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Fractional Distributions of Major-to-Ultratrace Elements in Coastal Seawater and Their Partitionings in Laboratory-Made Salts as Investigated by Inductively Coupled Plasma Atomic Emission Spectrometry and Inductively Coupled Plasma Mass Spectrometry with Aid of Membrane- and Ultra-filtration Techniques

Shan Ji, Tomoki Yabutani, Akihide Itoh, and Hiroki Haraguchi*

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8603

(Received November 29, 1999)

The coastal seawater sample was filtered with a membrane filter (pore size 0.45 μm), and the filtrate was further filtered with an ultrafiltration filter (molecular weight permeation limit of 10000 Da). Then, major-to-ultratrace elements in the particles which remained on the membrane filter, the membrane-filtered seawater, and the ultrafiltered seawater were determined by ICP-AES (inductively coupled plasma atomic emission spectrometry) and ICP-MS (inductively coupled plasma mass spectrometry). From these analytical results, the fractional distributions of each element in the particle, large molecule and small molecule fractions of seawater were estimated, where the distributions of the elements in the large molecule fraction were obtained as the differences between the elemental concentrations in membrane-filtered and ultrafiltered seawaters.

Furthermore, laboratory-made salts (Salts I—III) were prepared from original, membrane-filtered, and ultrafiltered seawaters. The concentrations of major-to-ultratrace elements in laboratory-made salts were also determined by ICP-AES and ICP-MS. It was found that alkali metals, alkaline earth metals, oxoanion-forming elements (V, Mo, W, U) and Cd were mostly contained in the small molecule fraction of seawater, and ca. 95—100% of them in salt, except for V, originated from those in the small molecule fraction. More than 50% of Al, Mn, Fe, Co, Ga, Y, rare earth elements (REEs) and Pb were contained as the particle constituents in seawater, but their intakes into salt were less than 50%. In addition, the fractional distributions of the following elements in the large molecule fraction of seawater were: Al 10%, Mn 4%, Fe 2%, Cu 23%, Zn 7%, Y 5%, REEs 3—15%, and Pb 30%. On the other hand, the intake factors of these elements in salt from the large molecule fraction were: Al 40%, Mn 5%, Fe 28%, Cu 20%, Zn 30%, Y 7%, REEs 5—30%, and Pb 55%. The results obtained in the present experiment suggest that the distributions of the elements in natural salt greatly depend on the chemical forms in seawater.

Salts have been utilized as an essential seasoning for human beings from ancient times.[1] Although natural salts are usually prepared from seawater or rock salts, seawater salts are generally used for cooking in Japan. According to the preparation methods, salts are classified into natural salts and purified salts. Such preparation methods influence the contents of *so-called* "minerals" (trace elements) in salts. In general, natural salts contain more mineral constituents than purified salts, because the former are directly condensed from seawater without any physicochemical pretreatments.[2]

In recent years, ICP-MS (inductively coupled plasma mass spectrometry) has been developed as a highly-sensitive analytical method for the multielement determination of trace elements in various samples.[3] The present authors have explored the methods for the multielement determination of trace elements in seawater by ICP-MS, where gallium coprecipitation,[4] aluminum coprecipitation[5] and chelating resin preconcentration[6,7] were examined as the preconcentration methods. Among these methods, it was found that the chelating resin preconcentration method was most effective for trace analysis of seawater, because major elements were to a large extent eliminated and no matrix element (coprecipitation carrier) was added.

Since trace elements in salts are the subject of interest from the viewpoint of nutrition and physiology, the present authors' group has dealt with the multielement determination of major-to-ultratrace elements in seawater salts.[8—10] In salt analysis, the chelating resin preconcentration method was applied to the determination of trace elements in the salt samples by ICP-MS. At the same time, major and minor elements in the salt samples were also determined by ICP-AES (inductively coupled plasma atomic emission spectrometry).

According to the results for various salt samples,[2] the concentrations of major-to-ultratrace elements in salts were different, depending on their sources and preparation methods. In addition, it was suggested that the distributions of such elements in natural salt were influenced by their dissolved states in seawater.[9,10] However, the salt samples obtained from the different sources were produced by different preparation methods. Thus, it is difficult to discuss comprehensively the partitionings of the elements between seawater and salt. Thus in the present experiment the coastal seawater collected off-shore of Nie in the Noto Peninsula was used for preparation of the salt samples to investigate the fractional distributions of the elements in seawater as well as their partitionings in natural salt. The seawater samples were separated into the particle, dissolved and small molecule fractions by using a membrane filter and an ultrafiltration filter. Then, the concentrations of major-to-ultratrace elements in the particle, dissolved and small molecule fractions of seawater were determined by ICP-AES and ICP-MS. Furthermore, salts were prepared from the original, membrane-filtered and ultrafiltration-filtered seawater samples in the laboratory, and the concentrations of major-to-ultratrace elements in these laboratory-made salts were also determined by ICP-AES and ICP-MS. From these experimental results, the fractional distributions of the elements in the different fractions of seawater and their partitionings between seawater and natural salt will be discussed in detail.

Experimental

Instrumentation. An ICP-MS instrument (model SPQ 8000A from Seiko Instruments, Chiba), composed of a quadrupole mass spectrometer, was used for the determination of trace and ultratrace elements in seawater and salts. An ICP-AES instrument of model Plasma AtomComp MKII (Jarrell Ash, Franklin, MA, USA), which included a polychromator with a Paschen–Runge mounting for simultaneous multielement detection (40 elements), was also used for the determination of major and minor elements in seawater and salts. The operating conditions of the ICP-MS and ICP-AES instruments are summarized in Table 1. These operating conditions were chosen after optimization of each instrumental parameter of both instruments. Ultrafiltration of the seawater samples was performed by using an ultrafiltration system of a tangential flow (Pellicon cassette system from Millipore, Bedford, MA, USA). An ultrafilter (ultrafiltration filter; Millipore) with the molecular weight permeation limit of 10000 Da made of cellulose acetate was used for ultrafiltration. The pH adjustment in the chelating resin preconcentration was carried out by using a pH meter (Twin pH meter from Horiba, Kyoto).

Chemicals. The standard solutions for standardization of the calibration curves in the ICP-AES and ICP-MS measurements were prepared from the single-element standard stock solutions (1000 $\mu g\,ml^{-1}$) for atomic absorption spectrometry,[10] purchased from Wako Pure Chemicals (Osaka). Nitric acid, acetic acid and ammonia solution used were of electronics industry reagent grade; these were obtained from Kanto Chemicals (Tokyo). Ammonium acetate, which was used for the pH adjustment, was prepared by mixing equivalent molar amounts of acetic acid and ammonia solution. Sodium hydroxide and nitric acid used for cleaning the ultrafiltration system were of analytical and electronics industry reagent grade, respectively, these were purchased from Kanto Chemicals. Methanol used for the same purpose was of analytical reagent grade (Wako Pure Chemicals).

The chelating resin used for preconcentration of trace elements in the seawater and salt water samples was a Chelex-100 resin (100—200 mesh; Bio-Lad Laboratories, Lichmond, CA, USA). The Chelex-100 resin was soaked in 5 M HCl (1 M = 1 mol dm^{-3}) for 5 d (changed daily), and rinsed with pure water, 2 M HNO_3 and pure water, in turn, before use. Pure water used throughout the present experiment was prepared by a Milli-Q purification system of model Milli-Q SP TOC (Nihon Millipore Kogyo, Tokyo).

Table 1. Operating Conditions for 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 $dm^3\,min^{-1}$
Auxiliary gas flow rate	Ar 1.0 $dm^3\,min^{-1}$
Carrier gas flow rate	Ar 1.0 $dm^3\,min^{-1}$
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 $dm^3\,min^{-1}$
Auxiliary gas flow rate	Ar 1.0 $dm^3\,min^{-1}$
Carrier gas flow rate	Ar 0.48 $dm^3\,min^{-1}$
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
Reception	3—10 times

Sample Pretreatment. The coastal seawater samples were collected off-shore of Nie in the Noto Peninsula on November 11, 1998, where the traditional natural salt preparation called "Agehama-en-den-ho" has been performed. The vessels for sample preservation were cleaned by soaking in 6 M HNO_3 for a week and then by rinsing with distilled water (5 times) and pure water (3 times).

The seawater samples were pretreated by the following procedures prior to laboratory-made salt preparation. The original seawater sample (ca. 30 dm^3) was divided into 3 portions (10 dm^3 each), which were taken in 3 different vessels (Vessels 1—3). The original seawater in Vessel 1 was directly subjected to preparation of salt (Salt I) without any filtration. The original seawater in Vessel 2 was filtered with a membrane filter (pore size 0.45 μm) just after sampling. The filtrate after filtration with the membrane filter corresponded to the dissolved fraction of seawater, which is hereafter referred to as "membrane-filtered seawater". The membrane-filtered seawater was subjected to preparation of salt (Salt II), which is usually considered to contain only the dissolved constituents in seawater. The original seawater in Vessel 3 was filtered first with the membrane filter and then with an ultrafilter. Since the permeation limit of the ultrafilter was 10000 Da in molecular weight (MW), the filtrate after ultrafiltration, which is hereafter referred to as "ultrafiltered seawater", contained only small molecular constituents (small molecule fraction) with MW smaller than 10000 Da. About 8.1 dm^3 of the ultrafiltered seawater was obtained from 10 dm^3 of original seawater, and it was subjected to preparation of salt (Salt III).

Preparation Procedure of Laboratory-Made Salts. Three kinds of salts (Salts I—III) were prepared from original, membrane-filtered, and ultrafiltered seawaters in the laboratory. The salts prepared in the laboratory are hereafter referred to as "laboratory-made salts". The preparation procedure and conditions for laboratory-made salts were decided by referring to the Agehama-salt preparation method. In the Agehama method, seawater is once evaporated to dryness on a sandy beach, and salt crystals collected together with sand are re-dissolved in original seawater. The supernatant of the re-dissolved seawater solution is subjected to preparation of salt with heating in an iron vessel. In the preparation of laboratory-made salts, however, the seawater samples were directly concentrated in a porcelain evaporating dish (1 dm^3 in volume) with heating on a hot plate for convenience of the laboratory experiment. The porcelain evaporating dish used for salt preparation was cleaned before use by soaking in 3 M HNO_3 for 3 d and washing with pure water. No significant blank values from the dish were detected in the present experiment.

First, 900 ml of each seawater sample was taken in a porcelain evaporating dish, and then heated at 220 °C for about 4 h on a hot plate under irradiation with an IR lamp, to reduce to ca. 120 ml in volume. After the material was kept standing overnight, only the supernatant was collected by pouring, and the precipitates (mostly $CaSO_4$) were removed. The preconcentration procedure mentioned above was repeated three times; and then ca. 360 ml of the supernatant solution was obtained from 2700 ml of original seawater. All the supernatant solutions were gathered together in the porcelain evaporating dish, and heated at 100 °C for about 1 h. When NaCl began to precipitate (crystalized), the heating temperature was lowered to 75 °C. Then, the residual solution was heated at 75 °C for 2 h and further heated at 55°C until most NaCl precipitated. At this stage, the residual solution became ca. 55 ml. Salt was obtained by filtering with a glass filter (G3). In order to avoid contamination, all the heating procedures described above were carried out in a clean chamber (Class 100).

In the laboratory-made salt preparation mentioned above, ca. 60.5 g of salt (Salt I) was obtained from 2700 ml of original seawater, which corresponded to a yield of about 71%. The purity of Salt I was 93.3% as NaCl. Other laboratory-made Salt II and Salt III samples were also prepared from the membrane-filtered and ultrafiltered seawaters, respectively, in a similar manner to Salt I. It should be noted here that Salts II and III did not contain particles at all.

Determination of Major-to-Ultratrace Elements in Seawater and Salt Samples. As mentioned earlier, original seawater was filtered with a membrane filter, and then the filtrate was further filtered with an ultrafilter. Thus, the membrance-filtered and ultrafiltered seawaters were obtained as the dissolved and small molecule fractions of seawater, respectively. After filtration, the pHs of the membrane-filtered and ultrafiltered seawaters were adjusted to ca. 1 by adding 0.1 M HNO_3. The determination of major-to-ultratrace elements in the seawater samples was carried out as described below.

Major and minor elements in each seawater sample were determined by ICP-AES after appropriate dilution. Trace and ultratrace elements in each seawater sample were determined by ICP-MS after chelating resin (Chelex-100) preconcentration, in a similar manner to that explained in previous papers.[6,7,10] In the present experiment, 250 ml of seawater was used for analysis, where preconcentration was performed at pH 6, using 0.2 g of the chelating resin.[7] Trace elements adsorbed on the resin were dissolved with 6 ml of 2 M HNO_3, and thus about 40-fold preconcentration was achieved. The internal standard elements (Ge, In, Re, and Tl) were added in the preconcentrated solution to be 10 ng ml^{-1} each, and the internal standard correction for matrix effect was made by the same method as that of Sawatari et al.[4]

Major-to-ultratrace elements in particles which remained on the membrane filter were also determined as the particle fraction by ICP-AES and ICP-MS after acid digestion, as reported previously.[9] In particle analysis, particles together with the membrane filter was digested with $HNO_3/HF/HClO_4$. The digested solution was heated to dryness, and the residue was dissolved in 10 ml of 2 M HNO_3.

In salt analysis, three kind of laboratory-made salts (Salts I—III) were dissolved in 0.1 M HNO_3 to become a 4% salt water solution. Three salt water solutions were analysed by ICP-AES and ICP-MS, in a similar manner to those in seawater mentioned above.

The blank values for trace elements in the analyses of the seawater, salt and particle samples were examined in the present experiment. Since the blank values were negligibly small or much smaller than the analytical values for all the samples, as obtained in the previous papers,[8—10] such data are not shown in Tables 2 and 3.

Results and Discussion

Fractional Distributions of Major-to-Ultratrace Elements in Original and Filtered Seawaters. As mentioned earlier, original coastal seawater was collected at the off-shore of Nie, Ishikawa Prefecture, in the Noto peninsula, and it was treated with a membrane filter and an ultrafilter. The following three kinds of seawater samples were obtained in the present experiment. They were subjected to the determination of major-to-ultratrace elements by ICP-AES and ICP-MS, as mentioned in the experimental section.

(1) Original seawater,
(2) Membrane-filtered seawater (dissolved fraction),
(3) Ultrafiltered seawater (small molecule fraction).

The analytical results for the dissolved, large molecule and small molecule fractions of seawater as well as for the particle fraction are summarized in Table 2. In Table 2, some data for the dissolved and particle fractions were cited from our previous paper,[10] and those for the small molecule fraction were newly obtained in the present experiment. The means and the standard deviations of the elements for the small molecule fraction were estimated from the 3 replicate measurements. The values for the large molecule fraction were obtained by subtracting the concentrations for the small molecule fraction from those for the dissolved fraction.

It is seen in Table 2 that 33 elements could be determined in the small molecule fraction over the wide concentration range from 9.75×10^6 ng ml^{-1} for Na to 0.0002 ng ml^{-1} for Eu, Tm, and Lu, although Pb was not detected in the small molecule fraction. In Table 2, the percentage ratios (D_{large} in %) of the concentrations of the elements in the large molecule fraction to those in the dissolved fraction are also shown in parentheses in the column of the large molecule fraction. The percentage ratio (D_{large}) of the large molecule fraction is calculated by Eq. 1:

$$D_{\mathrm{large}} = \{(C_{\mathrm{dissolved}} - C_{\mathrm{small}})/C_{\mathrm{dissolved}}\} \times 100\ (\%)\ , \qquad (1)$$

where $C_{\mathrm{dissolved}}$ and C_{small} are the concentrations of the elements in the dissolved and small molecule fractions, respectively.

Table 2. Analytical Results for the Concentrations of Major-to-Ultratrace Elements in Small Molecule, Large Molecule, Dissolved and Particle Fractions of Coastal Seawater as Determined by ICP-AES and ICP-MS

Element[a)]	Concentration / ng ml^{-1}				
	Small molecule[b)] fraction	Large molecule fraction		Dissolved[c)] fraction	Particle[d)] fraction
Na†	$(9.75 \pm 0.11)\times10^6$	0	(0)	9.75×10^6	116
K†	$(3.96 \pm 0.07)\times10^5$	−0.01	(−0.3)	3.95×10^5	24.6
Ca†	$(3.56 \pm 0.07)\times10^5$	0.06	(−1.7)	3.50×10^6	61.3
Mg†	$(1.10 \pm 0.02)\times10^6$	0.01	(−0.9)	1.09×10^6	40.1
Sr†	$(9.02 \pm 0.30)\times10^3$	−0.08	(−0.9)	8.94×10^3	0.89
Ba†	5.64 ± 0.32	0.26	(+4.4)	5.90	0.31
Al	0.72 ± 0.03	2.79	(+79.6)	3.51	26.1
Mn	0.76 ± 0.005	0.04	(+5.3)	0.80	0.87
V	1.56 ± 0.07	0.04	(+2.5)	1.60	n.d.[e)]
Fe	0.86 ± 0.04	0.44	(+33.6)	1.30	44.0
Co	0.005 ± 0.0001	0	(0)	0.005	0.015
Cu	0.22 ± 0.005	0.091	(+29.4)	0.31	0.070
Zn	0.92 ± 0.02	0.066	(+6.7)	0.99	0.233
Ga	0.005 ± 0.00004	0	(0)	0.005	0.021
Y	0.022 ± 0.0002	0.03	(+12.0)	0.025	0.026
Mo	11.8 ± 0.31	0.1	(+0.8)	11.9	n.d.[e)]
Cd	0.019 ± 0.0009	0	(0)	0.019	0.005
La	0.004 ± 0.00006	0.002	(+33.3)	0.006	0.018
Ce	0.0035 ± 0.00004	0.0015	(+30.0)	0.005	0.047
Pr	0.0011 ± 0.00003	0.0002	(+15.3)	0.0013	0.0053
Nd	0.005 ± 0.0001	0.001	(+16.7)	0.006	0.021
Sm	0.0010 ± 0.00003	0.0003	(+30.0)	0.0013	0.005
Eu	0.0002 ± 0.00006	0.0001	(+33.3)	0.0003	0.0011
Gd	0.0016 ± 0.00006	0.0003	(+15.8)	0.0019	0.0049
Tb	0.0003 ± 0.00002	0.0001	(+25.0)	0.0004	0.0012
Dy	0.0019 ± 0.00006	0.0005	(+26.3)	0.0024	0.0046
Ho	0.0005 ± 0.00001	0.0001	(+16.7)	0.0006	0.0009
Er	0.0016 ± 0.00001	0.0003	(+15.8)	0.0019	0.0028
Tm	0.0002 ± 0.000006	0.0001	(+33.3)	0.0003	0.0004
Yb	0.0015 ± 0.00002	0.0002	(+11.8)	0.0017	0.0028
Lu	0.0002 ± 0.000006	0.0001	(+33.3)	0.0003	0.0004
W	0.026 ± 0.002	0.001	(+3.7)	0.027	0.002
Pb	n.d.[e)]	0.043	(—)	0.043	0.099
U	2.93 ± 0.08	0.06	(+2.0)	2.99	n.d.[e)]

a) The elements with † were determined by ICP-AES. Other elements were determined by ICP-MS. b) Concentrations in ultrafiltered seawater. The values in parentheses are the percentage ratios of the concentrations of the elements in the large molecule fraction to those in the dissolved fraction, defined as $D_{\text{large}} = [(C_{\text{dissolved}} - C_{\text{small}})/C_{\text{dissolved}}]\times 100$ (%), where $C_{\text{dissolved}}$ and C_{small} are the concentrations of each element in membrane-filtered and ultrafiltered seawaters, respectively. c) Concentrations in membrane-filtered seawater; cited from Ref. 10. d) Concentrations in particles remained on a membrane filter; cited from Ref. 10. e) Not detected.

The concentrations of alkali and alkaline earth metals except for Ba in the small molecule fraction are almost the same as those in the dissolved fraction, within ±2% of D_{large}. These results indicate that almost all of these elements exist as the ionic forms in seawater. In addition, V, Mo, W, and U, which exist as oxoanions in seawater, also provided small D_{large}. The percentage ratios (D_{large}) of Co, Ga, and Cd in the large molecule fraction are also very small, which suggests their existences as the small organic molecule- or chloro-complex forms in the dissolved fraction of seawater. In other words, the concentrations of these elements in the large molecule fraction are extremely low, as is seen in Table 2. Other elements, especially Al, Fe, Cu, Y, rare earth elements (REEs) and Pb, showed large differences between their concentrations in the dissolved and small molecule fractions, which results in their large D_{large} values. These data indicate that the relatively large amounts of large molecules of these elements are contained in the dissolved fraction of seawater.

The fractional distributions of the elements in the small molecule, large molecule and particle fractions of original seawater are illustrated in Fig. 1, which were calculated from the data in Table 2. It should be noted here that more than 50% of Al, Mn, Fe, Co, Ga, Y, REEs, and Pb are contained in the particle fraction, among which the particle fractions of Al, Fe, and Ce are more than 90%. It is also seen from Fig. 1 that the fractional distributions of alkali and alkaline earth metals and oxoanion-forming elements in the particle

Table 3. Concentrations of Major-to-Ultratrace Elements in Laboratory-Made Salts Prepared from Original, Membrane-Filtered, and Ultrafiltrated Seawaters

Element[a]	Concentration / ng g^{-1}				
	Salt I	Salt II[b]		Salt III[c]	
Na†	$(3.67 \pm 0.03)\times10^8$	3.66×10^8	(1.00)	3.67×10^8	(1.00)
K†	$(3.22 \pm 0.12)\times10^6$	3.21×10^6	(1.00)	3.24×10^5	(1.01)
Ca†	$(3.14 \pm 0.05)\times10^6$	3.20×10^6	(1.02)	3.16×10^6	(1.01)
Mg†	$(7.54 \pm 0.21)\times10^6$	7.65×10^6	(1.01)	7.65×10^6	(1.01)
Sr†	$(7.48 \pm 0.25)\times10^4$	7.57×10^4	(1.01)	7.50×10^4	(1.00)
Ba†	91 ± 4.4	90.5	(0.99)	94.0	(1.03)
Al	141 ± 3.0	72.6	(0.51)	21.0	(0.15)
Mn	16.3 ± 0.08	9.06	(0.56)	8.37	(0.51)
V	3.84 ± 0.04	2.98	(0.78)	2.98	(0.78)
Fe	29.6 ± 3.6	23.9	(0.81)	15.9	(0.54)
Co	0.073 ± 0.007	0.061	(0.84)	0.063	(0.86)
Cu	2.20 ± 0.06	1.76	(0.80)	1.24	(0.56)
Zn	3.24 ± 0.01	3.07	(0.95)	2.22	(0.69)
Ga	0.019 ± 0.002	0.016	(0.84)	0.018	(0.95)
Y	0.198 ± 0.003	0.156	(0.79)	0.137	(0.69)
Mo	78.9 ± 0.8	77.0	(0.98)	76.9	(0.97)
Cd	0.573 ± 0.009	0.552	(0.96)	0.556	(0.97)
La	0.137 ± 0.002	0.113	(0.82)	0.078	(0.57)
Ce	0.195 ± 0.002	0.136	(0.70)	0.098	(0.50)
Pr	0.022 ± 0.0002	0.018	(0.82)	0.016	(0.73)
Nd	0.096 ± 0.002	0.076	(0.79)	0.066	(0.69)
Sm	0.029 ± 0.001	0.022	(0.76)	0.018	(0.62)
Eu	0.014 ± 0.0006	0.009	(0.64)	0.006	(0.42)
Gd	0.034 ± 0.001	0.025	(0.74)	0.021	(0.62)
Tb	0.005 ± 0.0001	0.0033	(0.66)	0.0028	(0.56)
Dy	0.033 ± 0.0002	0.025	(0.76)	0.022	(0.67)
Ho	0.006 ± 0.0003	0.0042	(0.70)	0.0036	(0.60)
Er	0.016 ± 0.0002	0.012	(0.75)	0.010	(0.63)
Tm	0.0019 ± 0.0001	0.0013	(0.68)	0.0011	(0.58)
Yb	0.134 ± 0.0002	0.0092	(0.69)	0.0086	(0.64)
Lu	0.0023 ± 0.0001	0.0017	(0.74)	0.0015	(0.65)
W	0.227 ± 0.013	0.233	(1.03)	0.236	(1.06)
Pb	2.22 ± 0.013	1.22	(0.55)	—[d]	(—)
U	17.6 ± 0.6	17.7	(1.01)	18.2	(1.03)

a) The elements with † were determined by ICP-AES. Other elements were determined by ICP-MS. b) The values in parentheses are the ratios of the concentrations of the elements in Salt II to those in Salt I. c) The values in parentheses are the ratios of the concentrations of the elements in Salt III to those in Salt I. d) Not detected.

fraction are negligibly small. The distributions of Cu, Zn, and Cd in the particle fraction are ca. 20%. In addition, the fractional distributions of Al, Cu, REEs (La, Tb, Tm, Lu), and Pb in the large molecule fraction were more than 10%, as is seen in Table 2, although only a few percentages of Mn, Fe, Zn, Y, and REEs (except for La, Tb, Tm, and Lu) were in the large molecule fraction. Thus, it is considered that these elements are dissolved to some extent as the large molecular forms in seawater.

Concentrations of Major-to-Ultratrace Elements in Laboratory-Made Salts. Three kinds of laboratory-made salts (Salts I—III), which were prepared from the original, membrane-filtered, and ultrafiltered seawaters, were dissolved in 0.1 M HNO_3 to be 4% salt water solutions. Then, major-to-ultratrace elements in these salt water solutions were determined by ICP-AES and ICP-MS, as mentioned earlier. The results are summarized in Table 3, where the concentrations of analyte elements are expressed as the concentration per 1 g of salt. In the case of Salt I, the mean values and the standard deviations for analyte elements are shown, these were estimated from the 3 replicate measurements. The ratios of the concentrations of the elements in Salt II or Salt III to those in Salt I are also shown in parentheses of the columns of Salt II and Salt III, respectively.

As is seen in Table 3, the concentrations of alkali and alkaline earth metals in Salt III are almost the same as those in Salt I and Salt II, within 3%. These results indicate that almost all of these elements in the orginal and membrane-filtered seawaters were transferred to Salt III, because they are in the ionic forms in seawater. The oxoanion-forming elements (Mo, W, and U) and Cd showed the similar behaviors to alkali and alkaline metals. However, V, which is also an oxoanion-forming element, was less by 22% in Salt II and Salt III than in Salt I. This fact may indicate that ca.

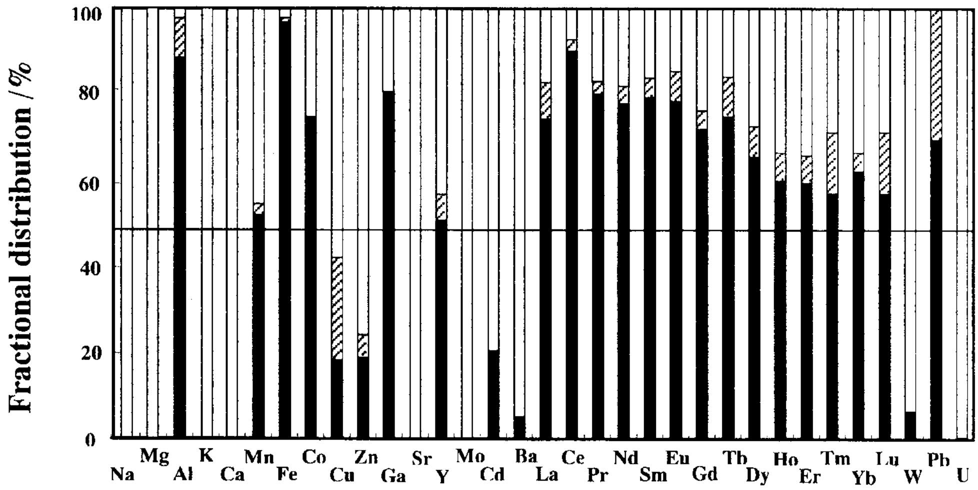

Fig. 1. Fractional distributions of analyte elements in small molecule, large molecule, and particle fractions of coastal seawater, collected at the off-shore of Nie, Ishikawa prefecture.
☐ small molecule fraction, ▨ large molecule fraction, ■ particle fraction.

20% of V in original seawater was in the particle fraction, although it could not be determined in the particle fraction, as mentioned earlier.

Other elements such as Al, Mn, Fe, Cu, Zn, Y, REEs, and Pb were considerally less in Salt II and Salt III than in Salt I, and, in general, they were also less in Salt III than in Salt II. These results mean that these elements exist partly as the particles and also as large molecules in seawater. This trend is apparently seen in Al. It should be noted here that biologically essential elements such as Mn, Fe, Co, Cu, and Zn exist to some extent as such large molecules in seawater.

Intake Factors of the Elements into Salt from Particle, Large Molecule and Small Molecule Fractions of Seawater. As described earlier, three different kinds of laboratory-made salts were prepared from original, membrane-filtered and ultrafiltered seawaters in the present experiment: (i) Salt I from original seawater, which contains particles, large molecules and small molecules, (ii) Salt II from the dissolved fraction, which contains large molecules and small molecules, and (iii) Salt III from the small molecule fraction, which contains only small molecules. Thus, it is considered that the concentrations of the elements in Salt I ($[\mathrm{M}]_{\mathrm{salt\ I}}$) include the contributions from particles, large molecules and small molecules. In a similar manner, $[\mathrm{M}]_{\mathrm{salt\ II}}$ and $[\mathrm{M}]_{\mathrm{salt\ III}}$ include the contributions from large molecules and small molecules and from only small molecules, respectively. In order to investigate the intakes of the elements in Salt I from the different fractions of seawater, the intake factors expressed by R_{particle}, R_{large}, and R_{small} were estimated, where the concentration of each element in Salt I was assumed to be 100%. The intake factors (R_{particle}, R_{large}, and R_{small}) of each element are defined by the following Eqs. 2, 3, and 4.

① R_{particle} is the intake factor from the particle fraction, which is expressed as the ratio (%) of the concentration of the element from the particle fraction to that in Salt I:

$$R_{\mathrm{particle}} = \{([\mathrm{M}]_{\mathrm{salt\ I}} - [\mathrm{M}]_{\mathrm{salt\ II}})/[\mathrm{M}]_{\mathrm{salt\ I}}\} \times 100\ (\%)\,. \quad (2)$$

② R_{large} is the intake factor from the large molecule fraction, which is expressed as the ratio (%) of the concentration of the element from the large molecule fraction to that in Salt I:

$$R_{\mathrm{large}} = \{([\mathrm{M}]_{\mathrm{salt\ II}} - [\mathrm{M}]_{\mathrm{salt\ III}})/[\mathrm{M}]_{\mathrm{salt\ I}}\} \times 100\ (\%)\,. \quad (3)$$

③ R_{small} is the intake factor from the small molecule fraction, which is expressed as the ratio (%) of the concentration of the element from the small molecule fraction to that in Salt I:

$$R_{\mathrm{small}} = ([\mathrm{M}]_{\mathrm{salt\ III}}/[\mathrm{M}]_{\mathrm{salt\ I}}) \times 100\ (\%)\,, \quad (4)$$

where $[\mathrm{M}]_{\mathrm{salt\ I}}$, $[\mathrm{M}]_{\mathrm{salt\ II}}$, and $[\mathrm{M}]_{\mathrm{salt\ III}}$ are the concentrations of each element in Salt I, Salt II, and Salt III, respectively, as shown in Table 3.

The intake factors of each element estimated by Eqs. 2, 3, and 4 are illustrated as bar graphs in Fig. 2. This figure indicates how much the elements in the particle, large molecule, and small molecule fractions of seawater were transferred to Salt I prepared from original seawater.

It is characteristically seen in Fig. 2 that Al and Pb in Salt I originated mostly from the particle and large molecule fractions. On the other hand, the intake factors of other elements from the small molecule fraction were more than 50%, which indicates that these elements in Salt I originated mainly from the small molecule fraction of seawater. Among them, almost 100% of alkali and alkaline earth metals, V, Mo, Cd, W, and U, whose fractional distributions as the small molecule fraction in original seawater were more than 80%, were taken in Salt I. Even in the case of Fe and REEs, more than 60% of them in Salt I originated from those in the small molecule fraction, although the fractional distributions of these elements in the small molecule fraction of seawater were less than 30%. As was described earlier, in seawater, Fe and REEs were mostly contained in the particle fraction. Thus, the larger abundances of Fe and REEs in Salt I suggest removal of particles together with $CaSO_4$ precipitates during the salt preparation procedure.

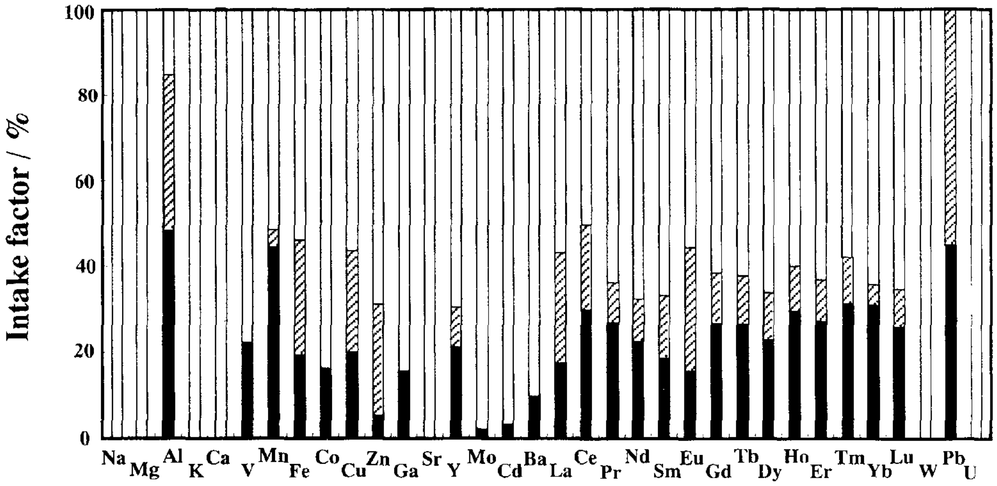

Fig. 2. Intake factors of analyte elements into laboratory-made salts from three different fractions of coastal seawater.
☐ small molecule fraction, ▨ large molecule fraction, ■ particle fraction.

The hatched parts of the bar graphs in Fig. 2 indicate the intake factors of the elements from the large molecule fraction of seawater. The intake factors of the elements in Salt I from the large molecule fraction were as follows: Al 40%, Mn 5%, Fe 28%, Cu 20%, Zn 30%, Y 7%, REEs 5—30%, and Pb 55%. On the other hand, the fractional distributions of these elements in the large molecule fraction of seawater were as follows: Al 10%, Mn 4%, Fe 2%, Cu 23%, Zn 7%, Y 5%, REEs 3—15%, and Pb 30%. Thus, it is stated here that these elements in the large molecular forms are relatively more abundant in Salt I than in seawater.

As is seen in Fig. 1, the fractional distributions of Al, Mn, Fe, Co, Ga, Y, REEs, and Pb in the particle fraction of seawater were more than 50%. On the other hand, the intake factors of Al, Mn, and Pb were 40—50%, while those of Fe, Co, Ga, Y, and REEs were ca. 20—30%. The fact that the values of the intake factors of these elements in salt are smaller than their fractional distributions in the particle fraction of seawater suggest removal of the particles during the salt preparation. The intake factor of V in salt from the particle fraction was ca. 20%, although V in the particle fraction of seawater could not be determined by ICP-MS, because ^{51}V was interfered with by ^{35}Cl^{16}O produced from $HClO_4$, which was used as a digestion reagent. On the other hand, V in salt water could be determined because it was preconcentrated with the chelating resin, so that spectral interference of ^{35}Cl^{16}O with ^{51}V became relatively smaller in preconcentrated salt water.

According to the results obtained in the present experiment, the intake factors of R_{large} and R_{small} for the elements in salt (Salt I) were almost the same as or larger than their fractional distributions in the small and large molecule fractions of seawater, but R_{particle} in salt became much smaller than the fractional distributions of the particle fraction in seawater. These results may be explained by the fact that the relatively large amounts of the particles in seawater were removed together with $CaSO_4$ precipitates produced during salt preparation, which results in the relatively lower concentrations of the elements consisting of the particles in salt. On the other hand, the elements in the small molecule fraction, which were not influenced by precipitation of $CaSO_4$, provided the larger intake fractors in salt. The elements from the large molecule fraction were also more abundant in salt than those in seawater. These results indicate that the elements in the large molecule fraction of seawater were to a large extent taken into salt.

It has been elucidated that most of the dissolved metallic elements in lake or pond water exist to a large extent in the small molecule fraction obtained after ultrafiltration, and also that the elements in the small molecule fraction are in the forms of large organic molecule-metal complexes (LOMMCs) with molecular weight (MW) of > 300000 Da and 10000—50000 Da.[11,12] LOMMCs with MW > 300000 Da are considered to be composed of hydroxide colloids of Al and Fe as core material, on which biogenic large organic molecules as well as various inorganic metal ions are adsorbed.[13] In order to explain this type of LOMMCs, a string-ball model was proposed by the present authors.[13] The study on LOMMCs in seawater has not been carried out yet. It may, however, be reasonable to consider that the elements in the large molecule fraction of seawater may be in the chemical forms similar to LOMMCs found in lake or pond water. Then, the elements existing as such LOMMCs in seawater may precipitate partly together with $CaSO_4$ and particle components before salt crystalization. However, LOMMCs are quite soluble in seawater, and thus the elements in LOMMCs may remain in the concentrated seawater solution. Consequently, they may be taken into salt as some aggregates or precipitates during evaporation of the seawater solution to produce NaCl crystals.

Conclusion

The fractional distributions of major-to-ultratrace elements in the particle, large molecule and small molecule fractions of seawater were investigated to elucidate their dissolved states in seawater. In addition, three kinds of laboratory-made salts were prepared from original, membrane-filtered and ultrafiltered seawaters. The intake factors of the elements from seawater were estimated from the concentrations of the elements in three different kinds of laboratory-made salts. The relationships between the fractional distributions and intake factors of the elements provided some information about the partitionings of the elements between seawater and salt, as well as about the dependence of the elemental compositions of natural salt on their chemical forms in seawater. Finally, it is conclusively stated from these results that a large number of elements, which are mineral nutrients in salt, are contained in natural salt together with biogenic organics at the trace concentration level.

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