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Geochemistry of Paleosols Formed under Oxic and Anoxic Conditions in Babeldaob Island, Palau

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Abstract

Two different types of paleosols (laterite vs. kaolinite types), developed on Eocene volcanic rocks in the Babeldaob Island, Palau, were examined in order to understand the behaviors of elements during soil formation under different redox conditions.

Laterite type paleosol on the Aimiliki volcanic rock was formed under ordinal atmospheric (oxic) condition. Si, Al, Mg, V, Fe, Mn, Cu, Co, Ni, Zn and Ge were leached out from the upper zone. It is noticeable that Fe is dissolved even under oxic condition. REEs increase slightly with advancing weathering. Th and U typically increase. Other elements show rather complicate pattern. On the other hand, kaolinite type paleosol on agglomerate and tuff of the Babeldaob volcanics might develop under anoxic condition, because the overlying lignite formation has absorbed the atmospheric oxygen from penetrating meteoric water. Many elements generally decrease upward, with the enrichment in the middle section. It is suggested that these elements have moved downward during the weathering. The most mobile elements such as K, Mg and Rb decrease uniformly upward in the section.

From the behaviors of relatively immobile elements, low pH as well as high P_{O_2} conditions were predicted for the laterite type paleosol developed on the Aimiriki volcanics, and slightly higher pH as well as lower P_{O_2} conditions for the kaolinite type paleosol on the Babeldaob volcanics. The Palauan data are compared with the Paleozoic and Precambrian paleosols reported previously. The comparison supports the suggestion made from the Pronto paleosol(NEDACHI *et al*., 1998) that the atmosphere at the Archean-Proterozoic boundary era was already oxic.

keywords:paleosol, geochemistry, Palau, laterite type, kaolinitetype.

Introduction

Soils develop in direct contact with the atmosphere, and weathering is a chemical reaction between meteoric water equilibrated with atmospheric gases, and rocks. Therefore, the soil chemistry is strongly affected by the atmospheric compounds such as carbon dioxide and oxygen gases. Paleosols have attracted attentions to many researchers to understand the ancient Earth’s environment, because the mineralogy and chemistry of paleosol were shaped in larger part by the contemporaneous atmosphere (HOLLAND, 1984). Especially, the loss or retention of Fe from paleosols has been used as a guide for the paleo atmospheric oxygen level (e.g., HOLLAND, 1984). Because ancient paleosols have been modified to various degree by various processes (diagenesis, metamorphism, and hydrothermal alteration) during their long history, however, it has been disputed as to whether the loss of Fe has occurred by anoxic weathering, by dissolution by organic acid, or by hydrothermal leaching (OHMOTO, 1996). Hence, the recent soils and young paleosols provide valuable information on the behaviors of various elements during soil formation. In this study, two contrasting types (laterite and ka-

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olinite types) of young paleosols developed on Paleogene volcanic rocks were studied.

Palau (Republic of Belau) is situated in the tropical zone and is composed of many islands, which construct a volcanic island arc between the Pacific and Philippine plates. Each island is enclosed with lagoons and reefs. Soils and paleosols are observed everywhere. Among them, relatively older weathering profiles were selected for this study. Weathering profiles of the kaolinite-montmorillonite type have often developed beneath the sediments in damp ground areas of Miocene age. As the overlying sediment contains many thin lignite beds, weathering might have proceeded under a reduced condition. A laterite type paleosol is also studied to compare the elemental behaviors during weathering under different redox conditions. The comparisons are expected to provide useful information in interpreting much older paleosol data, especially in attempt to put constraints on the atmospheric oxygen level during Precambrian.

Geological Outline of Babeldaob Island

Babeldaob Island, Palau, is comprised mainly of the volcanic rocks, lagoon sediments and coral reef. The volcanic rocks of Babeldaob Island erupted during Eocene and Oligocene, and debilitated at late Oligocene (TAYAMA, 1952). The volcanic rocks occur as lava, agglomerate, volcanic breccia, tuff breccia and tuff, with the composition of olivine basalt, hornblende-bearing two-pyroxene andesite and clinopyroxene hornblende dacite. These volcanic rocks are grouped into three formations; the Babeldaob volcanics (early Eocene), Aimiriki volcanics (late Eocene) and Almonagui volcanics (Oligocene) (TAYAMA and SHIMAKURA, 1937; TAYAMA, 1952). The SiO_2 contents of the volcanic rocks vary widely from 47% to 67%.

There are two types of volcanism; olivine tholeiite series and calc-alkaline series. NEDACHI *et al.*, (1996) described the trace element geochemistry of the volcanic rocks, and suggested that the volcanism was similar to those of the other island arc systems in the West Pacific region, especially that of the Mariana island arc system (TATSUMI *et al.*, 1983). The Palauan volcanism is characterized by the coexisting of two rock series, back-arc and front-arc series, in spite of the limited space and time. The patterns of the Babeldaob volcanics are similar to those in the back arc side of other island arc systems (TATSUMI *et al.*, 1983; YOSHIDA *et al.*, 1995). On the other hand, the Aimiriki agglomerate is similar to those in the volcanic front zone. Associated with these volcanisms, a small scale Zn-Au mineralization is observed in the southeastern end of Babeldaob Island. MILLER *et al.* (1987) pointed out that hydrothermal alteration in and near the veins was of neutral pH and potassic type. NEDACHI *et al.* (1996), from a fluid inclusion study, predicted the temperatures of about 320°C and the depth of about 1 km for the conditions of hydrothermal mineralization, and suggested that the main uplift movement was finished in Neogene.

The Galdog bed is found between the Babeldaob and Aimiriki volcanics in the northern area of Babeldaob Island. The Airai formation (Miocene) is scattered along the coastal line. The formation contains many thin lignite beds, which suggest that the formation has developed in damp grounds changed from lagoonal conditions in Miocene.

Weathering profiles of volcanic rocks are observed everywhere in Babeldaob Island. There are two types of paleosol. Laterite type weathering is well recognized everywhere, and kaolinite-montmorillonite type weathering is only beneath the Airai formation. The kaolinite type paleosol beneath the lignite formation changes gradually to the laterite type paleosol in the areas not overlain by lignite formation. Among many paleosols in Babeldaob Island, two places shown in Fig. 1 were selected for this work.

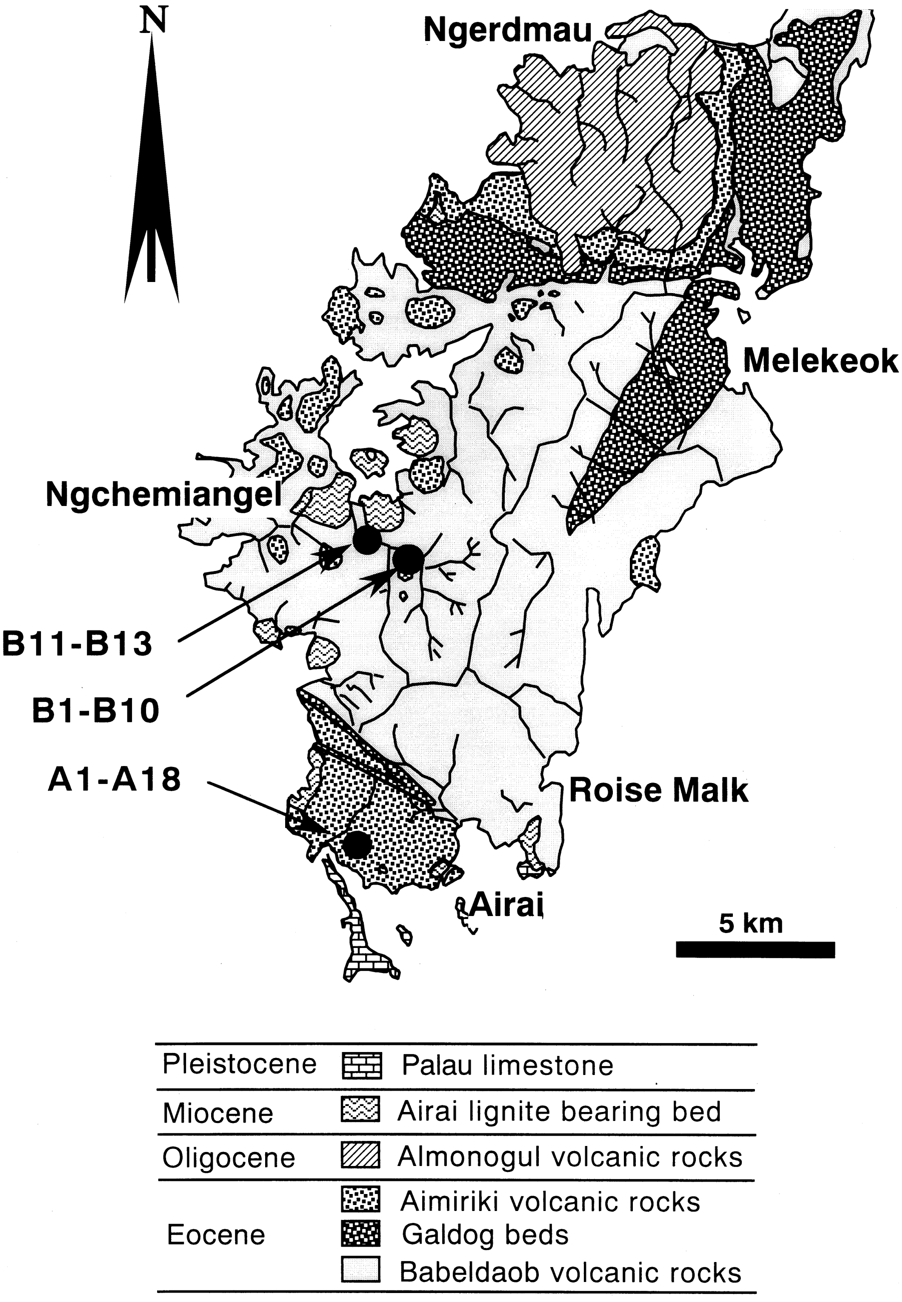


Fig 1. Geological map of the Babeldaob island, Palau, and sampling sites.

Sampling Sites

The samples, A1 to A18, were collected from the southern end of Babeldaob Island. Along the road, a steep road-cut exposes a clear profile of weathering. As shown in Fig. 2, the paleosols have developed on the Aimiriki volcanic rocks, and are overlain by a recent terrace deposit. The zonal arrangement, from the onion structure of fresh andesitic basalt, through yellowish colored layer, to reddish brown colored layer and to black colored paleosol is easily recognized on the section. All the layers without the crust of onion structure are almost unconsolidated. The upper part of the section is slightly eroded out and changed to modern soil. The boundary between the modern soil and paleosol is obscure. The fresh rock is an agglomerate with basaltic to andesitic composition, and contains olivine, clinopyroxene, orthopyroxene and plagioclase, with miner amounts of magnetite, apatite and others. According to X-ray diffraction analyses, Mg-chlorite, illinite, feldspar, epidote and other minerals are recognized in the paleosol near the fresh rock side, and kaolinite, carbonate, rutile, goethite, hematite and others are detected from the middle to upper parts of the paleosol. The mineral assemblage suggests that the weathering has proceeded under oxic environment. The cliff is almost vertical, and the distance from the terrace almost corresponds to the depth from the paleo-surface. The samples were collected along two traversed lines on the wall.

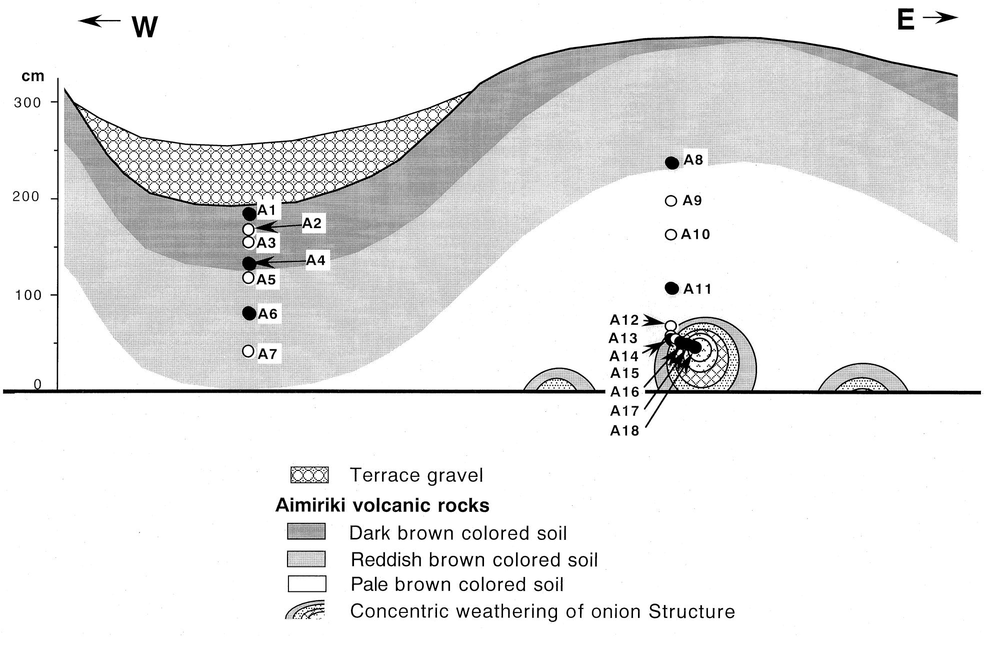


Fig 2. Schematic cross section of the paleosols on the Aimiriki volcanic rocks of Eocene Age, Babeldaob Island, Palau. Open and solid circles represent the location of the samples of which major, and major and trace elements were analyzed, respectively.

Another sampling site is located 10 km north of the first sampling site, where the samples, B1 to B10, were collected. A sketch of the sampling site is shown in Fig. 3. An agglomerate and tuff of the Babeldaob volcanics were weathered to form a paleosol. The Airai formation of

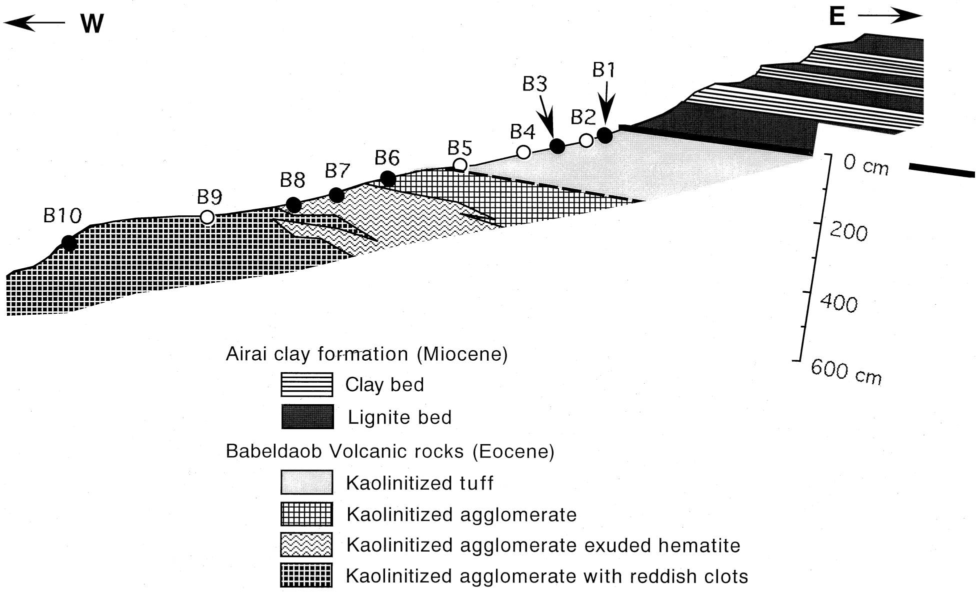


Fig 3. Schematic cross section of the paleosols on the Babeldaob volcanic rocks of Eocene Age, overlain by the lignite bearing Airai formation of Miocene Age, Babeldaob Island, Palau. Open and solid circles represent the location of the samples of which major, and major and trace elements were analyzed, respectively.

lignite-clay alternation overlies the volcanics and paleosol.

Kaolinite has dominantly formed in the paleosol. Illinite, quartz, rutile, hematite and others are also detected in the paleosol. Smectite is found in some of the sample. In spite of the intense mineralogical change, the original texture of phenocryst and other rock texture have clearly remained. The evidences suggest that the paleosol did not rework, and that both the tuff and agglomerate were weathered in situ. It might be better to call as “saprolith”. The paleosol is strongly removed the color as a whole, but shows spotted hematite red at the lower part. The hematite reddish color decreases toward the paleo-surface, and in the middle part of the outcrop, another hematite shows an irregular banded texture. The upper 200cm of the section is comprised mostly of homogeneous white colored kaolinite. The texture gradually disappears to be completely homogeneous at the top (about 20cm) of the section.

The age of the Airai formation is Miocene. There are three possible stages of weathering: 1) before deposition of the Airai formation under atmospheric (oxic) condition, 2) during and/or after the deposition of the Airai formation under anoxic condition, and 3) modern weathering. The land utilization by modern human suggests that the modern weathering might be only hematitization. The geological evidence suggests that the weathering proceeded at the stage of deposition of the Airai formation or much later. The existence of lignite in the Airai formation shows that the weathering has proceeded under anoxic environment (STUMM and MORGAN, 1981). The bedding of the lignite formation is slightly dipping toward south, and surface declines toward west. The parent fresh rock can not be observed in this section. The closest outcrop of fresh rock is 1.3 km north from the sampling site (Fig. 1). The samples, B11 to B13, collected from this outcrop, are regarded as parent rocks of the kaolinite type paleosol. The fresh rock is basaltic andesite of calc-alkaline rock series, and the main rock-forming minerals are plagioclase, clinopyroxene and orthopyroxene. Sometimes olivine or hornblende is observed. Magnetite, ilmenite and apatite are included as minor minerals.

Residual Elements in the Paleosols

The compositions of major and trace elements were obtained, using X-ray fluorescence method, ICP mass spectrometry and other methods. The results are shown in Tables 1 and 2. The changes of concentratios of major elements during weathering are shown in Fig. 4. The chemical behaviors roughly coincide with the microscopic observation and X-ray diffraction data. For example, the chemical profile of the laterite type paleosol differs from that of the kaolinite type paleosol. The chemical profile of major elements such as the decreases of MgO, Na2O and CaO coincides to the decomposition of major minerals such as plagioclase and pyroxene. In the section of kaolinite type paleosol, the chemical discontinuity corresponds to the boundary of tuff and agglomerate.

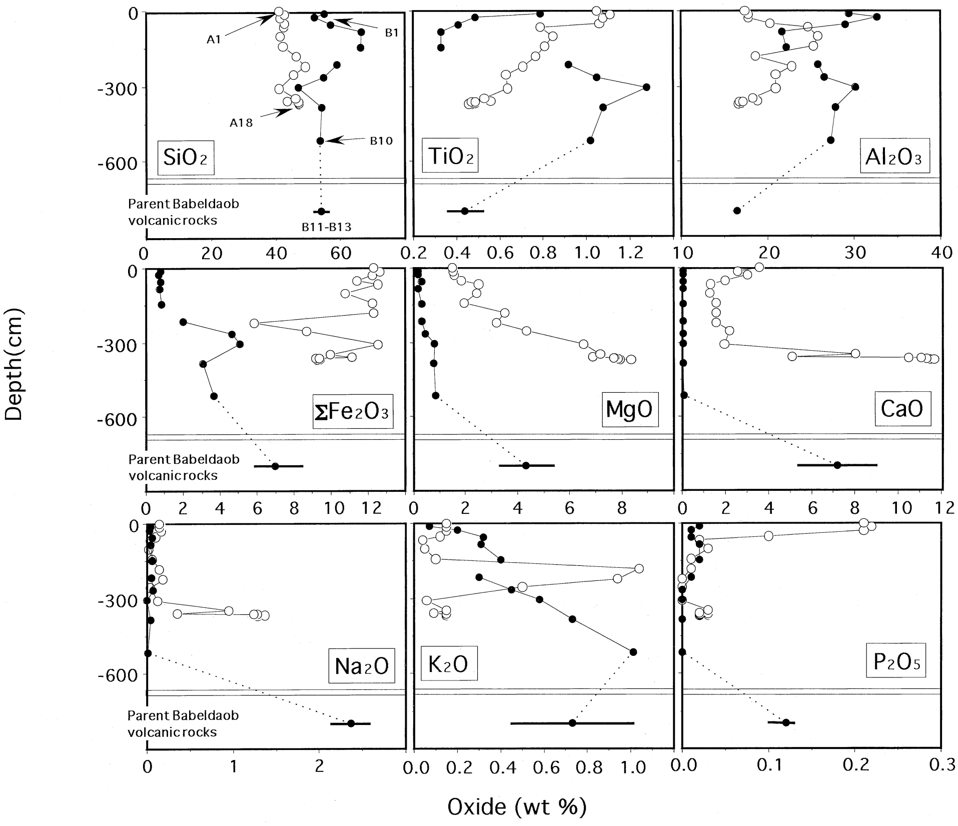


Fig 4. Variation of the contents of major element of the paleosols from Palau. Open and solid circles represent the paleosols on the Aimiriki volcanic rocks and on the Babeldaob volcanic rocks, respectively. The bar represents the deviation among three fresh samples.

Table 1. Compositions of major elements of the paleosols from Palau (wt%)

Formation	Aimiriki volcanic rocks										
Rock	Dark brown paleosol				Reddish brown paleosol				Pale brownish paleosol		
Sample No.	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11
Original No.	9510221	9510222	9510223	9510224	9510225	9510226	9510227	9510229	95102210	95102211	95102212
Depth (cm)	2	16	30	52	67	103	143	180	220	255	310
SiO2	41.33	42.79	41.62	42.87	42.53	41.63	42.48	46.51	49.32	45.58	41.25
TiO2	1.05	1.11	1.08	1.06	0.79	0.85	0.81	0.77	0.71	0.63	0.64
Al2O3	17.43	17.82	17.81	20.38	24.78	25.85	25.40	18.68	22.90	20.93	20.93
Fe2O3	12.27	12.62	12.22	11.41	12.52	10.76	12.23	12.27	5.85	8.70	12.54
MnO	0.14	0.16	0.16	0.11	0.10	0.08	0.12	0.07	0.04	0.21	0.17
MgO	1.51	1.52	1.56	1.83	2.50	2.44	1.95	3.52	3.20	4.37	6.54
CaO	3.60	2.58	3.07	2.01	1.34	1.29	1.59	1.60	1.59	2.20	1.97
Na2O	0.15	0.15	0.17	0.10	0.04	0.02	0.06	0.15	0.19	0.04	0.13
K2O	0.15	0.15	0.15	0.12	0.04	0.05	0.10	1.04	0.94	0.50	0.06
P2O5	0.21	0.22	0.21	0.10	0.02	0.03	0.01	0.01	tr	tr	tr
LOI	22.78	n.d.	n.d.	20.25	n.d.	18.59	n.d.	17.37	n.d.	n.d.	17.45
Total	100.62	79.11	78.04	100.24	84.66	101.57	84.74	101.97	84.74	83.16	101.67

Formation	Aimiriki volcanic rocks						
Rock		Skin of onion structure of basalt				Fresh basalt	
Sample No.	A12	A13	A14	A15	A16	A17	A18
Original No.	95102213	95102214	95102215	95102216	95102217	951022181	951022183
Depth (cm)	350	360	364	364	366	369	370
SiO2	46.20	43.73	47.13	47.09	47.30	47.45	47.40
TiO2	0.53	0.56	0.49	0.47	0.49	0.46	0.47
Al2O3	18.33	18.86	17.21	16.80	16.98	16.67	16.71
Fe2O3	9.97	11.12	9.39	9.18	9.40	9.29	9.40
MnO	0.14	0.20	0.14	0.14	0.15	0.15	0.15
MgO	7.17	6.90	7.69	7.75	7.87	7.93	8.37
CaO	8.01	5.10	10.51	11.07	11.35	11.65	11.50
Na2O	0.95	0.36	1.24	1.29	1.37	1.29	1.38
K2O	0.15	0.09	0.15	0.15	0.15	0.15	0.15
P2O5	0.03	0.02	0.03	0.02	0.03	0.02	0.02
LOI	n.d.	n.d.	6.46	n.d.	5.01	5.07	4.73
Total	91.48	86.93	100.42	93.94	100.08	100.13	100.30

Babeldaob volcanic rocks		
Kaolinitized tuff		
B1	B2	B3
95102613	95102612	95102611
10	25	55
55.29	52.17	57.02
0.79	0.49	0.41
29.42	32.69	28.98
0.76	0.67	0.80
0.01	0.01	0.01
0.16	0.19	0.30
0.04	0.03	0.04
0.04	0.03	0.06
0.07	0.20	0.32
0.02	0.01	0.01
13.54	n.d.	11.99
100.15	86.50	99.94

Formation	Babeldaob volacanic rocks									
Rock	Kaolinitized tuff		Kaolinitized aggromerate with reddish clots					Fresh andesite		
Sample No.	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13
Original No.	95102610	9510269	9510268	9510267	9510266	9510265	9510264	9510236	9510233	9510232
Depth (cm)	85	145	215	265	305	385	515	(other place)		
SiO2	66.70	66.36	58.98	54.93	47.13	54.25	53.84	52.10	56.96	57.59
TiO2	0.33	0.33	0.92	1.05	1.28	1.08	1.02	0.56	0.44	0.35
Al2O3	21.72	22.26	25.91	26.65	30.20	27.90	27.39	15.81	18.59	16.41
Fe2O3	0.74	0.81	2.02	4.65	5.07	3.07	3.67	9.16	6.78	5.55
MnO	0.01	0.02	0.01	0.01	0.02	0.02	0.02	0.16	0.16	0.18
MgO	0.19	0.31	0.30	0.44	0.81	0.75	0.85	5.88	4.39	3.06
CaO	0.05	0.05	0.04	0.04	0.03	0.05	0.07	9.87	6.68	5.51
Na2O	0.04	0.06	0.05	0.07	0.00	0.04	0.01	2.06	2.53	2.69
K2O	0.31	0.40	0.30	0.45	0.58	0.73	1.01	0.79	0.33	1.10
P2O5	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.09	0.13	0.13
LOI	n.d.	9.26	11.18	11.69	14.55	n.d.	12.63	n.d.	n.d.	n.d.
Total	90.11	99.88	99.72	100.00	99.66	87.88	100.51	96.46	97.00	92.57

Table 2. Compositions of trace elements of the paleosols from Palau (ppm)

Formation	Aimiriki volcanic rocks									Babeldaob volcanic rocks									
Sample No.	A1	A4	A6	A8	A11	A14	A16	A17	A18	B1	B3	B5	B6	B7	B8	B10	B11	B12	B13
Sc	50	61	75	54	55	45	47	40	40	16	7	6	20	25	27	28	n.d.	n.d.	n.d.
V	345	422	510	406	369	334	349	333	353	130	12	n.d.	171	256	268	221	210	85	89
Cr	416	469	505	279	298	344	333	327	312	246	13	n.d.	15	16	21	16	173	34	26
Co	36.4	38.9	44.6	49.1	48.1	62.8	56.0	56.6	70.5	5.7	3.6	12.2	22.5	6.4	6.0	10.6	137.9	25.5	43.5
Ni	76	100	149	108	145	114	123	122	124	23	19	n.d.	n.d.	8	15	30	n.d.	20	n.d.
Cu	56	96	260	102	258	167	216	163	162	21	8	12	7	30	17	19	51	6	n.d.
Zn	74	78	100	122	104	85	86	86	90	14	10	15	35	56	41	62	n.d.	99	n.d.
Ga	16	19	21	18	18	18	16	15	16	31	25	19	26	22	35	27	14	18	17
Ge	1.9	1.4	1.3	2.9	1.8	1.3	1.4	1.3	1.3	3.2	1.6	1.3	1.4	1.8	1.9	2.0	1.1	1.5	1.1
Rb	2.35	2.24	1.14	6.76	1.03	1.51	1.37	1.50	1.59	3.53	11.99	13.86	9.43	11.75	19.96	35.03	10.09	4.70	13.49
Sr	182.2	99.2	44.3	82.0	147.5	139.9	137.2	136.3	137.6	4.7	4.4	6.0	3.1	2.5	1.9	6.0	294.3	279.8	274.1
Y	19.6	18.6	16.5	19.0	11.1	11.0	11.3	10.8	11.0	27.9	21.3	24.5	17.9	10.0	16.8	11.7	17.3	18.5	20.3
Zr	39	39	28	37	21	16	16	15	16	326	253	226	146	160	224	157	61	105	111
Nb	0.64	0.53	0.28	0.40	0.19	0.11	0.13	0.09	0.11	7.06	6.11	5.27	2.83	3.52	4.25	3.36	0.92	3.33	3.15
Sn	0.8	0.6	0.6	1.0	0.5	0.9	0.3	0.3	1.0	1.4	1.5	1.0	0.9	1.3	1.5	1.4	1.0	0.6	0.5
Sb	0.50	0.72	0.07	0.30	tr	tr	tr	tr	tr	0.17	tr	tr	tr	tr	0.04	0.33	0.12	0.20	tr
Cs	0.20	0.12	0.07	0.18	0.04	0.03	0.05	0.05	0.05	0.39	0.90	0.51	0.27	0.44	0.59	0.69	0.38	0.20	0.47
Ba	37.3	29.8	18.1	85.4	85.9	22.0	19.5	19.4	20.8	9.5	7.1	9.7	12.6	13.5	9.1	11.1	101.0	46.0	127.4
La	2.83	2.53	1.46	1.78	1.03	0.87	0.86	0.79	0.91	7.77	13.29	52.66	24.84	14.11	3.26	13.94	4.70	7.71	9.12
Ce	6.90	6.47	3.31	3.07	2.76	2.33	2.13	2.12	2.29	11.23	11.11	53.88	34.21	21.53	6.79	31.02	10.83	18.89	21.33
Pr	0.99	0.86	0.59	0.60	0.38	0.36	0.38	0.37	0.40	2.01	2.03	9.10	6.06	2.96	0.71	2.91	1.31	2.07	2.41
Nd	6.14	5.72	3.66	3.75	2.50	2.60	2.45	2.48	2.59	9.41	8.90	38.09	26.68	12.47	3.99	13.09	7.86	10.93	12.67
Sm	2.02	2.01	1.60	1.35	1.02	0.92	1.00	0.97	1.07	2.54	1.91	5.50	4.08	1.69	0.83	1.73	2.21	2.61	2.84
Eu	0.66	0.60	0.50	0.48	0.36	0.40	0.36	0.38	0.41	0.49	0.34	1.59	1.11	0.31	0.21	0.41	0.71	0.93	0.85
Gd	1.59	1.58	1.28	1.03	0.88	0.87	0.80	0.74	0.81	1.91	1.45	3.55	2.37	1.25	0.75	1.17	2.07	2.42	2.64
Tb	0.43	0.39	0.34	0.30	0.23	0.21	0.22	0.22	0.23	0.51	0.40	0.62	0.46	0.19	0.20	0.20	0.43	0.47	0.54
Dy	3.33	3.17	2.70	2.46	1.78	1.78	1.74	1.67	1.70	3.49	3.12	3.69	2.99	1.57	1.98	1.41	2.53	2.65	3.00
Ho	0.73	0.77	0.65	0.60	0.42	0.41	0.41	0.41	0.41	0.97	0.74	0.85	0.74	0.34	0.57	0.41	0.58	0.57	0.62
Er	2.49	2.21	2.04	1.82	1.39	1.42	1.29	1.29	1.46	3.33	2.38	2.46	2.50	1.36	2.25	1.51	1.91	1.72	2.08
Tm	0.31	0.30	0.28	0.26	0.19	0.21	0.20	0.18	0.20	0.62	0.42	0.37	0.35	0.20	0.44	0.24	0.25	0.27	0.33
Yb	2.33	2.31	2.21	1.81	1.42	1.38	1.39	1.46	1.39	4.08	3.13	2.86	2.61	1.44	3.31	1.93	1.87	1.86	2.22
Lu	0.37	0.37	0.31	0.31	0.20	0.21	0.20	0.20	0.18	0.74	0.57	0.49	0.47	0.23	0.55	0.34	0.27	0.37	0.44
Hf	1.35	1.23	1.03	1.23	0.69	0.51	0.62	0.51	0.70	8.91	7.43	6.68	4.30	4.53	6.64	4.78	1.50	2.87	3.19
Ta	0.27	0.08	0.02	0.06	0.07	0.04	0.05	0.04	0.09	0.59	0.59	0.46	0.33	0.36	0.46	0.36	0.10	0.20	0.20
W	88.5	37.8	21.6	14.5	15.2	73.6	89.4	103.2	144.8	10.8	12.5	17.5	24.0	20.2	14.9	28.7	290.9	93.1	230.0
Tl	0.28	0.28	0.08	0.15	0.06	tr	tr	tr	tr	0.18	0.08	0.03	0.02	tr	0.11	0.10	0.09	tr	0.03
Th	1.70	0.75	0.34	0.41	0.23	0.13	0.12	0.11	0.09	4.30	4.64	3.96	2.21	2.53	3.06	2.64	0.88	1.37	1.43
U	3.90	3.11	1.43	2.12	1.32	0.11	0.06	0.03	0.06	1.85	1.56	1.20	0.76	1.21	1.14	0.84	0.23	0.47	0.52

During weathering, some elements have been removed from and others have remained in the original rock. Then from the concentration expressed in wt%, we can not judge whether the element has remained, has been added from other place, or has been removed. Usually the normalization by the concentration of the immobile element is adapted to evaluate true grain and loss. Al, Ti, and Cr have been commonly treated as immobile elements during weathering. Zr, Nb and Hf are proposed as more immobile elements, and the ratios among those elements were also used to identify the original rocks of paleosol (BRIMHALL and DIETRICH, 1987). Zr was used as an element for normalization in this study. The similar tendencies were obtained if Hf and Nb are used. Zr-normalized contents of the paleosols are plotted in Figs. 5 to 7 for the Aimiliki volcanics, and in Figs. 8 to 10 for the Babeldaob volcanics.

Chemical Profile of the Laterite Type Paleosols

Figs. 5 to 7 show the variation of Zr-normalized values of each element in the laterite type paleosols developed on the agglomerate of the Aimiriki volcanics.

Zr-normalized Si, Al, Mg, V, Fe, Mn, Cu, Co, Ni, Zn and Ge values decrease uniformly toward the unconformity. It is noticeable that Fe and Al are dissolved even under an oxic condition. Fe may have dissolved as Fe^{3+} irons.

Some elements do not show smooth trends through the section. Phosphorus decreases and increases toward the unconformity. The main P-bearing mineral in the parent rock is apatite. The decrease of phosphorus in the lower part of the section is related with the dissolution of apatite, but the P enrichment in the upper part might be due to biological activity. As there is no crystalline phase, phosphorus is probably adsorbed into clay minerals. K, Rb and Cs show rather complicate pattern. They are high in the middle part of the section. These elements decrease at early stage of weathering (the lower part of the section, around 300 cm from paleosol surface), increase at the middle stage (around 200 cm from the surface), decrease again, and increase near the surface of the paleosol. The decrease at early stage of weathering suggest that the enrichments of alkali elements at the middle stage is not by in situ chemical reaction, but that the alkali elements were added from the upper zones or from the overlying terrace (HOLLAND, 1984). These additions may not have been limited only to middle part, and the weaker enrichments are also recognized at near the top of the section. The enrichments near the top of the paleosol are recognized more easily on the light alkali elements (Na and K) than heavy alkali elements (Rb and Cs). The similar enrichments are recognized in the alkali earth elements; Ca and Sr. On the other hand, the elements of III and IV groups in the periodic table such as Nb and Hf, do not change through the section.

Fig. 7 shows the variation of REEs, Th and U, which increase toward the paleo-surface. It is said that uranium is dissolved and leached out from the parent rock under oxic environment, because U^{6+} is mobile. The enriched uranium might be interpreted by the addition from other place or overlying terrace at the stage later than that of weathering. The environment might change to anoxic, when the soil was migrated and was not supplied the atmospheric oxygen gas, which was completely consumed in the overlying formation. Other interpretation is the

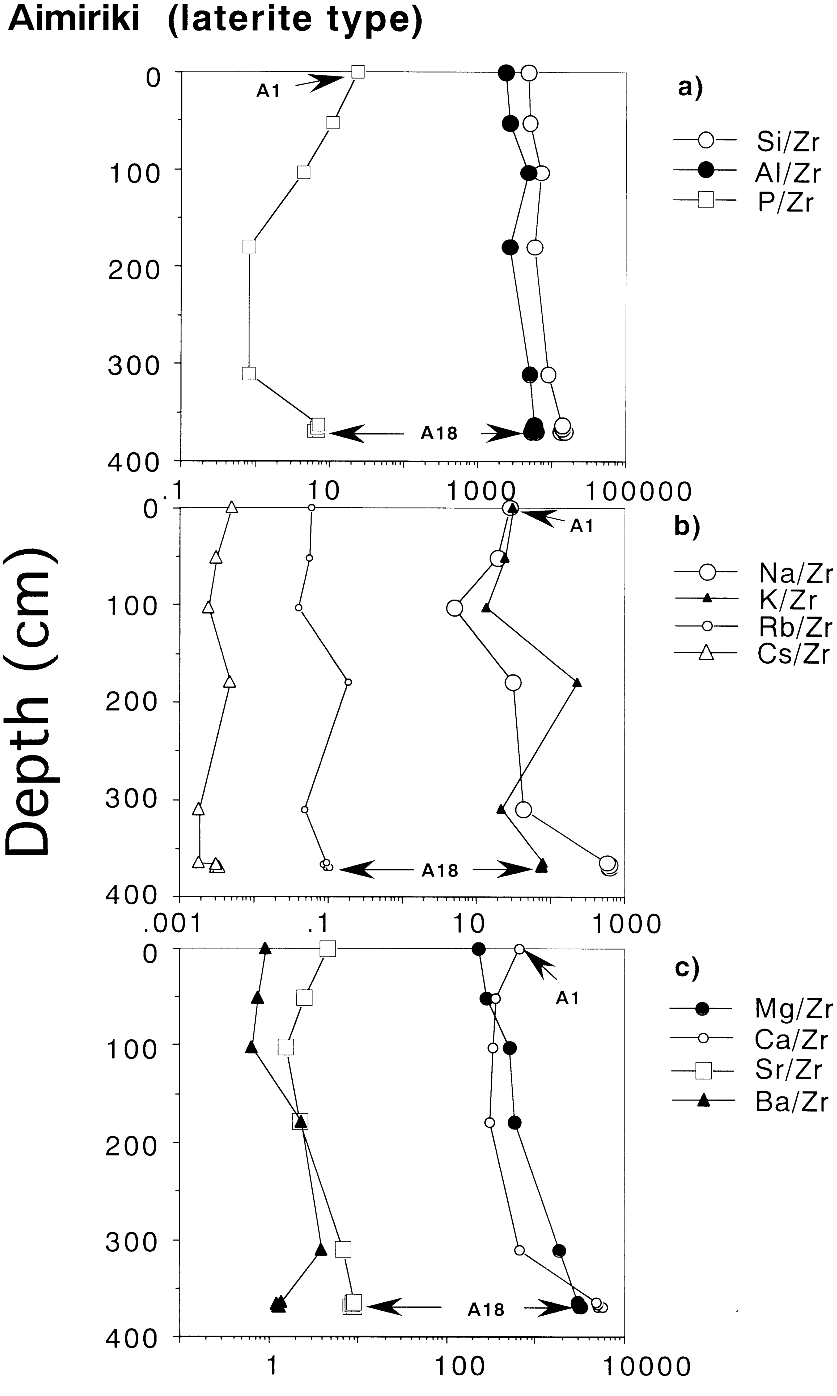


Fig 5. Variation of Zr-normalized contents of Si, Al, P, alkali and alkali earth elements of the paleosols on the Aimiriki volcanic rocks.

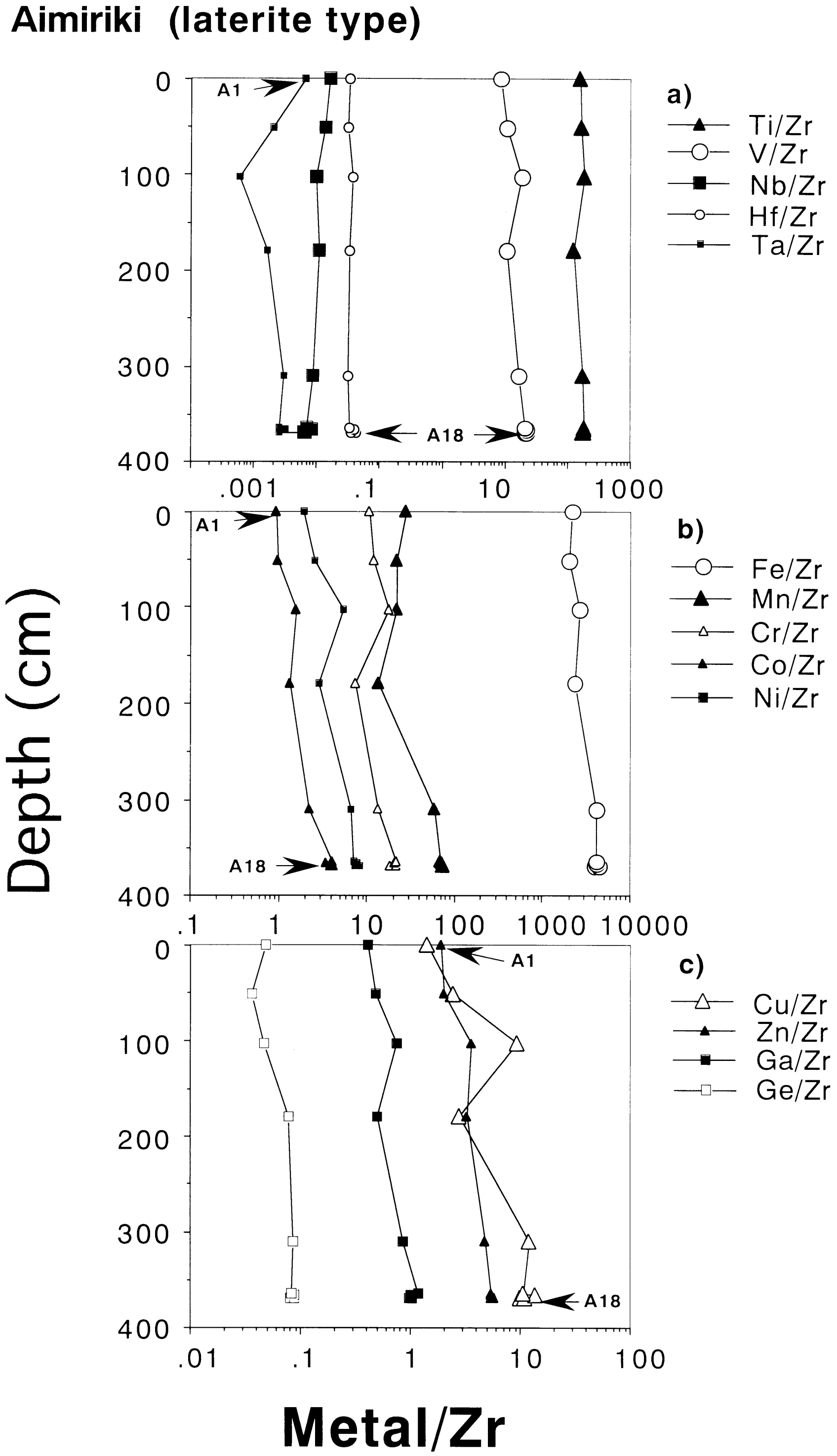


Fig 6. Variation of Zr-normalized contents of elements of the III and IV groups and transitional elements of the paleosols on the Aimiriki volcanic rocks.

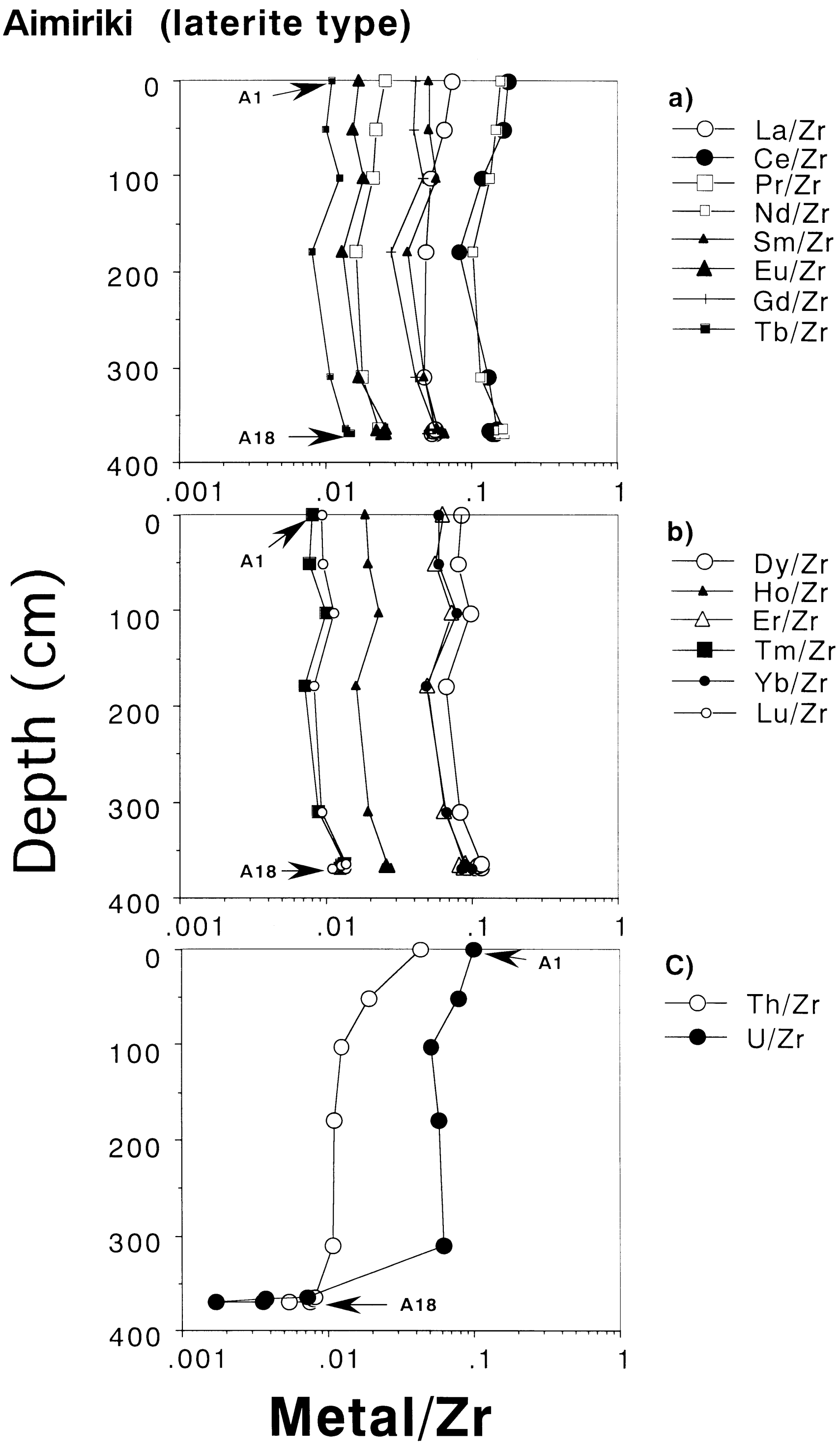


Fig 7. Variation of Zr-normalized contents of REEs, Th and U of the paleosols on the Aimiriki volcanic rocks.

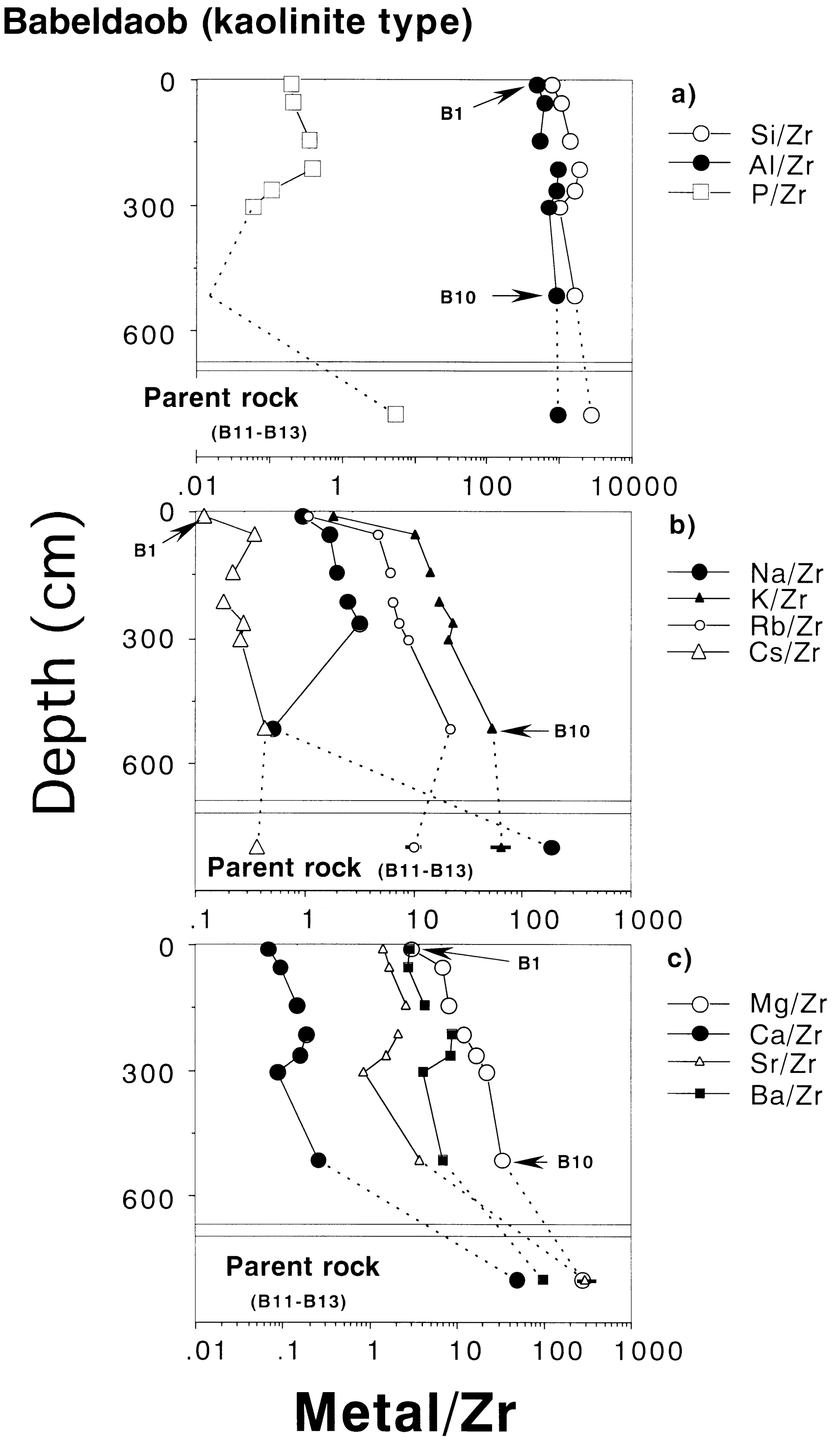


Fig 8. Variation of Zr-normalized contents of Si, Al, P, alkali and alkali earth elements of the paleosols on the Babeldaob volcanic rocks.

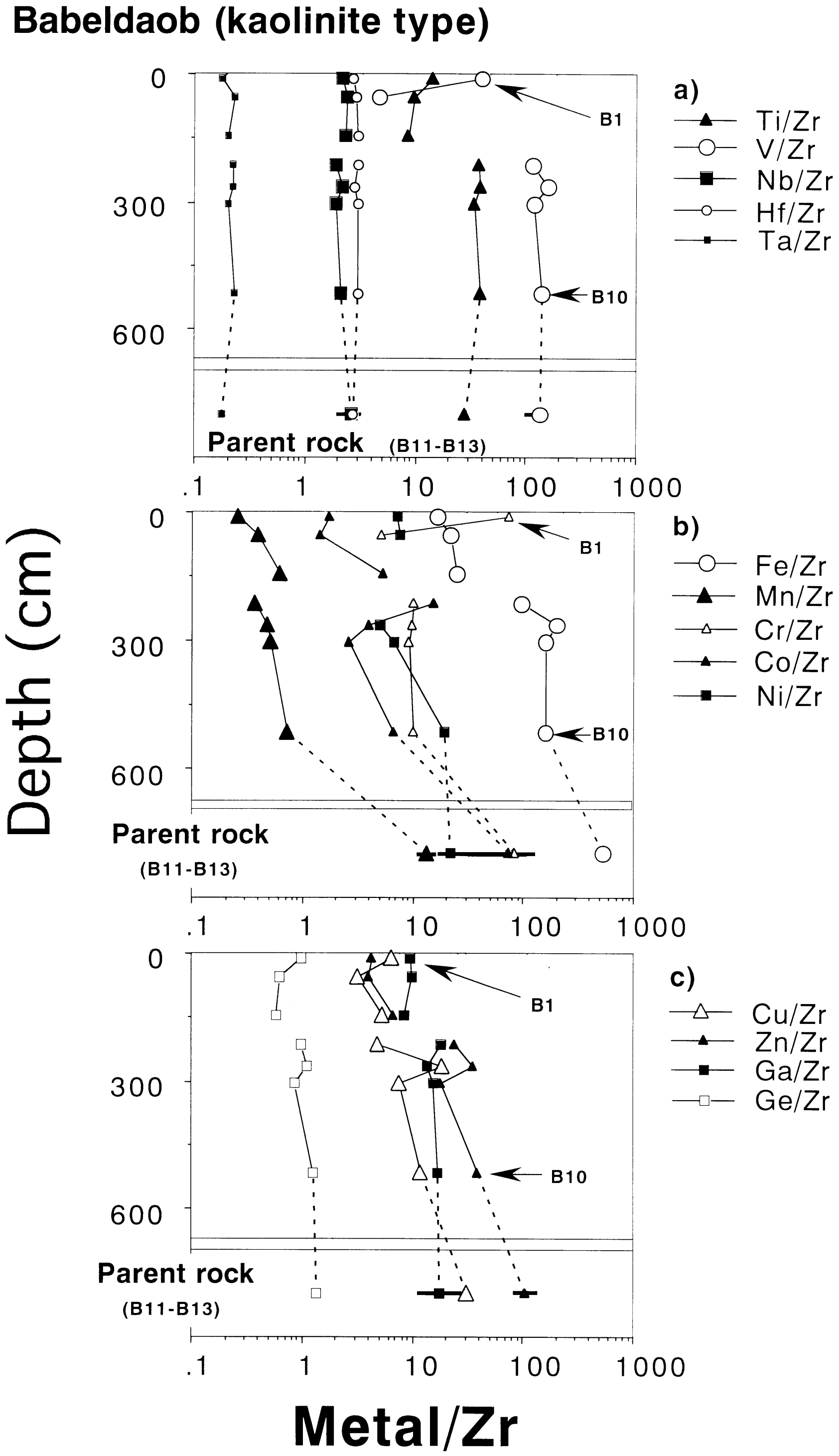


Fig 9. Variation of Zr-normalized contents of elements of the III and IV groups and transitional elements of the paleosols on the Aimiriki volcanic rocks.

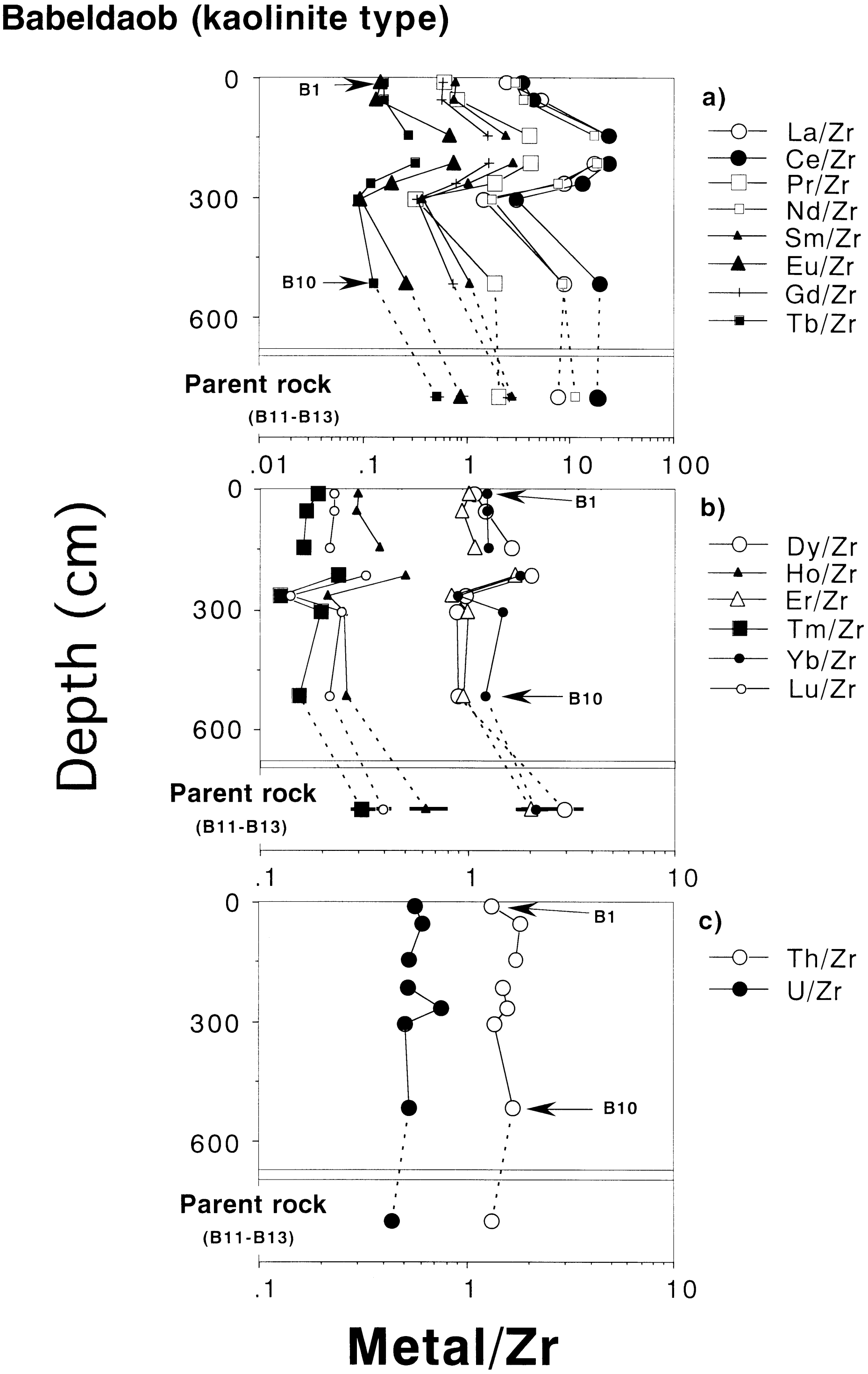


Fig 10. Variation of Zr-normalized contents of REEs, Th and U of the paleosols on the Aimiriki volcanic rocks.

formation of insoluble carbonate, such as $UO_2(CO_3)$. $UO_2(CO_3)$ is produced through the reaction of U^{6+} with HCO_3^- from overlying coral limestone, and is rather stable under oxic environment.

Kaolinite Type Paleosols Overlain by Lignite Deposits

Geochemistry of the paleosols on the Babeldaob volcanic rocks overlain by the Airai formation is rather complex. As shown in Fig. 9, Zr-normalized Nb and Hf are almost constant through the paleosol section, including the parent rock. But Zr-normalized Ti and Ga in the upper part of the section are distinctly lower than those of the lower part. The upper part originates in tuff, and the lower part in agglomerate. The profiles suggest that Ti and Zr have remained unchanged through weathering, and that the Ti/Zr ratios are fixed to the original compositions of both the rock which differ with each other.

Zr-normalized values of many other elements decrease toward the top of the paleosol section through a discontinuous jump. The distance of the discontinuous zone from the unconformity depends on the kind of element.

Fe decreases with advancing weathering, and jump off at the boundary from agglomerate to tuff with advancing weathering. Mn and Ni also decrease with advancing weathering, but jump up at the boundary from agglomerate to tuff.

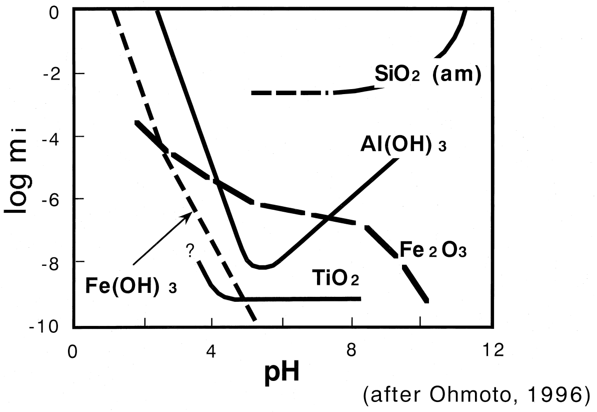
The values of Si, Al, Co, Zn, Cu, Ge, REEs, Ca, Sr and Ba also show similar tendency, but the positions of maximum values are beneath the boundary between tuff and agglomerate. These elements may have been dissolved from the upper part, and re-precipitated in the slightly lower part.

Phosphorus decreases from the parent rock to the lower part of paleosol, and increases toward the unconformity. As mentioned in the another section, the P-enrichment may be caused by biological activity.

Fig. 10 shows the variations of REEs, which decrease toward the top with the maximum values in the middle section. The LREEs profiles have the maximum values at 145 to 215 cm. Th and U are almost constant during weathering. As U^{4+} and Th are immobile under reduced environment, the profile well coincides with the existence of overlying lignite. In this case, the pattern would be similar to those of Hf, Nb and Ta.

Discussion

Some elements are easily dissolved and transported from rocks by low temperature water, and are precipitated again at the places of different chemical environment. The present study shows that these phenomena are frequently observed in young paleosol. OHMOTO (1996) compared the solubility of minerals comprised of rather immobile elements, showing that the solubility of SiO_2, $Al(OH)_3$, Fe_2O_3, $Fe(OH)_3$, and TiO_2 depends on pH as shown in Fig. 11. Although silica is less soluble at the pH below 9, SiO_2 is more mobile compared to Ti, Al and Fe



(after Ohmoto, 1996)

Fig 11. Thermodynamic solubilities of Fe, Al and Si compounds.

compounds under neutral condition. $Al(OH)_3$ is almost insoluble under neutral conditions, and $Fe(OH)_3$ and TiO_2 are less soluble than $Al(OH)_3$ under neutral or alkaline condition. However $Al(OH)_3$ is soluble more than SiO_2 under the pH less than 3.5, and $Fe(OH)_3$ might be also soluble more strongly under the pH less than 2.0. The dependency of solubility on pH affects the behavior of each element through weathering.

The geochemical profiles of each paleosol are compared together, using the content normalized by Zr and also normalized by the parent rock; $(Metal/Zr)_s$ /$(Metal/Zr)_p$. Where, the subscripts, s and p, represent sample and parent rock. Before discussion, the features shown in Fig. 11 are qualitatively expressed using $(Metal/Zr)_s/(Metal/Zr)_p$, assuming that Zr is completely insoluble. Fig. 12 is a model of behavior of Ti, Al, Fe and Si during weathering. The solubility of chemical compounds of Ti, Al and Fe^{3+} increase with decreasing pH(-6). Under same acid solution, TiO_2 is most insoluble and Al_2O_3 is most soluble among TiO_2, $Fe(OH)_3$ and Al_2O_3. In addition, as there are ferrous and ferric, the solubility of iron compounds is affected by P_{O_2}. A set of chemical trends of Si, Ti, Fe and Al should suggest the environment

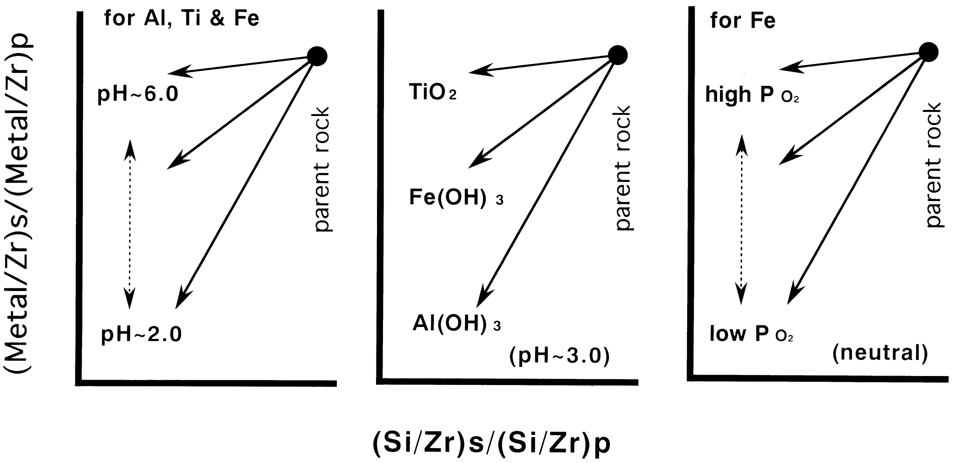


Fig 12. A model of behavior of Ti, Al, Fe and Si during weathering.

of weathering. For example, the environment of neutral and low P_{O2} can be expected, if both the (Al/Zr)s/(Al/Zr)P and (Ti/Zr)s/(Ti/Zr)P decrease gently with decreasing the (Si/Zr)s/(Si/Zr)P, but the (Fe/Zr)s/(Fe/Zr)P decrease more steeply than (Al/Zr)S/(Al/Zr)P with decreasing (Si/Zr)s/(Si/Zr)P.

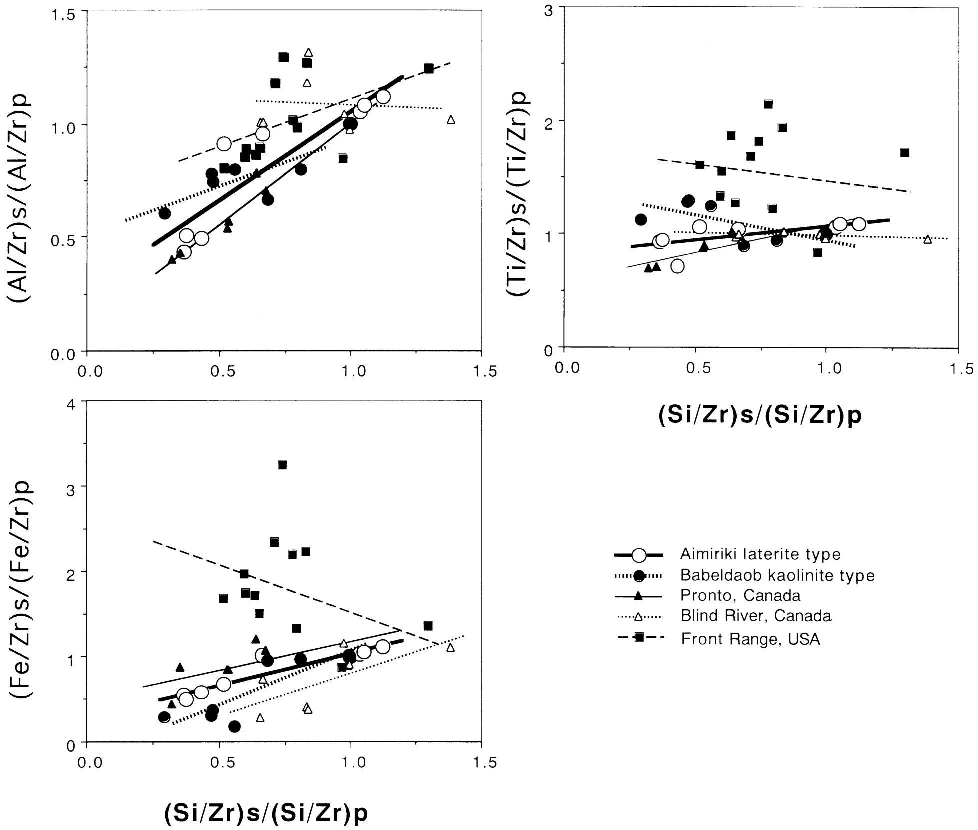


Fig 13. Comparisons of the variation of Zr-normalized values of Al, Fe and Ti versus Si, which are normalized by Zr and by parent rock.

The results of various paleosols are shown in Fig. 13. In the figure, lines represent the regression line estimated statistically. Although the deviations from the regression lines are rather large, some features and differences can be recognized. The(Al/Zr)s/(Al/Zr)P, (Fe/Zr)s/(Fe/Zr)P and (Ti/Zr)s/(Ti/Zr)P ratios generally decrease with decreasing (Si/Zr)s/(Si/Zr)P ratio (with advancing the weathering), but the decreasing manners slightly differ with each other.

The field evidence in Palau shows that the laterite type weathering on the Aimiriki volcanic rocks has proceeded under ordinal atmospheric condition (oxic condition). On the other hand, The kaolinite type weathering on the Babeldaob volcanics has advanced under anoxic conditions. The overlying lignite bed may have played a role of filter to reduce the surface water when O_2-saturated meteoric water penetrated through the ground. The difference of the environment affect the decreasing rate of (Fe/Zr)s/(Fe/Zr)P. The (Fe/Zr)s/(Fe/Zr)P for the laterite type is slightly lower than that for the kaolinite type. The (Al/Zr)s/(Al/Zr)P ratios of the laterite type are higher than that of the kaolinite type when the $(\mathrm{Si/Zr})_S/(\mathrm{Si/Zr})_P$ ratios are higher than ~0.5, but become much lower when the $(\mathrm{Si/Zr})_S/(\mathrm{Si/Zr})_P$ ratio decreases below ~0.5. On the other hand, the $(\mathrm{Ti/Zr})_S/(\mathrm{Ti/Zr})_P$ ratios of the laterite type decrease slightly, but those of the kaolinite type are almost constant or slightly increase with decreasing the $(\mathrm{Si/Zr})_s/(\mathrm{Si/Zr})_P$ ratios. The profiles suggest the low pH condition for laterite type and near neutral condition for the kaolinite type. Hence, the conditions for the laterite type weathering on the Aimiriki volcanic rocks might be of lower pH as well as higher P_{O_2}, and that for the kaolinite type weathering on the Babeldaob volcanics overlain by lignite might be of near neutral as well as lower P_{O_2}. The further mineralogical study should be obtained to confirm the weathering feature under different type.

The data of other paleosols of different ages are also plotted in Fig. 13 for comparison. The data are from Permian paleosol on granodiorite (Condie *et al.*, 1995) and Precambrian paleosols on the Archean granite at Pronto and on the Archean greenstone at Elliot Lake, Ontario, Canada (Nedachi *et al.*, 1998). These parent rocks are chemically and physically different from those in present study, and the absolute contents of constitutions affect their own behaviors as discussed by Holland (1984). The chemical profiles of the paleosols on the Archean granite from Pronto, Ontario, Canada, are very similar to those of the laterite type weathering. Condie *et al.*(1995) analyzed in detail the behaviors of REEs in the paleosol formed under high P_{O_2} conditions in the Front Range, USA. The Al, Fe, Ti, Si, and Zr behaviors in this paleosol (Fig. 12) suggest a neutral pH condition. However, the very large variation of $(\mathrm{Fe/Zr})_S/(\mathrm{Fe/Zr})_P$ ratios suggest some Fe addition during weathering.

In contrast, on the paleosols on greenstone at the Blind River area, the $(\mathrm{Al/Zr})_S/(\mathrm{Al/Zr})_P$ and $(\mathrm{Ti/Zr})_S/(\mathrm{Ti/Zr})_P$ are almost constant during weathering, but $(\mathrm{Fe/Zr})_S/(\mathrm{Fe/Zr})_P$ decreases with advancing weathering. Considering that ferrous mineral is more soluble than ferric mineral, the weathering condition on the Archean greenstone could be estimated to be almost same or slightly higher pH condition and same P_{O_2} condition with that of the kaolinite type paleosol in Palau. The reason of low P_{O_2} might be same with that of the kaolinite type paleosol in Palau. As P-enrichment is observed in the paleosol on the Archean greenstone, and as is observed some bio-activity might produce anoxic conditions there. However, attention should be paid to the wide deviations of data.

Conclusions

Behavior of various elements in two different types of paleosols on Eocene volcanic rocks at Babeldaob Island, Palau, was examined and compared with those of the old age.

In the laterite type paleosols on the Aimiriki volcanics, many elements were leached out from the upper zone. It is noticeable that Fe is dissolved even under oxic condition. REEs, Th and U typically increase with advancing weathering. Some alkali elements are leached out from the upper paleosols, and re-precipitated in the middle part.

In the kaolinite type paleosol on agglomerate and tuff of the Babeldaob volcanics, the ratios among Ti, Zr, Nb, Hf and Ta are almost constant, but differ between tuff and aggromerate. Zr-normalized values of many elements decrease toward the unconformity while jumping to maximum values at the middle part. The maximum Zr-normalized values of Si, Al, Co, Zn, Cu, Ge, Ba, Ca, Sr and REEs are recognized at slightly below the boundary between tuff and agglomerate. It is suggested that these elements have moved downward during soil formation. The contents of more mobile elements, such as K, Mg and Rb decrease uniformly toward top of the section. The chemical profile of paleosol strongly depends on the pH conditions as well as on the oxygen partial pressure.

From the diagrams of $(\mathrm{Al/Zr})_S/(\mathrm{Al/Zr})_P$, $(\mathrm{Fe/Zr})_S/(\mathrm{Fe/Zr})_P$ and $(\mathrm{Ti/Zr})_S/(\mathrm{Ti/Zr})_P$ ratios against $(\mathrm{Si/Zr})_S/(\mathrm{Si/Zr})_P$, low pH as well as high P_{O_2} conditions were estimated for the laterite type paleosol developed on the Aimiriki volcanics, and slightly high (but less than neutral) as well as low P_{O_2} conditions for the kaolinite type paleosol on the Babeldaob volcanics. The data from the Precambrian paleosols were compared, and it suggests that the atmosphere of the Archean-Proterozoic boundary era contained rather high oxygen.

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