surface waters. Therefore, regeneration rates, and correspondingly the production of organic selenide, are greatly reduced. As a result, organic selenide is not detected in oxic deep water. However, organic selenide does exist in deep water. We therefore suggest the possibility of the existence of organic selenide in deep water in the North Pacific. It is the difference of sample treatment for organic selenium determination between our method and Cutter and Bruland method. The amount of organic selenium was estimated by subtracting both selenite and selenate from the total amount of selenium, which was determined after wet-ashing decomposition with concentrated nitric and perchloric acid. In contrast, Cutter et al. estimated the amount of organic selenium by subtracting both selenite and selenate from the total amount of selenium, which were determined after

boiling 4 mol l<sup>-1</sup> hydrochloric acid sample solution, with potassium persulfate addition, for 1 hr (Cutter 1978). The potassium persulfate is a typical chemical reagent for decomposition of organic matter in natural water. However, potassium persulfate is not an effective reagent for the decomposition of organic matter in saline water (Gershey *et al.*, 1979; Alken 1992; Raimbault *et al.*, 1999). Alken has reported that the presence of chloride ion at concentrations greater than 0.02 mol l<sup>-1</sup> is shown to interface with analysis of aqueous dissolved organic carbon (DOC) concentrations by the wet oxidation method (Alken, 1992). In the case of a humic substance (Suwannee River Fulvic Acid) as dissolved organic matter in 0.10 mol l<sup>-1</sup> chloride ion, the recoveries of DOC were decreased to 72 - 76%. Generally, the concentrations of chloride ion in open ocean are approximately 1.95 × 10<sup>4</sup> mg l<sup>-1</sup> (1.82 mol l<sup>-1</sup>). If organic selenide exists as refractory selenium-humic acid complex in sea water, the amount of organic selenide may be underestimated by using wet-ashing decomposition with potassium persulfate. A humic substance, whether it is dissolved in water or present as a part of the solid phase in soil and sediments, has functional groups that are capable of acting as ligands in forming complexes with metals. Yamada and Hattori have reported that most soluble selenium species in soil are present as organic selenide with a molecular weight from 1000 to 5000, and it seems to exist in humic substances (Yamada and Hattori, 1989). In addition, they determined the concentrations of selenium and amino acid in the soluble fraction of soil humic acid by hydrolysis with hydrochloric acid. A positive high correlation was observed between selenium and amino acid, which

indicated that some selenium existed as seleno-amino acid in humic acid (Kang *et al.*, 1991). Abrams has suggested that some of the selenium in fulvic acid exists as seleno-methionine (Abrams and Burau, 1989). These results suggest that the organic selenide in deep water might exist as seleno-amino acids in humic acid and/or fulvic acid. The properties and behavior of dissolved organic matter in the western North Pacific Ocean was identified by three-dimensional excitation-emission matrix spectroscopy (Nakaguchi *et al.*, 2003). The fluorescence maximum peaks, which originated from marine humic-like substances, were detected. Fluorescent organic matter such as marine humic-like substances has been found to constitute 20 to 37 % of dissolved organic carbon in the deep layer of western North Pacific Ocean (Yamaguchi *et al.*, 2001). We investigated the relationship between the relative fluorescence intensity (R.F.I.) of organic matter and organic selenide in the South China Sea, and a relatively high and positive correlation was observed between R.F.I. and organic selenide concentrations ( $r=0.89$ ,  $n=19$ ). These results provide no evidence for the existence of selenium-humic acid complex in sea water. However, there is no denying the possibility of the existence of selenium-humic acid complex in sea water.

### 3.3 *The relationship between three selenium species and nutrients*

It is well known that selenium shows nutrient-type behavior. It indicates the utilization of selenium by phytoplankton in the surface ocean. In particular, selenite shows a silicate-type distribution (Measures, 1980). A correlation coefficient ( $r$ ) and significance

probability ( $p$ ) between three selenium species and nutrients are shown in Table 2. A high correlation coefficient was observed between selenite and silicate at all sampling stations. A high correlation coefficient was also observed between selenite and nitrite + nitrate, phosphate except for HY03 and 08. A high correlation coefficient was observed between selenate and silicate at HY03, 04, 08, 11, and 16. A high correlation coefficient was observed between selenate and nitrite + nitrate, and phosphate at HY16 and 18. These results suggest that the behavior of selenite is almost similar to that of silicate. Selenite has been supplied from particulate selenide (Se-II) via an oxidation of dissolved organic selenide (Cutter and Bruland, 1984). The correlation coefficients between selenite and silicate at HY03, 04, 06, 08, 09, and 11 were slightly higher than those between selenite and nitrite + nitrate, phosphate. These results indicate that a selenite-silicate compound is synthesized in a plankton shell, and then it dissolves from the plankton shell with decomposition of plankton body after the plankton dies. The correlation coefficient between selenite and silicate might be lower than 0.98~1.00 if the oxidation of particulate selenide to dissolved organic selenide is added to the regeneration process of selenite. The correlation coefficients between selenate and silicate are slightly lower than these between selenite and silicate. It is indicated that selenate was not directly supplied from plankton and it was supplied by oxidation of selenite. The correlation coefficients between selenate and silicate at HY06 ( $r=0.49$ ) and HY09 ( $r=0.63$ ) were lower than those of the other sampling stations. These results suggest that the oxidation

Table 2 Correlation coefficient and significance probability between three selenium species and nutrients

| Sampling station | selenite vs silicate |    |         | selenite vs nitrite + nitrate |    |         | selenite vs phosphate |    |         | Selenate vs silicate |    |         | Selenate vs nitrite + nitrate |    |         | Selenate vs phosphate |    |         | Organic Se vs silicate |    |        | Organic Se vs nitrite + nitrate |    |         | Organic Se vs phosphate |    |         |
|------------------|----------------------|----|---------|-------------------------------|----|---------|-----------------------|----|---------|----------------------|----|---------|-------------------------------|----|---------|-----------------------|----|---------|------------------------|----|--------|---------------------------------|----|---------|-------------------------|----|---------|
|                  | r                    | n  | p       | r                             | n  | p       | r                     | n  | p       | r                    | n  | p       | r                             | n  | p       | r                     | n  | p       | r                      | n  | p      | r                               | n  | p       | r                       | n  | p       |
| HY03             | 0.99                 | 23 | <0.0001 | 0.71                          | 23 | 0.0001  | 0.69                  | 23 | 0.0003  | 0.90                 | 23 | <0.0001 | 0.59                          | 23 | 0.0033  | 0.55                  | 23 | 0.0066  | 0.64                   | 23 | 0.0010 | 0.47                            | 23 | 0.0245  | 0.46                    | 23 | 0.0267  |
| HY04             | 0.98                 | 23 | <0.0001 | 0.78                          | 23 | <0.0001 | 0.77                  | 23 | <0.0001 | 0.96                 | 23 | <0.0001 | 0.65                          | 23 | 0.0009  | 0.63                  | 23 | 0.0012  | -0.04                  | 23 | 0.8583 | 0.18                            | 23 | 0.4047  | 0.15                    | 23 | 0.4895  |
| HY06             | 0.98                 | 23 | <0.0001 | 0.83                          | 23 | <0.0001 | 0.82                  | 23 | <0.0001 | 0.49                 | 23 | 0.0170  | 0.15                          | 23 | 0.4922  | 0.14                  | 23 | 0.5185  | 0.52                   | 23 | 0.0113 | 0.61                            | 23 | 0.0021  | 0.60                    | 23 | 0.0025  |
| HY08             | 0.97                 | 24 | <0.0001 | 0.69                          | 24 | 0.0002  | 0.67                  | 24 | 0.0004  | 0.84                 | 24 | <0.0001 | 0.50                          | 24 | 0.0131  | 0.47                  | 24 | 0.0217  | -0.49                  | 24 | 0.0146 | -0.19                           | 24 | 0.3862  | -0.19                   | 24 | 0.3853  |
| HY09             | 0.97                 | 22 | <0.0001 | 0.80                          | 22 | <0.0001 | 0.74                  | 22 | 0.0001  | 0.63                 | 22 | 0.0018  | -0.04                         | 22 | 0.8753  | -0.10                 | 22 | 0.6462  | 0.72                   | 22 | 0.0002 | 0.88                            | 22 | <0.0001 | 0.86                    | 22 | <0.0001 |
| HY11             | 0.97                 | 25 | <0.0001 | 0.88                          | 25 | <0.0001 | 0.81                  | 25 | <0.0001 | 0.95                 | 25 | <0.0001 | 0.63                          | 25 | 0.0007  | 0.51                  | 25 | 0.0086  | -0.63                  | 25 | 0.0008 | -0.20                           | 25 | 0.3444  | -0.11                   | 25 | 0.6015  |
| HY16             | 0.90                 | 21 | <0.0001 | 0.96                          | 21 | <0.0001 | 0.96                  | 21 | <0.0001 | 0.86                 | 21 | <0.0001 | 0.83                          | 21 | <0.0001 | 0.83                  | 21 | <0.0001 | 0.57                   | 21 | 0.0670 | 0.42                            | 21 | 0.0562  | 0.43                    | 21 | 0.0537  |
| HY18             | 0.95                 | 19 | <0.0001 | 0.97                          | 19 | <0.0001 | 0.97                  | 19 | <0.0001 | 0.73                 | 19 | 0.0004  | 0.83                          | 19 | <0.0001 | 0.82                  | 19 | <0.0001 | 0.14                   | 18 | 0.5788 | -0.13                           | 18 | 0.6605  | -0.14                   | 18 | 0.3820  |

of selenite to selenate did not occur smoothly at HY06 and 09. The correlation coefficients between selenite and nitrite + nitrate, phosphate are higher than those between selenite and silicate. The correlation coefficients between selenate and nitrite + nitrate, phosphate are also higher than these between selenate and silicate at HY16 and 18. These results indicate that selenite is supplied from not only the decomposition of plankton shell but also the decomposition of body fluid as soft tissue of plankton body. A high correlation coefficient was not observed between the three selenium species and nutrients except for HY09. A significant positive relationship was observed between organic selenide and nitrite + nitrate, phosphate at HY09. From this result we hypothesize that organic selenium is also supplied by the decomposition of plankton body fluid at HY09. These results suggest that the selenium regeneration processes differ at each sampling area. Selenite was supplied from both plankton shell and plankton body fluid. In particular, organic selenide was supplied by plankton body fluid at HY09. The behavior of selenite is related to the activity of marine phytoplankton. The difference in behavior of selenium in sea water may be due to the difference in the selenium requirements for plankton species. Selenium is primary concentrated from aqueous solution by bacteria and algae (Wrench and Measures, 1982; Foda *et al.*, 1983; Vandermeulen and Foda, 1988). Selenium requirements have been documented for some species of diatom and dinoflagellates (Harrison *et*

*al.*, 1988). Baines and Fisher have investigated the interspecific differences in the bioconcentrations of selenite by phytoplankton. Statistically significant differences in selenium concentrations were recognized among the algal divisions. The content of selenium in algal may vary in some species, depending on the phase of growth (Baines and Fisher, 2001). These investigation results suggest that selenium requirements and assimilation for marine phytoplankton differ among plankton species. The information obtained regarding plankton species at the sampling point will need to be considered in light of the regeneration process of selenium via microorganism action.

#### 4. Conclusions

Selenium species, selenite, selenate, and organic selenide in sea water were simultaneously determined in the eastern tropical, and subtropical South Pacific Ocean. Relatively high concentrations of selenite were observed at the surface water in the eastern tropical Pacific Ocean. These high concentrations might be due to an upwelling of selenite-enriched deep water. Relatively high concentrations of organic selenide were detected in deep water in the eastern tropical Pacific Ocean, possibly due to the presence of refractory selenium-humic acid complex. However, there is no evidence for the existence of selenium-humic acid complex. As such, we must determine the presence of selenium-humic acid complex in future. The correlation coefficients between selenite and nitrite + nitrate, phosphate

are higher than those between selenite and silicate at HY 16 and 18. These results might indicate that selenite is supplied from not only the decomposition of plankton shell but also the decomposition of body fluid as soft tissue of plankton body. The selenite/selenate ratio is not necessarily decreased with increasing total selenium concentrations in deep water below 2000 m, possibly due to the addition of selenium to deep waters via sinking particulate matter. Detailed information regarding the relationship between sinking particulate matter and dissolved selenium species will be necessary in the future to solve remaining problems related to selenium speciation.

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