Article

Geochemical profile of soil formation from serpentinite in Sekinomiya massif, southwest Japan

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Abstract

Weathering geochemical profile of serpentinite of the Sekinomiya massif of the Maizuru Terrane, southwest Japan was examined to describe element mobility of bed rock to weathered products (soil). The geochemical compositions of the vertical profile (about 3 m length) from bed rock serpentinite to soil via relatively weathered matter showed changes of element concentrations mostly related to the decrease in Mg contents during the weathering processes. The profile can be divided into three units; C, B and A in ascending order. The unit C (over 80 cm) is serpentinite and can be subdivided into two subunits (C1 and C2) according to the development of the fractures. The unit B (90 cm) is characterized by refining of the rocks with appearance of matrix clays. This unit is characterized by loss of the original structure and by color change to dark appearance. The unit A (1.2 m) is dark color soil, of which upper part is characterized by enrichment of organic matter. Weathering trends of serpentinite to soils were examined A-CN-K and A-C-M diagrams. The CIA values change from 72.57 to 84.70 with some variation. The trend of samples on the A-CN-K diagram apparently indicates systematic change in CaO, Na_2O and K_2O, although these elements show increasing in vertical profile. The linear array in A-C-M diagram also shows change in M component (Fe_2O_3 and MgO) during weathering process. Contents of TiO_2, Al_2O_3, P_2O_5 gradually increased upward from the upper part sample of subunit C2. Significant increase of Fe_2O_3 from the unit C (9.58 wt%) to unit B (30 wt%) was apparent. Decrease of MgO contents from the unit C (almost 45 wt% in this unit) to the unit B is great, and much decrease in the unit A (7.5 wt% at the top of this unit) is characteristic of the serpentinite weathering. In accordance to this decrease in MgO, Zr, Y, Sc, Th and As contents show increasing upward. Abrupt increase in concentrations of Cr and V in the unit B is characteristic feature in this profile. This may be due to concentrations of chromian spinel during weathering process.

Key words: serpentinite, weathering, soil formation, geochemistry, Sekinomiya massif

Introduction

Weathering is the first step of sedimentary process to form clastic fragments and fine particles which will become main part of sediments or sedimentary rock. Many studies have been done for weathering process of granitic rocks (Nesbitt *et al.*, 1980; 1997), but the examination of serpentinite was rare. A good example of profile from bed rock to weathered products (soil) via weathered rock occurs in the Sekinomiya massif (Agency of Natural Resources and Energy, 1988), southwest Japan (Fig. 1). Well exposed section of this profile (Fig. 2) is useful to understand geochemical weathering of ultramafic rocks in relation to release of mobile elements and enrichment of stable elements.

Study area and Sample collection

Serpentinite in the Inner Zone of southwest Japan occurs as lenticular bodies in tectonic zone (Fig. 1) which is the plate boundary of Meso-Paleozoic terranes (Ichikawa, 1990). The Sekinomiya massif is the one of the bodies occurring along the northern margin of the Maizuru Terrane (Hayasaka, 1990) and is a member of the Yakuno ophiolite (Ishiwatari, 1990).

The Sekinomiya massif is an elongated body with about 23 km east-west direction and 5 km north-south direction (Fig. 1). A tail shaped body is attached from eastern side of the main body with 7 km length. Petrologic description of the Sekinomiya massif has not been reported, and jadeite at Kahozaka of Oya-cho was nominated as Natural Monument designated by Hyogo Prefecture.

Examined outcrop is located at Ozaki of Sekinomiya area (134° 39′ 30″, 35° 22′ 30″).

The profile in this outcrop (Fig. 2, 3) consists of three units; C, B and A in ascending order. The unit C (over 3 m) is serpentinite which can be subdivided into two subunits (C1 and C2) according to the development of the fractures. The lower subunit, C1 is almost massive serpentinite and the overlying subunit with 40 cm is fragmented serpentinite (Fig. 2). The serpentinite partly yields small fragments of olivine. The unit B (90 cm) is characterized by refining of the rocks with appearance of matrix (clays). Disappearance of the original structure became clear toward upper portion in this unit and the color changes from dark greenish grey to dark reddish grey (Fig. 2). The unit A (1.3 m) is dark reddish grey soil, of which upper part (unit A2 with 50 cm length) is characterized by enrichment of organic matter (Figs. 2, 3, 4).

Seventeen samples were collected in this profile with 15 ~20 cm interval, in 1998 (Fig. 2, Table 1).

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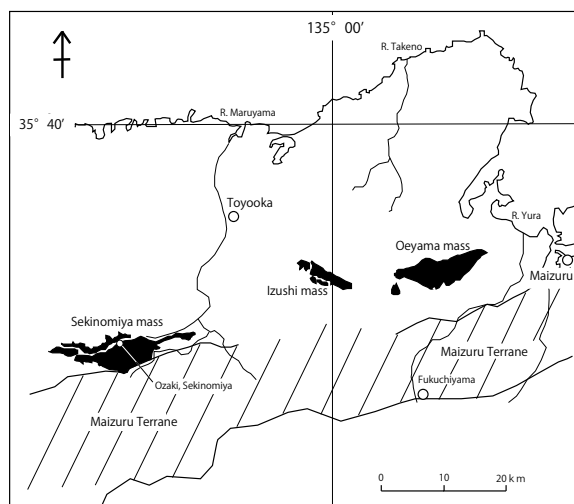
Fig. 1. Index map of the Sekinomiya massif, southwest Japan. Main ultramafic rock masses are indicated after Geological Survey of Japan, AIST (ed.), 2015. Locality of weathering profile of serpentinite at Ozaki in Sekinomiya is indicated.

Analytical procedures

All samples were analyzed by XRF, using Rigaku RIX-2000 spectrometer at Department of Geoscience, Shimane University.

Abundances of major elements (SiO_2, TiO_2, Al_2O_3, Fe_2O_3* (total iron expressed as Fe_2O_3), MnO, MgO, CaO, Na_2O, K_2O and P_2O_5) were determined on anhydrous basis, using ignited material from Loss on Ignition (LOI in Table 1). The glass beads were made using flux and ignited sample; flux ratio of 1:5. The procedure was followed to essentially that of Norrish and Hutton (1969) and followed by Sawada' method (Dr. Yoshihiro Sawada; Professor Emeritus of Shimane University).

Trace elements (As, Pb, Zn, Cu, Ni, Cr, Sr, Rb, Zr, Y, Th, Sc and TS; total sulfur) concentrations were determined by press powder briquettes method. After removal of roots and any other plant material, approximately 50 g of each sample was dried in an oven at 160˚C for 48 hrs to remove weakly-bound volatiles. The dried samples were then ground for 20 min in an automatic agate pestle and mortar grinder.

The XRF analyses were made on briquettes (about 5 g sample by a force of 200 kN for 60s), following the method of Ogasawara (1987). Average errors for all elements are less than±10% relative. Analytical results for GSJ standard JB-1a were acceptable compared to the proposed values (Imai *et al.*, 1996). Analytical results are indicated in Table 1.

Results

Geochemical compositions of serpentinite in this profile (Table 1) are characterized by significantly high contents of MgO (47.23 wt% at base), Ni (2921 ppm at base) and Cr (2618 ppm at base). SiO_2 contents do not show apparent variation in the profile ranging from 35.47 wt% in the subunit
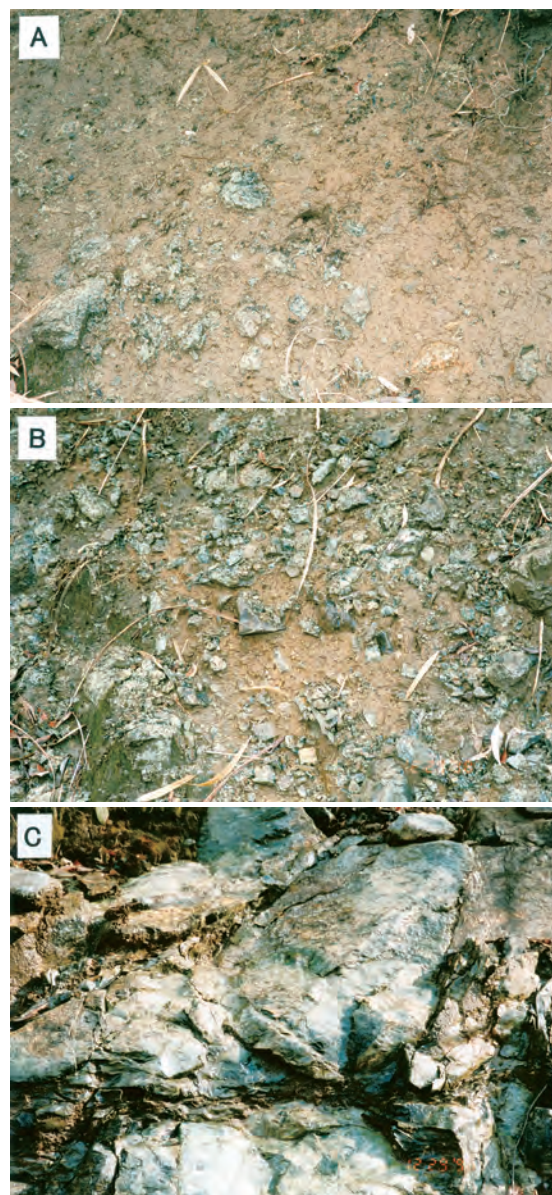
Fig. 2. Photos of serpentinite-soil profile of Sekinomiya massif, southwest Japan.
A; soil of weathered serpentinite, unit A1 (upper right) and upper part of unit B (lower left), B; fragmented weathered sertentinite and soil (lower part of unit B) and serpentinite (unit C1).

C2 to 50.21 wt% at the top sample of the profile (Table 1). Contents of Fe_2O_3 show great increase in the subunit C2 (30.06 wt%) and have high concentrations to the top sample with some variations. Contents of TiO_2, Al_2O_3, P_2O_5 gradually increased upward from the upper part sample of subunit C2. Zirconium, Y, Sc, Th and As contents show increasing upward.

Discussion and Conclusion

Weathering profile in A-CN-K and A-C-M diagrams

The intensity of weathering is indicated by Chemical

Table 1. Analytical results of serpentinite-soil profile of Sekinomiya massif, southwest Japan.

samples	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	LOI	CIA	As	Pb	Zn	Cu	Ni	Cr	V	Sr	Rb	Zr	Y	Th	Sc	TS
1	42.32	0.01	0.15	9.82	0.19	47.23	0.27				12.40		1	6	45	1	2921	2618	66	3	8	17	3	2	7	383
2	41.52	0.01	0.14	10.83	0.15	47.27	0.08				12.47		2	6	86	5	3068	2754	63	4	5	16	2	1	8	346
3	41.82	0.00	0.29	10.74	0.19	46.48	0.48				12.23		2	6	44	5	3229	2872	73	4	8	19	4	2	6	400
4	39.89	0.02	0.32	14.42	0.14	45.14	0.07				11.94		2	6	51	29	6127	2204	78	3	6	18	3	1	4	322
5	35.47	0.19	5.19	30.06	0.22	28.01	0.45	0.14	0.27	0.02	9.78	80.18	3	8	93	32	3728	5228	237	11	16	34	7	3	12	326
6	36.03	0.38	7.44	29.98	0.19	24.50	0.68	0.39	0.39	0.02	9.85	76.86	4	9	106	33	3233	7923	261	27	18	49	10	4	12	332
7	42.46	0.41	9.15	21.63	0.25	23.97	0.85	0.67	0.59	0.02	9.14	73.84	5	11	92	28	3441	4065	188	57	27	69	12	4	9	353
8	38.16	0.63	9.25	31.35	0.21	18.11	1.05	0.59	0.63	0.02	7.61	72.57	5	11	108	26	2631	8785	309	36	25	69	12	5	11	355
9	40.38	0.44	9.78	25.84	0.23	21.30	0.79	0.60	0.61	0.03	8.84	76.40	6	11	96	23	3046	4964	239	45	28	69	14	5	12	363
10	41.11	0.47	10.44	25.12	0.22	20.37	0.88	0.70	0.65	0.03	7.59	75.49	6	11	95	26	2970	4585	223	56	30	78	14	6	6	376
11	37.67	0.58	13.40	33.81	0.20	12.07	0.70	0.71	0.81	0.04	7.97	80.73	6	12	113	30	2396	7126	324	43	30	81	14	5	9	420
12	40.75	0.69	12.84	32.59	0.19	10.52	0.62	0.80	0.95	0.04	7.15	79.23	6	12	103	28	2103	6741	314	41	36	92	16	6	6	406
13	42.27	0.71	13.93	30.26	0.17	10.16	0.60	0.88	0.97	0.05	7.61	80.06	5	13	124	17	1859	5594	291	45	33	128	18	6	9	404
14	45.00	0.78	14.95	27.01	0.16	9.52	0.66	0.94	0.92	0.05	7.80	80.54	6	13	122	13	1924	4725	274	47	30	140	22	7	15	417
15	46.15	0.80	15.51	23.87	0.13	11.13	0.72	0.85	0.77	0.06	10.30	82.05	7	15	114	18	2130	3782	240	47	28	140	24	7	8	561
16	49.42	0.95	20.81	19.93	0.09	6.05	0.81	1.03	0.81	0.11	13.65	84.70	10	18	105	22	2178	2757	219	62	29	176	29	9	13	809
17	50.21	0.81	17.07	21.45	0.10	7.84	0.84	0.89	0.70	0.10	11.88	82.92	8	15	117	17	2270	3057	230	66	25	134	20	7	7	561

Index of Alteration (CIA) (Nesbitt and Young, 1984; 1989). The CIA value is calculated using molar proportions by the formula:

CIA=[Al2O3/(Al2O3+CaO*+Na2O+K2O)]x100 where CaO* is detrital CaO without apatite compositions (Fedo *et al.*, 1995). The CIA values increased from sample 7 of unit B (73.84) to the top sample 17 of unit A (82.92) with same variation (Table 1). The samples 5 and 6 have relatively higher values (80.18 and 76.86), even they are in the top of the unit C2 and base of the unit B. The weathering trend is indicated on the A-CN-K diagram (Fig. 5), of which plots show linear array from serpentinite to soils. Although the concentrations of CaO, Na2O and K2O are quite lower values for serpentinite, this trend indicates possible feldspar weathering in serpentinite.

Considering mafic elements mobility during the weathering, the A-C-M ternary plot (Nesbitt and Young, 1989) was examined. This diagram is drawn by apex A (Al2O3), C (CaO+Na2O+K2O) and M (Fe2O3+MgO) (Fig. 5) of which elements are given as molar values. The weathering trend from serpentinite to soil is more clearly indicated on this diagram, namely, the compositional array occurs from M corner to some composition along A-M join. This is suggestive of serpentinite weathering profile of gradual decrease of Fe2O3+MgO.

Vertical profile of weathering of serpentinite

To evaluate variation of elements during the weathering processes, the vertical profiles of elements which are normalized by the compositions of sample 1 of the unit C1 base are indicated (Fig. 3 for major elements, and Fig. 4 for trace elements). Apparent decrease is indicated for MgO (Fig. 3) as described concentration of this elements (Table 1). Contrastingly other major elements show increasing toward the top of unit A, excluding of MnO. Among these compositional changes, Al2O3, Fe2O3 and Na2O show significant increase in accordance with the decrease of MgO profile. Fe2O3 shows abrupt increase in unit B, but has gradual decrease toward the top sample in unit A, suggesting solution of iron in soil formation. The weathering trend in the A-C-M diagram was suggestive of decrease of Fe2O3+MgO, but MgO release can be a considerable change from the sample 5 of top

of C2. It can be said that MgO release was significant for compositional changes and properties of material (Bucher *et al.*, 2015) in the weathering process. Also refining and soil formation may concentrate finer minerals such as spinel and related iron minerals, thus Cu, Cr and V increased in C2 unit and within unit B. Serpetinized ultramafic rocks produce serpentine and brucite, and magnetite, of which Fe cannot be substituted in serpentine. The transformation of this process is significant for engineering geology for breakdown of rocks and alteration to soils (Umetsu, 1995; Katoh *et al.*, 2011; Undul and Tugrul, 2012). Magnesium is a main component of serpentine (Mg3Si2O5 (OH)4) and brucite (Mg (OH)2), and Mg can be release to pore water or grand water (Nakao *et al.*, 2011) during weathering. Contrastingly Fe is relatively immobile, if Fe was contained in magnetite.

As for the profile of trace elements (Fig. 4), Sr, Zr, Y, As Cu, Cr and V show considerable increase. Cupper content in serpentinite was low (1 pm) which abrupt increase in sample 4 of the top of the C1 unit.

Compositional changes from serpentinite to soils

To describe compositional changes by weathering process, the cross plot of concentrations of serpentinite (basal sample of unit C1) and soil (top sample of unit A) was given (Fig. 6). The plots in the area above the 1:1 line on this diagram are elements increased during the weathering. Aluminum, Ti and P lie significantly above the line, and Na, Zr, Sr, Y, Cu and As are also enriched. Silica and Fe also enriched among the higher contents of major elements (Fig. 6). The elements decreased were Mg, Ni, Mn suggesting solution of these elements during weathering process. Magnesium could be originally abundant in olivine and related minerals, thus decomposition of these minerals was considerably important in serpentinite weathering.
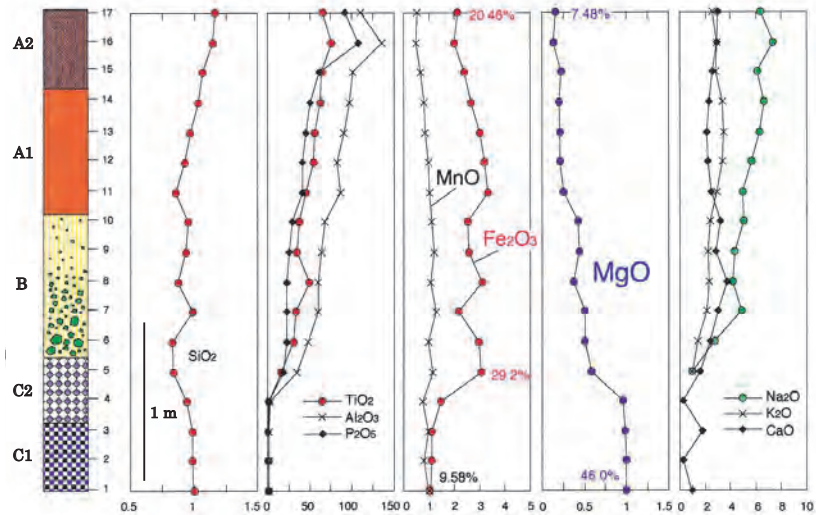
Fig. 3. Vertical changes of major elements in serpentinite-soil profile of Sekinomiya massif, southwest Japan. Plot data used normalized values by concentrations of basal sample of serpentinite in unit C1.
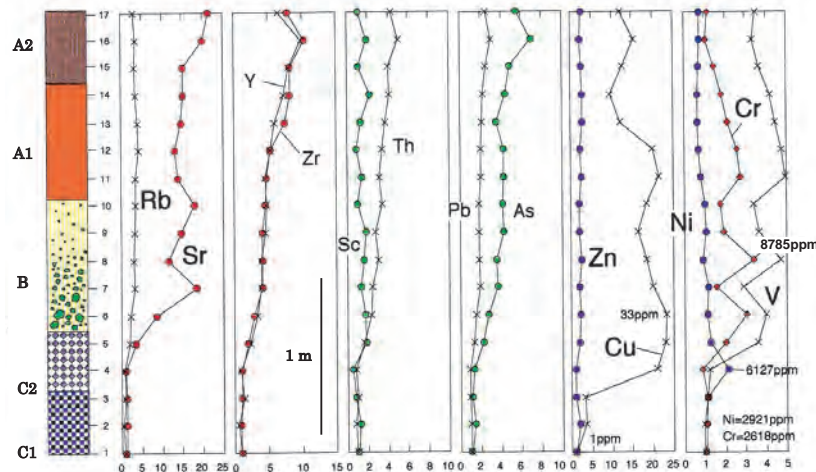
Fig. 4. Vertical changes of trace elements in serpentinite-soil profile of Sekinomiya massif, southwest Japan. Plot data used normalized values by concentrations of basal sample of serpentinite in unit C1.
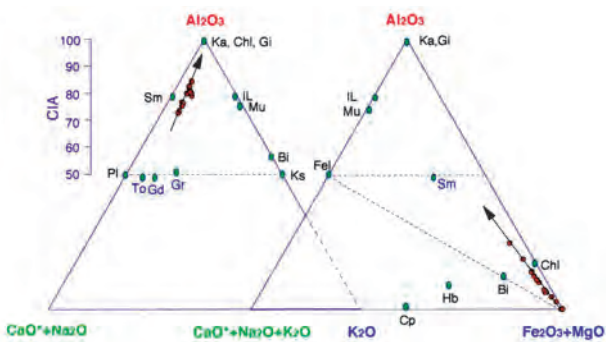
Fig. 5. A-CN-K and A-C-M diagrams for evaluation of serpentinite weathering of Sekinomiya massif, southwest Japan (see text).
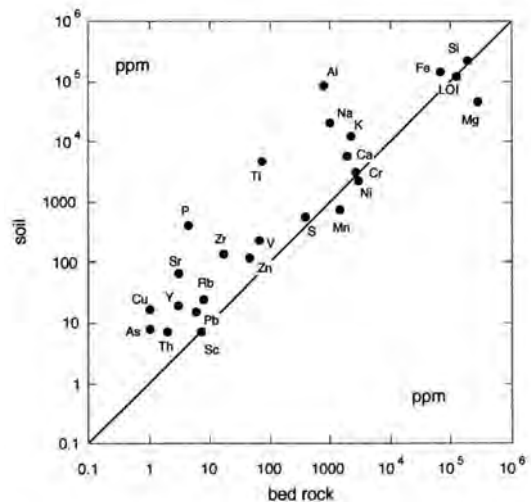
Fig. 6. Cross plot of geochemical contents of sepentinite (bed rock, base of unit C1) and soil (top of unit A) for examination of compositional changes by weathering process.

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（要　旨）

石賀裕明，2016．西南日本の関ノ宮岩体における蛇紋岩の土壌化に伴う地球化学的変化．島根大学地球資源環境学研究報告，34，89-93．

　　西南日本舞鶴帯の関ノ宮岩体の蛇紋岩において，風化作用による土壌化にともなう地球化学的組成の変化を検討し，母岩から風化産物（土壌）までの元素の移動を記述した．蛇紋岩からやや風化した岩石をへてその上位の風化産物までの断面は 10 m あり，元素組成の変化は MgO の存在量の減少に関連して変化する．この断面は岩相の特徴から上位から A, B, C の 3 ユニットに区分される．ユニット C は蛇紋岩の層で（厚さ 3 m 以上），劈開に沿った割れ目の発達によって 2 亜ユニットに区分される．ユニット B（90 cm）は風化による細粒化が進み，基質は粘土である．ユニット B は上方に向けてさらに初生の岩石構造が消滅し，破片化するとともに暗色に変化する．ユニット A は細粒化と有機物との混合が進んだ土壌である（厚さ約 1,2 m）．このユニットの上部は暗赤褐色を呈しさらに有機物量が増加する．

　　風化の程度を示す CIA 値は 72.57 から 84.70 まで変化しながら増加する．また，A-CN-K ダイヤグラムでは試料のプロットがトレンドを形成して，風化過程での系統的な組成変化を示す．さらに、A-C-M ダイヤグラムでは M から始まるトレンドを示し，この組成の減少を示す．しかし，Fe_2O_3 は分析値の垂直変化では逆に増加するので、このトレンドは MgO を含む鉱物の溶解によって形成されたことがわかる．

　　TiO_2, Al_2O_3, P_2O_5 などはユニット C2 から上方に向け次第に増加する．Na_2O, K_2O, CaO 等のほとんどが 1 wt% 以下と低い．Fe_2O_3 はユニット C（最下位の試料は 9.58 wt%）からユニット B（約 30 wt%）へと有意に増加する．MgO はユニット C（45 wt% 前後で変化しないが）からユニット B をへてユニット A（最上部試料で 7.5 wt%）では著しく減少する．MgO の著しい減少に関連して Zr, Y, Sc, Th, As などは上方の試料で増加する．Cr, V はユニット B で濃縮率の増加が顕著で，風化作用によるクロムスピネルの濃縮を示唆する．