Multi-Element Compositions of Marine Phytoplankton Samples from the Northern North Pacific and the Bering Sea

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ABSTRACT– Phytoplankton samples were collected from the northern North Pacific and the Bering Sea during the KH-97-2 Cruise by using a non-metal NORPAC P-25 (25-μm opening) attached a NGG52 pre-net (335-μm opening) and twelve samples were analyzed for Corg and Ntot, and for 14 major and trace elements by INNA. A sample collected in the Gulf of Alaska (Stn. 13) showed the highest Al content indicating a high content of lithogenic aluminosilicate and other eleven samples showed pelagic nature with low Al contents. For the eleven pelagic samples, extended Redfield ratios were tentatively obtained based on observed correlation with Se for most samples as follows: C : N : Se : Br : I : Fe : Zn : Cr = 106 : 11 : 0.00020 : 0.03~0.09 : 0.003~0.007 : 0.05~0.15 : 0.036 : 0.0045. A linearity between log (C_{PL}/C_{SW}) and log (C_{PL}/C_{RW}) (MKT plot) was observed for all samples with slope values ranging from 0.104 to 0.236 and relatively constant intercept values, 3.35 + 0.11 (1SD). The highest slope value was observed for the sample at Stn.13 with the highest Al content. More detailed studies will be needed to confirm the extended Redfield ratios and also the diversity of slope and intersept values of MKT plots of multi-elements in marine phytoplankton samples from different areas in open oceans.

***Key words**: marine phytoplankton, instrumental neutron activation analysis, multi-element composition, trace metals, MKT plot*

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INTRODUCTION

Biological production and its products are the starting materials of marine biogeochemical cycles of elements in marine environments. Marine organisms accumulate not only major (C, N, P, Si, S, etc.) but also trace biophile elements. Data on multi-element compositions of marine biological products, however, have been quite limited (e.g., Martin and Knauer, 1973; Bowen, 1979) especially for phytoplankton samples. Masuzawa et al. (1988) analyzed 24 major and trace elements of zooplankton species from the Japan Sea mostly by instrumental neutron activation analysis (INNA) and found a logarithmic linear relationship with a slope value of nearly zero between concentration ratios of plankton samples to mean seawater and to mean dissolved river water (MKT plot). Recently Masuzawa et al. (1999) reported 25 major and minor element compositions of phytoplankton samples collected from the coastal areas off Japan and showed significant effects of lithogenic aluminosilicate particles to these coastal phytoplankton samples and that MKT plot was applicable to these phytoplankton samples with some slope values. The purposes of the present study are to obtain multi-element compositions of phytoplankton samples collected from the pelagic areas of the northern North Pacific and the Bering Sea and to test the generality of multi-elemental compositions based on MKT plots to these samples.

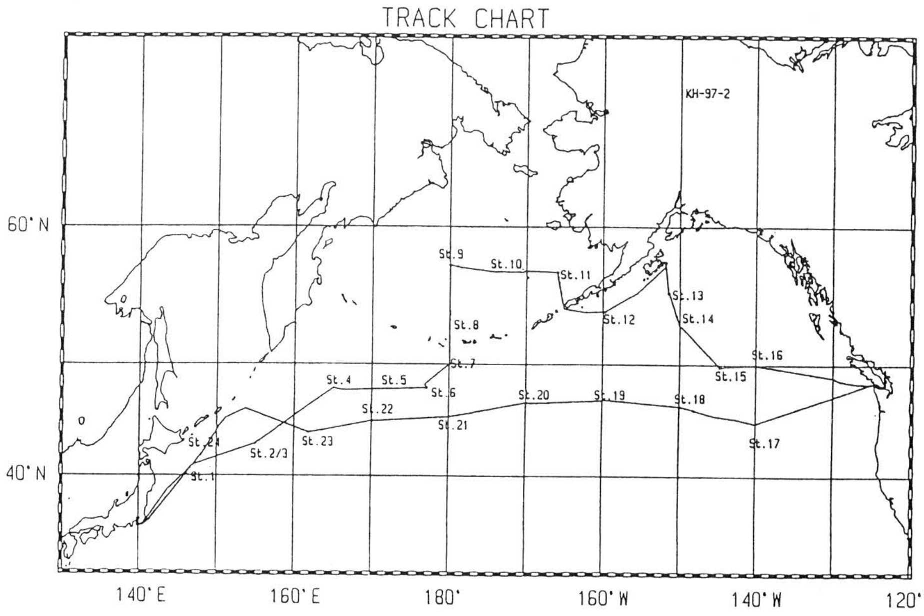

Fig. 1. Sampling locations of phytoplankton samples from the northern North Pacific and the Bering Sea during the KH-97-2 Cruise (Kawaguchi, 1998).

Table 1. Major and trace element compositions of phytoplankton samples collected from the North Pacific and the Bering Sea during the KH-97-2 Cruise.

Stn.		1	2/3	4	6	6	6	7	9	9	9	13	17
Area		WN Pacific			CN Pacific				Bering Sea			EN Pacific	
Latitude		41° 00.6'N	43° 01.2'N	48° 01.3'N	48° 00.9'N	48° 07.7'N	48° 06.3'N	50° 00.0'N	57° 24.0'N	57° 15.2'N	57° 15.6'N	55° 30.9'N	44° 59.9'N
Longitude		147° 01.1'E	155° 01.4'E	165° 03.5'E	177° 04.7'E	176° 34.2'E	176° 44.5'E	179° 59.4'E	179° 53.9'E	179° 55.1'E	179° 50.2'E	151° 26.4'W	139° 59.9'W
Water Depth		5149 m	5389 m	5809 m	4796 m	5497 m	5376 m	5858 m	3808 m	3814 m	3881 m	4889 m	4395 m
Sampling Depth		0-60 m	0-100m	0-50m	0-100m	0-90m	0-90m	0-50m	0-50m	0-50m	0-50m	0-50m	0-50m
Sampling Date		1997/7/11	1997/7/12	1997/7/14	1997/7/21	1997/7/22	1997/7/23	1997/7/24	1997/7/25	1997/7/25	1997/7/26	1997/8/6	1997/8/24
Sample Name		1bMQ	2/3aMQ	4AaMQ	6AbMQ	6BaMQ	6CaMQ	7aMQ	9AaMQ	9BaMQ	9CaMQ	13aMQ	17aMQ
PL No.		PL074	PL077	PL082	PL093	PL094	PL098	PL102	PL109	PL113	PL117	PL125	PL140
Corg	(%)	28.7	18.6	8.9	6.5	27.6	8.2	18.1	23.1	17.5	18.5	15.4	12.1
Ntot	(%)	5.21	3.00	1.14	0.75	4.41	1.05	3.90	2.89	2.29	2.30	2.24	1.27
C/N		5.52	6.19	7.82	8.63	6.26	7.88	4.65	7.99	7.65	8.03	6.89	9.51
Ca	(%)	6.4	2.7	-	3.1	5.8	3.7	5.1	2.4	-	-	1.4	-
Na	(%)	0.332	0.261	0.277	0.297	0.236	0.256	0.156	0.138	0.141	0.136	0.319	0.092
Cl	(%)	1.161	0.945	0.848	0.393	0.637	-	0.484	0.310	0.148	-	1.291	0.738
Al	(ppm)	1070	1220	1340	1180	950	1140	1130	1230	3400	1340	8660	1560
Fe	(ppm)	646	640	449	155	1644	195	789	1187	354	1156	4438	1032
Sr	(ppm)	312	282	-	181	346	219	-	135	145	165	155	2268
Br	(ppm)	890	387	230	248	754	238	1743	1089	938	882	560	391
I	(ppm)	164	64	68	48	123	38	317	109	100	121	148	150
Se	(ppm)	3.47	2.73	1.24	0.94	3.35	1.4	-	2.33	-	2.13	-	-
V	(ppm)	-	17.4	-	-	13.7	9.2	11.9	-	-	52.6	38.2	52.0
Cr	(ppm)	17.6	30.0	15.7	13.5	49.4	16.9	38.4	32.5	15.6	109	52.4	33.5
Co	(ppm)	0.44	0.46	0.13	-	0.45	0.19	0.38	-	0.33	0.50	1.74	0.45
Zn	(ppm)	123	457	95	90	520	139	383	225	153	338	236	361
Sc	(ppm)	0.121	0.175	0.286	0.017	0.075	0.017	0.071	0.133	0.044	0.058	1.44	0.075

MATERIALS AND METHODS

Phytoplankton samples were collected during the KH-97-2 Cruise of the R/V Hakuho Maru, University of Tokyo, from July to September 1997 (Kawaguchi, 1998; Fig. 1 and Table 1). Phytoplankton samples were collected from the euphotic zone using a non-metal NORPAC P-25 net (25-μm opening) attached a pre-net of NGG 52 (335-μm opening). Collected phytoplankton samples (25-335 μm) were concentrated and washed with 0.5M ammonium formate or with Milli-Q water to remove sea salts by centrifugation with a refrigerated centrifuge in a low temperature room at 0-4 °C. All centrifuged samples were stored in a freezer, carried back to the laboratory, and freeze- and vacuum-dried.

About 5 and 30 mg of Milli-Q washed and dried phytoplankton samples were subjected to INNA for short-lived and long-lived nuclides, respectively, by the comparator method (Koyama et al., 1987; Masuzawa et al., 1999) using the KUR reactor of Kyoto University. Standard solutions of 28 trace elements spotted on Millipore HA filters and a standard rock sample of Geological Survey of Japan (JB-1 or JB-1a; Imai et al., 1995) were irradiated together with the samples as recovery monitors for each element. Usually following 14 major and trace elements were analyzed for marine phytoplankton samples within errors of 5-15%: Ca, Al, V, Na, Cl and I (short-lived), and Fe, Sr, Br, Se, Zn, Co, Cr and Sc (long-lived). Organic carbon (Corg) and total nitrogen (Ntot) were determined with a Finnigan Tracer MAT after treating with HCl solution to remove inorganic carbon.

RESULTS AND DISCUSSION

Table 1 shows the analytical results of Corg, Ntot and 14 major and trace elements of 12 phytoplankton samples. The sample at Stn. 13 in the Gulf of Alaska (Fig. 1) showed the highest Al content, 8660 ppm, among the samples reported here. The station was very near to land (ca. 170 km) and its high Al content indicates a high content of lithogenic aluminosilicates and it will be discussed separately from other samples reported here. Table 2 summarizes the concentration ranges of phytoplankton samples for eleven pelagic samples and one coastal sample (Stn.13 in the Gulf of Alaska) from the northern North Pacific and the Bering Sea as well as those from coastal areas off Japan by INNA (Masuzawa et al., 1999), from eastern North Pacific by atomic absorption spectroscopy (Martin and Knauer, 1973) and those of marine phytoplankton compiled by Bowen (1979), where data for Cl, Br and Sc were not included.

Comparing with the chemical compositions of phytoplankton samples from coastal areas off Japan (Masuzawa et al., 1999), which were obtained by using the same sampling and analytical methods as those of this study, twelve elements (Mn, As, Sb, Ba, Cs, Th, Hf, U, La, Ce, Sm and Eu) were failed to be detected, and Al, Fe, Co and Sc contents were much lower because lithogenic aluminosilicate contents in the present samples collected mostly from pelagic areas were very low as indicted by low Al contents in the present samples, and most of these elements were mainly included in lithogenic aluminosilicates. Contents of Ca and Sr were much higher in the present pelagic samples than those from coastal areas off Japan. This suggests higher contents of calcium carbonate shells in the pelagic samples than in the coastal samples. Comparing with

Bowen's compilation, concentration ranges of phytoplankton samples reported here were higher for Ca, Al, Sr, V, Cr and Zn, and comparable for Fe, I, Se and Co (Table 2).

Table 3 shows a correlation matrix of 16 major and minor elements for the eleven pelagic samples reported here. Very high correlation coefficients were observed between Corg and Ntot and between Corg and Se. Several elements showed positive correlation with Se (Table 3) and some of them are plotted in Figs. 2 and 3, where good positive correlation was observed for most samples but sometimes not for all. Se has been considered to be a growth-limiting element for marine coccolithophorids (e.g., Dambara and Shiraiwa, 1999) or for coastal marine diatom (e.g., Price et al., 1987). This may be a possible reason for these better correlation of Se with several major and minor biologically important elements observed in Table 3 and Figs. 2 and 3.

Bruland et al. (1991) expanded Redfield ratios (C : N : P) to trace metals based on reported trace element contents of marine plankton samples (e.g., Martin and Knauer, 1973) and recommended the ratios of

$$C : N : P : Fe : Zn : Cu, Mn, Ni, Cd = 106 : 16 : 1 : 0.005 : 0.002 : 0.0004.$$

Based on the positive correlation of major and minor elements vs. Se for most of samples (Figs. 2 and 3), the following extended Redfield (atomic) ratios were tentatively obtained for pelagic phytoplankton samples from the northern North Pacific and the Bering Sea:

$$C : N : Se : Br : I : Fe : Zn : Cr =$$
$$106 : 11 : 0.00020 : 0.03\sim0.09 : 0.003\sim0.007 : 0.05\sim0.15 : 0.036 : 0.0045.$$

The obtained ratio for Zn was 0.036 and was comparable to that by Bruland et al. (1991), 0.002, but that for Fe is one order higher than that by Bruland et al. (1991). Iron has been considered to be a growth-limiting element in high-nutrient low-chlorophyll areas in open oceans (Martin et al., 1991). More detailed studies will be needed to confirm the extended Redfield ratios of trace elements in marine phytoplankton samples and also in different areas in open oceans.

A linearity between log (C_{PL}/C_{SW}) and log (C_{PL}/C_{RW}) has been observed for marine zooplankton species (Masuzawa et al., 1988) and settling particles (Masuzawa et al., 1989) as follows (MKT plot):

$$\log (C_{PL}/C_{RW}) = p + q \log (C_{PL}/C_{SW})$$

where C_{PL} is concentration in a plankton sample, C_{SW} average seawater concentration (Nozaki, 1997) and C_{RW} average dissolved river water concentration (Martin and Meybeck, 1979) for each element. Masuzawa et al. (1989, 1994) reported that the slope value, q, increased with increasing Al (clay) content in marine settling particles. MKT plots for typical three pelagic samples and one sample from the Gulf of Alaska (Stn. 13) are shown in Fig. 4. A linearity was observed for these twelve marine phytoplankton sample with slope values ranging from 0.104 to 0.236 and relatively constant intercept values, 3.35 + 0.11 (1SD). The highest slope value, 0.236, was observed for the highest Al content at Stn. 13. Fe is plotted at the right most side for all samples (Fig. 4), as found previously, showing the highest concentration ratio of iron in plankton samples to that in mean seawater. This suggests that iron is most likely limited easily in marine environments and consistent with the iron hypothesis (Martin et al., 1991). Multi-element analysis by INNA is useful to obtain almost 14 element compositions using about 35 mg of dried samples and

Table 2. Concentration ranges of major and trace elements of marine phytoplankton samples in ppm DM.

Area	*N Pacific* Bering Sea*	*G. of Alaska**	*Coastal area off Japan***	*EN Pacific*** I (no Ti)*	*II (high Ti)*	*III (high Sr)*	*Phytoplankton*****
Stn No.	*7*	*1*	*10*	*14*	*9*	*4*	
No.	*11*	*1*	*45*	*14*	*9*	*4*	
C	*65,000-287,000*	*154,000*					*225,000*
N	*7,500-52,100*	*22,000*					*63,000-110,000*
Ca	*ND-64,000*	*14,000*	*ND*	*4,000-9,000*	*3,300-10,000*	*3,100-12,600*	*6,100*
Na	*920-3,320*	*3,190*	*790-3,820*				*6,000*
Cl	*1,500-11,600*	*12,900*	*ND-119,000*				-
Al	*950-3,400*	*8,660*	*2310-17,500*	*7-630*	*230-2,850*	*11-177*	*38-440*
Fe	*155-1,644*	*4,438*	*1,180-5,890*	*51-380*	*520-3,120*	*116-2,780*	*220-1,500*
Sr	*ND-2,268*	*155*	*ND-221*	*90-260*	*53-127*	*383-3,934*	*70-700*
Br	*230-1089*	*560*	*42-1,237*				-
I	*38-317*	*148*	*ND-176*				*270*
Se	*ND-3.35*	-	*ND-2.61*				*3.5*
V	*ND-52.6*	*38*	*ND-38.5*				*3-5*
Cr	*13.5-109*	*52*	*ND-52*				*2.2-7.5*
Co	*ND-0.50*	*1.74*	*ND-1.54*				*0.38*
Zn	*90-520*	*236*	*ND-362*	*3-54*	*16-445*	*11-703*	*20-280*
Sc	*0.017-0.29*	*1.44*	*0.40-2.43*				-

** This work* *** Masuzawa et al. (1999)* **** Martin and Knauer (1973)* ***** Bowen (1979)*

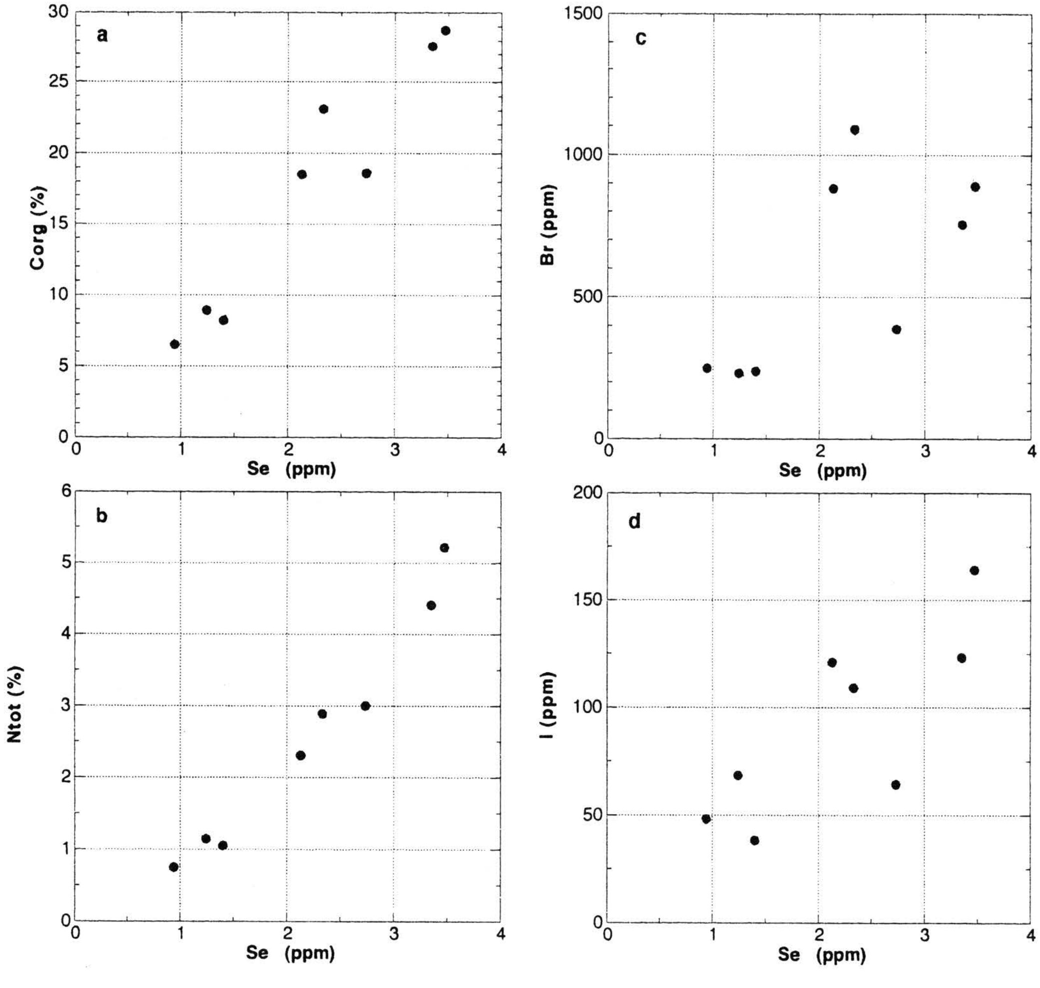

Fig. 2. Relationships of Corg *vs*. Se (a), Ntot *vs*. Se (b), Br *vs*. Se (c) and I *vs*. Se (d) in eleven phytoplankton samples collected from the northern North Pacific and the Bering Sea during the KH-97-2 Cruise.

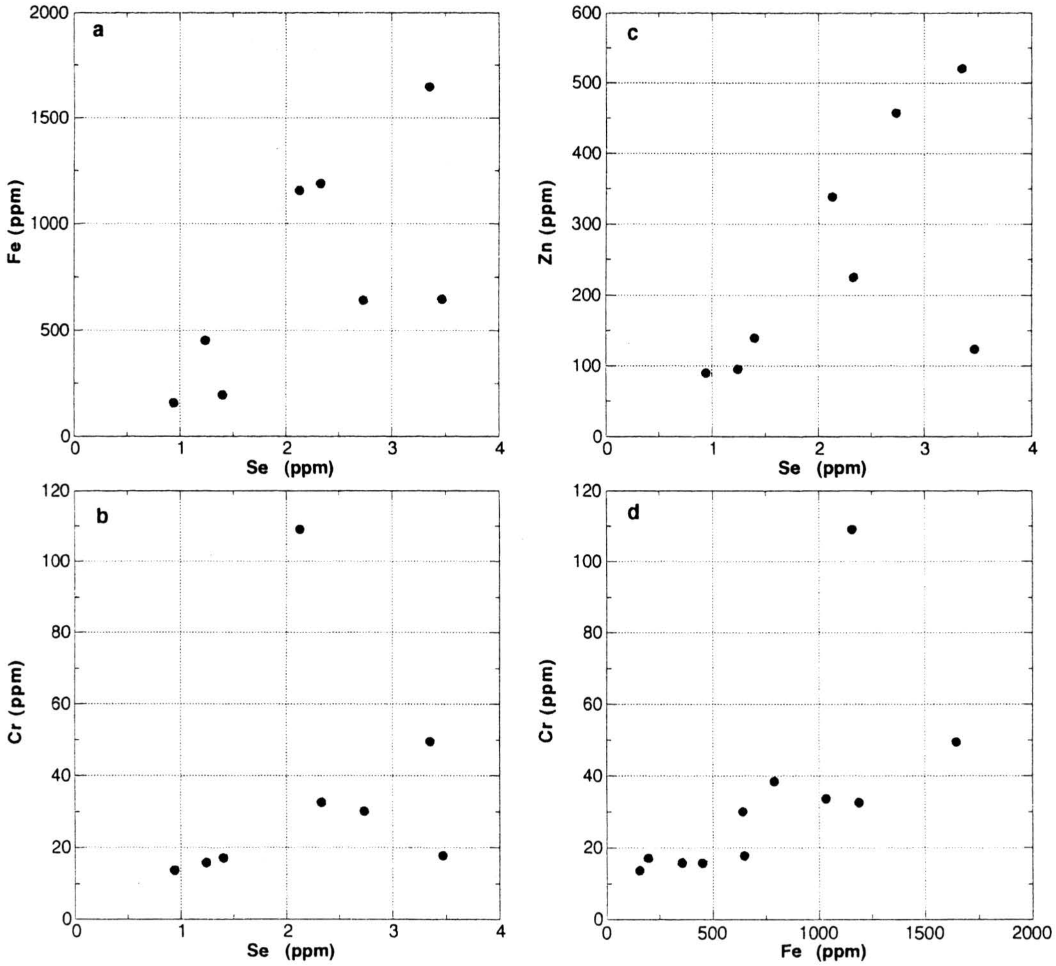

Fig. 3. Relationships of Fe *vs*. Se (a), Cr *vs*. Se (b), Zn *vs*. Se (c) and Cr *vs*. Fe (d) in eleven phytoplankton samples collected from the northern North Pacific and the Bering Sea during the KH-97-2 Cruise.

Table 3. Correlation matirix of 16 major and minor elements in 11 phytoplankton samples from the North Pacific and the Bering Sea.

	Corg	*Ntot*	*Ca*	*Na*	*Cl*	*Al*	*Fe*	*Sr*	*Br*	*I*	*Se*	*V*	*Cr*	*Co*	*Zn*
Corg															
Ntot	0.934														
Ca	0.548	0.723													
Na	-0.024	0.139	0.299												
Cl	0.228	0.338	0.483	0.575											
Al	-0.099	-0.205	-0.858	-0.408	-0.535										
Fe	0.665	0.509	0.299	-0.433	0.056	-0.289									
Sr	-0.221	-0.253	0.785	-0.457	0.231	-0.002	0.218								
Br	0.574	0.643	0.375	-0.428	-0.325	0.089	0.381	-0.310							
I	0.402	0.569	0.547	-0.370	-0.004	-0.099	0.355	0.436	0.850						
Se	0.962	0.982	0.636	-0.006	0.471	-0.577	0.669	0.714	0.666	0.798					
V	-0.147	-0.433	-0.338	-0.798	0.246	0.843	0.332	0.557	-0.144	-0.016	-0.098				
Cr	0.279	0.156	0.246	-0.450	-0.012	-0.177	0.626	-0.033	0.296	0.220	0.216	0.614			
Co	0.686	0.559	0.280	-0.300	0.171	-0.122	0.676	0.207	0.366	0.353	0.793	0.578	0.575		
Zn	0.440	0.419	0.143	-0.369	0.117	-0.246	0.742	0.275	0.288	0.370	0.606	0.002	0.526	0.683	
Sc	0.067	0.072	-0.121	0.257	0.532	-0.171	0.049	0.006	-0.170	-0.099	0.062	-0.053	-0.166	-0.329	-0.047

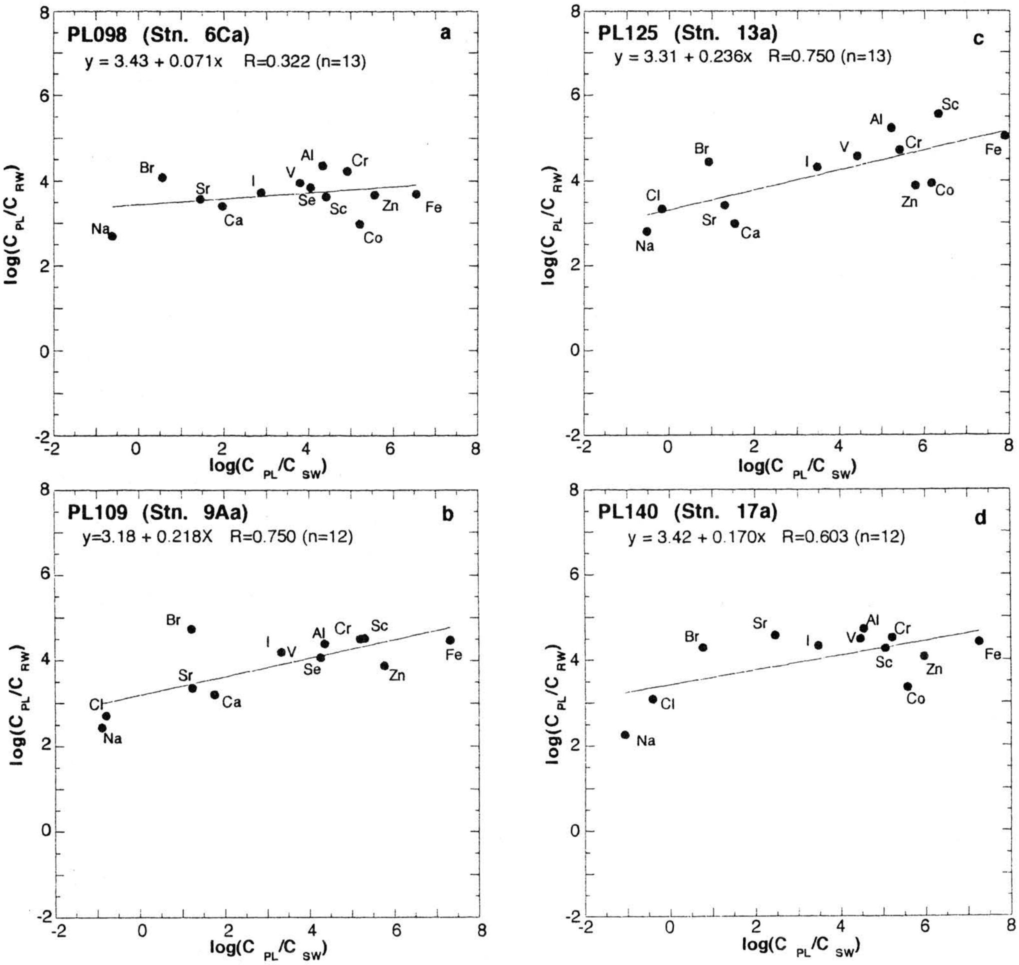

Fig. 4. Relationships between log (C_{PL}/C_{SW}) and log (C_{PL}/C_{RW}) (MKT plot) for phytoplankton samples collected at Stns. 6C (a), 9A (b), 13 (c) and 17 (d) from the northern North Pacific and the Bering Sea during the KH-97-2 Cruise.

made it possible to prepare MKT plots to understand the behaviors of trace elements with biological production in marine environments.

SUMMARY

Twelve phytoplankton samples collected from the northern North Pacific and the Bering Sea were analyzed for Corg and Ntot and 14 major and trace elements by INNA. Eleven samples showed pelagic nature with low Al contents and Se showed very high correlation coefficients with Corg and Ntot, and relatively high correlation coefficients with Br, I, Fe, Zn and Cr. Extended Redfield ratios were obtained tentatively based on the positive correlation with Se for most of samples as follows:

C : N : Se : Br : I : Fe : Zn : Cr = 106 : 11 : 0.00020 : 0.03~0.09 : 0.003~0.007 : 0.05~0.15 : 0.036 : 0.0045.

A linearity between log (C_{PL}/C_{SW}) and log (C_{PL}/C_{RW}) was observed for all samples with slope values ranging from 0.104 to 0.236 and relatively constant intercept values, 3.35 + 0.11 (1SD). The highest slope value, 0.236, was observed for the highest Al content at Stn.13. More detailed studies will be needed to confirm the extended Redfield ratios and also the diversity of slope and intercept values of MKT plots of trace elements in marine phytoplankton samples from different areas in open oceans.

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