Systematic Geochemical Study of the Soils, Litter, and Bedrock of a Permian Limestone Mountain, Central Japan

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Abstract

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The paper deals with the results of a systematic geochemical study of soils at Mt Kinshozan in Central Japan, a limestone area known for its well-preserved Permian fossils. Compared with the typical composition of the Japanese upper continental crust, here the soils were found depleted in Si, Ca, Na, Mg, and K and rich in Ti, Al, and Fe. They were enriched with some heavy metals (Cr, Ni, Cu, Pb, and Zn) detected also in the acetic-acid residue of the limestone collected from Mt. Kinshozan. Therefore, the residual materials produced through chemical weathering of the limestone bedrock may have significantly contributed to the soils formation. Concentrations of C_{total} were nearly identical to C_{org} and the relationship between C_{total} and Element/TiO_2 suggested a significant contribution of the litter to Si, Mg, Ca, and P in the soils.

Keywords: chemical composition; enrichment factor; nutrient; plant

In general, the properties of soil developed on limestone bedrock markedly differ from those formed on silicate bedrock and siliciclastic sediment. Limestone itself is significantly depleted in certain essential nutrients, such as K and Fe, which are essential for plant growth. Therefore, the supply of these nutrients from the chemical weathering of limestone bedrock is assumed to be limited. In addition, some elements (such as P) become immobile due to the formation of stable calcium compounds (Ström *et al.* 2005). Thus, soils developed on limestone bedrock are potentially unsuitable for vegetation. However, some plant species are able to tolerate the limited availability of nutrients and a high base status, which has resulted in the evolution of distinct vegetation dominated by calcicole (Ström *et al.* 2005). However, at the studied locality calcareous plants typical of such soils are not present, here the vegetation cover comprizes various non-calcareous plants like broad-leaved trees (*Quercus variabilis*) and conifers (*Chamaecyparis obtusa*).

Such distinct soils have been the subject of research for over one hundred years (Stace 1956), also in Japan a representative study by Yokoo (2007) came into being. The previous studies on these soils and related materials are, however, if not all, fragmentary and not systematically conducted. The present paper summarizes the results of a systematic geochemical study of the soils at Mt. Kinshozan in Central Japan. The objective was to obtain systematic geochemical data on the soils, litter, bedrock, and their acid residues, examine the data comprehensively, and provide description of biogeochemical features of the soils at Mt. Kinshozan.

MATERIAL AND METHODS

Sampling sites and local geology. Mt. Kinshozan has a maximum altitude of 217 m a.s.l. and is located in Ogaki City, Gifu Prefecture, in Central Japan (Figure 1). This area is in a warm-temperate zone, the annual mean air temperature in Ogaki City is 16.1°C, and annual precipitation is

2313.5 mm (Japan Meteorological Agency 2010). The natural vegetation cover is an evergreen broad-leaved forest with *Quercus variabilis*, but artificial forests composed of *Chamaecyparis obtusa* and *Cryptomeria japonica* dominate, followed by pine forests. Mt. Kinshozan is formed of a central unit of the Akasaka Limestone of Permian age, which contains an allochthonous block of up to the 250 m thick Funabuseyama Unit originating from coral reefs developed on a volcanic seamount. It contains abundant fossils such as Fusulinidae, Coelenterata, Mollusc, and Echinodermata (Goto *et al.* 1988).

In early August of 2010, soil, rocks, and litter samples were collected at two relatively flat localities with the same vegetation type (coniferous forest). At each site, three cores situated 1–2 m apart were selected for replicate sampling. In the laboratory, the core samples (40–45 cm long) were divided into 10–15 stratigraphic subsamples (80–160 g). Litter samples (33–81 g) were also collected. Limestone samples ($n = 3$) were taken from outcrops near the sampling localities.

Sample preparation. Soil samples were dried at room temperature, then sieved using a 2 mm screen, and crushed into less than 125 μm powder using an agate ball-mill. Litter samples were dried at 80°C for 24 h and then crushed into particles of less than 250 μm using ceramic milling. Acid residues in the limestone were obtained by dissolution of a crushed 1.4–1.6 kg sample with 25% acetic acid.

Soil properties (colour, pH, water content, and ignition loss). The pH of the soil samples was determined with a soil/water weight ratio of 1:2.5 using a glass electrode (Horiba pH/ion meter F-24, Horiba, Ltd, Kyoto, Japan). The water content of soils was determined by air drying for over 2 weeks and ignition loss was measured on ignition of samples at 600°C for over 2 h.

Major and minor elements. Soil samples were pulverized to less than 125 μm sample powder using an agate mortar, and then they were ignited at 600°C for 2 h. Rock samples were not ignited, although the process used was the same. Glass beads were made of a mixture of the sample powder (1.5 g) and lithium tetraborate (3.0 g). Major and minor components (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, K_2O, Na_2O, P_2O_5, As, Ba, Co, Cr, Cu, Zn, Nb, Pb, Rb, Sr, Th, Y, and Zr) were analyzed using a wavelength-dispersive X-ray fluorescence spectrometer (Panalytical Axios-N system, Spectris Co., Ltd, Tokyo, Japan). The acid residues were ignited at 900°C for 13 h after being pulverized to 125 μm. The mixing ratio with lithium tetraborate was 1:3. Litter samples of < 250 μm were subsequently ignited at 400°C for 4 h. The ignited sample of 0.5 g was mixed with 3.5 g of lithium tetraborate to make a glass bead. The elements analyzed in the litter samples were Si, Mg, Ca, K, P, Al, Na, Ba, Cr, Cu, Ni, Sr, and Zn. Using the standard rock samples, reagents, and their mixtures, the calibration curves were made. C_{total} and N_{total} of dried soil and litter samples were analyzed using an elemental analyzer (Amco, Flash2000 Eager Xperience Ver.1.02, Amco Incorporated, Tokyo, Japan).

Mineral composition. Soil samples collected from the surface (0–5 cm) and a deeper horizon (25–30 cm) were used for the mineral composition analysis. Additionally, the acid residues of limestone were subjected to X-ray diffraction (Rigaku MultiFlex; Rigaku Corporation, Tokyo, Japan) analyses, with a 2.0-s counting time per step.

RESULTS AND DISCUSSION

General characteristics of soils at Mt. Kinshozan. The soils at Mt. Kinshozan were mostly of dull brownish-yellow colour. The water content

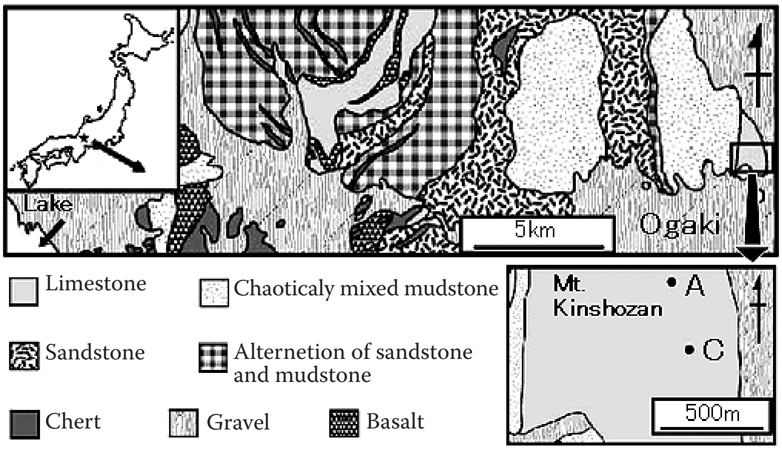

Figure 1. Sampling sites, and local geology of Mt. Kinshozan, Central Japan; the geological map is modified from 1/200 000 geological map "Gifu" (Wakita *et al.* 1992)

and ignition loss ranged 21–38% (28% on average), and 9–22% (15% on average), respectively. The pH value ranged 4.9–7.0 (6.3 on average). In almost all of the soil samples, clear peaks for quartz, plagioclase, mica, and K-feldspar were detected. Weak peaks for pyrite, hematite, gibbsite, and kaolinite were also detected in all the samples. Calcite was encountered only in the samples of topsoil. Contrary to the silicate-poor nature of the bedrock limestone, soils at Mt. Kinshozan are rich in silicate components (Table 1). SiO_2 is the most dominant component (40.19–46.49%). The order of abundance of other major components (except for C and N) is as follows:
$Al_2O_3 > Fe_2O_3 > K_2O > TiO_2 > MgO > CaO > P_2O_5 >$ $> MnO > Na_2O$.

In comparison with the major components, the order of concentration of the minor components is less uniform with Zn, Ba, Cr, Cu, and Zr concentration prevailing over that of Th, Nb, and Co (Table 1).

In order to preliminarily characterize the geochemical composition of the Mt. Kinshozan soils, comparisons with average compositions of Japanese soils (Yamasaki 2001) and the upper continental crustal composition (Togashi *et al.* 2000) were made (Table 1 and Figure 2). Compared with the average Japanese soils, those on limestone bedrock tend to be rich in Al_2O_3 and Fe_2O_3, and depleted in MgO, CaO, and Na_2O. A similar trend can be observed for the Mt. Kinshozan soils. Compared with the upper crustal composition, the analyzed soils are slightly depleted in SiO_2, significantly depleted in MgO, CaO, Na_2O, and K_2O, and significantly enriched with TiO_2, Al_2O_3, Fe_2O_3, P_2O_5. These patterns are consistent with the mobility trend of the major elements during weathering (Nesbitt *et al.* 1980).

Among the minor elements, concentrations of As, Cr, Nb, Ni, Pb, Rb, Th, and Zn tend to be higher in soils on limestone, whereas Sr concentration is higher in the average soil. The concentrations of other minor elements (Ba, Co, Cu, V, Y, and Zr) are nearly the same in both soil types. In the Mt. Kinshozan soils, concentrations of Ba, Co, and Zr are nearly the same as those in the average soil. Occurrence of the other minor elements in the Mt. Kinshozan soils tends to be higher. While this trend is again generally consistent with the average soil on limestone in Japan, concentrations of Cu and Y in the Mt Kinshozan soils are much higher.

Relationship between C_{total} and N_{total}. As can be seen in Figure 3a, C_{total} and N_{total} are highly positively correlated with each other (correlation coefficients = 0.99 at site A, 0.97 at site C), indicating incorporation of these elements exclusively in organic fractions. In other words, the concentrations of C_{total} of the analyzed soils predominantly represent amounts of organic matter, consistent with the fact that calcite, if present, occurs only as a minor component at these localities. Vertical profiles of C_{total}, N_{total} at site A are shown in Figure 3b. Both C_{total} and N_{total} concentrations decrease downward, although the details of pattern are not identical between sites and even cores. This feature can be seen also for site C samples (not shown here).

Chemical compositions of litter and their influence on soil components. Although litter at both sampling sites is derived mostly from coniferous trees, its composition is distinct (Table 2). The most abundant inorganic component in samples from site A was Si (as SiO_2, 49.95~58.2%), whereas the most abundant at site C was Ca (as CaO, 26.06~35.77%). The order of abundance of the subsequent components was common: Al_2O_3 $> Fe_2O_3 > K_2O$. Concentrations of Ti (as TiO_2) ranged 0.11–0.73%. Since Ti is not a nutrient element and is one of the most resistant elements during weathering, the detection of this element in the litter samples indicates the contamination of the silicate materials.

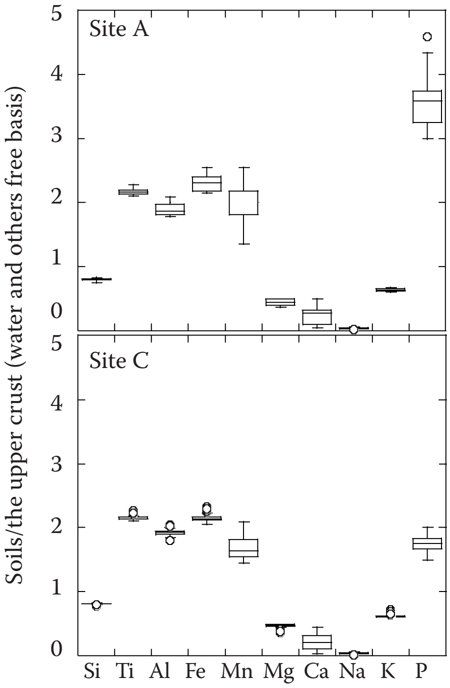

Figure 2. Box plots of major elements in the soils normalized to the upper crustal values

Table 1. Chemical composition of soils, limestones and their acid residues from Mt. Kinshozan

	Soils				Limestones			Acid residues		
	A	C	Jpn Soils*		B	C	E	B	C	E
	(*n* = 25) average		average 1	average 2	(*n* = 1)		(*n* = 4) average	(*n* = 1)		
SiO_2	43.91 ± 1.53	44.55 ± 1.31	53.3	51.11 ± 8.60	0.12	0.099	0.23 ± 0.09	38.82	70.94	42.92
TiO_2	1.09 ± 0.07	1.09 ± 0.05	0.9	1.02 ± 0.05	0.0026	0.0012	0.003 ± 0.001	1.75	0.50	1.06
Al_2O_3	22.55 ± 1.87	22.95 ± 1.35	18.5	24.71 ± 5.81	0.028	0.014	0.08 ± 0.04	22.24	11.42	18.29
Fe_2O_3	10.13 ± 0.93	9.46 ± 0.56	7.95	10.33 ± 2.22	0.016	0.014	0.03 ± 0.02	6.74	4.20	8.13
MnO	0.18 ± 0.02	0.15 ± 0.02	0.13	0.14 ± 0.09	0.0002	0.0013	0.007 ± 0.005	0.0040	0.0217	0.0179
MgO	0.91 ± 0.08	0.96 ± 0.06	1.56	0.56 ± 0.29	0.20	1.96	0.43 ± 0.08	3.24	0.67	1.73
CaO (%)	0.73 ± 0.40	0.68 ± 0.36	2.18	0.42 ± 0.34	53.52	52.21	54.15 ± 1.27	12.14	7.36	16.01
Na_2O	0.10 ± 0.03	0.10 ± 0.02	1.13	0.22 ± 0.13	n.d.	n.d.	n.d.	0.50	1.97	0.86
K_2O	1.25 ± 0.08	1.23 ± 0.09	1.44	1.90 ± 0.28	0.0033	n.d.	0.009 ± 0.006	5.67	0.95	2.96
P_2O_5	0.35 ± 0.03	0.17 ± 0.01	0.15	0.20 ± 0.11	0.0068	0.0031	0.011±0.002	8.41	1.51	11.70
C	3.76 ± 2.00	3.60 ± 1.75	3.48	1.53 ± 1.18						
N	0.26 ± 0.14	0.27 ± 0.10	0.21	0.16 ± 0.08						
LOI	14.87 ± 4.00	14.22 ± 2.88	13.2	9.35 ± 2.92						
As	73 ± 16	49 ± 6	12.3	43 ± 12	n.a.	n.a.	n.a.	n.d	n.d	n.d
Ba	406 ± 22	393 ± 17	348	371 ± 46	n.a.	n.a.	n.a.	1006	172	677
Co	20 ± 1	23 ± 2	18.2	23 ± 5	n.a.	n.a.	n.a.	11	11	8
Cr	252 ± 27	300 ± 25	65.8	162 ± 51	n.a.	n.a.	n.a.	23503	4465	5708
Cu	313 ± 54	168 ± 20	47.9	53 ± 17	n.a.	n.a.	n.a.	452	314	298
Nb	15 ± 1	18 ± 1	10.2	20 ± 2	n.a.	n.a.	n.a.	33	13	31
Ni	76 ± 7	88 ± 5	25.8	80 ± 23	n.a.	n.a.	n.a.	515	553	753
Pb (ppm)	241 ± 42	129 ± 4	21.8	47 ± 6	n.a.	n.a.	n.a.	147	29	80
Rb	98 ± 7	103 ± 7	69.9	162 ± 30	n.a.	n.a.	7 ± 8	513	64	144
Sr	77 ± 6	56 ± 3	186	91 ± 46	872	592	258 ± 83	640	283	314
Th	11 ± 1	12 ± 1	8.99	21 ± 3	n.a.	n.a.	n.a.	13	7	9
V	210 ± 18	216 ± 14	184	179 ± 30	n.a.	n.a.	n.a.	4990	257	926
Y	70 ± 3	70 ± 10	21.2	36 ± 17	n.a.	n.a.	n.a.	1671	122	397
Zn	434 ± 53	346 ± 26	89.3	187 ± 72	14	12	4 ± 2	3269	2624	2926
Zr	284 ± 12	286 ± 8	211	266 ± 53	42	30	14 ± 4	384	149	266

Samples of B and E are from the other site than A and C; *average 1 and average 2 indicate data of all soils and those on limestone bedrocks, respectively; LOI – loss on ignition; n.d. – not detected; n.a. – not analyzed

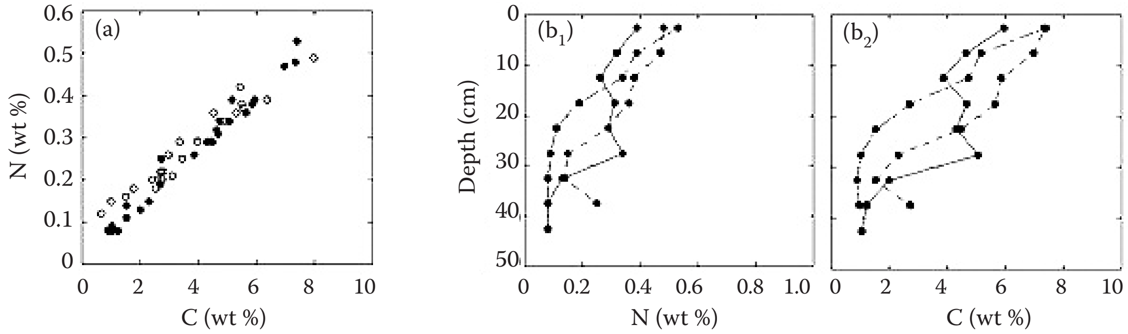

Figure 3. Relationship between concentrations of C_{total} and N_{total} in the soils (a), and vertical profiles of N_{total} (wt%) (b_1), C_{total} (wt%) (b_2) in individual core samples collected from the two sites; ●: Site A, ○: Site C

Zinc was the most abundant among the analyzed trace elements, ranging 320–430 ppm at site A and 360–405 ppm at site C. With the exception of Ba, Sr is subsequently abundant (125–177 ppm). Concentrations of Cr, Cu, Ni, and Pb were lower than 200 ppm, except for Cr in the three samples from localities C. Zirconium (Zr) was detected in all samples. Concentrations of Zr tended to be higher at site C (65–166 ppm) than at site A (25–32 ppm).

As discussed in the previous section, concentrations of C_{total} represent the amount of organic matter in the soil. Thus the relationship of other elements to C_{total} could provide some implications for contributions of litter to the bulk soil compositions. Although contribution or dilution by litter can be inferred to some degree from correlation coefficients with C_{total} (e.g., −0.84~−0.65 for C_{total}-TiO_2 and −0.86~−0.79 for C_{total}-Al_2O_3), more precise description of the contribution of litter to the major element composition of soil could be made based on TiO_2-normalized values. As shown in Figure 4a, TiO_2 shows a clear inverse relationship with C_{total}. Ti is not a bio-essential element and its concentrations in plants are extremely low. In soils, Ti is contained exclusively in inorganic mineral fractions that are derived from weathering residues of limestone bedrock and eolian dust (Stoorvoge *et al.* 1997). Therefore, an increase in organic matter in soils would result in a superficial decrease in bulk Ti concentrations, as shown in the plot pattern in Figure 4a. TiO_2-normalized values could offset such a dilution effect by organic fractions. For the selected major nutrient elements, the relationships of TiO_2-normalized values with C_{total} diagram are shown in Figures 4b–f. Several features are recognizable:

(1) Si and Mg show the same plot pattern. TiO_2-normalized values, except for samples from one core from site A (encircled in the figures), increase with an increase in concentrations of C_{total}, but tend to saturate above a C_{total} concentration of 4%.

(2) Ca and P show a clear positive correlation with C_{total}, while the slope and the lowest values for P_2O_5/TiO_2 are distinct between the two sites.

Table 2. Chemical compositions of litters (ashed)

		Litters	
		A	C
		(*n* =3) average	
Si		24.91 ± 2.0	9.90 ± 2.79
Ti		0.08 ± 0.01	0.30 ± 0.12
Al		1.41 ± 0.20	4.97 ± 1.67
Fe		0.95 ± 0.13	2.86 ± 1.00
Mn		0.25 ± 0.03	0.13 ± 0.02
Mg		0.37 ± 0.02	0.50 ± 0.04
Ca	(%)	13.18 ± 1.99	24.24 ± 5.08
Na		n.d	0.04 ± 0.01
K		0.62 ± 0.08	0.91 ± 0.16
P		0.38 ± 0.06	0.30 ± 0.06
C			
N		0.93 ± 0.07	0.53 ± 0.17
H		5.19 ± 0.20	5.54 ± 0.21
Ba		312 ± 69	205 ± 58
Co		n.d.	19 ± 4
Cr		70 ± 9	170 ± 47
Cu		55 ± 1	98 ± 11
Nb		n.d.	12 ± 2
Ni		32 ± 3	64 ± 15
Pb	(ppm)	51 ± 7	106 ± 26
Rb		n.a.	n.a.
Sr		141 ± 14	174 ± 5
V		27 ± 3	86 ± 34
Y		13 ± 2	29 ± 7
Zn		383 ± 57	378 ± 24
Zr		27 ± 5	108 ± 52

n.d. – not detected; n.a. – not analyzed

(3) K does not correlate with C_{total}. K_2O/TiO_2 values are nearly constant, although the values are distinct between the two sites.

The patterns described above could be explained in the context of the degree of litter contribution to bulk soil composition (ratios of organic/inorganic fractions).

Ca and P show a clear positive correlation with C_{total} (0.94–0.97 for Ca and 0.85–0.87 for P), indicating their derivation from an organic fraction. In particular, Ca concentrations at sites A and C are likely to be controlled exclusively by an organic fraction, because the regression lines intercept very close to the origin (–0.0017 for A and –0.0575 for C). This is consistent with the high Ca concentrations in litter (Table 2). P, on the other hand, is assumed to be contained in inorganic fractions to a larger degree because the regression lines intercept the P_2O_5/TiO_2 axis. This is consistent with the detection of apatite in some soil samples. The "background" P_2O_5/TiO_2 values, that are represented by the intercepts at the P_2O_5/TiO_2 axis, are not identical at sites A and C. The difference in the background values may be attributed to different P concentrations in the weathering residues of bedrock limestone at these two sites (Table 1). Concentrations of Si and Mg in the soils also appear to be influenced by organic fractions. Notably, these elements do not show the linear relationship with C_{total} since the variation of C_{total} concentrations reflects the gradual decomposition of litter (respiration); decomposition of the litter is propelled as deeper burial. Thus, the pattern shown in Figure 5b, c suggests that during the early stage of litter decomposition, Si and Mg released from the decomposed litter are not immediately washed down and away or recycled. In the case of Si, this may be explained by the retention of plant opal in soils (BIRKELAND 1983), but it is uncertain why Mg shows a similar behaviour. Although K is one of major nutrients for plants, as are Ca and P, its TiO_2-normalized values do not show any correlation with C_{total}. This can be explained by much lower concentrations of K compared with Ca in litter (Table 2). In the soils studied here, K is contained largely in inorganic fractions. In other words, the contribution of litter to the bulk K concentration is negligible.

Heavy metal enrichment. As described earlier, the Mt. Kinshozan soils are rich in Cr, Ni, Cu, Pb, and Zn. To assess the heavy metal enrichment, the enrichment factors are calculated using the following equation and shown as box plots in Figure 5:

Enrichment factor (EF) = $(Element/TiO_2)_{sample}/(Element/TiO_2)_{crust}$

The soil samples are commonly characterized by having the highest EF for Pb, followed by Cu or Zn; the EF for Cr and Ni tend to be lower at each locality.

The heavy metal enrichment is one of the most important characteristics of the Mt. Kinshozan soils. Soil, in general, is subjected to various sources of

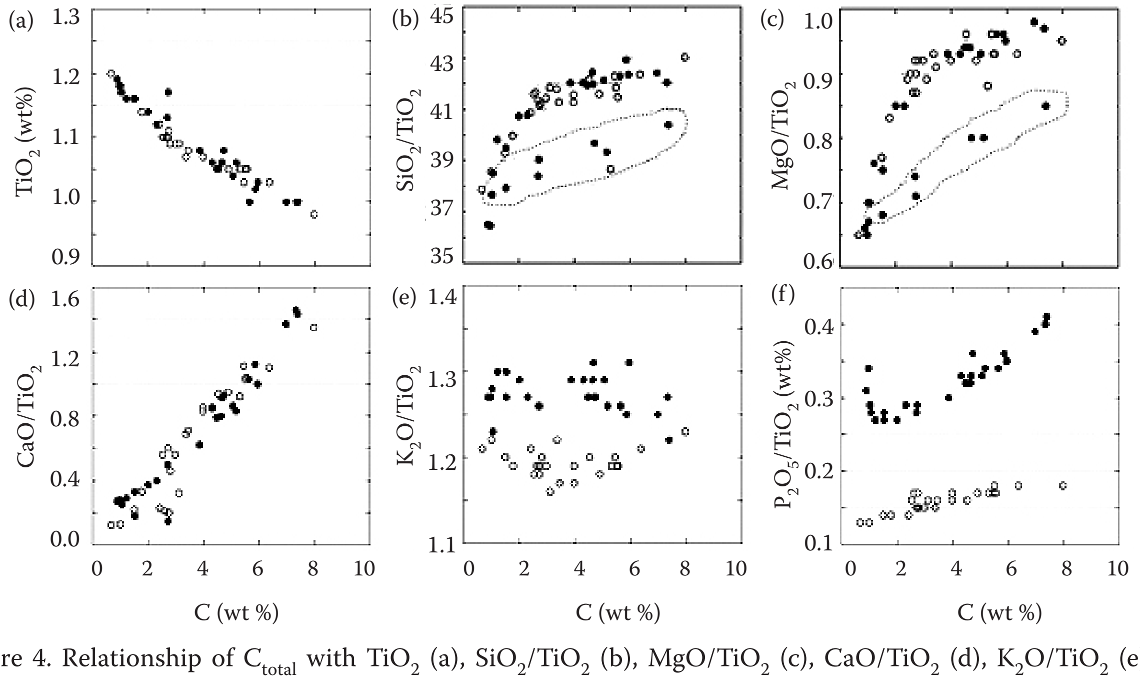

Figure 4. Relationship of C_{total} with TiO_2 (a), SiO_2/TiO_2 (b), MgO/TiO_2 (c), CaO/TiO_2 (d), K_2O/TiO_2 (e) and P_2O_5/TiO_2 (f); ●: Site A, ○: Site C

heavy metal contamination, including that from fertilizers, traffic, and factory pollution (Harrison *et al.* 1981). One of the most pronounced sources of heavy metals is vehicle-related dust (Adachi & Tainosho 2004). In the case of Mt. Kinshozan, such sources of heavy metal enrichment are negligible, as the sampling sites are located within forests and the traffic load is quite low. Since the soil is rich in organic matter derived largely from vegetation, the effect of bioaccumulation needs to be considered. However, as evident from the chemical data of litter and as assumed from the C_{total} concentrations in the soils, the effect should be negligible (Tables 1 and 2). Instead, it is most likely that heavy metals in the soils are at least partially derived from bedrock limestone. Although limestone exhibits very low heavy metal concentrations, its acid residues may be rich in heavy metals. Indeed, acid residues of Mt. Kinshozan limestone are enriched with heavy metals such as Cr, Cu, Ni, Pb, and Zn (Table 1). Retention and accumulation of residual materials during chemical weathering of limestone may have contributed, at least partially, to the high concentrations of heavy metals in the soils. The EF for Cr and Pb in the acid residues of Mt. Kinshozan limestones were much higher and lower, respectively, and the enrichment pattern of Cr, Ni, Cu, Pb, and Zn was distinct between the soils and the residues.

CONCLUSION

In this study, we performed a systematic geochemical study of soils and related materials at three sites (coniferous forest zone and broad-leaved forest zone) of the Permian limestone mountain called Mt. Kinshozan in Central Japan, which was accreted to the continent in the middle Jurassic period. The following results and implications were obtained:

(1) The Mt. Kinshozan soils are siliceous and their properties are distinct from typical calcareous soils.

(2) Compared with the composition of the Japanese upper continental crust, the soils are depleted in Si, Ca, Na, Mg, and K, but riched in Ti, Al, and Fe.

(3) Concentrations of C_{total} are nearly identical to C_{org}. The relationship between C_{total} and Element/TiO_2 suggests the presence of Si, Mg, Ca, and P. In particular, Ca in soils may be contained exclusively in organic fractions.

(4) The soils are characterized by the enrichment with certain heavy metals such as Cr, N, Cu, Pb, and Zn. The heavy metals are at least partially derived from the residual materials of limestone bedrock subjected to chemical weathering.

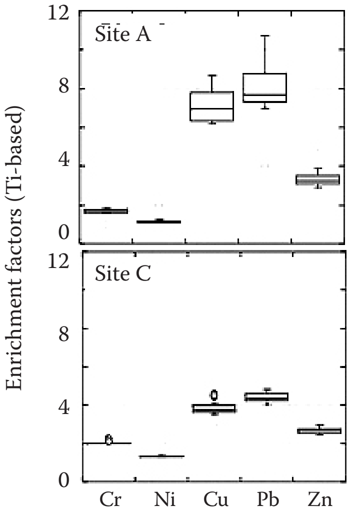

Figure 5. Box plots of enrichment factors for selected heavy metals. See the text for calculation of the enrichment factors

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