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Journal of Asian Earth Sciences 29 (2007) 685–697
Journal of Asian Earth Sciences
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Geochemistry of surface sediments in the southwestern East/Japan Sea

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Received 2 August 2005; received in revised form 31 March 2006; accepted 7 April 2006

Abstract

We analyzed 77 surface sediment samples collected in the southwestern East/Japan Sea from the Korea Strait through the Ulleung Basin and the Korea Plateau for grain size, calcium carbonate, organic carbon, and major (Na, Mg, Al, Fe, K, Ca, and Ti) and trace elements (P, Mn, Sr, Li, Sc, V, Cr, Co, Ni, Zn, Cu, and Pb).

The chemical composition of the surface sediments was found to be highly variable spatially. Cluster analysis of surface sediment chemical compositions indicated five major geochemical sedimentary environments: basin, lower slope, coast and upper slope, inner shelf, and outer shelf. Continental-shelf sediments were rich in shell fragments and had relict and coarse-grained characteristics. Recent fine-grained sediments were only distributed in coastal, slope, and basin areas. Concentrations of Al, K, Ca, Ti, Cr, and Sc were highest in the coastal and upper slope areas and decreased with water depth. Elemental ratios using major and trace elements indicated that coastal and upper slope detrital sediments were mixtures of sediments derived from the Changjiang (Yangtze) and Nakdong Rivers. Although the concentrations of organic carbon, P, Mn, V, Co, Ni, Cu, and Pb increased with water depth, their distribution patterns indicated authigenic (V, Cu, and Pb) and diagenetic (Fe, P, Mn, Co, and Ni) origins. The distribution pattern with water depth suggested that the chemical composition of surface sediment was determined by sedimentologic and geochemical processes, such as the supply of detrital and biogenic materials, and authigenic and post-depositional diagenetic processes in sediments.

Keywords: East/Japan Sea; Sediment; Elements; Chemical composition

1. Introduction

Marine sediments are composed of terrestrial materials transported by rivers, atmospherically driven dusts, and particles formed in situ biologically or inorganically (Chester, 1990). Particulate materials experience many processes, including interaction with seawater, during transport from their source areas to depositional sites. Therefore, the chemical composition of marine sediments reflects the particulate material source, the reactions between particulate and dissolved phases during transport and sedimentation, and the post-depositional changes resulting from diagenetic reactions in the sediments (Calvert and Pedersen, 1993). In nearshore sediments, chemical composition is mainly controlled by sedimentologic parameters such as grain size, mineralogical composition, and calcium carbonate and organic carbon contents (Calvert, 1976; Chester and Aston, 1976; Cho et al., 1999). In deep-sea sediments, chemical composition is determined by such factors as the proximity to continents, reactivity between particulate and dissolved components within the oceanic water column, biological activities, water depth, and deep water circulation patterns (Chester, 1990). The sedimentation rate and physicochemical properties, e.g., redox state, of bottom water overlying sediments also influence the chemical composition of sediments (Piper and Isaacs, 1996; Morford and Emerson, 1999).

The East/Japan Sea is a marginal sea in the northwestern Pacific Ocean. Despite its small spatial dimensions,

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1367-9120/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jseaes.2006.04.009

the sea has many characteristics of the open ocean, such as the existence of a subpolar front, warm and saline northward currents, deep water formation via convective and brine rejection processes, and active biological processes (Seung, 1992; Kim et al., 2002; Min and Warner, 2005). Topographically, shallow and deep seas coexist in the East/Japan Sea, where nearshore and deep-sea sedimentation occurs. Therefore, it is expected that East/Japan Sea sediments have high spatial variation in chemical composition. However, there have been few reports regarding the chemical composition of these sediments, except for nearshore surface sediments close to the Korean Peninsula (Lee et al., 1989) and deep core sediments from one or two sites in the East/Japan Sea (Masuzawa and Kitano, 1977; Kato et al., 1983). Therefore, the present study investigated the chemical composition of surface sediments in the southwestern East/Japan Sea, where shallow and deep seas coexist, based on the spatial distribution of individual elements and statistical analyses of the chemical data.

2. Environmental setting

The East/Japan Sea is a semi-enclosed marginal sea consisting of three major basins deeper than 2000 m (the Japan, Yamato, and Ulleung basins) that are separated by the Korea Plateau, the Oki Bank, and the Yamato Rise (Fig. 1a). The East/Japan Sea is connected to the North Pacific, the Sea of Okhotsk, and the East China Sea by the Korea, Tartarsky, Tsugaru, and Soya Straits, respectively, which have water depths less than 120 m.

This study examined the southwestern part of the East/Japan Sea from 128°45′E to 133°00′E and 33°30′N to 38°00′N. The study area is topographically differentiated into northern and southern parts by a boundary at approximately 35.5°N (Fig. 1b). The southern part is characterized by shallow water depths of less than 200 m (120 m on average) and is divided further into an inner continental-shelf covered with recent sediments and an outer continental-shelf covered with relict sediments (Park, 1985; Lee et al., 1989; Choi and Park, 1993). The relict sediments are coarse-grained sediments with high calcium carbonate content and were deposited during the last glacial period when sea level was at least 100 m below its present level. The high calcium carbonate content is attributable to shell fragments (Choi, 1989; Lee et al., 1989; Choi and Park, 1993).

The northern part of the study area is characterized by rapid changes from a narrow continental-shelf and slope to a relatively large basin-plain, i.e., the Ulleung Basin with depths exceeding 2000 m. The Ulleung Basin is a deep, bowl-shaped back-arc basin. The basin borders the steep continental slope of the Korean Peninsula and the Korea Plateau to the west and north. To the south and east, the Ulleung Basin borders the Japanese Arc and the Oki Bank, characterized by a gentle slope and broad shelf. To the northeast of the basin, the Ulleung Interplain Gap (UIG) is located between the islands of Ulleung and Dok. The UIG is approximately 3000 m deep and 70 km wide and connects the Ulleung Basin to the Japan Basin (Lee et al., 1996; Chough et al., 2000).

The Tsushima Warm Current (TWC) enters the East/Japan Sea through the Korea Strait and flows out to the North Pacific through the Tsugaru and Soya straits. When entering the East/Japan Sea, the TWC splits into two distinct branches: the Nearshore Branch (NB) along the Japanese coast and the East Korean Warm Current (EKWC) along the Korean coast. The EKWC separates from the coast, typically at 37–38°N where it meets the North Korean Cold Current (NKCC), and forms the Subpolar Jet that meanders eastward across the East/Japan Sea and then flows out through the Tsugaru Strait to the North Pacific. In the cold water region, the NKCC and the Liman Current flow to the south along the western boundary of the Japan/East Sea (Uda, 1934; Seung, 1992; Mooers et al., 2005).

Thermohaline circulation of the East/Japan Sea initiates after the formation of deep water by wintertime convection and brine rejection to the south offshore from Vladivostok. Part of the water spreads into the Japan Basin north of 40°N, and another part is transported southward to the Ulleung Basin and spreads into the Yamato Basin through the UIG (Kim and Seung, 1999; Senjyu et al., 2005). Deep and fast circulation results in a well-mixed water mass, with the cold (<1 °C), oxygen-rich (>210 μM), and vertically homogeneous deep water below the thermocline depth in the East/Japan Sea; this water has been regarded as a single water mass called the East Sea (or Japan Sea) Proper Water (Uda, 1934). However detailed analyses of temperature–salinity (T–S) structures have revealed three water masses: central water (CW), deep water (DW), and bottom water (BW) (Kim et al., 1991, 1996). The deep water ventilation time has been reported to be 80–100 years (Kim and Kim, 1996; Kumamoto et al., 1998).

3. Materials and methods

3.1. Samples

Surface sediments were collected during two cruises in May 1993 and October 1995 aboard the R/V Eardo using a Van Veen grab sampler (Fig. 1b). The 1993 cruise covered the southern part of the study area (33°30′–36°00′N), and the 1995 cruise covered the northern part (36°30′–38°00′N). Sediments of the upper 2 cm were subsampled with a plastic spoon and stored in clean vinyl bags to prevent possible contamination. The sediments were oven-dried at 60 °C (the 1995 samples were freeze-dried at −70 °C). After drying completely, the sediment samples were powdered in an agate mortar with a pestle for further chemical analysis.

3.2. Analytical procedures

The grain size of sediments was determined using dry sieving and sedimentation methods (Carver, 1971). The $CaCO_3$ content was determined gasometrically (Gross,

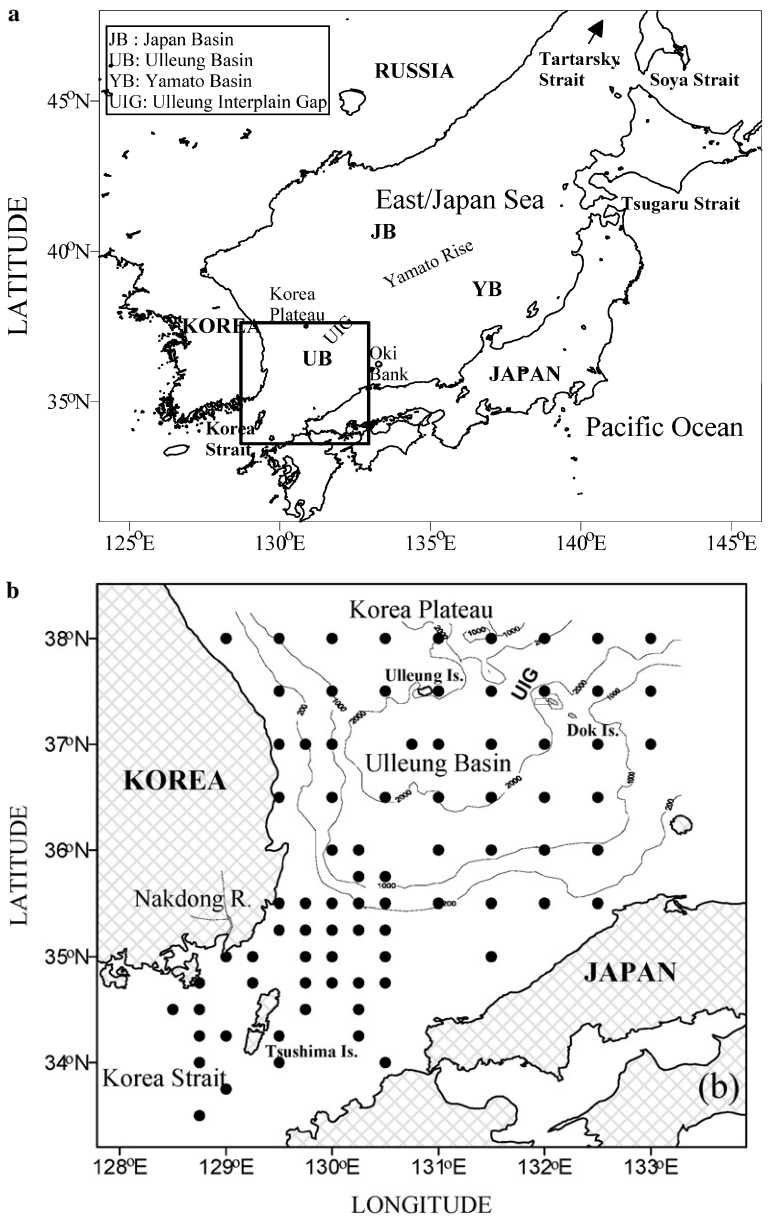

Fig. 1. East/Japan Sea (a) and sampling sites of surface sediments in the southwestern East/Japan Sea (b).

1971). The accuracy and precision of the analytical method, checked against certified reference material BCSS-1 from the National Research Council of Canada (NRCC), were within ±5%. The organic carbon content was quantified using the wet oxidation method with potassium dichromate as an oxidant. The accuracy and precision of this method were within ±7%. To determine the concentrations of major elements (Na, Mg, Al, Fe, K, Ca, and Ti) and trace elements (P, Mn, Sr, Li, Sc, V, Cr, Co, Ni, Zn, Cu, and Pb), the powdered samples were digested with a mixture of HF, HNO_3, and $HClO_4$ at a ratio of 4:4:1 in low-pressure Teflon digestion vessels and heated on a ceramic hot plate at 180 °C until the mixed solutions were completely dried. Then, 1% HNO_3 was added to the vessels, and elemental concentrations were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES; model ICPS-1000III, Shimadzu). The Pb concentration was measured using inductively coupled plasma mass spectrometry (ICP-MS; model PQ3, VG Elemental Ltd.). For reliable analytical results, standard sediment reference materials, i.e., MAG-1 (U.S. Geological Survey) and BCSS-1 (NRCC), were analyzed together with the sediment samples. The accuracy and precision of our analytical techniques were within ±10%.

4. Results

4.1. Spatial distribution of sedimentological and geochemical parameters in sediments

The mean grain size of the surface sediments showed wide spatial variation, ranging from 0.94 to 10.33 ϕ [where,

$\phi = -\log_2$ (diameter in mm)]. The spatial distribution of the mean grain size resembled the isobathymetric lines of the study area (Fig. 2). Fine-grained sediments (mean grain size not less than 8 ϕ) were distributed over the northern part of the study area (north of 35.5°N), the Ulleung Basin, and the continental slopes surrounding the Ulleung Basin. The finest-grained sediments were found on the lower continental slope areas bordering the southern Ulleung Basin. Fine-grained sediments were also found along coastal areas from Pusan to Pohang, Korea. Coarse-grained sediments with mean grain sizes less than 4 ϕ were found in the southern part of the study area, particularly in the Korea Strait and the Japanese-side continental shelves.

The distribution of calcium carbonate also showed great spatial variation; low concentrations (<1%) were found in the northern deep areas and high concentrations (>30%) were identified in the southern part. Concentrations of calcium carbonate were usually high in coastal areas and low in deep seas, but the highest concentration of calcium carbonate in this study was found on the outer continental shelves in the Korea Strait at water depths of at least 100 m. Most carbonates in these areas consisted of deeply or moderately weathered shell fragments, indicating that the high carbonate content sediments in these areas are relict sediments that were deposited during the last glacial period (Choi, 1989).

The distribution of organic carbon concentrations was similar to that of mean grain size. High organic carbon concentrations (>1.5%) were found in deep northern parts of the study area. The sediments of the Korea Plateau and the UIG contained very high concentrations of organic carbon (>2.5%). Meanwhile the sediments in the southern part, except for coastal areas, had low organic carbon concentrations (<1%).

The highest concentrations of Al, Mg, and K were found on the upper continental slope bordering the southern Ulleung Basin at approximately 36°N (Fig. 2). The lowest concentrations of K, Mg, and Al were identified on the outer continental shelves over the Korea Strait and near Tsushima Island where the most coarse-grained sediments were distributed. The concentrations of K, Mg, and Al were not as high in sediments of the central to northern Ulleung Basin where the finest-grained sediments were deposited. Concentrations of Na were high in the northern part and low in the southern part of the study area. The highest Na concentrations were distributed on the Korea Plateau and the areas near Ulleung Island.

The distribution of Fe concentrations resembled the isobathymetry of the study area. Fe-rich sediments occurred along the Korean coasts and in areas between the UIG and the continental slope bordering the southern and southwestern Ulleung Basin. Meanwhile, low

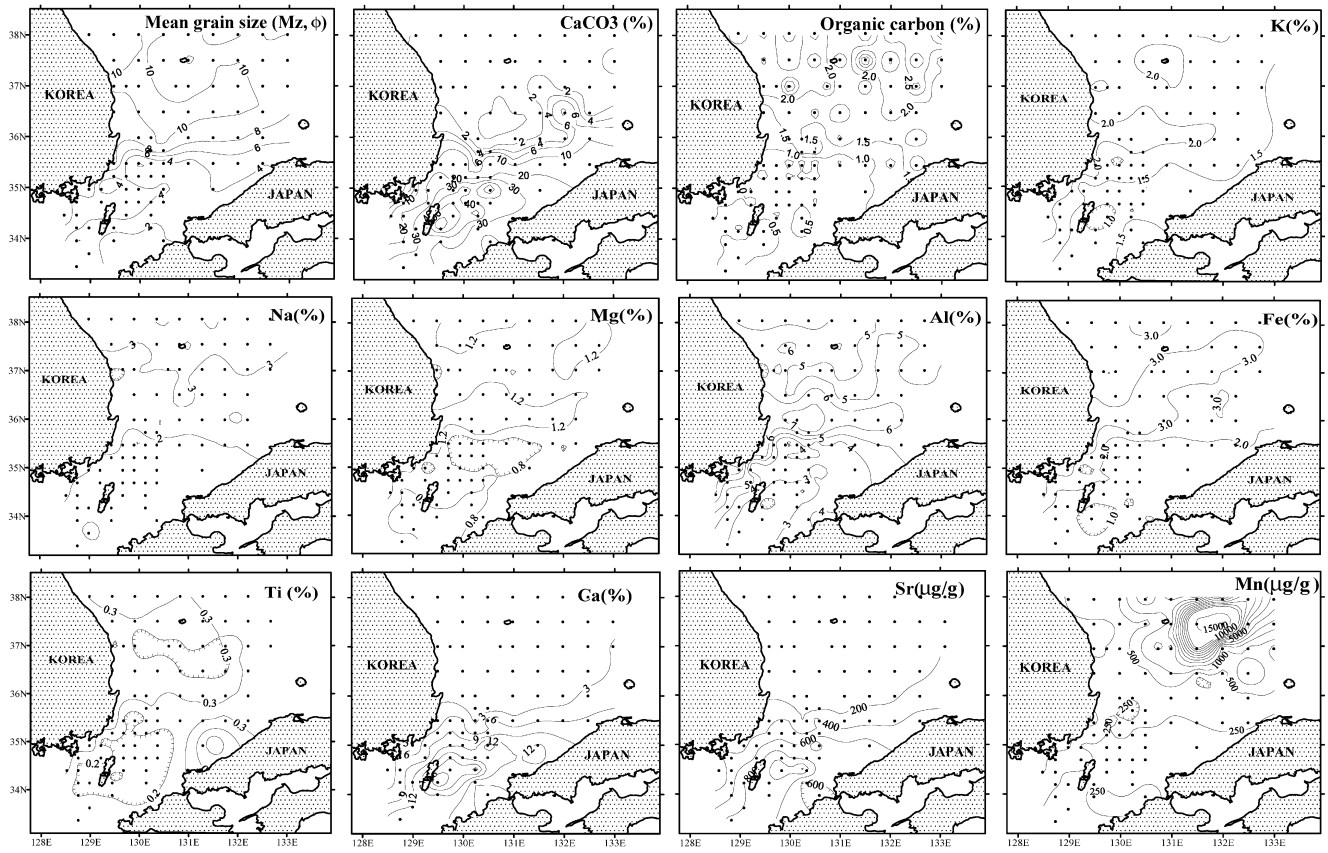

Fig. 2. Spatial distribution of mean grain size (ϕ), calcium carbonate (%), organic carbon (%), major (%), and trace (μg/g) elements in the surface sediments.

concentrations of Fe were distributed on the outer and inner continental shelves over the Korea Strait.

The distribution of Ca and Sr was almost the same as that of carbonates; high concentrations were found in the Korea Strait and near Tsushima Island, while concentrations were low in the northern part of the study area. The high concentrations of Ca and Sr in the southern part were caused by widespread shell fragments.

The spatial distributions of Cr and Sc were similar to that of Al; high concentrations were found along the Korean coasts and on the continental slope bordering the southern Ulleung Basin at 36°N (Fig. 3). As with the distribution of Al, the concentrations of Cr and Sc were lower in the UIG and the central Ulleung Basin than in the continental slope areas near 36°N. These findings reflect the dilution of detrital materials by biogenic materials in these areas.

The concentrations of V, Zn, Cu, and Pb increased gradually from the Korea Strait to the eastern margin of the Ulleung Basin. The lowest concentrations of these elements were found on the outer continental shelf areas in the Korea Strait.

The concentrations of Mn, Co, and Ni were fairly high along the Korean coasts (Figs. 2 and 3). High concentrations of Mn, Co, and Ni were also found between the Ulleung Basin and the UIG. The concentrations of these elements were distributed concentrically around the UIG; the concentrations of these elements decreased rapidly with distance from the center of the concentric circle. The highest relative concentration of Mn, in the center of the concentric circle, was greater than 2%. Maximum concentrations of Co and Ni were 44 and 93 μg/g, respectively.

High concentrations of P were found in sediments around Tsushima Island and in the eastern Korea Strait, through which the Tsushima Warm Current (TWC) enters the East/Japan Sea. High concentrations of P not less than 600 μg/g were also found along the Japanese coasts. The highest P concentrations were found in the northern part of the study area. The sediments of the Ulleung Basin and the UIG contained more than 900 μg/g concentrically around the UIG.

Sedimentation rates for the study area have been determined using $^{210}Pb_{ex}$ and ^{137}Cs methods and shown to range

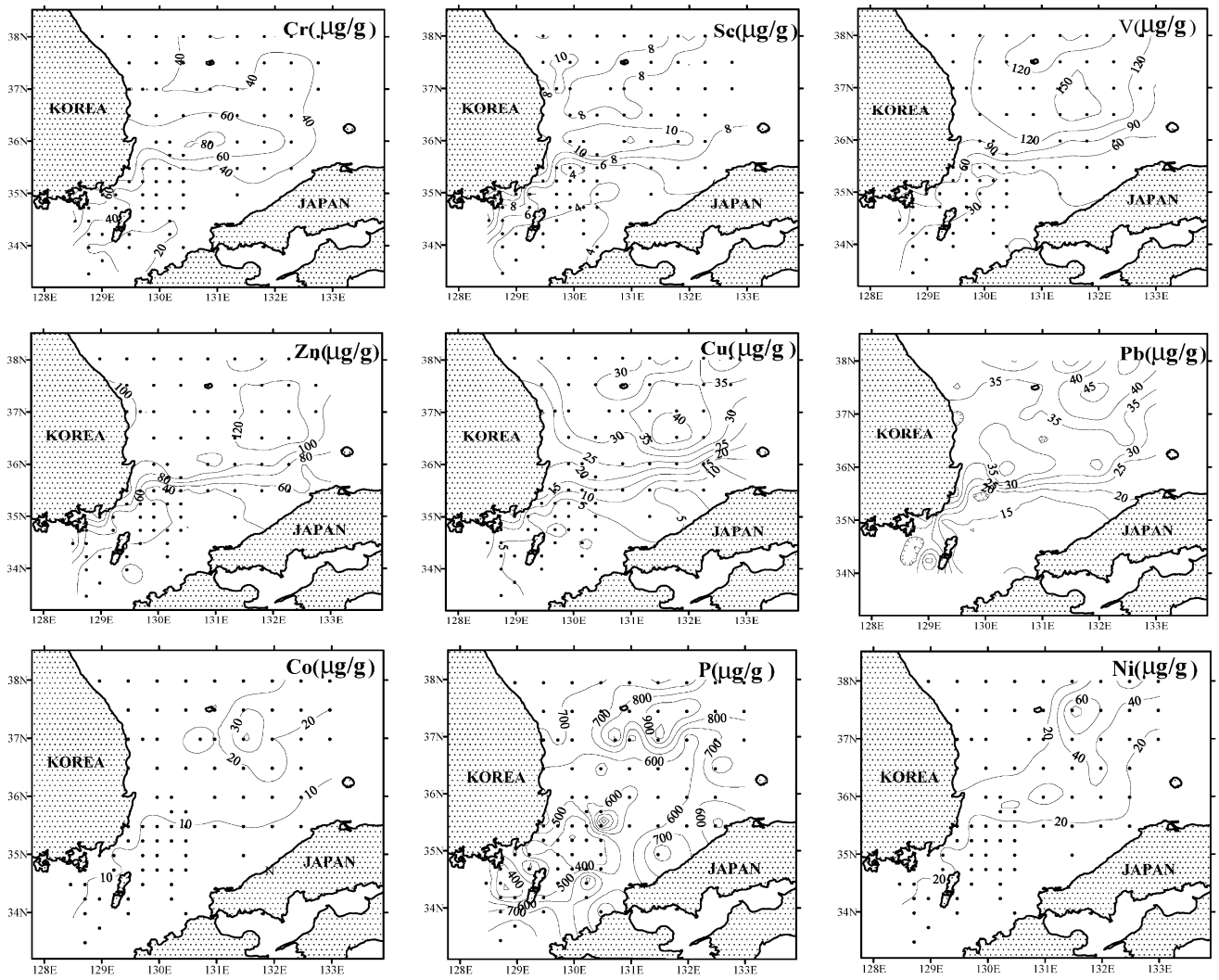

Fig. 3. Spatial distribution of trace elements (μg/g) in the surface sediments.

from 0.02 to 0.6 cm yr^{-1} (KBSI, 1993; Hong et al., 1997; Cha et al., 2005). The lowest sedimentation rates were found in the Ulleung basin area. The highest rates were found in continental-shelf areas near Kampo. Moving toward the Ulleung Basin from Kampo, sedimentation rates decreased rapidly in a radial pattern (Fig. 4). Sedimentation rates were related to water depth, and their relationship can be described by the following exponential equation, based on the data reported in the above three studies:

$$S = 0.674 \times e^{-0.00128D} (r^2 = 0.70, n = 22), \quad (1)$$

where S is the sedimentation rate (cm yr^{-1}), and D is the water depth (m). The southwestern side of the study area, however, showed distinctly higher sedimentation rates.

5. Discussion

5.1. Classification of geochemical sedimentary environments by cluster analysis

Cluster analysis is a multivariate procedure for detecting natural groupings in data. It serves, therefore, as a useful tool for classifying a set of objects into subgroups, even when the number and types of subgroups are unknown. The southwestern East/Japan Sea is characterized by great topographic variation. The TWC passes by the southern part of the study area through the Korea Strait, and a branch of deep cold water that forms off Vladivostok enters the Ulleung Basin through the UIG. Thus, it is anticipated that the physicochemical conditions of the bottom water overlying the sediments vary greatly with area and may have a significant influence on the composition of surface sediments (Morford and Emerson, 1999). Moreover, there are widespread relict sediments on the outer continental shelves between Korea and Japan. The different physical, chemical, and sedimentological conditions are reflected in the spatial distributions of sediment compositions in the study area. Therefore, we carried out a hierarchical cluster analysis to determine the number of true groups into which the study area should be divided. Ward's minimum variance method and the Euclidean distance were used (Danielsson et al., 1999). The dendrogram from the hierarchical cluster analysis showed that the study area could be reasonably divided into five zones. Knowing the number of true groups of sampling sites in the study area, we performed K-means clustering for more quantitative grouping. As a result of cluster analyses, surface sediments in the study area were classified into five sediment types: basin, lower slope, coastal and upper slope, inner continental-shelf, and outer continental-shelf sediments (Fig. 5).

Table 1 summarizes the elemental composition of the sediments in the five geochemical sedimentary environments as well as those of typical nearshore and deep-sea fine-grained sediments, and sediments of the seas surrounding the Korean Peninsula (the Yellow and South Seas).

5.1.1. Basin sediments (Type I)

Basin sediments covered the central and northeastern part of the Ulleung Basin to the UIG at depths greater than 2000 m (Fig. 5). Sedimentation rates for basin sediments were lower (less than 0.1 cm yr^{-1}) than rates for other types of sediments. Type I sediments were very fine-grained and characterized by high clay and organic carbon contents and

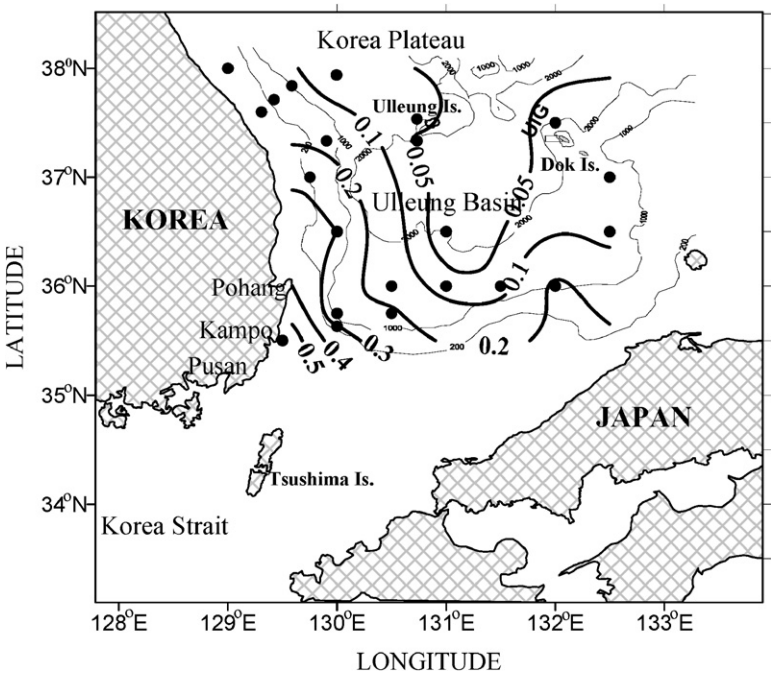

Fig. 4. Contour of sedimentation rates (cm yr^{-1}) in the study area estimated from $^{210}Pb_{ex}$ and ^{137}Cs dating methods. Data for core sites and sedimentation rates were from KBSI (1993); Hong et al. (1997); and Cha et al. (2005).

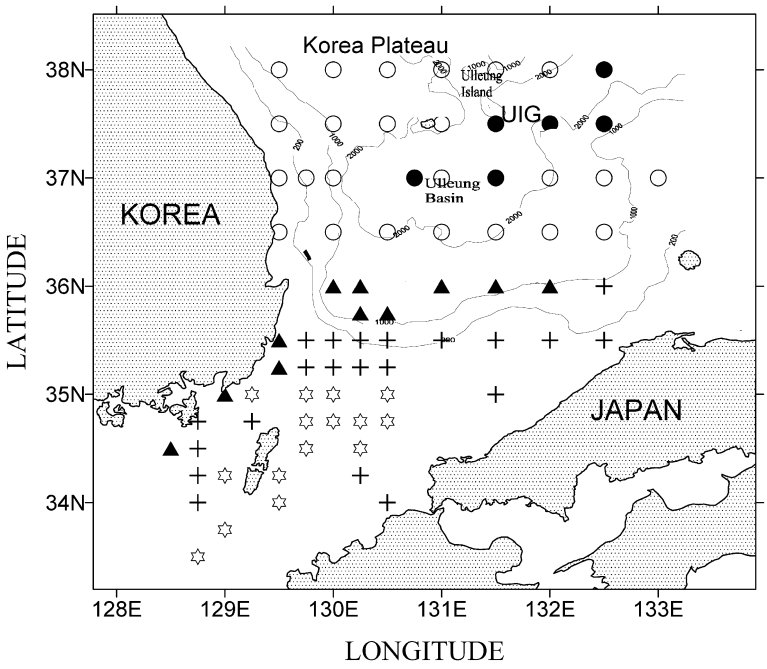

Fig. 5. Distribution of classified surface sediment types in the southwestern East/Japan Sea. Type I: Basin sediments (●). Type II: Lower slope sediments (○). Type III: Coastal and upper slope sediments (▲). Type IV: Inner continental-shelf sediments (+). Type V: Outer continental-shelf sediments (☆).

Table 1
Elemental composition of the sediments around the Korean Peninsula

Element	Unit	Yellow Sea of Korea[a]	South Sea of Korea[a]	Near-shore mud[b]	Deep-sea clay[b]	Type I	Type II	Type III	Type IV	Type V
Depth	(m)					2165	1310	773	210	120
Organic C	(%)	0.3	0.5			2.7	2.0	1.7	0.7	0.4
$CaCO_3$	(%)	0.8	18.9			0.9	1.1	5.4	15	42
Clay	(%)					82	76	67	11	9
Mz	(ϕ)					9.8	9.4	8.5	3.7	3.6
Na	(%)	0.77	0.83	4	4	3.2	3.0	2.7	1.6	1.4
Mg	(%)	0.59	1.04	2.1	1.8	1.2	1.1	1.4	0.7	0.8
Al	(%)	5.75	5.24	8.4	9.5	4.8	5.3	7.2	4.3	2.7
Fe	(%)	2.17	2.55	6.5	6	3.2	2.8	3.3	1.7	1.4
K	(%)	2.87	2.04	2.5	2.8	1.7	1.9	2.2	1.7	1.2
Ca	(%)	0.72	8.1	2.9	1	0.4	0.8	2.2	6.8	15.2
Ti	(%)	0.25	0.23	0.5	0.57	0.28	0.30	0.33	0.24	0.16
P	(μg/g)	349	617	550	1400	980	650	580	520	490
Mn	(μg/g)	360	420	850	6000	11000	810	410	280	210
Sr	(μg/g)	178	509	160	250	100	100	180	430	830
Sc	(μg/g)			12	20	8.6	8.5	11.5	5.2	3.6
V	(μg/g)	45	58	145	150	140	120	97	36	24
Cr	(μg/g)	37	53	60	100	39	44	77	37	27
Co	(μg/g)	7	12	13	55	30	15	17	8.4	6.7
Ni	(μg/g)	17	25	35	200	54	14	39	14	10
Zn	(μg/g)	40	61	92	120	120	110	110	40	40
Cu	(μg/g)	9	11	56	200	38	31	20	5.4	3.9
Pb	(μg/g)			22	200	43	34	35	18	16
Fe/Al		0.38	0.49	0.77	0.63	0.68	0.54	0.46	0.40	0.53

Type I: Basin sediments.
Type II: Lower slope sediments.
Type III: Coastal and upper slope sediments.
Type IV: Inner continental-shelf sediments.
Type V: Outer continental-shelf sediments.
[a] Cho et al. (1999).
[b] Chester (1990).

low Al concentrations, even though Al is generally abundant in fine-grained detrital sediments (Calvert, 1976). This indicated a low supply of detrital materials and a high supply of biogenic materials to these areas. Type I sediments had very high concentrations of Mn, P, Co, and Ni and high Fe/Al ratios (Table 1, Fig. 3). Pb and V were also enriched in these sediments (Fig. 3). The very high concentration of Mn and high Fe/Al ratios indicated a highly oxidized surface layer in Type I sediments.

5.1.2. Lower slope sediments (Type II)

Type II sediments covered the Korea Plateau and the continental slope areas bordering the Ulleung Basin to the west, south, and east. However, the upper part of the continental slope south of the Ulleung Basin did not have Type II sediments. Sedimentation rates of Type II sediments were relatively low, except near the Korean Peninsula (Fig. 4). Type II sediments were fine-grained and characterized by high clay, high organic carbon, and low Al contents. As with Type I sediments, this trend is attributed to a low supply rate of detrital material. Mn, P, Zn, Cu, and Pb levels were also enriched in Type II sediments, but less than in Type I sediments. Based on the chemical and sedimentologic characteristics, Type II sediments were transitional between Type I and Type III sediments.

5.1.3. Coastal and upper slope sediments (Type III)

Type III sediments covered the Korean-side coastal areas from Pusan to Pohang and the upper part of the continental slope bordering the Ulleung Basin to the south. Sedimentation rates were very high in these areas (Fig. 4). Type III sediments were fine-grained and characterized by high Al, Fe, K, Sc, and Cr concentrations. These elements are abundant in detrital minerals, and the concentrations of these elements were comparable to those in typical nearshore mud deposits (Table 1). The Al, Fe, Cr, V, Co, Ni, Zn, and Cu concentrations in the study area were higher than those in the Yellow and South Seas around the Korean Peninsula. This may be a result of the granulometric effects: type III sediments were much more fine-grained than sediments from the Yellow and South Seas.

5.1.4. Inner continental-shelf sediments (Type IV)

Type IV sediments covered the inner continental-shelf areas between Korea and Japan (Fig. 4), excluding the areas around Tsushima Island. The chemical composition of Type IV sediments, with the exception of Mg that was abundant both in fine-grained sediments and carbonate sands, was transitional between Type III and Type V sediments: very coarse-grained, fairly high $CaCO_3$, Ca, and Sr contents, and a very low Al concentration. Most sites classified as having Type IV sediments had water depths shallower than 150 m and were beaches or underwater areas during the last glacial period when sea level was approximately 100 m lower than at present. As post-glacial sea level rise changed these areas into the present marine environment, recent sediments covered the relict sediments. Thus, Type IV sediments consisted of sandy relict sediments and muddy recent sediments. Based on $CaCO_3$ and detrital components, the chemical composition of these sediments was similar to that of sediments from the South Sea of Korea (Table 1).

5.1.5. Outer continental-shelf sediments (Type V)

Type V sediments covered the outer continental-shelf and shelf break areas around Tsushima Island, sites that were shallower than 100 m in water depth. Type V sediments were very coarse-grained and contained numerous shell fragments, leading to high calcium carbonate (>40%), Ca and Sr concentrations. Concentrations of Al, Zn, Cr, and Sc were very low, because these elements are mainly associated with fine-grained detrital sediments. The chemical and granulometric compositions indicated that Type V sediments were relict sediments that were deposited in coastal areas during the glacial age and remained intact during the subsequent period of rapid sea level rise.

5.2. Characteristics of recent fine-grained coastal sediments

The chemical composition of sediment is determined by its sources, particle-water interactions during transport and deposition, and post-depositional diagenesis (Calvert and Pedersen, 1993). Anthropogenic materials may also influence the chemical composition of sediments. In the case of nearshore sediments, the chemical composition may vary depending on the mineralogy, inorganic and organic carbon contents, and grain size variations of the sediments (Calvert, 1976; Chester and Aston, 1976; Chester, 1990; Cho et al., 1999). Sedimentation rates, bottom water chemistry, and the depth of the redox interface in sediments also affect sediment chemical composition (Bodur and Ergin, 1994; Morford and Emerson, 1999). In the case of deep-sea sediments, the proximity to sources of detrital materials greatly affects sediment composition.

Before evaluating the processes responsible for the spatial variation in chemical composition of coastal to basin sediments from the East/Japan Sea, we characterized the nature of coastal sediments by comparing concentrations and metal/Al ratios with possible source-related sediments. Table 2 lists the metal/Al ratios of coastal sediments from the East/Japan Sea and those of possible source-related sediments. In nearshore detrital sediments, the metal/Al ratio varied with sediment origin for sediments that did not undergo post-depositional diagenesis and compositional mixing in the sea. The ratios of Mn, Sr, Cu, Pb, and P to Al varied greatly in the study area [Table 2; % relative standard deviation (%RSD) > 10], possibly because of mixing with calcium carbonate (Sr), pollutants (Cu, Pb), and organic matter (P) and post-depositional diagenesis (Mn). Because other metal/Al ratios were relatively constant in the study area and intermediate among those of possible source sediments, coastal sediments in the study area are

Table 2
Metal/Al ratios in Type III sediments and possible source-related sediments

		Type III Coastal & Upper slope sediment			Yellow Sea of Korea[a]	South Sea of Korea[a]	Changjiang R. SPM[b]	Nakdong R. SPM[c]
		Mean ($n = 10$)	stdev	%RSD				
Mg/Al	(%/%)	0.20	0.01	7	0.10	0.20	0.21	0.11
Fe/Al	(%/%)	0.46	0.01	3	0.38	0.49	0.62	0.46
K/Al	(%/%)	0.30	0.02	7	0.50	0.39	0.27	0.22
Ti/Al	(%/%)	0.047	0.003	5	0.043	0.044	0.080	0.050
P/Al	(μg/g/%)	79.5	8.2	12	61	118	196	96
Mn/Al	(μg/g/%)	57	19	32	63	80	138	143
Sr/Al	(μg/g/%)	27.0	14.0	53	31	97	12	16
Sc/Al	(μg/g/%)	1.6	0.1	6				1.30
V/Al	(μg/g/%)	12.9	1.0	8	7.8	11.1	16.9	8.9
Cr/Al	(μg/g/%)	10.4	0.7	7	6.4	10.1	12.1[d]	5.7
Co/Al	(μg/g/%)	2.3	0.2	7	1.2	2.3	2.2	1.5
Ni/Al	(μg/g/%)	5.2	0.4	7	3.0	4.8	7.2[e]	2.9
Zn/Al	(μg/g/%)	14.8	1.0	7	7.0	11.6	17.0	15.5
Cu/Al	(μg/g/%)	2.7	0.5	20	1.6	2.1	7.2	3.4
Pb/Al	(μg/g/%)	4.8	0.8	16			5.1	4.5

[a] Cho et al., 1999.
[b] Gaillardet et al., 1999.
[c] Choi and Cho, 2001.
[d] Huang et al., 1992.
[e] Zhang, 1999.

considered to be well-mixed deposits derived from several surrounding source materials.

Combined metal ratios and isotopic compositions have been used to identify the origin of nearshore sediments in the seas surrounding the Korean Peninsula, especially for the Yellow Sea (Yang et al., 2003, references therein). Metal ratios with low variability (%RSD < 10) were selected and combined as two variables: one for major elements and the other for trace elements. Using possible source-related sediments, coastal and upper slope sediments were examined based on these two variables (Fig. 6). As shown in Fig. 6, three end-members were identified: the Changjiang (Yangtze) River, Nakdong River, and Yellow Sea sediments. Coastal and upper slope sediments were also along the line between the Changjiang River and the Nakdong River. South Sea sediments fell below the line connecting the Changjiang River and Yellow Sea sediments. This distribution indicates that coastal and upper slope detrital sediments are mixtures of sediments borne from the Changjiang and Nakdong Rivers, while the South Sea sediments are mixtures of materials transported from the Yellow Sea and the Changjiang River. These mixing relationships seem reasonable, because the Changjiang River may affect the East/Japan Sea as well as the South Sea in terms of freshwater and sediments. Furthermore, the Nakdong River is very close to coastal areas of the study area and is located at the southernmost part of the East/Japan Sea, which enables the direct input of sediments to the coastal area. However, in the mixing diagram (Fig. 6), the closest point to the Nakdong River end-member was collected at the site closest to the Nakdong River (Fig. 5). If a two end-members mixing equation was

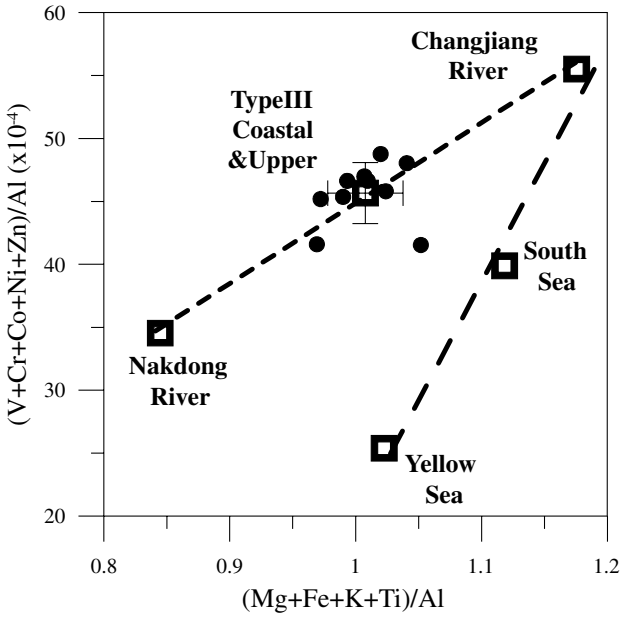

Fig. 6. The mixing diagram showing the provenance of Type III coastal and upper slope sediments based on (Mg + Fe + K + Ti)/Al and (V + Cr + Co + Ni + Zn)/Al ratios. Metals with relatively low variable metal/Al ratios (%RSD < 10) in Type III sediments were selected. Possible mixing lines were also drawn as dotted lines.

applied to that sample to obtain the quantitative estimate for its origin, the proportion of materials from the Nakdong River would be estimated as only two-thirds, a questionable result given the proximity of the site to the Nakdong River. Therefore, this mixing diagram should be considered tentative, because the chemical composition of each end-member has some variability, and the mixing

diagram does not quantitatively estimate the proportion of source materials. Nevertheless, based on geochemical tools using major and trace elements, the origin of coastal and upper slope sediments can be identified qualitatively as mixtures of materials derived from the Nakdong and Changjiang Rivers.

5.3. Elemental distributions in fine-grained recent sediments from nearshore to deep sea

The study area sediments were composed of recent fine-grained sediments in the northern part and relict or mixed relict and recent sediments in the southern part. The recent fine-grained sediments were widely distributed from the coastal areas through the continental-shelf, continental slope, and deep basin. Three characteristic environments were classified based on elemental and environmental factors: coastal and upper slope sediments, lower slope sediments, and basin sediments. In the above discussion, coastal and upper slope sediments were regarded as detrital sediments originating from the Nakdong and Changjiang Rivers. What processes are thus responsible for the variation in chemical composition in each depositional environment? Because the environmental factor with the greatest difference among the three sediment categories was water depth, the change in sediment metal concentrations with water depth may suggest the governing processes. In the study area, the sedimentation rate was also closely related to water depth. Fig. 7 shows the variation in concentrations and metal/Al ratios with water depth. Aside from coastal and upper slope sediments, the mean grain size was scattered but nearly constant.

Masuzawa et al. (1989) reported four groups of elements in settling particles in the Japan Sea based on the variation in concentrations and metal/Al ratios with relation to water depth: refractory (Al, Sc, La, Th, Hf, V, Ta, K, Rb, and Cs), biogenic (Ba, Ca, and Sr), scavenged (Mn, Ce, Fe, and Co), and biogenic-scavenged (As, Sb, Se, Ag, Zn, and Br). Elements can also be categorized into four groups based on the variation trend with water depth in surface sediments; however, this method groups some elements differently. Elements in the first group decrease in concentration with water depth but have a constant metal/Al ratio (Sc and Cr). Because these elements are lithophilic and abundant in detrital minerals, it is thought that detrital sediments are diluted by biogenic materials, resulting in a decreased concentration and constant metal/Al ratios with depth. Elements of the second group decrease in concentration and metal/Al ratios with increasing water depth (Ca, Sr, and $CaCO_3$). In the third group, the concentration and metal/Al ratios of elements increase steadily with increasing water depth (organic carbon, V,

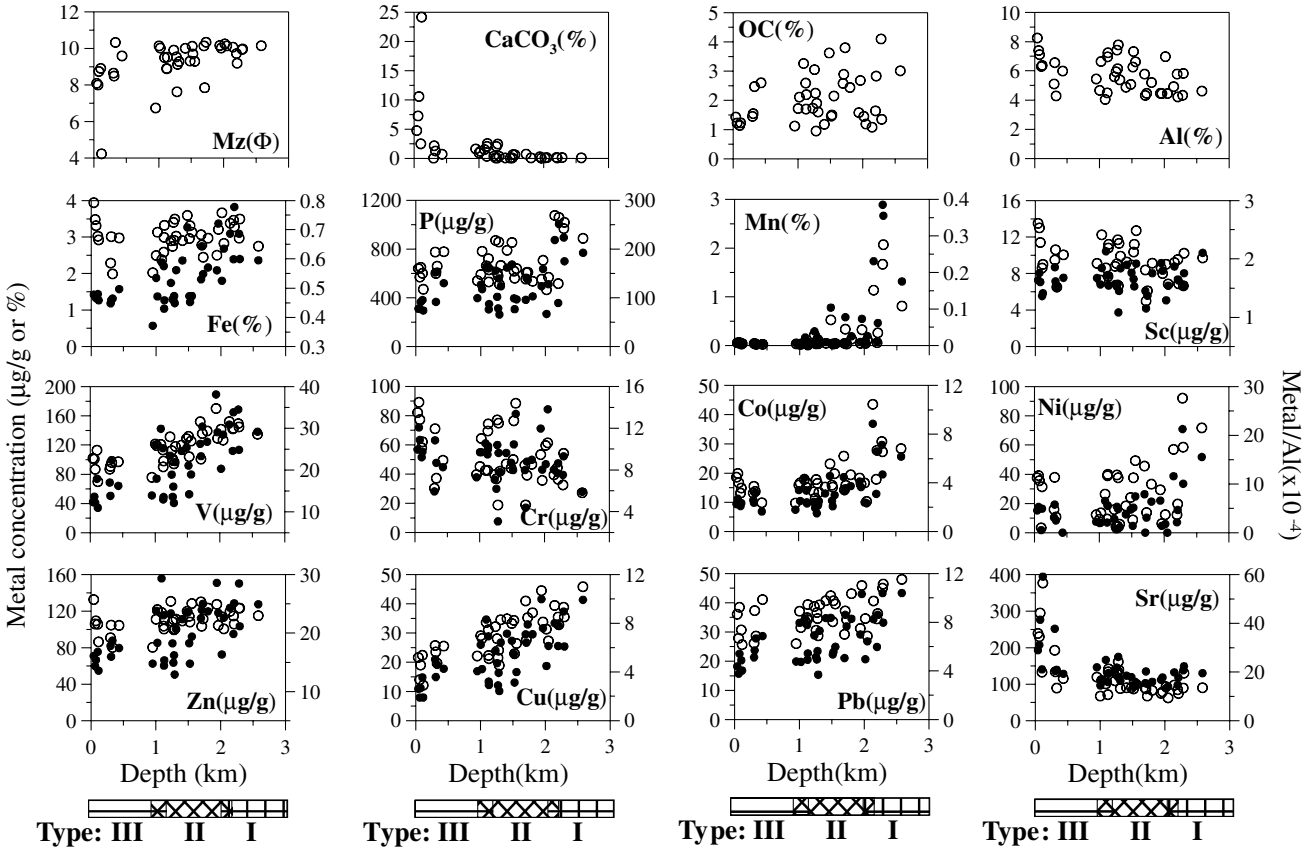

Fig. 7. Variation of mean grain size (Mz), contents of $CaCO_3$ and organic carbon, and concentration of major and trace elements (open circle) in recent fine-grained sediments plotted against water depth. Metal/Al ratios (closed circle) are also drawn based on the right *y*-axis scale.

Cu, and Pb). The steady increase of concentration and metal/Al ratio with water depth may indicate that the water column scavenges these metals. Because sedimentation rates also decrease with water depth, longer residence in a water column results in particles more enriched in metals in basin areas. Therefore, this group can be categorized as an authigenic component. In the fourth group, element concentration and metal/Al ratios increase rapidly in basin sediments (Fe, Mn, P, Co, and Ni). Precipitation of Mn oxides is considered responsible for the rapid changes in these elements. Mn is highly responsive to redox changes and is enriched at the redox interface through the repeated redox cycle: burial with sediments, reductive dissolution, upward migration, and reprecipitation (Froelich et al., 1979; Marin and Giresse, 2001). In the study area, Mn was enriched in the near-surface sediments, particularly in areas between the Ulleung Basin and the UIG, which usually have suboxic conditions within the sediment column. The other elements were likely to be co-precipitated with Mn oxides. Masuzawa et al. (1989) reported that biogenic-scavenged elements of the fourth group have constant concentrations but decreasing metal/Al ratios with increasing water depth. In this study, we did not find elements that had decreasing metal/Al ratios with water depth, except for detrital and biogenic elements. In the surface sediments, elements of diagenetic origin after deposition were categorized in the fourth group.

The highest concentration of organic carbon was found in the basin areas, which also had the highest concentrations of Mn-oxide related metals. As noted above, the UIG is a passage by which deep water formed in the northern part of the East/Japan Sea, and containing plentiful dissolved oxygen, enters the bottom of the Ulleung basin. Sedimentary organic carbon levels are usually low in deep-sea sediments covered with an oxic surface layer. In this study, the finding that basin sediments had the highest relative organic carbon contents (up to 4%) implies that there is some mechanism preserving organic materials in these sediments. The fairly high sedimentation rate relative to common deep-sea sedimentation rates may be a possible mechanism. The high sedimentation rate may prevent the bottom water oxygen from penetrating deeply into sediments, leading to well-preserved organic materials and causing diagenetically mobilized Mn to reprecipitate near surface sediments.

5.4. Contribution of authigenic metals to deep basin sediments in the East/Japan Sea

The contribution of authigenic metals was estimated using a constant-flux model assuming constant vertical flux of hydrogeneous metals and a horizontal supply of coastal detrital sediments. The following equations were applied:

$$F_t = F_a + F_d \quad (2)$$

$$C_t \times S \times \rho = F_a + C_d \times S \times \rho \quad (3)$$

$$C_t = F_a/(S \times \rho) + C_d, \quad (4)$$

where subscripts t, a, and d represent total, authigenic, and detrital, respectively, and F, C, S, and ρ denote flux ($\mu g\ cm^{-2}\ yr^{-1}$), concentration ($\mu g\ g^{-1}$), sedimentation rate ($cm\ yr^{-1}$), and dry bulk density ($g\ cm^{-3}$), respectively. Using Eq. (4), the constant value of F_a can be estimated from the relationship between C_t and $(S \times \rho)^{-1}$. If the dry bulk densities in sediments are similar and can be assumed to be constant, then constant authigenic fluxes (F_a) for some metals may be estimated from the relationship between C_t and the inverse of sedimentation rate (S^{-1}). In addition, the intercept of the y-axis in the regression line can be regarded as the concentration of metal in the coastal detrital sediment.

To obtain spatially-averaged fluxes for the study area, the sedimentation rate at each site was calculated using water depth with regression Eq. (1), which describes the relationship between sedimentation rate and water depth.

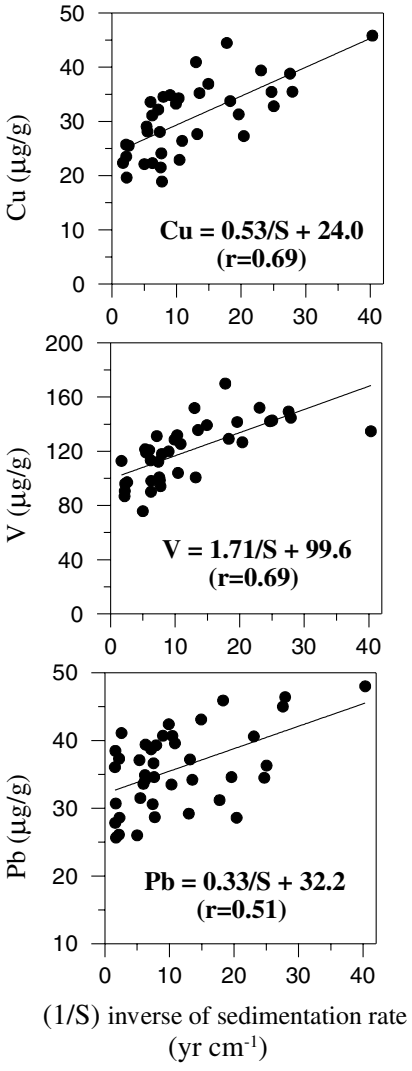

Fig. 8. Scatter plots of metal concentrations in surface sediments plotted against the inverse of sedimentation rates. The least squared regression lines and equations are also shown.

The dry bulk density in the core surface sediments was 0.41 ± 0.12 ($n = 16$) g cm^{-3}, calculated from the water content and assumed grain density (Cha et al., 2005). Metal concentrations were plotted against the inverse of the sedimentation rate. Least squared regression lines and equations were depicted in Fig. 8. The intercepts of the y-axis for Cu, V, and Pb were 24.0, 99.6, and 32.2 μg/g, respectively, and correspond to values in coastal and upper slope detrital sediments (Table 1). Authigenic fluxes estimated using the slopes of the regression lines and the above dry bulk density were 0.22, 0.72, and 0.14 μg cm^{-2} yr^{-1} for Cu, V, and Pb, respectively. The dissolved Cu concentration in the water column of the study area ranged from 0.13 to 0.37 μg kg^{-1} with a mean of 0.20 μg kg^{-1} (Yang, 1997). For a mean water depth of approximately 1500 m, the residence time of Cu in the East/Japan Sea was estimated to be approximately 85.9–245 yr (mean 132 yr) using a simple one-box, steady-state model. The authigenic flux of Cu estimated above was 10 times higher than that found in Nares Abyssal Plain red clays (Thompson et al., 1984). In addition, the calculated residence time of Cu was about 20 times shorter than the mean oceanic residence time (~2400 yrs), but similar to the ventilation time (80–100 yr) of deep water in the East/Japan Sea. These findings may have resulted from the relatively greater supply of detrital materials close to the continent, even though the study area has a deep basin.

6. Summary and conclusions

Surface sediments in the study area were classified into five types based on statistical analyses of chemical data: basin sediments, lower continental slope sediments, coastal and upper continental slope sediments, inner continental-shelf sediments and outer continental-shelf sediments. The basin and lower slope sediments were characterized by high levels of organic carbon, Fe, Mn, P, V, Co, Ni, Zn, and Cu, similar to typical deep-sea mud. The outer continental-shelf sediments had the characteristics of carbonate sands, with high Ca and Sr concentrations and very low levels of Al and trace elements. The coastal and upper slope sediments were similar to nearshore mud, with high concentrations of Al, K, Mg, and trace elements. Combined metal/Al ratios of major and trace elements suggested that these sediments were mixtures of materials from the Nakdong and Changjiang Rivers. Finally, the inner continental shelf sediments had chemical compositions transitional between the outer continental-shelf and the coastal and upper slope sediments.

In summary, the chemical composition of coastal sediments, including upper slope sediments, in the East/Japan Sea was more affected by the supply, transport, and preservation of detrital sediments than by diagenetic processes in the sediments. In contrast, the chemical composition of basin sediments was more influenced by post-depositional diagenetic and authigenic processes than by sedimentation of detrital sediments.

Acknowledgments

This study was partly supported by KORDI research "Carbon cycle in the East Sea-1; Ulleung basin (PE92400)". The authors thank to Dr. Shigeyoshi Otosaka of Japan Atomic Energy Research Institute and the editor for their critical reviews of the manuscript.

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