Partitionings of Major-to-Ultratrace Elements in Bittern as Determined by ICP-AES and ICP-MS with Aid of Chelating Resin Preconcentration

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The concentrations of major-to-ultratrace elements in bittern, which was obtained after seawater concentration in the salt preparation process, were investigated by ICP-AES (inductively coupled plasma atomic emission spectrometry) and ICP-MS (inductively coupled plasma mass spectrometry) with and without the aid of chelating resin preconcentration. As a result, 34 elements in bittern could be determined in the concentration range from 10^7 to 10^{-3} ng mL^{-1} with good RSDs (less than 5%) for most analyte elements. Based on the experimental results, the concentrations of the elements in bittern were compared with those in seawater. Furthermore, the distribution factors of major-to-ultratrace elements in bittern were estimated to elucidate the partitionings of those elements among the calcium precipitate, the salt and the bittern from coastal seawater. The results suggest that the concentrations of the elements in bittern significantly depended on their chemical forms in seawater. For example, K and Mg in ionic form, V, Mo, W, and U in oxoanion form, and Cu and Zn in complex form with organic molecules in seawater, were much more partitioned in bittern than in salt.

Seawater has been utilized as a natural resource for our lives. One of the utilizations of seawater is to prepare table salt because of the high content of dissolved salts.[1] As is well known, table salt is obtained as a crystalline precipitate after seawater concentration, while bittern is obtained as the supernatant (the residual solution phase) after salt precipitation. Generally, in such a process, when seawater is evaporated by solar radiation or thermal heating, calcium precipitates ($CaSO_4$ and $CaCO_3$) are first removed, and then NaCl is produced as a crystalline precipitate. Bittern has been traditionally utilized as a solidifying reagent to make bean curd, which has been a kind of nutritious food since ancient times. It has been reported that bittern was often added into purified salt to increase the mineral constituents.[2] Recently, it is also known that bittern is added to drinking water to prepare mineral water. However, there have been few reports about the multielement determination of trace elements in bittern. Therefore, it is the subject of interest from the viewpoint of nutritional chemistry to determine major-to-ultratrace elements in bittern for elucidating the partitionings of the elements in bittern as well as the roles of the ingredients in salt and their products.

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] However, the determination of trace metals in samples like seawater and bittern is still difficult, because the high salt contents in these samples cause instrumental drift, isobaric polyatomic interference, signal suppression, and clogging of the sample introduction system in ICP-MS. In order to overcome these problems, the present authors have explored various analytical methods, such as gallium coprecipitation,[4] aluminum coprecipitation,[5] and chelating resin preconcentration,[6,7] for the multielement determination of trace elements in seawater by ICP-MS. Among these methods, it was found that the chelating resin preconcentration method was the most effective for trace element analysis of seawater because major elements were efficiently eliminated and no carrier (coprecipitation reagent) was required.

In the present experiment, bittern is defined as the residual solution obtained after seawater concentration by 49.1-fold in volume, where most of the Ca and Na are removed in the salt production process, while most of the Mg and K remain.[8–11] In the present experiment, thus, the chelating resin preconcentration in a batch method was applied to the determination of trace elements in the bittern samples by ICP-MS. At the same time, major elements in the bittern samples were also determined by ICP-AES (inductively coupled plasma atomic emission spectrometry).

In order to discuss comprehensively the partitionings of the elements (minerals) among calcium precipitates, salt (product) and bittern (residual solution) from seawater (raw material), the experiment for salt and bitten preparation was performed in the laboratory. Coastal seawater collected off-shore of Nie in the Noto Peninsula was used for the preparation of salt in the laboratory, where bittern was obtained as the residual solution after precipitation of calcium precipitates and NaCl crystal. The major-to-ultratrace elements in coastal seawater, laboratory-made salt and bittern were determined by ICP-AES and ICP-MS with and without the aid of chelating resin preconcentration. Since the results for coastal seawater and laboratory-made

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Table 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 16.0 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 point	3 points/peak
number of scans	100
ICP-AES Jarrell Ash Plasma AtomComp Mk II	
Plasma conditions:	
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 L min^{-1}
Nebulizer:	Cross-flow type
observation height	18 mm
Data acquisition:	
integration time	10 s
accumulation	3 times
repetition	3 times

salts have already been reported elsewhere,[10] the results for bittern will be mainly discussed in detail in the present paper.

Experimental

Instrumentation. An ICP-MS instrument (SPQ 8000A, Seiko Instruments, Chiba), which was composed of a quadrupole mass spectrometer, was used for the determination of trace and ultratrace elements in bittern. An ICP-AES instrument (Plasma AtomComp MkII, Jarrell-Ash, Franklin, MA, U.S.A.) equipped with the polychromator of a Paschen-Runge mounting for simultaneous multielement detection (40 channels) was also used for the determination of major and minor elements in bittern. The operating conditions of the ICP-MS and ICP-AES instruments are summarized in Table 1. These operating conditions were chosen after the optimization of the instrumental parameters of each instrument. The pH adjustment in the chelating resin preconcentration was carried out by using a non-contact type pH meter (Twin pH meter B212; Horiba, Kyoto).

Chemicals. The standard solutions for making the calibration curves in the ICP-AES and ICP-MS measurements were prepared from the single-element standard stock solutions (1000 μg mL^{-1}) for atomic absorption spectrometry, which were purchased from Wako Pure Chemicals (Osaka). Taking into consideration the chemical stabilities and polyatomic interferences in the ICP-MS and ICP-AES measurements, the standard solutions were separated into five groups, which are summarized in Table 2. Nitric acid, acetic acid, and an ammonia solution of high-purity grade were purchased from Kanto Chemicals (Tokyo). Ammonium acetate, which was used for the pH adjustment, was prepared by mixing equivalent molar amounts of diluted acetic acid and diluted ammonia solution.

Table 2. Compositions of Standard Solutions for Simultaneous Multielement Determination for ICP-MS and ICP-AES Measurements

Group	Element	Concentration /ng mL^{-1}
ICP-MS measurement[a)]		
Std. 1	Al, Ti, V, Co, Pb	50
	Dy, Ho, Er, Tm, Lu	5
Std. 2	Fe, Cu, Zn, Cd	50
	La, Ce, Pr, Nd, Yb	5
Std. 3	Mn, Mo, Sn	50
	Y, Sm, Eu, Gd, Tb, U	5
ICP-AES measurement		
Std. 4	Na	100000
	K, Ca, Mg	50000
	Sr, Ba	10000
Std. 5	Al, Ti, Pb, Fe, Cu, Zn, Mn, Mo	5000

a) Each of the multielement standard solutions for ICP-MS measurement contains Ge, In, Re, and Tl (10 ng mL^{-1} each) as internal standard elements. Stds. 1, 2, 3, and 5 are in 2 M HNO_3 solutions, while Std. 4 is in 0.1 M HNO_3 solution.

The chelating resin used for preconcentration of trace elements in the bittern samples was a Chelex-100 resin (100–200 mesh; Bio-Rad Laboratories, Richmond, CA, U.S.A.). The Chelex-100 resin was soaked in 5 M HCl for 5 days (changed daily), and then rinsed sequentially with pure water, 2 M HNO_3, and pure water before use. The pure water used throughout the present experiment was prepared by a Milli-Q Purification system (Milli-Q SP TOC; Nihon Millipore Kogyo, Tokyo).

Coastal Seawater Sample and Preparation Procedure of Laboratory-Made Salts. The coastal seawater sample was collected off-shore of Nie in the Noto Peninsula on November 11, 1998.[11] The vessels for sample preservation were cleaned by soaking in 6 M HNO_3 for a week, and then rinsing with distilled water (5 times) and pure water (3 times).

Coastal seawater was directly subjected to concentration for salt preparation without any filtration. In salt preparation, when seawater in a glass beaker was heated on a burner and concentrated by about 8 fold, calcium precipitates were first obtained. The residual solution (so-called "kan-sui" in Japanese) was further concentrated by about 5-fold to precipitate salt, and then bittern was obtained as the supernatant after salt precipitation. In this laboratory-made salt preparation procedure, 60.5 g of salt and 55 mL of bittern were obtained from an initial 2700 mL of seawater, which corresponded to a yield of about 71% as salt. The purity of laboratory-made salt was 93.3% as NaCl.[11]

Determination of Major-to-Ultratrace Elements in Bittern Samples. The major-to-ultratrace elements[3] in seawater and salts were determined by ICP-AES and ICP-MS after chelating resin preconcentration, and have been reported elsewhere already.[6,7,10,11]

In bittern analysis, 10 and 20 mL of bittern were diluted to 250 mL each of 0.1 M HNO_3 solutions, which were used for the determination of trace elements (Al, V, Mn, Fe, Co, Cu, Zn, Mo, Cd, W, and U) and ultratrace elements (Ga, Y, rare earth elements (REEs), and Pb) in bittern, respectively. Trace and ultratrace elements in each bittern sample were determined by ICP-MS after chelating resin preconcentration. Major elements in bittern were determined by ICP-AES after appropriate dilution.

Table 3. The Recoveries, Analytical Detection Limits, and Blank Values of Analyte Elements Obtained by ICP-MS with Aid of Chelating Resin Preconcentration

Element	m/z	Recovery /%	Analytical detection limit /ng mL^{-1}	R$_{BD}$ [a)]	Blank[b)] /ng mL^{-1}	R$_{BB}$ [c)]
Al	27	80.8	0.16	173	0.54	51
V	51	55.8	0.03	953	n.d.	—[d)]
Mn	55	75.9	0.04	25	0.08	13
Fe	57	53.8	1.2	8.8	n.d.	—[d)]
Co	59	99.3	0.002	55	0.008	14
Cu	63	98.5	0.02	525	0.11	95
Zn	66	103	0.05	468	0.3	78
Ga	71	79.3	0.0003	4.3	n.d.	—[d)]
Y	89	101	0.0002	215	0.006	7
Mo	98	41.3	0.005	94400	0.008	59000
Cd	111	97.5	0.002	48	0.003	32
La	120	102	0.0002	41	0.0011	7
Ce	139	101	0.0003	35	0.0012	9
Pr	140	101	0.0001	14	0.0002	7
Nd	141	100	0.0004	11	n.d.	—[d)]
Sm	143	96.5	0.0002	3	n.d.	—[d)]
Eu	147	95.1	0.0001	16	n.d.	—[d)]
Gd	151	92.6	0.0002	10	n.d.	—[d)]
Tb	157	95.2	0.0001	4	n.d.	—[d)]
Dy	159	95.3	0.0002	25	n.d.	—[d)]
Ho	163	95.6	0.0001	15	n.d.	—[d)]
Er	165	95	0.0002	45	0.0002	45
Tm	167	94.8	0.0001	17	n.d.	—[d)]
Yb	169	95	0.0001	100	n.d.	—[d)]
Lu	173	94.5	0.0001	25	n.d.	—[d)]
W	184	51.6	0.005	214	n.d.	—[d)]
Pb	208	95.1	0.002	28	0.011	5
U	238	80.1	0.004	27500	0.013	8460

a) The values (R$_{BD}$) are the ratios of the concentrations of the elements in bittern, shown in Table 4, to the analytical detection limits of those elements. b) n.d.; not detected. c) The values (R$_{BB}$) are the ratios of the concentrations of the elements in bittern, shown in Table 4, to the blank values of those elements. d) Not available.

As mention earlier, in the present experiment, 10 or 20 mL of bittern was used for analysis after dilution to 250 mL, depending on the concentrations of the elements in bittern, where preconcentration was performed at pH 6 using 0.2 g of the chelating resin in a similar manner to that for seawater.[7] Trace elements adsorbed on the resin were eluted with 6 mL of 2 M HNO_3 after rinsing with a 2 M sodium acetate solution and pure water. The internal standard elements (Ge, In, Re, and Tl) were added into the preconcentrated solution to achieve 10 ng mL^{-1} each, and the matrix effect correction by the internal standard method was made in the same manner as that reported by Sawatari et al.[4]

Results and Discussion

Analytical Figures of Merit of Chelating Resin Preconcentration/ICP-MS Method. The recoveries, analytical detection limits, and blank values for the trace elements obtained in the present experiment are summarized in Table 3. The recovery values in Table 3 were cited from Ref. 10, where those values were obtained by adding 1 or 10 ng mL^{-1} of standard elements in seawater, and performing the chelating resin preconcentration procedure described previously.[10] As can be seen in Table 3, the recoveries of Al, Co, Cu, Zn, Ga, Y, Cd, REEs, Pb, and U (23 elements) in chelating resin preconcentration were larger than or almost equal to 80%. These recoveries were in fairly good agreement with those reported in the previous paper.[7] On the contrary, the recoveries of V, Mo, and W were below 60%. In general, oxoanion-forming elements such as V, Mo, and W provided poor recoveries in chelating resin preconcentration, which may be ascribed to their low adsorption abilities on the chelating resin at the pH condition (pH 6) employed in the present experiment. The recoveries of Mn and Fe were 75.9 and 53.8%, respectively. The relatively poor recoveries of Fe and Mn may be due to the formation of stable hydroxo- and/or chloro-complexes in bittern.[7,12]

The analytical detection limits of trace elements in Table 3 were calculated from their instrumental detection limits, taking into consideration their concentration factors and recoveries. In the present experiment, the instrumental detection limit was estimated as the analyte concentration corresponding to 3-fold the standard deviation (σ) of the intensities obtained from a 10-times repeated measurement of the blank solution (0.1 M HNO_3 solution) at each m/z. The analytical detection limits of major and minor elements obtained by the ICP-AES measurements at each wavelength were estimated in a

Table 4. Concentrations of Major-to-Ultratrace Elements in Bittern Prepared from Coastal Seawater

Element[a]	Concentration in bittern /ng mL^{-1}	RSD /%	Concentration in coastal seawater[b] /ng mL^{-1}	R_{BS}[c]	D_{bittern}[d] /%
Na†	6.08×10^{7}	2.9	9.75×10^{6}	6.2	12.7
K†	1.53×10^{7}	3.9	3.95×10^{5}	38.7	78.9
Ca†	1.53×10^{5}	2.6	3.50×10^{6}	0.04	0.1
Mg†	4.44×10^{7}	5.2	1.09×10^{6}	40.7	83
Sr†	2.07×10^{3}	4.8	8.94×10^{3}	0.2	0.5
Ba†	5.1	5.8	5.93	0.86	1.8
Al	27.7	3.6	29.6	0.94	1.9
V	28.6	4.8	1.6	17.9	36.4
Mn	1	5	1.67	0.6	1.2
Fe	10.6	3.2	45.3	0.23	0.5
Co	0.11	4.1	0.02	5.5	11.2
Cu	10.5	1.9	0.38	27.6	56.3
Zn	23.4	2.6	1.22	19.2	39.1
Ga	0.0013	7.2	0.026	0.05	0.1
Y	0.043	2.2	0.051	0.84	1.7
Mo	472	5.2	11.9	39.7	80.8
Cd	0.095	1.9	0.024	4	8.1
La	0.0081	4.1	0.024	0.34	0.7
Ce	0.0105	3.1	0.052	0.2	0.4
Pr	0.0014	2.8	0.0066	0.21	0.4
Nd	0.0044	2.1	0.027	0.16	0.3
Sm	0.0015	5.4	0.0063	0.24	0.5
Eu	0.0006	4.8	0.0014	0.43	0.9
Gd	0.0016	4.2	0.0068	0.24	0.5
Tb	0.0004	5.8	0.0016	0.25	0.5
Dy	0.005	5.3	0.007	0.71	1.5
Ho	0.0015	7.2	0.0015	1	2
Er	0.0089	5.2	0.0047	1.9	3.9
Tm	0.0017	9.8	0.0007	2.4	4.9
Yb	0.011	4.6	0.0045	2.4	6.3
Lu	0.0025	5.9	0.0007	3.6	7.3
W	1.07	8.3	0.029	36.9	75.1
Pb	0.056	3.2	0.142	0.39	0.8
U	110	4.8	2.99	36.8	74.9

a) The elements with † were determined by ICP-AES. Other elements were determined by ICP-MS after chelating resin preconcentration. b) Cited from Ref. 10. c) R_{BS} is the ratio of concentrations of the elements in bittern to those in coastal seawater. d) D_{bittern} is the distribution factor defined by Eq. 2.

similar manner to those in the case of ICP-MS. As shown in Table 3, the analytical detection limits for 28 trace elements were in the concentration range from 1.2 ng mL^{-1} for Fe to 0.0001 ng mL^{-1} for Lu.

The blank values in Table 3 were estimated by measuring the apparent signal intensities of the blank solution in ICP-MS after the same preconcentration was carried out for a test solution of 0.1 M HNO_3. The blank values for V, Fe, Ga, REEs (except for La, Ce, and Pr), and W were lower than the analytical detection limits. Although the blank values for other elements in Table 3 were higher than their analytical detection limits, the ratios (R_{BB}) of the elemental concentrations in bittern to their blank values were larger than 10 for most elements, except for Y, La, Ce, Pr, and Pb. In the cases of Y, La, Ce, Pr, and Pb, their R_{BB} values were also larger than 5, and the RSDs were in the range from 2.2 to 4.1%. Thus, it was considered that the blank values of trace elements did not significantly affect their analytical results.

Concentrations of Analyte Elements in Bittern. As discussed above, the chelating resin preconcentration method employed in the present experiment is an effective method for the multielement determination of trace elements in bittern. In the present experimental procedure, trace elements in the original bittern were preconcentrated to 3.3 fold by the chelating resin method. Furthermore, the total concentrations of matrix elements (Na, K, Ca, and Mg) in the analysis solution were below 200 µg mL^{-1} after chelating resin preconcentration, and then the signal suppression of these analyte elements due to the matrix effect could be corrected by the internal standard method.[4]

The analytical results for bittern are summarized in Table 4, together with the RSD values for three independent experiments. About 30 trace elements in bittern were determined in the concentration range from 10^{3} to 10^{-3} ng mL^{-1} by ICP-MS. In addition, the concentrations of analyte elements in coastal seawater, which was the raw material for salt preparation,

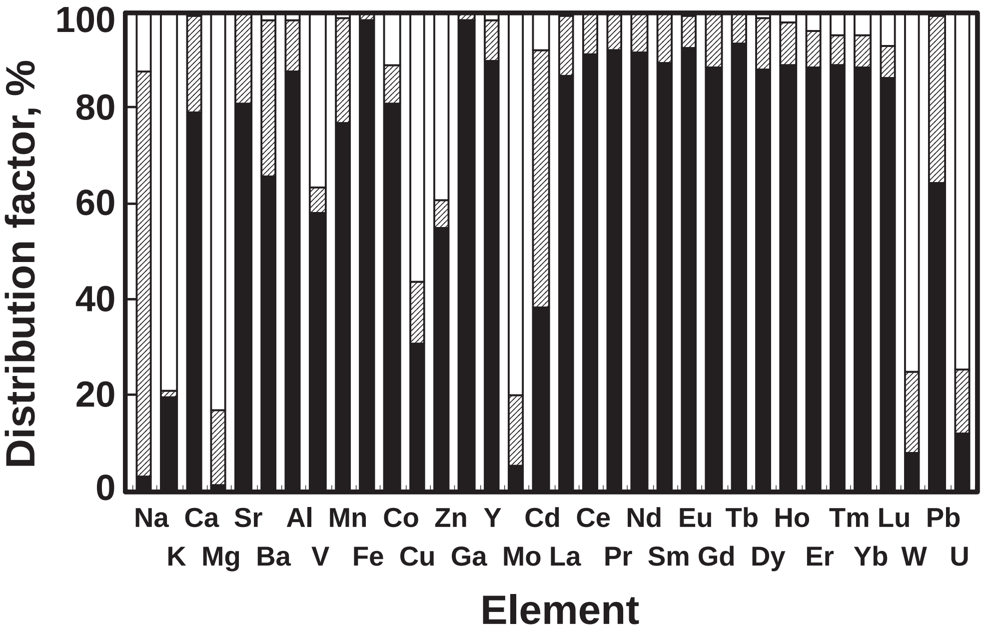

Fig. 1. Distribution factors of analyte elements in calcium precipitate, salt and bittern in salt preparation process. ■, calcium precipitate; ▨, salt; □, bittern.

are also shown in Table 4.[11] Consequently, 34 elements in bittern as well as in coastal seawater were determined in the concentration range from 10^7 to 10^{-3} ng mL^{-1} by ICP-AES and ICP-MS with and without chelating resin preconcentration. As can be seen in Table 4, RSDs for most analyte elements were smaller than or almost equal to 5%. These results indicate that these elements were determined with good reproducibility. The RSDs for Ga, Ho, Tm, and W were 7.2, 7.2, 9.8, and 8.3%, respectively. The poor precision for Ga was attributed to its low concentration close to the detection limit, while the precisions for ^{165}Ho and ^{169}Tm might be affected by polyatomic interferences with ^{149}Sm^{16}O and ^{153}Eu^{16}O, respectively. In the case of W, the poor precision was mainly due to the low recovery and relative low concentration in bittern.

In order to discuss the relationships between the concentrations of the elements in bittern and the chemical forms in coastal seawater, the concentration ratios (R_{BS}) of the elements in bittern to those in coastal seawater were calculated, and they are shown in Table 4. The R_{BS} values of Mg and K were 40.7 and 38.7, respectively. In the salt preparation process, 55 mL of bittern was obtained from 2700 mL of seawater, which indicates that bittern was concentrated by approximately 49 times in volume. These results mean that ca. 81% of Mg and ca. 77% of K in seawater remained in the liquid phase (bittern) during the salt preparation process; in another words, the concentrations of Mg and K in bittern were higher by 40.7- and 38.7-fold than those in seawater, respectively. On the other hand, the R_{BS} values of Ca, Sr, and Ba were 0.04, 0.2, and 0.86, respectively, which indicate that their concentrations were substantially lower than those in coastal seawater. This is because they formed precipitates such as $CaCO_3$, $CaSO_4$, $SrSO_4$, and $BaSO_4$ when seawater was concentrated by ca. 8 fold. Thus, it can be stated here that alkaline earth elements except for Mg are removed from the liquid phase before NaCl precipitation. The R_{BS} value of Na was 6.2, smaller than those of Mg and K, but much larger than those of Ca, Sr, and Ba. These results suggest that Na was more concentrated in bittern than in seawater, which is attributed to the fact that bittern is regarded as a saturated solution of NaCl even after the separation of salt crystals.

The R_{BS} values of Al, Mn, Fe, Ga, and Pb were in the range from 0.05 to 0.94. This indicates that their concentrations in bittern were lower than those in coastal seawater. These facts support the conclusion mentioned in earlier papers,[10,11] in which it was stated that most of these elements except Pb in coastal seawater were coprecipitated together with calcium precipitates in the forms of hydroxides and/or particles during salt preparation, because these elements were mostly contained in the particulate fraction of coastal seawater.[11] As shown in Fig. 1, ca. 35% of Pb was taken into salt, although the reason was not clear.

The R_{BS} values of typical transition elements, such as Cd, Co, Cu, and Zn, were 4, 5.5, 27.6, and 19.2, respectively. The quite large R_{BS} values of these elements suggest that these transition elements remained in the liquid phase (bittern) because of their easy formation of chloro-complexes, such as $CoCl^+$, $CdCl^+$, $CuCl^+$, and $ZnCl^+$ in seawater,[13] and stable chloro-complexes, such as $CoCl_4{}^{2-}$, $CdCl_4{}^{2-}$, $CuCl_4{}^{2-}$, and $ZnCl_4{}^{2-}$, in bittern. In addition, Cu and Zn in seawater existed more in the large organic molecule fraction than in the small molecule fraction. The existence of Cu and Zn as their complexes with biogenic large organic molecules in bittern was elucidated after ultrafiltration using an ultrafilter with a molecular permeation limit larger than 10000 Da in the previous paper.[11] Then, Cu and Zn provided larger R_{BS} values than Co and Cd, whose complexation abilities with biogenic large organic molecules are generally smaller than those of Cu and Zn.

Furthermore, V, Mo, W, and U in bittern, which were present mainly in soluble oxoanion forms ($VO_4{}^{3-}$, $MoO_4{}^{2-}$, $WO_4{}^{2-}$, and $[UO(CO_3)_3]^{2-}$) in seawater, provided large R_{BS}

values of 17.9, 39.7, 36.9, and 36.8, respectively. These results indicate that most of these elements remained as oxoanions in the liquid phase (bittern) during the salt preparation process.

It is interesting to note that the R_{BS} values of heavy REEs were slightly larger than Y and light REEs. According to the study on chemical speciation of REEs in lake water,[14] heavy REEs were more soluble than light REEs because heavy REEs provide larger stability constants in complex formation with biogenic organic molecules, compared to light REEs. Thus, the larger R_{BS} values for heavy REEs than those for light REEs suggest that heavy REEs in seawater might be more in the forms of metal complexes with biogenic organic molecules than light REEs and remain more in the liquid phase (bittern) during the salt preparation process.

Partitionings of the Elements into Calcium Precipitate, Salt, and Bittern from Coastal Seawater in Salt Preparation Process. The partitionings of the elements into salt from coastal seawater in the salt preparation process have already been reported elsewhere.[10,11] According to these papers, it is known that only 10–20% of most elements were taken into salt from coastal seawater, and then it was supposed that some metal elements (Al, Mn, Fe, etc.) and REEs were removed together with calcium precipitates,[14] while other elements (Mg, K, V, Mo, W, U, etc.) remained in bittern. In order to prove the above elemental distributions, the distribution factors (D_{bittern}) of analyte elements into calcium precipitates, salt, and bittern from coastal seawater were estimated to discuss their partitionings in bittern from seawater. As mentioned earlier, 60.5 g of salt and 55 mL of bittern were obtained from 2700 mL of coastal seawater. Therefore, the distribution factors of analyte elements in calcium precipitates, salt, and bittern, which were expressed as D_{Ca} (%), D_{salt} (%), and D_{bittern} (%), respectively, were calculated by Eqs. 1, 2, and 3, as follows:

$$D_{\mathrm{salt}}\ (\%) = \{([\mathrm{M}]_{\mathrm{salt}} \times 60.5) / ([\mathrm{M}]_{\mathrm{seawater}} \times 2700)\} \times 100\ (\%), \tag{1}$$

$$D_{\mathrm{bittern}}\ (\%) = \{([\mathrm{M}]_{\mathrm{bittern}} \times 55) / ([\mathrm{M}]_{\mathrm{seawater}} \times 2700)\} \times 100\ (\%), \tag{2}$$

$$D_{\mathrm{Ca}}\ (\%) = 100\ (\%) - D_{\mathrm{salt}}\ (\%) - D_{\mathrm{bittern}}\ (\%), \tag{3}$$

where $[\mathrm{M}]_{\mathrm{salt}}$ ($\mu g\,g^{-1}$), $[\mathrm{M}]_{\mathrm{seawater}}$ ($\mu g\,mL^{-1}$), and $[\mathrm{M}]_{\mathrm{bittern}}$ ($\mu g\,mL^{-1}$) are the concentrations of the element in salt, those in coastal seawater, and those in bittern, respectively. The results for D_{bittern} are summarized in the last column of Table 4. Since the results for D_{salt} have been reported in the earlier papers,[10,11] the D_{Ca} values could be obtained from Eq. 3.

In order to consider the elemental distributions, the results for D_{bittern}, D_{salt}, and D_{Ca} are schematically illustrated as bar graphs in Fig. 1. This figure indicates the partitionings of analyte elements in calcium precipitates, salt, and bittern from coastal seawater during the salt preparation process. It can be characteristically seen in Fig. 1 that ca. 75–85% of Mg, K, Mo, W, and U from seawater remained in bittern and more than 10% of these elements were taken into salt. On the other hand, 35–55% of V, Cu, and Zn remained in bittern, but other elements except for Na and Co from seawater were taken into bittern less than 10%. In addition, more than 10% of Al, Mn, Sr, Cd, Ba, Eu, and Pb were taken into the salt fraction. As a result, more than 80% of Al, Ca, Mn, Fe, Co, Ga, Sr, Y, and REEs were removed together with calcium precipitates, maybe, due to coprecipitation as hydroxide colloids or carbonate precipitates. These facts agree with the conclusion obtained in previous papers.[10,11]

It is noted from the results in Fig. 1 that 35–55% of V, Cu, and Zn in seawater remained in bittern, while only 5–15% of them were taken into salt, as stated in the previous papers.[10,11] Thus, it can be stated that about 30–60% of these elements are also removed together with calcium precipitates in the salt preparation procedure. Major chemical species of V in seawater are also considered as VO_4^{3-}, but V provides more complicated chemical species such as VO_2^{+}, VO_3^{-}, and $V_2O_7^{4-}$, in weakly alkaline solutions like seawater.[12] Thus, some unstable species of V may be adsorbed on colloidal particles in seawater more than stable oxoanions of Mo, W, and U,[15] and then they may be taken into calcium precipitates in the salt preparation process. As for Cu and Zn, it was suggested earlier that most of them existed as large organic molecule-metal complexes (LOMMCs) in seawater.[11] When seawater is concentrated, some parts of them may form colloidal particles, which results in their coprecipitation with calcium precipitates. However, the rest of them may remain as soluble LOMMCs in the liquid phase (bittern) during the salt preparation process. As shown in Fig. 1, the amounts of REEs (rare earth elements) in bittern were very small, but it should be noted here that the amounts of heavy REEs in bittern were larger than those of light REEs. These facts also suggest the existence of LOMMCs in the bittern, because heavy REEs have larger complexing abilities with biogenic large organic molecules than light REEs.[16]

Conclusion

The concentrations of 34 elements in bittern were determined by ICP-AES and ICP-MS with and without the aid of chelating resin preconcentration. The distribution factors of analyte elements into bittern from coastal seawater were estimated from the data of bittern and seawater obtained in the present experiment to discuss the partitionings of analyte elements among calcium precipitates, salt, and bittern from seawater during the salt preparation process. It can be conclusively stated here from the results in Fig. 1 that the elements in seawater are first removed with calcium precipitates (■), then with salt (▨), and finally remain in bittern (□) in the salt preparation process. The elements such as Mg, K, V, Mo, W, U, Cu, and Zn, which are more soluble elements because of simple ionic species (Mg and K), oxoanions (V, Mo, W, and U), or complex compounds (LOMMCs; Cu and Zn) in seawater, remained much more in bittern, and then provided larger distribution factors: 75–85% for Mg, K, Mo, W, and U, and 35–55% for V, Cu, and Zn. Since the biological or physiological impacts of these elements in bittern may also depend on chemical forms, it is desirable to promote chemical speciation analysis of them, especially in terms of biogenic organic molecules by MALDI-TOFMS and ESI-MS.[17]

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