

Geochemical Features of Soil and Plant Cover in the Zone of Recent Explosive Volcanism

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Abstract—Geochemical specialization of the soil and plant cover has been revealed in the vicinity of the active Karymsky volcano (the eastern coast of the Kamchatka Peninsula), where the concentrations of most trace elements in the soil are lower than their clarkes but those in plants exceed their contents commonly recorded in living matter. Freshly deposited volcanic ash is enriched with movable forms of trace elements. As a result of hypergenic processes, they are dissolved and transferred to ground and surface waters, which accounts for a rich mineral composition of vegetation.

Key words: soils, plants, active volcanism, geochemistry.

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The effect of volcanism on soil formation and plant development is usually attributed to periodic fallout of volcanic ash (which overlays the existing soil and plant cover), with such an episode being followed by a long period of relative “rest.” However, specific conditions of soil formation and vegetation development in the vicinity of permanently active volcanoes are also of major interest.

The purpose of this study was to reveal specific features of these processes in the zone of continuous volcanic ash fallout in the vicinity of the active Karymsky Volcano on the eastern coast of the Kamchatka Peninsula. The particular tasks were as follows: to characterize specific features of soils and vegetation accounted for by regional volcanic activity; to reveal geochemical specialization of soil genetic horizons, volcanic ashes, and local vegetation; and to estimate possible correlations among trace element contents in fresh volcanic ash, soils, and plants growing on them.

OBJECTS AND METHODS

Studies were performed in the vicinity of Karymskoe Lake located in the caldera of the Akademii Nauk volcano, 6 km from the active Karymsky volcano, which are structurally included in the Karymsky volcanic center of the East Kamchatka volcanic belt.

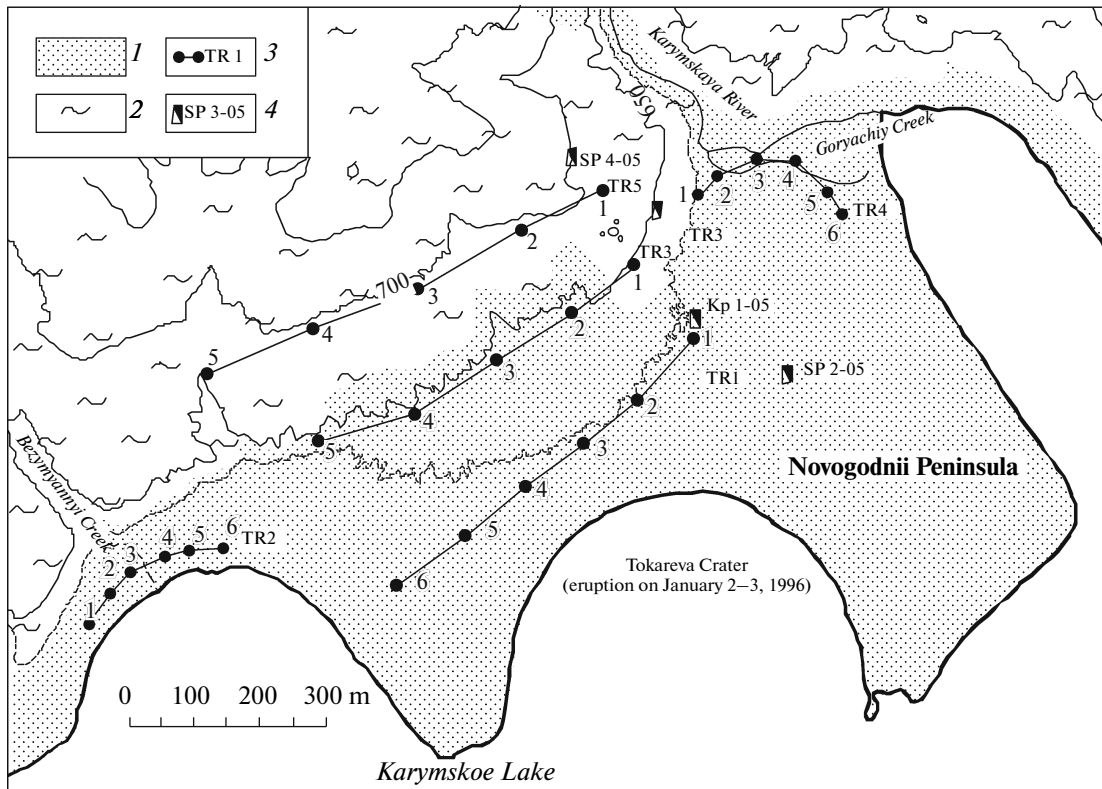
Two simultaneous eruptions in this middle-mountain area took place in early January 1996, one at the

top of the Karymsky volcano and the other in the north of Karymskoe Lake, in the Akademii Nauk caldera (Fedotov, 1996). The underwater eruption involved an abundant discharge of basaltic pyroclastic material, which changed the shoreline contour by forming the Novogodnii Peninsula at the northern lake shore and added a new mineral horizon of medium depth (2–5 cm) to the upper part of the soil profile throughout the area surrounding the lake. Ash from the continuously erupting Karymsky volcano contributes to recent organomineral soil horizons.

The climate of the study region is moderately continental. Its annual average parameters are as follows: air temperature –2 to –4°C, precipitation 500–700 mm, and humidity factor (by Ivanov) over 1.33.

The vegetation is dominated by shrub alder and subalpine herb–reed grass meadow communities. Volcanic ashes from the Karymsky volcano (mainly andesitic) have served as soil-forming rock for both recent and buried organogenic soil horizons.

Soils, volcanic ashes, and plants (reed grass *Calamagrostis langsdorffii*, which is ubiquitous in the region) were studied in four soil pits and five geochemical transects (Fig. 1). Soil pits SP1 and SP2 on the Novogodnii Peninsula were used to analyze the upper horizons of volcanic ash deposits, while pits SP3 and SP4 were dug through the entire thickness of the



Schematic map of the study region: (1) essentially bare areas with pioneering plant groups, (2) areas covered by shrub alder and meadow associations, (3) ecogeochemical transects with numbers of stations, and (4) basic soil pits.

Holocene soil–pyroclastic cover characteristic of this territory.

Geochemical transects were established to analyze the distribution pattern of trace elements in soils and plants under different landscape conditions, both on the Novogodnii Peninsula (transects TR1–TR4) and on the hill slope adjoining it on the northwest (TR5).

To study geochemical features of the loose soil–pyroclastic cover, we selected the most typical soil and ash horizons. In well-developed soils around Karymskoe Lake (formed throughout the Holocene), these were the sod (root-inhabited) horizon, buried humus horizons, and buried ash (andesitic) horizons. In the Novogodnii Peninsula formed by products of recent eruptions, we distinguished surface andesitic ash recently discharged from the Karymsky volcano and compacted basaltic ash from the underwater eruption in Karymskoe Lake.

We identified different elementary landscapes on the peninsula. According to Perel'man's (1975) nomenclature, they are as follows:

– transeluvial, geochemically weakly subordinate (the middle part of the peninsula, transect TR1);

– transeluvial, geochemically subordinate (hill slope adjoining the peninsula on the northwest, TR5);

– transeluvial accumulative (the inland part of the peninsula at the slope base, TR3);

– trans-superaqual, geochemically weakly subordinate (Goryachiy Creek valley with thermal springs at the northern margin of the peninsula, TR4); and

– trans-superaqual, geochemically subordinate (overmoistened alluvial cone of the Bezmyannyi Creek in the west of the peninsula, TR2).

To estimate geochemical specialization of genetic soil horizons, recent ash layers, and vegetation growing in the study area, we calculated the clarkes of concentrations (CCs) of trace elements as the ratios of their geometric mean contents in the above objects to the clarkes of these elements in corresponding media. For andesitic ashes from the Karymsky volcano, recently deposited or buried, we accepted the mean contents of trace elements in intermediate rocks; for basaltic ash from the underwater eruption in Karymskoe Lake, their mean contents in continental basalts; the corresponding parameters for plants were inferred from data on the occurrence of chemical elements in living matter (Solovov et al., 1990), and those for the

Table 1. Clarkes of concentration (CCs) of trace elements in ashes, soil horizons, and plants in the vicinity of Karymskoe Lake (gross contents)

Element	Ash, soil horizon						Plants				
	Freshly deposited ash from Karymsky volcano, <i>n</i> = 6	Andesitic ash from Novogodnii Peninsula, <i>n</i> = 22	Basaltic ash from Novogodnii Peninsula, <i>n</i> = 12	Surface sod horizons, <i>n</i> = 7	Buried humus horizons, <i>n</i> = 8	Buried ash horizons, <i>n</i> = 10	Transect TR5, <i>n</i> = 5	Transect TR1, <i>n</i> = 6	Transect TR2, <i>n</i> = 6	Transect TR4, <i>n</i> = 6	Transect TR5, <i>n</i> = 5
Sr	0.35	0.35	0.75	0.36	0.45	0.23	1.51	2.26	0.65	0.94	1.12
Mn	0.53	0.59	0.64	0.57	0.81	0.62	0.33	0.35	0.37	1.98	3.67
Cr	0.09	0.41	0.42	0.13	0.12	0.16	0.91	0.91	1.08	1.23	1.29
V	0.62	0.63	0.43	0.57	0.99	0.57	38.66	27.88	17.15	28.84	26.84
Ni	0.25	0.61	0.43	0.29	0.25	0.34	4.12	4.55	4.65	6.28	10.4
Co	0.37	0.49	0.6	0.33	1.25	0.37	5.51	4.37	2.82	5.64	3.51
Cu	0.66	1.2	0.89	0.94	3.69	1.18	0.74	1.27	0.69	1.16	1.87
Ag	0.67	0.39	0.28	0.4	0.36	0.46	0.26	1.39	1.12	1.3	2.21
Zn	1.01	1.11	0.81	0.94	1.2	0.89	0.36	0.48	0.4	0.66	1.48
Pb	0.83	0.72	0.56	0.94	0.68	0.81	1.17	0.86	0.9	0.93	1.90
Mo	0.97	0.88	0.60	0.99	0.47	0.86	0.52	0.44	0.51	3.91	0.70
Sc	0.22	0.24	0.28	0.2	1.24	0.26	2.56	1.82	1.66	2.03	1.11

buried humus horizon, from data on their occurrence in continental soils (Lukashev and Lukashev, 1967).

We compared relative contents of movable trace elements in andesitic ash from the Karymsky volcano (ubiquitous in the surface soil horizons) and in freshly deposited ashes (not yet leached with precipitation). This allowed us to estimate the directions and rates of geochemical transformations of these ashes in the soil–pyroclastic cover under the effect of hypergenic processes involving the transition of dissolved trace elements to contiguous media, including live phytomass.

Samples from the soil pits were used to determine the following parameters: pH_{water} , hydrolytic acidity, humus content (by Tyurin's method); movable forms of Si, Fe, and Al (by Tamm's method); and exchangeable Ca and Mg (by a complexometric method). Chemical soil properties were analyzed as described in manuals by Peterburgskii (1968) and Arinushkina (1970).

Soil and ash samples were analyzed for the gross contents of trace elements and the contents of their soluble forms; plant samples, for the composition of ash trace elements.

Total (gross) concentrations of trace elements were determined by complete spectral analysis in a DFS-

458 diffraction spectrograph. Measurements were made on a three-phase arc discharge, introducing the sample by a spilling method. Movable forms of trace elements were extracted from lithochemical samples with 1M HNO_3 (solid-to-liquid ratio 1 : 10), and their contents in extracts were determined by inductively coupled plasma mass spectrometry (ICP-MS).

RESULTS AND DISCUSSION

Specific Features of Soils Formed in the Recent Ash Fallout Zone

A distinctive feature of soils formed in the vicinity of Karymskoe Lake is that they are stratified and polygenetic: their profile consists of four superimposed elementary profiles, each containing organogenic horizons and distinct layers of weakly transformed ash from the Karymsky volcano.

The lower part of the soil profile contains an ochreous illuvial–metamorphic horizon (B_{ochr}) formed by mid-Holocene ash discharged from the Karymsky volcano during the early first period of its activity, approximately 6100 years ago (Braitseva and Melekestsev, 1989). This is characteristic of volcanic ochreous soils segregated by Sokolov (1973) into an individual soil type.

The upper part of the profile contains a series of horizons—O, A_dO, C, II [A_d1], II [A_d2], and II [A_d3]—consisting of pyroclastic material discharged during recent eruptions of the Karymsky volcano and the catastrophic underwater eruption in Karymskoe Lake.

Mesomorphological and physicochemical properties of upper soil horizons provide evidence that they are poor in finely dispersed organic matter (humus content 1.2–1.5%). The organic component is represented by dead (slightly transformed) or live roots of herbaceous plants, which consolidate volcanic ash into dense, well-formed sod. Continuous fallout of pyroclastic material from recent eruptions of the volcano prevents effective transformation of organic matter, since it is known that a “rest” period of no less than 100 years is necessary for the development of mature organogenic soil horizons under such conditions (Zakharikhina, 2006).

On the whole, these soils are characterized by a low base saturation degree, weakly acid pH values (4.9–5.8), and the fulvate composition of humus (with prevalence of movable fulvic acids). They are also subject to illuvial processes: newly formed organomineral compounds are leached down the soil profile, being partially fixed in its middle and lower parts.

Well-developed organogenic horizons containing appreciable amounts of humic substances occur only in the middle part of the soil profile, beginning from a depth of about 40–50 cm. Being interposed by Holocene ashes from the Karymsky volcano, they consist of three layers. The deepest layer, horizon III [A], corresponds to a long interval (about 2300 years) between two major periods of volcanic activity. The content of humus in these buried horizons is about 16–17% in soils under shrub alder vegetation and 3–

4% under meadow vegetation. Live plant roots in them are sparse.

As noted above, the Novogodnii Peninsula on the southeastern shore of Karymskoe Lake was formed as a result of volcanic activity. It is covered by a 10- to 12-cm layer of loose andesitic ash from the Karymsky volcano, which overlays compacted basaltic ash discharged during the underwater eruption. Colonization of this territory by pioneering plants proceeds slowly. Volcanic ashes have weakly acid to almost neutral pH values (5.4–6.8) and are very poor in humus (fractions of one percent), which is brought by runoff from the adjacent hill slope. The humus has a fulvate composition. The content of sesquioxides, which indicate the presence of movable soil-formation products, is very low.

Geochemical Features of Genetic Soil Horizons and Volcanic Ash Layers under Conditions of Recent Ash Fallout

Volcanic ashes forming the soil–pyroclastic cover of the study area, including as yet unleached (fresh) varieties of andesitic ashes from the Karymsky volcano, proved to have lower total contents of almost all trace elements included in analysis, compared to their average concentrations in corresponding rocks (Table 1). A slight excess of CC over unity (up to 1.2) was observed for Cu and Zn in andesitic ash from the Novogodnii Peninsula and for Cu in similar buried ash from the pit on the adjoining hill slope. Buried humus horizons showed accumulation of Cu relative to its crustal abundance (CC = 3.69); Co, Zn, and Sc were also in a slight excess over the corresponding clarke values. Trace elements contained in different components of the soil–pyroclastic cover were grouped in ranked (priority) series with respect to CC value (in descending order). These series are as follows:

Ash, soil horizon	Priority trace element series	
Freshly deposited andesitic ash from the Karymsky volcano	$\frac{Zn}{CC > 1} > \frac{Mo, Pb, Ag, Cu, V, Mn, Co, Sr, Ni, Sc, Cr}{CC 1-0}$	
Novogodnii Peninsula, transect TR1	Andesitic ash	$\frac{Cu, Zn}{CC > 1} > \frac{Mo, Pb, V, Ni, Mn, Co, Cr, Ag, Sr, Sc}{CC 1-0}$
	Basaltic ash	$\frac{-}{CC > 1} > \frac{Cu, Zn, Sr, Mn, Mo, Co, Pb, V, Ni, Cr, Ag, Sc}{CC 1-0}$
Soils on hill slope, transect TR5	Surface sod horizons	$\frac{Cu, Mn, Zn}{CC > 1} > \frac{V, Co, Sc, Sr, Mo, Pb, Ag, Ni, Cr}{CC 1-0}$
	Buried humus horizons	$\frac{Cu, Mn, V, Co}{CC > 1} > \frac{Sc, Zn, Sr, Ni, Mo, Cr, Ag, Pb}{CC 1-0}$
	Buried ash (andesitic) horizons	$\frac{Cu}{CC > 1} > \frac{Zn, Mo, Pb, Mn, V, Ag, Co, Ni, Sc, Sr, Cr}{CC 1-0}$

The arrangement of elements in these series is indicative of general trends common to all mineral (mainly mineral) formations:

- Cu, Zn, Mo, and Pb consistently tend to occur at the beginning of the series;
- V, Ni, Mn, and Co occupy intermediate positions in the series;
- Sc and Cr occur at the end of the series; and
- positions of Ag and Sr vary between the series.

In organogenic formations (buried humus horizons), these trends do not hold true except for Cu occurring at the beginning and Cr at the end of the series. This may be due to a more complex genesis of these horizons, which was apparently accompanied by

redistribution of trace elements, formation of complex organomineral compounds, and illuvial processes, with these elements being leached and resorbed from ground waters by organic matter.

A different picture is observed while analyzing data on CCs for the vegetation growing in different elementary landscapes (Table 1). Irrespective of growing conditions, the majority of trace elements detected in plants proved to be in excess over their clarkes in living matter. The priority series of these elements for the vegetation of different landscapes were compiled as described above (Sc is absent, since its concentrations in all samples were below the detection limit). They are as follows:

Landscape (transect)	Priority trace element series
Transeluvial, geochemically weakly subordinate (TR1)	$\frac{V}{CC > 10} > \frac{Ag, Cu, Pb, Sr, Ni}{CC 1-10} > \frac{Zn, Co, Mn, Mo, Cr}{CC < 1}$
Transeluvial, geochemically subordinate (TR5)	$\frac{Ag}{CC > 10} > \frac{V, Mn, Cu, Ni, Zn, Pb}{CC 1-10} > \frac{Sr, Mo, Cr, Co}{CC < 1}$
Transeluvial accumulative (TR3)	$\frac{Ag, V}{CC > 10} > \frac{Cu, Sr, Ni}{CC 1-10} > \frac{Pb, Zn, Mn, Co, Mo, Cr}{CC < 1}$
Trans-superaqual, geochemically weakly subordinate, thermal springs (TR4)	$\frac{Ag, V}{CC > 10} > \frac{Mo, Cu, Mn, Ni, Zn, Pb}{CC 1-10} > \frac{Sr, Co, Cr}{CC < 1}$
Trans-superaqual, geochemically subordinate (TR2)	$\frac{Ag}{CC > 10} > \frac{V, Cu, Ni}{CC 1-10} > \frac{Pb, Zn, Sr, Mn, Mo, Cr, Co}{CC < 1}$

These series show similarity in the arrangement of trace elements, which reflects geochemical specialization of vegetation in the zone of current volcanic ash fallout in Kamchatka. Thus, elements such as Ag, V, Cu, and Ni consistently occupy leading positions ($CC > 1$), while Cr, Co, and Mo occur at the end of the series ($CC < 1$). However, the series for plants growing under the influence of thermal springs on the Novogodnii Peninsula (TR4) is richer in elements accumulated in large excess, with Mo and Mn shifting toward the beginning of the series. This fact indicates that thermal springs may serve as an additional, local source of chemical elements incorporated by vegetation in regions of active volcanism.

The leading positions of Ag, Cu, and, to a lesser extent, Ni in the series may be explained by the fact that the coefficients of biological absorption (A_x) for these metals are, on average, higher than those for other elements, this applying to all terrestrial plants (Perel'man, 1975). However, such an explanation does not hold for V: although its absorption coefficient is low ($A_x < 1$), this metal occupies a prominent position in the series. On the other hand, elements such as Mo, Zn, and Sr have high absorption coefficients, but their

concentrations in the test plant (*C. langsdorffii*) are often insufficient. An explanation to these facts apparently lies in specific physiological features of this species.

Since migration of chemical elements in the rock–soil–plant system takes place when they are dissolved, it is of interest to consider the distribution pattern and behavior of movable forms of trace elements in soils and volcanic ashes of the study region. Volcanic ash at the moment of eruption has a high sorption capacity, and its particles adsorb considerable amounts of various trace elements from the gaseous phase (Basharina, 1958; Gushchenko, 1965; Markhini et al., 1963; Tovarova, 1958).

Freshly deposited (unleached) andesitic ashes from the Karymsky volcano are markedly enriched with movable forms of trace elements (both qualitatively and quantitatively), compared to all horizons studied in the soil–pyroclastic cover (Table 2). The average contents of these forms (relative to the gross contents of corresponding elements) reach the highest values in the following kinds of ash (data on movable Ag are absent):

Table 2. Contents of trace elements in movable forms relative to their gross contents in soils and volcanic ashes in the vicinity of Karymskoe Lake, %

Ash, soil horizon	Sr	Mn	Cr	V	Ni	Co	Cu	Zn	Pb	Mo	Sc
Freshly deposited ash from Karymsky volcano, $n = 6$	7.31	2.51	5.40	1.70	16.62	14.45	24.19	2.72	7.03	3.93	5.03
Andesitic ash from Novogodnii Peninsula, $n = 22$	5.88	4.02	1.01	1.60	5.77	6.78	5.77	1.76	3.98	3.94	10.07
Basaltic ash from Novogodnii Peninsula, $n = 12$	5.64	2.77	0.33	0.71	3.46	4.63	3.08	1.70	3.06	4.77	12.29
Surface sod horizons, $n = 7$	3.25	1.55	5.29	2.49	6.34	4.02	9.15	1.55	5.23	4.12	4.85
Buried humus horizons, $n = 8$	3.45	1.31	1.45	0.91	3.69	2.34	4.89	1.70	4.80	2.66	2.64
Buried ash horizons, $n = 10$	5.28	2.11	7.40	4.92	7.52	5.24	9.03	2.16	6.54	3.65	6.58

– fresh andesitic ash: Cu (24.19%), Ni (16.62%), Co (14.45%), Sr (7.31%), Pb (7.03%), and Zn (2.72%);

– andesitic ash from the Novogodnii Peninsula: Mn (4.02%);

– basaltic ash from the Novogodnii Peninsula: Sc (12.29%) and Mo (4.77%); and

– buried ash horizons: Cr (7.40%) and V (4.92%).

Comparing the relative contents of movable trace elements in andesitic ashes included in the surface horizons of the soil–pyroclastic cover with those in freshly deposited ash from the Karymsky volcano, it is possible to estimate the direction and rate of geochemical transformation of fresh ash in the course of hypergenic processes. On the basis of such a comparison, we constructed the following geochemical formulas for different elementary landscapes of the study area:

Landscape (transect)	Geochemical formulas of leaching and repeated accumulation of trace elements in the course of hypergenic transformation of soil-forming andesitic ashes
Transeluvial, geochemically weakly subordinate (TR1)	$\frac{\text{Cr}(0.13) - \text{Cu}(0.29) - \text{Ni}(0.44) - \text{Co}(0.70) - \text{Pb}(0.72) - \text{Zn}(0.98)}{\text{V}(1.08) - \text{Mo}(1.23) - \text{Sr}(1.34) - \text{Mn}(2.44) - \text{Sc}(2.76)}$
Transeluvial, geochemically subordinate (TR5)	$\frac{\text{Co}(0.29) - \text{Ni}(0.34) - \text{Cu}(0.41) - \text{Zn}(0.43) - \text{Sr}(0.46) - \text{Mn}(0.50) - \text{Sc}(0.70) - \text{Pb}(0.72) - \text{Cr}(0.76) - \text{Mo}(0.96)}{\text{V}(1.01)}$
Transeluvial accumulative (TR3)	$\frac{\text{Cu}(0.24) - \text{Ni}(0.28) - \text{Cr}(0.31) - \text{Co}(0.57) - \text{Pb}(0.62) - \text{Mo}(0.75) - \text{Sr}(0.77) - \text{Zn}(0.83)}{\text{V}(1.39) - \text{Sc}(1.84) - \text{Mn}(2.58)}$
Trans-superaqual, geochemically weakly subordinate, thermal springs (TR4)	$\frac{\text{Cu}(0.23) - \text{Ni}(0.27) - \text{Co}(0.30) - \text{Cr}(0.32) - \text{Zn}(0.34) - \text{Pb}(0.37) - \text{V}(0.50) - \text{Sr}(0.57)}{\text{Mn}(1.06) - \text{Mo}(1.15) - \text{Sc}(1.55)}$
Trans-superaqual, geochemically subordinate (TR2)	$\frac{\text{Cr}(0.11) - \text{Cu}(0.21) - \text{Ni}(0.42) - \text{Co}(0.43) - \text{Pb}(0.65) - \text{Zn}(0.68) - \text{Sr}(0.70) - \text{Mo}(0.87)}{\text{Mn}(1.16) - \text{V}(1.19) - \text{Sc}(1.98)}$

The numerator of these formulas shows the series of trace elements for which the relative contents of movable forms proved to be lower in transformed ashes than in their fresh analogs, providing evidence for their dispersion in the zone of hypergenesis. Corresponding content ratios are shown in parentheses after element

names (the higher the ratio, the lower the rate of dispersion). The set of trace elements leached from ashes at the highest rates remains fairly constant in different elementary landscapes. It includes Cr (89%), Cu (79%), Ni (72%), and Co (71%); then follow Zn (66%) and Pb (63%). A noteworthy fact is that the loss

Table 3. Correlations between average percent contents of soluble trace elements in freshly deposited ash from the Karymsky volcano and in formations of the soil–pyroclastic cover in the vicinity of Karymskoe Lake ($n = 11$, $r5\%cr = 0.602$)

Ash, soil horizon		1	2	3	4	5	6
Freshly deposited ash from Karymsky volcano	1	1					
Andesitic ash from Novogodnii Peninsula	2	0.401	1				
Basaltic ash from Novogodnii Peninsula	3	0.026	0.901	1			
Surface sod horizons	4	0.830	0.339	0.114	1		
Buried humus horizons	5	0.688	0.437	0.236	0.741	1	
Buried ash horizons	6	0.706	0.316	0.118	0.913	0.616	1

Note: n is the number of elements included in calculations, and $r5\%cr$ is the critical value of correlation coefficient at 5% confidence level. Statistically significant correlations are in boldface.

of movable trace elements from ashes increases under the influence of thermal springs (transect TR4) and flowing water (transect TR2).

In the series of elements shown in the numerator, the relative contents of movable forms are higher in transformed than in fresh ashes, with their ratio exceeding unity. This may be evidence for secondary accumulation of these elements, which include Mn, Sc, V, Mo, and Sr. In most cases, however, the excess over unity is small and may well be accounted for by element's inertness in hypergenic processes. The highest degrees of secondary accumulation are characteristic of Mn (2.58) and Sc (2.76) in surface ash layers on the Novogodnii Peninsula. Most of inert elements are anionogens, which accounts for their low mobility in local landscapes characterized by acid or weakly acid pH of soils and ashes.

On the whole, geochemical formulas for transformed andesitic ashes in different elementary landscapes of the Novogodnii Peninsula (transects TR1–

TR4) are more similar to each other than to the formula for the adjoining hill slope (the transeluvial, geochemically subordinate landscape, TR5), although general trends are the same in both cases. This is evidence that hypergenic geochemical processes on the peninsula and the adjoining hill slope may differ in direction. In particular, the leaching of Mn and Sc from ashes on the slope apparently accounts for their accumulation in transformed andesitic ashes on the peninsula (see above).

Thus, movable trace elements deposited with erupted volcanic ashes rapidly dissolve and enter surface and ground waters, but they are also partly fixed in the soil. This follows from correlations between their contents in fresh ashes and soil horizons, which were revealed by compiling corresponding geochemical series of elements ranked in order of decreasing average content of movable forms relative to the total element's content. These series are as follows:

Freshly deposited ashes from the Karymsky volcano

Transect TR1

Transect TR2

Transect TR3

Transect TR4

Transect TR5 (sod horizons)

Transect TR5 (buried humus horizons)

Transect TR5 (buried ash horizons)

Cu–Ni–Co–Sr–Pb–Cr–Sc–Mo–Zn–Mn

Sc–Co–Sr–Ni–Cu–Mn–Pb–Mo–Zn–Cr

Sc–Ni–Co–Sr–Cu–Pb–Mo–Mn–Zn–Cr

Sc–Co–Mn–Cu–Sr–Ni–Pb–Mo–Zn–Cr

Sc–Cu–Mo–Ni–Co–Sr–Mn–Pb–Cr–Zn

Cu–Ni–Cr–Pb–Sc–Mo–Co–Sr–Mn–Zn

Cu–Pb–Ni–Sr–Mo–Sc–Co–Zn–Cr–Mn

Cu–Ni–Cr–Sc–Pb–Sr–Co–Mo–Zn–Mn

To estimate the degree of similarity (or difference) between these series, we calculated corresponding rank correlation coefficients (Table 3). The series for surface sod horizons and buried humus horizons showed a significant positive correlation with each other and with the series for freshly deposited volcanic ash. This may be explained by soil formation under conditions that remained similar during the Holocene: these soils developed mainly from ashes

erupted by the Karymsky volcano in different periods and enriched with movable trace elements in the course of eruption. No positive correlation was revealed between the series for fresh ashes and transformed pyroclastic deposits on the Novogodnii Peninsula, since volcanogenic movable elements had already been leached from the latter by atmospheric precipitation.

CONCLUSIONS

(1) The recent catastrophic eruption in Karymskoe Lake and continuous activity of the Karymsky volcano accounted for the formation of specific soils in the surrounding area. Recent horizons of these soils practically lack finely dispersed organic matter capable of supplying elements necessary for plant growth. Regular fallout of pyroclastic material prevents effective transformation of organic matter in the soil.

(2) All components identified in the soil–pyroclastic cover of the study area are characterized by reduced contents of most trace elements, compared to their clarkes in corresponding lithospheric media. Irrespective of landscape conditions of plant growth, the majority of trace elements determined in plants showed an excess over their clarkes for living matter. The highest parameters of biological absorption are characteristic of Ag, V, and, to a lesser extent, Cu.

(3) Freshly deposited varieties of andesitic ashes from the Karymsky volcano, which form loose surface horizons of the study area, are markedly enriched with movable forms of trace elements (both qualitatively and quantitatively), compared to all horizons of the soil–pyroclastic cover. In these ashes, which have not yet been affected by hypergenic processes, the average relative contents of many trace elements in movable forms (percentages of total contents) reach the highest values. In particular, this concerns Cu (24.19%), Ni (16.62%), Co (14.45%), Sr (7.31%), Pb (7.03%), and Zn (2.72%).

As a result of hypergenic geochemical processes in the soil–pyroclastic cover, movable forms of most trace elements are leached from freshly deposited ashes and transferred in dissolved form to contiguous media, including live phytomass. This secondary dispersion is most intense in cases of Cr, Cu, Ni, and Co. Conversely, V, Sr, Mn, Sc, and, to a lesser extent, Mo behave as inert elements under landscape conditions of the Novogodnii Peninsula. Moreover, their contents may even increase slightly due to input with runoff from adjoining hill slopes.

(4) Volcanic ash particles during eruption effectively adsorb trace elements from the gaseous phase. When the ash settles, movable forms of these elements rapidly dissolve and enter surface and ground waters, which accounts for a rich mineral composition of vegetation in the study region.

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REFERENCES

- Arinushkina, E.V., *Rukovodstvo po khimicheskomu analizu pochv* (Manual of Soil Chemical Analysis), Moscow: Mosk. Gos. Univ., 1970.
- Basharina, L.A., Analysis of Gaseous Emissions from the Klyuchevskoi and Shiveluch Volcanoes, *Byull. Vulkanol. Stantsii*, 1958, no. 27, pp. 3–8.
- Braitseva, O.A. and Melekestsev, I.V., The Karymsky Volcano: History of Formation, Dynamics of Activity, and Long-Term Prognosis, *Vulkanol. Seismol.*, 1989, no. 2, pp. 14–31.
- Fedotov, S.A., On the Simultaneous Eruption of Two Kamchatka Volcanoes in January 1996, *Zemlya i Vselennaya*, 1996, no. 3, pp. 60–65.
- Gushchenko, I.I., *Peply Severnoi Kamchatki i usloviya ikh obrazovaniya* (Ashes of Northern Kamchatka and Conditions of Their Formation), Moscow: Nauka, 1965.
- Lukashev, K.I. and Lukashev, V.K., *Geokhimicheskie poiski elementov v zone gipergeneza* (Geochemical Search for Elements in the Hypergenesis Zone), Minsk: Nauka i Tekhnika, 1967, pp. 52–54.
- Markhinin, E.K., Tokarev, P.I., Pugach, V.B., and Dubik, Yu.M., Eruption of the Bezmyannyi Volcano in the Spring of 1961, *Byull. Vulkanol. Stantsii*, 1963, no. 34, pp. 12–36.
- Perel'man, A.I., *Geokhimiya landshafta* (Landscape Geochemistry), Moscow: Vysshaya Shkola, 1975.
- Peterburgskii, A.V., *Praktikum po agronomicheskoi khimii* (Practical Course in Agricultural Chemistry), 6th ed., Moscow: Kolos, 1968.
- Sokolov, I.A., *Vulkanizm i pochvoobrazovanie* (Volcanism and Soil Formation), Moscow: Nauka, 1973.
- Solovov, A.P., Arkhipov, A.Ya., Bugrov, V.A., et al., *Spravochnik po geokhimicheskim poiskam poleznykh iskopaemykh* (Manual on Geochemical Prospecting for Extractable Resources), Moscow: Nedra, 1995.
- Tovarova, I.I., On the Efflux of Water-Soluble Substances from Pyroclastics of the Bezmyannyi Volcano, *Geokhimiya*, 1958, no. 7, pp. 683–686.
- Zakharikhina, L.V., Soil Formation on Acid and Basic Volcanic Ashes of Different Ages, *Pochvovedenie*, 2006, no. 9, pp. 1229–1236.