報告番号 甲第 4822 号

Multielement Profiling Analysis of Trace Metals in Seawater as Studied by Inductively Coupled Plasma Mass Spectrometry

Tomoki Yabutani

①

Multielement Profiling Analysis of Trace Metals in Seawater as Studied by Inductively Coupled Plasma Mass Spectrometry

Tomoki Yabutani

September, 2000

Contents

Chapter 1 Introduction

1-1 Marine Chemistry of Trace Elements

The earth is believed to be only one planet with liquid water among the planets in the universe. It has been speculated that the ocean was created about 4 billion years ago, and that the origin of life on the earth began in the ocean 3.8 billion years ago. The ocean occupies about 70% of the earth's surface, and it would be *ca.* 4000 m in depth, if the elevation of the earth was averaged. The ocean contains about 96% of water on the earth, and thus the ocean is the largest reservoir of water. The ratio of thermal capacity of seawater to that of air is approximately 1000 : 1. Therefore, the heat capacity of surface seawater in 5 m depth of the whole ocean is almost equivalent to that of the earth's atmosphere. Seawater contains a large quantity of various organisms and materials. For example, the content of carbon dioxide in the ocean, which is a green-house gas, is 50-times more than that in the atmosphere.1) Consequently, the ocean plays many important roles in global climate changes and geochemical cycles of various materials.

Seawater provides high ionic strength, containing about 35 g kg^{-1} of salts. The concentrations of the elements in the Pacific Ocean are presented in the order to the higher concentration in Table 1-1, along with the types of distribution patterns of vertical concentration profiles.2) As is seen in Table 1-1, the elemental concentrations in typical open seawater are in the wide range from about 2% for Cl to 0.0000001 μg l^{-1} for Ir. In seawater, 6 major dissolved ions of Na$^+$, Cl$^-$, SO$_4^{2-}$, Mg^{2+}, Ca^{2+}, and K$^+$ make up 99% of all inorganic ions. The major elements have nearly constant ratios to salinity in all over the sea and have long residence times, because major ions are little affected by biological or human activities. In contrast, all other elements exist at the extremely low concentrations and in various chemical forms such as inorganic ions, colloids, organicmolecule-chelates and so on.

According to the vertical concentration profiles of the elements in the ocean, trace elements can be classified into three groups: (i) conservative-type, (ii) nutrient-type, and (iii) scavenged-type.3) The schematic diagrams of the vertical concentration profiles for these distribution types of the elements in the ocean are shown in Fig. 1-1. This classification of the elements is hereafter referred to as the marine-chemical classification. As will be described below, the vertical concentration profiles of the elements in the ocean reflect the behaviors of the elements in biochemical and physicochemical cycles.

Table 1-1 The average concentrations and distribution patterns of the elements in Pacific Ocean.

Element	Concentration[a]/μg l^{-1}	Type of distribution[b]	Element	Concentration[a]/ μg l^{-1}	Type of distribution[b]
Cl	19350000	c	Ti	0.0065	s+n
Na	10780000	c	La	0.0056	n
Mg	1280000	c	Ge	0.0055	n
S	898000	c	Nb	0.005	?
Ca	412000	c	Hf	0.0034	?
K	399000	c	Nd	0.0033	n
Br	67000	c	Pb	0.0027	s
B	13000	c	Ta	0.0025	?
Sr	7800	c	Ag	0.002	n
Si	2800	n	Co	0.0012	s
C	800	n	Ga	0.0012	s+n
Li	180	c	Er	0.0012	n
Rb	120	c	Yb	0.0012	n
P	62	n	Dy	0.0011	n
I	58	c	Gd	0.0009	n
Ba	15	n	Sc	0.0007	(s+n)
Mo	10	c	Ce	0.0007	s+n
N	6	n	Pr	0.0007	n
U	3.2	c	Sm	0.00057	n
Be	2	s+n	Sn	0.0005	s
V	2	c	Ho	0.00036	n
As	1.2	r+n	Lu	0.00023	n
Ni	0.48	n	Tm	0.0002	n
Zn	0.35	n	Eu	0.00017	n
Cs	0.306	c	Tb	0.00017	n
Cr	0.21	c	Hg	0.00014	(s+n)
Sb	0.2	c	Rh	0.00008	n
Cu	0.15	s+n	Pd	0.00006	n
Se	0.1	r+n	Te	0.00005	r+s
Cd	0.07	n	Pt	0.00005	(c)
Al	0.03	s	Bi	0.00003	s
Fe	0.03	s+n	Au	0.00002	(c)
Mn	0.02	s	Th	0.00002	s
Y	0.017	n	In	0.00001	s
Zr	0.015	s+n	Ru	0.000005	?
Tl	0.013	c	Os	0.0000002	?
W	0.01	c	Ir	0.00000013	?
Re	0.0078	c			

a) Cited from Ref. 2.

b) c: conservative-type, n: nutrient-type, s; scavenged-type, r; redox-controlled-type.

It can be seen in Fig. 1-1(a) that the vertical concentration profiles of the conservative-type elements are almost constant with depth of the ocean. The distributions of this type of the elements receive little influences from biochemical and physicochemical cycles. Thus, the conservative-type elements have long residence time in relation to the mixing time of seawater. As is seen in Table 1-1, the conservative elements mostly include the elements which exist in seawater as the major and minor elements as well as simple ions and oxoanion-forming elements.

The nutrient-type elements have strong interaction with phytoplanktons and biogenic particles. Most of nutrient-type elements are "biologically essential elements". Thus, it is considered that the nutrient-type elements are taken up by phytoplanktons for their growth in the surface layer of the ocean, where photosyntheses of phytoplanktons are performed under solar radiation. The vertical profiles of the nutrient-type elements are shown in Fig. 1-1 (b), which are strongly correlated to those of P, N, and Si.[4] Their concentrations are extremely low in surface waters due to direct uptake by phytoplanktons, and then gradually increase with depth due to decomposition of organic phases in detritus during their settling. The vertical profiles of Cd correlates closely with that of P, while the vertical profile of Zn does with that of Si. The vertical profiles of P and Cd show more rapid increase with depth, compared to those of Si and Zn. Since P and Cd may be distributed in soft organic tissue of organisms, they are easily decomposed and then re-dissolved in seawater. On the other hand, since Si and Zn are cycled with skeletal phases of organism, they are decomposed slowly.

The scavenged-type elements are generally contained in low-solubility species, and they also strongly interact with suspended particulate matters in seawater. Therefore, the residence times of the scavenged-type elements in seawater are estimated to be a few hundred years, and thus shorter than the oceanic stirring time (10^3 years)[5]. It is seen in Fig 1-1(c) that the concentrations of the scavenged-type elements often show the maximum in surface layer of the ocean and near the coastal areas because of the supply of terrestrial materials from the atmosphere and the rivers. Then, they decrease with depth of the ocean and distance from the terrestrial lands.

The elements are classified into a redox-controlled-type elements in some occasion, such as As, Cr, and Sb, with the different oxidation states, because they often reflect the different redox conditions in seawater. The concentration ratio of each element in the different oxidation states is easily changed by the redox potential in marine environment. Therefore, these elements are regarded as the tracers for the oxidative/reductive conditions in seawater.

As has been described so far, the concentrations, vertical profiles, and oxidation states of the elements give us key to understand the marine environment. As a result, the elements, not only major elements but also trace elements, in seawater can be the excellent indicators for the study on marine chemistry.

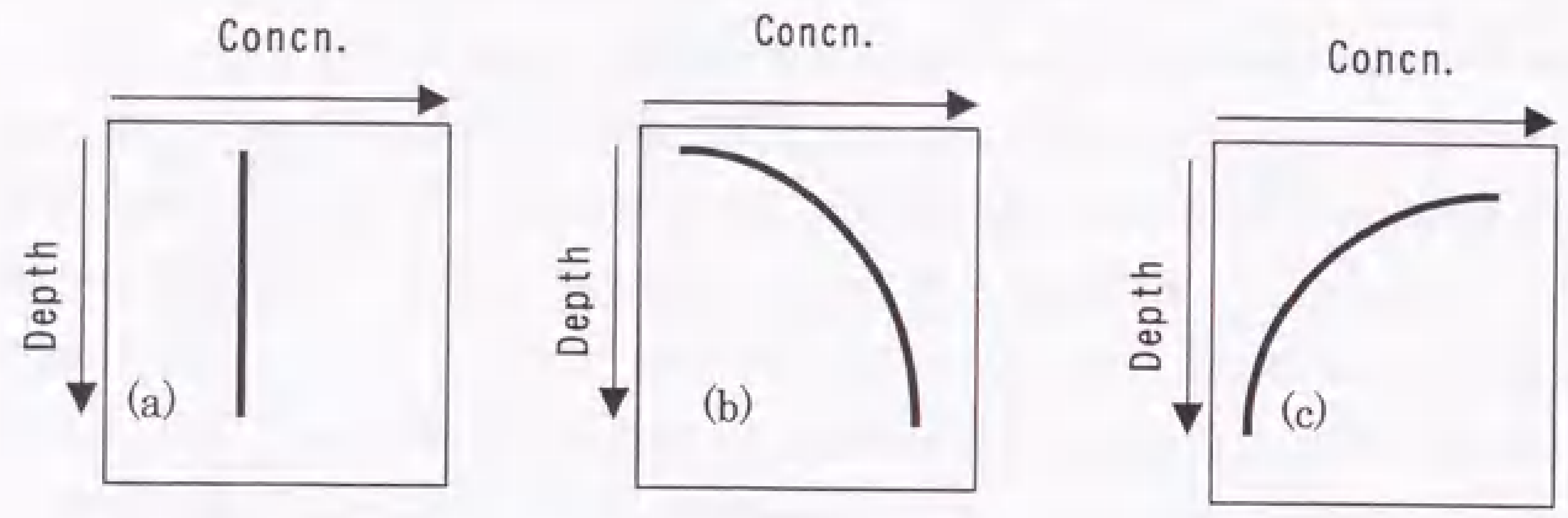

Fig. 1-1 Schematic diagrams of vertical concentration profiles for distribution types of elements in seawater.

(a) conservative-type element, (b) nutrient-type element , (c) scavenged-type element.

1-2 Historical Aspects in Development of Analytical Methods for Trace Elements in Seawater

It is considered that the modern marine chemistry began from the world-round cruise of H. M. S. Challenger from 1872 to 1875.[6] Dittmar analyzed 70 water samples collected during the cruise. He found from the analytical data that the ratios of the concentrations of major elements were almost constant in all over sea areas.[6]

In 1920s, Fritz Haber, who is famous as the pioneer of artificial ammonia synthesis, tried to recover gold from seawater for recoup of Germany's World War I debt. Unfortunately, as gold could hardly be recovered from seawater, his attempt had met with failure. The cost for recovery of gold from seawater was much more expensive than the cost estimated at the beginning of his trial. After about 10 years, Haber noticed that the concentration of Au in seawater was much less than 4 μg l^{-1}, which had been the accepted concentration in those days.[7] However, the 0.004 μg l^{-1} as the concentration of Au, which was obtained by Haber, was still 2 orders of magnitude higher than the concentration reported in 1990s.[8] This was a story of the beginning of marine chemistry in 1920s, when the analytical techniques for the determination of trace metals at the ppb level as the elemental concentration in seawater had not been established.

Since that time, various analytical methods for the accurate and precise determination of trace elements in seawater have been explored by many researchers until today.[9] However, the determination of trace elements in seawater is still one of the most difficult subjects in analytical chemistry and marine chemistry, because the concentrations of most of trace elements in seawater are extremely low with the presence of high contents of major elements.

The historical changes of the reported concentration values of the elements in seawater are summarized in Table 1-2.[2,9-12] In Table 1-2, the data for most elements at the upper ppm (mg l^{-1}) or sub-ppm level as the concentration have not been changed until now, but the concentrations of most heavy metals such as Ni, Zn, Cr, Cu, Fe, and Co have significantly been lowered with the years from 1965 to 1997. The decrease of the concentrations of trace elements with the years was in coincidence with development of the highly sensitive analytical methods as well as of clean technology for the determination of trace elements.

Table 1-2 Historical changes of reported concentration values of the elements in seawater.

Element	Concentration / μg l⁻¹			
	1965[a]	1975[b]	1983[c]	1997[d]
Li	170	180	178	180
Be	0.0006	0.0056	0.0002	0.0002
B	4600	4440	4400	4400
C	28000	28000	26000	26000
N	500	640	420	600
O		2400	2400	2800
F		1300	1300	1300
Na	10500000	10770000	10780000	10780000
Mg	1350000	1290000	1280000	1280000
Al	10	2	1	0.03
Si	3000	2200	3100	2800
P	70	60	62	62
S	885000	905000	898000	898000
Cl	19000000	19350000	19353000	19350000
K	380000	399000	399000	399000
Ca	400000	412000	415000	412000
Sc	0.004	0.0006	<0.001	0.0007
Ti	1	1	<0.001	0.0065
V	2	2.5	<1	2
Cr	0.05	0.03	0.33	0.21
Mn	2	0.2	0.01	0.02
Fe	10	2	0.04	0.03
Co	0.1	0.02	0.002	0.0012
Ni	2	0.56	0.48	0.48
Cu	3	0.25	0.12	0.15
Zn	10	4.9	0.39	0.35
Ga	0.03	0.03	0.01	0.0012
Ge	0.07	0.05	0.005	0.0055
As	3	3.7	2	1.2
Se	0.4	0.2	0.17	0.1
Br	65000	67300	67000	67000
Rb	120	120	124	120
Sr	8000	7900	7800	7800
Y	0.3	0.013	0.013	0.017
Zr		0.03	<1	0.015
Nb	0.01	0.01	0.001	0.005
Mo	10	10	11	10
Ru		0.0007	0.0005	0.000005
Rh				0.00008
Pd			0.003	0.00006
Ag	0.04	0.04	0.003	0.002
Cd	0.11	0.11	0.07	0.07
In	20	0.00011	0.0002	0.00001
Sn	0.8	0.004	0.0005	0.0005
Sb	0.5	0.24	0.2	0.2
Te				0.00005
I	60	60	59	58

Table continues

Table 1-2. Continued

Element	Concentration / μg l⁻¹			
	1965[a]	1975[b]	1983[c]	1997[d]
Cs	0.5	0.3	0.0003	0.306
Ba	30	13	11.7	15
La	0.0029	0.0034	0.004	0.0056
Ce	0.0013	0.0012	0.004	0.0007
Pr	0.0064	0.00064	0.0006	0.0007
Nd	0.0023	0.0028	0.004	0.0033
Sm	0.00042	0.00045	0.0006	0.00057
Eu	0.00011	0.00013	0.0001	0.00017
Gd	0.006		0.0008	0.0009
Tb		0.00014	0.0001	0.00017
Dy	0.00073	0.00091	0.001	0.0011
Ho	0.00022	0.00022	0.0002	0.00036
Er	0.00022	0.00087	0.0009	0.0012
Tm	0.00013	0.00017	0.0002	0.0002
Yb	0.00052	0.00082	0.0009	0.0012
Lu	0.00012	0.00015	0.0002	0.00023
Hf		0.007	<0.008	0.0034
Ta		0.002	<0.0025	0.0025
W	0.1	0.1	<0.001	0.01
Re		0.004	0.004	0.0078
Os				0.0000002
Ir				0.00000013
Pt				0.00005
Au	0.004	0.004	0.011	0.00002
Hg	0.03	0.03	0.006	0.00014
Tl	0.01	0.019	0.012	0.013
Pb	0.03	0.03	0.001	0.0027
Bi	0.02	0.02	0.01	0.00003
Th	0.05	0.001	0.0007	0.00002
U	3	3.2	3.2	3.2

a) Cited from Ref. 10, b) Cited from Ref. 11, c) Cited from Ref. 12, d) Cited from Ref. 2.

From 1950s to 1970s, analytical atomic spectrometry was developed in succession[9]; flame atomic absorption spectrometry (FAAS), electrothermal atomization atomic absorption spectrometry (ETAAS), and inductively coupled plasma atomic emission spectrometry (ICP-AES). As a result, trace analysis at the ppb level could be carried out after 1970s.

Walsh and Alkemade proposed independently atomic absorption spectrometry (AAS) in 1955.[13,14] Then, ETAAS was developed by L'vov in 1965.[15] ETAAS has great advantages in high sensitivity and small sample volume injection. The detection limits of ETAAS for most elements were superior to those for classical flame atomic absorption spectrometry (FAAS). However, it has some disadvantages because of the single-element analysis, severe chemical interferences by major elements, and insufficient excitation of refractory elements such as Mo and W. Holak *et al.* reported a new method using hydride generation for the AAS measurement in 1968.16) The hydride generation method provides high sensitivity for the hydride-forming elements such as As, Se, Sb, Sn, Ge, Te, Bi and Pb, compared to conventional FAAS. Then, the hydride generation method coupled with other analytical methods (FAAS, ETAAS, ICP-AES) has been extensively applied to the determination of hydride-forming elements.

ICP-AES was proposed by Fassel in USA and Greenfield in UK in 1965.17,18) The argon ICP has some important spectrochemical properties such as high plasma excitation temperature (4500-8000 K) and high electron number density (n_e=10^{14}-10^{15} cm^{-3}).19) These characteristics of the argon ICP lead to efficient atomization and ionization of almost all elements as well as less chemical interferences by matrix elements, compared to other chemical flames. Furthermore, the ICP has a unique plasma structure called " doughnut structure", in which the plasma temperature and the electron number density in the central channel are lower than those in the outer plasma region. This structure of the plasma allows effective and reproducible introduction of the sample solution into the plasma and reduction of self-absorption of the emission lines. As a result, ICP-AES can provide rapid multielemental detection capability with the wide dynamic ranges of the calibration curves up to 5 orders of magnitude.

In 1978, the intercomparison works, in which 49 laboratories joined to analyze two kinds of the seawater samples with the nanomolar level concentrations of trace metals, were conducted by the International Oceanographic Commission. Unfortunately, the analytical results for Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn showed the wide deviations between the laboratories and reseachers.20) These poor precisions of the analytical values for trace elements suggested some contamination during sample collection and storage. After this work, clean technology for trace analysis of seawater have been interested in by many marine chemists in the world. In the mid-1980s, the metal-free sampling bottles such as Go-Flo sampling bottles and MERCOS sampling bottles, all parts of which were made from Teflon, were developed to avoid sample contamination.21,22) Advances in clean technology for trace analysis of seawater have led to achieve the accurate analytical values for some trace elements at the extremely low concentration levels in 1980s, as seen in Table 1-2. In 1983, then, seawater standard reference material for the intercalibration of analytical data were issued from National Research Council of Canada.23) Analysis of seawater reference

material enables us to estimate the validation and reliability of the analytical data obtained by some newly developed analytical methods.

Inductively coupled plasma mass spectrometry (ICP-MS) was developed by the Fassel's group in 1980.24) The argon ICP is an efficient ionization source for most metallic elements because of its high plasma temperature. ICP-MS provides some excellent analytical feasibilities such as multielement detection capabilities with high sensitivity and wide linear dynamic ranges of the calibration curves. Development of ICP-MS has allowed us to perform multielemental analysis routinely at the ppt level. Today, ICP-MS and ICP-AES are extensively used in a variety of the scientific fields. In 1997, compilation of the reliable concentrations of almost all elements in open seawater was firstly reported by Nozaki2), which will greatly contribute to future development of marine chemistry.

1-3 Current Issues and Topics in Study on Trace Elements in Seawater

1-3-1 Multielement profiling analysis of seawater sample

In last decade, trace elements in seawater has attracted a great deal of attention from the viewpoint of global climate changes, bio-resources, local environmental pollution and global material cycles. As has been mention so far, it has been proved that almost all elements in the periodic table exist in seawater.2) The concentrations of major elements are almost constant in the whole ocean, while those of trace elements are often changeable in each local costal or ocean area. It is, thus, considered that the distributions of trace elements in the ocean reflect the biochemical and physicochemical processes of the marine environment. In consequence, analysis of trace elements in seawater provides us some useful information for marine chemistry.

In 1993, a report of " Application of Analytical Chemistry to Oceanic Carbon Cycle Studies" was published from the Committee on Oceanic Carbon Oceanic Studies Board in National Research Council in USA.25) Carbon cycle has very close relation to bioactivities and global climate changes of the earth. In the report, the items, whose concentrations should be monitored for elucidation of carbon cycles in the ocean, were proposed.25) The items concerning to trace metal analysis are summarized in Table 1-3. Iron in seawater is considered to cause the limiting bioproductivity in many areas of the ocean.26) Aluminum and Pb are considered as the tracers for exchanges of terrestrial materials between the atmosphere and the

Table 1-3. Demanded monitoring items with relation to trace metals for Oceanic Carbon Cycle Studies.

Item	Concentration in seawater	Measurement precision at present	Demanded measurement frequency
Fe	<0.05~2.5 nmol/kg	5%	every hour
Zn	0.05~10 nmol/kg	0.05 nmol/kg	everyday
Cu	0.5~40 nmol/kg	0.1 nmol/kg	every day
Al	0.4~40 nmol/kg	0.2 nmol/kg	every day
Pb	5~175 pmol/kg	1 pmol/kg	every day
Mn	0.1~4 nmol/kg	?	every hour

ocean.[27,28] The concentrations of Cu and Zn, which are known as the biologically essential elements, are highly affected by the bioactivities of phytoplanktons and organic particles.[4] The changes of the concentration of dissolved Mn in the ocean often correlate with the influx from the hydrothermal plume.[29] However, limited knowledge is available on the nature, interactive processes, and biological impacts of other trace elements. For comprehensive knowledge about the processes involving the multielement interactions and the complexities of bioavailability, it is considered that multielemental marine chemistry should be essentially developed.

A research on marine pollution caused by heavy metals is one of the most important topics in marine chemistry. Since the kinds and amounts of the pollutants and new chemical substances emitted to the atmosphere and hydrosphere are so many and so large today, compared to those before, as a result of great development of industrial activities, the risk of exposure to hazardous chemicals and heavy metals for man and living organisms is substantially increasing today. Therefore, the concentration measurements of not only toxic elements (Pb, Hg, and Cd) but also other elements are strongly required to monitor the environmental pollution.

Therefore, in order to understand the influences on the human health as well as living organisms in seawater, the concentration distributions of various elements in the global ocean is necessary to be monitored with high temporal and spatial resolution. Consequently, the analytical methods for simple sample preparation and multielement determination of trace elements in seawater is really required. Thus, the present author would like to offer multielement profiling analysis of major-to-ultratrace elements in seawater as a new methodology for marine-chemical research.

1-3-2 Multielement determination of trace elements in seawater by ICP-MS

It is now known that almost all elements exist in seawater.[2] The concentrations of the elements in open seawater were shown in Fig. 1-2, along with the detection limits obtained by ICP-AES and ICP-MS.[32] The concentrations of the elements in seawater are distributed in the wide concentration range from 1% for Na to 0.0000001 μg l^{-1} for Ir. As can be seen in Fig. 1-2, the detection limits for most elements obtained by ICP-MS are generally lower than 2 or 3 orders of magnitude of those by ICP-AES. Therefore, it can be stated here that ICP-MS is the most powerful analytical method for the multielement determination of trace elements in seawater. As for trace analysis of seawater by ICP-MS, although the system for direct introduction of the sample with high salt concentration into the plasma has been developed,[33,34] and thus the direct determination of trace elements in original-seawater by ICP-MS is still difficult to be performed. In the direct introduction of seawater

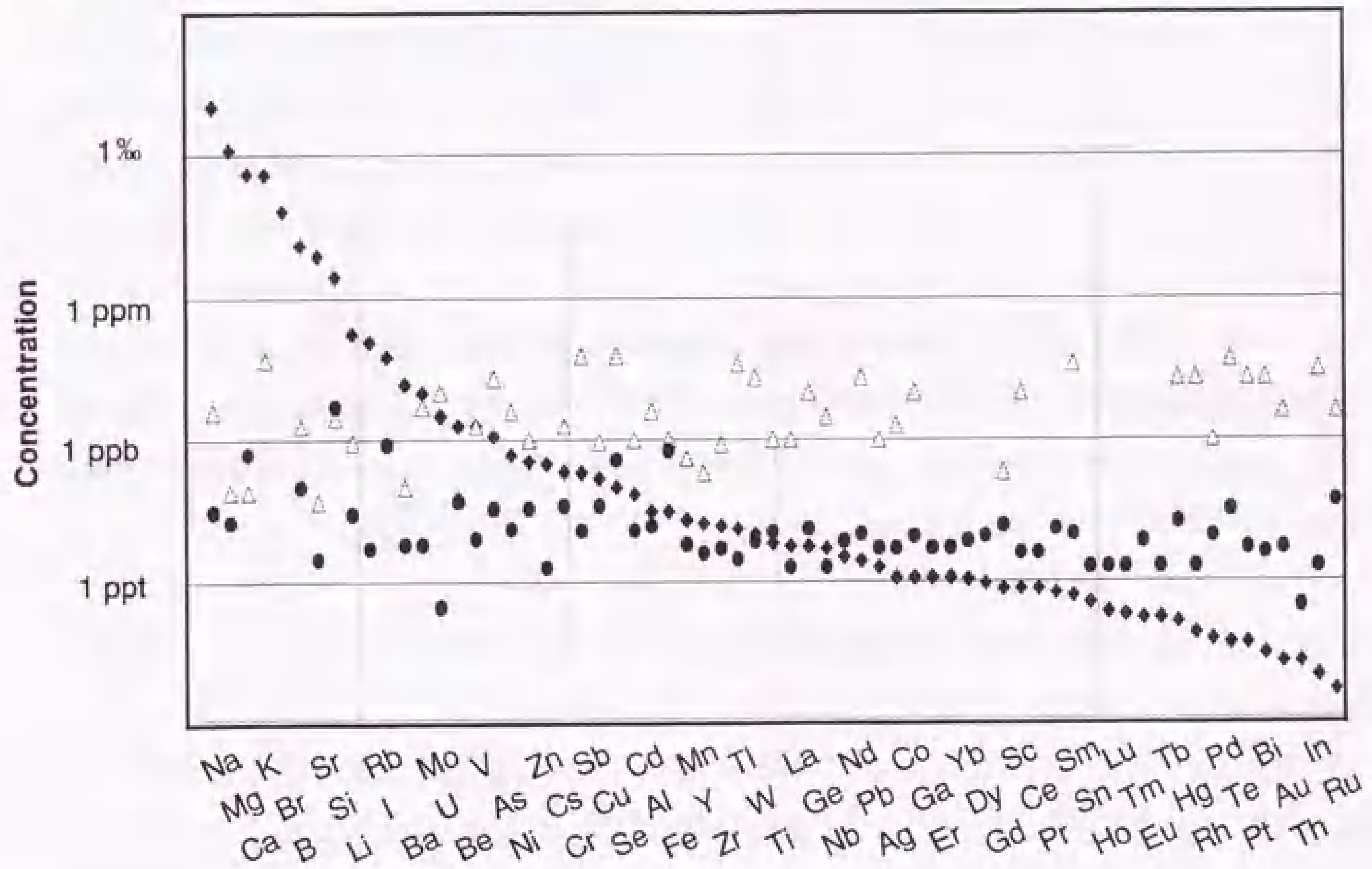

Fig. 1-2 Concentrations of the elements in open seawater and the detection limits obtained by ICP-AES and ICP-MS.

◆; Concentration of elements in open seawater (Cited from Ref. 2), ●; Detection limit obtained by ICP-MS (Cited from Ref. 32), △; Detection limit obtained by ICP-AES (Cited from Ref. 32).

into ICP-MS, high content of salts in seawater causes serious problems such as cloggings of the sampling and skimmer cones, contamination of the ion lens system, matrix effects such as suppression of analyte signals, and polyatomic ion interferences. Furthermore, it can be seen in Fig. 1-2 that the concentrations of most trace elements in seawater are at the low ppt or sub-ppt level, which are close to or below the limits of determination obtained by ICP-MS. As a result, some appropriate preconcentration of trace elements as well as separation of major elements in seawater is usually required for the multielement determination of trace elements.

As the preconcentration methods, the techniques such as coprecipitation, chelating resin preconcentration, and solvent extraction have been examined for seawater analysis prior to the ICP-MS measurement.[35] In addition, the hydride generation method combined with ICP-MS is recognized to make possible highly sensitive analysis for hydride-forming elements such as As, Se, Sn, and Sb in environmental samples.[36,37]

In the multielement determination of trace elements in seawater, it is desirable to determine at 20 trace elements simultaneously. However, an analytical method for the simultaneous determination of the elements in two elemental groups such as (i) transition elements and rare earth elements (REEs), and (ii) oxoanion- and hydride-forming elements have not been reported yet.

In consequence, the preconcentration methods used in the study on multielement profiling analysis of trace elements in seawater are summarized as follows; (i)non-selective multielement preconcentration, (ii) effective elimination of matrix elements, and (iii) larger concentration factor.

1-4 Objective of the Present Research

In the present study, the primary aim of the research is to establish multielement profiling analysis of trace elements in the ocean. As has been described so far, the concentrations of trace elements in seawater so often reflect some changes of the marine environment. The investigation on trace elements in seawater is, therefore, the important subject from the viewpoints of elucidation of material cycles, bioactivity, and marine pollution in the open and coastal sea areas. In such a purpose, it is desirable to determine the concentrations of trace elements as many as possible. The first objective of the present research, hence, is to explore the analytical methods for the simultaneous multielement determination of major-to-ultratrace elements in

seawater.

In Chapters 2-4, the analytical methods for the multielement determination of trace metals in seawater by ICP-MS are described. Since ICP-MS has excellent analytical features such as multielement detection capability and wide dynamic range, the application of ICP-MS to seawater analysis is suitable for this purpose. However, direct injection of seawater sample into ICP-MS often causes serious matrix effects to analyte elements and severe influences on the ICP-MS instrument (cloggings of skimmer/sampling cones and the plasma touch, and contamination of the ion lens system) due to matrix elements in seawater. Furthermore, the detection limits of ICP-MS are not low enough to determine some trace elements in seawater directly. In the present study, hence, the pretreatment methods for preconcentration of trace elements as well as elimination of matrix elements have been extensively investigated and explored for the multielement determination of trace elements by ICP-MS.

In Chapter 2, a preconcentration method for the multielement determination of trace elements in seawater by ICP-MS has been investigated with aid of chelating resin preconcentration. In this study, the experimental conditions for chelating resin preconcentration were optimized to obtain the better recoveries and the larger concentration factors for most analyte elements as well as effective separation of matrix elements. As a result, the preconcentration factor of *ca.* 40-fold in volume was obtained, with reduction of the total concentration of matrix elements less than 200 mg l^{-1}. The recovery values were larger than 80 % for 22 elements among 29 elements examined.

Chapter 3 focused on the determination of hydride- and oxoanion-forming elements, because it was found throughout the study reported in Chapter 2 that the hydride- and oxoanion-forming elements could not be recovered well by chelating resin preconcentration. In this study, La (lanthanum) coprecipitation has been applied to the preconcentration of those elements.

In Chapter 4, a tandem preconcentration method, in which chelating resin adsorption and La coprecipitation were cooperatively employed for preconcentration, was developed as a pretreatment method for simultaneous multielement determination of trace elements in seawater by ICP-MS. In tandem preconcentration method, the original seawater sample (250 ml) was subjected to chelating resin preconcentration, and then the filtrate after chelating resin preconcentration was further subjected to La coprecipitation. As a result, most transitional elements and REEs as well as the hydride- and oxoanion-forming elements could be determined with good accuracy and precision.

In Chapters 5 and 6, the multielement determination and multielement profiling analysis of trace elements in coastal and open sea areas were carried out for the elucidation of the biological and physicochemical roles of trace elements in the ocean as well as for the investigation of marine pollution.

In Chapter 5, the multielement concentration monitoring of trace metals in surface seawater collected at the sampling stations along the ferry track between Osaka and Okinawa were performed by ICP-MS after chelating resin preconcentration. The surface seawater samples were collected by an automated sampling system for on-board sampling, which was installed on the bottom of a ferryboat. According to the thus obtained results, it was found that most of trace metals especially below the 0.01 $\mu g\ l^{-1}$ as the dissolved and total concentrations sensitively reflected the environmental pollution in the Osaka Bay and Seto Inland Sea areas, as well as near the Bungo Canal and the outlet of Kagoshima Bay.

In Chapter 6, the multielement determination of major-to-ultratrace elements in surface seawater collected form the West Pacific Ocean, the West Australian Sea and the Antarctic Ocean was performed by ICP-MS and ICP-AES. Trace and ultratrace elements in the seawater samples were preconcentrated with the chelating resin and La coprecipitation. As a result, it was found that the nutrient-type elements such as Zn, Cu, Cd and Fe were enriched in surface seawater around the Antarctic Ocean, compared to those in the West Pacific Ocean. On the contrary, the scavenged elements (Mn, Co, and Ce) showed the opposite reversed distributions in the Antarctic Ocean, and the conservative elements (V, Mo, W, and U) were uniform in any sea areas.

In Chapter 7, the findings obtained by the present research, are briefly summarized, and future prospective of marine-chemical research on trace elements in described in conclusion. The present author would be offer the following research subjects for future development of marine chemistry; (I) all-elements determination, (ii) speciation of trace elements, and (iii) Global mapping of trace elements in the ocean and coastal sea areas.

References

1) J. P. Riley and R. Chester, "Chemical Oceanography", Academic Press, London (1983).
2) Y. Nozaki, *EOS Trans. AGU*, **78**, 221 (1997).
3) H. Whitfield and D. R. Turner, "Aquatic Surface Chemistry", ed. W. Stumn, John Wiley & Sons, New York, pp. 457 (1987).
4) K.W. Bruland, K. J. Orians, and J. P. Cowen, *Geochim. Cosmochim. Acta*, **58**, 3171 (1994).
5) K. W. Bruland, "Chemical Oceanography", eds. J. P. Riley and R. Chester, Academic Press, London, pp. 157-220, (1983).
6) W. Dittmar, "Report on the Scientific Results of the Exploring Voyage of the H. M. S. Challenger, Physics and Chemistry, Vol. 1", H. M. Stationery Office, London, (1884).
7) F. Haber, *Z. Angew. Chemie*, **40**, 303 (1927).
8) K. K. Falkner and J. M. Edmond, *Earth. Planet. Sci. Lett.*, **208**, 98 (1990).
9) H. Haraguchi, *Bull Chem. Soc. Jpn.*, **72**, 1163 (1999).
10) B. Mason, " Principles of Geochemistry." (1966).
11) J. P. Riley and G. Skirrow, " Chemical Oceanography" Vol. I, Academic Press (1975).
12) M. S. Quinby-Hunt and K. K. Turekian, *EOS Trans. AGU*, **64**, 130 (1983).
13) A. Walsh, *Spectrochim. Acta*, **7**, 108 (1955).
14) C. T. J. Alkemade and J. M. W. Milatz, *J. Opt. Soc. Jpn*., **45**, 583 (1955).
15) B. L'vov, *Spectrochim .Acta*, **17**, 761 (1961).
16) W. Holak, *Anal. Chem*., **41**, 1712 (1968).
17) R. H. Wendt and V. A. Fassel, *Anal. Chem*., **37**, 920 (1965).
18) S. Greenfield, L. L. Jones, and C. T. Berry, *Analyst,* **89**, 713 (1964).
19) H. Haraguchi, "Fundamentals and Applications of Inductively Coupled Plasma Atomic Emission Spectrometry (in Japanese)", Kodansha, Tokyo (1986).
20) P. G. W. Jones, C. W. Baker, and J. Olafsson, "ICES Cooperative "Report. No. 125, pp. 33 (1983).
21) K. W. Bruland, R. P. Franks, G. A. Knauer, and J. H. Martin, *Anal. Chim. Acta.*, **105**, 233 (1979).
22) P. Freimann, *Mar. Chem.*, **14**, 43 (1983).
23) S. S. Berman, R. E. Sturgeon, J. A. H. Desauliers, and A. P. Hykytiuk, *Mar. Pollut. Bull.*, **64**, 69 (1983).

24) R. S. Houk, V. A. Fassel, G. D. Flesch, H. J. Svec, A. L. Gray, and C. E. Taylor, *Anal. Chem.*, **52**, 2283 (1980).

25) National Research Council, "Applications of Analytical Chemistry to Oceanic Carbon Cycle Studies", National Academy Press, Washington D. C., (1993).

26) J. H. Martin and S. E. Fitzwater, *Nature*, **331**, 341 (1988).

27) R. Chester and K. J. T. Murphy," Metals in the Marine Atmosphere in Heavy Metals in the Marine Environment", eds. P. S. Rainbow and R. W. Furness, Boca Raton, pp. 27, (1990).

28) P. Burt-Ménard, "The Role of Air-Sea Exchange in Global Cycling", ed. P. Burt-Ménard, NATO ASI Series, D. Reidel Pub. Co., pp. 477 (1985).

29) G. Thompson, "Chemical Oceanography", Vol. 8, eds. J. P. Riley and R. Chester, Academic Press, London, pp. 72, (1983).

30) J. M. Edmond, *Rev. Geophysics Supp.*, 645 (1991).

31) P. A. Rona, K. Boström, L. Laubier, and K. L. Jr. Smith, "Hydrothermal Process at Seafloor Spreading Centers", Plenum Press, New York, (1983).

32) H. Haraguchi, E. Fujimori, and K. Inagaki, "Free Radicals and Antioxidant Protocols", ed. D. Armstrong, Humana Press, Totowa, pp. 389-441, (1998).

33) A, Montaser, M. G. Minnich, J. A. McLean, H. Liu, J. A. Caruso, and J. M. McLeod, "Inductively Coupled Plasma Mass Spectrometry", ed. A. Montaser, pp. 114, (1999).

34) A, Montaser, J. A. McLean, H. Liu, and J. M. Mermet, "Inductively Coupled Plasma Mass Spectrometry", ed. A. Montaser, pp. 26, (1999).

35) C. Vandecasteele and C. B. Block, "Modern Methods for Trace Elements Determination", John Wiley & Sons., Chichestar, pp. 9-53 (1993).

36) T. Tanizaki, K. Baba, K. Kadokami, and R. Shinohara, *Bunseki Kagaku*, **46**, 849 (1997).

37) S. J. Santosa, H. Mokudai, and S. Tanaka, *J. Anal. At. Spectrom.*, **12**, 409 (1997).

Chapter 2 Multielement Determination of Trace Elements in Coastal Seawater by Inductively Coupled Plasma Mass Spectrometry with Aid of Chelating Resin Preconcentration

2-1 Introduction

Nowadays, it is known that almost all stable–isotope elements in the major-to-ultratrace concentration range exist in seawater.[1] Although trace elements in seawater are extremely low, the concentration variations of such elements often reflect the physicochemical or biochemical changes in the sea. Thus, the accurate determination of trace elements in seawater is still important to elucidate the kinetic behaviors of the elements or to evaluate environmental pollution in the sea. It is, therefore, desirable to determine the major–to–ultratrace elements as many as possible for comprehensive appreciation of the distributions of trace elements and their multielement correlation in the marine environment.

Inductively coupled plasma mass spectrometry (ICP-MS) has analytical features such as simultaneous multielement detection capability with high sensitivity and wide linear dynamic ranges of the calibration curves, 5-6 orders of magnitude for most metallic elements. Consequently, ICP-MS has been extensively applied to the determination of trace elements in seawater. Since concentrations of trace elements in seawater are very low, compared to those of major (matrix) elements such as Na, K, Mg, and Ca, separation of matrix elements and preconcentration of trace elements should be performed prior to the determination of trace elements in seawater. As the separation and/or preconcentration methods, coprecipitation,[2-6] chelating resin adsorption,[7-17] and solvent extraction[18,19] have been widely employed in seawater analysis. In general, the elements such as Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb[3-5, 8, 9, 16, 19] and rare earth elements (REEs)[10, 11, 13, 14, 18] were separately determined by the analytical methods so far developed. However, there have been a few reports in which both of the transition elements and rare earth elements were determined at the same time.[2, 15]

Several works using the Chelex 100 resin for preconcentration of trace elements in coastal seawater have been reported in terms of REEs[10, 11] and other metallic elements (Al, Ti, Mn, Fe, Co, Ni, Zn, Y, Mo, Cd, and Pb).[20-22] The Chelex 100 resin which is a chelating resin with the iminodiacetate groups has rather non-selective adsorption capability for a variety of elements, although most metallic elements show slightly different pH dependences of the recoveries in chelating resin preconcentration. Thus, the experimental conditions for the multielement determination of trace elements in seawater should be optimized to obtain better recoveries and larger concentration factors for most analyte elements.

In the present paper, hence, chelating resin preconcentration of trace elements has been further investigated in detail, to assist their multielement determination by ICP-MS. In addition, the present analytical method was applied to the multielement analysis of coastal seawater certified reference material CASS-3, issued from National Research Council of Canada, and of off-shore seawater collected from the Ise Bay.

2-2 Experimental

2-2-1 Instruments

An ICP-MS instrument of model SPQ 8000A (Seiko Instruments Inc., Chiba) was used for the determination of trace elements ; it consisted of a quadrudpole-type mass spectrometer. An ICP-AES of model Plasma AtomComp MKII (Jarrell-Ash, Franklin, MA, USA) with a polychromator was also used for the simultaneous multielement determination of major and minor elements. The instrumental components and operating conditions are shown in Table 2-1. These operating conditions were chosen after optimization of each instrumental parameter in the ICP-MS and ICP-AES instruments. A pH meter of model twin pH meter from Horiba (Kyoto) was used for pH adjustment.

2-2-2 Chemicals

Nitric acid, acetic acid, and aqueous ammonia solution used were of electronic industrial grade (Kanto Chemicals Co., Tokyo). The multielement standard solutions were prepared by mixing the single-element standard stock solutions (1000 mg l^{-1}) of analyte elements for atomic absorption spectrometry, purchased from Wako Chemicals Co. The multielement standard solutions used for the ICP-MS measurement are listed in Table 2-2. The compositions of the elements in the standard solution were chosen, taking into consideration the stabilities of the elements dissolved in the 2 M HNO_3 solution as well as correction of polyatomic ion interferences. Since Ti and W were unstable in the HNO_3 solution, the standard solutions of these elements were prepared as the 1 M HCl solution for the former and the pure water solution for the latter. The Chelex 100 resin in 100-200 mesh was purchased from Bio-Rad Laboratories (USA). The resin was soaked in 5 M HCl which was changed 5-times every 12 h, and washed with water before use. Purified water used throughout the present experiment was prepared by a Milli-Q purification system.

2-2-3 Seawater samples

Coastal seawater reference material CASS-3 obtained from National Research Council of Canada was analysed for evaluation of the present analytical method. The coastal seawater samples collected at about 1 km off-shore from Tokoname (Aichi Prefecture) in the Ise Bay were also subjected to the present experiment. The seawater samples were filtrated with a membrane filter (pore size ; 0.45 μm) immediately after sampling, and then acidified to pH 1 with nitric acid. A polyethylene bottle used for collection and preservation of the seawater samples were

Table 2-1. Operating conditions for ICP-MS and ICP-AES instruments.

ICP-MS	Seiko SPQ 8000A
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 16 l min^{-1}
Auxiliary gas flow rate	Ar 1.0 l min^{-1}
Carrier gas flow rate	Ar 1.0 l min^{-1}
Sampling depth	12 mm
Nebulizer :	concentric type
Sample uptake rate	1.0 ml min^{-1}
Data acquisition :	
Dwell time	10 ms / channel
Data points	3 points / peak
Number of scans	100
ICP-AES	Jarrell-Ash Plasma AtomComp MK II
Plasma conditions :	
Incident power	1.0 kW
Coolant gas flow rate	Ar 17 l min^{-1}
Auxiliary gas flow rate	Ar 1.0 l min^{-1}
Carrier gas flow rate	Ar 0.48 l min^{-1}
Observation height	18 mm
Nebulizer :	cross-flow type
Sample uptake rate	1.2 ml min^{-1}
Polychromator :	Paschen-Runge mounting
Focal length	75 cm
Grating	2400 grooves / mm
Entrance slitwidth	25 μm
Exit slitwidth	50 μm

Table 2-2. The compositions of the standard solutions for ICP-MS measurement[a].

No.	Element	Concentration
(1)	Al, V, Co, Ga, Zr, Pb	50 μg l^{-1}
	Dy, Ho, Er, Tm, Lu, Bi	5 μg l^{-1}
(2)	Mn, Mo, Sn, U, Th	50 μg l^{-1}
	Sm, Eu, Gd, Tb	5 μg l^{-1}
(3)	Cr, Fe, Ni, Cu, Zn, Y, La, Ce, Pr, Nd	50 μg l^{-1}
	Cd, Yb	5 μg l^{-1}
(4)	Ti	50 μg l^{-1}
(5)	W	50 μg l^{-1}
(6)	Ca[b]	50 mg l^{-1}

a) The all standard solutions except for Ti and W were of 2 M HNO_3. The standard solutions of Ti and W were of 1 M HCl (Ti) and pure water (W), respectively.

b) This standard solution was used for correction of isobaric ion interferences with ^{57}Fe and ^{59}Co due to $^{40}Ca^{16}O^{1}H$ and $^{43}Ca^{16}O$.

soaked in 6 M HNO_3 for more than 1 week and rinsed with pure water before use.

2-2-4 Preconcentration procedure

The following preconcentration procedure for the coastal seawater samples was established as a recommended method after optimization, as will be described later. First, 250 ml of the seawater sample was taken in a beaker, and then the pH of the sample solution was adjusted to 6.0 with acetic acid and aqueous ammonia solution. Next, 0.2 g (dry weight) of the chelating resin was added into it, and then the solution was stirred with a magnetic stirrer for 2 h. The resin was collected on a glass filter (1.4 cm, i.d.), and washed with 10 ml of water and 8 ml of 1 M ammonium acetate (pH 6.0) to reduce major elements adsorbed on the resin. After washing with 10 ml of water, trace elements were eluted with 6 ml of 2 M HNO_3, into which 0.5 ml of a mixed solution of Ge, In, Re, and Tl (100 μg l^{-1} each) was added as the internal standard elements for correction of matrix effects due to major elements.[3, 25]

In the recovery test, 5 ml of the mixed standard solution containing the analyte elements (5 mg l^{-1} – 2 μg l^{-1}) were added into 250 ml of the seawater sample solution, and the experimental procedure described above was carried out to estimate the recovery values.

2-3 Results and Discussion

In order to perform the accurate and precise determination of trace elements in seawater, less contamination, efficient removal of matrix salts, large concentration factor, and good recoveries of analyte elements should be taken into consideration in the chelating resin preconcentration. Therefore, in the case of chelating resin preconcentration using the Chelex 100 resin, the following conditions are usually investigated : (i) resin amounts, (ii) pH dependence, (iii) stirring time, (iv) volume of ammonium acetate solution needed to eliminate matrices (Ca, Mg) adsorbed on the resin, and (v) volume of the eluent solution. In the present experiment, the experimental conditions of (ii), (iv), and (v) were investigated by using 250 ml of the seawater sample. The other conditions such as (i) amount of resin (0.2 g) and (iii) stirring time (2 h) were chosen after the reference.[10]

2-3-1 pH dependence of recoveries of trace elements in seawater

The recoveries of various analyte elements were examined in the pH range of 2-8, where the preconcentration procedure described in the experimental section was carried out. The results are illustrated in Fig. 2-1a-d. Four types of characteristic behaviors of analyte elements were observed when the pH was varied. As can be seen in Fig. 2-1a, the recoveries of Ti, V, Fe, Mo, Sn, and W were maximum near pH 4. The recovery curves in Fig. 2-1b show that the recoveries of Al, Y, and REEs increased in the pH range of 2-5, and they were the largest near pH 5-6. On the other hand, Fig. 2-1c shows that the recoveries of Cu, Ni, Zn, and Co increased with the pH increase from 2 to 4, and they were almost constant at larger than 80% values in the pH range of 4-8. As is shown in Fig. 2-1d, the recoveries of Mn and Cd were constant at *ca.* 60% and *ca.* 100% above pH 6, while that of Cr was very poor in the pH range of 2-8.

It is further seen in Fig. 2-1 that the recoveries for most elements were generally very low in the pH range of 2-3. Since the iminodiacetate functional groups of the resin rarely dissociate proton at the lower pH, trace elements are prevented from adsorbing on the chelating resin through the complex formation,[23] which results in the poor recoveries of most heavy metals. It should be noted here that the recoveries of V, Mo, and W which form oxoanions decreased in the higher pH region. The following elements provided the largest recoveries at pH 3 for Sn, 4 for Ti, 4 for Fe, 6 for Al, and 5-6 for REEs. These pHs are close to the pH value at which hydroxides of these elements begin to precipitate.[24] Accordingly, these results indicate that the coordinations of the hydroxy groups with these elements increase at the higher pH, and thus the complex formations of these elements with the chelating resin are prohibited.

Next, the recoveries of Mn and Cd in seawater and in the aqueous solution were investigated at pH 4. As is seen in Fig. 2-1d, the recoveries of these elements were 4.0% for Mn and 19.8% for Cd in seawater. On the other hand, they were 38.7% for Mn and 78.7% for Cd in water. The results that the recoveries of Mn and Cd in the aqueous solution is larger at pH 4 than those in seawater may be explained by the formation of chloro-complexes of these elements in seawater.

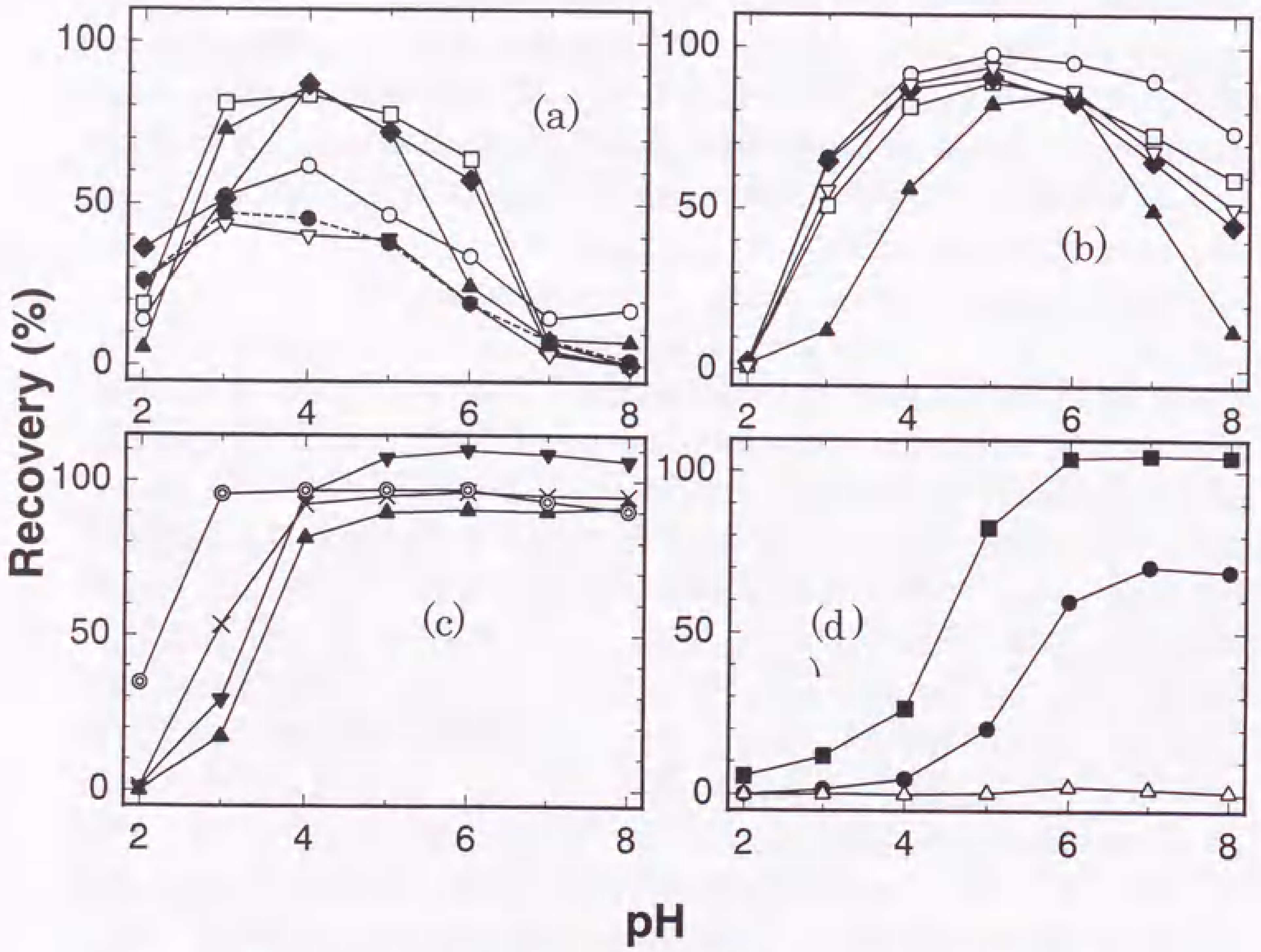

Fig. 2-1 pH dependence of the recoveries of trace elements in chelating resin preconcentration.

(a)▲ : Ti , □ : V, ○ : Fe, ◆ : Mo, ● : Sn, ▽ : W,
(b)▲ : Al, ○ : Y, □ : La, ◆ : Tb, ▽ : Lu,
(c)▲ : Co, × : Ni, ◎ : Cu, ▼ : Zn,
(d)△ : Cr(VI), ● : Mn, ■ : Cd.

Table 2-3. Recoveries of trace elements in chelating resin preconcentration at pH 4 and pH 6.

Element	pH 4		pH 6	
	Recovery/ %	RSD[a] / %	Recovery / %	RSD[a] / %
Al	48.7	14.7	72.6	0.6
Ti	86.0	5.7	27.8	21.2
V	87.6	10.8	63.9	6.8
Cr	0.6	13.1	8.0	12.0
Mn	4.0	8.0	53.9	3.0
Fe	91.8	7.9	55.9	17.4
Co	83.1	6.1	97.1	0.8
Ni	87.0	9.5	91.0	3.8
Cu	97.0	6.3	96.0	1.5
Zn	90.9	5.1	93.9	3.5
Ga	73.1	6.8	67.6	14.5
Y	80.9	5.4	91.3	1.9
Zr	38.5	5.7	14.3	2.2
Mo	86.1	10.7	57.8	9.1
Cd	19.8	13.0	85.5	4.4
Sn	52.9	7.9	33.0	2.7
La	80.4	5.3	89.3	1.3
Ce	82.0	5.2	87.9	1.6
Pr	84.8	5.2	89.5	1.4
Nd	82.3	5.0	88.8	1.1
Sm	85.5	5.4	90.8	1.7
Eu	86.6	4.9	91.4	2.0
Gd	79.6	4.7	89.4	1.7
Tb	87.0	4.7	92.8	1.7
Dy	80.6	4.9	90.0	2.2
Ho	81.0	4.6	90.3	2.0
Er	80.4	4.8	91.7	1.1
Tm	79.9	4.4	91.2	2.3
Yb	75.6	4.5	89.1	2.3
Lu	79.8	4.6	93.4	1.6
W	69.5	3.7	43.2	4.9
Pb	74.5	6.0	94.1	3.2
U	74.4	4.4	81.1	4.1

a) The RSDs were calculated from three replicate preconcentration procedures.

As is seen in Fig. 2-1, the larger recoveries of almost all elements were obtained in the pH range of 4-6. Thus, the recoveries of analyte elements at pH 4 and pH 6 were further examined in detail to decide the optimum pH value for simultaneous multielement preconcentration. The recoveries for 33 elements at pH 4 and pH 6 are summarized in Table 2-3. It is seen from Table 2-3 that the recoveries were more than 80% for 19 elements at pH 4 and for 22 elements at pH 6, respectively. The recoveries for Al, Mn, Co, Ni, Zn, Cd, Y, REEs, Pb, and U are larger at pH 6 than at pH 4. The relative standard deviations (RSDs) of almost all elements, except for Ti, Fe, and Ga, were also better at pH 6 than at pH 4. Accordingly, pH 6 was employed for simultaneous preconcentration of trace elements in seawater.

2-3-2 Removal of matrix elements adsorbed on the chelating resin.

It is known that alkaline earth elements are significantly adsorbed on the resin[10, 20, 21] when seawater is treated with the Chelex 100 resin. It has been, thus, proposed that alkaline earth elements retained on the resin should be removed by washing the resin with ammonium acetate aqueous solution so as to minimize matrix effect to analyte elements in the ICP-MS measurement.[10, 20, 21] However, when an excess amount of the buffer solution is used for washing the resin, significant amounts of analyte elements might be lost in this washing process.

Thus, removal of matrix elements was examined by using various volumes of ammonium acetate solution. The results are summarized in Table 2-4. Without washing, the concentrations of Na, Ca, and Mg were 50 mg $\mathrm{l^{-1}}$, 259 mg $\mathrm{l^{-1}}$, and 465 mg $\mathrm{l^{-1}}$, respectively. In this case, the total concentration of matrix elements was about 800 mg $\mathrm{l^{-1}}$. Table 2-4 shows that the concentrations of matrix elements decreased with increasing volume of ammonium acetate solution. The total concentration of Mg and Ca was below 200 mg $\mathrm{l^{-1}}$, when the washing volume was more than 8 ml. When the total concentration of matrix elements was 200 mg $\mathrm{l^{-1}}$, the signal intensities of most analyte elements in the ICP-MS measurement were suppressed by about 20%, compared to those for the matrix-free solution. However, the signal suppression at this level could be corrected by the internal standard method employed in the present experiment.

Table 2-4. Concentrations of major elements and the recoveries of trace elements in the analysis solution after chelating resin preconcentration.[a]

Element	Volume of ammonium acetate soln. / ml					
	0		8		15	
(A) Concentration of major element						
Na[b]	50.8	$\mathrm{mg\ l^{-1}}$	—[c]	$\mathrm{mg\ l^{-1}}$	—[c]	$\mathrm{mg\ l^{-1}}$
Ca[b]	259		85.0		65.3	
Mg[b]	465		95.2		84.0	
K[b]	—[c]		—[c]		—[c]	
Sr[b]	3.11		0.59		0.57	
Ba	0.0035		0.0005		0.0004	
(B) Recovery of trace element						
Al	87.8	%	86.2	%	83.5	%
Mn	58.0		55.8		59.9	
Co	99.6		98.1		100.4	
Ni	97.0		96.5		99.2	
Zn	100.2		96.7		98.7	
Cd	92.9		96.0		95.6	
La	96.1		95.3		92.5	
Eu	93.1		94.4		86.0	
Lu	94.9		92.6		82.3	
U	87.6		86.5		84.8	

a) The analysis solution was obtained by the recommended preconcentration procedure described in the experimental section.
b) Measured by ICP-AES.
c) Not detected.

The recoveries for Al, Mn, Co, Ni, Zn, Cd, and U were almost constant with and without washing. However, the recoveries for REEs decreased by about 10%, when the resin was rinsed with 15 ml of ammonium acetate solution. As a result, taking into consideration both removal of major elements and the recoveries of trace elements, the compromised washing volume of ammonium acetate solution was chosen to be 8 ml.

The elution of trace elements from the resin was investigated by eluting each 2-ml fraction of 2 M HNO_3. Almost all elements were completely removed with 4 ml of 2 M HNO_3. Since at least 5 ml of the sample solution was necessary for the ICP-MS measurement, analyte elements on the resin were eluted with 6 ml of 2 M HNO_3.

2-3-3 Correction of polyatomic and divalent ion interferences.

In the ICP-MS measurement, major elements in the sample solution often cause spectral interferences with analyte elements due to polyatomic and divalent ions.[26] Thus, polyatomic and divalent ion interferences to all analyte elements were examined.

Table 2-5. Polyatomic and divalent ions and their interference correction coefficients for each analyte element in the ICP-MS measurement after chelating resin preconcentration.

element	polyatomic and divalent ion	interference correction coefficient[a)] ng l^{-1} / μg l^{-1}
^{57}Fe	$^{40}Ca^{16}O^{1}H$, $^{40}Ca^{17}O$	3.02
^{59}Co	$^{43}Ca^{16}O$	5.4×10^{-4}
^{111}Cd	$^{95}Mo^{16}O$	1.75
^{157}Gd	$^{141}Pr^{16}O$	123
^{159}Tb	$^{143}Nd^{16}O$	2.01

a) The correction coefficient is defined as the ratio of the apparent concentration (ng l^{-1}) of the interfered element provided by 1 μg l^{-1} of the interference element which produces polyatomic or divalent ions shown in the table.

The ions subjected to correction in the present experiment are listed in Table 2-5, together with their interference correlation coefficients. The interference correction coefficients (ng l^{-1} / μg l^{-1}) in Table 2-5 are expressed as the apparent analyte concentration (ng l^{-1}) which is provided by 1 μg l^{-1} of each interferent element at the mass number of analyte element. As is shown in Table 2-5, ^{57}Fe and ^{59}Co overlap with $^{40}Ca^{16}O^{1}H$ and $^{43}Ca^{16}O$.[27)] The interference of $^{95}Mo^{16}O$ with ^{111}Cd is not negligible because the ratio of Mo to Cd in seawater is usually ca. 300. Although monoxide ions of light REEs often interfere with heavy REEs, the interference of $^{141}Pr^{16}O$ with ^{157}Gd was particularly severe in the present experiment.[28)]

The following simple formula was used for correction of polyatomic ion interference, where the correction coefficient is assumed to be a linear function of the concentration of analyte element examined : [27,29)]

$$C_{cor} = C_{obs} - F \times C_{int} \qquad (1)$$

where C_{cor}, C_{obs}, F, and C_{int} are the corrected concentration of analyte element (ng l^{-1}), the observed concentration of analyte element (ng l^{-1}), interference correction coefficient (ng l^{-1} / μg l^{-1}), and the concentration of the inteferent element (μg l^{-1}).

When $F \times C_{int}$ is comparable to or larger than C_{obs}, a large error may be caused in estimation of the corrected concentration of analyte element. In Table 2-5, the ratio of ($F \times C_{int}$) to the observed concentration (C_{obs}) was larger than 1 in the cases of Fe, while those of other elements were much smaller than 1. Thus, the concentration of Fe in Table 2-7 was shown in the parentheses just for reference.

2-3-4 Analytical figure of merit.

In order to evaluate the lower limit of determination by the present method, the analytical detection limits were estimated from the instrumental detection limits, taking into account the concentration factor and the recovery values. The instrumental detection limits were obtained as the concentration of analyte element corresponding to 3-fold the standard deviation (3σ) of background signal intensities for the blank solution (2 M HNO_3), where the standard deviation was calculated from the 10-times repeated measurements at each mass number. The analytical detection limits estimated are shown in Table 2-6. As can be seen in Table 2-6, the analytical detection limits for 33 elements were in the range from 0.1 μg l^{-1} of Fe to 0.000007 μg l^{-1} of Ho. The poor detection limits of ^{52}Cr and ^{57}Fe may be ascribed to large background intensities due to isobaric molecular ions such as $^{40}Ar^{12}C$ and $^{40}Ar^{16}O^{1}H$,[30)] respectively, together with their low recovery values (Cr : 8.0%, Fe : 55.9%).

The blank values in the present method are also summarized in Table 2-6. The blank values were almost negligible because they were much lower than the abundances of analyte elements in seawater.

Table 2-6. Analytical detection limits and blank values obtained by ICP-MS with chelating resin preconcentration.

Element	m/z	Analytical detection limit[a)] μg l^{-1}	Blank value μg l^{-1}	Element	m/z	Analytical detection limit[a)] μg l^{-1}	Blank value μg l^{-1}
Al	27	0.005	0.070	La	139	0.00002	0.00029
Ti	47	0.04	0.05	Ce	140	0.00002	0.00018
V	51	0.0003	0.0007	Pr	141	0.000008	0.000044
Cr	52	0.02	—[b)]	Nd	146	0.00002	0.00008
Mn	55	0.0004	0.0058	Sm	147	0.00003	0.00004
Fe	57	0.1	—[b)]	Eu	151	0.00001	0.00002
Co	59	0.0001	0.001	Gd	157	0.00007	0.00003
Ni	62	0.0009	0.0086	Tb	159	0.00001	0.00002
Cu	63	0.0002	0.0036	Dy	163	0.00002	0.00004
Zn	68	0.002	0.039	Ho	165	0.000007	0.000015
Ga	69	0.00005	0.00020	Er	166	0.00002	0.00003
Y	89	0.00001	0.00017	Tm	169	0.000008	0.000015
Zr	90	0.008	—[b)]	Yb	174	0.00003	—[b)]
Mo	95	0.004	—[b)]	Lu	175	0.000009	0.000014
Cd	111	0.0001	0.0007	W	184	0.0003	—[b)]
Sn	118	0.0008	0.016	Pb	208	0.0001	0.011
				U	238	0.04	0.05

a) Analytical detection limits were calculated from instrumental detection limits, taking into account the concentrated factor(41.7) and recovery values.

b) Not detected.

2-3-5 Determination of trace elements in coastal seawater reference material (CASS-3)

Trace elements in coastal seawater reference material CASS-3 were determined by the present analytical method. The results are summarized in Table 2-7, along with the certified and reference values.$^{12, 15, 31, 32)}$ As is seen in Table 2-7, the concentrations of 29 elements (Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Y, all-REEs, W, Pb, and U) in CASS-3 were obtained in the present study. In addition, since Ti and W provided the recovery values below 50% and the correction percentage of isobaric ion interference for Fe was larger than 50%, the concentrations of these elements were seemingly less reliable, and then they are shown in the parentheses for reference in Table 2-7. Although we also tried to determine Cr, Ga, Zr, and Sn, their concentrations were below the analytical detection limit. It is seen in Table 2-7 that the relative standard deviations (RSDs) for 27 elements in CASS-3 were less than 10%.

The analytical results for Mn, Co, Ni, Cu, Zn, Mo, Cd, and Pb were in rather good agreement with the certified values issued from NRC. As for the elements whose certified values have been not issued from NRC, their concentrations were compared with the literature values for CASS-3$^{12, 32)}$ or CASS-2.$^{15, 31)}$ It is seen in Table 2-7 that the analytical results for Al and V were also in good agreement with the literature values. Since the concentrations of REEs for CASS-3 have been not reported so far, the literature values for REEs in CASS-2 are listed in Table 2-7. As is seen in Table 2-7, the concentrations of REEs in CASS-3 were much higher than those in CASS-2.

2-3-6 Determination of trace elements in the coastal seawater collected from the Ise Bay

The analytical method explored in the present experiment was also applied to the determination of trace elements in the coastal seawater sample collected off-shore of the Ise Bay near Tokoname. The results are summarized in Table 2-7. The analytical values for 29 elements were also obtained in the concentration range over 5 orders of magnitude from 9.20 μg l^{-1} of Mo to 0.000320 μg l^{-1} of Tm. The RSDs for the analytical values were below 10% except for Ti, V, Mn, Fe, Mo, W, and Pb. The concentrations of V, Mo, and U in coastal seawater from the Ise Bay were almost at the same levels as those in CASS-3. These results indicate that V, Mo, and U exist as the stable oxo-ions, and thus it can be considered that they are well mixed and keep their concentrations almost constant over all the sea areas of the world. The concentrations of Al, Mn, and Pb are relatively higher in the Ise Bay, compared to those in CASS-3, while those of Cd and REEs are lower. Aluminum, Mn, and Pb are known as the anthropogenic elements : thus the higher concentrations of these elements in the coastal area of the Ise Bay may be caused by the terrestrial supply or artificial pollution.

Table 2-7. Analytical results for trace elements in coastal seawater reference material CASS-3 and Ise Bay seawater sample determined by ICP-MS after chelating resin preconcentration.

Element	CASS-3		Ise Bay seawater
	concentration$^{a)}$	certified or literature value	concentration$^{a)}$
	μg l^{-1}	μg l^{-1}	μg l^{-1}
Al	0.32 ± 0.03	0.389$^{b)}$	2.11 ± 0.11
Ti	(0.10 ± 0.03)		(0.15 ± 0.03)
V	1.43 ± 0.04	1.50$^{c)}$, 2.49$^{d)}$	1.39 ± 0.20
Mn	2.71 ± 0.17	2.51 ± 0.36	4.35 ± 1.09
Fe	(2.3 ± 0.4)	1.26 ± 0.17	(0.8 ± 0.1)
Co	0.038 ± 0.003	0.041 ± 0.009	0.056 ± 0.004
Ni	0.39 ± 0.01	0.386 ± 0.062	1.32 ± 0.11
Cu	0.48 ± 0.01	0.517 ± 0.062	0.62 ± 0.01
Zn	1.38 ± 0.03	1.24 ± 0.25	1.68 ± 0.11
Y	0.024 ± 0.0004		0.034 ± 0.002
Mo	9.98 ± 0.71	8.95 ± 0.26	9.20 ± 1.75
Cd	0.032 ± 0.002	0.030 ± 0.005	0.012 ± 0.0009
La	0.014 ± 0.0004	0.00510$^{e)}$	0.0075 ± 0.0004
Ce	0.0061 ± 0.0003	0.00159$^{e)}$	0.0048 ± 0.0003
Pr	0.0021 ± 0.00004	0.00052$^{e)}$	0.0013 ± 0.00009
Nd	0.0089 ± 0.0001	0.00222$^{e)}$	0.0057 ± 0.0003
Sm	0.0069 ± 0.0003	0.00191$^{e)}$	0.0013 ± 0.00005
Eu	0.00037 ± 0.00002	0.00007$^{e)}$	0.00027 ± 0.00003
Gd	0.0021 ± 0.0001	0.00046$^{e)}$	0.0023 ± 0.0002
Tb	0.00030 ± 0.00002	0.00006$^{e)}$	0.00035 ± 0.00003
Dy	0.0020 ± 0.00008	0.00050$^{e)}$	0.0028 ± 0.0001
Ho	0.00051 ± 0.00003	0.00015$^{e)}$	0.00070 ± 0.00006
Er	0.0016 ± 0.00002	0.00040$^{e)}$	0.0021 ± 0.00012
Tm	0.00025 ± 0.00002	0.00006$^{e)}$	0.00032 ± 0.00002
Yb	0.0016 ± 0.00009	0.00048$^{e)}$	0.0022 ± 0.00008
Lu	0.00027 ± 0.00001	0.00007$^{e)}$	0.00037 ± 0.00001
W	(0.012 ± 0.001)		(0.037 ± 0.007)
Pb	0.0095 ± 0.0007	0.012 ± 0.004	0.032 ± 0.006
U	3.35 ± 0.09	2.84	3.54 ± 0.19

a) The mean value and standard deviation obtained by 3-times measurements. Data in the parentheses are the results for the elements with the recovery values lower 50% or isobaric ion interference correction larger than 50%.

b) Literature value for CASS-2, cited from Ref. 31.

c) Cited from Ref. 32.

d) Cited from Ref. 12.

e) Literature values for CASS-2, cited from Ref. 15.

2-3-7 REE patterns of coastal seawater

There are no saline water reference materials for which the concentrations of REEs are certified. Thus, the REE distribution patterns which are shown as the relative concentrations of REEs normalized to their concentrations in chondrite or shale[10, 33] are often examined in order to evaluate internal consistency of the REEs data. Such REE patterns for CASS-3, CASS-2 and Ise Bay seawater are shown in Fig. 2-2, where the concentrations of REEs were normalized to those in Post Australian Average Shale.[34] As is seen in Fig. 2-2, the REE patterns show the quite smooth curves. It is noted here that the concentrations of heavy REEs are relatively higher than those of light REEs, and the negative anomalies of Ce are clearly observed for all seawater samples, in similarity to the previous reports.[10, 33] A high concentration of Sm was observed for CASS-3 in the present work. Such high concentration of Sm was also reported for CASS-2 in the previous work.[15] Jarvis et al.[15] suggested that the high concentration of Sm in CASS-2 might be due to contamination occurred at some stage in preparation procedure of the reference material. Since the concentration of Sm in the off-shore seawater from the Ise Bay was not relatively high, it may be reasonable to consider that Sm in CASS-3 and CASS-2 was contaminated during preparation of these reference materials.

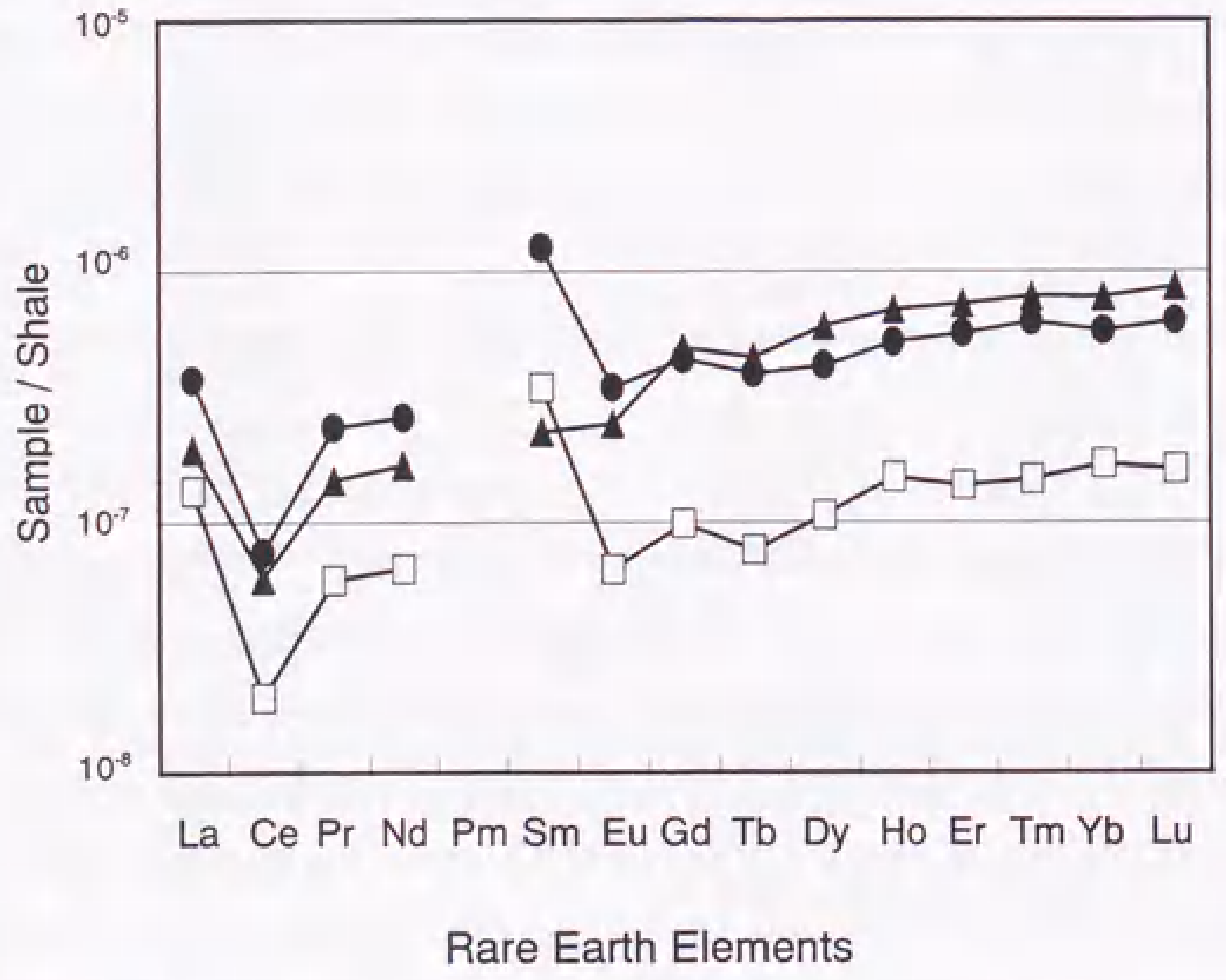

Fig. 2-2 Shale-normalized REE patterns of coastal seawaters.

● : CASS-3, ▲ : Ise Bay seawater, □ : CASS-2 (cited from Ref.15)

2-4 Conclusion

The concentrations of 29 elements in the coastal seawater samples could be determined by ICP-MS after chelating resin preconcentration. The analytical values for most elements in coastal seawater reference material (CASS-3) were in rather good agreement with the certified values (Mn, Co, Ni, Cu, Zn, Mo, Cd, and Pb). These results indicate that the present method is reliable enough to apply to the multielement determination of trace elements in seawater. The concentrations of V, Mo, and U are at almost the same level in the coastal seawater samples from both CASS-3 and the Ise Bay. In terms of REEs, their concentrations obtained in the present experiment were almost the same in both CASS-3 and the coastal seawater from the Ise Bay, although they were quite different from the literature values of CASS-2. In addition, it was found from the comparison of the REE patterns that the concentration of Sm in CASS-3 and CASS-2 was remarkably high, perhaps due to contamination.

References

1) Y. Nozaki, *EOS Trans. AGU,* **78**, 221-225 (1997).

2) H. Sawatari, T. Hayashi, E. Fujimori, A. Hirose, and H. Haraguchi, *Bull. Chem. Soc. Jpn*., **69**, 1925-1931 (1996).

3) H. Sawatari, E. Fujimori, and H. Haraguchi, *Anal. Sci.*, **11**, 369-374 (1995).

4) J. Wu and E. A. Boyle, *Anal. Chem.*, **69**, 2464-2470 (1997).

5) J. Wu and E. A. Boyle, *Anal. Chim. Acta*, **367**, 183-191 (1998).

6) J. W. McLaren, K. W. M. Siu, J. W. H. Lam, S. N. Willie, P. S. Maxwell, A. Palepu, M. Koether, and S. S. Berman, *Fresenius J. Anal. Chem*., **337**, 721-728 (1990).

7) Y. Sohrin, S. Iwamoto, S. Akiyama, T. Fujita, T. Kujii, H. Obata, E. Nakayama, S. Goda, Y. Fujishima, H. Hasegawa, K. Ueda, and M. Matsui, *Anal. Chim. Acta*, **363**, 11-19 (1998).

8) S. N. Willie, Y. Iida, and J. W. McLaren, *At. Spectrosc*., **19**, 67-72 (1998).

9) M. Wells and K. Bruland, *Mar. Chem*., **63**, 145-153 (1998).

10) H. Sawatari, T. Toda, T. Saizuka, C. Kimata, A. Itoh, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **68**, 3065-3070 (1995).

11) P. Möller, P. Dulski, and J. Luck, *Spectrochim. Acta*, **47B**, 1379-1387 (1992).

12) K. Yang, S. Jiang, and T. Hwang, *J. Anal. At. Spectrom.*, **11**, 139-143 (1997).

13) D. S. R. Murty and G. Chakrapani, *J. Anal. At. Spectrom.,* **11**, 815-820 (1996).

14) L. Halicz, I. Gavrieli, and E. Dorfman, *J. Anal. At. Spectrom.,* **11**, 811-814 (1996).

15) K. E. Jarbis, J. G. Williams, E. Alcantara, and J. D. Wills, *J. Anal. At. Spectrom*., **11**, 917-922 (1996).

16) D. B. Taylor, H. M. Kingston, D. J. Nogay, D. Koller, and R. Hutton, *J. Anal. At. Spectrom,*. **11**, 187-191 (1996).

17) A. Seubert, G. Petzold, and J. W. McLaren, *J. Anal. At. Spectrom*., **10**, 371-379 (1996).

18) M. B. Shabani, T. Akagi, H. Shimizu, and A. Masuda, *Anal. Chem*., **62**, 2709-2714 (1990).

19) G. J. Batterham, N. C. Munksgaard, and D. L. Parry, *J. Anal. At. Spectrom.,* **12**, 1277-1280 (1997).

20) C. J. Cheng, T. Akagi, and H. Haraguchi, *Anal. Chim. Acta*, **198**, 173-181 (1987).

21) H. M. Kingston, I. L. Barnes, T. J. Bredy, T. C. Rains, and M. A. Champ, *Anal. Chem*., **50**, 2064 – 2097 (1978).

22) S.Pai, T. Fang, C. Chen, and K. Jeng, *Mar. Chem*., **29**, 295-306 (1990).

23) D. Leyden and A. Underwood, *J. Phys. Chem*., **68**, 2093-2097 (1964).

24) G. Charlot, authorized translation by R. C. Mullay, “Qualitative Inorganic Analysis” London : Methuen, New York : John Wiley & Sons, pp.153-186, pp.221-241 (1954).

25) W. Doherty, *Specrochim. Acta*, **47B**, 263-280 (1989).

26) M. A. Vaughan and G. Horlick, *Appl. Spectrosc*., **40**, 434-445 (1986).

27) A. R. Date, Y. Y. Cheung, and M. E. Stuart, *Spectrochim. Acta*, **42B**, 3-20 (1987).

28) F. Vanhaecke, C. Vandecasteele, H. Vanhoe, and R. Dams, *Microchim. Acta*, **108**, 41-51 (1992).

29) M. A. Vaughan and G. Horlick, *Appl. Spectrosc*., **44**, 587-593 (1990).

30) S. H. Tan and G. Horlick, *Appl. Spectrosc.*, **40**, 445-460 (1986).

31) I. Roduskin and T. Rush, *J. Anal. At. Spectrom*., **12**, 1181-1185 (1997).

32) G. Chapple and J. P. Byrne, *J. Anal. At. Spectrom*., **11**, 549-553 (1997).

33) H. J. W. de Baar, M. P. Bacon, P. G. Brewer, and K. W. Bruland, *Geochim. Cosmochim. Acta*, **49**, 1943-1959 (1985).

34) S. R. Taylor and S. M. McLennan, “The Continental Crust : Its Composition and Evolution. An Examination of the Geochemical Record Preserved in Sedimentary Rocks”, Blackwell (1985).

Chapter 3 Simultaneous Multielement Determination of Hydride- and Oxoanion-Forming Elements in Seawater by Inductively Coupled Plasma Mass Spectrometry after Lanthanum Coprecipitation

3-1 Introduction

The concentration levels of major elements such as Na, Mg, K, and Ca in seawater are almost constant all over the sea, while those of trace elements often show some local distributions and characteristic behaviors. In addition, the concentration variations of such trace elements often reflect some physicochemical and/or biochemical changes in the sea,1) even though their concentrations in seawater are extremely low. Thus, the accurate determination of trace elements in seawater is still important to elucidate their roles in the aquatic system or to evaluate environmental pollution in the sea. It is, therefore, desirable to determine as many as possible of major-to-ultratrace elements for comprehensive appreciation of the distributions of trace elements and their multielement correlation in the marine environment.

Inductively coupled plasma mass spectrometry (ICP-MS) has been developed as an analytical method for the determination of trace and ultratrace elements. This method has excellent analytical features, such as simultaneous multielement detection capability, extremely high sensitivity and wide linear dynamic ranges for most metallic elements. Consequently, ICP-MS has been extensively applied to the analyses of various kinds of samples including seawater. However, major elements such as Na, K, Mg, and Ca in seawater often cause serious matrix interferences with trace elements in the ICP-MS measurement.1,2) Therefore, various pretreatment methods for both preconcentration of trace elements and elimination of major elements have been developed to perform the accurate determination of trace elements at the μg l^{-1} or ng l^{-1} level by ICP-MS. As the preconcentration methods for trace elements in seawater, coprecipitation2,3), chelating resin preconcentration4-8), and solvent extraction method9,10) have been widely employed so far. The present authors reported that 29 elements in coastal seawater could be simultaneously determined by ICP-MS with the multielement preconcentration method using a chelating resin.4) However, it was found that the hydride-forming elements (As, Se, Sb, Sn, and Bi) and oxoanion-forming elements (Cr and W) could not be determined by the chelating resin preconcentration method because of the poor recoveries of these elements. Among these elements, some of the hydride-forming elements have been usually determined with a hydride generation method.[11-13] Unfortunately, however, the hydride generation method is not adequate as a pretreatment technique for the simultaneous multielement determination of trace elements in seawater by ICP-MS.

Lanthanum coprecipitation, which has been used for the preconcentration of trace elements in river water[14-16] and industrial waste water[17] in inductively coupled plasma atomic emission spectrometry (ICP-AES) or atomic absorption spectrometry (AAS), can efficiently preconcentrate the hydride-forming elements. However, lanthanum coprecipitation has not been applied to the preconcentration of such elements at the ultratrace level in ICP-MS. In addition, the coprecipitation capability of lanthanum for the elements such as Cr, V, Mo, W, and U, which mostly exist as oxoanion compounds in seawater, has not been examined yet.

In the present study, hence, lanthanum coprecipitation was applied to the preconcentration of hydride- and oxoanion-forming elements for the simultaneous multielement determination by ICP-MS. The pH dependence of the coprecipitation efficiencies, spectral interferences due to lanthanum as a carrier, and analytical figures of merit in lanthanum coprecipitation preconcentration were investigated for the multielement determination of hydride- and oxoanion-forming elements by ICP-MS. The coprecipitation efficiencies for Cr, As, Sb, and Se with the different oxidation states were also examined, because the effects of the oxidation states on the recoveries in lanthanum coprecipitation have not been reported except for Se.[16] In order to evaluate the analytical reliability, the present lanthanum coprecipitation/ICP-MS method was applied to the analysis of coastal seawater reference material (CASS-3) issued from National Research Council of Canada (NRC). In the present experiment, Mn and Y were also determined by the lanthanum coprecipitation/ICP-MS method, because their certified and reference values are provided for CASS-3.

3-2 Experimental

3-2-1 Instruments

An ICP-MS instrument model SPQ 8000A (Seiko Instruments Inc., Chiba) was used for the determination of trace elements; it consisted of a quadrudpole-type mass

spectrometer. An ICP-AES instrument model Plasma AtomComp MKII (Jarrell-Ash, Franklin, MA, USA) with a polychromator of Paschen-Runge mounting was also used for the simultaneous multielement determination of major and minor elements. The instrumental components and operating conditions are shown in Table 1. These operating conditions were chosen after optimization of each instrumental parameter in the ICP-MS and ICP-AES instruments. A model twin pH meter from Horiba (Kyoto) was used for pH adjustment.

3-2-2 Chemicals

Nitric acid and aqueous ammonia solution used were of electronics industry grade (Kanto Chemicals, Tokyo). The multielement standard solutions for standardization of the calibration curves were prepared by mixing the single-element standard stock solutions (1000 μg l^{-1}) of each element for atomic absorption spectrometry, purchased from Wako Chemicals (Osaka). The standard stock

Table 3-1. Operating conditions for ICP-MS and ICP-AES instruments

ICP-MS : Seiko SPQ 8000A	
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 16 l min^{-1}
Auxiliary gas flow rate	Ar 1.0 l min^{-1}
Carrier gas flow rate	Ar 1.0 l min^{-1}
Sampling depth	12 mm from load coil
Nebulizer:	concentric type
Sample uptake rate	1.0 ml min^{-1}
Data acquisition :	
Dwell time	10 ms/channel
Data points	3 points/peak
Number of scans	100
ICP-AES : Jarrell-Ash Plasma AtomComp MK II	
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 20 l min^{-1}
Auxiliary gas flow rate	Ar 1.0 l min^{-1}
Carrier gas flow rate	Ar 0.48 l min^{-1}
Observation height	18 mm above load coil
Nebulizer:	cross-flow type
Sample uptake rate	1.2 ml min^{-1}
Polychromator:	Paschen-Runge (75 cm focal length)
Grating	2400 grooves/mm
Entrance slit width	25 μm
Exit slit width	50 μm

solutions for Cr(III), As(V), Sb(III), Sb(V), and Se(VI) were prepared as follows: the Cr(III) solution was prepared by dissolving high purity metal of guaranteed reagent grade (Nakarai Tesque, Kyoto) in 3 M HCl solution, As(V) solution by dissolving potassium arsenate of chemical grade (Wako Chemicals) in pure water, Sb(III) solution by dissolving dipotassium bis(tartrato) diantimonate(III) of extra grade (Wako Chemicals) in 3 M HCl solution, Sb(V) solution by dissolving potassium hexahydroxoantimonate of guaranteed reagent grade (Nakarai Tesque) in 3 M HCl solution, and Se(VI) solution by dissolving sodium selenate of extra grade (Wako Chemicals) in pure water. The lanthanum solution for the coprecipitation carrier was prepared by dissolving 3 g of $La(NO_3)_3$ (extra grade; Wako Chemicals) in 100 ml of 0.1 M HNO_3 so as to provide 10 g l^{-1} of La. Purified water used throughout the present experiment was prepared by a Milli-Q purification system (Nihon Millipore Kogyo, Tokyo).

3-2-3 Seawater samples

Coastal seawater reference material CASS-3 was obtained from the National Research Council of Canada (NRC) for evaluation of the present analytical method. Some coastal seawater samples collected at about 1 km off-shore from Tokoname (Aichi Prefecture) in Ise Bay were also used for the recovery test in the present experiment. The artificial seawater, which was used for the recovery test of Cr, As, Sb, and Se with different oxidation states, was prepared by dissolving 23.4 g of NaCl, 10.6 g of $MgCl_2 \cdot 6H_2O$, 1.40 g of $CaCl_2 \cdot 2H_2O$, and 3.92 g of Na_2SO_4 (extra grade; Wako Chemicals) in 1 l of pure water after the reference[18)].

3-2-4 Preconcentration procedure

The following preconcentration procedure for trace elements in the coastal seawater samples was established after optimization, as will be described later. First, 250 ml of the coastal seawater sample was taken in a beaker; into this, 2 ml of the lanthanum solution (10 g l^{-1}) was added. Then the solution was stirred with a magnetic stirrer for *ca.* 5 min. After pH adjustment of the sample solution to 9.5 with aqueous ammonia solution, the sample solution was kept standing for 2 h to complete precipitation. The precipitate which formed was collected on a PTFE membrane filter (pore size 0.45 μm) by filtration. After washing with 30 ml of pure water, the precipitate was dissolved with 90 ml of 2 M HNO_3; into this, 10 ml of mixed solution of Ge, In, Re, and Tl (100 μg l^{-1} each) was added as the internal standard elements for correction of matrix effect due to major elements.[3)] Consequently, 2.5-fold preconcentration was achieved by the present procedure. This solution was used as the analysis solution to the ICP-MS and ICP-AES measurements.

When the recoveries of Cr, As, Se, and Sb with different oxidation states were investigated, the artificial seawater was used to avoid the disturbances caused by these elements with natural abundances in seawater. Two kinds of recovery test solutions were prepared in order to avoid the oxidation–reduction reactions among the elements. One of them was the solution for the lower oxidation states and the other for the higher oxidation states. Proper amounts of the standard stock solutions of Cr(III), As(III), Sb(III), and Se(IV) were added to the artificial seawater to prepare 250 ml of the test solution for the lower oxidation state, and those of Cr(VI), As(V), Sb(V), and Se(VI) were added to another sample of artificial seawater to prepare 250 ml of the test solution for the higher oxidation state. These two test solutions were subjected to the lanthanum coprecipitation procedure mentioned above.

The polyatomic ion interferences due to Ca, which remained as a matrix element in the analysis solution, were corrected by the interference correction coefficient method.[4)]

3-3 Results and Discussion

3-3-1 pH dependence of removal of major elements and recoveries of trace elements in lanthanum coprecipitation

The removal of major elements (Na, K, Mg, and Ca), and recoveries of trace elements and La in lanthanum coprecipitation were examined in the pH range of 9.1-9.9, where the preconcentration procedure described in the experimental section was carried out. Since lanthanum hydroxides begin to precipitate near pH 8 and a large amount of Mg precipitates above pH 10[19)], the pH dependence of removal of major elements was examined in the pH range 9-10. The concentrations of major elements such as Na, Ca, and Mg which remained in the analysis solution after lanthanum coprecipitation are shown in Fig. 3-1. The concentration of Mg was less than 10 mg l^{-1} below pH 9.5, while it increased to 1000 mg l^{-1} at pH 9.9, while those of Na and Ca were less than 10 mg l^{-1} and that of K was below the detection limit in the pH range of 9.1-9.9. Thus, the pH dependence at pH values above 10 was not examined because introduction of the solution containing more than 1000 mg l^{-1} of Mg into the argon ICP caused serious problems (e.g., cloggings of the plasma torch and the sampling interface) in the ICP-MS instrument.

The recoveries of V, Mn, Sb(V), W, and U as well as La in the pH range of 9.1-

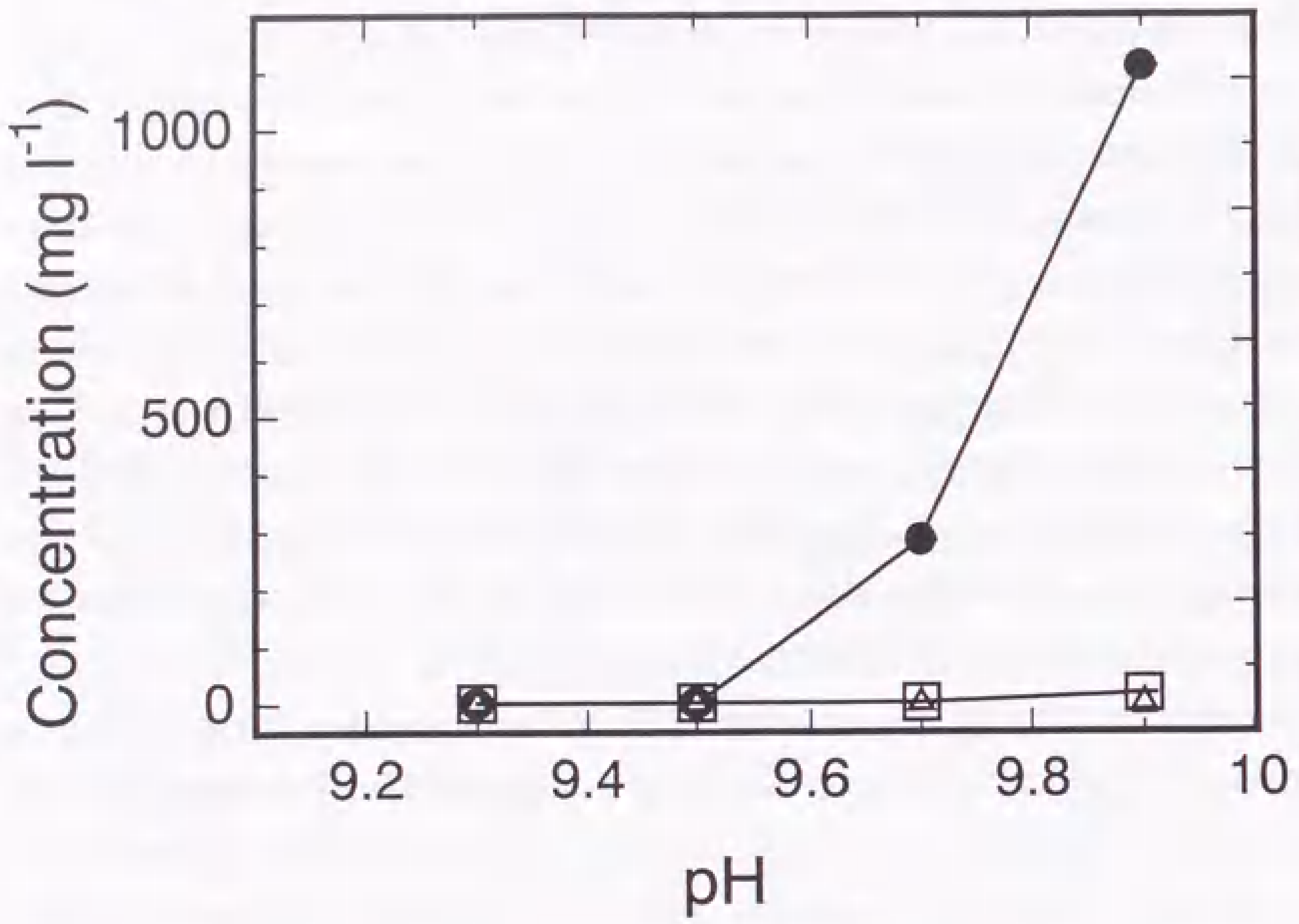

Fig. 3-1 pH dependence of the concentrations of major elements in the analysis solution after La coprecipitation.

● : Mg, □ : Ca, △ : Na.

9.9 are shown in Fig. 3-2, as some typical examples. It is seen in Fig. 3-2 that La was recovered almost 100% in the whole pH range of 9.1-9.9. This result indicates that La is suitable enough as the coprecipitation carrier in the pH range of 9.1-9.9. The recoveries of V, Sb(V), W, and U were almost constant, larger than 85%, while that of Mn provided the maximum value of about 85% near pH 9.5.

In consequence, taking into consideration both the removal efficiencies of major elements and the recoveries of trace elements, we chose pH 9.5 as the optimum pH for lanthanum coprecipitation of trace elements in seawater. Under the optimum conditions, the recoveries of almost all the trace elements examined here were more than 85%, and the total concentration of major matrix elements (Na, K, Mg, Ca) originated from seawater was less than 20 mg l^{-1} in the analysis solution.

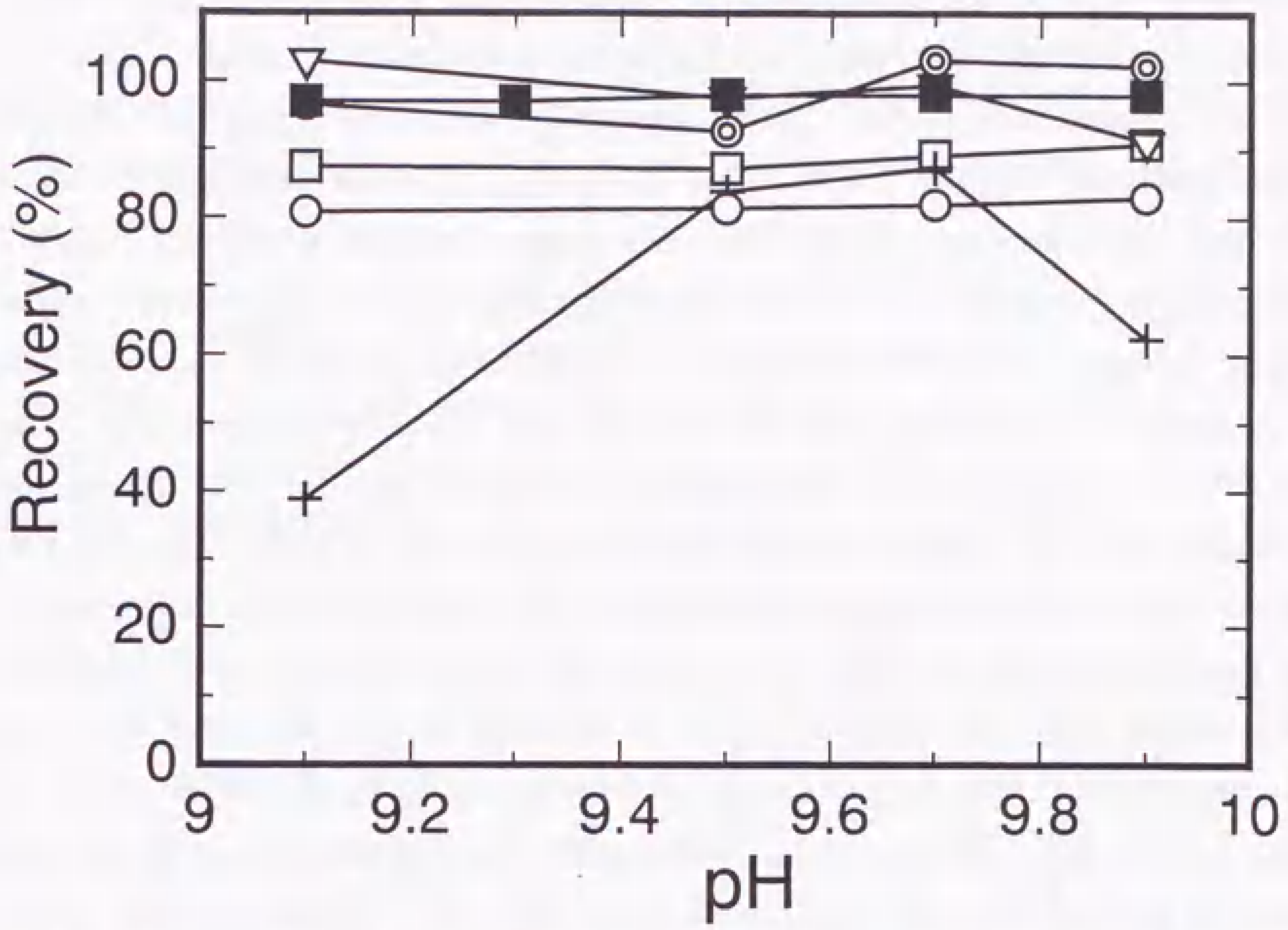

Fig. 3-2 pH dependence of recoveries of La and trace elements in La coprecipitation.
■ : La, □ : V, + : Mn, ◎ : Sb, ○ : W, ▽ : U.

3-3-2 Spectral interferences of lanthanum in ICP-MS measurement

In the ICP-MS measurement, matrix elements in the analysis solution often cause spectral interference with analyte elements, when they provide some polyatomic and divalent ions. In the present coprecipitation method, the concentration of La used as the coprecipitation carrier was *ca.* 200 mg l^{-1} in the analysis solution, and then it became a matrix element in the analysis solution. Thus, possible interferences of polyatomic and divalent ions due to La were examined by measuring the ICP-MS spectrum over the whole mass range. In Fig. 3-3, the ICP-MS spectra in the m/z ranges of 65-79 and 141-180 are illustrated, when 200 mg l^{-1} of lanthanum solution in 2 M HNO_3 and the blank solution (2 M HNO_3) were introduced into the plasma. The ICP-MS spectrum in the mass range of 80-140 was not shown in Fig. 3-3, because no significant polyatomic ion peaks due to La were observed in this mass range. The largest peak observed in the mass range of 65-79 is ascribed to the divalent ion of $^{139}La^{2+}$ near m/z 69, where the major isotope of ^{69}Ga (60.11%) is observed. Thus, the determination of Ga by the lanthanum coprecipitation/ICP-MS method is not possible by the measurement of major isotope of ^{69}Ga, and then Ga should be determined at m/z 71 with the abundance of 39.89%. In the spectrum in the mass range of 140-180, the polyatomic ions of ^{139}La^{14}N, ^{139}La^{16}O, ^{139}La^{17}O, ^{139}La^{18}O, and ^{139}La^{16}O^{1}H were observed in the mass range between 153 to 158. The peaks observed at m/z 141 and 142 corresponded to ^{141}Pr and ^{142}Ce, respectively, which were concomitant elements in the lanthanum solution. Two smaller peaks were also observed at m/z 171 and 179; these were attributed to polyatomic ions of ^{139}La^{16}O$_2^+$ and ^{139}La^{40}Ar$^+$, respectively. The polyatomic ion species of La observed in the m/z range 140-180 caused the interferences with rare earth elements, especially Eu, Gd, and Tb, and thus the lanthanum coprecipitation/ICP-MS method could not be applied to the determination of rare earth elements at the trace level. Since rare earth elements can be effectively preconcentrated with the chelating resin, it is better to use the chelating resin preconcentration/ICP-MS method for the determination of rare earth elements, as reported previously.[4] In consequence, the divalent and polyatomic ions of La were not prone to interfere with the elements listed in Table 3-2. Furthermore, no severe polyatomic ion interferences of ^{35}Cl^{16}O and ^{40}Ar^{35}Cl with ^{51}V and ^{75}As, respectively, were observed.

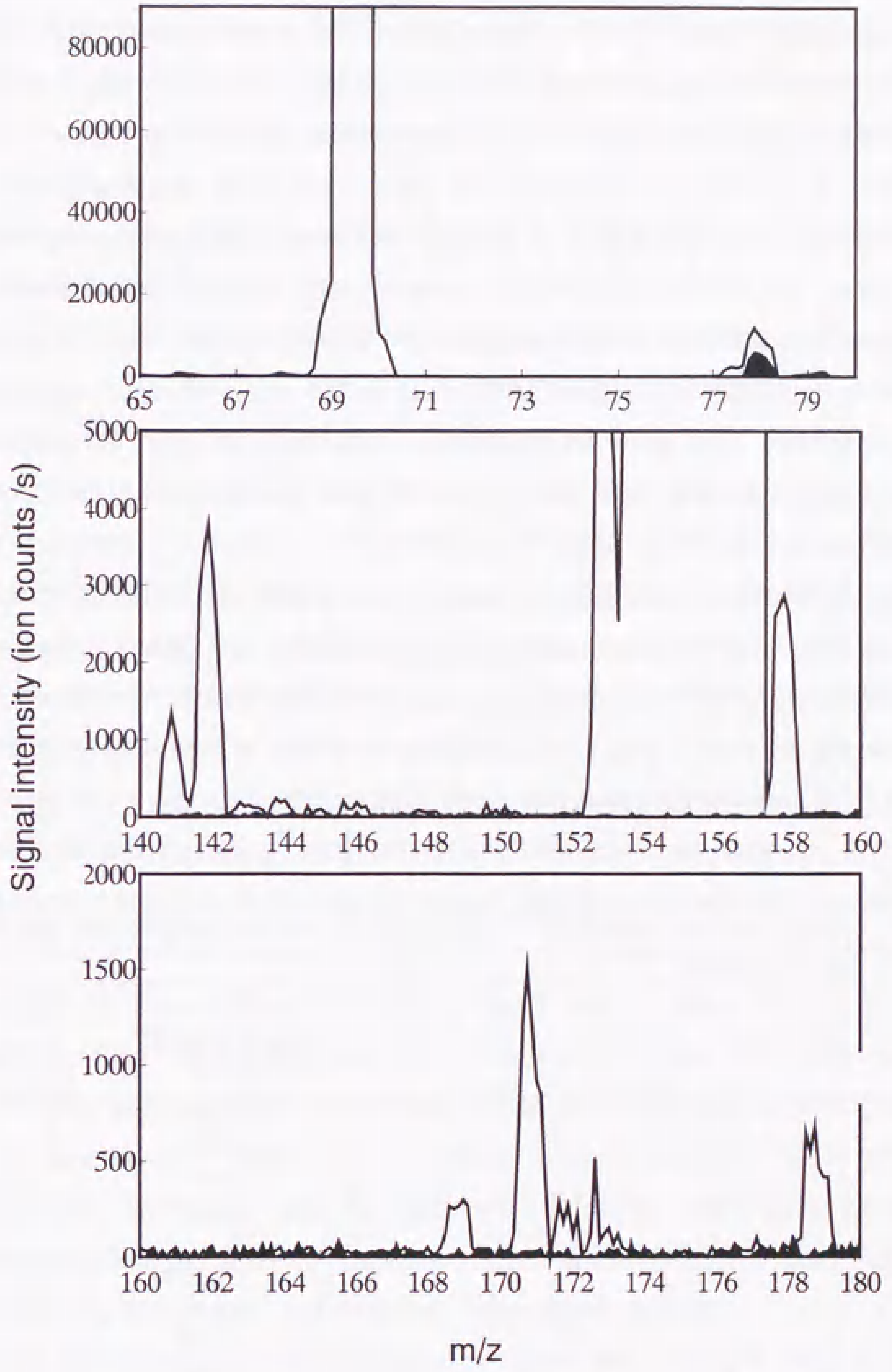

Fig. 3-3 ICP-MS spectra of 200 mg l^{-1} La solution in the mass range of m/z 65-79 and 140-180.

white spectrum : 200 mg l^{-1} of La solution in 2 M HNO$_3$.

black spectrum : 2 M HNO$_3$ blank solution.

3-3-3 Analytical figures of merit

In order to evaluate the lower limit of determination by the present method, the analytical detection limits were estimated from the instrumental detection limits, taking into account the concentration factors and the recovery values. The instrumental detection limits of analyte elements were obtained as the concentrations corresponding to 3-fold the standard deviation (3σ) of the background signal intensities for the blank solution (2 M HNO_3), where the standard deviation (σ) was calculated from the 10-times repeated measurements at each mass number. The analytical detection limits of analyte elements are shown in Table 3-2. It is seen from Table 2 that the analytical detection limits were in the range from 0.2 µg l^{-1} for Se to 0.0001 µg l^{-1} for Bi. The poor detection limit of Se (m/z 82) may be ascribed to the large background intensity due to polyatomic ion ($Ar_2H_2^+$) and the low isotope abundance (^{82}Se 9.2%).

In the lanthanum coprecipitation method, the lanthanum solution with the high concentration (200 mg l^{-1}) added into the sample solution may provide the large blank values. Compared to the detection limits, however, the blank values caused by the lanthanum solution were negligibly small for the analyte elements except for Y. In the case of Y, La provided contamination corresponding to the concentration of Y (0.026 µg l^{-1}) in seawater. The total blank values caused from the whole preconcentration procedure were also examined. They were 0.32 µg l^{-1} for Cr, 0.031 µg l^{-1} for Y, 0.009 µg l^{-1} for Sb, 0.0011 µg l^{-1} for W, and 0.0004 µg l^{-1} for Bi, respectively. These blanks might be caused by the contamination introduced at some stages in the preconcentration procedure and/or by the impurities of the lanthanum carrier.

Table 3-2. Analytical detection limits obtained by La coprecipitation and ICP-MS measurements.

Element	m/z	Analytical detection limit[a] µg l^{-1}
V	51	0.005
Cr	52	0.03
Mn	55	0.02
As	75	0.003
Se	82	0.2
Y	89	0.0007
Mo	95	0.04
Sn	116	0.002
Sb	121	0.004
W	184	0.0009
Bi	209	0.0001
U	238	0.05

a) Analytical detection limits were calculated from the instrumental detection limits, taking into account the recovery values and concentration factor (2.5) obtained by the present coprecipitation method.

3-3-4 Recoveries and coprecipitation behaviors of hydride- and oxoanion-forming elements in seawater.

As mentioned earlier, pH 9.5 was chosen as the optimum pH for lanthanum coprecipitation, and thus the recovery values for trace elements in seawater were estimated by carrying out lanthanum coprecipitation at 9.5. The results for the recovery test are summarized in Table 3-3, where the recovery values of analyte elements obtained by gallium coprecipitation[3)] and chelating resin (Chelex 100) preconcentration[4)] are also shown. The recoveries of analyte elements except for Cr, As, Se, and Sb were examined using the coastal seawater sample, where the coprecipitation procedure described in the experimental section was carried out. As for Cr, As, Se, and Sb, the artificial seawater sample was used for the recovery test because they have different oxidation states. As reported previously[3,4)], the gallium coprecipitation and chelating resin preconcentration methods have not been applied to the preconcentration of hydride- and oxoanion-forming elements with some exceptions because of their poor recoveries. In gallium coprecipitation, the recoveries of Cr(III), Mn, As(III), Y, Sn, and Sb(III) were much poorer than those in lanthanum coprecipitation. The recoveries of oxoanion-forming elements in gallium coprecipitation were slightly lower than those in lanthanum coprecipitation. As mentioned previously[5)], the chelating resin preconcentration also provided the extremely poor recoveries of the elements listed in Table 3-3 except for Y. Consequently, the lanthanum coprecipitation method was more efficient for preconcentration of hydride- and oxoanion-forming elements.

It is seen in Table 3-3 that the recovery values for V, Cr(III), Mn, As(III), As(V), Se(IV), Y, Sn, Sb(III), Sb(V), W, Bi, and U were larger than 80%, although those for Mo, Cr(VI), and Se(VI) were less than 30%. In the cases of As and Sb, the recoveries were about 100% regardless of their oxidation states. On the other hand, the recoveries of Cr(VI) and Se(VI) were *ca.* 30% and 1.4%, respectively, while those of Cr(III) and Se(IV) were *ca.* 100%. The results in the recovery test for Se agreed well with those reported in the reference.[16)] Under the oxidizing conditions of coastal

Table 3-3. Recoveries of trace elements in La coprecipitation at pH 9.5.

Element	Recovery /%		
	present work[a]	Ga coprecipitation[b]	chelating resin preconcentration[c]
V	85.9 ± 0.5	32	63.9
Cr(III)	106[d]	98	
Cr(VI)	27.1[d]		8.0
Mn	100 ± 1	104	53.9
As(III)	102[d]	95	
As(V)	100 ± 0.2		
Se(IV)	92.0 ± 5.3		
Se(VI)	1.4[d]		
Y	99.4 ± 4.3	99	91.3
Mo	16.0 ± 0.8	1	57.8
Sn(II)	98.1 ± 2.8	97	33.0
Sb(III)	96.7[d]	1	
Sb(V)	97.6 ± 2.2		
W	92.5 ± 0.8		43.2
Bi	96.2 ± 0.9		
U	97.5 ± 1.1	82	81.1

a) The mean values and standard deviations were estimated from 3-times preconcentration procedures.

b) The recovery values for Ga coprecipitation, cited from Ref. 3.

c) The recovery values for chelating resin (Chelex 100) preconcentration at pH 6, cited from Ref. 4.

seawater, Cr(VI), As(V), Se(VI), and Sb(V) with the higher oxidation state are generally more dominant in seawater than those with the lower oxidation states.[20,21] The excellent recoveries for As(V) and Sb(V) may allow one to determine As and Sb in seawater as their total concentrations by the present method. On the contrary, the poor recoveries for Cr(VI) and Se(VI) in lanthanum coprecipitation unfortunately made it difficult to determine Cr and Se in seawater. The relative standard deviations of the recovery values for V, Mn, As(V), Se(IV), Sn, Sb(V), W, Bi, and U were within 5%. This means that these elements were effectively preconcentrated by lanthanum coprecipitation.

Among the oxoanion-forming elements, Cr(III), V, W, and U were found to be almost completely recovered with lanthanum coprecipitation, but Cr(VI) and Mo were recovered less than 30%. It was reported that oxoanions which have hydroxyl group(s) such as $HM^{VI}O_4^-$ type ion are more efficiently adsorbed on the surface of metal-hydroxide colloids than those with dissociated hydroxyl group(s) (e.g., $M^{VI}O_4^{2-}$ type ions), because the hydroxyl groups in oxoanions may coordinate with metal-hydroxide colloids through hydrogen bondings.[22] At pH 9.5, Cr(VI) and Mo may be in the forms of CrO_4^{2-} and MoO_4^{2-} in the sample solution, while Cr(III), V, W, and U may be in the chemical forms such as $Cr(OH)_3$, $NaHVO_4^-$, HWO_4^-, and $UO_2(OH)_3^-$, respectively.[23,24] As a result, Cr(III), V, W, and U can be almost completely coprecipitated with lanthanum hydroxide colloids because their chemical forms have some hydroxyl groups in them. On the contrary, Cr(VI) and Mo are poorly coprecipitated because they have no hydroxyl groups.

The coprecipitation behaviors of As, Sb, and Se in different oxidation states may be explained in analogy to the mechanisms described above. In seawater, As(III), As (V), Se (IV), Sb (III), and Sb (V) may be in the forms of $As(OH)_3$, $HAsO_4^{2-}$, $HSeO_3^-$, $Sb(OH)_3$, and $Sb(OH)_6^-$, respectively.[24] These types of oxo-compounds may be efficiently adsorbed on the hydroxide colloids because they have hydroxyl groups in them. As a result, As(III), As(V), Se(IV), Sb(III), and Sb(V) were completely coprecipitated at all with lanthanum hydroxide colloids. On the other hand, Se(VI), which is in the form of SeO_4^{2-}, was hardly coprecipitated with lanthanum hydroxide colloids.

3-3-5 Determination of trace elements in coastal seawater reference material.

Trace elements in coastal seawater reference material CASS-3 were determined by the present lanthanum coprecipitation/ICP-MS method. The results are summarized in Table 3-4, along with the certified and literature values. In Table 3-4, As and Sb were estimated as the total concentrations [As (III+V) and Sb (III+V)] because they provided the same recovery values regardless of their oxidation states although they may exist in the higher oxidation states in seawater.[20,21] Eight elements (Mn, Mo, As, U, V, Y, Sb, and W) in CASS-3 could be determined by the present lanthanum coprecipitation/ICP-MS method. In Table 3-4, the analytical value of Mo is shown in the parentheses for reference, because its recovery value was poor. Since the concentration levels of Cr, Se, Sn, and Bi in seawater were below the analytical detection limits, they could not be determined by the lanthanum coprecipitation/ICP-MS method. Thus, the larger preconcentration factor is required for lanthanum coprecipitation to determine such elements at the ultratrace level. The relative standard deviations (RSDs) for the elements in Table 3-4 were less than 10% even at the low concentration level. The analytical results for Mn, As, and U were in fairly good agreement with the certified or information values issued from NRC, although the concentration of U was slightly higher than the reference value.

Since the certified values for V, Y, Sb, and W have not been issued from NRC, their analytical results were compared with the literature values for CASS-3[4,25,26] or the averaged concentration values for open seawater.[27] The analytical results for V, Y, and Sb were in good agreement with the literature values for CASS-3. Furthermore, the concentration of W was almost the same as that in open seawater. This indicates that W is kept almost constant in concentration all over the sea area in the world, since it exists in the stable oxoanions as the dissolved form.

Table 3-4. Analytical results for trace elements in coastal seawater reference material CASS-3 determined by ICP-MS after La coprecipitation.

Element	Concentration[a] µg l^{-1}	Certified value and literature values µg l^{-1}	Open seawater reference values[f] µg l^{-1}
Mn	2.67 ± 0.05	2.51 ± 0.36	0.02
As (III + V)	1.12 ± 0.04	1.09 ± 0.07	1.2
Mo	(14.4 ± 1.7)	8.95 ± 0.26	10
U	3.29 ± 0.07	2.84[b]	3.2
V	1.46 ± 0.05	1.50[c]	2.0
Y	0.0258 ± 0.0013	0.0237[d]	0.017
Sb (III + V)	0.150 ± 0.004	0.12[e]	0.2
W	0.0117 ± 0.0007		0.010

a) The means and standard deviation obtained from 3-times independent determination. Data in the parentheses are the results for the elements of which recoveries were lower than 50%.
b) Information value issued from NRC.
c) Cited from Ref. 24.
d) Cited from Ref. 4.
e) Cited from Ref. 25.
f) Cited from Ref. 27; open seawater.

3-4 Conclusion

It has been proved that the lanthanum coprecipitation/ICP-MS method is useful for the multielement determination of hydride- and oxoanion-forming elements as well as some trace elements in seawater. Eight elements (Mn, As, Mo, U, V, Y, Sb, W) in coastal seawater reference material CASS-3 could be determined by the present method, and their analytical values fairly agreed well with the certified or reference values. Since the determination of As, Sb, and W in seawater is not possible by the chelating resin preconcentration/ICP-MS method, the present lanthanum coprecipitation method may be employed as a complimentary method for the chelating resin preconcentration/ICP-MS method.

References

1) H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 2772 (1999).

2) H. Sawatari, T. Hayashi, E. Fujimori, A. Hirose, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **69**, 1925 (1996).

3) H. Sawatari, E. Fujimori, and H. Haraguchi, *Anal. Sci.*, **11**, 369 (1995).

4) T. Yabutani, S. Ji , F. Mouri, H. Sawatari, A. Itoh, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 2253 (1999).

5) H. Sawatari, T. Toda, T. Saizuka, C. Kimata, A. Itoh, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **68**, 3065 (1995).

6) P. Möller, P. Dulski, and J. Luck, *Spectrochim. Acta*, **47B**, 1379 (1992).

7) D. B. Taylor, H. M. Kingston, D. J. Nogay, D. Koller, and R. Hutton, *J. Anal. At. Spectrom.*, **11**, 187 (1996).

8) A. Seabert, G. Petzold, and J. W. McLaren, *J. Anal. At. Spectrom.*, **10**, 371 (1995).

9) M. Shabani, T. Akagi, H. Shimizu, and A. Masuda, *Anal. Chem.*, **62**, 2709 (1990).

10) G. J. Batterham, N. C. Munksgaard, and D. L. Parry, *J. Anal. At. Spectrom.,* **12**, 1277 (1997).

11) M. O. Andreae, J. Asmode, P. Foster, and L. Van't dack, *Anal. Chem.*, **53**, 1766 (1981).

12) T. Tanizaki, K. Baba, K. Kadokami, and R. Shinohara, *Bunseki Kagaku,* **46**, 849 (1997).

13) S. J. Santosa, H. Mokudai, and S. Tanaka, *J. Anal. At. Spectrom.*, **12**, 409 (1997).

14) M. Thompson, B. Pahlavanpour, and L. T. Throne, *Water Res.*, **15**, 407 (1981).

15) G. H. Tao and E. H. Hansen, *Analyst*, **119**, 333 (1994).

16) H. Saisho and T. Fujiwara, *Anal. Sci.*, **6**, 619 (1990).

17) K. Himeno, T. Yanagisawa, T. Yuki, and Y. Nakamura, *Bunseki Kagaku*, **33**, T43 (1984).

18) G. Lyman and R.H. Fleming, *J. Mar. Res.*, **3**, 136 (1940).

19) G. Charlot, authorized translation by R. C. Mullay, "Qualitative Inorganic Analysis" London : Methuen, New York : John Wiley & Sons, pp.172 (1954).

20) M. O. Andreae, *Deep-Sea Res.*, **25**, 391 (1978).

21) J. J. Middelburg, D. Hoede, H. A. Van Der Sloot, C. H. Van Der Weijden, and J. Wijkstra, *Geochim. Cosmochim. Acta*, **52**, 2871 (1988).

22) H. Yamazaki, S. Gouda, and Y. Nishikawa, *Bunseki Kagaku*, **29**, 58 (1980).

23) H. Yamazaki, K. Tsujimoto, S. Gouda, K. Hiraki, and Y. Nishikawa, *Bunseki Kagaku*, **28**, 424 (1979).

24) D. R. Turner, M. Whitfield, and A. G. Dickson, *Geochim. Cosmochim. Acta*, **45**, 855 (1981).

25) G. Chapple and J. P. Bylne, *J. Anal. At. Spectrom.*, **11**, 549 (1996).

26) H. Falk, R. Geerling, B. Hattendorf, K. Krengel-Rothensee, and K. Schmidt, *Fresenius J. Anal. Chem.*, **359**, 352 (1997).

27) T. Nozaki, *EOS. Trans. AGU*, **78**, 221. (1997).

Chapter 4 Multielement Determination of Trace Elements in Seawater by Inductively Coupled Plasma Mass Spectrometry after Tandem Preconcentration with Cooperation of Chelating Resin Adsorption and Lanthanum Coprecipitation

4-1 Introduction

Nowadays, the concentration levels of almost all the elements in seawater have been elucidated by persistent efforts of a large number of scientists, using various kinds of analytical techniques.[1] Consequently, it has been found that trace and ultratrace elements in seawater show some characteristic vertical concentration distributions in the ocean, reflecting the physicochemical conditions and biological activities in marine environments, while major and minor elements are kept at almost uniform concentration level horizontally and vertically in the ocean. Then, the kinetic behaviors of various trace elements can be well understood from such elemental distributions in the ocean.[1] For example, Fe, Mn, and Al are interacting with settling particulates and play an important role in the transport of trace elements in the ocean.[2] It is also known that Fe, Cu, Zn, Ni, and Cd show strong relationships with bio-activities in the ocean.[3] In addition, As, Se, and Sb exist in various oxidation states, reflecting the redox conditions in seawater.[4,5] Thus, a variety of trace elements in seawater can be some good indicators to monitor the changes of the marine ecosystems. Therefore, it is considered that the knowledge of the concentrations and distributions for trace elements as many as possible are helpful to elucidate not only the physicochemical and bio-geochemical phenomena but also environmental pollution in the open and coastal sea areas.[6]

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most powerful analytical methods for the determination of trace elements with a wide linear dynamic range of 5-6 orders of magnitude, extremely high sensitivity, and multielement detection capability.[7] However, the determination of trace elements in seawater is quite difficult without any preconcentration even by ICP-MS, because their concentrations are generally below the $\mu g\ l^{-1}$ level. In addition, the high salt contents of seawater make it difficult to nebulize the seawater sample directly into the plasma in the ICP-MS measurement. Therefore, a pretreatment method for preconcentration of trace elements together with removal of matrix elements is inevitably required to determine a variety of trace and ultratrace elements in seawater.[7]

The present authors have tried to establish the analytical methods for the multielement determination of major-to-trace elements by plasma spectrometry.[7-9] It has been shown that the chelating resin preconcentration method has excellent analytical features of non-selective multielement preconcentration for many trace elements in seawater, along with efficient removal of matrix elements such as Na, K, Ca, and Mg.[10-12] Then, about 30 elements such as Al, V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Y, rare earth elements (REEs), Pb, and U, which were in the concentration range from 10 μg l^{-1} to 0.1 ng l^{-1}, could be determined by the chelating resin preconcentration/ICP-MS method.[10-12] However, it was found that the chelating resin provided the poor recoveries for oxoanion- and hydride-forming elements. The present authors also investigated the coprecipitation methods using Ga, Al and La.[13-16] Then, it was found that La coprecipitation was useful for preconcentration of oxoanion- and hydride-forming elements such as As, Se, Mo, Sb, W, V, and U,[16] which could be determined simultaneously by ICP-MS. Accordingly, complementary use of the chelating resin preconcentration and La coprecipitation comes into idea about further efficient multielement preconcentration for trace elements in seawater.

In the present paper, hence, we developed a tandem method for multielement preconcentration of trace elements in seawater, where chelating resin preconcentration was first applied to the original seawater, and then La coprecipitation was applied to the filtrate after the chelating resin preconcentration. In order to evaluate the analytical reliability of the present tandem preconcentration/ICP-MS method, it was applied to the analysis of open seawater reference material (NASS-4) issued from National Research Council of Canada (NRC).

4-2 Experimental

4-2-1 Instruments

An ICP-MS instrument of model SPQ-8000A (Seiko Instruments, Chiba), which consisted of a quadrupole-type mass spectrometer, was used for the determination of trace elements. The ICP-MS instrument equipped with a concentric nebulizer allowed us to determine 30 elements (or m/z) simultaneously. The operating conditions of the ICP-MS instruments are shown in Table 4-1. The mass numbers (m/z) for analyte elements in the ICP-MS measurement were the same as those in the previous papers.[12] A model twin pH meter from Horiba (Kyoto) was used for pH adjustment.

Table 4-1. Operating conditions for ICP-MS instrument.

ICP-MS :	Seiko SPQ 8000A
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 16 l min^{-1}
Auxiliary gas flow rate	Ar 1.0 l min^{-1}
Carrier gas flow rate	Ar 1.0 l min^{-1}
Sampling depth	12 mm from load coil
Nebulizer:	concentric type
Sample uptake rate	1.0 ml min^{-1}
Data acquisition :	
Dwell time	10 ms/channel
Data points	3 points/peak
Number of scans	100 times

4-2-2 Chemicals

Nitric acid, hydrochloric acid, acetic acid, and aqueous ammonia solution used were of electronics industry grade, purchased from Kanto Chemicals (Tokyo). The multielement standard solutions for making the working calibration curves were prepared from the single-element standard stock solutions (1000 μg l^{-1}) for atomic absorption spectrometry (Wako Chemicals, Osaka) except for As(V) and Sb(V).[12] The standard stock solutions for As(V) and Sb(V) were prepared by dissolving potassium arsenate of analytical reagent grade (Wako Chemicals) in pure water and potassium hexahydroxoantimonate of guaranteed reagent grade (Nacalai Tesque, Kyoto) in 3 M HCl solution, respectively. In the cases of Cr, As, and Sb, which have two different oxidation states, only Cr(VI), As(V), and Sb(V) were investigated in the present experiment, because they are dominant oxidation states in seawater. In addition, in the case of Se, Se(IV) was almost completely recovered by La coprecipitation,[12] while Se(VI) was not. The La solution as a coprecipitation carrier was prepared by dissolving 3 g of La$(NO_3)_3$ (extra pure grade; Wako Chemicals) in 100 ml of 0.1 M HNO_3 so as to be 10 g l^{-1} of La solution.

The Chelex 100 resin in 100-200 mesh was purchased from Bio-Rad Laboratories (Richmond, CA, USA). The resin was soaked in 5 M HCl, changing the HCl solution 5-times every 12 h, and washed with pure water before use.

Purified water used throughout the present experiment was prepared by a Milli-Q purification system (Nihon Millipore Kogyo, Tokyo).

4-2-3 Seawater samples

Open seawater reference material NASS-4 was obtained from National Research Council of Canada (NRC) for evaluation of the present analytical method. The coastal seawater samples collected at about 1 km off-shore from Tokoname (Aichi Prefecture) in the Ise Bay were also used for the preliminary experiments of the present analytical method. The coastal seawater samples examined were filtrated with a membrane filter (pore size 0.45 µm) immediately after sampling, and then acidified to pH 1 with nitric acid. These seawater samples were preserved in the polyethylene bottles, which were soaked in 6 M HNO_3 for more than 1 week and rinsed with pure water before use.

4-2-4 Experimental procedures of tandem preconcentration

The flow chart of the tandem preconcentration method is shown in Fig. 4-1. The procedure was established as a recommended method for preconcentration of trace elements in the seawater samples, taking into account the experimental conditions of the chelating resin preconcentration and La coprecipitation methods, reported in the previous papers.[12,16]

First, 250 ml of the seawater sample was subjected to chelating resin preconcentration where the pH of the sample solution was adjusted to 6.0 with acetic acid and aqueous ammonia solution. After adding 0.2 g of the chelating resin (dry weight) into the sample solution, the solution was stirred with a magnetic stirrer for 2 h, and filtered with a glass filter (1.4 cm i.d.). At this time, the filtrate was collected in a polypropylene bottle. Then, the resin was rinsed with 10 ml of pure water and 8 ml of 1 M ammonium acetate solution to reduce major elements such as Na, K, Ca, and Mg partly adsorbed on the resin. These rinsing solutions were also collected in the polypropylene bottle, in which the filtrate had already been stored. After washing with 10 ml pure water again, trace elements adsorbed on the resin were eluted with 6 ml of 2 M HNO_3, into which the internal standard elements (Ge, In, Re, and Tl; 100 µg l^{-1} each) in HNO_3 solution were added for correction of matrix effects due to major elements. Then, the 41.7-fold concentration factor in volume was achieved in the chelating resin preconcentration.

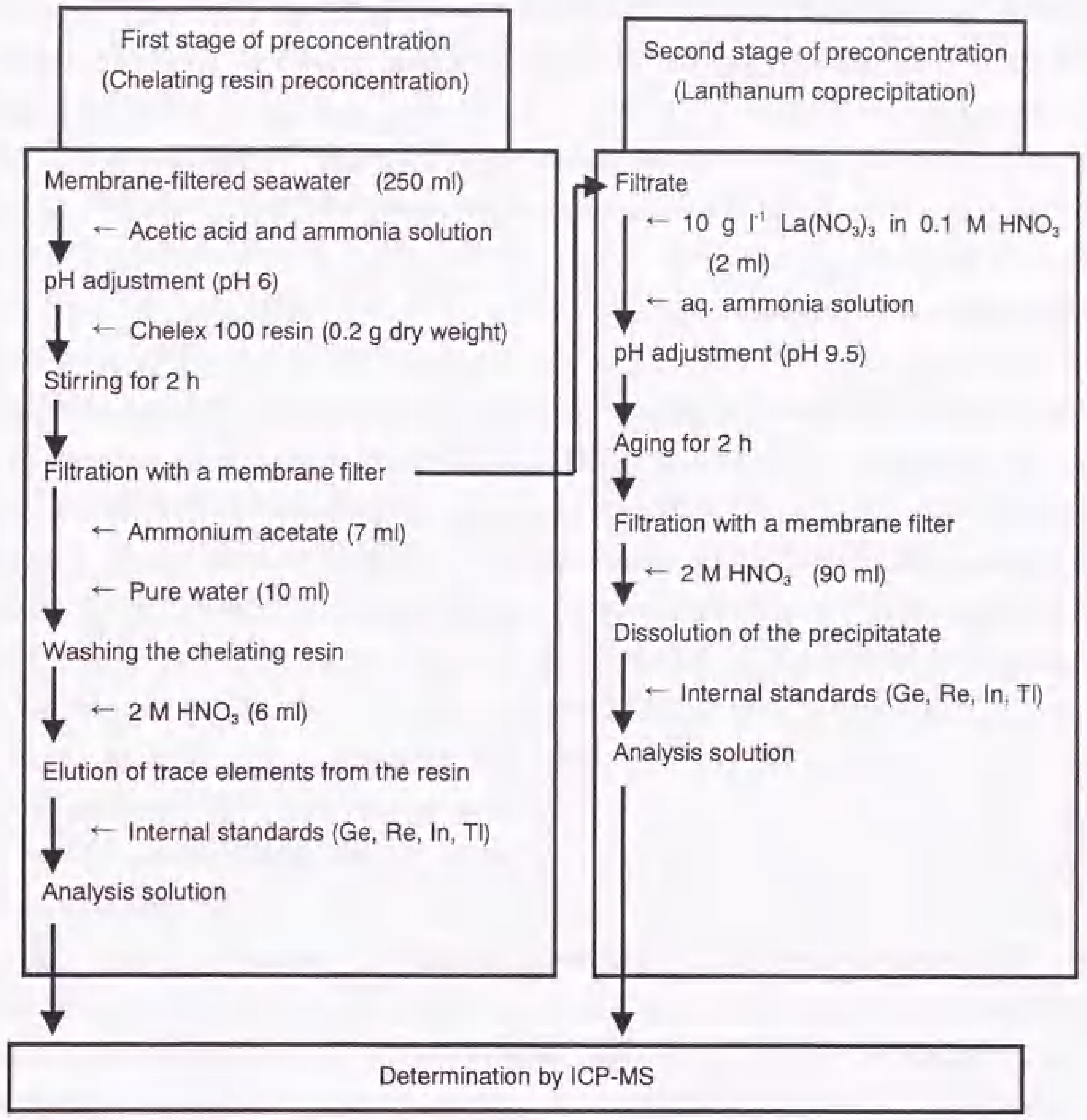

Fig. 4-1 Flow chart of the tandem preconcentration method, followed by ICP-MS measurement.

As the second stage of tandem preconcentration, the mixture of the residual seawater sample (*c.a.* 280 ml) of the filtrate and rinsing solutions collected after chelating resin preconcentration was then subjected to La coprecipitation. Two ml of La solution (10 g l^{-1}) was added in the residual seawater sample as a coprecipitation carrier. After adjustment of pH of the sample solution to 9.5 with aqueous ammonia solution, the solution was stirred with a magnetic stirrer for *ca*. 5 min. The sample solution was kept standing for 2 h. Then, the precipitate formed was collected on a PTFE membrane filter (pore size 0.45 μm), and washed with 30 ml of pure water. The precipitate was dissolved with 90 ml of 2 M HNO_3, into which 10 ml of the mixed solution of Ge, In, Re, and Tl (100 μg l^{-1} each) was added for the internal standard correction of matrix effects in the ICP-MS measurement. Consequently, 2.5-fold preconcentration was achieved in the La coprecipitation procedure.

4-3 Results and Discussion

4-3-1 Analytical Figures of Merit of Tandem Preconcentration/ICP-MS Method

The analytical figures of merit of the present tandem preconcentration method, in which chelating resin adsorption and La coprecipitation was cooperatively employed, were investigated by using the coastal seawater sample collected in the Ise Bay. The recoveries, analytical detection limits, and blank values obtained by the tandem preconcentration/ICP-MS method are summarized in Table 4-2, together with those obtained only by the chelating resin preconcentration/ICP-MS method. In Table 4-2, R_{ch} indicates the recovery obtained by chelating preconcentration, and R_{total} does the accumulative sum of the recoveries obtained by chelating resin preconcentration and La coprecipitation, *i.e.*, by the whole experimental procedure of tandem preconcentration. Similarly, DL_{ch} and DL_{La} are the analytical detection limits obtained by ICP-MS after chelating resin preconcentration and tandem preconcentration, respectively. It should be noted here that DL_{La} is the analytical determination limit estimated only by considering the concentration factor in La coprecipitation.

It is seen in Table 4-2 that the recoveries (R_{ch}) of Co, Ni, Cu, Zn, Y, Cd, REEs, Pb, and U in chelating resin preconcentration were larger than 80%, and their relative standard deviations (RSDs) were less than 5%. These recoveries and RSD values were fairly in good agreement with those reported in the previous paper.[12] Since the elements listed above were concentrated sufficiently only by chelating resin preconcentration, further preconcentration was not required for them. On the contrary, the recovery values (R_{ch}) of Al, Ti, V, Cr, Mn, As, Se, Mo, Sn, Sb, W and Bi were found below *ca.* 60%. In general, oxoanion- and hydride-forming elements such as Cr, V, Mo, As, Se, Sb, W, and Bi provided the poor recoveries in chelating resin preconcentration, which may be ascribed to their low adsorption abilities on the chelating resin. In the cases of Al, Ti, Mn, and Sn, their poor recoveries may be ascribed to the formation of relatively stable hydroxo- or chloro–complexes in seawater.[12,17)] Then, La coprecipitation was consecutively performed to recover these elements in the residual seawater sample as the second stage of the tandem preconcentration.

The accumulative recovery values (R_{total}) of 12 elements obtained by tandem preconcentration are summarized in Table 4-2. As is seen in Table 4-2, in particular, the recoveries of Ti, V, As, Se, Sb, W, and Bi were substantially improved to be larger than 80%, although those of other elements were also larger than 60%. Under these conditions, the relative standard deviations (RSDs) of all the elements examined were within 6%, except for Ti. The RSD of R_{total} for Ti was about 30%, although its recovery was 92.6%. The poor reproducibility of Ti in tandem preconcentration might be ascribed to its adsorption on the surface of the polypropylene bottle during preservation, because hydrolysis of Ti may easily occur in weekly acidic solution.[18)] The recoveries of Al, Cr(VI), Mn, Mo, and Sn were still in the range from 60 to 80% after the present tandem preconcentration. However, the RSDs for their recovery values throughout the whole tandem preconcentration procedure were kept below 5%, even though the preconcentration process became more complicated because of combination of the two different preconcentration methods.

The analytical detection limits shown in Table 4-2 were estimated from the instrumental detection limits obtained by ICP-MS, taking into account the concentration factors and the recovery values of each preconcentration procedure.[12)] The instrumental detection limits were defined as the concentration corresponding to 3-fold standard deviation of the background signal intensities for the blank solution (2 M HNO_3), where the standard deviation was calculated from the 10–times repeated measurements at each mass number. It is seen in Table 4-2 that the analytical detection limits (DL_{ch}) obtained by ICP-MS after chelating resin preconcentration were in the range from 3 μg l^{-1} for Se to 0.00006 μg l^{-1} for Tm and Tb. The poor detection limits for Se, Sb, and As were ascribed to their low recoveries (Se 0.1%, Sb 0.04%, and As 2.5%) as well as to the large background signals of at m/z 82 due to $^{40}Ar^{40}Ar^{2}H$ in the case of ^{82}Se. The blank values for analyte elements caused in chelating resin preconcentration were negligibly small, compared to the analytical detection limits except for Al, Ni, Sn, and Pb. The large blank values for Al, Ni, Sn, and Pb might be caused by contamination from the laboratory environment.

Table 4-2. Analytical figures of merit for trace elements in the tandem preconcentration method.

Element	Chelating resin preconcentration				Tandem preconcentration			
	R_{ch} [a] /%		DL_{ch} [b]/μg l^{-1}	Blank [c]/μg l^{-1}	R_{total} [d]/%		DL_{La} [e]/μg l^{-1}	Blank [c]/μg l^{-1}
	Mean	RSD [f]			Mean	RSD [f]		
Al	54.6	0.8	0.002	0.052	62.5	0.8	0.6	n.d.
Ti	27.8	21.2	0.08	n.d.	92.6	30.5	3	n.d.
V	61.3	2.1	0.001	n.d.	85.5	3.4	0.01	n.d.
Cr (VI)	3.2	23.2	0.04	n.d.	64.7	4.1	0.02	0.92
Mn	53.9	3.1	0.002	0.007	77.7	5.0	0.05	n.d.
Co	101	0.7	0.00009	0.00050				
Ni	97.2	0.9	0.0009	0.013				
Cu	97.8	0.1	0.0007	n.d.				
Zn	100	0.9	0.003	n.d.				
As(V)	2.5	16.3	0.4	n.d.	104	4.4	0.03	n.d.
Se (IV)	0.1	50.5	3	n.d.	92.0	5.0	0.06	n.d.
Y	95.8	0.6	0.00001	0.0002				
Mo	55.3	3.2	0.002	n.d.	70.2	2.7	0.01	n.d.
Cd	95.1	2.5	0.00006	0.0007				
Sn	33.0	2.7	0.0003	0.030	69.7	3.4	0.01	n.d.
Sb(V)	0.04	29.2	1	n.d.	104	4.2	0.008	n.d.
La	102	2.2	0.00002	0.00024				
Ce	97.8	1.4	0.00004	0.00036				
Pr	99.7	0.4	0.00001	0.00003				
Nd	90.5	1.2	0.00004	n.d.				
Sm	88.0	1.6	0.00004	n.d.				
Eu	87.1	0.5	0.00001	n.d.				
Gd	85.7	1.8	0.00002	n.d.				
Tb	86.6	1.6	0.000006	n.d.				
Dy	85.9	2.5	0.00001	n.d.				
Ho	86.7	1.2	0.000007	n.d.				
Er	85.0	1.1	0.00002	n.d.				
Tm	85.7	1.1	0.000006	n.d.				
Yb	84.9	0.8	0.00001	n.d.				
Lu	87.8	1.3	0.000007	n.d.				
W	43.2	4.9	0.0002	0.0010	98.0	3.8	0.002	0.004
Pb	93.1	1.1	0.0003	0.011				
Bi	30.8	14.5	0.00003	n.d.	85.0	5.5	0.002	n.d.
U	94.2	2.5	0.0008	0.0010				

a) R_{ch} is the recovery value obtained by chelating resin preconcentration.
b) DL_{ch} is the analytical detection limit obtained by the chelating resin preconcentration/ICP-MS method.
c) n.d. : Not detected.
d) R_{total} is the recovery value obtained by tandem preconcentration.
e) DL_{La} is the analytical detection limit obtained by the La coprecipitation/ICP-MS method.
f) The RSDs were calculated from three replicate preconcentration procedures.

The analytical detection limits (DL_{La}) are shown in Table 4-2. As is seen in Table 4-2, DL_{La} was in the range from 3 μg l^{-1} for Ti to 0.002 μg l^{-1} for W and Bi. In general, DL_{La} was inferior to DL_{ch}, because the concentration factor of La coprecipitation was smaller by *ca*. 20-fold than that of chelating resin preconcentration. However, the analytical detection limits of the oxoanion- and hydride-forming elements such as Cr(VI), As(V), Sb(V), and Se(IV) obtained after La coprecipitation were better than their DL_{ch}, because their recoveries were improved up to *ca.* 60% for Cr(VI) and *ca.* 100% for As(V), Sb(V) and Se(IV) after the tandem preconcentration procedures.

The blank values caused from the tandem preconcentration procedures were also very low except for Cr(VI), although there was a possibility that the consecutive La coprecipitation method would provide the additional blanks. The large blank value of Cr(VI) was ascribed to contamination introduced during La coprecipitation procedure, as reported previously.[16)]

Taking into account the analytical figures of merit in the present tandem preconcentration/ICP-MS method, analyte elements were classified into three groups. The first group consists of the elements which provided more than 80% of R_{ch} values, and they can be determined only by chelating resin preconcentration, followed with the ICP-MS determination. Although the R_{ch} values of Al, Mo and Mn were about 50%, these elements belong to the first group, because their recovery values were not improved after tandem preconcentration, and also because their detection limits (DL_{ch}) obtained by the chelating resin preconcentration/ICP-MS were one order of magnitude better than those by the La coprecipitation/ICP-MS (DL_{La}).

The second group consists of Ti, V, Sn, W, and Bi, whose recoveries were in the range from 30% to 80% after chelating resin preconcentration, but they were improved to be larger than 80% after tandem preconcentration. They were determined either by the chelating resin preconcentration/ICP-MS or by the tandem preconcentration/ICP-MS. In the cases of these elements, thus, the analytical data could be obtained by two different preconcentration procedures, which allowed us to complementarily evaluate the accuracies of analytical values.

The third group consists of Cr, As, Se, and Sb. Their R_{ch} values were below 10%, but their recoveries were improved to be above 60% after the tandem preconcentration. Thus, it is preferable to determine these elements by the tandem preconcentration/ICP-MS method.

4-3-2 Determination of trace elements in open seawater reference material (NASS-4)

The tandem preconcentration/ICP-MS method explored in the present study was applied to the multielement determination of trace elements in open seawater reference material NASS-4. The analytical results are summarized in Table 4-3, along with the certified and literature values. As is seen in Table 4-3, the concentrations of 32 elements were obtained in the concentration range over 5 orders of magnitude from 9.6 μg l^{-1} for Mo to 0.00018 μg l^{-1} for Tm. Since the recovery values of Ti, Sn, and W were smaller than 50% in chelating resin preconcentration, the concentrations of these elements were seemingly less reliable so that they are shown in parentheses as the reference values. Arsenic, Se, and Sb could be determined by the tandem preconcentration/ICP-MS method, in addition to the data obtained by chelating resin preconcentration. However, the analytical result of Se was still less reliable because of its poor detection limit. As for V and W, their analytical results obtained by both the chelating resin and tandem preconcentration agreed well with each other. These results would assure the validity of the present tandem preconcentration method. Chromium (VI) and Bi could not be determined even by the present tandem method, because their concentrations were below the detection limits. It is seen in Table 4-3 that the relative standard deviations (RSDs) of the analytical values for analyte elements were smaller than 15% even at their extremely low concentration levels, except for Al and Pb. The poor precision for these two elements might be caused by the high blank values.

It is seen in Table 4-3 that the analytical values for Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, and U were in good agreement with the certified values issued form NRC, although the Zn concentration obtained here was slightly higher than the certified value. The analytical results for Al, V, and Sb, whose certified values have not been issued, were in the same concentration ranges as the literature values.[19,20] As for other elements such as Ti, Y, Sn, REEs, and W, there are no certified or literature values, and thus the analytical values obtained here are the first data reported for these elements in NASS-4. The analytical results for REEs including Y and La are considered to be quite reliable, because their concentrations are much higher than their analytical detection limits, in addition to their small RSDs below 10%.

Table 4-3. Analytical results for the concentrations of trace elements in open seawater reference material of (NASS-4) and Ise Bay seawater obtained by ICP-MS measurement after the tandem preconcentration method.

Element[a]	Concentration /μg l^{-1}		
	NASS-4		Ise Bay Seawater
	Observed values[b]	Certified or literature values	Observed values[c]
Al	0.15 ± 0.09	0.246[d]	1.4
Ti	(0.16)		(0.12)
Ti†	n.d.		n.d.
V	1.8 ± 0.2	1.26[d],1.49[e]	1.5
V†	1.5 ± 0.1		1.5
Cr†	n.d.	0.115 ± 0.01	n.d.
Mn	0.43 ± 0.04	0.38 ± 0.023	5.2
Co	0.0089 ± 0.0014	0.009 ± 0.001	0.042
Ni	0.22 ± 0.01	0.228 ± 0.009	0.67
Cu	0.20 ± 0.01	0.228 ± 0.011	0.40
Zn	0.16 ± 0.02	0.115 ± 0.018	1.23
As†	1.26 ± 0.01	1.26 ± 0.09	1.44
Se†	0.10 ± 0.01	0.018	
Y	0.019 ± 0.001		0.026
Mo	9.6 ± 1.2	8.84 ± 0.6	9.6
Cd	0.019 ± 0.002	0.016 ± 0.003	0.01
Sn	(0.006)		(0.071)
Sn†	n.d.		n.d.
Sb†	0.14 ± 0.01	0.440[e]	0.21
La	0.010 ± 0.001		0.0067
Ce	0.0041 ± 0.0003		0.0043
Pr	0.0016 ± 0.0001		0.0014
Nd	0.0073 ± 0.0004		0.0052
Sm	0.0032 ± 0.0002		0.0012
Eu	0.00025± 0.00003		0.00025
Gd	0.0015 ± 0.0001		0.0022
Tb	0.00023± 0.00003		0.00031
Dy	0.0016 ± 0.0001		0.0023
Ho	0.00042± 0.00004		0.00057
Er	0.0014 ± 0.00004		0.0019
Tm	0.00018± 0.00002		0.0003
Yb	0.0012 ± 0.0001		0.0020
Lu	0.0002 ± 0.00003		0.00037
W	(0.011 ± 0.002)		(0.039)
W†	0.010 ± 0.001		0.037
Pb	0.008 ± 0.003	0.013 ± 0.005	0.029
Bi	n.d.		(0.0017)
Bi†	n.d.		n.d.
U	3.0 ± 0.3	2.68 ± 0.12	3.5

a) The values with † were obtained by ICP-MS measurement after the tandem preconcentration method, and others by ICP-MS measurement after chelating resin preconcentration.

b) The observed values (means) and standard deviations were obtained from 3-times measurements, where n.d. means "not detected.". Data in the parentheses are the results for the elements of which recoveries were less than 50%.

c) The observed values are the means estimated from 2-times measurements. Data in parentheses are the results for the elements, whose recoveries were less than 50%.

d) Literature values cited from ref. 19.

e) Literature values cited from ref. 20.

4-3-3 Comparison of elemental concentrations in open and coastal seawater samples

The concentrations of trace elements in open seawater reference material NASS-4 obtained in the present experiment were compared with those in coastal seawater reference material CASS-3, which were reported in the previous papers.[12,16] The open seawater reference material NASS-4 was collected at about 30 km off-shore of Halifax harbor in Canada, while coastal seawater reference material CASS-3 was collected at seashore. The elemental concentration profiles of NASS-4 and CASS-3 are shown in Fig. 4-2, in the order of the elements with the concentrations from the higher to the lower for open seawater. From this figure, Ti, Se, and Sn were omitted by lack of the analytical results for Se and Sn in CASS-3 and also because of their poor reliabilities in the present experiment. In addition, the concentrations of trace elements in coastal seawater collected in the Ise Bay were also plotted in this figure as the reference data. The seawater sample from the Ise Bay used in the preliminary experiment was also analyzed by the present tandem preconcentration/ICP-MS method. The analytical results are summarized in Table 4-3. The analytical values for the seawater sample from the Ise Bay almost agreed with those reported in previous papers,(12,16) although they were slightly different from each other because of the different sampling seasons.

It is seen in Fig. 4-2 that the concentrations of Mo, U, V, As, Sb and W in NASS-4 were almost coincident with those in CASS-3 as well as with those in coastal seawater from Ise Bay excepted for W. Since these elements exist as the stable oxoanions in seawater, their concentrations are uniform as the stationary elements in seawater all over the sea areas in the world.(1,6,21) In another words, the consistencies of the concentrations of these stationary elements in three different seawater samples may guarantee the accuracy and reliability of the data obtained by the tandem preconcentration/ICP-MS method for the determination of trace elements in seawater. On the other hand, the difference between the concentration values for W in the coastal seawater samples between the Halifax harbor and Ise Bay may be caused by the different human activities in the local areas, because the concentration for W in seawater is low enough to reflect the anthropogenic pollution in the coastal sea areas.(6)

The concentrations of other elements in open seawater were generally lower than those in coastal seawater. In particular, the concentrations of Mn, Ni, Cu, Al, Zn, Cd, and Co were significantly higher in coastal seawater than in open seawater, except for Cd in the coastal seawater from the Ise Bay. The results for Mn and Al may indicate that these elements in the dissolved forms supplied from the terrestrial land would be rapidly adsorbed onto particulates and/or colloids in coastal seawater. Such characteristic behaviors of Al and Mn were also observed in the Tokyo Bay[22] and Seto Inland Sea.(23) Thus, it can be stated here that Al and Mn are easily taken into some colloids, which results in their short residence times in seawater, compared to those for other elements.(2) On the other hand, the high concentrations of Ni, Cu, Zn, Cd, and Co in coastal seawater may be caused by anthropogenic emission, because they are widely used in modern industries as alloys, catalysts, electrical materials and so on, although they are in relatively low abundances in earth crust. The concentrations of rare earth elements (REEs) were slightly higher in coastal seawater than in open seawater.[1,24] These results may suggest that REEs are constantly supplied into seawater from the terrestrial sources.

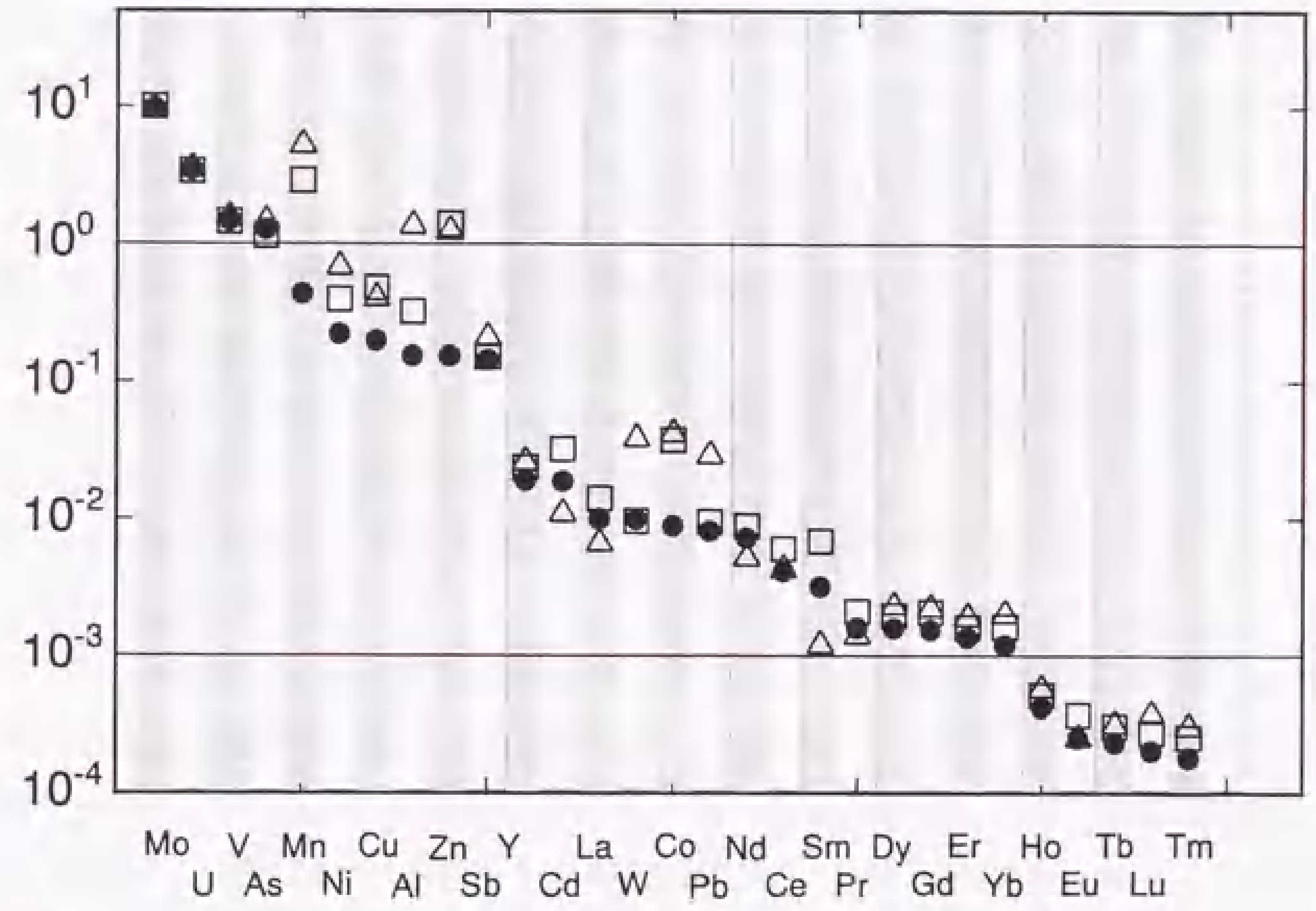

Fig. 4-2 Concentration distributions of trace elements in seawater reference materials (NASS-4 and CASS-3) and coastal seawater from Ise Bay.

● : NASS-4, △ : CASS-3 (cited from Refs. 12 and 16),

□ : Ise Bay seawater.

4-4 Conclusion

The tandem preconcentration/ICP-MS method with cooperative use of chelating resin adsorption and La coprecipitation has been explored for the determination of trace and ultratrace elements in open seawater. As a result, 32 elements could be determined in the concentration range over 5 orders of magnitude from 9.6 $\mu g\ l^{-1}$ for Mo to 0.00018 $\mu g\ l^{-1}$ for Tm, when the present tandem pre-concentration/ ICP-MS method was applied to the analyses of open seawater reference material (NASS-4) as well as coastal seawater. The analytical results for Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Cd, U and V were fairly in good agreement with the certified or literature values. These results indicate that the present method is reliable enough to apply to the multielement determination of trace elements in seawater. Since the present method requires only 250 ml for the simultaneous determination of more than 30 elements, it is very useful for multielement profiling analysis of open and deep seawater,7) which helps to elucidate the characteristic and kinetic behaviors of trace elements in marine environments in relation to biological activities, terrestrial material supply, anthropogenic pollution and so on.

References

1) Y. Nozaki, *EOS Trans. AGU*, **78**, 221, (1997).
2) K.W. Bruland, K. J. Orians, and J. P. Cowen, *Geochim. Cosmochim. Acta,* **58**, 3171 (1994).
3) K. W. Bruland, *Earth. Planet. Sci. Lett*., **47**, 176 (1980).
4) M. O. Andreae and P. N. Froelich, *Tellus*, **36**, 121 (1984).
5) D. R. Turner, M. W. Whitfield, and A. G. Dickson, *Geochim. Cosmochim. Acta*, **45**, 855 (1981).
6) T. Yabutani, F. Mouri, and H. Haraguchi, *Anal. Sci.*, **16**, 675, (2000).
7) H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 1163 (1999).
8) H. Haraguchi, A. Itoh, S. Ji, and T. Yabutani, *Environ. Sci.* **13**, No.3 (2000). in press
9) H. Haraguchi, *Chemistry Todays (Gendai Kagaku)*, **2000**, (No. 6), 16.
10) C. J. Cheng, T. Akagi, and H. Haraguchi, *Anal. Chim. Acta*, **198**, 173 (1987).
11) H. Sawatari, T. Toda, T. Saizuka, C. Kimata, A. Itoh, and H. Haraguchi, *Bull. Chem. Soc. Jpn*., **68**, 3065 (1995).
12) T. Yabutani, S. Ji , F. Mouri, H. Sawatari, A. Itoh, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 2253 (1999).
13) T. Akagi and H. Haraguchi, *Anal. Chem*., **62**, 81 (1990).
14) H. Sawatari, E. Fujimori, and H. Haraguchi, *Anal. Sci*., **11**, 369 (1995).
15) H. Sawatari, T. Hayashi, E. Fujimori, A. Hirose, and H. Haraguchi, *Bull. Chem. Soc. Jpn*., **69**, 1925 (1996).
16) T. Yabutani, S. Ji , F. Mouri, A. Itoh, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **73**, 895 (2000).
17) G. Charlot, authorized translation by R. C. Mullay, "Qualitative Inorganic Analysis", Methuen and John Wiley Sons, London and New York, (1954), pp.153-186, pp.221-241.
18) S. Takagi, "Qualitative Analytical Chemistry (Teisei Bunseki Kagaku)" Nankodo, (1964), pp..482.
19) I. Roduskin and T. Ruth, *J. Anal. At. Spectrom*., **12,** 1181 (1997).
20) G. Chapple and J. P. Byrne, *J. Anal. At. Spectrom*., **11,** 549 (1997).
21) Y. Sohrin, M. Matsui, and E. Nakayama, *Geochim. Cosmocim. Acta,* **63**, 3457 (1999).
22) T. Akagi and H. Haraguchi, *Geochem. J*., **28**, 81 (1994).

23) T. Akagi and H. Haraguchi, *Chikyuukagaku(Geochemisitry)*, **18**, 81 (1984).
24) J. Zhang and Y. Nozaki, *Geochim. Cosmochim. Acta,* **62**, 1307 (1998).

Chapter 5 Multielement Concentration Monitoring of Trace Metals in Seawater along the Ferry Track between Osaka and Okinawa as Investigated by ICP-MS and ICP-AES

5-1 Introduction

The marine environment is a very important field for bio-resources such as fish, shells and sea weeds. In addition, the marine or ocean environment exerts great influences on climatic changes on the local and/or global scale. Thus, the conservation of the marine environment has received great interest from the viewpoints of resources and climate changes. However, the pollution of the marine environment due to hazardous chemicals and heavy metals are often caused by our human activities. Therefore, the monitoring of the marine environment is really necessary for environmental conservation. Since the concentrations of trace metals in seawater are in general extremely low,1,2) they so occasionally reflect some changes of the aquatic environment due to the biological activities or the environmental pollution from some anthropogenic sources.1) Thus, the concentration changes of trace metals in coastal and open seawater can often be the good indicators for environmental monitoring. Seawater sampling in coastal and open sea areas, however, is generally a difficult and tedious work. Thus, development of a convenient sampling system for seawater is really required for such marine environmental monitoring.

As reported in our short communication,3) an automated sampling system for the on-board collection of surface seawater, which was installed on a ferryboat (Kuroshio-maru; Kansai Kisen, Osaka, Japan), was developed, and it was employed for the automated seawater sampling along the ferry track between Osaka and Okinawa.4) Then, the concentrations of dissolved trace metals in surface seawater collected at 17 sampling points were determined by ICP-MS (inductively coupled plasma mass spectrometry) after chelating resin preconcentration,3) in a manner similar to the previous works.5-7) It was found that W, Cd and La, whose concentrations dissolved in open seawater were below 0.01 μg l^{-1}, provided the higher concentrations in the Seto Inland Sea area near to Osaka Bay as well as in the coastal sea areas near to Bungo Canal and Kagoshima Bay. In the present experiment, hence, further investigation on multielement concentration monitoring of major-to-ultratrace elements in the dissolved and acid-soluble forms was carried out by ICP-MS and ICP-AES.

5-2 Experimental

5-2-1 Sampling and pretreatment of seawater samples

The seawater samples were collected at 5 m below the surface water through a stainless pipe line which was set up on the bottom of the ship. These seawater samples were collected at 17 sampling stations along the ferry track between Osaka and Okinawa during December 5-7, 1996. The sampling locations and the water qualities such as temperature, salinity, and dissolved oxygen (DO) are summarized in Table 5-1. The sampling locations are also illustrated in Fig. 5-5, which will be shown later. Among the sampling stations, the No. 1~No. 3 stations are in the East part of Seto Inland Sea, which is the sea area between the Honshu and Shikoku Islands.

Table 5-1. Sampling locations, sampling dates, and hydrographic data of seawater samples.

Station No.	Location Longitude (E)	 Latitude (N)	Temperature ℃	Salinity ‰	Dissolved oxygen mg l^{-1}	Sampling date
1	135° 05’	34° 28’	17.2	32.993	7.61	Dec 5, 1996
2	134° 58’	34° 12’	18.0	33.420	7.49	Dec 5, 1996
3	134° 50’	33° 48’	18.4	33.743	7.98	Dec 5, 1996
4	134° 04’	33° 09’	21.1	34.440	8.14	Dec 6, 1996
5	132° 50’	32° 42’	20.8	34.550	6.81	Dec 6, 1996
6	132° 11’	32° 24’	19.8	34.550	7.20	Dec 6, 1996
7	131° 48’	31° 58’	21.1	34.510	6.88	Dec 6, 1996
8	131° 22’	31° 20’	21.1	34.485	6.72	Dec 6, 1996
9	130° 42’	30° 57’	19.4	34.760	6.25	Dec 6, 1996
10	130° 31’	30° 43’	22.1	34.325	6.88	Dec 6, 1996
11	130° 21’	30° 27’	21.8	34.312	6.85	Dec 6, 1996
12	130° 14’	30° 12’	21.8	34.303	6.96	Dec 6, 1996
13	130° 06’	29° 54’	22.7	34.233	6.78	Dec 6, 1996
14	129° 59’	29° 36’	23.5	33.943	6.69	Dec 6, 1996
15	129° 46’	29° 01’	23.4	34.220	6.75	Dec 6, 1996
16	129° 13’	28° 22’	23.6	34.198	7.03	Dec 7, 1996
17	128° 25’	27° 27’	24.3	34.115	7.02	Dec 7, 1996

A part of seawater sample at each sampling point was filtered with a membrane filter (pore size 0.45 μm) immediately after sampling, and the remainder of the seawater sample was non-filtered. Both of these filtered and non-filtered samples were acidified to pH *ca.*1 by adding conc. HNO_3. The concentrations of analyte metals in the seawater samples with and without filtration are hereafter referred to as the dissolved and total concentrations, respectively. All the seawater samples were preserved in the high-density polyethylene bottles, which were cleaned by soaking in 6 M HNO_3 for more than a week and washing with pure water prior to use.

5-2-2 Instrumentation

An ICP-MS instrument of model SPQ 8000A (Seiko Instruments, Chiba, Japan), which consisted of a quadrupole-type mass spectrometer, was used for the

Table 5-2 The instrumental components and operating conditions of ICP-MS and ICP-AES instruments

ICP-MS Seiko SPQ 8000A	
Plasma conditions:	
Incident RF power	1.0 kW
Coolant gas flow rate	Ar 16 l min^{-1}
Auxiliary gas flow rate	Ar 1.0 l min^{-1}
Carrier gas flow rate	Ar 1.0 l min^{-1}
Sample uptake rate	1.0 ml min^{-1}
Nebulizer	Concentric type
Sampling depth	12 mm
Data acquisition:	
Dwell time	10 ms/channel
Data points	3 points/peak
Number of scans	100
ICP-AES Jarrell-Ash Plasma AtomComp Mk II	
Plasma conditions:	
Incident RF power	1.0 kW
Coolant gas flow rate	Ar 20 l min^{-1}
Auxiliary gas flow rate	Ar 1.0 l min^{-1}
Carrier gas flow rate	Ar 0.48 l min^{-1}
Sample uptake rate	1.2 ml min^{-1}
Nebulizer	Cross-flow type
Observation height	18 mm
Data acquisition:	
Integration time	10 s
Accumulation time	3 times
Repetition	3-10 times

determination of trace metals in seawater. An ICP-AES of model Plasma AtomComp MkII (Jarrel Ash, Flanklin, MA, USA) was also used for the determination of major and minor elements. The instrumental components and operating conditions of the ICP-MS and ICP-AES instruments are shown in Table 5-2. These operating conditions were chosen after optimization of each instrumental parameter. A pH meter of model twin pH meter from Horiba Seisaku-sho (Kyoto, Japan) was used for the pH measurement. This pH meter was of non-contact type in order to avoid contamination from electrode materials.

5-2-3 Chemicals

The chemicals such as nitric acid, hydrochloric acid, acetic acid, and aqueous ammonia solutions were of electronics industry grade, purchased from Kanto Chemicals (Tokyo, Japan). The multielement standard solutions used for making the working calibration curves were prepared from the single-element standard solutions (1000 mg l^{-1}) of analyte metals for atomic absorption spectrometry from Wako Chemicals (Osaka, Japan). The compositions of the multielement standard solutions were similar to those used in the previous work.5)

The chelating resin (Chelex 100) in 100-200 mesh was purchased from Bio-Rad Laboratories (Lichmond, CA, USA). The resin was soaked in 5 M HCl for about one week, changing every day, and washed with pure water before use. Pure water used throughout the present experiment was prepared by a Milli-Q purification system (Nihon Millipore Kogyo, Tokyo, Japan).

5-2-4 Preconcentration procedure of trace metals in seawater

Trace metals in both filtered and non-filtered seawater samples were preconcentrated by using a chelating resin (Chelex 100) prior to the determination by ICP-MS, in a manner similar to the previous papers.5-7) In preconcentration procedure, 250 ml of the seawater sample was taken in a glass beaker, and the pH of the sample was adjusted to pH 6 by using acetic acid solution and aqueous ammonia solution. Then, 0.2 g (dry weight) of the chelating resin was added to the seawater sample, and the sample solution was stirred for 2 h with a magnetic stirrer. The chelating resin was then collected on a glass filter (G4) by filtration, and it was rinsed with 8 ml of 1 M ammonium acetate solution to elute any Mg and Ca partly adsorbed on the resin. Finally, analyte metals adsorbed on the chelating resin were eluted with 6 ml of 2 M HNO_3 solution, into which 0.5 ml of a mixed solution of Ge, In, Re, and Tl (100 μg l^{-1} each) was added as internal standard elements to correct matrix effects due to co-existing major elements. As a result, about 40-fold preconcentration in volume was

achieved. Thus obtained solutions are hereafter referred to as the analysis solutions for the ICP-MS measurements. In consequence, 28 trace metals could be determined by the present method.

In addition, major elements such as Na, K, Mg and Ca were determined by ICP-AES after appropriate dilution of the seawater samples with pure water.

5-3 Results and Discussion

5-3-1 Analytical figures of merit

The analytical detection limits of trace metals obtained by the present analytical method are summarized in Table 5-3, together with the blank values, where only Fe was measured by ICP-AES. These analytical detection limits were estimated as follows, in a manner similar to the previous work.5) First, the instrumental detection limits were obtained as the concentrations of analyte metals corresponding to 3-times the standard deviation (3σ) of the blank signal intensities at each m/z in the ICP-MS measurement, when 2 M HNO_3 was nebulized as the blank solution into the plasma. The standard deviation (σ) was calculated from the 10-times repeated measurements. Then, the analytical detection limits were estimated from the instrumental detection limits, taking into account the preconcentration factors and the recovery values in the chelating resin preconcentration. As is seen in Table 5-3, the analytical detection limits for 28 analyte elements were in the range from 0.02 μg l^{-1} of Ti to 0.000006 μg l^{-1} of Ho. The blank values in the present method were almost negligible because they were much lower than the abundances of analyte elements in seawater. The relative standard deviations, for example, for V, Mn, Ni, Cu, Mo, Cd, La, Eu, Lu, W, and U in the dissolved forms were 5.4, 5.4, 2.6, 4.8, 6.6, 7.8, 5.6, 8.9, 4.5, 3.1, and 1.6%, respectively, in replicate measurements (n=3) at their concentration levels in open seawater, as reported previously.3)

5-3-2 Concentrations of dissolved trace metals in surface seawater

First, the surface seawater samples filtered with the membrane filters were subjected to the determination of dissolved trace metals by ICP-MS after chelating resin preconcentration. Here, dissolved trace metals indicate analyte metals in membrane-filtered surface seawater. The analytical results for 28 trace metals are summarized in Table 5-4. In Table 5-4, the data for the average concentrations of trace metals in the seawater samples collected at the No.1～No.3 stations (inland sea area) and at other stations (No.4～No.17; Kuroshio current zone) are separately shown

Table 5-3 Analytical detection limits and blank values for analyte metals obtained by the chelating resin preconcentration/ICP-MS method.

Element	m/z or wave length	Analytical detection limit $\mu g\ l^{-1}$	Blank value $\mu g\ l^{-1}$
Al	27	0.003	0.262
V	51	0.0007	0.0004
Mn	55	0.0005	0.0045
Fe	259.9 nm [a]	0.002	0.028
Co	59	0.0002	0.0023
Ni	62	0.003	0.027
Cu	63	0.002	< 0.006
Zn	66	0.003	0.018
Y	89	0.00002	0.00013
Mo	98	0.0005	— [b]
Cd	111	0.0002	< 0.0006
La	139	0.00001	0.13
Ce	140	0.00003	0.16
Pr	141	0.000009	0.009
Nd	146	0.00004	0.09
Sm	147	0.00004	0.01
Eu	151	0.00001	— [b]
Gd	157	0.00003	0.02
Tb	159	0.000008	— [b]
Dy	163	0.00002	— [b]
Ho	165	0.000006	— [b]
Er	166	0.00002	0.03
Tm	169	0.000007	0.013
Yb	174	0.00002	0.01
Lu	175	0.000008	0.012
W	184	0.00003	0.00046
Pb	208	0.0002	0.0124
U	238	0.0004	— [b]

a) The wavelength of Fe II emission line.
b) Not detected.

as the concentrations in the inland and open sea areas, respectively. In addition, the literature values for the dissolved concentrations of trace metals in seawater collected in the different sea areas[2, 8-11] are also shown in Table 5-4.

As is seen in Table 5-4, the concentrations of dissolved trace metals in inland sea area were in the range of 17.7 $\mu g\ l^{-1}$ of Zn to 0.00017 $\mu g\ l^{-1}$ of Eu, while those in

Kuroshio current zone were in the range from 10.2 $\mu g\ l^{-1}$ of Mo to 0.000044 $\mu g\ l^{-1}$ of Eu and Tm. The concentrations of most trace metals except for V, Mo and U were significantly higher in the inland sea area near Osaka Bay than in the Kuroshio current zone. These results indicate that seawaters in the inland sea area are clearly polluted

Table 5-4 Comparison of concentrations of trace elements in the present work and in the previous works.

Element	This work				Reported		
	Concentration/ $\mu g\ l^{-1}$				Concentration/ $\mu g\ l^{-1}$	Area	(Reference)
	Inland Sea[a)]		Kuroshio current[b)]				
	Dissolved	Total	Dissolved	Total			
Al	3.39	22.4	2.17	2.11			
V	1.74	2.06	1.59	1.71	1.7	Okinawa	(8)
Mn	1.1	3.1	0.34	0.41	0.09-0.7	Kuroshio current	(9)
					0.03	North. Pacific	(10)
Fe	7.4	33.1	2.9	18.1	0.8	Kuroshio current	(11)
Co	0.060	0.062	0.049	0.048	0.02-0.05	Kuroshio current	(11)
Ni	5.53	9.68	2.9	3.0	0.5	Kuroshio current	(11)
Cu	3.81	3.85	0.97	1.17	0.02-0.1	Kuroshio current	(9)
Zn	17.7	14.7	8.4	8.2	0.02-0.1	Kuroshio current	(9)
Y	0.024	0.044	0.006	0.008	0.011	Sagami Bay	(2)
Mo	9.5	10.7	10.2	10.7	10	Okinawa	(8)
Cd	0.015	0.02	0.0052	0.0053	0.0014	Kuroshio current	(11)
La	0.0043	0.034	0.0010	0.0017	0.0022	Sagami Bay	(2)
Ce	0.0018	0.042	0.00053	0.0018	0.0014	Sagami Bay	(2)
Pr	0.0007	0.0052	0.00022	0.00044	0.00045	Sagami Bay	(2)
Nd	0.0031	0.022	0.00065	0.0015	0.0019	Sagami Bay	(2)
Sm	0.00075	0.0045	0.00010	0.00033	0.00047	Sagami Bay	(2)
Eu	0.00017	0.00093	0.000044	0.00015	0.00012	Sagami Bay	(2)
Gd	0.0014	0.0057	0.00026	0.00056	0.00062	Sagami Bay	(2)
Tb	0.00023	0.00083	0.000053	0.00014	0.00012	Sagami Bay	(2)
Dy	0.0018	0.0057	0.00035	0.00067	0.00065	Sagami Bay	(2)
Ho	0.00044	0.0012	0.000083	0.00019	0.00018	Sagami Bay	(2)
Er	0.0016	0.0037	0.00035	0.00053	0.00058	Sagami Bay	(2)
Tm	0.00023	0.00053	0.000044	0.00011	0.000081	Sagami Bay	(2)
Yb	0.0017	0.0042	0.00028	0.00053	0.00046	Sagami Bay	(2)
Lu	0.00026	0.00060	0.000051	0.00010	0.000077	Sagami Bay	(2)
W	0.034	0.084	0.012	0.019	0.01	Okinawa	(8)
Pb	0.30	1.1	0.063	0.19			
U	3.65	3.67	3.37	3.65	3.3	Okinawa	(8)

a) Mean values of analytical data for surface seawater collected at the No. 1-No. 3 sampling stations.
b) Mean values of analytical data for surface seawater collected at the No. 4-No. 17 sampling stations.

by some artificial sources due to the material flows through the rivers. As reported previously,[3)] the oxoanion-forming metals such as V, Mo and U, which were at the concentration level higher than 1 μg l^{-1}, showed almost the uniform concentration distributions at all the sampling stations. On the other hand, the concentrations of W which is also the oxoanion-forming element, were higher by about 3-fold in the inland sea area than in the Kuroshio current zone.[3)] These results suggest that the influences from some anthropogenic sources are not detected at the μg l^{-1} level within the experimental error, while such influences can be sensitively detected at the lower ng l^{-1} level. The similar trends can also be seen for trace metals such as Cd, Pb and all REEs (rare earth elements). Furthermore, trace metals such as Al, Mn, Fe, Ni, Cu and Zn, whose concentrations were above the μg l^{-1} level, provided the higher concentrations in the inland sea area than in the Kuroshio current zone. These results may be interpreted by the fact that large amount of use of metals in the modern industry causes accumulation of such metals as the anthropogenic pollution in the bay area. However, it is considered that some parts of Al, Fe, and Mn in the bay area were increased by the supply of terrestrial clay minerals from the rivers. The concentrations of V, Co, Mo, and Cd in Kuroshio current zone were in good agreement with the literature values.[8,9,11)] The concentrations of other analyte elements were slightly different from the literature values, although their differences for each element were within one order of magnitude. These facts mean that the concentrations of dissolved trace metals determined in the present study were at the reasonable levels. On the other hand, the concentrations of Cu and Zn were relatively larger even in Kuroshio current zone than literature values.[2,9)] These high concentrations of Cu and Zn suggest that the pollution caused by human activities was relatively large in seawater along the ferry track between Osaka and Okinawa.

5-3-3 Total concentrations of trace metals in surface seawater

The total concentration here is defined as the concentration of trace metal in surface seawater acidified prior to filtration with a membrane filter. Thus, trace metals dissolved from the particulates, in addition to the dissolved fraction, are contained in the total concentrations. Such total concentrations of trace metals in surface seawater examined in the present experiment are also summarized in Table 5-4, where the data for the inland sea area and the Kuroshio current zone are also separately shown in a manner similar to their dissolved concentrations. The total concentrations of trace metals in surface seawater were in the range from 33.1 μg l^{-1} of Fe to 0.00053 μg l^{-1} of Tm in the Inland sea area, and in the range from 18.1 μg l^{-1} of Fe to 0.00010

μg l^{-1} of Lu, respectively. Generally, the total concentrations of trace metals were significantly higher than their dissolved concentrations, especially in the inland sea area near Osaka Bay. Of course, these results are reasonable because trace metals additionally dissolved from particulates by acidification with nitric acid are contained in the total concentrations. It is also noted here that the total concentrations of trace metals in the inland sea area were higher than those in the Kuroshio current zone, which almost belongs to open sea of the West Pacific Ocean.

In Fig. 5-1, the concentration distributions of Mn, Cd, and REEs (La, Ce, Gd, Eu, Ho, Lu) for both the total and dissolved concentrations are shown for comparison. It is seen in Fig. 5-1 that the total concentrations of all the elements except for Cd are significantly higher at the No. 1~No. 3 stations in the inland sea area than at other stations, and also they are markedly higher than the dissolved concentrations. These results indicate that the suspended particles are more distributed in the inland sea area than in open sea area. The similar trends that the total concentrations of Mn and Fe were significantly higher than their dissolved concentrations were observed in the Tokyo Bay.[9,12)]

In the case of Cd, both the total and dissolved concentrations were almost similar to each other at all the sampling stations, although the concentrations were higher in the inland sea than in the open sea. This fact may indicate that Cd in surface seawater is mostly in the soluble form, maybe, in $CdCl_4^-$.

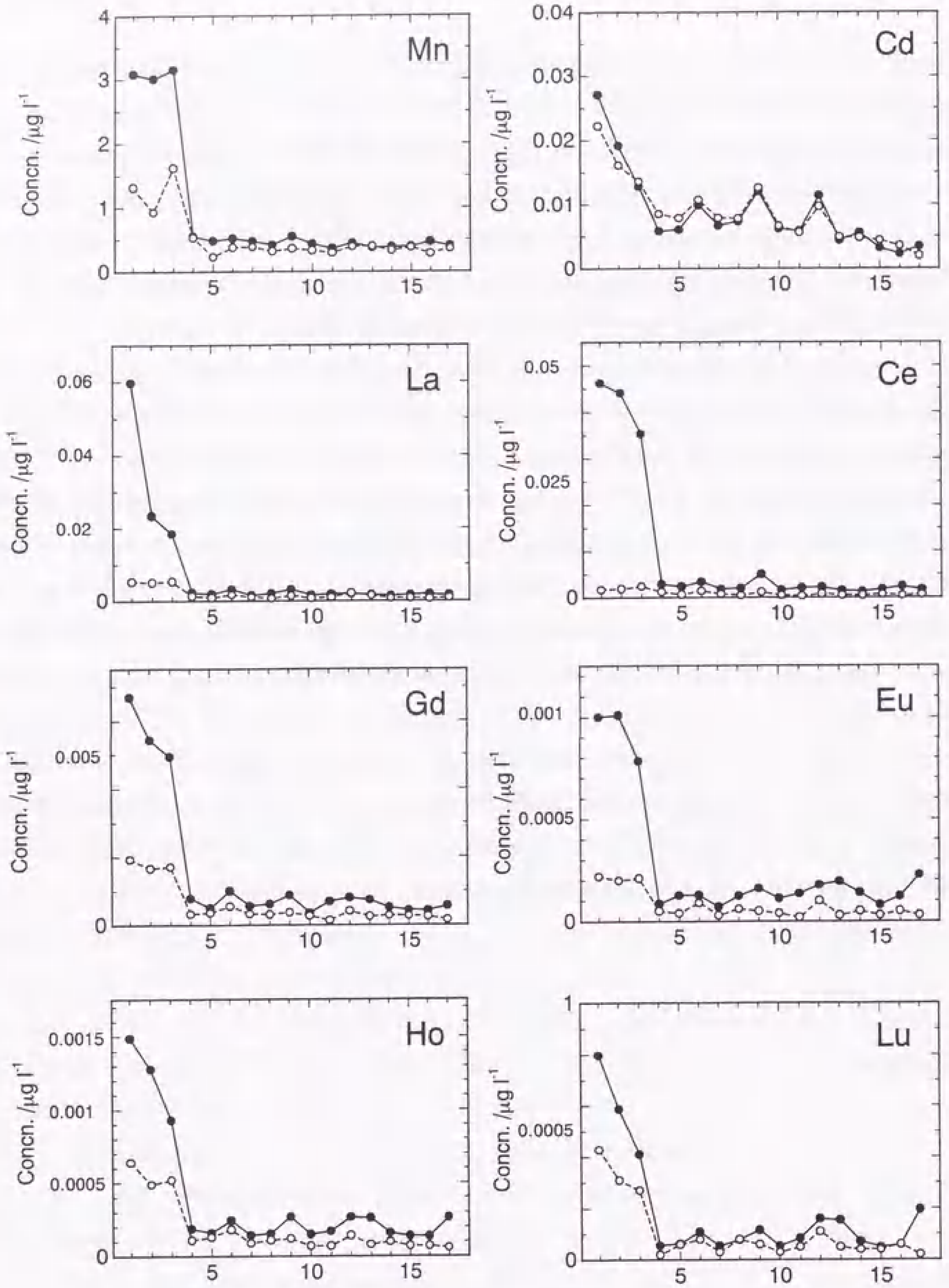

Fig. 5-1 The concentration distributions of trace metals (Mn, Cd and REEs) at various sampling stations.

●; total concentration, ○; dissolved concentration.

5-3-4 Concentration variations of oxoanion-forming metals in surface seawater along the ferry track from Osaka to Okinawa

The distributions of the total and dissolved concentrations of Mo, U, V, and W in surface seawater samples collected at the 17 sampling stations are shown in Fig. 5-2. As reported previously,[3] the mean dissolved concentrations of Mo, U, and V in all the seawater samples examined were 10.2±1.7 μg l^{-1}, 3.38±0.49 μg l^{-1} and 1.60±0.17 μg l^{-1}, respectively. These concentration levels were quite reasonable, compared to the literature values as the concentrations of Mo, U, and V dissolved in seawater,[2] although some fluctuations of the concentrations were observed, probably, because of their poor recoveries in chelating resin preconcentration.[5,6] It is seen in Fig. 5-2 that the dissolved concentrations of W was at the 0.01 μg l^{-1} level in the open sea area, which were lower by *ca.* 3 orders of magnitude than those of Mo, U, and V. Under these conditions, the dissolved concentration of W was significantly higher at Stns. 1-3 in the inland sea area than those at all other sampling stations in the open sea area.

The variations of the total concentrations of Mo, U, V and W in the surface seawater at the 17 sampling points along the ferry track from Osaka to Okinawa are also shown in Fig. 5-2. It is seen in Fig. 5-2 that the total concentrations of Mo, U, and V are almost at the same concentration levels in surface seawater from Osaka to Okinawa. However, the extremely high total concentrations were observed for W near Osaka Bay in the inland sea area, which were higher by almost 10-fold than those in open sea near to the Okinawa Islands. In addition, the total concentrations of W were also significantly high at Stn. 6 near to the Bungo Canal and at Stn. 9 near to the exit of Kagoshima Bay. It is stated here from the results in Fig. 5-2 that the markedly high concentrations of W were commonly observed at the sampling stations near to industrial areas with large populations. These results certainly indicate some anthropogenic pollution caused by human and industrial activities. The similar concentration profiles were also observed for Mn and REEs, as is seen in Fig. 5-1.

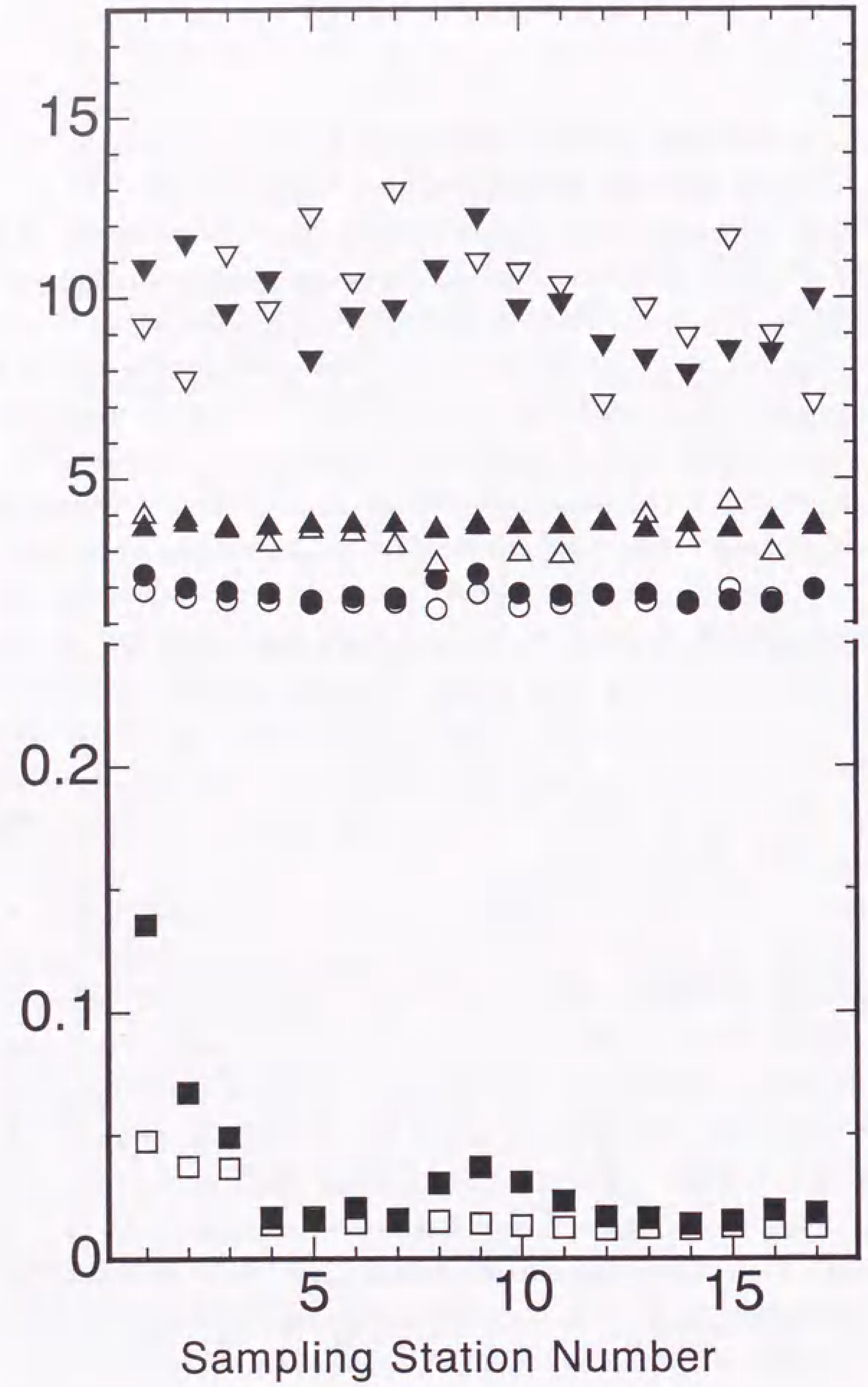

Fig. 5-2 The concentration distributions of Mo, U, V, and W in surface seawater along the Okinawa ferry track between Osaka and Okinawa.

▽,▼; Mo, △,▲; U, ○,●; V, □,■; W
The solid marks indicate their total concentrations.
The open marks indicate their dissolved concentrations.

5-3-5 Acid-soluble fractions of trace metals in surface seawater

As described in the experimental section, the surface seawater samples acidified before and after filtration with a membrane filter were subjected to the determination of the total and dissolved concentrations, respectively. Thus, the differences between the total and dissolved concentrations of trace metals correspond to their acid-soluble concentrations in surface seawater. Therefore, the acid-soluble fractions of trace metals were estimated as the ratios (%) of the acid-soluble concentrations to the total concentrations. Such acid-soluble fractions of trace metals in surface seawater are shown in Fig. 5-3, separately in the terms of the inland sea area (●: Stn. 1~Stn. 3) and open sea area (△: Stn.10~Stn.17).

In open sea area, REEs generally provided the large acid-soluble fractions more than 50%, while Al, transition metals (Cu, Mn, Ni, Co, Zn, Cd) and oxoanion-forming metals (U, Mo, V) provided the small acid-soluble fractions less than 25%. These results suggest that REEs are much more contained as the acid-soluble forms in the suspended particulates in surface seawater of open sea area, while oxoanion-forming metals and Cd in open seawater exist mostly as the soluble forms. In the cases of Al

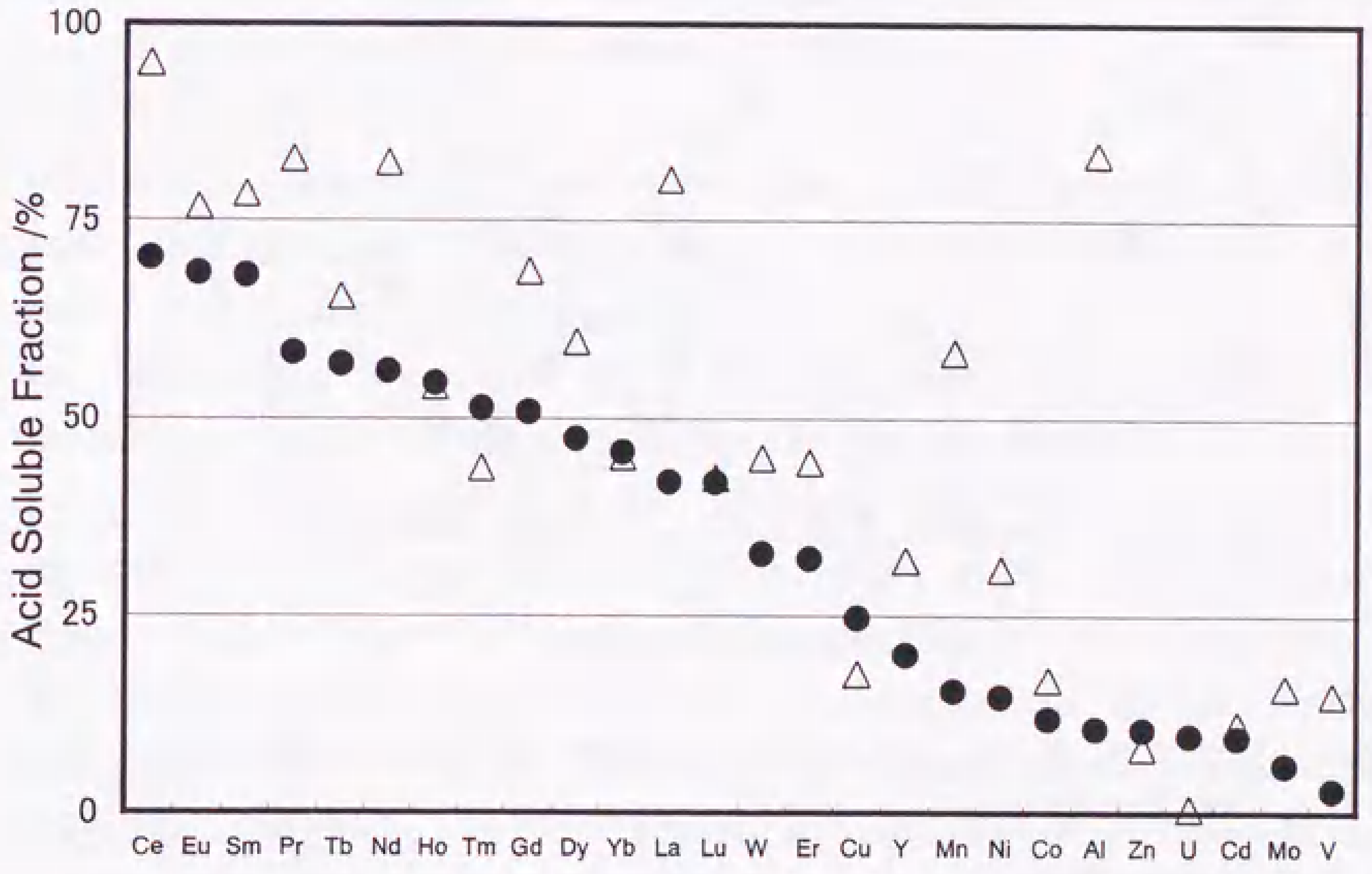

Fig. 5-3 The acid-soluble fractions of trace metals in surface seawater collected in open sea and inland sea areas.

△; the mean concentration from Stn. 1 to Stn. 3 (Inland Sea area), ●; the mean concentration from Stn.10 to Stn. 17 (open sea area).

and transition metals, it is considered that they are in the fine colloidal particles which may pass the membrane filter.

In inland sea area, the acid-soluble fractions of trace metals showed some characteristic behaviors, which were different from those in open sea area. The acid-soluble fractions of REEs are significantly larger in inland sea area than in open sea area. However, the acid-soluble fractions of light-REEs (La, Ce, Pr) are generally much larger than those of heavy-REEs (Tm, Yb, Lu). According to the study on chemical speciation of REEs in lake water,[13] heavy-REEs are more soluble than light-REEs because heavy-REEs provide the larger stability constants in complex formation with biogenic organic molecules, compared to light-REEs. In addition, Al and Mn showed markedly large acid-soluble fractions in inland sea area. These results suggest that Al and Mn in surface seawater of Inland sea are mostly in the colloidal forms of hydroxides and/or oxides, which are easily soluble even in weak acid. As mentioned earlier, the similar trends were observed in terms of Mn and Fe in seawater collected in Tokyo Bay.[9,12] The acid-soluble fractions of W, Y, Ni, Co, Mo, and V in inland sea area are also larger than those in open sea area. Thus, trace metals which provided the large acid-soluble fractions may exist as the colloidal forms of hydroxides and/or oxides forms adsorbed on the suspended mineral particulates.

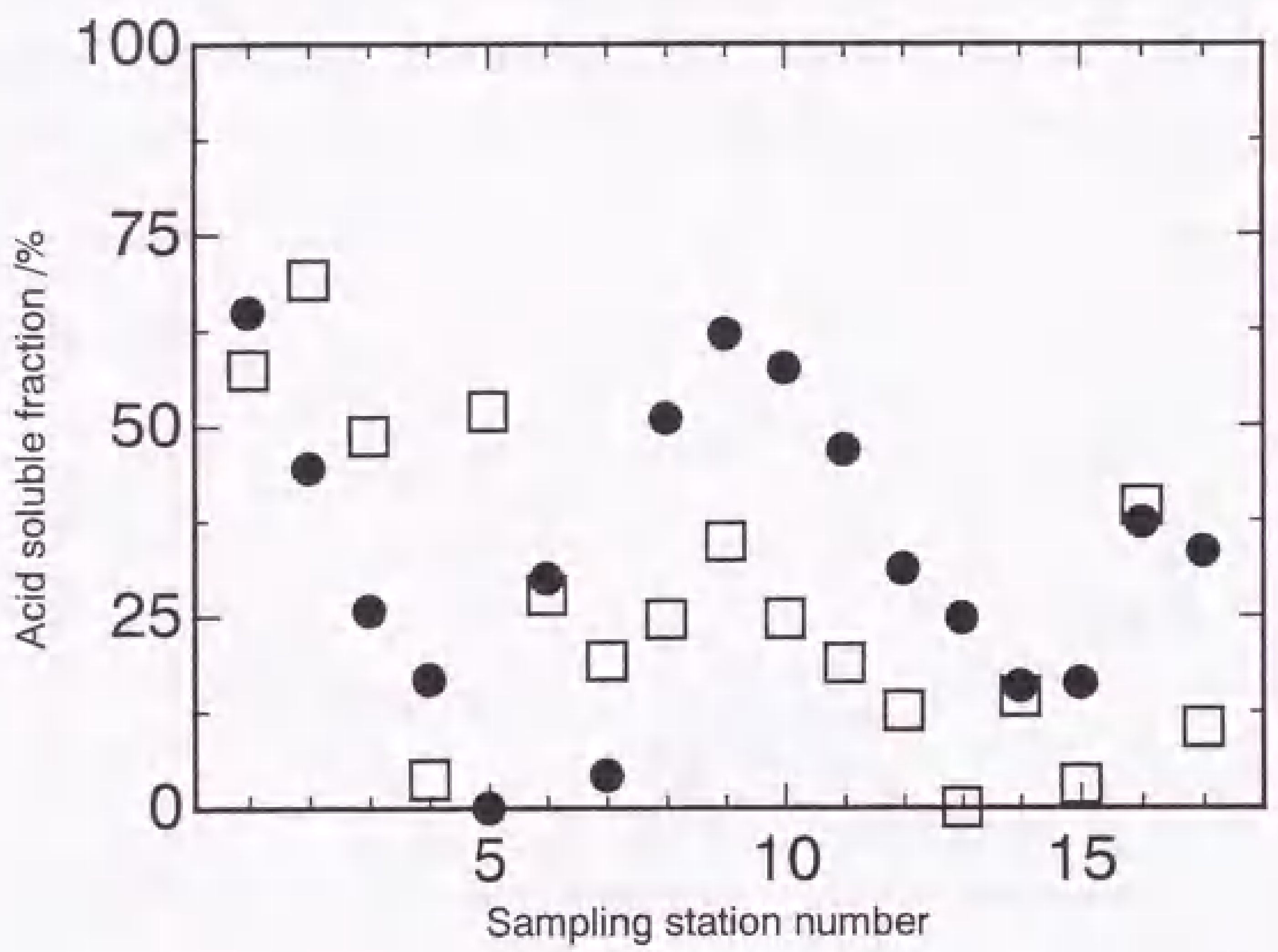

Fig. 5-4 Variations of the acid-soluble fractions of Mn and W through the sampling stations.
□; Mn, ●; W.

The variations of the acid-soluble fractions for Mn and W in surface seawater along the ferry track from Osaka to Okinawa are also shown in Fig. 5-4. As is seen in Fig. 5-4, the acid soluble fractions of Mn and W showed remarkable changes along the track examined. It is noted that the acid-soluble fractions of Mn and W were higher not only in inland sea area, but also in open sea area, especially near Bungo Canal (Station No. 6) and the exit of Kagoshima Bay (Station No. 9). The acid-soluble fractions of W were significantly large near Station No. 9. The active volcano Mt. Sakuragima is located near Kagoshima Bay, and thus it is considered as one of the possibilities that the supply of volcanic ashes may cause such larger acid soluble fractions of W near Station No. 9.

5-3-6 Variations of dissolved and total concentrations of W, Cd, and La along the ferry track between Osaka and Okinawa

As has been discussed so far, various trace metals in the dissolved and acid-soluble forms showed significant concentration changes in inland sea and open sea areas. In Fig. 5-5, the variations of the dissolved and total concentrations of W, Cd, and La in surface seawater along the ferry track from Osaka to Okinawa are shown as the 3-dimentional illustrations, where the total concentrations are shown as the accumulative sum of the dissolved and acid-soluble concentration. It is clearly seen in Fig. 5-5 that both dissolved and total concentrations of W are significantly high in the inland sea area near Osaka Bay (Stations No. 1-No. 3). In addition, such concentrations of W are also relatively high near to Bungo Canal (Station No. 6) and the exit of Kagoshima Bay (Station No. 9). These results indicate that emission of W from anthropogenic sources due to human and industrial activities in big cities with large population can be sensitively detected as environmental pollution because of its low concentration (below 0.01 $\mu g\ l^{-1}$) in original seawater. It should be noted that the concentrations of Mo, U, and V, which were above 1 $\mu g\ l^{-1}$, were almost constant through the ferry track examined. As is seen in Fig. 5-5, the trends similar to the case of W were also observed in the cases of Cd and La, whose concentrations in open sea were at the lower ng l^{-1} or sub-ng l^{-1} level.

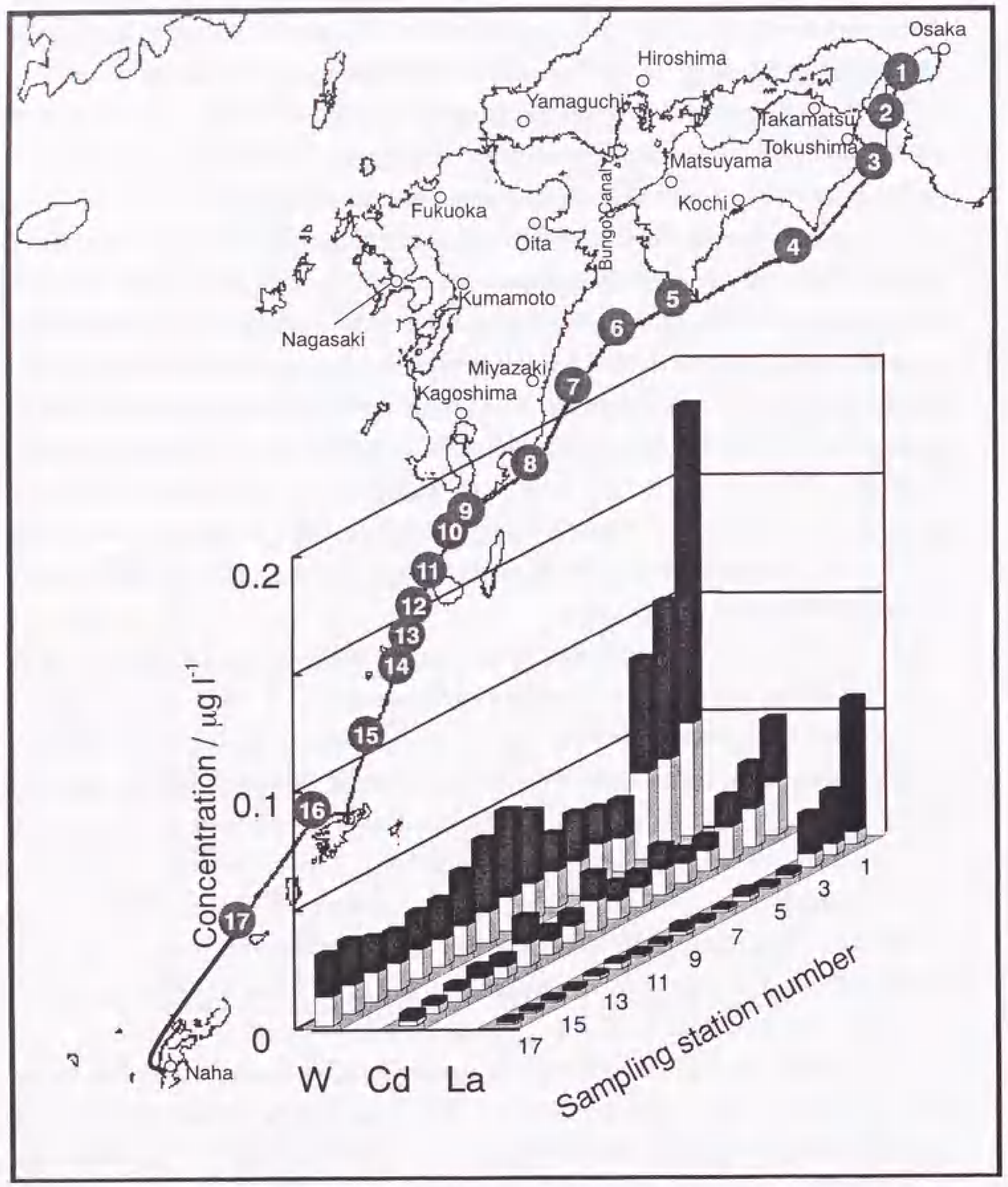

Fig. 5-5 The variations of the dissolved and total concentrations of W, Cd, and La in the surface seawater along the Okinawa ferry track between Osaka and Okinawa.

The total concentrations correspond to the accumulative sums of dissolved and acid-soluble concentrations.
The white part of the bar indicates the dissolved concentration.
The black part of the bar indicate the concentration of the acid-soluble fraction.

5-4 Conclusion

The concentration monitoring of the dissolved and total concentrations of 28 trace metals in the surface seawater along the ferry track between Osaka and Okinawa were carried out by the determination by ICP-MS after chelating resin preconcentration. These results show that most of trace metals were significantly higher in the inland sea area than in open sea area. In addition, it was elucidated from the acid-soluble fractions of trace metals in open and inland sea areas that the large parts of Al, Fe, and Mn in the inland sea area existed as the colloidal forms of hydroxides and/or oxides adsorbed on the suspended particulates. Furthermore, REEs provided the large acid-soluble fractions in all the sea areas, although the acid-soluble fractions of heavy-REEs were smaller in the inland sea area than those of light-REEs.

As a consequence, it can be conclusively stated here that some artificial pollution from the terrestrial areas are sensitively observed for trace metals (Cd, W and REEs) below the 0.01 μg l^{-1} concentration level in coastal or semi-open seawater, although such pollution is difficult to be observed for trace metals with the concentrations above the 1 μg l^{-1} level because their pollution levels are within the standard deviations of the analyte concentrations. It should also be pointed out that the multielement concentration monitoring of trace metals in surface seawater in the coastal and open sea areas provide many meaningul information not only about environmental pollution but also about the chemical forms of trace metals dissolved in seawater.

Acknowledgment

The present research was supported by the Grant-in-Aid from the Science and Technology Agency of Japan. The present authors express sincere thanks to Dr. Masayuki Kunugi (National Institute for Environmental Studies) and Dr. Hiroaki Tao (National Institute for Resources and Environment) for providing the seawater samples examined in the present study.

References

1. H.Haraguchi and T. Akagi, ed. S. J. Haswell, "Atomic Absorption Spectrometry—Theory, Design and Applications", pp. 125-157 Elsevier, Amsterdam, (1991).
2 J .Zhang and Y. Nozaki, *Geochim. Cosmochim. Acta*, **62**, 1307 (1998).
3. T. Yabutani, F. Mouri, and H. Haraguchi, *Anal. Sci.*, **16**, 675 (2000).
4. A. Harashima (*ed.*), *"Collected data of high temporal- spatial resolution marine biogeochemical monitoring from ferry tracks : Seto Inland Sea(Jan. 1996-Nov. 1997) and Osaka-Okinawa (Jan. 1996-Mar. 1998)"*, CGER-DO21(CD-ROM)-'99, (1999).
5. T. Yabutani, S. Ji, F. Mouri, H. Sawatari, A. Itoh, K. Chiba and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 2253 (1999).
6. H. Sawatari, T. Toda, T. Saizuka, C. Kimata, A. Itoh and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **68**, 3065 (1998).
7. H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 1163 (1999).
8. Y. Sohrin, M. Matsui and E. Nakayama, *Geochim. Cosmochim. Acta*, **63**, 3457 (1999).
9. T. Akagi, T. Kodama, H. Haraguchi, K. Fuwa and H. Tsubota, *Geochem. J.*, **20**, 127 (1986).
10. W. M. Landing and K. W. Bruland, *Earth Planet. Sci. Lett.*, **49**, 45 (1980).
11. K. Shitashima and H. Tsubota, *Geochem. J.*, **24**, 283 (1990).
12. T. Akagi, K. Fuwa and H. Haraguchi, *Anal. Chim. Acta*, **177**, 139 (1985).
13. H. Haraguchi, A. Itoh, C. Kimata and H. Miwa, *Analyst*, **123**, 773 (1998).

Chapter 6 Enrichment of Nutrient-type Trace Elements in Surface Seawater of Antarctic Ocean with Occurrence of Natural Seawater Circulation

6-1 Introduction

These days, the vertical distributions of almost all major-to-ultratrace elements in open sea have been clarified, especially in the North Pacific Ocean, by the great efforts of Nozaki.[1] According to the vertical distributions, various elements show the characteristic distribution profiles, reflecting their physicochemical properties and the biological activities in the ocean. In consequence, the elements are classified mainly into three groups from their vertical distribution patterns; (i) nutrient-type elements, (ii) scavenged-type elements, and (iii) conservative-type elements. The classification mentioned above are hereafter referred to as the marine-chemical classification of the elements. In the vertical distributions of the nutrient-type elements, their concentrations are lower in the upper layer of water column (0-300 m) and higher in the lower water column(below *ca.* 300 m). On the other hand, the scavenged-type elements show the reversed profiles of the vertical concentration distributions because of their fast settling-down with the particulates. In the vertical distributions of the conservative-type elements, their concentrations are almost constant from the surface to the bottom. It is well known that the lower concentrations of the nutrient-type elements can be correlated with biological activities of diatoms (phytoplanktons). That is, phytoplanktons require the intake of the nutrient-type elements for their growth.

In general, the concentrations of trace elements in seawater are extremely low. Therefore, the accurate determination of trace elements in seawater has been quite difficult until recent years. However, the recent development of ICP-MS (inductively coupled plasma mass spectrometry) allows us to determine a variety of trace elements simultaneously with good accuracy and precision,[2] when some appropriate preconcentration is performed. For such purposes, the present authors have developed the chelating resin preconcentration and La coprecipitation methods for the multielement determination of more than 30 elements in seawater by ICP-MS.[3-5]

Then, such preconcentration methods were successfully applied to the determination of trace elements in the open and coastal seawater samples.

In the present paper, the study on the multielement determination of trace elements in seawater was extended to the analyses of the surface seawater samples colleted in the Pacific Ocean, the West Australian Sea and the Antarctic Ocean, in order to elucidate the concentrations of trace elements and their differences in the sea areas of the Southern Hemisphere. The special interest of the present research was focused on the elemental distributions in the Antarctic Ocean in relation with the biological activities.

6-2 Experimental

6-2-1 Seawater samples

The surface seawater samples were collected at the 11 sampling stations in the West Pacific Ocean, the West Australian Sea and the Antarctic Ocean by the marine observation ship “Shirase”, which belonged to the Maritime Self-Defense Force (Tokyo, Japan). The locations of the sampling stations are summarized in Table 6-1, together with the hydrographic data such as seawater temperature, salinily, dissolved oxygen (DO), and chlorophyll *a* contents. The sampling stations at No. 2 and No. 3 were close to the equator near the Philippine islands. The variations of seawater temperature, DO and chlorophyll *a* contents are also illustrated in Fig. 6-1, which will be shown later.

Table 6-1. Data for sampling locations, temperature, salinity, dissolved oxygen, and Chlorophyll *a*.

Station No.	Location latitude	 longitude	Seawater temperature ℃	Salinity ‰	Dissolved oxygen mg l^{-1}	Chlorophyll *a* μg l^{-1}
1	12°29' N	129°19' E	27.88	34.57	6.8	0.53
2	2°33' N	121°19' E	28.84	34.43	6.25	0.95
3	5°55’ S	116°52’E	29.25	34.40	5.88	1.46
4	11° 42' 0' S	116°52' E	29.42	35.05	5.89	1.38
5	17°42' S	114°08' E	25.92	35.34	6.15	1.22
6	22°44' S	113°07' E	23.39	35.73	6.36	1.62
7	27°58' S	113°07' E	21.57	35.89	6.32	1.6
8	45°28' S	109°54' E	10.13	34.19	8.64	7.46
9	50°23' S	109°54' E	3.82	34.11	11.09	21.91
10	59°11' S	100°40 E	0.51	34.21	12.82	14.19
11	60°04' S	131°52 E	2.87	33.89	11.86	5.44

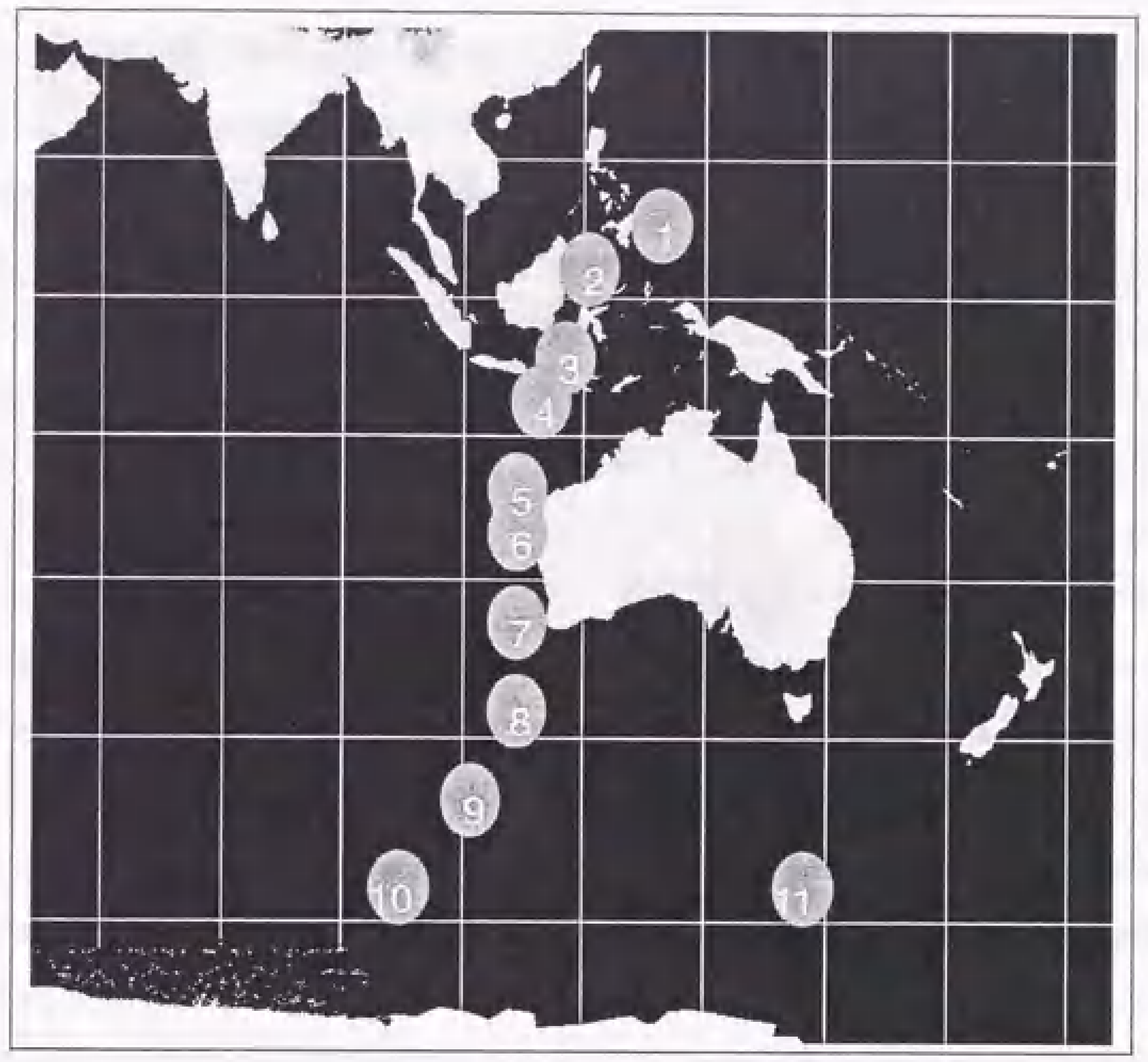

Fig. 6-1 The locations of the sampling stations from West Pacific Ocean to Antarctic Ocean.

The numbers in the figure correspond to the sampling stations listed in Table 6-1.

The surface seawater samples were filtered with the membrane filters (pore size 0.45 μm) immediately after sampling and then preserved in the high density polyethylene bottles, which were kept in a cold room (-20℃). After thawing, the seawater samples were acidified to pH *ca.*1 by adding conc. HNO_3. Then, the samples were subjected to the following determination of trace elements by ICP-MS.

6-2-2 Chemicals

Nitric acid, acetic acid, and aqueous ammonia used were of electronics industry grade, purchased from Kanto Chemicals (Tokyo, Japan). The multielement standard solutions for making the working standard curves were prepared from the standard stock solutions of analyte elements for atomic absorption spectrometry (Wako Chemicals, Osaka, Japan). in the manner similar to the previous work.2)

The chelating resin (Chelex-100) in 100-200 mesh, used for preconcentration, was purchased from Bio-Rad Laboratories (Richmond, CA, USA). The chelating resin was cleaned prior to use by soaking in 5 M HCl, which was changed 5-times every 12 h, and by washing with pure water finally. Pure water used throughout the present experiment was prepared by a Milli-Q purification system (Nihon Millipore Kogyo, Tokyo, Japan).

6-2-3 Preconcentration procedure

The surface seawater samples were subjected to the following tandem preconcentration of trace elements, which was developed in our labolatory.7) In the tandem preconcentration, the chelating resin preconcentration was first applied to the original seawtater, and then La coprecipitation was applied to the filtrate after the chelating resin preconcentration. The preconcentration procedure for trace elements in seawater was almost the same as that described in the previous paper.7) In preconcentration, first, 250 ml of the surface seawater sample was used and 0.2 g (dry weight) of the chelating resin was added into seawater after pH adjustment at 6. Finally, trace elements adsorbed on the chelating resin were eluted with 6 ml of conc. HNO_3, which resulted in *ca*. 40-fold preconcentration. In the second stage of tandem preconcentration, then the filtrate after the chelating resin preconcentration was subjected to La coprecipitation. Two ml of La solution (10 g l^{-1}) was added in the filtrate as a coprecipitation carrier. Then, the sample solution was adjusted to pH 9.5 with aqueous ammonia solution. After collection of the precipitate, the precipitate produced was dissolved in 90 ml of 2 M HNO_3, into which 10 ml of the mixed solution of Ge, In, Re, and Tl (100 $\mu g\ l^{-1}$ each) was added for the internal standard correction of matrix effects in the ICP-MS measurement. Consequently, 2.5-fold preconcentration was achieved in the La coprecipitation procedure. In the estimation of the analytical results, the recoveries of all analytes except for As and Sb in the chelating resin preconcentration and those of As and Sb in the tandem preconcentration were taken into account.

6-2-4 Instrumentation

An ICP-MS instrument of model SPQ 8000A (Seiko Instruments, Chiba, Japan), which consisted of a quadrupole-type mass spectrometer, was used for the determination of trace elements. The resolution of the ICP-MS instrument was *ca*. 350 at each mass unit. The operating conditions of the ICP-MS instrument was almost the same as those employed in the previous papers.3-5) The matrix effects due to major and minor elements in seawater, especially due to Mg and Ca, were corrected by the internal standard correction method,6) where Ge, In, Re and Tl were used as the internal standard elements. In the determination of REEs by ICP-MS, polyatomic ion interferences due to their oxides and/or hydroxides were also corrected by the interference correction coefficient method.

6-3 Results and Discussion

6-3-1 Water qualities of surface seawater in the oceans

As mentioned in the experimental section, the surface seawater samples were collected at 11 the sampling stations in the West Pacific Ocean, the West Australian Sea and the Antarctic Ocean. The locations of the sampling stations are shown in Fig. 6-1. In order to know the fundamental water qualities of all the seawater samples, water temperature, salinity, DO (dissolved oxygen), and chlorophyll *a* contents were measured by the conventional analytical methods, and the results are summarized in Table 6-1. The experimental data for such water qualities are also illustrated in Fig. 6-2 as the distributions in the sea areas examined. As is seen in Fig. 6-2(a), the chlorophyll *a* contents remarkably increased at the sampling stations No. 8-No. 11 in the Antarctic Ocean area, compared to other sea areas. Such increase of chlorophyll *a* indicates that the population of diatoms, one of phytoplanktons, was much larger in the Antarctic Ocean. In other words, the biological activities were much more higher in the Antarctic Ocean than in other sea areas, even though the climate of the Antarctic Ocean was very cold, as is seen in the data of water temperature in Table 6-1.

It is also noticed from Fig. 6-2(b) that DO contents in the Antarctic Ocean was above 10 ml l^{-1}, while it was about 6 ml l^{-1} in the West Pacific Ocean and the West Australian Sea. Such large DO contents in the Antarctic Ocean suggest that kinetic movement for aeration is taking place in the surface layer there to promote dissolution of air into seawater.

In addition, the water temperature distribution in three sea areas is shown in Fig. 6-2(c). As is seen in Fig. 6-2(c), the water temperature was *ca*. 30℃ in the tropical sea areas of the West Pacific Ocean near the equator. However, the water temperature decreased below 5℃ at the No. 9～ No. 11 stations in the Antarctic Ocean. It is known that the specific gravity of salt seawater is the maximum near ice point. Thus, surface seawater in the Antarctic Ocean is quite heavy, which results in down-flow of seawater from the surface to the deep sea. As a result, water circulation between the surface seawater and the deep seawater may take place naturally in the Antarctic Ocean.

6-3-2 Concentrations of trace elements in surface seawater collected from the Pacific Ocean and the Antarctic Ocean

The observed concentrations of trace elements in surface seawater collected

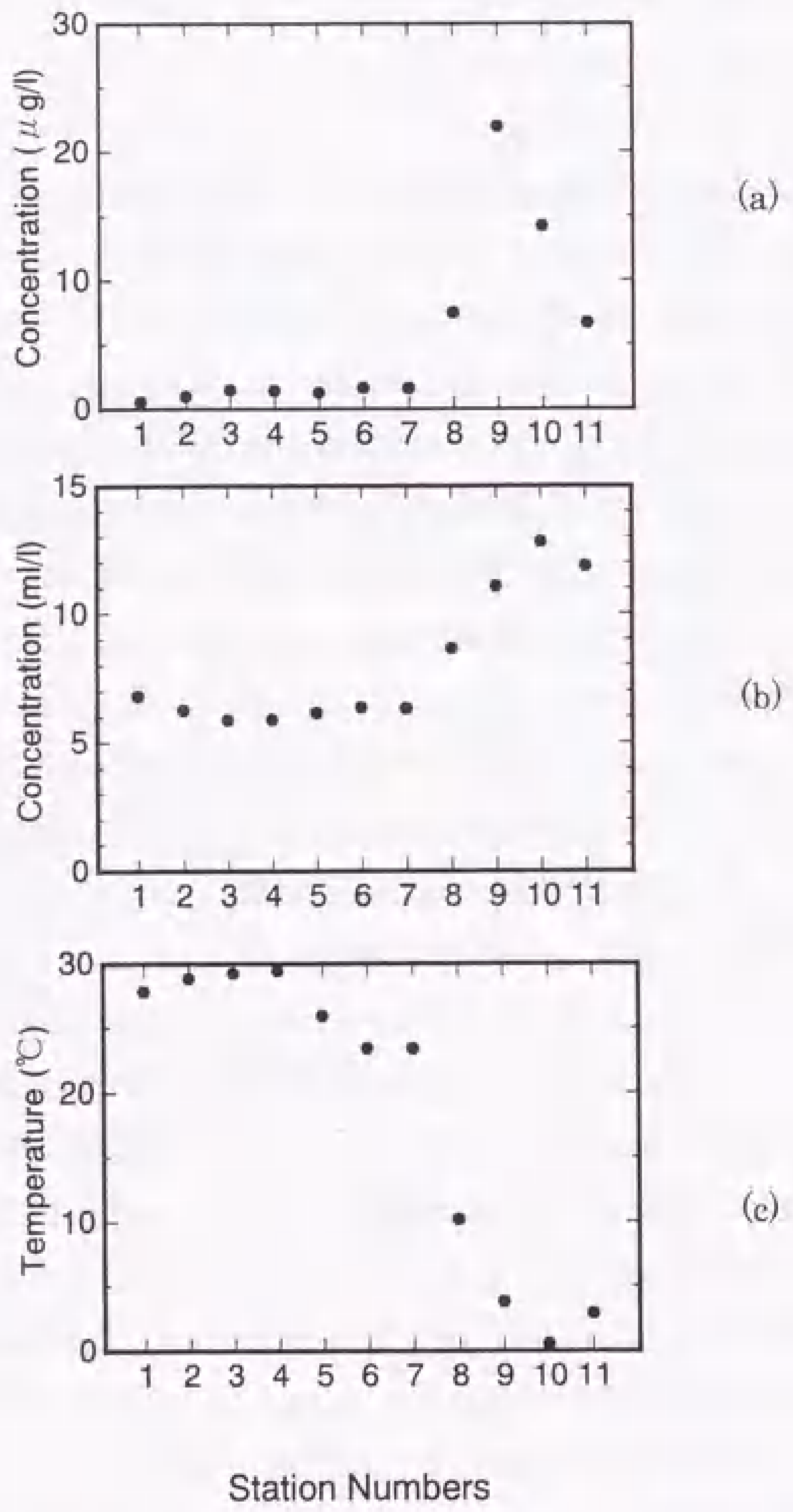

Fig. 6-2 Profiles of chlorophyll *a* contents, dissolved oxygen (DO), and water temperature in the surface seawater.

(a) chlorophyll *a*, (b) dissolved oxygen, (c) seawater temperature.

from the Pacific Ocean and the Antarctic Ocean are summarized in Table 6-2, along with the literature values. In Table 6-2, the marine-chemical classification of the elements are also shown in the last column. The concentrations obtained in the present experiment are the analytical values for surface seawater collected at the No. 1 and No. 11 sampling stations in the Pacific Ocean and the Antarctic Ocean, respectively. In the case of the Pacific Ocean, the seawater samples for the present experiment were collected for the West Pacific Ocean, exactly say, South-west Pacific Ocean, while those for the literatures were collected from the North Pacific Ocean.

As for surface seawater in the West Pacific Ocean (No. 1 station), the analytical values for oxoanion-forming elements such as V, As, Mo, Sb, W, and U agreed well with the literature values, although the values obtained by the present experiment were slightly higher than the literature values. Since these oxoanion-forming elements generally provide almost the constant concentrations in every open sea area, the agreement between the present analytical values and the literature ones suggest the validity of the analytical methods employed in both experiments. It is also seen in Table 6-2 that the concentrations of oxoanion-forming elements in the Pacific Ocean and the Antarctic Ocean were almost consistent with each other. On the other hand, the analytical values of Mn, Co, and Zn in the present experiment for the Pacific Ocean are higher more than 2-fold, compared to the literature values, while those of Ni and Cd in the present experiment were less than a half of the literature ones. The concentrations of Cu in both the present and literature values were almost at the same level. It is noticed that the concentration of Pb in the present experiment was extraordinarily higher than the literature value. The similar trend is also seen in the data for the Antarctic Ocean. Although the reasons were not clear, there might be a possibility of contamination of Pb in the present experiment during the sample storage or the sample pretreatment. In the analysis of open seawater reference material CASS-3, issued from National Research Council of Canada, we obtained the analytical values of 0.0008 μg l^{-1} for Pb, whose certified value is 0.0013 μg l^{-1}.[7)] Taking into consideration these results, contamination of Pb was possibly caused during sample storage.

In the case of rare earth elements (REEs) including Y, the present analytical values for the Pacific Ocean were generally higher except for Ce and Sm than the literature values. Since there is no certified reference material for REEs in seawater, comparison of the analytical values for REEs can not be made anymore. However, further discussion about the concentrations of REEs in seawater will be given later.

Table 6-2. Concentrations and distribution types of trace elements in Pacific Ocean and Antarctic Ocean.

Element	Concentration / μg l^{-1}						Distribution type[h]
	Pacific Ocean			Antarctic Ocean			
	Present work[a]		Reported value[b]	Present work[c]		Reported value	
V	2.5	[1.3]	2	2.3			c
Mn	0.087	[4.4]	0.02	0.034	[8.5]	0.004[d]	s
Co	0.0043	[3.6]	0.0012	0.0020	[1.3]	0.0015[d]	s
Ni	0.17	[0.35]	0.48	0.33	[1.8]	0.18[e]	n
Cu	0.14	[0.93]	0.15	0.15	[1.5]	0.10[e]	n+s
Zn	0.85	[2.4]	0.35	2.93	[42]	0.07[e]	n
As	1.3	[1.1]	1.2	1.8			n+r
Y	0.013	[0.76]	0.017	0.018			n
Mo	11.2	[1.1]	10	10.7			c
Cd	0.033	[0.47]	0.07	0.042	[0.66]	0.063[f]	n
Sb	0.17	[0.89]	0.19	0.14			c
La	0.0022	[0.39]	0.0056	0.0041	[2.7]	0.0015[g]	n
Ce	0.0020	[2.9]	0.00070	0.0014	[1.7]	0.0008[g]	n+s
Pr	0.00055	[0.79]	0.00070	0.00065			n
Nd	0.0022	[0.67]	0.0033	0.0030	[2.6]	0.0011[g]	n
Sm	0.00062	[1.1]	0.00057	0.00056	[2.5]	0.00022[g]	n
Eu	0.00014	[0.82]	0.00017	0.00016	[2.5]	0.00006[g]	n
Gd	0.00066	[0.73]	0.00090	0.00095	[2.6]	0.00036[g]	n
Tb	0.00016	[0.94]	0.00017	0.00015			n
Dy	0.00097	[0.87]	0.00111	0.0012	[2.5]	0.00048[g]	n
Ho	0.00024	[0.67]	0.00036	0.00034			n
Er	0.00071	[0.59]	0.0012	0.0012	[2.6]	0.00046[g]	n
Tm	0.00012	[0.60]	0.00020	0.00018			n
Yb	0.00047	[0.39]	0.00119	0.0011	[2.9]	0.00038[g]	n
Lu	0.000091	[0.40]	0.00023	0.00020	[3.4]	0.000059[g]	n
W	0.013	[1.3]	0.0099	0.012			c
Pb	0.13	[43.3]	0.003	0.037	[28.5]	0.0013[f]	s
U	4.3	[1.4]	3.1	4			c

a) Analytical data for surface seawater collected at the No.1 sampling station (See Fig. 6-1). The values in parentheses are the ratios of the present data to the reported values.

b) Data for surface seawater in the North Pacific Ocean, cited from Ref. 8.

c) Mean values of analytical data for surface seawater collected at the No. 8~No. 11 sampling stations (See Fig. 6-1). The values in parentheses are the ratios of the present data to the reported values.

d) Ref. 9 (Antarctic Ocean), e) Ref. 10 (Antarctic ocean), f) Ref. 11 (Weddel Sea), g) Ref. 12 (Antarctic Ocean).

h) The signs of c, s, n, and r indicate the conservative-, scavenged-, nutrient-, and redox-controlled-type elements, respectively.

In the case of the Antarctic Ocean, the literature values for trace elements were obtained from several literature sources. Thus, it is quite difficult to compare the analytical values with the literature values. Even so, it can be stated here that the analytical values in the present experiment are almost at the same concentration levels as the literature values, except for Mn, Co, Zn, and Pb, although the present analytical values are higher by 2-3 times than the literature values, except for Cd. In general, the concentrations of trace elements are largely different in different sea areas, depending on the local conditions of material supplies and bioactivities. Thus, further research on the concentrations of trace elements in seawater is really required to obtain some comprehensive understanding of trace element chemistry around the Antarctic Ocean.

6-3-3 Distributions of the concentrations of trace elements in the oceans

The concentrations distributions of trace elements in surface seawater collected at the 11 sampling stations are shown in Figs. 6-3~6-7. In the figures, the distributions are shown separately in each group of marine-chemical classification of the elements. In the following sections, the characteristics of the distributions of each type's elements will be discussed to elucidate the elemental populations in these sea areas.

Nutrient-type elements: The concentration distributions of the nutrient-type elements, such as Ni, Cd, Zn, Cu, and As at the 11 sampling stations in three sea areas are shown in Fig. 6-3. It is seen in Fig. 6-3 that Ni and Cd provided the clearly higher concentrations in the Antarctic Ocean than in other sea areas, although Cd was quite higher at the No.1 sampling station in the West Pacific Ocean. It is also seen in Fig. 6-3(c) that the concentration of Zn was rather high in the range of 2〜4 μg l^{-1} at all the stations except for the No. 1 station. The concentration of Cu was at almost the same level of *ca.* 0.2 μg l^{-1} through the sampling stations, while it was slightly higher at the No. 2 and No. 3 stations. As will be described later, Cu has the properties of both nutrient- and scavenged-types. Since the concentrations of Cu were smaller in the Antarctic Ocean, Cu may act rather as the scavenged-type elements in this sea area. On the other hand, the concentrations of As were slightly higher in the Antarctic Ocean than in other sea areas. Thus, it can be stated that As acts rether as the nutrient-type element in the Antarctic Ocean area.

Scavenged-type elements: The concentration distributions of Mn and Co, in surface seawaters at the sampling stations are shown in Fig. 6-4. According to the marine-chemical classification, Mn and Co are the scavenged-type elements. As is seen in Fig. 6-4(a), the concentration of Mn in the Antarctic Ocean was rather lower than in the West Pacific Ocean and the West Australian Sea. On the other hand, the concentration of Co at the No.9～No.11 stations in the Antarctic Ocean was not necessarily low, compared to other oceans. Since the concentrations of Co in surface seawater were fluctuating on the whole, maybe, because of their low concentration close to the analytical detection, it may be difficult to make exact comparison of the analytical data for Co.

Conservative-type elements: As the examples of the conservative-type elements, the distributions of the concentrations of Mo, V, U, W, and Sb in surface seawater collected at the 11 sampling stations are shown in Fig. 6-5. As is well known, the

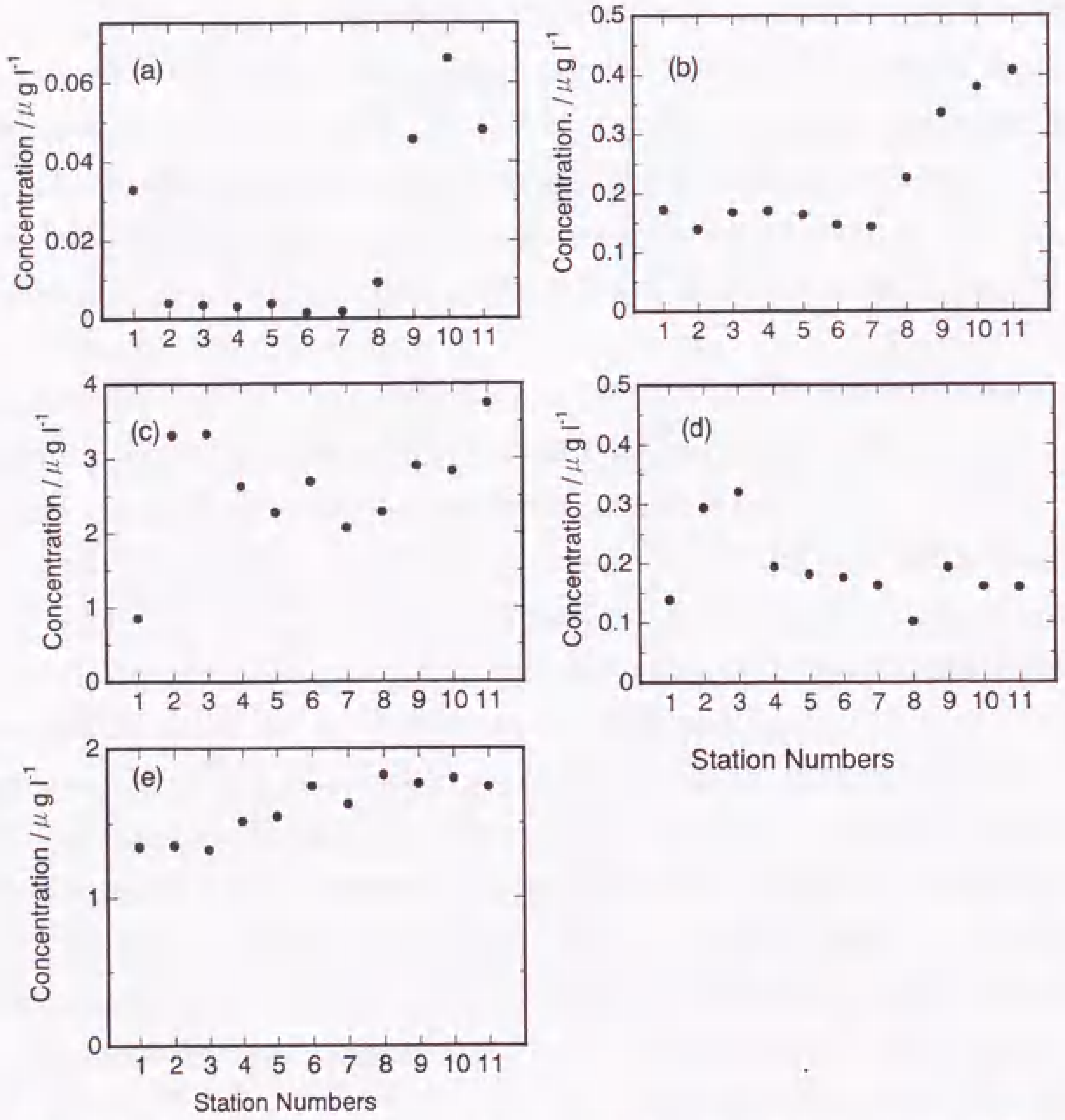

Fig. 6-3 The concentration distributions of nutrient-type elements in surface seawater from West Pacific Ocean to Antarctic Ocean.
(a) Cd, (b) Ni, (c) Zn, (d) Cu, (e) As.

vertical distributions of the conservative-type elements provide the uniform concentration profiles. That is, their concentrations are almost constant from the surface to the bottom in the water column of open sea. It is noted here that the concentrations of Mo, V, U, W, and Sb were almost constant at all 11 sampling stations, although the concentrations of these elements show some fluctuations because of the low recoveries in the chelating resin preconcentration. These results indicate that the conservative-type elements in the ocean are also uniform not only vertically but also horizontally.

Yttrium and rare earth elements: According to the marine-chemical classification, REEs except for Ce belong to the nutrient-type elements, while Ce is a scavenged-type elements. The concentration distributions of REEs including Y in surface seawater of the oceans are shown in Fig. 6-5. Since REEs mostly belong to the nutrient-type elements, it is seen in Fig. 6-6 that Y, La, Pr, Ho and Lu provided the higher concentrations in the Antarctic Ocean (No. 9-No. 11). On the other hand, while Ce

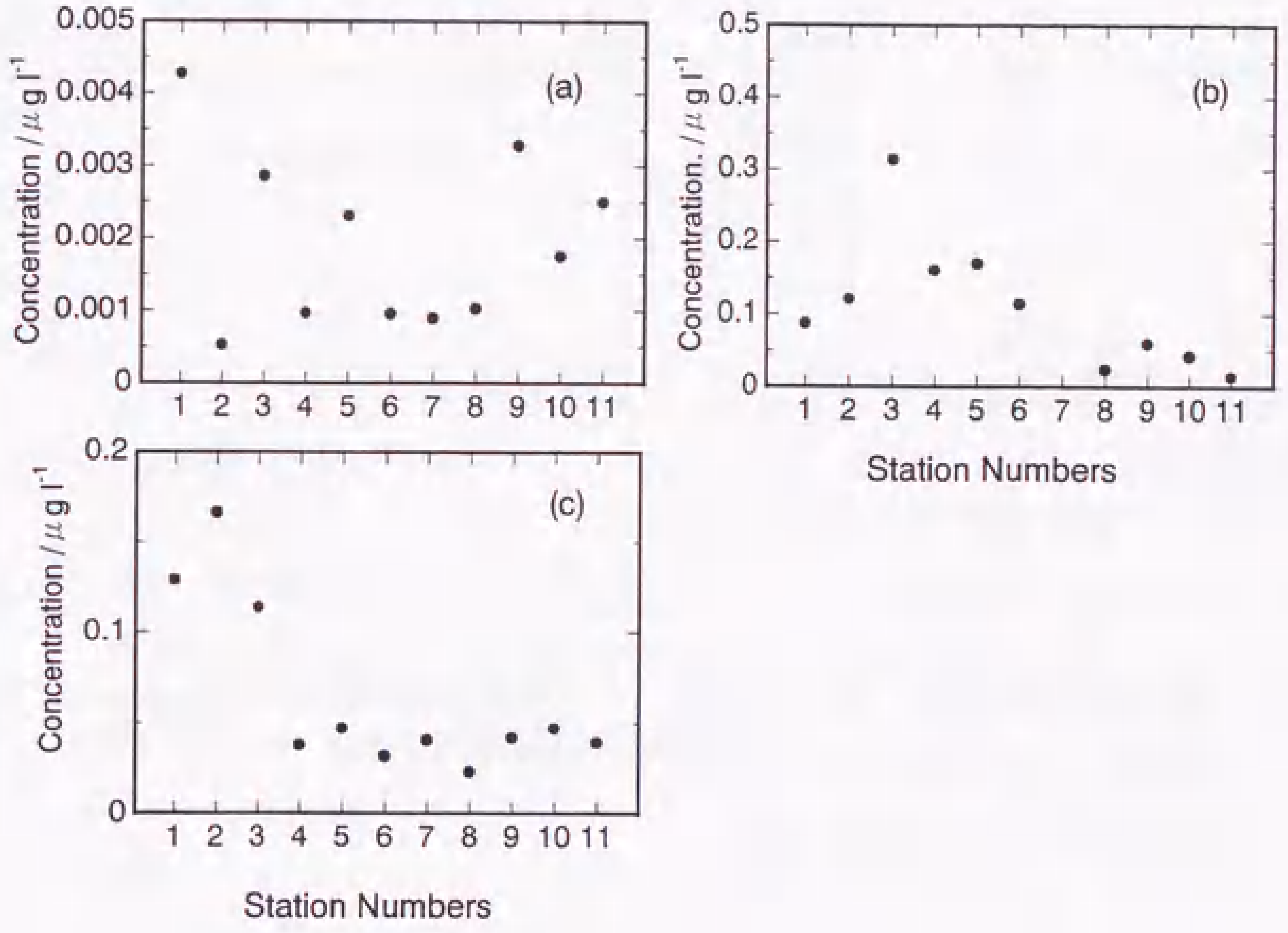

Fig. 6-4 The concentration distributions of scavenged-type elements in surface seawater from West Pacific Ocean to Antarctic Ocean.
(a) Mn, (b) Co, (c) Pb.

provided the higher concentrations in the West Pacific Ocean and the West Australian Sea. The trends of these concentration distributions of Y and REEs agree with those observed for other nutrient-type and scavenging-type elements.

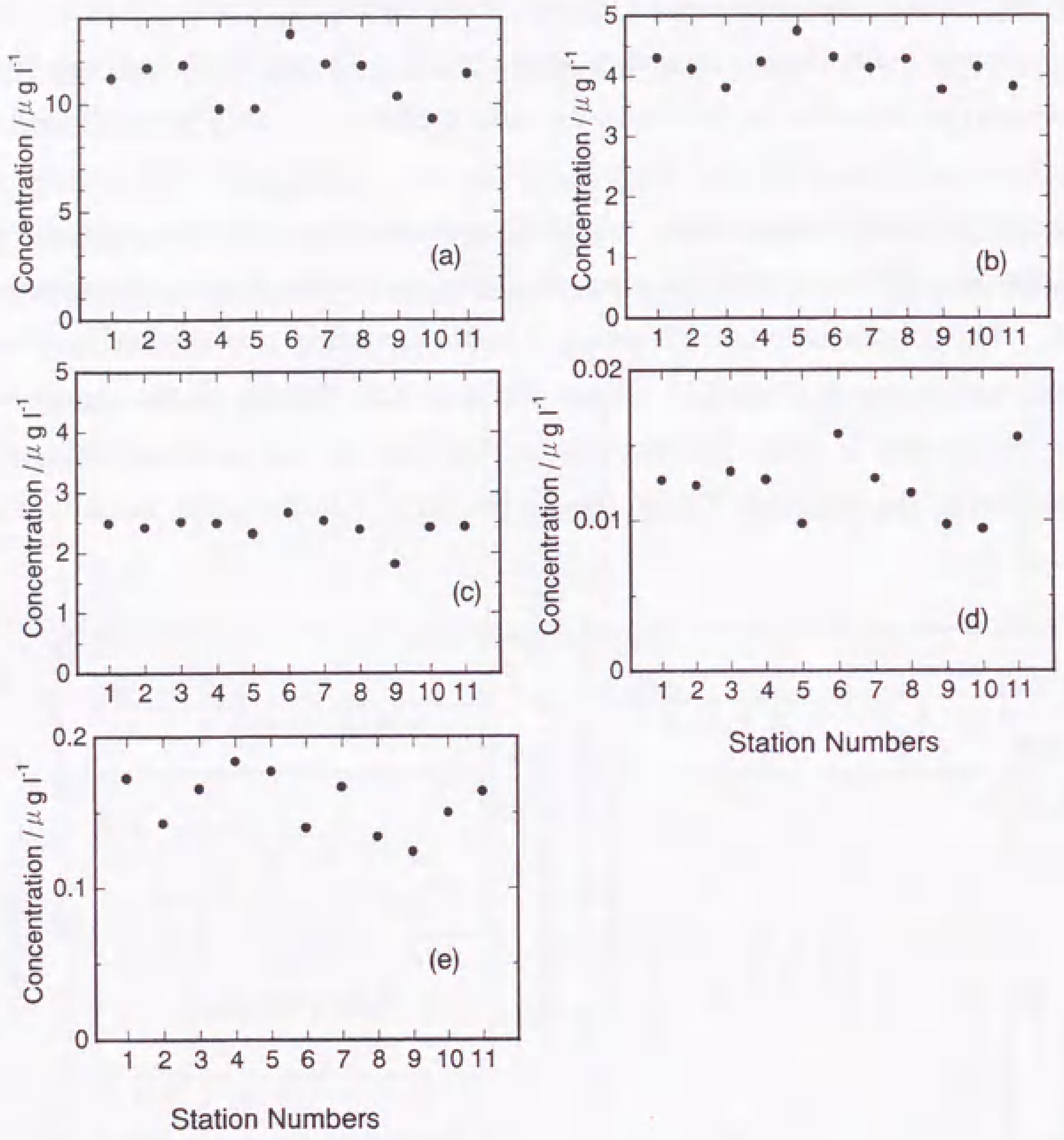

Fig. 6-5 The concentration distributions of conservative-type elements in surface seawater from West Pacific Ocean to Antarctic Ocean.

(a) Mo, (b) U, (c) V, (d) W, (e) Sb.

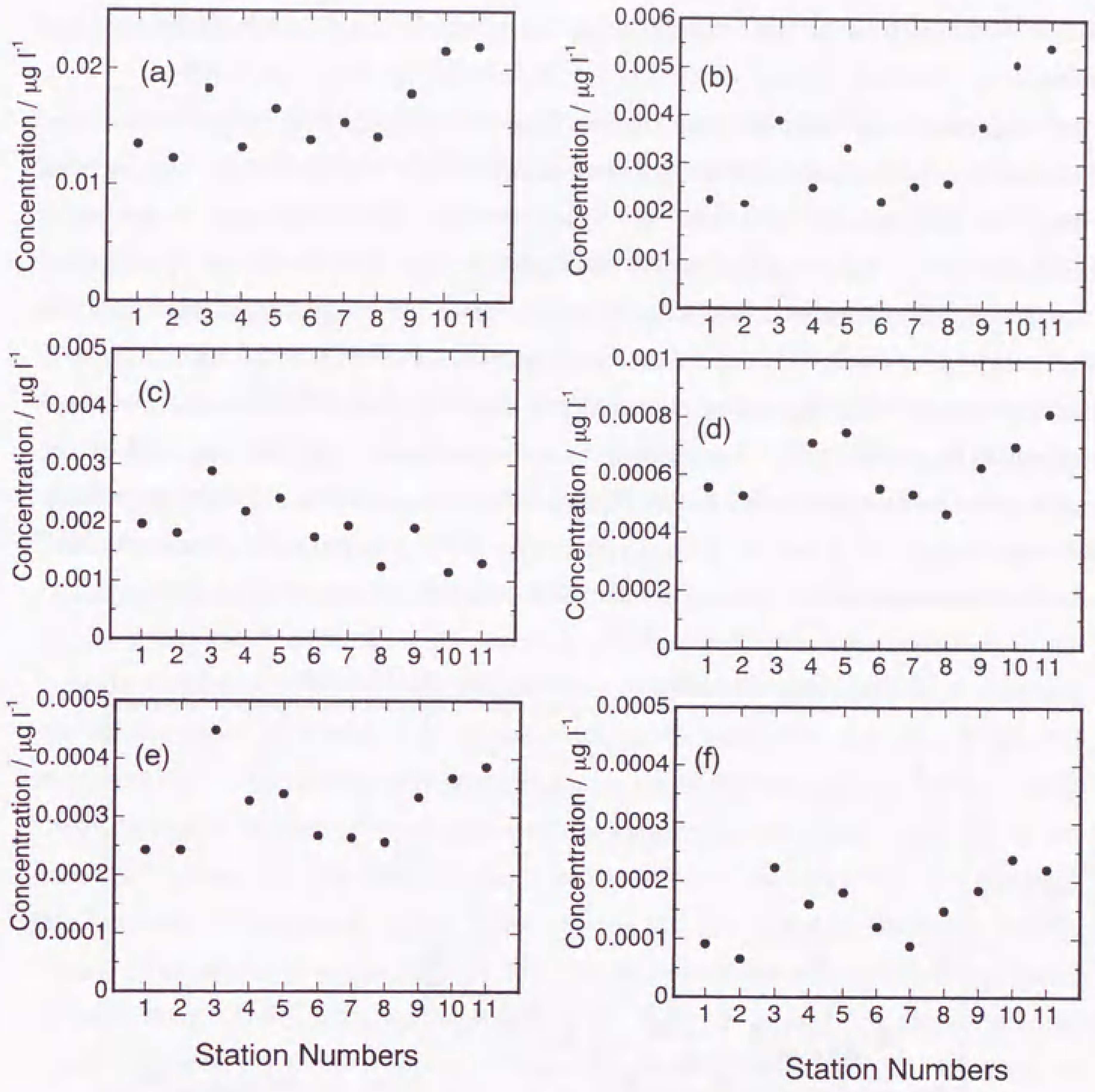

Fig. 6-6 The concentration distributions of Y and rare earth elements in surface seawater from West Pacific Ocean to Antarctic Ocean.

(a) Y, (b) La, (c) Ce, (d) Pr, (e) Ho, (f) Lu.

6-3-4 Comparison of the concentrations of trace elements in the difference sea areas

In order to compare the concentrations of trace elements in three sea areas, the ratios of the concentrations of analyte elements in surface seawater at the No. 5 (West Australian Sea) and No. 11 (Antarctic Ocean) sampling stations to those at the No. 1 (West Pacific Ocean) sampling station are shown in Fig. 6-7, where the elements are arranged by the marine-chemical classification. In the figure, the signs *a*〜*e* indicate the types of the distributions of the elements in open seawater; *a* is the nutrient-type, *b* the type having the propaties of both nutrient- and redox-controlled-types, *c* the type having the properties of both nutrient- and scavenged-types, *d* the scavenged-type, and *e* the conservative-type. Of course, if the concentrations of the elements are almost the same in any sea areas, the ratio is one in Fig. 6-7. It is typically seen in Fig. 6-7 that the conservative-type elements such as V, Mo, Sb, W and U are almost equal to each other in the tree different sea areas.

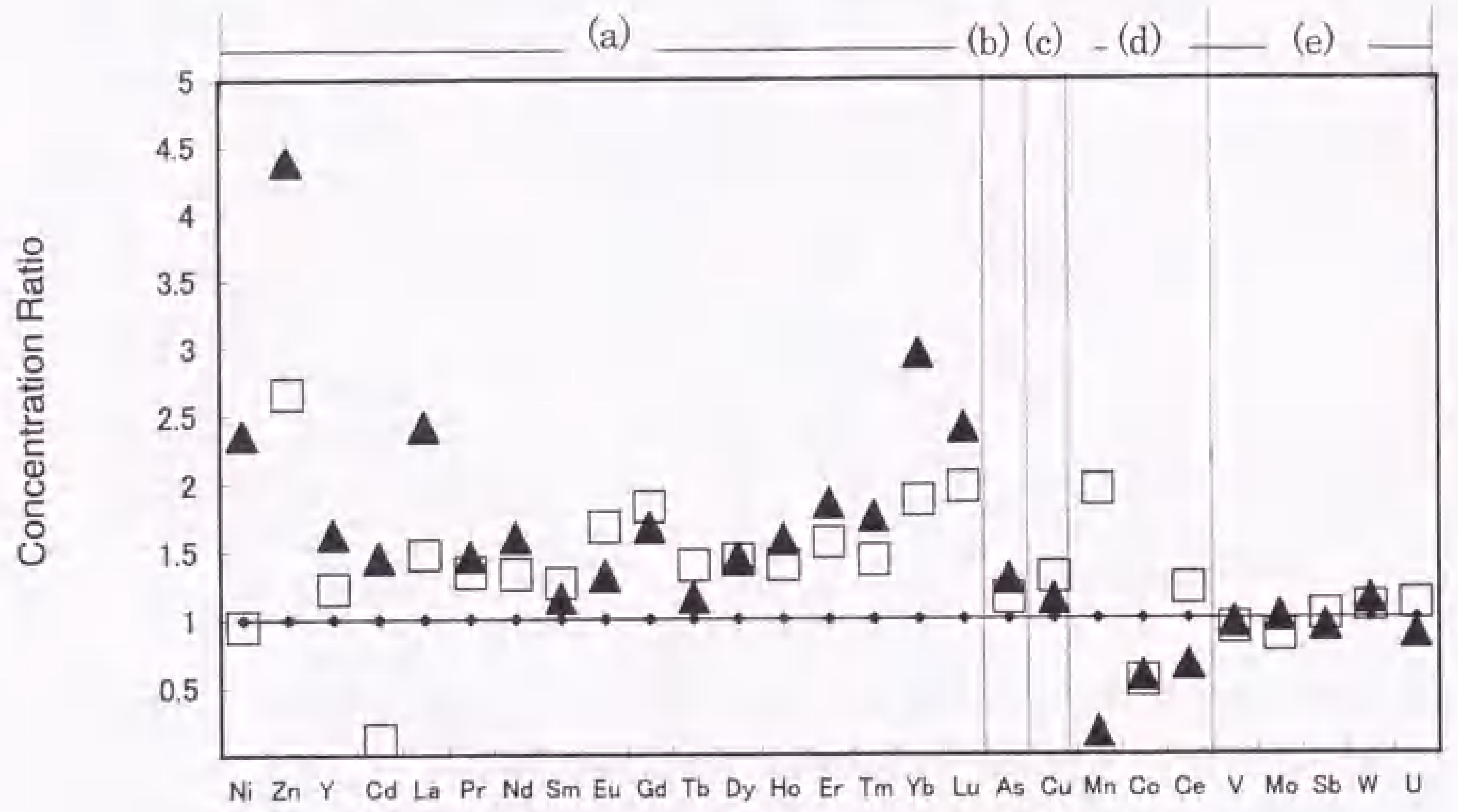

Fig. 6-7 Comparisons of concentration ratios of analyte elements in surface seawaters from Antarctic Ocean and West Australian Sea to those from West Pacific Ocean.

□ ; West Australian Sea, ▲; Antarctic Ocean.

The signs of (a), (b), (c), (d), and (e) indicate the distribution types of trace element in open sea.

(a) nutrient-type, (b) type having the properties of both nutrient- and redox-controlled-types, (c) type having the properties of both nutrient- and scavenged-types, (d) scavenged-type, (e) conservative-type.

It is noted here that the nutrient-type elements in surface seawater generally provided the higher concentrations in the Antarctic Ocean and the West Australian Sea than in the West Pacific Ocean, although Cd in the West Australian Sea was exceptional. In addition, the concentrations of As and Cu, which are the elements having the properties of both nutrient- and redox-controlled-types and of both nutrient- and scavenged-type, respectively, were slightly higher in the Antarctic Ocean and the West Australian Sea than in the West Pacific Ocean. On the other hand, the concentrations of Mn, Co and Ce which are the typical scavenged-type elements, were clearly lower in the Antarctic Ocean than in the West Pacific Ocean, although the concentrations of Mn and Ce were higher in the West Australian Sea than in the West Pacific Ocean.

According to the experimental results shown in Fig. 6-7, it is conclusively stated that the nutrient-like type elements generally provide the higher concentrations in the Antarctic Ocean than in the West Pacific Ocean, while the scavenged-type elements provide the lower concentrations in the Antarctic Ocean. On the other hand, the concentrations of the conservative-type elements are almost the same in any sea areas. These situations for the nutrient-type and scavenged-type elements observed in the Antarctic Ocean and the West Pacific Ocean result in the reversed concentration distributions of them, compared to those in open sea, for example, the North Pacific Ocean. The higher concentrations of the nutrient-type elements as well as the lower concentrations of the scavenged-type elements may be caused by the continuous supplies of deep seawater to the surface layer by some natural circulation of seawater in he Antarctic Ocean.

6-3-5 REE patterns observed in three sea areas

Since REEs show the typical elemental distributions followed by the law of Oddo-Harkins,[2] their original concentration distributions are in a saw-tooth pattern, i.e., higher for the element with even atomic number than for ones with the neighboring odd atomic numbers. Thus, normalization of REEs in the samples to those in some reference materials (e.g., chondrite) is often made to smooth the distribution pattern of REEs, which is called "REE pattern". In the present study, the concentrations of REEs in surface seawater collected from three different sea areas were normalized by those in PAAS (Post Australian Average Shale).[13] Such REE patterns for the samples from the No. 1, No. 2, No. 5 and No. 11 sampling stations are shown in Fig. 6-8. In all the seawater samples, Ce showed the remarkable negative anomaly. Such a negative anomaly of Ce indicates the relatively less population of Ce, compared to other REEs. As mentioned earlier, Ce is one of the scavenged-type elements. Thus, it is considered that Ce is rapidly decreased from surface seawater by the scavenging effects of the suspended particulates, which results in the cerium anomaly.

The other characteristic features seen in Fig. 6-8 is that the populations of heavy-REEs provide much higher than those of light-REEs. Such higher populations of heavy-REEs were observed in lake water[14] and human blood serum.[15] According to the results for lake water and human blood serum,[14,15] it is considered that the higher populations of heavy-REEs can be interpreted by the complex formation with biogenic large organic molecules such as proteins. This may be true for REEs in seawater.

As another characteristic features, it is seen in Fig. 6-8 that the populations of REEs are larger in the Antarctic Ocean than in the West Australian Sea and the West Pacific Ocean. This can be seen clearly in the case of heavy-REEs. As described earlier, REEs except for Ce belongs to the nutrient-type elements. Thus, the deep-seawater supply to the surface layer in the Antarctic Ocean results in the larger populations of REEs dissolved in seawater. On the other hand, the populations of Ce in surface seawater were slightly smaller in the Antarctic Ocean than in the West Pacific Ocean. Such less population of Ce in the Antarctic Ocean was already seen in Fig. 6-6 because of the reversed distribution of the scavenged-type element.

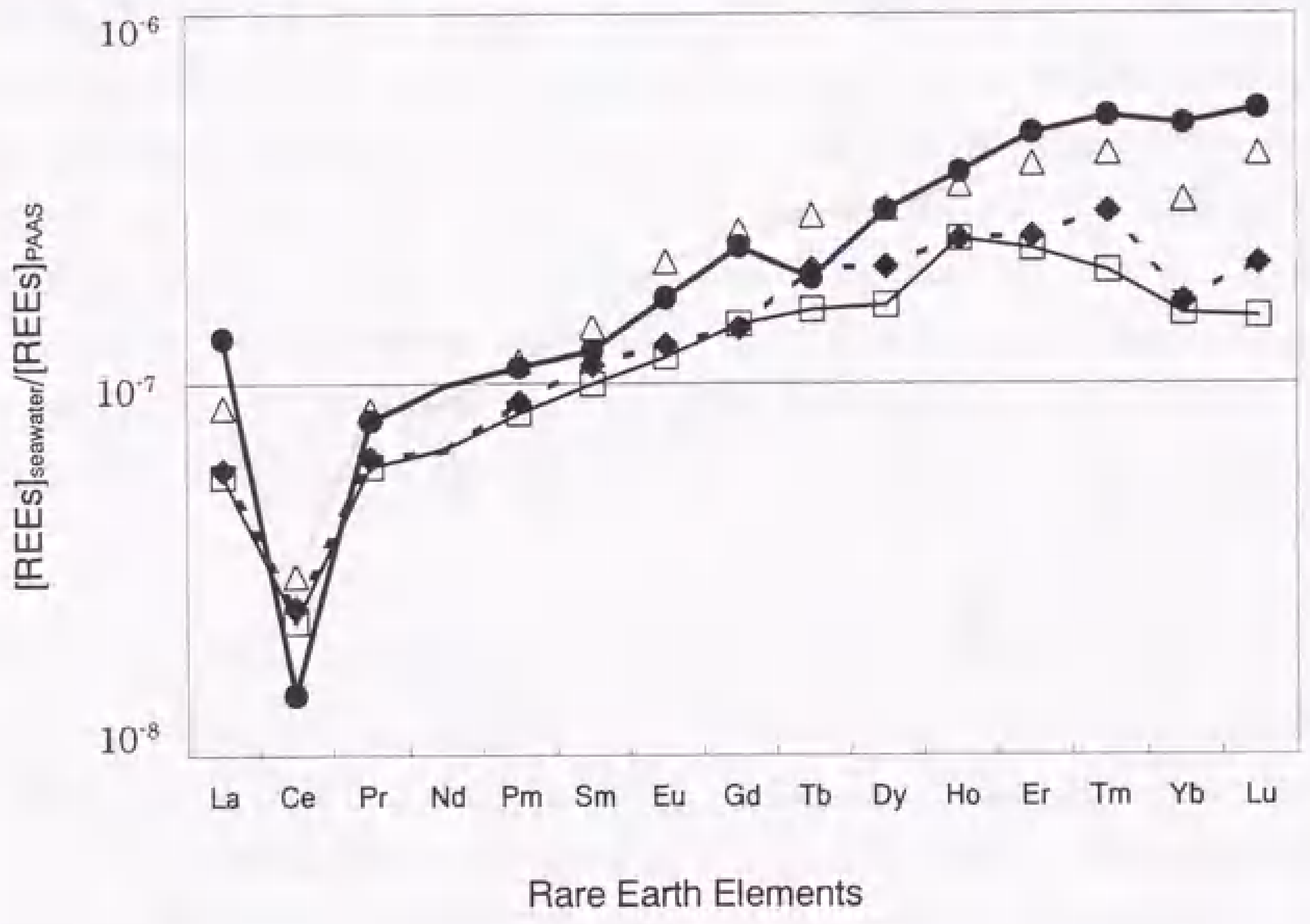

Fig. 6-8 PAAS-shale normalized REE patterns for surface seawaters from different sea areas.

◆; No. 1 station in West Pacific Ocean,□; No. 2 station in Philippine Sea, △; No. 5 station in West Australian Sea, ●; No. 11 station in Antarctic Ocean.

6-4 Conclusion

The concentrations of trace elements in surface seawater collected in the West Pacific Ocean, West Australian Sea and the Antarctic Ocean were determined by ICP-MS after the tandem preconcentration using chelating resin adsorption and La coprecipitation cooparetively. It was found that the concentrations of the nutrient-type elements were generally higher in the Antarctic Ocean than in the West Pacific Ocean, while those of the scavenged-type elements were lower in the Antarctic Ocean than in the West Pacific Ocean. On the other hand, the concentrations of the conservative-type elements were almost constant in any sea areas examined. Then, it was found that these concentration distributions of the nutrient-type and scavenging-type elements in the Antarctic Ocean were reversed, compared to those usually observed in open sea such as the North Pacific Ocean. These results may be interpreted by the fact that vigorous seawater circulation between surface seawater and deep seawater takes place in the Antarctic Ocean because of cold temperature of seawater as well as the diluted salinity. Then, the nutrient-type elements are continuously supplied to the surface layer from the deep sea by natural pumping. Such enrichment of the nutrient-type elements, maybe, together with nitrogen, silicone, and phosphorus, produces the fertile marine environment for phytoplanktons, which helps to grow the animal planktons and other fishes through the food chains in the sea. Such seawater circulation and enrichment of the nutrient-type elements is substancial to keep the oceans fertile for marine bio-production.

Acknowledgment

The present authors express sincere thanks to Dr. Midorikawa in the Agency of Meteorology for his providing the seawater samples examined in the present experiment.

References

1) Y. Nozaki, *EOS. Trans. AGU*, **78**, 221 (1997)..
2) H. Haraguchi, *Bull Chem. Soc. Jpn.*, **72**, 1163 (1999).
3) T. Yabutani, S. Ji, F. Mouri, H. Sawatari, A. Itoh, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 2253 (1999).
4) H. Sawatari, S. Toda, T. Saizuka, C. Kimata, A. Itoh, and H. Haraguchi, *Bull Chem. Soc. Jpn.*, **68**, 3065 (1995).
5) T. Yabutani, S. Ji, F. Mouri, A. Itoh, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **73**, 895 (2000).
6) H. Sawatari, E. Fujimori, and H. Haraguchi, *Anal Sci.*, **11**, 369 (1995).
7) T. Yabutani, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, submitted.
8) J. R. Donat and K. W. Bruland, "Trace Elements in Natural Waters" eds. B. Salba and E. Steins, CRC Press, London, pp.255-256 (1995).
9) J. H. Martin, R. M. Gordon, and S. E. Fitzwater, *Nature*, **345**, 156 (1990).
10) B. H. Löscher, *Mar. Chem.*, **67**, 67 (1999).
11) S. Westerland and P. Öhman, *Geochim. Cosmochim. Acta.*, **55**, 2127 (1991).
12) C. R. German, T. Masuzawa, M. J. Greaves, M. Elderfield, and J. M. Edmond, *Geochim. Cosmochim. Acta.*, **59**, 1551 (1995).
13) S. M .McLeman, "Geochemistry and Mineralogy of Rare Earth Elements", ed. B. R. Lipin and G. A. Mckey, pp. 169-200, the Mineralogy Society of America, Washington D. C. (1989).
14) H. Haraguchi, A. Itoh, and C. Kimata, *Analyst*, **123**, 773 (1998).
15) K. Inagaki and H. Haraguchi, *Analyst*, **125**, 191 (2000).

Chapter 7 Conclusion and Future Prospect

In the present study, the analytical methods for the simultaneous multielement determination of major-to-ultratrace elements in seawater were developed by using ICP-MS. In order to preconcentrate the trace elements at the extremely low concentration levels as well as to eliminate a large amount of matrix elements, chelating resin preconcentration, La coprecipitation, and a tandem preconcentration method with combination of chelating resin adsorption and La coprecipitation were explored for seawater analysis. As a result, more than 30 elements in seawater could be determined simultaneously, where only 250 ml of a seawater sample was used for analysis. The concentration values of the elements determined in the present study as well as those cited from the literature are summarized in Fig. 7-1, along with the detection limits of the elements obtained by ICP-MS. As can be seen in Fig. 7-1, the elements such as transition elements, rare earth elements, oxoanion- and hydride-forming elements were simultaneously determined by the present methods. However, it is still difficult to determine Cr, Se, the elements in the platinum group, Hf, Ta, Ir, Os *etc*, because the concentrations of these elements are lower by 3-5 orders of magnitude than the detection limits obtained by ICP-MS, and also because most of them suffer from severe matrix effects or spectral interferences in the ICP-MS measurement.

From what has been mentioned above, it is desirable to develop an analytical method for the all-elements determination. In all-elements analysis, a new efficient preconcentration method with high concentration factors (*ca.* 100~1000-fold) as well as the improvement of the analytical sensitivities of ICP-MS have to be developed with a new analytical concept. For example, a micro-sample analysis with ICP-MS should be explored in combination with an extremely efficient preconcentration method, when the sample in a limited volume, such as the open or deep seawater sample, is analyzed.

It was found from the present study that the concentration distributions of trace elements at the ppt (ng l^{-1}) level sensitively reflected marine pollution and bioactivities in the ocean and coastal sea areas. As mentioned in Chapter 5 and Chapter 6, the spatial distributions of trace elements clearly revealed the anthropogenic pollution in the local areas around Japan and enrichment of the nutrient-type elements due to the upwelling of deep seawater in the Antarctic Ocean. Therefore, it is very important to draw the global map of the concentration distributions of trace elements in the ocean. Such a global map is called "global mapping of the elements", which may be helpful to understand the global climate change, marine pollution, and production of bio-resource. It should be stressed that a rapid and simple method for the determination of trace elements is substantially required to achieve the global mapping of the elemental distributions. For example, the automated on-board sampling system, which was mentioned in Chapter 5, may help to perform the worldwide survey of the distribution of trace elements in the ocean. A project for the collection of seawater samples and *in situ* monitoring of the pollutants along the tracks of the commercial trade ships in all over the sea area is now in progress. In future, an automated on-board analytical system for sample collection and the determination of trace elements should be also explored to obtain the analytical data with a highly spatial and temporal resolution. Such an automated system can be certainly used to achieve the global mapping of trace elements.

Speciation for chemical species of trace elements in seawater is another important and challenging theme in marine chemistry. The geochemical cycles of trace elements in the ocean are strongly dependent on their chemical forms as well as on the local marine environments. Seawater contains various kinds of species and organisms in a variety of chemical forms. However, since the concentrations of the species are extremely low and dissolved organic compounds are generally so unstable as to be decomposed during the sample storage and the separation processes, speciation of trace elements is still one of the very difficult subjects in analytical chemistry. Thus, development of a new hyphenated system for inorganic trace analysis and separation of the chemical species is really desired to characterize the chemical species and related materials of trace elements in the ocean.

As a future prospect in marine chemistry as well as analytical chemistry for further development of marine science, three subjects, which were proposed above, are summarized in Fig. 7-2. Such subjects are; (i) All-element determination, (ii) Global mapping of the element in the ocean, and (iii) Characterization by chemical speciation and imaging analysis. In conclusion, I would like to stress that harmonious progress in the research on the all-elements determination, global mapping for major-to-trace elements and characterization including chemical speciation for species will give us enormous and wonderful information for comprehensive understandings of our ocean.

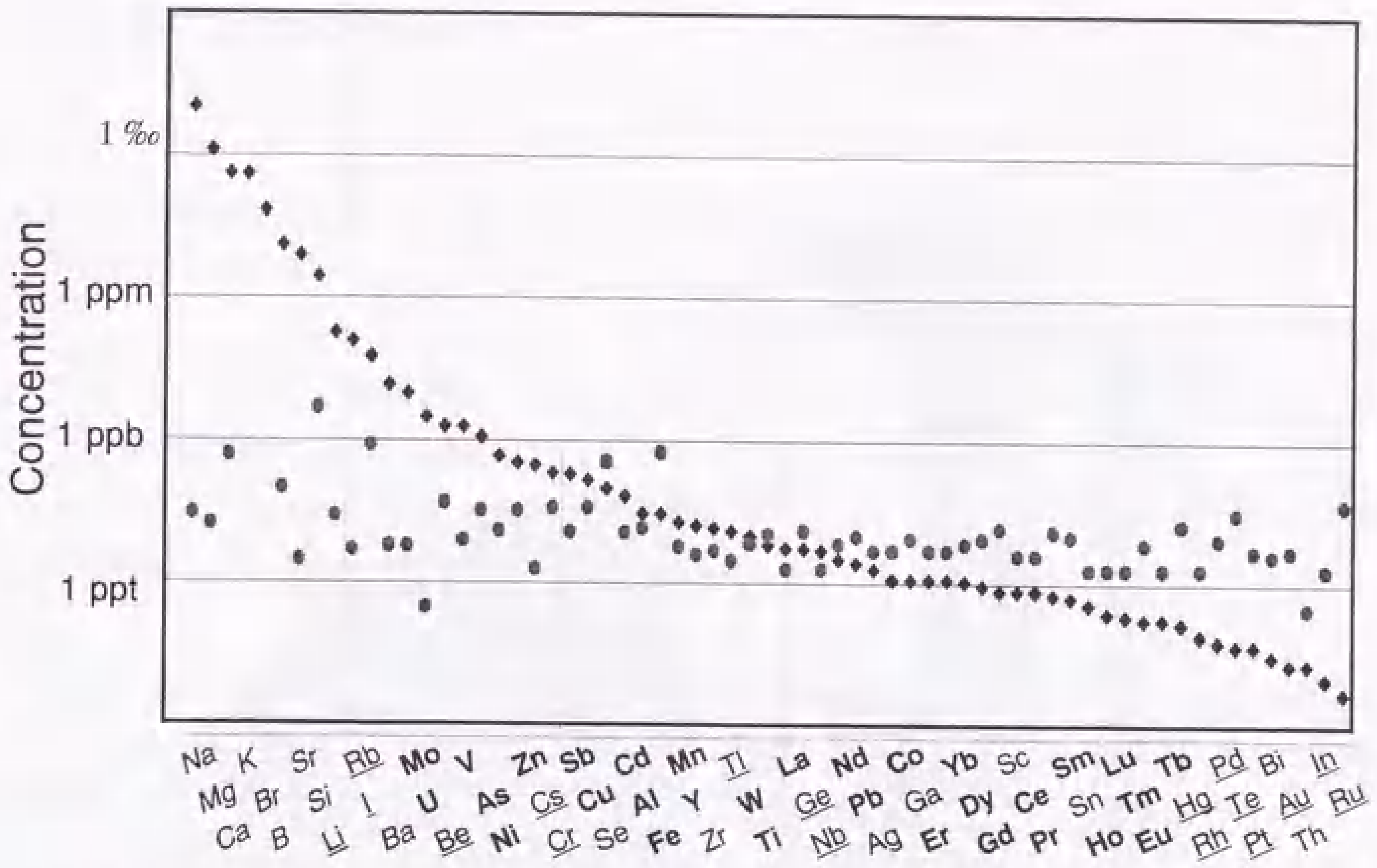

Fig. 7-1 The concentration distributions of the elements in seawater and the detection limits obtained by ICP-MS.

◆; the concentration of the elements in the ocean. (Cited from Ref. 2 in Chapter 1)

●; the detection limit of the element obtained by ICP-MS.(Cited from Ref. 32 in Chapter 1)

M; the element which can be determined by chelating resin preconcentration/ICP-MS, La coprecipitation/ICP-MS, or the tandem preconcentration/ICP-MS method.

M; the element which can be determined directly by ICP-AES or ICP-MS.

M; the elements which can be detected by chelating resin preconcentration/ICP-MS, La coprecipitation/ICP-MS, or the tandem preconcentration/ICP-MS method.

M; the elements which can be not be determined by the method examined in present study.

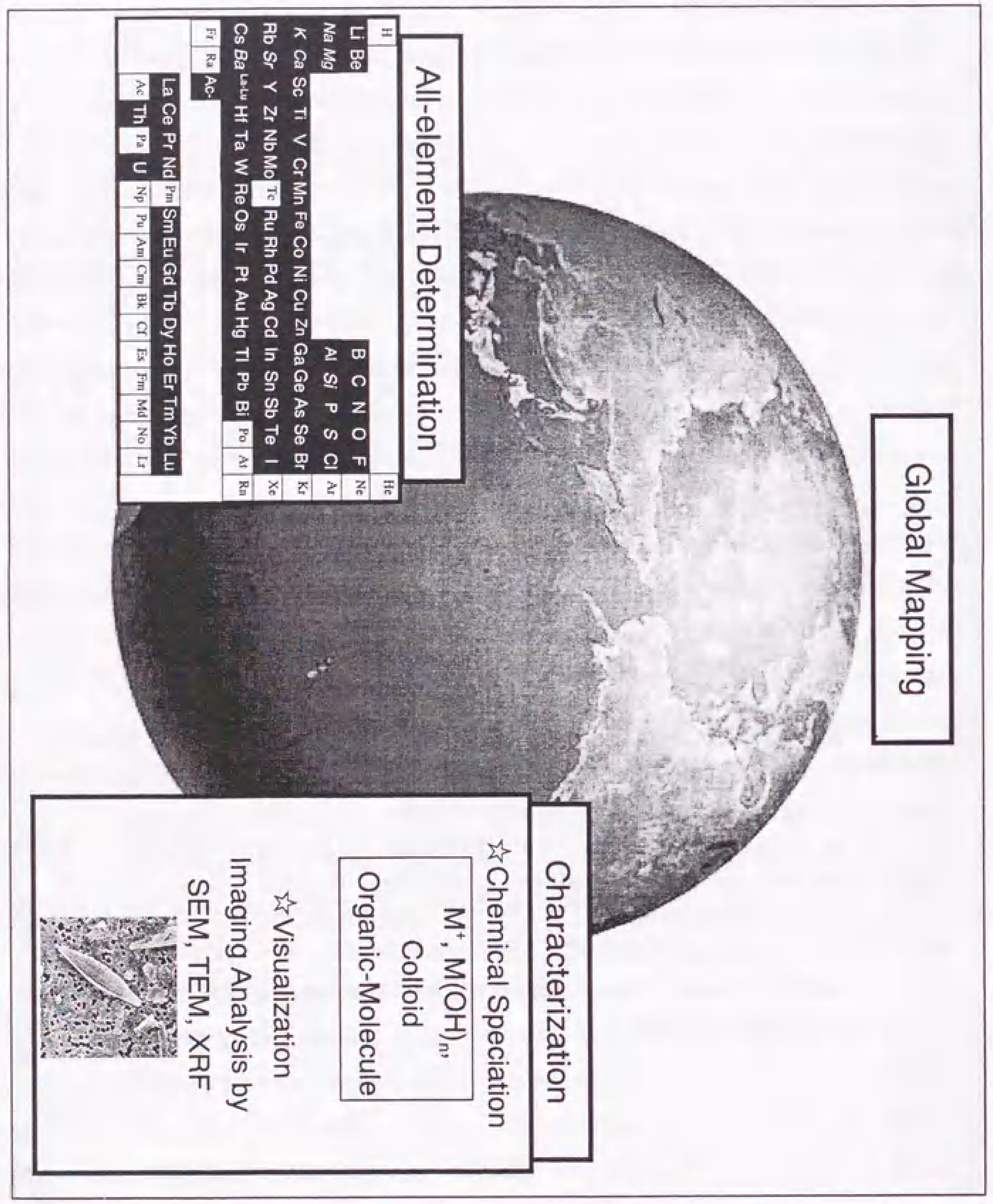

Fig. 7-2 Schematic Diagram for future prospect of analytical and marine chemistry in marine science.

List of Publications

1.Original Papers

1. Multielement Determination of Major-to-Trace Elements in Natural Solar Salt by ICP-AES and ICP-MS after Chelating Resin Preconcentration.
   S. Ji, C. Kimata, T. Yabutani, A. Itoh, E. Fujimori, K. Chiba, and H. Haraguchi : *Biomed. Res. Trace Elements*, **8**(1), 37-46, (1997).

2. Multielement Determination of Trace Elements in River Water Certified Reference Matericals (JAC 0031, JAC 0032) by ICP-MS and ICP-AES with Chelating Resin Preconcentration.
   A. Itoh, K. Iwata, S. Ji, T. Yabutani, C. Kimata, H. Sawatari, and H. Haraguchi: *Bunseki Kagaku*, **47**(2), 109-117 (1998).

3. Multielement Determination of Trace Elements in Coastal Seawater by Inductively Coupled Plasma Mass Spectrometry with Aid of Chelating Resin Preconcentration.
   T. Yabutani, S. Ji, F. Mouri, H. Sawatari, A. Itoh, K. Chiba, and H. Haraguchi : *Bull. Chem. Soc. Jpn*., **72**(10), 2253-2260 (1999).

4. Multielement Analysis of Insoluble Particulates in Solar Salts by ICP-AES and ICP-MS in Relation to Geochemical Consideration.
   S. Ji, T. Yabutani, F. Mouri, C. Kimata, A. Itoh, K. Chiba, and H. Haraguchi: *Bunseki Kagaku*, **48**(10), 897-908 (1999).

5. Distributions of Elements into Natural Salt from Coastal Seawater in a Natural-salt Preperation Process.
   S. Ji, T. Yabutani, A. Itoh, K. Chiba, and H. Haraguchi : *Bunseki Kagaku*, **49**(2), 111-120 (2000).

6. Multielement Determination of Major-to-Ultratrace Elements in Common Salts by Inductively Coupled Plasma Atomic Emission Spectrometry and Inductively Coupled Plasma Mass Spectrometry.
   S. Ji, T. Yabutani, A. Itoh, and H. Haraguchi : *Bull. Soc. Sea Water Sci. (Nihon Kaisui Gakkaishi)*, **54**(2), 117-125 (2000).

7. Simultaneous Multielement Determination of Hydride- and Oxoanion-Forming Elements in Seawater by Inductively Coupled Plasma Mass Spectrometry after Lanthanum Coprecipitation.
   T. Yabutani, S. Ji, F. Mouri, A. Itoh, K. Chiba, and H. Haraguchi : *Bull. Chem. Soc. Jpn.*, **73**(4), 895-901 (2000).

8. Fractional Distributions of Major-to-Ultratrace Elements in Coastal Seawater and Their Partitioning in Laboratory–made Salts as Investigated by Inductively Coupled Plasma Atomic Emission Spectrometry and Inductively Coupled Plasma Mass Spectrometry with Aid of Membrane– and Ultrafiltration Techniques.
   S. Ji, T. Yabutani, A. Itoh, and H. Haraguchi. : *Bull. Chem. Soc. Jpn.*, **73**(5), 1179-1186 (2000).

9. Concentration Variations of Trace Metals in Surface Seawater along the Ferry Track between Osaka and Okinawa as Determined by ICP-MS after Chelating Resin Preconcentration.
   T. Yabutani, F. Mouri, and H. Haraguchi : *Anal. Sci.*, **16**(7), 675-676 (2000).

2. Reviews

1. Multielement Profiling Analysis of Seawater from the Viewpoint of Bio-marine Chemistry.
   Trans. Res. Institute Oceanochem., **13**(1), 16-29 (2000).
   H. Haraguchi, T. Yabutani, S. Ji, and K. Inagaki.

2. Studies on Bio-geochemical and Environmental Behaviors of Trace Elements — Chemical Speciation of Trace Elements in Natural Water.
   Environ. Sci. : **13**(3), 313-328 (2000).
   H. Haraguchi, A. Itoh, S. Ji, and T. Yabutani.

Acknowledgment

The author wishes to express his deepest gratitude and appreciation to ***Prof. Dr. Hiroki Haraguchi***, Graduate School of Engineering, Nagoya University, for his fruitful discussion, continuous instruction and encouragement during the period of the author's Ph. D course in Nagoya University.

The author would like to express his sincere gratitude to ***Prof. Dr. Shin Tsuge***, ***Prof. Dr. Shin-ichi Hirano***, and ***Dr. Hajime Ohtani***, Graduate School of Engineering, Nagoya University, for their valuable advice and suggestions.

The author is much obliged to ***Dr. Koichi Chiba***, Graduate School of Engineering, Nagoya University, for his valuable discussion and continuous supports during the period of the author's Ph. D course in Nagoya University.

The author is also indebted to ***Mr. Akihide Itoh*** and ***Dr. Shan Ji, Mr. Eiji Fujimori***, Graduate School of Engineering, Nagoya University, and ***Dr. Hideyuki Sawatari***, Miyagi University of Education, for their important suggestions and technical advice.

The author feels much fortunate to have had the opportunity to collaborate with ***Dr. Tomonari Umemura, Dr. Rong Wei, Dr. Kazumi Inagaki, Dr. Akiko Hokura, Ms. Chisen Kimata, Mr. Kosuke Iwata, Mr. Fumihiko Mouri, Ms. Miwa Kawai, Mr. Toru Ozaki, Mr. Masayoshi Hasegawa, Mr. Taisuke Nagasawa, and Mr. Hiroshi Yamada*** who are members of the Haraguchi's laboratory in Nagoya University, and wishes to express for their gratitude to above members.

Finally, the author would like to thank ***his parents, grandmother, brother and sister*** for their continuous supports at any time.