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Zoning and Geochemical Characterization of Volcanic Soils on Kamchatka

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Abstract—The paper presents the first data on the zoning of modern volcanic soils on the Kamchatka Peninsula according to the age and composition of volcanic ashes in which the surface organogenic horizons of the soils were formed. The following soil provinces are recognized: Northern, Central, Western, and Southeastern. Parameters of their regional geochemical background (concentrations of trace elements) are determined. The main factor controlling the background concentrations of trace elements in these soils is the composition of the ashes underlying the soils. The geochemical specifics of the surface organogenic horizons of volcanic soils on Kamchatka may be variably affected only by the concentrations of trace elements whose average contents in magmatic rocks are the highest: Cr, Cu, Mn, Sc, Zn, Co, V, and Ag. The maximum concentrations of excess elements were determined in the soils underlain by ashes of basic composition, and the minimum concentrations of these elements occur in the soils formed in silicic ashes. All soil provinces recognized on Kamchatka are characterized by pervasively elevated Cu concentrations. It is proposed to identify volcanic soils formed in the peninsula in ashes of various composition with the application of a multiplicative geochemical coefficient.

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INTRODUCTION

Conditions under which soils are formed on the Kamchatka Peninsula are related to the activity of volcanic centers which produced eruption material of various compositions.

The soil-forming rocks of most soils on Kamchatka are volcanic ashes. In contrast to the development of a profile of postlithogenic (normal and residual) soils, a process that involves the progressive replacement of the underlying rocks by soils with the consumption of chemical elements of the rocks, a profile of volcanic soils progressively grows upward due to the periodically supplied pyroclastic material newly fallen on the surface (synlithogenic soil production). Since volcanic soils are most widely spread in the region, we assumed them as the basis for delineating the zoning of the soil cover (no such zoning has been outlined). Soils whose genesis was not controlled predominantly by volcanism (alluvial, paludal, and mountain tundra soils) cover much smaller areas on Kamchatka.

Another distinctive feature of volcanic soils is the polygenetic character of their profiles, with these profiles consisting of a number of superimposed elementary soil profiles, whose genesis is related to the periodically occurring covering of the surface with ash material.

At the same time, the character of the soil-forming processes, which are adequate to the modern climatic conditions, comprehensively reflects the surface organogenic horizon of the soils, which is generated on volcanic ashes of various compositions. In this sense, this horizon is characteristic of the soil type and was assumed as the basis for delineating the regional soil zoning. The latter includes the following four major regional soil provinces of Kamchatka: Northern, Central, Western, and Southeastern.

Ecological–geochemical studies, soil monitoring, and exploration for mineral deposits with the use of lithochemical guides are carried out with the broad application of the regional background concentrations of trace elements in soils.

Currently available reference materials on the background concentrations of trace elements in soils in various bioclimatic zones within the territory of the former Soviet Union [1] and the schematic map of the biogeochemical zones and provinces of this territory [2] provide no data on volcanic soils.

Our research was centered on delineating the zoning of volcanic soils on Kamchatka and the estimation of their geochemical characteristics in relation to the composition and age of the volcanic ashes in which these soils were formed.

This task was accomplished through solving the following problems:

(1) We applied available literature [3] and our own data on the occurrence of identified volcanic ashes of various compositions and ages to outline the zoning of soils on the peninsula according to their surface organogenic horizon that was formed in these ashes, with the recognition of soil provinces.

(2) We evaluated the variations in the regional background concentrations of trace elements in the most ubiquitous soil varieties within the provinces depending on their structure and physicochemical characteristics, which, in turn, depend on the type of vegetation under which the soils were formed.

(3) We compared volcanic soils on Kamchatka with zonal soils in various bioclimatic zones within the territory of the former Soviet Union.

(4) We calculated the parameters of the regional background concentrations of trace elements in the surface organogenic horizons of volcanic soils in the provinces and determined their geochemical specifics relative to the concentrations of trace elements in soils on continents.

(5) We identified the major factors that control the trace element composition of volcanic soils.

METHODS

Our study was carried out using comparative geographical and comparative chronological methods, as well as the studying of the morphological, physicochemical, and chemical characteristics of the soils. Volcanic ashes were identified with the application of the mesomorphological method. Areas in which volcanic ashes occur and in which surface organogenic horizons of soils were formed were specified by sampling along a number of soil profiles in various parts of the peninsula.

The geochemistry of volcanic soils on Kamchatka was studied with the application of the method of standard reference areas in which the most typical landscape–geochemical conditions occur that are typical of the recognized soil provinces.

We studied the modern organogenic horizon that was formed in near-surface ashes of various compositions and according to which soil zones were distinguished.

Soils were sampled within areas of 10×10 m (using the envelope method) and along soil geochemical profiles that were run across the most typical elementary landscape territories.

Bulk concentrations of trace elements in the horizon were determined by spectral analysis. Concentrations of elements below the detection limits of spectral analysis (Se, Te, As, Sb, Hg, and others) were analyzed by ICP-MS and atomic absorption. Spectral analysis was carried out at the Analytical Center of the Bronnitsy Geological–Geochemical Expedition and the Central Laboratory of OJSC Kamchatgeologiya; atomic-absorption and ICP-MS analyses were made at the Sector of Research and Production Work of the Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements.

The overall dispersed occurrence of trace elements in soils is characterized by their background concentrations outside obvious lithochemical anomalies, which were used as the basis for the evaluation of the geochemical specifics of soils in the recognized provinces.

Parameters of the geochemical backgrounds were determined by calculating the geometric mean values of trace element concentrations (GMC) and standard multipliers (ε) as a measure of the dispersion of the values used in our calculations. The background sets consisted of samples taken far away from exposures of orebodies at mineral deposits and geochemical anomalies.

For the volcanic soils of all of the provinces, we determined parameters of their regional geochemical background. In order to evaluate trace element variations in soils of various elemental landscapes, we calculated the values of the local geochemical background concentrations from the sampling data on the most typical areas with a homogeneous landscape within the Central and Southeastern soil provinces.

In order to identify the geochemical specifics of volcanic soils on Kamchatka, the values of the regional geochemical background of trace elements were compared with the values of their zonal background, which reflects the distribution of elements in the major soil types typical of the soil–bioclimatic zones on continents [1].

The geochemical specifics of modern volcanic soils in the soil provinces of the Kamchatka Peninsula was evaluated by calculating the clarkes of concentrations (CC) of trace elements as the ratios of the regional background concentrations to the overall abundance of trace elements in soils on continents [4]. Soils are regarded as containing elevated concentrations of certain elements if their CC > 1.

ZONING OF SOILS ON KAMCHATKA IN CORRELATION WITH THE COMPOSITION AND AGE OF VOLCANIC ASHES IN WHICH THE SOILS ARE PRODUCED

At present, extensive volcanological information is available on the isotopic age of ash beds and corresponding volcanic events based on the carbon isotopic dating of organogenic horizons underlying and overlying the ash beds [3, 5–8]. Tracing the occurrence of identified near-surface ash beds (Fig. 1), we delineated the zoning of volcanic soils on the peninsula whose subsurface horizons were formed in ashes of various age, composition, and eruption source.

The northeastern part of the peninsula and its eastern shore north of Kronotskii Volcano belongs mostly to the area of soils produced in pyroclastic deposits of the northern group of volcanoes on Kamchatka. The activity of these volcanoes (Shiveluch, Klyuchevskoi, Bezymyannyi, and Tolbachik) was often associated with the repeated eruptions of insignificant amounts of pyroclastic material of predominantly andesite and basaltic andesite composition. The surface organogenic soil horizons of this territory were formed in relatively young ash deposits, whose age ranges from ~30 to 967 yr. Their origin was associated with the systematic introduction of newly fallen pyroclastic material supplied by the modern eruptions of active volcanoes in the form of thin coatings at the surface of the soils.

In Fig. 1, the western boundary of areas with ashes of the northern volcanic group (shown as inferred) runs across the upper reaches of large rivers of the eastern coast.

However, data obtained on the farthest northwestern part of the peninsula indicate that the ashes of these eruptions occur over much greater areas. Our soil–geobotanical studies (conducted together with the geobotanist V.Yu. Neshataev, St. Petersburg Foresting Academy) at Cape Utkholot revealed that the forest and marsh soils contain ash lamina of sandy clay composition and whitish color. These lamina were most reliably identified there in peat layers several meters thick at oligotrophic bogs. Their number (four) corresponds to the number of the major eruptions of Shiveluch Volcano in the Holocene [5]. In addition, the characteristic color of the ashes, their granulometric composition, and the significant distance of this territory from other possible sources (volcanic centers) led us to identify the ashes as eruption products of Shiveluch Volcano during its discrete activity periods. Obviously, the areas where soils are generated in volcanic ashes of the northern group of volcanoes extend to the western shore of Kamchatka.

Soils in the central and southeastern parts of the peninsula were formed in ashes from volcanoes on southern Kamchatka, whose activity was characterized by rare significant caldera-forming eruptions. The products of these eruptions have a predominantly silicic (rhyodacite) composition. Young pyroclastic material was not supplied to this territory for a long time. The surface organogenic horizons of these soils were generated in old enough (for soil-forming processes) ashes: in the rhyodacite ashes supplied by eruptions of Opala Volcano (~1400 yr) in the central part and in ashes of analogous composition from Ksudach volcano (~1760 yr) in the western part. Our data on the upper reaches of the Aga River indicate that the western boundary of ashes from Ksudach Volcano is located at a significant distant east of the boundary shown in Fig. 1, and is probably, along the Sredinnyi Range of Kamchatka, because no ash of this eruption was found in the upper reaches of the Aga River.

The western coast occurs at a significant distance from active volcanic centers. Tephrochronological data indicate that this whole area belongs to the zone of soils whose genesis was not related to any significant covering of the surface with ash material.

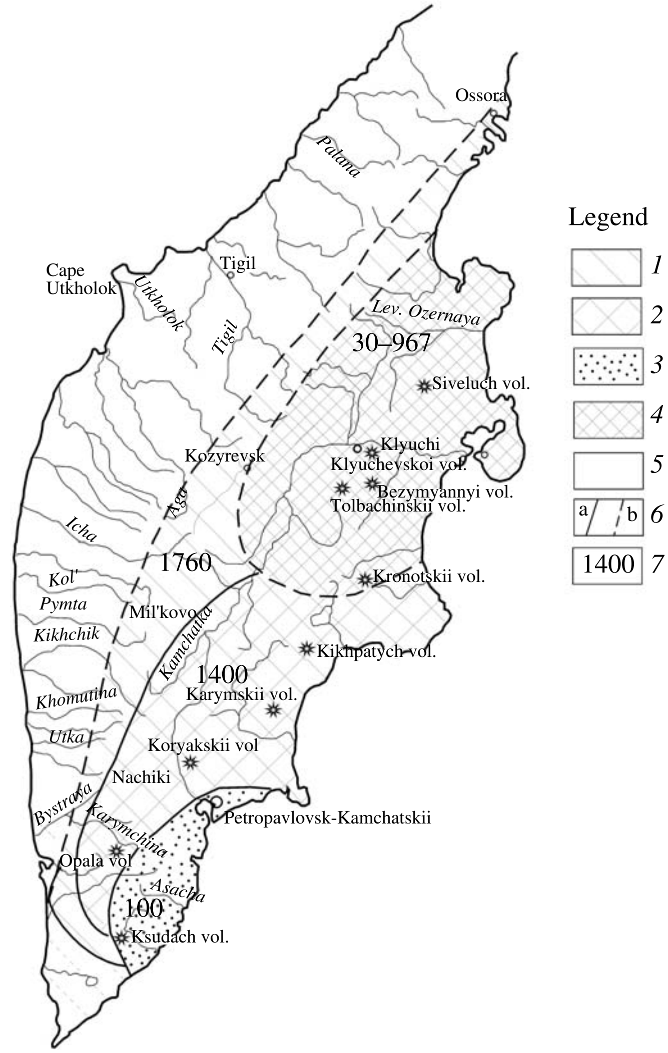

Fig. 1. Schematic map of subsurface volcanic ashes on the Kamchatka Peninsula [3, 5–8].

(*1–3*) Areas with ashes from the following volcanoes: (*1*) Ksudach, 236 A.D. ~ 1760 years ago; (*2*) Opala, 606 A.D.—1400 years ago; (*3*) Ksudach, 1907 A.D.—100 years ago; (*4*) zone of ashes from volcanoes of the northern group; (*5*) zone without any significant covering of its surface with volcanic ashes; (*6*) zone boundaries: (a) identified, (b) inferred; (*7*) age of near-surface ash (roughly).

At the same time, on southwest Kamchatka, we found a thin lamina of volcanic ash in the upper part of the soil profile, beneath the surface humus horizon. This lamina is not shown in the schematic tephrochronological maps [9]. The ash has a light loamy granulometric composition, a pale gray color, and a rhyolite–dacite composition. The ash occurs over a fairly extensive territory, from the Bystraya River in the south to the Aga River in the north. The isotopic age of this rock is ~2920 yr (O.A. Braitseva, personal communication). Its affiliation with any identifiable volcanic event remains obscure as of the present. The silicic composition of the ash, its relatively old age, and the fairly large area over which it occurs led us to provisionally relate the genesis of this ash to significant caldera-forming eruptions of volcanoes on southern Kamchatka.

In general, it can be concluded that soils on central, southern, and southwestern Kamchatka were commonly formed in silicic ashes from volcanoes on southern Kamchatka, whereas soils on northern Kamchatka were generated in basic and intermediate ashes from volcanoes of the northern group.

The area of silicic ashes from volcanoes on southern Kamchatka includes a small field in the farthest southeast of the peninsula in which surface soil horizons were formed in relatively young ash (from the 1907 eruption) from Ksudach Volcano. In contrast to most products of older eruptions of the volcano, this material has an intermediate–basic and basic composition. The underlying part of the soil profile consists of silicic pyroclastic material.

Based on the aforementioned differences in the composition and age of the surface volcanic ashes in which modern soil horizons were formed, we recognized the following four soil provinces of the Kamchatka Peninsula [Fig. 2]:

(1) Northern province. The upper soil horizons were formed in ashes of andesite composition from volcanoes in the northern group on Kamchatka; the age of the ashes is ~30–967 yr.

(2) Central province. The upper soil horizons were formed in ashes of rhyodacite composition from Opala Volcano (the age of the ash is ~1400 yr) and in ashes of analogous composition from Ksudach Volcano (the age of the ash is ~1760 yr).

(3) Western province. The upper soil horizons were formed in ashes of rhyodacite composition from unknown volcanoes, dated at ~2920 yr.

(4) Southeastern province. The upper soil horizons were formed in ashes of basaltic andesite composition from Ksudach Volcano (the age of the ash is ~100 yr).

In the absence of sufficient data on the occurrence of soils that developed in ashes from Ksudach Volcano, these soils were provisionally classed with the Central soil province.

Modern soil-forming processes in the Central and, partly, Northern and Southeastern provinces are locally complicated by the recurrent falls of young ashes from active volcanoes (Karymskii, Kikhpinych, Avachinskii. Kronotskii, and others). The soils of these zones are at the initial stage of their genesis, show unusual geochemical features, their genesis depends on the character of eruptions of certain volcanoes, and the geochemistry of these soils differs from that of soils in the host provinces.

SPECIFICS OF THE VOLCANIC IL-FORMING PROCESSES

As was mentioned above, the soil-forming rocks of all volcanic soils on Kamchatka are weakly weathered volcanic ashes. It is known that, in the course of eruption and further transport from the source to their falling areas, ashes adsorb chemical compounds, including trace elements [10–13], which later determine the geochemical composition of the soils which form in the ashes.

This is corroborated by the results of our earlier studies in the vicinity of the active Karymskii Volcano [14], where modern geochemical characteristics of the volcanic soils in the zone of active explosive volcanism are controlled by the composition of newly fallen ashes and, first of all, by the concentrations of soluble species of trace elements that are adsorbed on ash particles.

The ability of a soil to adsorb elements of various genesis is largely controlled by its physicochemical characteristics, first and foremost, the content of highly dispersed organic matter in the soil (humus itself—the organic colloids of the soil have higher adsorption capacities than those of mineral particles), the saturation of the soil in bases, and the pH of the soil water extract. The higher these parameters, the higher the adsorption capacity of the soil.

Differences in these characteristics of the surface organogenic horizons of volcanic soils directly depend on the vegetation growing in this soil. Coarse-humus horizons are formed in soils in stone birch (Erman's birch) forests, while soddy horizons develop beneath meadows. The soils in alder elfin woodland and mountainous tundra cenoses are high-humus moldy.

All volcanic soils on Kamchatka are generally characterized by the high contents of organic matter, are acidic or weakly acidic, and contain low concentrations of bases. Among the aforementioned soil varieties, soils at elfin woodlands and mountainous tundra are the richest in organic matter. The C concentrations in their mold horizons reach ~15–20%. Thereby, the soils of alder elfin woodlands typically have the lowest pH of the soil water extract (no higher than 4.22) and the lowest (for volcanic rocks) contents of bases (1.7–5.9%). The soils of mountainous tundra are characterized by very high pH values (4.8–5.0) and are slightly richer in bases (15–18%).

The lowest contents of organic matter usually occur in soils in stone-birch forests (7–11% C), their pH varies from ~5.9 to 6.5, and these soils contain intermediate concentrations of bases (20–30%).

The C concentrations in the surface soddy soil horizons of meadows are 10–17%, the soils contain 35–55% bases, and their pH is near-neutral.

Table 1. Regional geochemical background of trace elements in volcanic soils in the Northern soil province (GMC in ppm)

Element	GMC n = 450	ε	Element	GMC n = 450	ε	Element	GMC n = 450	ε
Li	28.11	1.34	Zn	37.31	1.94	Sn	1.66	1.47
Be	1.08	1.34	Ga	12.32	1.36	Sb	0.70*	1.35
B	17.52	1.37	Ge	0.63	1.40	Te	<0.06*	–
P	2965.35	1.51	As	6.64*	1.46	Cs	1.23*	1.39
Sc	9.98	1.70	Se	<3*	–	Ba	326.54	1.65
Ti	2953.8	1.28	Sr	139.14	1.30	Yb	1.10	1.31
V	92.37	1.52	Y	7.80	1.46	W	0.31*	1.38
Cr	43.39	1.32	Zr	150.58	1.23	Tl	0.19*	1.39
Mn	547.66	1.50	Nb	3.12	1.22	Pb	6.27	1.27
Co	6.03	1.46	Mo	1.72	1.23	Bi	0.13*	1.28
Ni	18.14	1.47	Ag	0.06	1.35	Th	1.40*	1.28
Cu	58.86	1.30	Cd	0.14*	1.25	U	0.72*	1.28

Note: Dashes mean no data available, asterisks mark data obtained by ICP-MS; n—here and in other Tables corresponds to number of samples.

BACKGROUND TRACE ELEMENT CONCENTRATIONS IN MODERN VOLCANIC SOILS ON THE KAMCHATKA PENINSULA

Northern Soil Province

As was mentioned above, modern soil horizons in the Northern soil province are formed in ashes erupted by the central group of volcanoes on Kamchatka, with these ashes having a predominantly andesite composition and relatively young age.

The geochemical examination of the soils was carried out in this province on the northern part of the Kamchatka Peninsula, in the upper reaches of the Levaya Ozernaya River, over an area >100 km^2, in which elementary landscapes typical of this province occur.

Parameters of the regional geochemical background were calculated using samples taken from the most typical volcanic soil types of the area:

(1) layered ocher coarse humic soils in stone birch forests

(2) and ocher typical mold soils in alder elfin woodland forests.

The results of our calculations are summarized in Table 1.

Central Soil Province

The geochemistry of the surface soil horizon in the Central soil province, which was generated in silicic rhyodacite ashes from Opala Volcano, was studied in the middle reaches of the Karymchina River, at an area of >140 km^2.

The most widely spread types of volcanic soils in the area are as follows:

(1) ocher typically mold soils in alder elfin woodlands,

(2) layered ocher coarse-humic soils in stone-birch forests,

(3) ocher typically soddy soils in sub-Alpine meadows and meadows in the forest zone,

(4) and mountain-tundra soils in mountainous tundras.

The parameters of the chemical elements' geochemical background in modern organogenic horizons of the aforementioned soil types are listed in Table 2.

The maximum background concentrations are fairly evenly distributed between soil types, do not display any pronounced tendencies, and are distributed at random.

The lowest values of the background concentrations of most trace elements are, conversely, prone to occur only in certain soil types: layered ocher coarse-humic soils in stone-birch forests or ocher soils typical mold soils in alder elfin woodlands. The former are characterized by relatively low contents of organic matter, whereas the soils in alder elfin woodlands (which have high C contents) are either relatively poor in bases or are acidic or weakly alkaline. These issues can be regarded as additional factors enhancing the migration ability of certain trace elements and their removal from these soils. The exceptions are Mo and Ag, whose minimum background concentrations were found in the soils in mountain meadows and mountain tundra. Explanations of this should be searched for in the properties of these elements: the mobility of Mo decreases with decreasing pH, and extremely low Ag concentrations in soils predetermine an insignificant role of the environment in the migration of this element.

The background concentrations of such elements as Te, Se, As, Sb, and Hg, which were identified only in

Table 2. Parameters of the local geochemical background of trace elements in volcanic soils of the Central soil province (GMC in ppm)

Element	Soils in alder elfin woodlands		Soils in stone-birch forests		Soils in sub-Alpine meadows and meadows in the forest zone		Soils in mountainous tundra	
	GMC ($n = 108$)	ε	GMC ($n = 75$)	ε	GMC ($n = 52$)	ε	GMC ($n = 93$)	ε
Sc	7.36	1.29	5.62	1.21	7.02	1.28	7.71	1.28
V	74.59	1.24	58.10	1.32	70.20	1.33	63.33	1.70
Cr	7.91	1.45	9.59	1.41	6.10	1.56	8.43	1.68
Mn	523.94	1.42	572.93	1.45	560.04	1.40	574.77	1.60
Co	3.77	1.49	5.26	1.36	5.37	1.51	6.43	1.60
Ni	6.27	1.39	6.52	1.28	7.66	1.41	7.14	1.35
Cu	43.12	1.26	32.91	1.35	39.70	1.31	36.71	1.60
Zn	25.56	1.52	51.19	1.37	47.02	1.47	57.06	1.56
As	1.79*	1.17	–	–	–	–	–	–
Se	<0.5*	–	–	–	–	–	–	–
Sr	76.69	1.18	74.18	1.23	92.66	1.47	80.23	1.34
Mo	1.03	1.52	1.90	1.21	0.92	1.43	0.98	1.42
Ag	0.08	1.39	0.09	1.51	0.06	1.21	0.06	1.23
Sb	<1*	–	–	–	–	–	–	–
Te	0.001*	1.41	–	–	–	–	–	–
Hg	0.02*	1.76	–	–	–	–	–	–
Pb	8.91	1.16	13.14	1.30	9.71	1.22	10.51	1.32

Note: Dashes mean no data available, asterisks mark data obtained by atomic absorption.

the soils in alder elfin woodlands (which are the most widely spread in this territory), are extremely low and roughly equal to or lower than the detection limit of atomic absorption.

The variations in the background concentrations of elements (GMC_{max}/GMC_{min}) in the recognized varieties of volcanic soils are shown below as a sequence of elements ranked according to this parameter:

Zn (2.23) – Mo (2.06) – Co (1.71) – Cr (1.57) – Ag (1.5) – Pb (1.47) – Sc (1.37) – Cu (1.31) – V (1.28) – Ni (1.22) – Mn (1.1) – Sr (1.08).

The comparatively low values of these variations allowed us to combine the selections for which the local background values were calculated and to evaluate parameters of the single regional geochemical background of trace elements in volcanic soils in the Central soil province (Table 3).

Western Soil Province

The Western soil province is mostly distant from centers of active volcanism, its near-surface ash layer has a rhyodacite composition, and the ash is the oldest. The parameters of regional geochemical background for soils in this province were calculated from sampling data on a representative territory of approximately 70 km^2 in the upper reaches of the Icha River (Table 4).

The background selection is compiled of analyses of samples taken from the modern organogenic horizon of volcanic ocher typical soils in stone-birch forests and alder elfin woodlands (these soils are most widely spread in the province).

Southeastern Soil Province

Geochemical characteristics of soils in the Southeastern soil province (which were formed in basaltic andesite ashes from Ksudach Volcano) were studied in a territory of approximately 20 km^2 in the upper reaches of the Asacha River.

The sampling was carried out in areas with the most ubiquitous volcanic ocher typical soils in stone-birch forests, alder elfin woodlands, and meadows of the forest zone.

The calculated background concentrations of trace elements of the modern organogenic horizons of these volcanic soils are reported in Table 5.

As follows from these data, no soils obviously enriched or depleted in most of the trace elements can be recognized among the soil varieties: the maximum and minimum background concentrations of the elements are distributed evenly. The variations in the background concentrations of some of the elements display relatively high values. The elements can be ranked

Table 3. Parameters of the regional geochemical background of trace elements in volcanic soils of the Central soil province (GMC in ppm, $n = 120$)

Element	GMC	ε	Element	GMC	ε	Element	GMC	ε
Li	24.98	1.25	Ni	6.92	1.28	Nb	3.98	1.19
Be	<1	–	Cu	40.66	1.50	Mo	1.56	1.36
B	12.08	1.48	Zn	45.26	1.44	Ag	0.08	1.39
P	1341.08	1.46	Ga	10.15	1.35	Sn	2.07	1.12
Sc	6.60	1.28	Ge	1.09	1.36	Sb	<1*	–
Ti	1924.10	1.41	As	1.79*	1.17	Te	0.001*	1.41
V	69.66	1.47	Se	<0.5*	–	Ba	295.83	1.45
Cr	10.72	1.43	Sr	65.14	1.17	Yb	1.00	1.00
Mn	515.10	1.57	Y	6.44	1.38	Hg	0.02*	1.76
Co	5.89	1.52	Zr	61.02	1.15	Pb	10.51	1.40

Note: Dashes mean no data available, asterisks mark data obtained by atomic absorption.

Table 4. Parameters of the regional geochemical background of trace elements in volcanic soils of the Western soil province (GMC in ppm, $n = 40$)

Element	GMC $n = 493$	ε	Element	GMC $n = 493$	ε	Element	GMC $n = 493$	ε
Li	30	1.23	Ga	10	1.24	Sb	0.25*	–
Be	1.1	1.12	As	4.2*	–	Te	<0.02*	–
Sc	5	1	Se	1.4*	–	Cs	3.7*	–
Ti	3000	1.34	Sr	40	1.45	Ba	200	1.33
V	61.4	1.2	Y	10	1.38	Yb	1	1.4
Cr	17.7	1	Zr	155.67	1.19	W	1.4*	–
Mn	400	1	Nb	4.5	1.43	Tl	0.25*	–
Co	5.9	1.31	Mo	1.3	1.35	Pb	10	2.34
Ni	6.6	1.3	Ag	0.1	1.1	Bi	1.19	1.26
Cu	40	1.43	Cd	0.11*	–	Th	2.0*	–
Zn	21.2	1.31	Sn	2	1	U	1.1*	–

Note: Dashes mean no data available, asterisks mark data obtained by ICP-MS.

according to this parameter in the form of the following sequence:

Ag(2.86) – Sr(2.5) – Mn(2.47) – Sn(2.07) – Ti(1.86) – Yb(1.77) – Ba(1.67) – Li(1.67) – Y(1.63) – Zr(1.59) – Pb(1.55) – Co(1.5) – Cu(1.44) – V(1.43) – Zn(1.35) – Ga(1.2) – Mo(1.2) – Cr(1.12) – Ni(1.01) – Sc (1.00).

Reasons for these geochemical features of modern volcanic soils in the Southeastern soil province should be searched for in the contrasting compositions of ashes in the soil profile. Basaltic andesite near-surface ashes are ubiquitously underlain by a soil profile with laminas of silicic volcanic ashes alternating with buried humus horizons. The root system of plants penetrating the soils to a significant depth intersects silicic volcanic products, and this results in the development of compositionally complicated biogeochemical and hydrogeochemical processes of migration. Consequently, the near-surface soil horizons locally include domains with elevated concentrations of elements typical of basic ashes alternating with domains from which these elements were removed and in which elements from deeper silicic horizons were redeposited. This may result in a significant scatter of the values of the local geochemical background.

The calculated parameters of the regional geochemical background of trace elements in modern volcanic soils in the Southeastern province (based on the whole database) are presented in Table 6.

REGIONAL CHARACTERISTICS OF THE TRACE-ELEMENT COMPOSITION AND GEOCHEMICAL SPECIFICS OF SOIL PROVINCES ON KAMCHATKA

The comparison of the background concentrations of elements in the near-surface horizons of volcanic

Table 5. Local geochemical background of trace elements in varieties of volcanic soils in the Southeastern soil province (GMC in ppm)

Element	Soil in stone-birch forests	Soils in alder elfin woodlands	Soils in meadows of the forest zone
	GMC (n = 10)	GMC (n = 5)	GMC (n = 5)
Li	(15.00)	25.00	17.50
Sc	15.00	15.00	15.00
Ti	1861.21	1000.00	1000.00
V	91.47	70.00	100.00
Cr	156.51	175.00	175.00
Mn	1732.05	700.00	1250.00
Co	10.00	10.00	15.00
Ni	5.92	6.00	6.00
Cu	59.16	85.00	60.00
Zn	92.59	85.00	125.00
Ga	14.56	15.00	12.50
Sr	200.00	80.00	90.00
Y	12.25	10.00	7.50
Zr	135.54	100.00	85.00
Mo	1.46	1.75	1.50
Ag	0.07	0.15	0.2
Sn	1.86	1.00	0.90
Ba	227.95	150.00	250.00
Yb	2.21	1.50	1.25
Pb	12.25	15.00	19.00

Note: n shows the number of integrate samples involved in the calculations.

soils on Kamchatka with the background concentrations in zonal soils in the territory of the former Soviet Union is illustrated in Table 7.

The relations of the regional and zonal backgrounds of certain elements were determined to broadly vary depending on the types of the compared zonal soils and the affiliation of the volcanic soils to certain soil provinces.

Compared to the zonal soils of the former Soviet Union, volcanic soils on Kamchatka usually

(1) have persistently elevated Cu regional background concentrations;

(2) have similar Pb concentrations;

(3) have pervasively lower concentrations of such elements as Cr, Ni, Sr, Sn, Mo, and Ag; and

(4) have generally lower concentrations of trace elements (except for Cu) in the soils formed in silicic ashes (the Central and Western provinces) than in most types of the zonal soils.

It should be mentioned that the volcanic soils show absolute maxima in the background concentrations of P and As in the Northern province and of Mn and Zn in the Southeastern province.

In order to evaluate the geochemical specifics of modern volcanic soils in the soil provinces distinguished on the Kamchatka Peninsula, we calculated the CC values of trace elements contained in these soils (Table 8).

Our calculations demonstrate that the values of CC for Sn are prone to be high in all volcanic soils on Kamchatka. At the same time, the comparison of our data with the composition of zonal soils in the former Soviet Union (see Table 7) shows that the background Sn concentrations in the volcanic soils are notably lower than the background concentrations of this element in all types of zonal soils. The reason for this inconsistency is that the values of Sn concentrations in soils on continents used to calculate CC (1.1 ppm [4]) were underestimated and much lower than those quoted elsewhere: up to 10 ppm [15]. Obviously, the detected elevated Sn concentrations in volcanic soils on Kamchatka are an artifact, and hence, this element was excluded for the list of excess elements.

Based on the data of Table 8, we established geochemical formulas for distinguishing soil provinces on Kamchatka. The numerators of these formulas include elements (except Sn) whose regional background concentrations are higher than their concentrations in zonal soils on continents (CC > 1), and the denominators list elements whose concentrations are lower than in continental zonal soils (CC < 1). Ele-

Table 6. Parameters of the regional geochemical background of trace elements in volcanic soils of the Southeastern soil province (GMC in ppm, n = 20)

Element	GMC	ε	Element	GMC	ε	Element	GMC	ε
Li	17.98	1.30	Ni	5.78	1.20	Mo	1.54	1.26
Sc	15.00	1.00	Cu	63.77	1.30	Ag	0.11	1.85
Ti	1426.16	1.42	Zn	90.94	1.33	Sn	1.43	1.42
V	85.82	1.21	Ga	14.75	1.22	Ba	198.52	1.36
Cr	166.85	1.30	Sr	135.05	2.11	Yb	1.87	1.29
Mn	1236.13	1.57	Y	11.23	1.22	Pb	12.01	1.38
Co	10.60	1.17	Zr	118.98	1.24			

Table 7. Comparison of background concentrations (ppm) of trace elements in volcanic soils on Kamchatka and zonal soils in the former Soviet Union [1]

Element	Soils in bioclimatic zones of the former Soviet Union					Soil provinces on Kamchatka			
	podsolic	gray forest	black	chestnut	gray	Northern	Central	Southeastern	Western
Li	23.5	26.4	33.8	34.2	37.2	28.1	25.0	18.0	–
Be	1.5	3	3.2	4	1	1.1	0.5	–	–
B	5.8	12.3	19.7	30	46	17.5	12.1	–	–
P	700	1500	700	700	700	2965.4	1341.1	–	–
Ti	4045	4400	4780	4075	1990	2953.8	1924.1	1426.2	3000.0
V	63.5	118	145	79	86	92.4	69.7	85.8	61.4
Cr	180	250	286	328	467	43.4	10.7	166.9	17.7
Mn	715	1025	885	722	725	547.7	515.1	1236.1	400.0
Co	8.4	12.4	13.2	11.7	6.9	6.0	5.9	10.6	5.9
Ni	23.2	30.3	72.1	46	19	18.1	6.9	5.8	6.6
Cu	15.3	23.5	28.9	15.8	24	58.9	40.7	63.8	40.0
Zn	41.3	60	62	52.3	50	37.3	45.3	90.9	21.2
As	3	4.7	5.9	5.2	2.5	6.6	1.8	–	–
Sr	238	258	260.4	287	305	139.1	65.1	135.1	40.0
Zr	150	442	299	420	112	150.6	61.0	119.0	100
Mo	1.7	3.2	4.2	3.2	3	1.7	1.6	1.5	1.3
Ag	0.1	0.3	0.5	0.4	–	0.1	0.1	0.1	0.1
Sn	2.9	2.8	3.2	3.3	4	1.7	2.1	1.4	2.0
Pb	11.5	12.5	13.2	10.0	6.3	6.3	10.5	12.0	10.0

Note: Dashes mean no data available.

ments in the formulas are ranked according to their CC (shown in parentheses).

Southeastern province:

$$\frac{\text{Cr}(2.78) - \text{Cu}(2.77) - \text{Mn}(2.47) - \text{Sc}(1.88) - \text{Zn}(1.52) - \text{Co}(1.18) - \text{Ag}(1.1)}{\text{V}(0.95) - \text{Mo}(0.77) - \text{Ga}(0.74) - \text{Yb}(0.62) - \text{Sr}(0.61) - \text{Li}(0.6), \text{Pb}(0.6) - \text{Y}(0.45) - \text{Zr}(0.4), \text{Ba}(0.4) - \text{Ti}(0.39) - \text{Ni}(0.29)}.$$

Northern province:

$$\frac{\text{Cu}(2.56) - \text{Sc}(1.25) - \text{Mn}(1.1) - \text{V}(1.03)}{\text{Li}(0.94) - \text{Ni}(0.91) - \text{Mo}(0.86) - \text{Ti}(0.8) - \text{Cr}(0.72) - \text{Co}(0.67) - \text{Ba}(0.65) - \text{Sr}(0.63) - \text{Zn}(0.62), \text{Ga}(0.62) - \text{Ag}(0.6) - \text{Zr}(0.50) - \text{Yb}(0.37) - \text{Y}(0.31), \text{Pb}(0.31)}.$$

Central province:

$$\frac{\text{Cu}(1.77) - \text{Mn}(1.03)}{\text{Sc}(0.83), \text{Li}(0.83) - \text{Ag}(0.80) - \text{Mo}(0.78) - \text{V}(0.77) - \text{Zn}(0.75) - \text{Co}(0.65) - \text{Ba}(0.59) - \text{Pb}(0.53) - \text{Ti}(0.52) - \text{Ga}(0.51) - \text{Ni}(0.35) - \text{Yb}(0.33) - \text{Sr}(0.30) - \text{Y}(0.26) - \text{Zr}(0.20) - \text{Cr}(0.18)}.$$

Western province:

$$\frac{\text{Cu}(1.74)}{\text{Ag}(1.00) - \text{Ti}(0.81) - \text{Mn}(0.80) - \text{V}(0.68) - \text{Co}(0.66) - \text{Mo}(0.65) - \text{Sc}(0.63) - \text{Ga}(0.50). \text{Pb}(0.50). \text{Li}(0.50) - \text{Y}(0.40) - \text{Ba}(0.40) - \text{Zn}(0.35) - \text{Zr}(0.33), \text{Yb}(0.33), \text{Ni}(0.33) - \text{Cr}(0.30) - \text{Sr}(0.18)}.$$

The formulas presented above reflect the geochemical specifics of soils in the distinguished soil provinces of Kamchatka, and their analysis led us to the following conclusions:

(1) volcanic soils formed in intermediate and, particularly, silicic ashes, which are predominant in the soil cover of Kamchatka, are generally depleted in trace elements relative to soils on continents;

(2) variably elevated concentrations in soils on Kamchatka are typical of the following eight elements (of those examined in the course of our research): Cr, Cu, Mn, Sc, Zn, Co, V, and Ag; all of them are more typical of basic magmatic rocks (including P and As, mentioned above in comparison with zonal soils);

(3) trace elements typomorphic of silicic magmatic rocks (Pb, Li, Ba, Mo, and others) are depleted in the volcanic soils, including those formed immediately in silicic ashes, perhaps, because these elements are sig-

Table 8. Concentrations of trace elements in soils on continents and the CC of these elements in volcanic soils on Kamchatka

Element	Concentration in soils on continents, ppm [4]	Soil provinces on the Kamchatka Peninsula and CC of elements in their soils			
		Southeastern	Northern	Central	Western
Li	30	0.6	0.94	0.83	(0.50)
Sc	8	*1.88*	*1.25*	0.83	0.63
Ti	3700	0.39	0.8	0.52	0.81
V	90	0.95	*1.03*	0.77	0.68
Cr	60	*2.78*	0.72	0.18	0.30
Mn	500	*2.47*	*1.1*	*1.03*	0.80
Co	9	*1.18*	0.67	0.65	0.66
Ni	20	0.29	0.91	0.35	0.33
Cu	23	2.77	*2.56*	*1.77*	*1.74*
Zn	60	*1.52*	0.62	0.75	0.35
Ga	20	0.74	0.62	0.51	0.50
Sr	220	0.61	0.63	0.3	0.18
Y	25	0.45	0.31	0.26	0.40
Zr	300	0.4	0.5	0.2	0.33
Mo	2	0.77	0.86	0.78	0.65
Ag	0.1	*1.1*	0.6	0.8	1.00
Sn	1.1	*1.3*	*1.51*	*1.88*	*1.82*
Ba	500	0.4	0.65	0.59	0.40
Yb	3	0.62	0.37	0.33	0.33
Pb	20	0.6	0.31	0.53	0.50

nificantly depleted in all of the examined types of volcanic ashes, from basic to silicic, which, in turn, likely reflects the overall geochemical specifics of multistage volcanism on the Kamchatka Peninsula;

(4) volcanic soils in all provinces are characterized by pervasively elevated Cu concentrations, which is most contrastingly pronounced in the soils formed in intermediate and basic ashes;

(5) the number of elements enriched in the soils depends on the composition of the ashes in which these soils are formed: the overall number of these elements is prone to increase in the sequence silicic–intermediate–basic ashes, which is completely consistent with the aforementioned affiliation of these elements with basic magmatic rocks;

(6) the number of elements depleted in the soils and the degree of their depletion increase in the opposite direction; i.e., from basic to silicic ashes.

The reasons for the ubiquitously elevated Cu concentrations in soils on Kamchatka require further examination. It should be mentioned that high Cu concentrations are characteristic not only of the volcanic soils discussed herein but also of natural waters on Kamchatka, a fact that should be regarded as a distinctive regional feature.

With regard to the discovered high activity of trace elements typomorphic of basic magmatic rocks in the origin of the geochemical specifics of volcanic soils on Kamchatka, it is worth noting the deficit in Ni in all of the distinguished soil provinces. The most contrasting depletion in this element (CC = 0.29) was detected in soils formed in basic ashes, a fact that can be accounted for only by initially low Ni concentrations in these ashes.

The depletion in Ni of modern soils in the Western province is consistent with the silicic composition of the ashes underlying the soils but is at variance with the metallogenic specifics of this part of Kamchatka. This soil province includes an extensive Ni-bearing metallogenic zone, a fact contributing to further support for the idea that the geochemical composition of the regional soils is controlled by the composition of volcanic ashes in which these soils were formed but not by the composition of the geological basement, in contrast to the classic situation with soil-forming processes.

The geochemical formulas presented above reflect the geochemical specifics of the volcanic soils and are shown (in a concise form) in the schematic map of soil provinces on Kamchatka (Fig. 2). The numerators of the formulas show all of the predominant trace elements whose CC > 1, and the denominators list only the most deficient elements whose CC << 1.

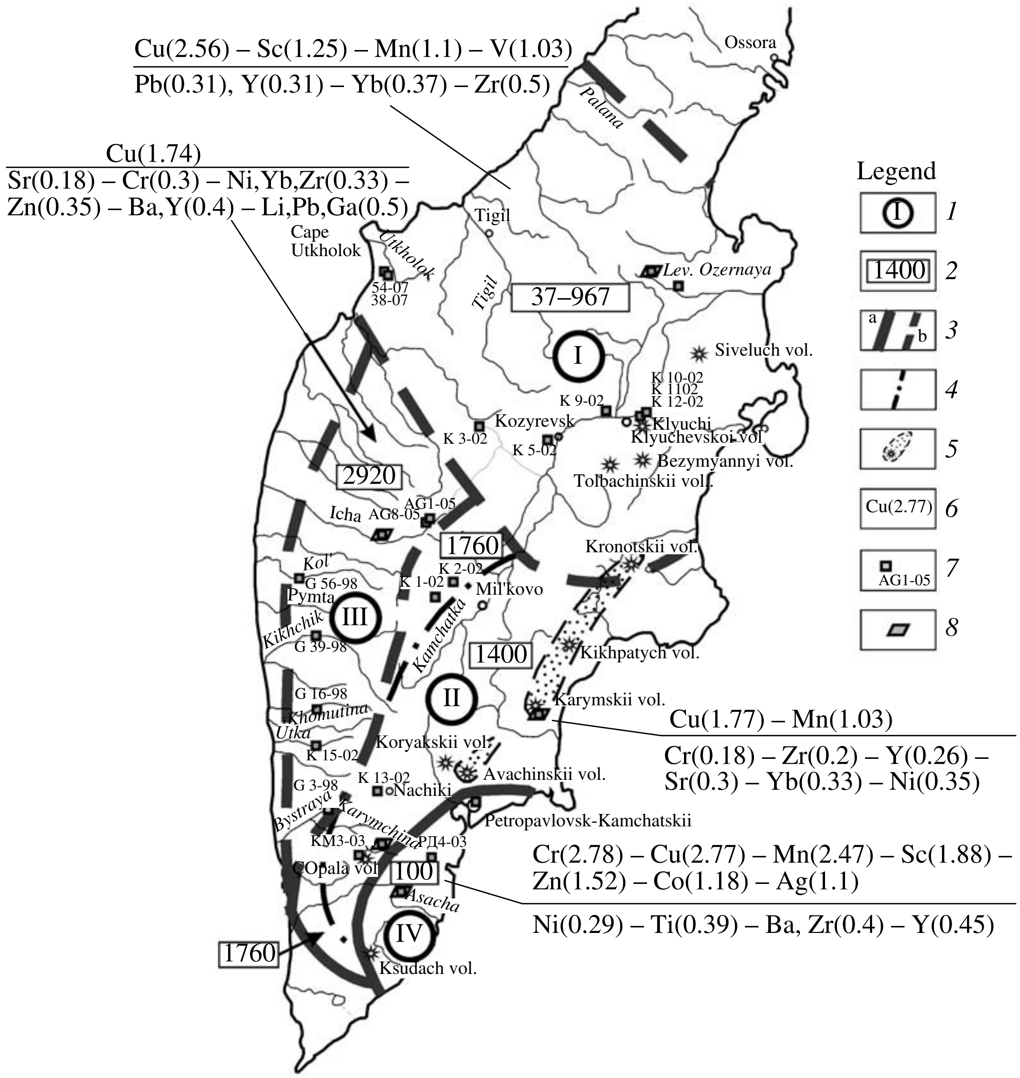

Fig. 2. Schematic map of soil zoning and geochemical specifics on the Kamchatka Peninsula.
(*1*) Soil provinces (composition of near-surface ashes): (I) Northern (ashes of andesite composition), (II) Central (ashes of rhyodacite composition), (III) Western (ashes of rhyodacite composition), (IV) Southwestern (ashes of basaltic andesite composition); (*2*) age (years) of near-surface ashes; (*3*) boundaries of soil provinces: (a) established, (b) inferred; (*4*) boundaries between soils formed in ashes of identical complex from Opala and Ksudach volcanoes in the Central soil province; (*5*) local areals of moderrn ashes near active Kamchatka volcanoes; (*6*) numerals in parentheses in the geochemical formulas show the clarkes of concentrations of elements in soils of the provinces relative to the contents of these elements in soils on continents [4]; (*7*) location of reference soil profiles run to specify the occurrence of marker ash beds and their numbers; (*8*) areas where detailed soil studies were carried out.

The results obtained on the geochemical characteristics of the volcanic soils can be utilized in disputable situations, when the soils cannot be visually identified according to the composition of the ashes in which these soils were formed. This problem can be solved using the multiplicative geochemical coefficient, which involves a great number of elements behaving similarly in the soils in question. This makes it possible to enhance the "desired signal" and suppress the "random noise," which may be related, for example, to the inaccuracy of the analytical data and local variations in the trace-element composition depending on the sampling site.

In order to identify volcanic soils on Kamchatka, we derived a multiplicative coefficient which includes trace elements characterized by a pervasive decrease in concentration from soils formed in basic ashes to soils developing in silicic ashes:

$$\gamma = Cu \cdot Cr \cdot Mn \cdot V \cdot Sr \cdot Co \cdot Sc/10^{10},$$

where symbols of elements denote their mean geometric concentrations in the soils (in ppm);

the division of the coefficient by 10^{10} does not modify the meaning of the this coefficient and is done to reduce its value.

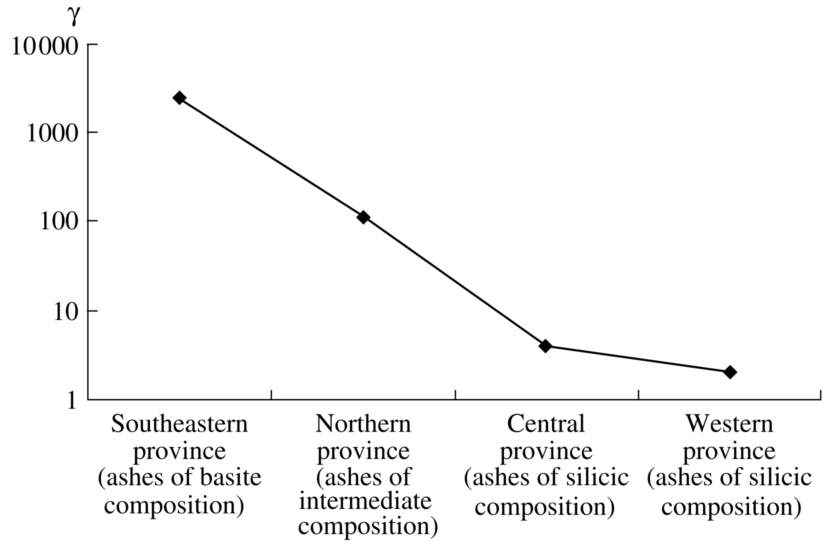

Fig. 3. Variations in the multiplicative coefficient γ for volcanic soils in soil provinces of Kamchatka formed in ashes of various composition.

Our calculations yielded the following γ values of the soil provinces and, correspondingly, the volcanic soils formed in ashes of various composition:

Southeastern province, ashes of basic composition —2425.9;

Northern province, ashes of intermediate composition—108.0;

Central province, ashes of silicic composition—3.96;

Western province, ashes of silicic composition—2.05.

Based on these values, we constructed a plot for the γ values (Fig. 3), which can be applied to identify volcanic soils on Kamchatka.

The scatter of the γ values indicates that geochemical characteristics make it possible to accurately identify soils formed in ashes of basic, intermediate, and silicic composition. It is, however, problematic whether this coefficient can be used to identify the affiliation of the soils to the Central or Western provinces, because its values for these provinces are similar.

The main difficulty in the geochemical identification of soils formed in silicic ashes is their general depletion in trace elements, including those typomorphic of silicic magmatic rocks. Studies in this field should be continued, and soils should be analyzed for a wider spectrum of elements and the application of more sensitive and accurate analytical techniques.

Our geochemical results for volcanic soils on Kamchatka indicate that their original geochemical specifics are controlled by the composition of ashes that provided the mineral basis for the development of these soils. This factor controlled the predominant-component composition and background concentrations of trace elements in the soils of the distinguished soil provinces.

The geochemistry of the surface organogenic horizons of volcanic soils also depended on their consistency and physicochemical properties, which, in turn, differed depending on the type of vegetation under which the soils were formed. These properties controlled mostly the variations in the local geochemical background of trace elements in soils of various elementary landscapes in the distinguished soil provinces.

CONCLUSIONS

(1) Our data on the surface organogenic horizons of volcanic soils on Kamchatka that were formed in volcanic ashes of various composition and age led us to distinguish the following four soil provinces of the peninsula: Northern, Central, Western, and Southeastern.

(2) Differences in the composition of ashes that served as the mineral basis of the volcanic soils formed in them are reflected in differences in the geochemistry of the soil provinces.

(3) We determined the regional geochemical background concentrations of trace elements in volcanic soils for each province, with these background concentrations controlled mostly by the trace-element composition of the volcanic ashes in which the soils developed.

(4) The consistency of the soils depends on the type of vegetation beneath which the soils are formed and controls the generally insignificant variations in the local geochemical background of trace elements within the soil provinces.

(5) Relative to the zonal soils of the former Soviet Union, volcanic soils of Kamchatka are generally

richer in Cu, have similar concentrations of Pb, and are pervasively poorer in such elements as Cr, Ni, Sr, Sn, Mo, and Ag.

(6) The geochemical specifics of soils produced in ashes of various composition are predetermined solely by trace elements typical of basic magmatic rocks.

(7) Trace elements typomorphic of silicic magmatic rocks are deficient in volcanic soils of all of the soil provinces, including those formed immediately in silicic ashes.

(8) The number of excess elements in the soils increases from 1 to 8 in the sequence silicic–intermediate–basic soil-forming ashes. The number of deficient elements and the extent of their deficit increase in the opposite direction.

(9) All of the provinces are characterized by pervasively occurring elevated concentrations of Cu, a phenomenon most clearly pronounced in soils produced in intermediate and basic ashes.

(10) The geochemical identification of volcanic soils formed in ashes of various composition can be accomplished with a multiplication coefficient, which includes trace elements characterized by a pervasive decrease in concentration in the sequence of soils formed in basic volcanic ashes to those in silicic ashes.

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