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Article

Major and trace element geochemistry of beach sands from northern Kyushu, Japan

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Abstract

The geochemical compositions of beach sand samples from seventeen locations in northern Kyushu were determined by X-ray fluorescence analysis. The results show that SiO_2, Al_2O_3 and CaO were the three most abundant elements, with contents averaging 77.24 wt%, 10.62 wt% and 4.76 wt%, respectively. Concentrations of K_2O, Na_2O and Fe_2O_3 were next in abundance. The high SiO_2 contents reflect the abundance of quartz, and high K_2O and Na_2O contents relative to Al_2O_3 indicates presence of significant K-feldspar and sodic plagioclase. Correlations between CaO, Sr and MgO are attributed to abundance of biogenic carbonate material. The combination of these mineral phases leads to dilution of all other elements, and nearly all trace elements (including heavy metals) are present at levels well below those in average Upper Continental Crust.

Key words: Major and trace elements, beach sand, northern Kyushu, composition, geochemistry, quartz, feldspar

Introduction

Beaches are functional links between the land and the sea. The composition of beach sand sediments and their geochemical variation is regulated by multiple factors, including waves, wind, long shore currents, climate, relief, and source composition. A sequence of pocket beaches separated by headlands shape the coastline of the Genkai Sea in the northern part of Kyushu, Japan. These beaches are considered to be stable because they exist as sandy beach despite little supply of sediment from rivers (Kojima *et al*., 1986).

Work on the composition of beach sands has previously been carried out at various locations around Honshu. These studies include examining the geochemical composition of beach sands from Tottori (Bah *et al*., 2011a), major and trace element composition of sands from pocket beaches in western Yamaguchi (Bah *et al*., 2011b) and in Shimane (Ishiga *et al*., 2010). In the latter study, Ishiga et al. (2010) examined the characteristics of pocket beaches in the western San'in coast of southwest Japan, and evaluated the geochemical maturity of the beach sands. The goal of this present study is to characterize the major and trace element compositions of beach sand samples collected from fifteen beaches in the coastal zone of the northern Kyushu along the shoreline of Fukuoka and Saga prefectures.

Study area

The study area is situated on the northern coast of Fukuoka and Saga Prefectures, Kyushu Island, in an area open to the southern part of the Sea of Japan (Fig. 1). Samples were collected at the following locations: Ashiya, Namitsu, Monakata, Katusuurahama, Tsuyazaki, Miyaji, Koga, Singu, Wajiro, Nagahama, Ikinomatsubara, Imajuku, Itoshima, Nijo, Shikaka, and Karatsu. The shoreline in the study area is fringed with broad sandy beaches and wetlands (essentially estuaries) and intertidal mud flats. However, large areas of the shoreline have been reclaimed for agricultural, infrastructural and urban development.

The geological basement in northern Kyushu consists of a variety of sedimentary, metamorphic rocks and igneous rocks (both volcanic and plutonic) (Fig. 1), all of which are located in the Southwest Japan Arc (inner arc). The main lithotypes in the basement adjoining the sample sites are Triassic to Jurassic sedimentary rocks and younger plutonic rocks. Paleogene sediments are also significant in the coastal strip from Shingu to Ashiya (Fig. 1). In the lowlands, poorly developed alluvial flats, Pleistocene terraces, and several faults bordering mountains suggest that Quaternary crustal movements played an important part in the geomorphic development of the region.

Sample collection

Fifteen sites in Fukuoka Prefecture and two in Saga Prefecture were chosen for beach sand sediment sampling (Figs. 1 and 2). Sampling was carried out at moderate to low tides, based on tidal information for Hakata, available from the Japan Meteorological Agency. Surface sand sediment samples weighing 300 to 500 g were collected from the foreshore zone at depths of about 0-5 cm, using a hand trowel. Beach widths were measured using a linen tape, and beach slope measured with an inclinometer. Thirty beach sand samples were collected from the mid-tide level of beaches

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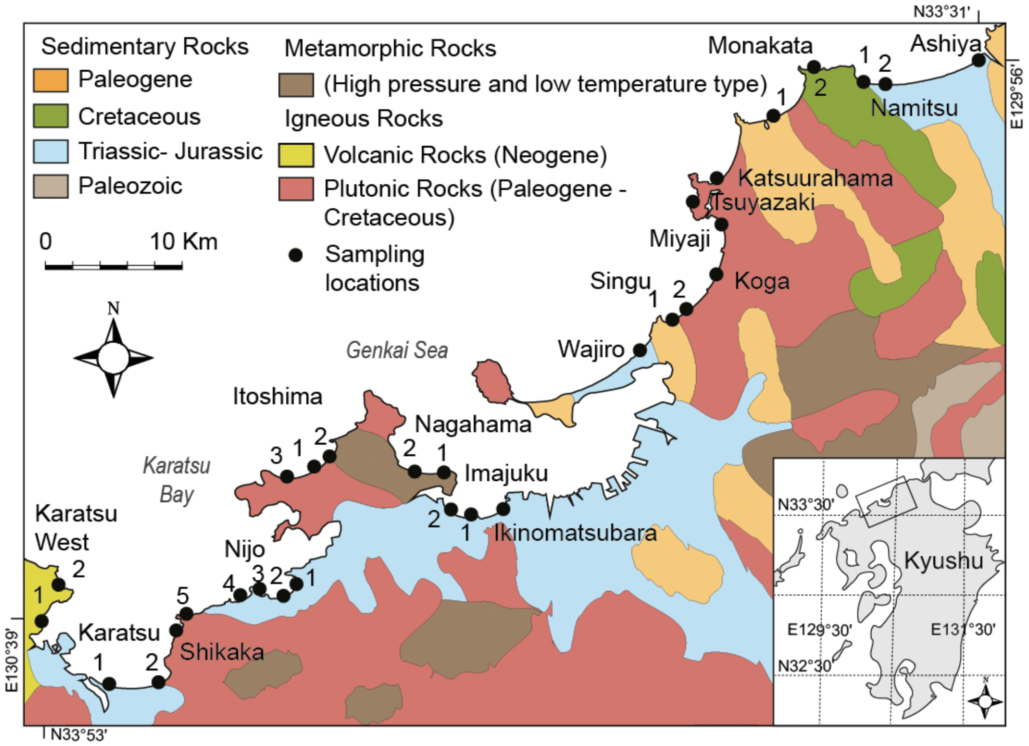

Fig. 1. Map showing sample locations and distribution of sedimentary, metamorphic and plutonic rocks in northern Kyushu. (GLGArcs: Introduction to the Landforms and Geology of Japan)

on April 27th and 28th, 2012.

Materials and sample preparation

Two analytical methods were used to determine the compositions of the beach samples. X-ray fluorescence spectrometry (XRF) was used to determine the major oxide and trace element compositions, and loss on ignition (LOI) was used as an estimate of the organic matter and carbonate contents of each sample.

Approximately one-third of each sample was transferred to Pyrex beakers, covered with aluminum foil to allow air circulation, and dried in an oven at 110˚C for 24 hours. Once dried, sub-samples of the sediments were crushed in an automatic agate mortar and pestle grinder to produce a powder suitable for analysis. The mortar and pestle were cleaned between samples with water, and dried with ethanol. Pressed powder pellets and fused glass discs were prepared from the crushed samples for trace element and major oxide analysis, respectively.

The pressed powder pellets were prepared by pressing the powdered samples into 40 mm diameter plastic rings, using a force of 200 kN for about 60 s in an automatic pellet press (E-30 T. M Maekawa).

For the fused glass discs and loss on ignition (LOI), about 10 g of crushed sample was dried in open glass vials in an oven for 24 hours at 110˚C to remove unbound moisture before determining the LOI content. LOI can be used to estimate the organic matter and carbonate contents of sediments (Heiri *et al*., 2001). The LOI determinations were made by transferring about 5 g of dried sample to previously weighed porcelain crucibles, and the overall weight recorded. The samples were then ignited in a muffle furnace for at least 2 h at 1050˚C. After ignition, the porcelain crucibles were cooled in a dessicator, and reweighed. The weight differential was calculated and reported as a percent loss. The ignited samples from the LOI procedure were manually disaggregated in an agate pestle and mortar, transferred to glass vials, and stored in a 110˚C oven for at least 24 h before the preparation of fused glass discs.

The fused glass discs were prepared using the 2:1 method (Kimura and Yamada, 1996) in an NT-2000 automatic bead sampler. For this, 1.8000 ± 0.0005 g of the ignited sample was mixed with 3.6000 ± 0.0005 g of flux, also previously heated at 110˚C for 24 hours. The mixture was thoroughly mixed in an agate mortar, and then fused in a platinum crucible. This produced single-phase glass beads for the XRF analysis.

The XRF analyses were made at Shimane University using an automated RIX 2000 system (Rigaku Denki Co. Ltd.). The major oxides (SiO_2, TiO_2, Al_2O_3, Fe_2O_3*, MnO, MgO, CaO, Na_2O, K_2O, and P_2O_5) were determined from the fused glass discs, and 18 trace elements (As, Pb, Zn, Cu, TS, Ni, Cr, V, Sr, Y, Nb, Zr, Th, Sc, F, Br, I, and Cl) were obtained using the pressed pellet method (Ogasawara, 1987).

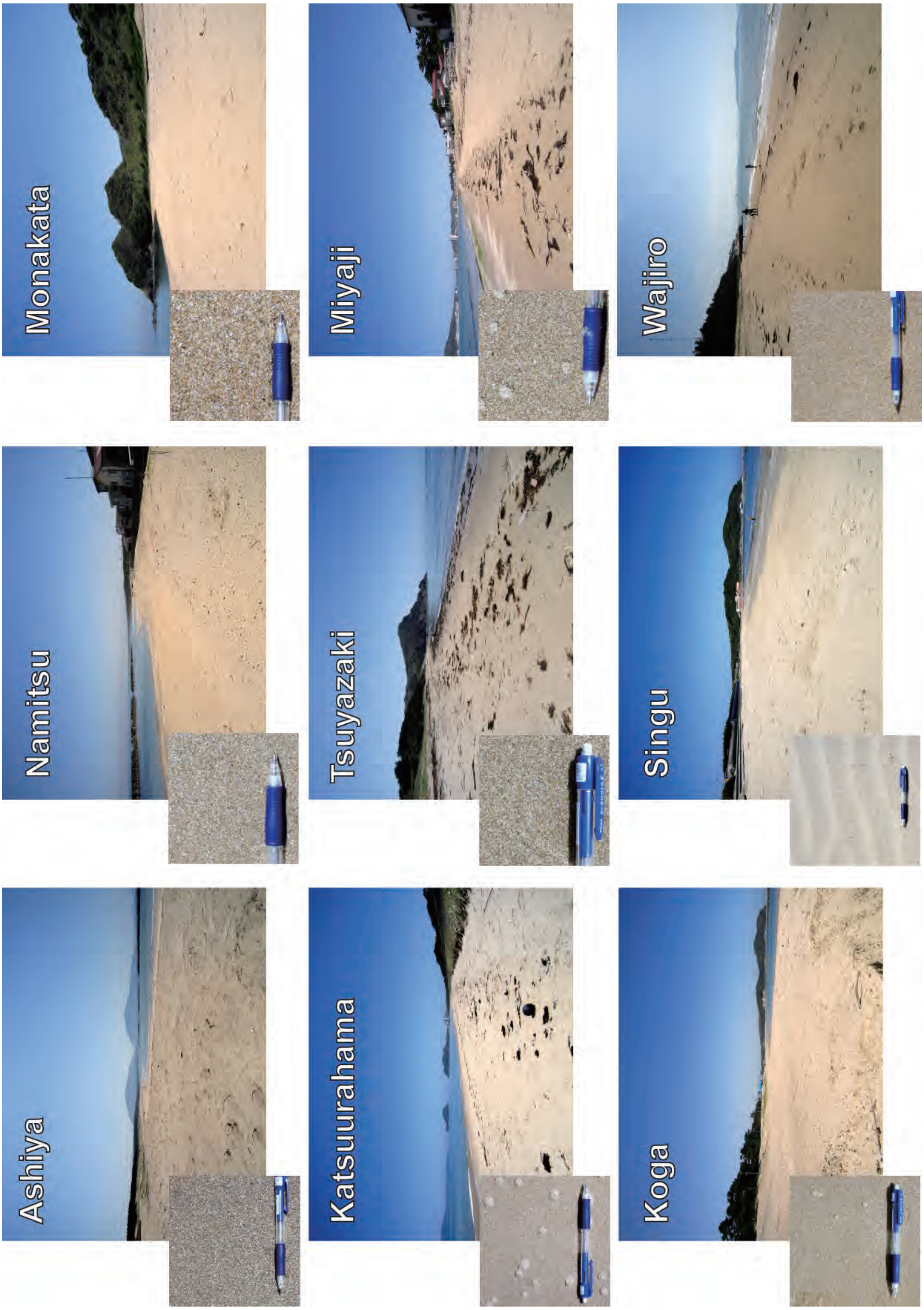

Fig. 2a. Photographs of beaches sampled along the shoreline of Fukuoka and Saga Prefectures in northern Kyushu.

Fig. 2b. Photographs of beaches sampled along the shoreline of Fukuoka and Saga Prefectures in northern Kyushu.

Results and discussion

Major and trace element analyses of the north Kyushu beach sands are listed in Table 1. The beach sands have moderate to high SiO_2 contents, with abundances ranging from 54.43 wt% to 91.23 wt%, and averaging 77.24 wt%, well above the 66.62 wt% present in the average Upper Continental Crust (UCC) reported by Rudnick and Gao (1995). The higher values in the beach sands reflects their quartz content. The next most abundant element, Al_2O_3, ranges from 4.71 wt% to 18.35 wt%, averaging (10.62 wt%), less than in UCC (15.40 wt%). In most samples CaO contents are low (<5 wt%) and less than UCC (4.76 wt%), reflecting low shell contents. Samples from Ashia and Munakata-1 are exceptions, with higher CaO contents of 13.47 wt% and 28.43 wt%, respectively. Among the remaining major elements K_2O (average 2.97 wt%, range 1.63-4.64 wt%), Na_2O (2.17 wt%, range 0.87-3.63 wt%) and Fe_2O_3 (1.35 wt%, range 0.31-3.97 wt%) are the next most abundant. Other major elements (MgO, TiO_2, MnO, and P_2O_5) are less abundant, and average values for all are less than in UCC. Loss on ignition (LOI) data in Table 1 are presented to indicate variations in organic matter and calcium carbonate content of the beach sands sediment. Average LOI was low, averaging only 3.45 wt%. However, relatively high LOI values of 10.87 wt% and 18.78 wt% were observed at Ashiya and Munakata-1, consistent with the very high CaO contents in these samples.

Table 1 also shows the concentration of trace elements in the beach sands. Chlorine has the highest content, averaging 2920 ppm, and ranging from 44 ppm to 10660 ppm, followed by total sulfur (TS) averaging 871 ppm, with range from 405 ppm to 2260 ppm. Strontium contents are significant, averaging 382 ppm and ranging from 76 ppm to 989 ppm, whereas iodine (I) content varies from three ppm to 3630 ppm, averaging 145 ppm. Fluorine contents range from 11 ppm to 340 ppm, and zirconium from eight ppm to 67 ppm. The average content of vanadium and chromium are 27 ppm and 20 ppm respectively, well below the values in UCC (97 and 92 ppm, respectively). Concentrations of other trace elements such as As, Pb, Zn, Cu, Ni, Y, Th, Sc, and Br are less than 20 ppm on average, and also below the abundances in UCC.

Major elements contents for all samples are plotted as a function of SiO_2 content in Fig. 3. The negative correlation for all the major elements except K_2O reflects silica dilution due to elevated quartz contents. The SiO_2-K_2O plot shows considerable scatter (Fig. 3). However, positive correlation between K_2O and Al_2O_3 in the beach sands suggests that K_2O abundances are controlled by variation in K-feldspar contents derived from the granitoids in the area. High K_2O content relative to Al_2O_3 in sediments implies greater feldspar content (Alagasamy *et al*., 2009). Strong linear increase of the Na_2O_3/Al_2O_3 ratio with increasing Al_2O_3 (Table 2), also suggests significant sodic plagioclase content. Weak

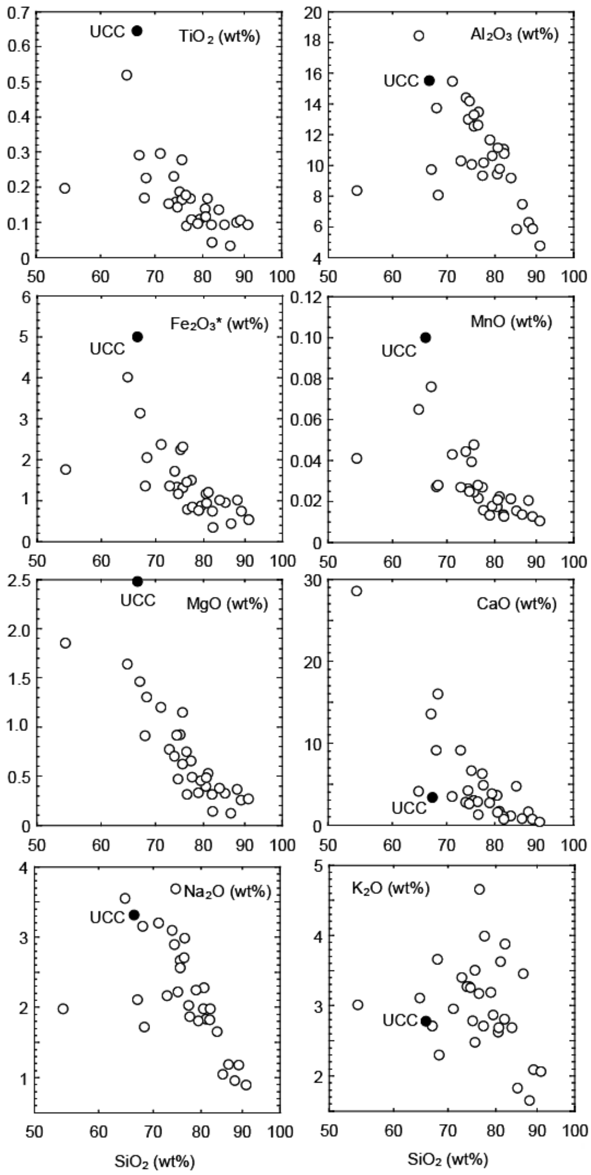

Fig. 3. Major element-SiO_2 variations in beach sand samples from Fukuoka and Saga prefectures, northern Kyushu. UCC = Upper Continental Crust (Rudnick and Gao, 2003).

positive correlations were found between Al_2O_3 and Cu, Zn and V (Fig. 4) suggesting that the abundances of these elements are controlled by the limited silt and clay fractions present in the beach sands.

Correlations involving CaO may be attributed to biogenic carbonates. The strong and positive correlations seen between Sr-CaO, Sr-MgO and Sr-LOI (Table 2) suggest that strontium is associated with CaO and MgO in biogenic carbonate material. The strong negative correlation (r = -0.80) between CaO and Zr is probably accidental, and may be due to concentration of CaO in coarser shell-rich samples. Trace elements with significant negative correlation with SiO_2 are Zn (r = -0.53), Cu (r = -0.50), TS (r = -0.52), Sr (r = -0.81) and Sc (r = -0.63) (Table 2), reflecting the significant quartz dilution in these beach sands.

Table 1: Geochemical composition of beach sands from northern Kyushu. LOI = loss on ignition; UCC = Upper Continental Crust (Rudnick and Gao, 2003). Major element concentrations in weight percent, trace element concentrations in ppm.

	Major elements (wt%)										wt%	Trace elements (ppm)																
Sample	SiO_2	TiO_2	Al_2O_3	$Fe_2O_3^*$	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	As	Pb	Zn	Cu	Ni	Cr	V	Sr	Y	Nb	Zr	Th	Sc	TS	F	Br	I	Cl
Fukuoka Prefecture (*n* =26)																													
Ashiya	67.12	0.29	9.64	3.11	0.08	1.45	13.47	2.09	2.70	0.06	10.87	23	14	26	3	–	11	41	556	16	3	37	1	30	1724	101	11	11	6197
Namitsu 1	88.25	0.10	6.21	0.99	0.02	0.36	1.50	0.94	1.63	0.01	5.58	20	13	21	4	–	31	36	423	14	2	46	2	21	1535	49	12	23	10660
Namitsu 2	75.17	0.18	9.98	2.21	0.04	0.91	6.49	2.20	2.77	0.04	1.87	15	12	14	2	–	23	14	181	11	2	46	2	6	674	35	5	36	1007
Munakata 1	54.43	0.19	8.28	1.73	0.04	1.84	28.43	1.96	3.00	0.08	18.78	11	11	18	6	–	5	17	989	14	–	–	2	46	2260	–	9	3	5232
Munakata 2	85.39	0.09	5.76	0.92	0.01	0.32	4.62	1.03	1.81	0.03	3.58	17	12	13	2	–	7	8	337	9	1	46	2	13	724	206	3	26	–
Katsuurahama	89.25	0.10	5.81	0.72	0.01	0.25	0.61	1.16	2.07	0.01	0.98	8	12	13	2	–	21	–	115	10	3	53	3	–	742	11	30	3630	–
Tsuyazaki	80.87	0.13	9.34	1.13	0.02	0.39	3.53	1.96	2.61	0.02	2.58	12	13	16	2	–	–	16	365	13	2	54	3	11	665	227	4	24	–
Miyaji	77.56	0.16	9.25	1.46	0.03	0.65	6.13	2.01	2.70	0.04	5.02	13	12	19	6	–	7	24	433	13	2	47	3	18	1017	172	7	19	2239
Koga	84.03	0.13	9.11	0.98	0.02	0.37	1.02	1.64	2.67	0.02	0.93	10	15	18	5	1	30	26	241	15	4	55	2	6	569	89	5	36	–
Singu 1	81.41	0.16	9.67	1.18	0.02	0.52	1.59	1.82	3.61	0.02	1.22	10	16	17	3	–	25	15	247	15	3	54	2	5	530	61	5	27	–
Singu 2	82.32	0.09	10.98	0.72	0.01	0.31	0.96	1.81	2.79	0.01	1.25	11	16	17	6	1	25	17	300	16	2	45	2	8	802	131	9	32	3962
Wajiro	91.23	0.09	4.71	0.50	0.01	0.26	0.29	0.87	2.05	0.00	0.82	8	12	12	2	2	21	–	79	9	3	46	1	–	763	60	11	33	4021
Ikinomatsubara	86.74	0.03	7.40	0.41	0.01	0.11	0.68	1.17	3.44	0.01	0.55	3	18	12	0	–	2	–	183	13	2	56	1	–	405	131	3	28	–
Imajuku 1	82.40	0.04	10.67	0.31	0.01	0.13	0.60	1.97	3.86	0.01	0.58	3	19	15	1	–	11	–	231	16	2	53	1	–	564	21	7	34	1984
Imajuku 2	76.67	0.09	13.38	0.76	0.02	0.31	1.15	2.97	4.64	0.02	0.91	3	21	20	2	0	2	–	274	17	3	60	1	3	598	104	9	27	1895
Nagahama 1	68.12	0.17	13.65	1.33	0.03	0.90	8.99	3.14	3.64	0.05	5.92	6	13	18	8	–	13	19	654	14	1	25	2	22	955	143	6	18	44
Nagahama 2	74.48	0.16	12.92	1.30	0.03	0.91	4.04	2.88	3.26	0.04	2.45	6	13	17	6	15	38	26	464	14	2	39	1	13	704	34	8	23	2730
Itoshima 1	72.93	0.15	10.19	1.33	0.03	0.76	9.04	2.15	3.39	0.04	6.49	7	13	16	6	–	19	19	557	14	2	38	2	27	1182	48	6	25	1817
Itoshima 2	79.66	0.11	10.56	0.85	0.02	0.44	3.70	1.79	2.85	0.02	3.92	9	15	16	5	–	33	23	434	16	3	45	2	18	1151	89	8	29	4777
Itoshima 3	77.84	0.10	10.10	0.81	0.02	0.48	4.79	1.85	3.97	0.03	3.70	9	16	13	4	–	9	2	410	15	2	45	3	12	805	–	8	22	2397
Nijo 1	75.72	0.27	12.47	2.29	0.05	1.14	2.90	2.65	2.46	0.04	1.13	4	13	23	7	15	42	62	316	14	5	58	2	13	687	340	9	23	2812
Nijo 2	71.23	0.29	15.39	2.34	0.04	1.19	3.36	3.19	2.94	0.02	1.28	4	15	24	9	14	43	62	386	14	4	48	2	12	586	34	8	21	288
Nijo 3	81.01	0.11	11.05	0.91	0.02	0.47	1.47	2.26	2.67	0.02	0.84	4	17	15	5	4	14	10	223	13	3	55	2	6	652	–	10	29	3005
Nijo 4	75.72	0.16	13.21	1.28	0.02	0.61	2.92	2.55	3.49	0.04	1.34	8	15	16	6	3	20	13	354	14	3	49	1	6	503	–	5	28	–
Nijo 5	79.20	0.09	11.58	0.73	0.01	0.32	2.64	2.23	3.17	0.02	2.26	8	17	15	4	2	19	12	365	16	3	41	2	9	662	–	5	30	693
Shikaka	76.50	0.17	12.54	1.42	0.03	0.74	2.73	2.69	3.16	0.02	1.29	4	15	20	7	9	26	31	359	15	4	44	2	8	568	31	6	23	380
Saga Prefecture (*n* =4)																													
Karatsu 1	64.77	0.52	18.35	3.97	0.06	1.63	4.03	3.54	3.09	0.03	2.73	5	15	45	20	7	24	109	419	15	6	54	2	14	788	59	8	14	2737
Karatsu 2	73.96	0.23	14.31	1.70	0.04	0.69	2.71	3.08	3.25	0.02	1.40	8	16	22	6	3	21	38	369	13	4	49	2	9	561	103	6	26	–
Karatsu West 1	74.69	0.14	14.10	1.14	0.02	0.46	2.51	3.68	3.24	0.03	1.50	8	15	19	2	–	17	14	382	13	3	56	2	8	665	–	7	35	1685
Karatsu West 2	68.46	0.22	8.00	2.02	0.03	1.30	15.91	1.70	2.29	0.07	11.77	13	11	20	2	–	20	34	816	12	1	8	3	43	2081	–	8	15	3674
Average	77.24	0.16	10.62	1.35	0.03	0.67	4.76	2.17	2.97	0.03	3.45	9	14	18	5	6	20	27	382	14	3	47	2	15	871	99	8	145	2920
Maximum	91.23	0.52	18.35	3.97	0.08	1.84	28.43	3.68	4.64	0.08	18.78	23	21	45	20	15	43	109	989	17	6	60	3	46	2260	340	30	3630	10660
Minimum	54.43	0.03	4.71	0.31	0.01	0.11	0.29	0.87	1.63	0.00	0.55	3	11	12	0	0	2	2	79	9	1	8	1	3	405	11	3	3	44
UCC	66.62	0.64	15.40	5.04	0.10	2.48	3.59	3.27	2.80	0.15	–	5	17	67	28	47	92	97	320	21	12	193	11	14	621	557	2	1	370

Table 2: Coefficient of determination (R^2) of beach sands from northern Kyushu ($R^2 > \pm 0.50$, $n = 22$, bold numbers are significant).

	SiO_2	TiO_2	Al_2O_3	$Fe_2O_3^*$	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	As	Pb	Zn	Cu	Ni	Cr	V	Sr	Y	Nb	Zr
TiO_2	**-0.66**																				
Al_2O_3	**-0.53**	**0.59**																			
$Fe_2O_3^*$	**-0.69**	**0.96**	0.49																		
MnO	**-0.71**	**0.87**	0.47	**0.94**																	
MgO	**-0.89**	**0.82**	0.37	**0.86**	**0.84**																
CaO	**-0.78**	0.29	-0.11	0.40	0.43	**0.75**															
Na_2O	**-0.61**	**0.56**	**0.95**	0.49	**0.50**	0.43	0.02														
K_2O	-0.30	-0.06	**0.56**	-0.11	-0.01	-0.04	-0.05	**0.53**													
P_2O_5	**-0.84**	0.44	0.12	**0.56**	**0.55**	**0.81**	**0.90**	0.26	0.01												
As	-0.01	0.05	-0.49	0.22	0.23	0.16	0.35	-0.44	**-0.57**	0.32											
Pb	**0.19**	-0.22	0.40	-0.28	-0.17	-0.41	**-0.50**	0.26	**0.67**	**-0.50**	-0.51										
Zn	**-0.53**	**0.90**	**0.63**	**0.84**	**0.77**	**0.64**	0.12	**0.56**	0.02	0.24	0.01	0.06									
Cu	**-0.50**	**0.78**	**0.67**	**0.66**	**0.54**	**0.57**	0.09	**0.55**	0.09	0.19	-0.24	-0.01	**0.81**								
Cr	0.07	0.34	0.27	0.26	0.16	0.16	-0.28	0.19	-0.31	-0.14	-0.06	-0.21	0.25	0.34							
V	-0.36	**0.91**	**0.56**	**0.83**	**0.72**	**0.60**	-0.04	0.44	-0.15	0.05	-0.18	0.03	**0.94**	0.78	0.45						
Sr	**-0.81**	0.33	0.11	0.38	0.38	**0.70**	**0.88**	0.21	0.04	**0.86**	0.26	-0.39	0.25	0.25	-0.13	0.05					
Y	-0.23	0.08	**0.50**	0.05	0.14	0.04	-0.08	0.35	**0.61**	-0.05	-0.23	**0.68**	0.33	0.32	0.03	0.22	0.14				
Nb	-0.22	**0.60**	**0.59**	0.47	0.49	0.34	-0.37	**0.50**	0.08	-0.21	-0.38	0.30	**0.63**	**0.60**	0.47	**0.69**	-0.27	0.27			
Zr	0.42	-0.10	0.13	-0.17	-0.07	-0.40	**-0.80**	0.07	0.16	**-0.67**	-0.34	0.44	0.02	0.02	0.00	0.11	**-0.79**	0.12	0.49		
Th	0.00	0.18	-0.11	0.11	-0.07	0.05	0.07	-0.09	-0.29	0.08	0.16	-0.33	0.10	0.13	0.06	0.01	0.11	-0.23	-0.01	-0.08	
Sc	**-0.63**	0.21	-0.37	0.30	0.30	**0.65**	**0.89**	-0.26	-0.28	**0.82**	0.39	**-0.61**	0.11	0.02	-0.22	0.09	**0.94**	-0.14	-0.43	**-0.81**	0.09

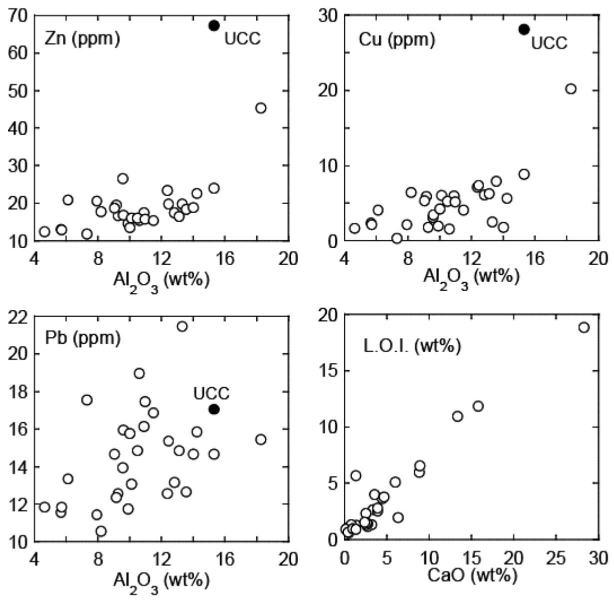

Fig. 4: Relationship between Zn, Cu and Pb with Al_2O_3, and CaO with LOI in beach sand samples from Fukuoka and Saga prefectures in northern Kyushu.

Conclusions

The results show the major and trace element compositions of beach sand sediments from northern Kyushu are characterized by high SiO_2 contents due to relative concentration of quartz, and relatively high K_2O and Na_2O associated with feldspars. CaO contents are generally low, although enrichments occur in a few samples due to presence of shell material. Abundances of the remaining major elements show strong negative correlation with SiO_2, reflecting silica dilution. Among the trace elements Cl, TS, Sr, I, F and Zr are the most abundant, but contents of most of the trace elements are less than in average UCC.

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（要　旨）

Bah Mamadou Lamine Malick・Sansfica Marlyn Young・石賀裕明 , 2012 北部九州の海浜砂の主元素および微量元素の地球化学的検討．島根大学地球資源環境学研究報告，31，1-8

北部九州の海浜砂について 17 地点において蛍光 X 線分析による地球化学組成の検討を行った．SiO_2, Al_2O_3 と CaO が主な主元素であり，それぞれの平均値は 77.24 wt%, 10.62 wt% と 4.76 wt% である．K_2O, Na_2O と Fe_2O_3 はこれに次ぐ組成である．高い SiO_2 含有量は石英によるものであり，Al_2O_3 に対する高い K_2O と Na_2O 含有量はカリ長石や曹長石を代表するものと言える．CaO と Sr および MgO との相関は生物起源の炭酸塩の寄与を示す．これら 3 種類の鉱物が砂粒子として存在することにより，微量元素濃度（重鉱物を含む）は希釈される．そのため UCC と比較した場合にはその濃度は乏しい．