

# Biogeochemical cycles of selenium in Antarctic water\*

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**Abstract**—Both vertical and horizontal profiles of total dissolved selenium, dissolved organic and inorganic selenium, including Se(IV) and Se(VI), as well as particulate selenium in seawater were obtained on a basis of newly developed separation technique from Antarctic Ocean, where the production of deep waters occurs. The results exhibited that the concentrations of Se(IV) and Se(VI) were elevated and the total concentration in the surface of the high latitude waters (1.31 nmol/L) was above those at lower latitudes (1.09 nmol/L) and also that previously reported from the Southern Ocean (1.18 nmol/L, Suzuki, 1987). Preliminary investigation using specifically designed microlayer-sampler, that was first employed to identify the main biogeochemical processes, revealed Antarctic Ocean being functioning as a potential source as selenium in sea-air exchange. The mean life time of the selenium, detected as Se(IV) in deep water, was also estimated rather shorter than the residence time of the water mass, based on the samples collected from the cruise of China's Sixth Scientific Expedition.

**Keywords:** Antarctic waters; selenium; biogeochemical cycle; microlayer.

## 1 Introduction

Selenium is one of the few trace elements existing in variable oxidation states in seawater, i. e. selenate or Se(VI), selenite or Se(IV) and selenide that is usually operationally taken as organic selenium. Only selenate is the dominant form in oxic seawater based on thermodynamic calculation (Sillen, 1961). However, the substantial presence of selenite, Se(IV), has been verified in recent decade (Suzuki, 1987; Measures, 1980; Takayanagi, 1985; Cutter, 1984; 1994), which apparently proposes a possible cycle of the element that

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may be somehow different from theoretically stable occurrences under the condition of redox potential of seawater but related to the biogeochemical cycles in the oceans. In this paper, evidence were given by viewing the spacial distributions of selenium, its speciations in water column and, in particular, total selenium in microlayer that was the first of studies designed to address whether processes in high latitude affect the element and geochemical signature.

## 2 Sampling and analysis

Water samples, over 29 vertical profiles, were obtained from the cruise of China's Sixth Scientific Expedition in Eastern Antarctic Ocean, Summer/1990. Separation of the speciations of the element was done immediately after sampling, using newly-developed separation technique, i. e. Se(IV), Se(VI) and organic selenium. Particle matter ( $>0.45 \mu\text{m}$  Millipore HA) was also collected for selenium analysis at station C-10. The selenium in microlayer was investigated in this cruise and the results were presented. All the samples were reserved in refrigerator and carried back to the base laboratory for determination of selenium conducted by Fluorospectrometer, Zhejiang Physics and Chemistry Institute. Analysis of particulate selenium was performed by PIXE, Institute of Low Energy Physics, Beijing.

## 3 Results and discussion

### 3.1 Total dissolved selenium in surface water

Results showed an average of 1.31 nmol/L of total dissolved selenium found from 42 surfacewater samples, which was appreciably higher than the average of the 30 surface water samples along the equatorial Pacific, 1.09 nmol/L, from Philippine Sea to Hawaii, 1990, and also higher than the value (1.18 nmol/L) observed by Suzuki and Sigumura from the area adjacent to the study area, 1987. The vertical profiles are given in Fig. 1, which showed that the concentration of the total selenium was fairly constant except station B-5 and B-6 where upwelling might not be neglected along the slope. As contrast, total selenium were relatively lower but constantly increased with the depth at the Pacific Equator (Fig. 2).

### 3.2 Inorganic selenium in seawater

Suzuki and Sugimura (1976) were the first successfully separating the speciations of the element in seawater and exhibiting the ratio of tetra-valent ion to the total was 0.2 to 0.6 in surface water, and 0.2 to 0.5 in the deep, whereas total selenium increased with depth from 0.76 nmol/L to 2.53 nmol/L, and Se(VI) was raised even three times that in surface. All the observation was however made on Northwest Pacific Ocean and suggested a potential role of biogeochemical reactions determining the chemical forms of the element at different depths of the ocean.

In Antarctic Ocean, we found that the presence of the inorganic selenium was about 72% of the total selenium in the surface water. The vertical profiles of nutrients and oxygen indicated water column were well oxygenated in 50m depth. Contrary to the thermodynamic prediction, Se(IV) appeared through whole oxic layer (Fig. 1), and reached a broad maximum around 0.35 nmol/L beneath the mixed layer. Within the surface water, the ratio of Se

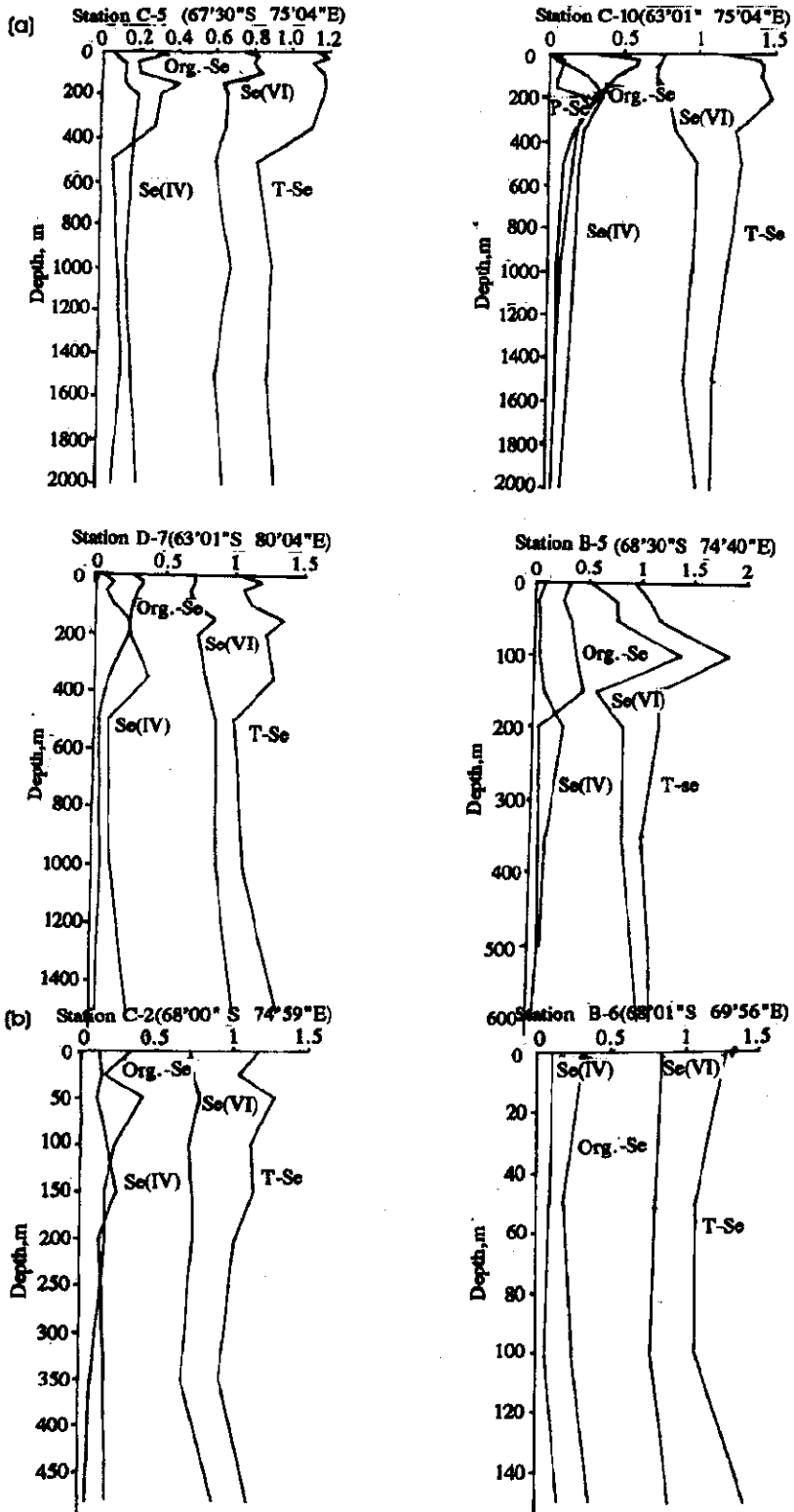


Fig. 1 Vertical distributions and speciations of selenium in Antarctic Ocean (nmol/L)

(IV) to Se(VI) was 10%, which however was approved to be 14% in equatorial Pacific using the similar separation method. The mechanism behind the deficiency of the selenite in such an eutrophic area was still unknown. A possible explanation however was the preferential uptake of Se(IV) over Se(VI) during the seasonal plankton blooms (Wrench, 1982) in summer of the Antarctic. Taking that into account, the profiles of Se(IV) could be expected being nutrient-like, and removed or consumed in surface or sub-surface and subsequently regenerated in deeper water as demonstrated by our observations at all profile stations. Another relevant consequence was that the deficiency of Se(IV) might give rise to the secondary uptake of Se(VI) as reported in oligotrophic regions (Cutter, 1984), which occurred also in upper layer of the high latitude water (Fig. 1).

Selenate was the major species through water column and the concentration risen steadily from the depth of 100m, above the maximum of Se(IV), and remained rather constant below 500m, but the ratio to total dissolved selenium became higher up to 90% at the deep water.

### 3.3 Organic selenium in seawater

Organic form of the metals existing in seawater has been considered a precursor of the degree being involved with the biotic processes, though it has been controversial in view of the determination since the methods applied by different author might not be compatible. Sugimura and Suzudi (1978; 1985) reported that about 37% of selenium was presented as organic complexes or covalent compounds in seawater using Amberlite XAD-2 resin and active carbon, which could even be as high as 80% in Pacific Ocean while it was defined as the difference between total selenium and inorganic selenium (Cutter, 1984). Employing GDX-102 resin, we came to the conclusion that total dissolved selenium was comprised of 37% of organic selenium in surface water of Antarctic Ocean, but 26% in equatorial Pacific Ocean. The difference could be accounted for not only by the zonal difference in biological processes, but by the possibility that organic selenium might not be coherent to similar compound. Cutter and Bruland (Cutter, 1984) and Takayanagi and Wong (Takayanagi, 1985) suggested that the organic selenium might be seleno-amino acid in dissolved peptides that was the most labile fraction of the organic complexes and subject to the decomposition or transformation with the conveying belt from surface to the bottom sediment, hence if it could be identified, the organic fraction of the selenium could be taken as the measure of the movement rate of water mass. Antarctic Ocean, as one of the two origins of water masses in the world where the high productivity certainly results in an enrichment of the dissolved organic matter, would accumulate organic selenium in surface waters as long as the transfer rate is not as fast as biological production rate in the summer. Our investigation showed a pronounced maximum of the organic selenium in the surface, 0.42 nmol/L, which was 0.28 nmol/L in equa-

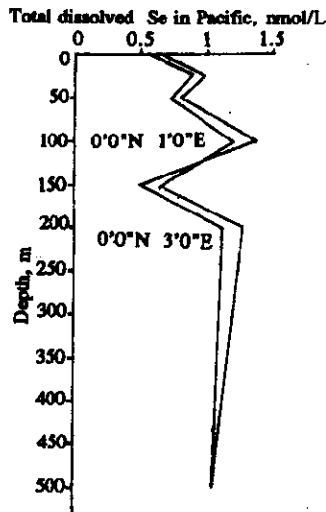


Fig. 2 Vertical distributions of selenium in Equatorial Pacific (nmol/L)

torial Pacific. However, below 1000m, the fraction of the organic selenium was almost undetectable, somehow different from inorganic forms as already discussed.

### 3.4 Particulate selenium, microlayer selenium and selenium in sea-air exchange

Particulate selenium, as collected at station C-10, displayed a maximum concentration at depth of 200m with 0.21 nmol/L, and absolutely lower both in surface (<1m) and the depth below 1000m, the range of which varied from less than 1% to 14% of total dissolved selenium, close to those reported from Northwestern Pacific (Suzuki, 1987). It was likely that the distributions of the speciation could be affected by the uptake of selenite in surface water and zooplankton grazing with fecal pellet production in subsurface water, by viewing of two peaks of the particulate selenium at depth of 25m and 200m respectively.

A reverse relation existed between the particulate and organic selenium in upper water (100m—350m), which might imply a possible interconversion between those two forms of selenium, i. e. the initial step of the regeneration of the element from the biogenic particles was the production of the dissolved organic selenium (Cutter, 1982). Now comes an interesting question that if the less fraction of the organic selenium in surface water was due to the losses by sea-air exchange and hydrolysis such as the mechanism leading to the production of dissolved carbonyl sulfide. To exam the assumption, the determination was made on the few volume of the microlayer of the seawaters (within 50  $\mu\text{m}$  layer). The results revealed that the microlayer bore 0.65 nmol/L of the total dissolved selenium, only half of the average value detected from underlying waters.

The dramatic reduction of selenium in the microlayer approved significant losses of selenium to the stratosphere via the exchange such as sulfate aerosols, considering the concentration of the nitrate, 44  $\mu\text{mol/L}$  in the microlayer as determined as two-fold of that from surface water, and the Redfield ratio of carbon to selenium which was assumed  $106:4.8 \times 10^{-4}$  (Cutter, 1984). This paper could not provide direct evidence to answer what kind of speciation would help to transfer selenium into the air. It, however, could be predicted that the most part of the selenium within the microlayer might exist in inorganic form since, as elucidated in foregoing discussion, the enrichment of the nitrate hinted the less feasibility of the depletion on Se(IV), even Se(VI) in the air-touched layer. In another words, following up the regeneration of the biotic particle, it was most likely that the fraction of the selenium lost into the overlying air could be the organic selenium.

### 3.5 Biogeochemical cycling of selenium in seawater

Selenium is not a typical metallic element nor thorough bio-limiting one, and controlled by various processes with season and depth in the ocean, the biogeochemical behaviors of the element in most of cases are fairly complex. One of the challenging models was put forward by Cutter (Cutter, 1982), which could be testified by the occurrence of maxima of organic-Se, Se(IV), particulate-Se(VI) at progressively great depth, i. e. when organic-Se was the initial product during the oxidation of the particulate organic matter, it should be concentrated at the shallow depth or younger waters. This model seemed still applicable even in the high latitude waters, i. e. station C-10, where organic-Se was located above the maxima of

nitrate and phosphate, the final products of the regeneration process in surface water. At deeper depth, Se(IV) reached maximum as a result of the oxidation of dissolved organic selenium from somewhat older water mass of the Antarctic Winter Water remaining along the depth. Whereas in bottom water, organic-Se almost disappeared but Se(VI) became dominant, up to 90% of the total dissolved selenium, probably due to its longer residence time.

To better understand mixing processes occurred over the water column, a temperature vs. salinity diagram was constructed in Fig. 3 which showed that only remaining Antarctic Winter Water was of stable S-T structure, from 100m to 350m, above which a pycnocline existed as a barrier to transport particulate matter, and hence resulted in a maximum of particulate selenium along the layer boundary.

The total selenium and the speciations, within the stable layer (100m — 350m), are presented in Fig. 4. It could be found that both selenite and organic selenium were non-conservative element like in the intermediate water where the input rate of the species from the mixed layer or the upwelling was not negligible. Moreover, the transformation rate of particulate to dissolved selenium might be also responsible for the non-conservative of Se(IV), which could be approximately estimated to be 0.01/a according to the Redfield ratio (Cutter, 1984) and the concentration of Se(IV) in deep water, which was 0.14 nmol/L. Based upon that, the mean life of selenite, with respect to its oxidation rate, could be referred as 180 years in deep water, which is really short relative to the general residence time of the deep water as of 1500 years. Therefore it became understandable that selenium, or selenite, presented as non-conservative and disappeared in deeper water where biological uptake might not significantly exist.

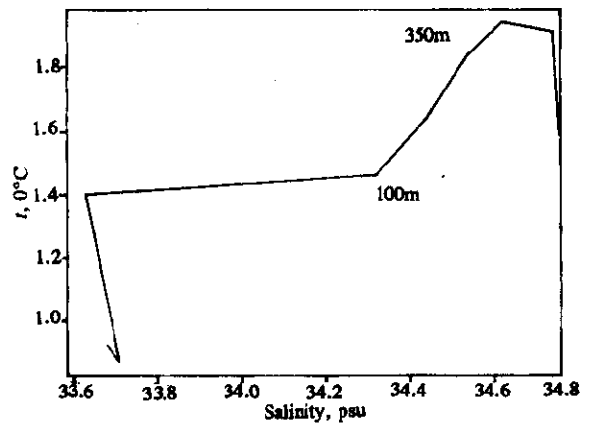


Fig. 3 *In situ* temperature vs. salinity (station C-10)

## 4 Conclusions

Selenium concentration was higher than those previously reported from the surface water of eastern Antarctic Ocean, which might be contributed mostly from an enrichment of organic selenium due to high productivity that also helped volatilization losses via organic selenium within microlayer—an indirect evidence that Antarctic Ocean might be the source of the selenium as aerosol into the overlying air layer. The distributions of selenite and particulate selenium could be accounted for by the oxidation and particulate transport in subsurface, the dissolution of the particle or the regeneration back to the dissolved state. The substantial low selenite in deep water could be explained by its fairly short mean life according to Cutter & Bruland's model (Cutter, 1984).

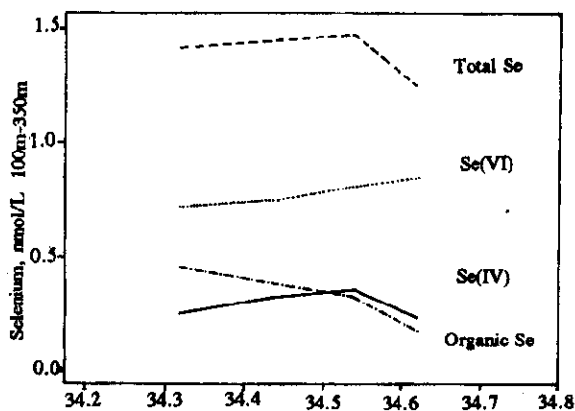


Fig. 4 Total selenium and its speciations vs. salinity within Antarctic Winter Water

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