

The Alteration of Effusive Rocks Due to Acidic Leaching by Shallow Thermal Waters: The Baranskii Geothermal System, Iturup Island

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Abstract—This paper discusses patterns that are observable in the alteration of effusive rocks that were discharged by Baranskii Volcano (central Iturup Island) under the action of sulfate chloride as well as acidic and ultra-acidic water (in the Kipyashchaya Rechka thermal brook). We acquired data on changes in the chemical and mineralogic composition of the rocks, structural features, porosity, and petrophysical properties. The dynamics of leaching and the leaching phase in a flowing acidic (ultra-acidic) geothermal environment are described. We note that the mechanism that is responsible for hydrogen sulfate leaching of rocks at the ground surface may be largely analogous to the generation of secondary quartzites (mono-quartzites) in the zones of ascending acidic gas flows above small gabbro–diorite and diorite intrusions.

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INTRODUCTION

Rocks are intensely altered in present-day hydrothermal (geothermal) systems in areas of Quaternary volcanism. Thermal water leaches out the primary components of volcanic rocks, such as glass, feldspar, and mafic minerals, and replaces them with secondary minerals that are more stable under changed temperature, pressure, and composition of the hydrothermal solution involved. One hydrothermal metasomatic process that occurs is hydrogen sulfate leaching, which usually takes place in the shallow zone of hot hydrothermal systems under the action of ascending acidic (ultra-acidic) sulfate and sulfate chloride waters whose temperature is $\leq 100^\circ\text{C}$. Hydrogen sulfate leaching and the generation of opalite facies rocks is a phenomenon that occurs widely and has been extensively studied to understand mineral alteration [Eroshchev-Shak, 1992; Karpov, 1991; Korzhinskii, 1955; Korobov, 1994; Lebedev, 1979; *Metasomatizm...*, 1998; Naboko et al., 1965; Rusinov, 1989; Reyes, 1990]. It is common knowledge that the main new formations in the zone of hydrogen sulfate leaching include siliceous minerals (opal, tridymite, cristobalite, chalcedony, and quartz), sulfates (gypsum, barite, alunite, and jarosite), clay minerals (kaolinite and halloysite), native sulfur, and hydroxides of iron and aluminum. However, one usually records the end products of this process as a whole or for each phase of hydrogen sulfate leaching, while the dynamics of rock alteration (the removal/introduction of chemi-

cal elements, phases in the generation of the mineral composition, porosity, pore-space structure, and petrophysical properties of the rocks concerned) is still little known.

The present study is based on results from an investigation of alluvium in the Kipyashchaya Rechka Brook that originates on the slope of the Baranskii active andesitic volcano (central Iturup Island) and that traverses the eponymous geothermal system. Multidisciplinary geological and geochemical studies of this system [Korobov, 1994; Ladygin and Rychagov, 1995; Rychagov, 1993; Rychagov et al., 1993] revealed a well-defined zoning in the alluvial boulders and pebbles of the thermal brook in the form of yellow, light grey, and darker concentric bands ranging between a few millimeters and a few centimeters in width. It was found that this phenomenon was only typical of rock samples taken in flowing acidic environments (the sampling sites were in this brook below the discharges of springs with ultra-acidic sulfate and sulfate chloride thermal waters, as well as the Golubye and Kipyashchie Lakes). It thus appears that nature itself has performed an experiment there for us to tackle several issues that are traditionally very important, both theoretically and practically, in the study of any geothermal system, viz., What are the character and directivity of hydrothermal alteration of rocks in the zones of active circulation of hydrothermal solutions? Can one quantitatively estimate the intensity of rock alteration in a flowing acidic

environment? What are the mechanisms that are responsible for the generation of metasomatic zoning under these conditions? Can one estimate the rate of rock alteration *in situ*? We note at once that the last issue is still at the stage of being properly formulated and is not considered in the present paper.

The goal of this study was to identify patterns in the variation of the compositions, structures, and properties of effusive rocks under the action of flowing acidic to ultra-acidic thermal water and to investigate the mechanisms that are responsible for the generation of metasomatic zoning that arise from hydrogen sulfate leaching of rocks.

GEOLOGIC SETTING

The central part of Iturup Island, South Kurils, contains the Baranskii active andesitic volcano, which belongs to the structure of the Ivan Groznyi volcanic range. At the northwestern slope and base of the volcano is the eponymous hydrothermal system, whose central part contains the Okeanskoe geothermal field [Pchelkin, 1988]. The system has a high temperature and is currently at the progressive halogen–sulfate–carbon-dioxide phase of evolution [Rychagov, 1993]. The bottom of the geologic section is composed of psephosammite and agglomerate tuffs and lavas that consist of andesites from the Parusnyi Series of Neogene age. These are penetrated by diorites and gabbro diorites; it is supposed that the subvolcanic bodies of these rocks are related to a deep-seated magma source and supply heat to the hydrothermal system. The aquifer sequence consists of micro- and macrofragmental tuffites, tuffs, and lavas that consist of andesites from the Lebedin Series of Lower Quaternary age, which overlie the Parusnyi rocks with no apparent angular unconformity. These rocks are fairly permeable to thermal water, whose action helped to shape the hydrothermal metasomatic zoning that is typical of geothermal systems during the progressive phase of their evolution. The section contains, from the bottom to top, the following parts: secondary quartzites (garnet quartz, mono-quartz, and muscovite–cerisite–quartz mineral associations), moderate-temperature propylites (wairakite–calcite, lomontine–quartz, prehnite–calcite, and quartz–chlorite–calcite associations), argillites (quartz–chlorite–smectites), and opalites [Korobov, 1994; Rychagov et al., 1993]. The zones differ in the reworking of parent rocks and in their petrophysical properties [Ladygin and Rychagov, 1995; Frolova et al., 1999; Ladygin et al., 2000]. The opalite zone is shallow and is formed by hydrogen sulfate leaching; it is a few tens of meters thick, reaching values as great as 200 m in fault zones.

The most intensive alteration, as far as hydrothermal clays and mono-opalites, occurs in thermal fields around boiling springs, mudpots, steam jets, and in steaming patches. Several groups of thermal springs form the origin of Kipyashchaya Rechka Brook. The

brook is 1.4 km long, flows in a shallow valley that is filled with rudaceous volcanogenic deposits, and empties into the Sernaya River. The hydrochemical features of this brook are determined by the water of Kipyashchie Springs and by Lakes Golubye. The temperature of the spring water is 81–95°C (reaching 98°C), the total mineral content varies between 1.9 and 5.8 g/L, the pH is between 0.7 and 1.7, the Eh is between +200 and +590 mV, and the composition is sulfate and sulfate chloride with high concentrations of Na and K [Znamenskii and Nikitina, 1985]. The springs boil due to the emission of free gases: hydrogen sulfide, methane, hydrogen, carbonic-acid gas, and nitrogen; these are fluorescing owing to native fine sulfur found in the water. The water composition in the brook is formed from a mixture of thermal waters from these springs and from other groups of springs downstream (Vodopadnye, Kotel, Nizhnie, Ust'evye, and Skrytye) with cold meteoric waters. The brook water remains acidic due to the large total discharge of the springs (roughly ≥ 100 L/s). The discharge rate at the brook mouth is 200 L/s and the water has a temperature of 30–32°C. The brook water has a daily rate of about 60 t of dissolved material, including about 15 t of hydrogen sulfate [Znamenskii and Nikitina, 1985].

An abundance of large, semi-rounded and rounded rock fragments (as large as 10–20 cm across) of effusive rocks ranging from basaltic andesites to dacite andesites was found in the upper reaches of Kipyashchaya Rechka Brook. When split, the boulders and pebble both show a well-defined zonal structure emphasized by successive change of color from dark grey to white in several bands (Fig. 1a, samples A-4, B-8, S-2, and L-1). Some samples exhibit zones with pronounced iron content, making the rock yellow, ginger, or brown (samples V-6 and V-2). It was noted that practically all boulders of effusive rocks in the brook bed are to varying degrees subject to geochemical alteration. One encounters both slightly altered boulders with one or two barely visible altered zones and completely altered rocks, which are white, unconsolidated, and strongly porous.

We selected the most typical samples of boulders and pebbles with the greatest numbers of altered zones for investigation. The fragments were downstream along the brook at distances of 100–200 m from the discharge of the thermal springs. Each sample showed (visible by color and textural features) three to five zones 1–3 cm wide separated by clear-cut boundaries between the center and the outer edges. The central parts of the samples retained their red color, while the edge zones were lighter in varying degrees. The zone boundaries were concentrically zonal and were frequently curved in intricate shapes. The concentric zoning is disturbed by cracks that allow alterations to penetrate into the center of sample (see Fig. 1b). Some tentative results were derived previously and reported by Frolova et al. [2001].

METHOD OF STUDY

Six samples were selected for a detailed laboratory study; these were boulders composed of effusive rocks of basaltic andesite (V-2, A-4, and S-2), of andesite (B-8 and L-1), and of dacitic andesite (V-6). The material from each zone was studied in laboratories at the Chair of Engineering and General Geology of the Faculty of Geology of Moscow State University using a polarization microscope (Olympus BX41) in transmitted and reflected light, X-ray fluorescent analysis (Analyst E.N. Samarin), X-ray diffractometry (DRON-3 diffractometer, Analyst V.G. Shlykov), and microprobe analysis with a Camscane-4DV electron microscope (Chair of Petrology of Moscow State University). Morphological analysis was used to study changes in pore space (Analyst A.A. Sasov). For each sample we measured the porosity at intervals of 2 mm from the center to the edge. For each zone the measured quantities included morphologic characteristics, such as the relative pore area, mean pore size, the shape coefficient, and the number of pores. The shape coefficient is the ratio of the major to minor axes of the ellipse that fits the image of a pore:

$$K\phi = b/a,$$

where a and b are the major and minor axes, respectively.

The coefficient in question varies between 1 (for isometric pores) and 0.01 for very elongated pores.

Cubes or rectangular prisms were cut from each zone of all samples; between 3 and 20 items were obtained for each. The following petrophysical properties were measured: rock density (ρ), density of the solid phase (mineral density) (ρ_s), porosity (n), water absorption (W), open porosity (n_o), compressional velocity (V_p), strength under uniaxial compression (R_c), and magnetic susceptibility (χ). For samples L-1 and V-2 we also measured compressional velocities at cross sections (in addition to measurements on cubes) using point sensors (an Ul'trazvuk instrument) (see Fig. 1a). All determinations were carried out using the standard procedures [Laboratornye raboty..., 2008].

RESULTS

The samples can be divided into two sets. Color varies progressively in the samples of set I (S-2, B-8, L-1, and A-4), from dark grey and black at the center to milky white and snow white at the edges (see Fig. 1). The samples of set II (V-2 and V-6) also show color variation and lighter colors, but unlike the preceding set, there is a ginger or brown layer due to accumulation of iron hydroxides, followed by a lighter layer. Below, we provide a detailed petrographic and petrophysical characterization of the samples we studied according to this separation into two sets.

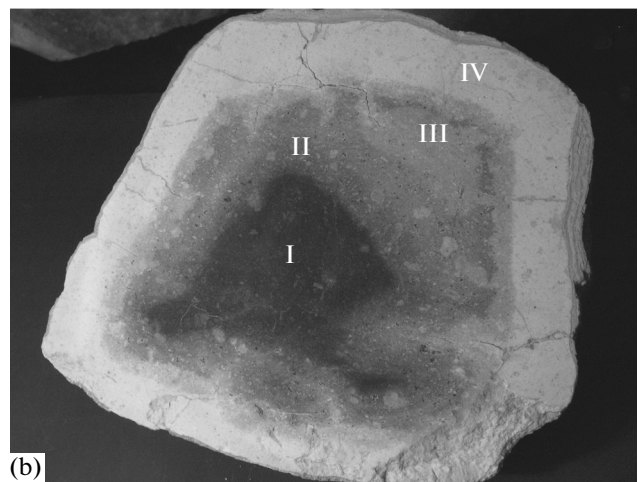
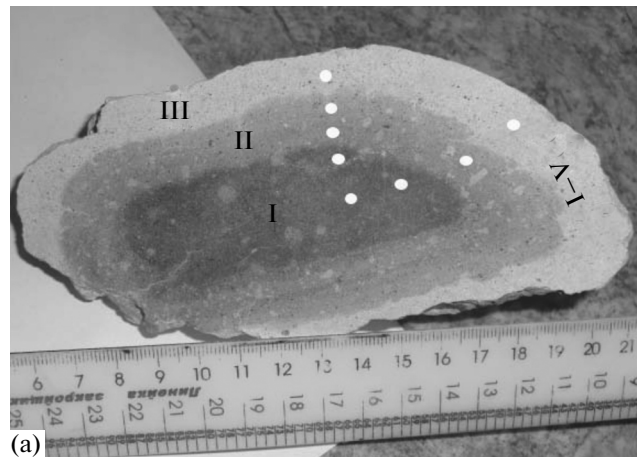


Fig. 1. Zonal structure of rock fragments in Kipyashchaya Rechka Brook.

a sample L-1, dots mark the locations where the velocities of compressional and shear waves were determined; *b* the most typical sample with microcracks that disturb the concentric zonality.

Samples of set I

Porphyric basaltic andesite (S-2). The rock is dark crimson, has porphyric texture and massive structure. Upon the background of an aphanitic groundmass one discerns plagioclase phenocrysts 1–2 mm across, larger crystals (5–6 mm) are less frequent. The pyroxene crystals reach 2 mm. Phenocrysts make up about 25–40%. The groundmass is hyalopilitic intersertal and the plagioclase microlites are up to 0.1 mm across.

The samples have three zones: the central is a dark crimson (I), a light crimson (II), and the outer is a rose–white one (III). The central parts of the samples (I) contain 30–40% plagioclase consisting of labradorite, as revealed by X-ray analysis, and as much as 30% pyroxenes. The minerals are mostly fresh (Fig. 2a), but the central parts of some crystals have been affected by secondary alteration. The pyroxene crystals have opaque margins. The clinopyroxenes contain dark

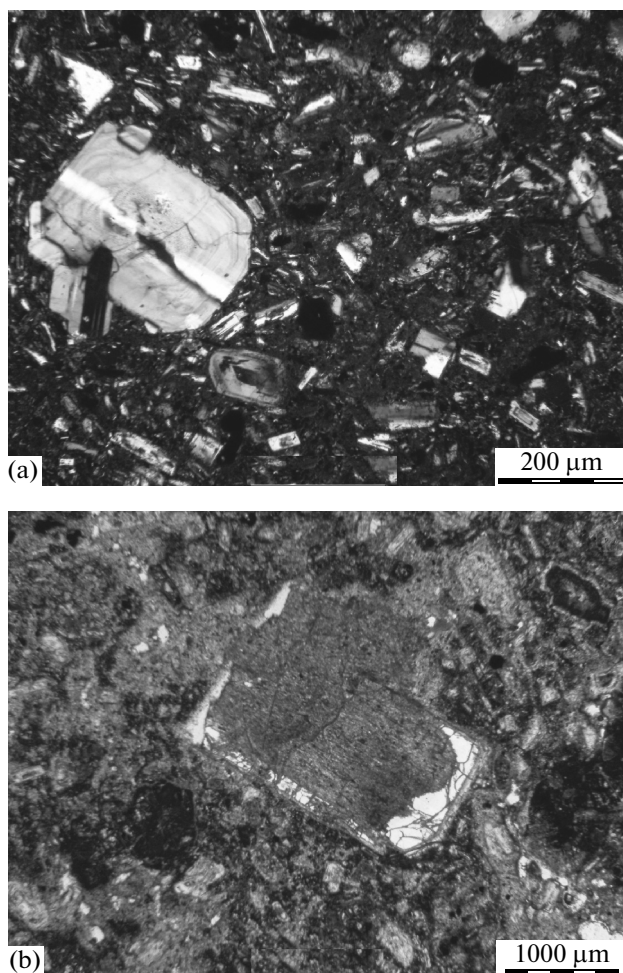


Fig. 2. Porphyritic basaltic andesite (sample S-2).

a central zone, one can clearly see a good degree of preservation for plagioclase crystals, crossed nicols; *b* outer zone, pseudomorph replacement of plagioclase crystals and groundmass with amorphous siliceous substance, crossed nicols.

patches, which are presumably composed of a clay mineral. It is quite probable that this phenomenon was not due to hydrogen sulfate leaching but to previous alteration. Volcanic glass is less stable under alteration, with cryptocrystalline cristobalite developing in the central part of the sample with a concentration of 22% (Table 1). Zone II has a plagioclase concentration that is twice as low, with the plagioclase being replaced with siliceous minerals. The amount of cristobalite increases to reach 69%. In the outer zone II the rock has been completely replaced with siliceous minerals (see Fig. 2b). One discerns some plagioclase phenocryst relicts, with most crystals being replaced with silica as pseudomorphs. There are also some pyroxene grains with typical tortuous microcracks filled with silica.

Microprobe analysis revealed variation in matrix composition from zone I to zone III. Most major components are transported away, Al from 17.6 to 4.9%, Fe

from 4.1 to 0.6%, Mg from 2 to 0.2%, Ca from 5.8 to 0.6%, and Na from 3.4 to 0.8% with a concomitant increase of Si from 63.5 to 84.8%. The concentrations of K (1.6–2.2%) and of Ti (0.5–1%) remain constant.

Morphological analysis applied to rock porosity revealed that this parameter increases gradually from the center of the sample (16.5%) toward the edge zone (39%). There is a certain (insignificant in the case under consideration) compaction at zone boundaries. The mean pore size increases from the center (30 μm) toward edges (45 μm) of the samples, but zone II is notable for large pores (54 μm). The number of pores also increases from the center to the outer zone as leaching proceeds, but the pore shape remains practically the same (Table 2).

The rock density decreases stepwise from the center toward the edges: 2.54 \rightarrow 2.17 \rightarrow 1.78 g/cm^3 ; porosity increases by a factor of 3, from 12 to 36% (see Table 2). We note that the porosity derived theoretically coincides with the results of morphological analysis. Compressional velocity decreases along with decreasing density and increasing porosity: 4.2 \rightarrow 2.65 \rightarrow 2.2 km/s . The strength decreases by a factor of 5, from 106 to 22 MPa. Magnetic susceptibility has low values in the central zone (4.9×10^{-3} –3 SI) and very low values (as low as 0.7×10^{-3} SI) in the edge zone, where the greatest reworking is observed.

Andesite (B-8) This is a dark grey rock, dense and massive. Five zones have been identified in the sample, the color successively varies from dark grey at the center (I) toward white in the outer zone (V). The rock has a serial-porphyric texture, the phenocrysts are dominated by plagioclase with some monoclinic pyroxene. The plagioclase is labradorite. The phenocrysts are 0.3 to 3 mm long. Glomerophytic intergrowths occur. The groundmass is intersertal with many smaller (≤ 0.05 mm) plagioclase and pyroxene crystals. The percentage of ore minerals can reach 5–7%.

Partial replacement of labradorite crystals with siliceous minerals occurred in zone I (the inner). In zone II the phenocrysts are to a greater extent replaced with adularia and silica. Some “islands” of primary minerals remained. The matrix is a brown solid mass. The rocks in zones II through V have been completely altered and are largely composed of siliceous minerals (cristobalite and opal). Some patches in plagioclase were replaced with allophane and gypsum. Relicts of pyroxene crystals remain in zone V. When viewed in transmitted light using crossed nicols, the rock is found to be a homogeneous, dark grey, optically isotropic mass with slightly translucent pyroxene and plagioclase crystals.

The amount of primary minerals successively diminishes from the central zone to the outer zones, as revealed by X-ray diffraction methods; for plagioclase the decrease is from 40% to 10% and for pyroxene it is from 20–40% to complete absence, although pyroxene relicts can still be seen in thin sections. The percentage of tridymite increases from 12–15% to 30–35%, with

Table 1. The mineral composition of samples deduced from X-ray diffractometry (wt %)

Sample	Zone	Minerals						
		primary		secondary				
		Pl	Pr	Tr	Cb	Qu	Alb	Ad
V-2	1	41	22	16–18	23			
	2	31	17–18	14–15	35			
	3	28	10–12	15–20	37			
V-6	1	20			15–17	57–60		
	2	51			13	31		
	3	9			18	71		
	4				15	75	3	6
S-2	1	40	32		22			
	2	22			69			
B-8	1	40–42	20–24	12–15	20			
	2	20	40	20	23			
	3	20	13	35	22			
	4	20		30–32	39	5		
A-4	1	14		6	55			
	2	21			68	2		
	3			7–10	90			

Abbreviations: Pl plagioclase, Pr pyroxene, Tr tridymite, Cb cristobalite, Qu quartz, Alb albite, Ad adularia. The determinations were carried out at the Faculty of Geology of Moscow State University, Analyst V.G. Shlykov. Quantitative analysis was only applied to crystalline material (X-ray amorphous substances were disregarded).

the figures for cristobalite being from 20 to 39% (see Table 1). The chemical composition of the matrix appreciably varies from the center toward the edges of a sample, as inferred from microprobe analyses. The concentration of Si varies in this order: 64.3 → 82.8 → 89.9 → 94.9 → 89%. The percentage of Al decreases from 17.7% at the center to 1–2% in zones III through V. Outward transport of Fe, Mg, Ca, Na, and K from the center to the periphery of a sample also occurs (Table 3). The rock density successively decreases from the inner to the outer zone: 2.78 → 2.60 → 2.32 → 2.12 → 1.83 g/cm³. The values of V_p decrease from 4.0 to 1.75–2.1 km/s, but the overall pattern of compressional velocity that decreases from zone to zone is somewhat disturbed (see Table 2).

The variation of porosity in this sample is peculiar. The porosity increases very slightly in the first three zones, from 5 to 9%, but zone IV shows a sharp jump up to 23%. For zone V the porosity values obtained by two methods (by calculation and using morphological analysis) are discrepant, with the calculated value being 19% and that derived by morphological analysis being up to 70% (Figs. 3a, 3b). This may be due to a nonuniform distribution of pores, because morphological analysis tends to yield overestimated values under such circumstances. The pore size remains constant in zones I through IV (19–28 μm) and increases up to 53 μm in

the outer zone. The number of pores increases. Magnetic susceptibility in zones I and II is high (30×10^{-3} SI), while farther away, in zones III and IV, it decreases to $(21–23) \times 10^{-3}$ SI and rapidly drops to 0.4×10^{-3} SI in the outer zone.

Finely porphyric andesite (L-1) The rock is grey and dense. The plagioclase phenocrysts measure 0.5 mm across on the average, with certain individual crystals reaching 4.5 mm. The pyroxenes are small (within 0.5 mm) and infrequent. The sample shows three zones. The central zone (I) mostly contains fresh plagioclase crystals, with the pyroxene being very slightly altered. The groundmass is composed of volcanic glass with some plagioclase microlites. In some patches the volcanic glass has been replaced with siliceous minerals, which are expressed in outward appearance as lighter-colored rock. Such patches are distributed in a chaotic manner and are rounded in outline. These lighter patches alternate with darker ones that are unaffected by alteration.

The plagioclase and pyroxene phenocrysts in zones II and III have been completely altered, only the “outlines” are extant. The volcanic glass is also dark and optically isotropic, but it has been completely reworked and presumably replaced with opal. The “outlines” of plagioclase phenocrysts and fragments of pyroxene

Table 2. Variation in morphological characteristics and in petrophysical properties of rocks in accordance with the identified zones

Sample #	Zone	Morphologic parameters				Petrophysical properties									
		relative pore area, %	pore size, μm	shape coefficient	number of pores	density, g/cm^3	density of solid particles, g/cm^3	porosity, %	hygroscopic humidity, %	open porosity, %	velocity of compressional waves in dry condition*, km/s	velocity of compressional waves in water-saturated condition, km/s	velocity of compressional waves in dry condition**, km/s	uniaxial compressive strength, MPa	magnetic susceptibility $\times 10^{-3}$ SI units
V-2	1	24.5	47	0.53	183	2.28	2.87	21	1	11	3.8	4.25	—	—	29
	2	44.5	46	0.57	341	2.12	2.70	21	2.1	11	3.2	3.7	3.7	51	3.1
	3a	52	50	0.63	336	1.72	2.61	34	3.2	19	1.95	2.85	2.4	22	0.5
	3a					1.52	2.51	39	3	31	1.5	1.9	1.8	7	0.3
V-6	1	24.4	37	0.53	289	2.40	2.68	10	1.1	9	3.15	4.1	—	80	0.6
	2	31.1	39	0.64	339	2.23	2.66	16	0.9	10	2.65	3.45	—	24	0.5
	3	46.4	51	0.61	289	1.96	2.65	26	0.9	20	—	2.3	—	8	0.4
	4	74.3	75	0.69	214	1.65	2.78	41	1.1	27	2.15	2.3	—	4	0.4
	5	—	—	—	—	1.42	2.76	49	1.1	37	1.55	1.8	—	3	0.35
S-2	1	14.8	30	0.6	262	2.54	2.88	12	0.3	5	4.2	4.8	—	106	4.9
	2	35	54	0.58	195	2.17	2.88	25	1.4	19	2.65	2.8	—	34	1.7
	3	39	45	0.58	316	1.78	2.80	36	2.8	27	2.20	2.55	—	22	0.7
B-8	1	4.1	22	0.61	134	2.78	2.96	6	0.9	1.5	4.0	4.9	—	181	30
	2	9	28	0.55	188	2.60	2.73	5	1.4	4.8	2.55	—	—	79	30
	3	6.5	19	0.66	284	2.32	2.55	9	2.1	8.2	2.45	3.65	—	40	21
	4	20	27	0.57	461	2.12	2.75	23	3.2	12	1.75	2.75	—	38	23
	5	78	53	0.67	454	1.83	2.26	19	—	18	2.10	3.1	—	55	0.4
L-1	1	—	—	—	—	2.65	2.85	7	0.76	—	—	—	4.6	—	—
	2	—	—	—	—	2.1	2.60	19	3.51	—	—	—	2.5	—	—
	3	—	—	—	—	1.35	2.40	44	4.27	—	—	—	1.75	—	—
A-4	1	16.5	34	0.6	241	1.96	2.35	17	—	15	2.85	3.6	—	—	19
	2	25.9	38	0.59	292	1.64	2.23	26	2.8	23	2.45	3.2	—	15	4
	3	64.5	76	0.58	184	1.51	2.15	30	3.5	24	1.80	2.6	—	13	0.2

The determinations were carried out by these authors at the Faculty of Geology of Moscow State University. Method of determining V : * on cubic samples, ** on plates using point sensors.

grains remain in zone III. Judging from color differences, the plagioclase crystals and volcanic glass have been replaced with various modifications of silica.

Similarly to the other samples, the density increases from the inner (I) to the outer (III) zone: $2.65 \rightarrow$

$2.10 \rightarrow 1.35 \text{ g}/\text{cm}^3$. The density of the solid phase decreases as the primary minerals and volcanic glass are being replaced with silica: $2.85 \rightarrow 2.60 \rightarrow 2.40 \text{ g}/\text{cm}^3$. Porosity increases by a factor of six, from 7 to 44%. The density decrease and the generation of secondary

Table 3. The chemical composition of the matrix and plagioclase in samples studied by microprobe analysis (wt %)

Sample #	Patch investigated	Zone	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O ₃	K ₂ O
V-2	M	1	70	0.5	12.2	3.1	1.1	2.5	2.8	1.8
		2	78.1	0.8	9.3	2.0	0.1	0.9	2.6	2.6
		3	80.7	0.5	8.6	0.6	0.1	0.7	2.3	3.7
	Pl	1	53.8	0.1	28.3	0.8	0.2	10	5.7	0.4
		2	64.6	N.d.	19.5	0.4	N.d.	1.0	3.9	0.5
		3	55.7	0.05	27.7	0.6	0.2	9.4	6.0	0.2
B-8	M	1	64.3	0.5	17.7	3.1	1.6	6.1	3.7	1.6
		2	82.8	0.6	6.8	2.7	1.0	1.0	1.7	1.8
		3	89.9	0.7	2.1	0.5	N.d.	0.9	0.5	0.6
		4	94.9	0.7	2.4	0.5	0.2	0.7	0.8	0.2
	Pl	1	51	0.05	31.5	0.5	N.d.	13	3.4	0.2
		2	54.3	N.d.	29.2	0.3	0.5	10.7	4.8	0.3
		3	62	0.2	15.7	0.4	0.1	1.4	2.3	0.4
		4	97.2	0.2	1.2	0.2	N.d.	0.2	0.3	0.2
A-4	M	1	84.5	0.5	3.8	2.0	0.2	0.4	0.8	0.3
		2	84	0.6	6.8	2.0	0.1	0.5	1.4	0.3
		3a	91.7	0.5	1.5	0.5	0.2	0.4	0.5	0.02
		3	92.5	0.6	1.7	0.2	0.2	0.3	0.5	0.5
	Pl	1	54.3	0.1	28.6	0.7	0.4	10.2	5.1	0.2
		2	54.5	0.1	28.3	0.5	0.3	10.3	5.1	0.1
		3	53.2	0.1	29.7	0.5	0.2	11.2	4.7	0.1

M matrix (groundmass); Pl plagioclase. Plagioclase composition: andesine (Ca_{48.1}Na_{49.8}K_{2.1}) in sample V-2, labradorite (Ca_{66.9}Na_{32.0}K_{1.1}) in sample B-8, not determined (abbr. n.d.) in sample A-4. These investigations were carried out by these authors at the Faculty of Geology of Moscow State University.

porosity make the compressional velocity decrease from 4.6 to 1.75 km/s (see Table 2).

Porphyric basaltic andesite (A-4) The rock has porphyric texture and fine-porous structure. The phenocrysts consist of plagioclase and pyroxenes ranging between 0.1 and 1–2 mm across. They make as much as 30–40% of the total rock volume. Three zones can be identified in the sample. Many phenocrysts found in the first (inner) zone have been leached out and their relationship to a specific rock-forming mineral can only be extracted from their relict forms. Phenocrysts were replaced selectively, similarly to the other samples. The groundmass is intersertal hyalopilitic and is finely crystallized. The volcanic glass has been devitrified and replaced with silica; it is brown optically isotropic substance. Microprobe analysis corroborated a considerable alteration of the groundmass, with 84.5% of it being SiO₂. The concentrations of the other major elements are not high: 3.8% for Al, 2% for Fe, 0.2% for Mg, 0.4% for Ca, 0.8% for Na, and 0.3% for K (see Table 3).

Similarly to the other samples, the degree of reworking increases from zone I to zone III. The outer zone is

light beige and the porphyric texture is preserved; the structure is fine-porous and the porosity increases. The concentration of SiO₂ in the matrix becomes as high as 92.5%. X-ray analysis revealed the outer zone to be composed of siliceous minerals (7–10% tridymite and 90% cristobalite, see Table 1). Pyroxene relicts are preserved in all zones, although most of their volume has been replaced with silica.

Morphological analysis revealed that the porosity increases from the inner zone to the outer by a factor of four, from 16 to 65%. Patches of greater density were observed at zone boundaries; these patches are probably due to precipitation of dense amorphous silica in the pores. The pore size increases from 34 to 75 μm, with the shape coefficient being constant (see Table 2). Compared with the other samples, the central part has a relatively low density (1.96 g/cm³), decreasing to 1.51 g/cm³ in the edge zone. The value of V_p decreases from 2.85 km/s to 1.8 km/s. The variation in these properties is due to replacement affecting the groundmass, with the most intensive replacement occurring in the edge zone. Iron is leached out and the ore minerals

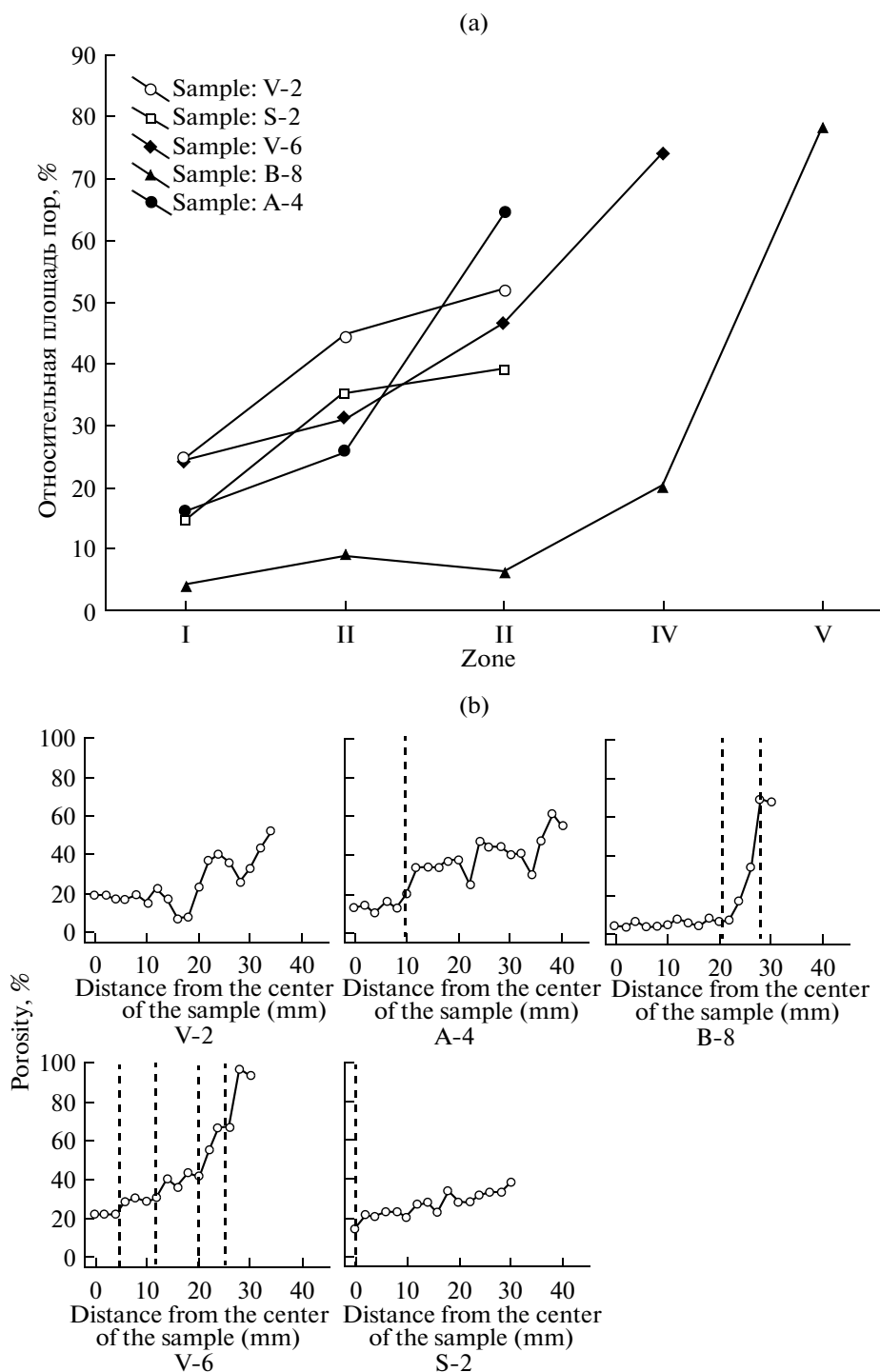


Fig. 3. Variation of rock porosity, revealed by morphological analysis.

a average porosity for individual zones; *b* porosity profile from central parts of samples to the outer zones.

are decomposed, leading to a magnetic susceptibility decrease from 19×10^{-3} SI to 0.2×10^{-3} SI (see Table 2).

Samples of Set II

Porphyric basaltic andesite (V-2) The rock is dark grey with a porphyric texture a massive structure and no

visible open pores. Color variation highlights three zones: the central, dark grey (I), a ginger band up to 1.5 cm wide (II), and the outer, light grey and beige, zone (III). The color largely depends on the alteration in the groundmass. Porphyric phenocrysts consist of plagioclase (1–3 mm, up to 5 mm in the longer dimension), less frequently of pyroxene (up to 1 mm). The

Table 4. The chemical composition of zonal samples studied by X-ray fluorescence analysis (wt %)

Sample #	Zone #	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	CaO	MgO	K ₂ O	
V-2	1	54.13	0.68	22.88	8.1	5.87	1.89	0.96	Set II
	2	56.38	0.75	11.96	4.99	3.56	1.38	1.5	
	3	58.42	1	11.51	6.61	1.43	1.14	1.46	
	4	65.9	0.94	7.82	2.62	1.39	0.67	1.39	
V-6	1	62.37	0.54	11.05	3.22	1.9	0.89	1.64	
	2	65.16	0.54	10.37	2.85	1.2	0.7	1.53	
	3	68.66	0.64	10.35	3.32	0.81	0.62	1.58	
	4	70.09	0.67	11.61	3.52	0.42	0.54	1.65	
	5	64.83	0.81	12.77	4.55	0.14	0.59	1.56	
S-2	1	57.12	0.7	24.92	7.74	6.4	2.04	0.67	
	2	69.95	0.95	16.03	7.34	3.83	1.95	0.74	
	3	71.06	1.34	7.1	2.94	1.17	0.65	0.9	
V-8	1	59.02	0.85	18.3	8.78	5.95	2.18	0.97	Set I
	2	74.11	0.98	13.73	8.65	4.08	2.05	0.64	
	3	85.37	0.96	7.19	6.85	2.22	1.59	0.65	
	4	87.74	1.1	3.24	5.63	1.22	1.1	0.45	
	5	83.98	1.24	1.15	3.97	0.81	0.87	0.21	
L-1	1	60.19	0.69	23.94	8	5.73	2.39	1	
	2	77.51	1.05	3.89	7.16	1.67	1.52	0.67	
	3	85.24	1.4	N.d.	1.27	0.45	0.27	N.d.	
A-4	1	54.17	0.7	21.82	7.62	1.65	1.69	1.02	
	2	58.85	1.04	11.4	3.95	0.25	0.45	0.62	
	3a	80.47	1.17	587	0.25	0.45	N.d.	0.19	
	3	89.4	1.35	0.25	N.d.	N.d.	N.d.	N.d.	

We list the most significant and variable components; n.d. below detection threshold. The determinations were carried out at the Faculty of Geology of Moscow State University, Analyst E.N. Samarin.

porphyric texture is also preserved in the outer zone, but in this zone the phenocrysts have been replaced in a pseudomorphous manner with secondary minerals and are visible as outlines upon the background of a lighter groundmass.

Investigations of thin sections and an analysis of chemical and mineral compositions showed that the intensity of alteration increases toward the outer zone. X-ray diffractometry (see Table 1) revealed that the percentage of primary minerals decreases from the center toward the edges. The decrease is from 41 to 28% for plagioclase and from 22 to 10% for pyroxene. This is due to replacement of these minerals with secondary minerals, primarily with low-temperature modifications of SiO₂ (cristobalite, tridymite, and opal). It should be noted that the high concentration of siliceous minerals (about 40%) that mostly replace the matrix (volcanic glass) is observed, even at the very center of the sample (see Table 1). This provides evidence that either the rock had been previously subjected to hydrothermal alteration or else the alterations reached the

center of the boulder. However that may be, the rock is no longer a fresh basaltic andesite. The concentration of siliceous minerals increases to reach 52–57% in the outer zone; this is due to the generation of cristobalite, while the amount of tridymite remains the same.

Thermal water removes most major components from the rock, the changes are from 22.9 to 7.8% for Al₂O₃, from 8.1 to 2.6% for FeO, from 1.9 to 0.7% for MgO, and from 5.9 to 1.4% for CaO. On the other hand, the concentration of SiO₂ increases from 54% in the inner zone to 66% in the outer (Table 4).

It was noticed that the character of the variation differs between the matrix, the plagioclases, and the pyroxenes. It can be seen in thin sections that considerable changes have affected the plagioclase phenocrysts. The plagioclases in the central zone are affected the least. However, there is some selective alteration, with some crystals being affected to a greater degree, while in others all changes occur along microcracks. This may have been related either to different plagioclase compositions or to a selective hydrothermal process, with

andesine relicts remaining in the second and third zones because they were replaced with cristobalite, opal, and tridymite, with adularia being involved to a lesser degree. The pyroxene composition varies little from the central zone to the outer one, some partial dissolution occurs in weakened places that correspond to defects in the crystals along with replacement with silica. The replacement front (from a primary mineral to a secondary one) is well pronounced; its width is a few tenths of a micron. Considerable amounts of pyroxene remain in all zones, including the outer zone.

The matrix has SiO_2 increasing from 70% in the central part to 80% in the outer zone (see Table 3). The high concentration of silica in the central part of the sample corroborates a significant hydrothermal metasomatic alteration of the rock. The concentrations of most components decrease from the center (zone I) toward the edges (zone III): Al_2O_3 (from 12.2 to 8.6%), FeO (from 3.1 to 0.6%), MgO (from 1.1 to 0.1%), CaO (from 2.5 to 0.7%), and Na_2O (from 2.8 to 2.3%). The concentration of K_2O exhibits the opposite trend, increasing from 1.8 to 3.7%. This seems to be due to groundmass microlites being replaced with adularia. The amount of titanium remains constant. Volcanic glass is partially altered in the central zone while being completely transformed and replaced with a cristobalite aggregate in all the other zones. Taken as a whole, the dynamics of the variation of chemical composition for the rock and for its matrix are similar, although the figures are slightly different (see Tables 3 and 4).

Morphological analysis showed that secondary porosity is generated during hydrogen sulfate leaching, with the porosity values increasing from 24% in the central part of the sample to 52% in the outer zone (see Table 2 and Fig. 3a). The pore size changes little, but the number of pores is significantly greater. The pores become more isometric, as indicated by the change in the shape coefficient from 0.53 to 0.63. The porosity varies progressively along a cross section from the central part of the sample toward the edges (see Fig. 3b). The general trend of stepwise increase in porosity at zone boundaries is broken by local patches of higher density (similarly to sample S-2). The formation of these patches is probably due to precipitation and concentration of siliceous material there.

The rock properties vary in accordance with the mineral transformations (see Table 2). The density decreases progressively from 2.28 g/cm^3 in the central part of the sample to 1.52 g/cm^3 in the edge zone. The third zone, which was identified visually, exhibits a clear-cut division into two subzones, 1.6–1.9 g/cm^3 (IIIa) and 1.3–1.6 g/cm^3 (IIIb). The density of solid particles, which reflects the chemical composition of the rock, progressively diminishes according to the zones: 2.87 \rightarrow 2.70 \rightarrow 2.61 \rightarrow 2.51 g/cm^3 . This resulted from decomposition of the denser primary minerals and of volcanic glass and from the generation of light siliceous minerals. Leaching inflates the porosity by two

times, from 21 to 39%. In accordance with the variation in density and porosity the compressional velocity V decreases: 3.85 \rightarrow 3.2 \rightarrow 1.95 \rightarrow 1.5 km/s. The rock loses its magnetic properties under hydrogen sulfate leaching, which is due to the outward transport of iron and to the decomposition of mafic and ore minerals (magnetite, titanomagnetite, and ilmenite). In the sample under discussion the magnetic susceptibility decreases by two orders of magnitude from the inner zone to the outer (29×10^{-3} SI to 0.3×10^{-3} SI).

Porphyric dacite andesite (V-6) The rock is dark grey with a porphyric texture and a massive structure. The groundmass contains lighter plagioclase phenocrysts with the longer dimension equal to 4–6 mm on average. The groundmass is hyalopilitic. Five zones can be distinguished in this sample. The rock becomes progressively lighter as one proceeds from the central part (I) toward the edge zone (V). The last zone shows alternating white, beige, and yellow colors, the structure is changed in that larger pores are produced by leaching, which affected plagioclase phenocrysts. The rock becomes less resistant.

This is the only sample in which the bulk chemical composition varies little and the matrix is not subject to appreciable changes in composition. In particular, 72–75% of the matrix is SiO_2 and its composition experiences practically no changes as one proceeds from the inner part to the outer part. The rock had probably been altered previously, before it came into the brook, or else it had long been in an acidic running-water environment, so that all the changes have been smoothed out. Thin sections show that the groundmass was replaced with a cryptocrystalline siliceous aggregate.

X-ray phase analysis revealed that the central part of the sample contains 50% plagioclase, which is andesine. Andesine crystals contain small leached-out patches filled with a clay mineral (supposedly dickite). Some patches in the crystals have been replaced with silica. The amount of plagioclase gradually diminishes from the center to the edge of the sample, until it completely disappears in the outer zone. As far as zone III (inclusive) there are some preserved remains of plagioclase, while in IV and V they have been completely replaced, with only outlines (shadows) remaining of the primary crystals that have been replaced with siliceous minerals as pseudomorphs. In the outer zone (V), 90% consists of siliceous minerals (cristobalite and quartz); there are also some small amounts of adularia, which has replaced andesine. The amount of Fe increases in the outer zone (from 1.1% at the center of the sample to 6.3% in the outer zone), while that of Ca decreases (from 1.2 to 0.4%), as does that of Al (from 14.1 to 10.7%). Intensive ferruginization makes the outer zone brown and yellow.

Pyroxene is present in all zones. There are patches in pyroxene crystals (zones I and II) that are filled with siliceous minerals, while clay minerals develop along

cracks. Some pyroxene relicts are also preserved in the outer zone (V).

The leaching generates secondary porosity, whose values increase from 24% in the central part of the sample to 74% in the edge zone (as inferred from morphological analysis) (see Fig. 3a). Porosity increases in a stepwise fashion in accordance with the zones identified (see Fig. 3b). Pores increase from zone to zone from 37 to 75 μm . The shape coefficient increases from 0.53 to 0.69 (see Table 2), indicating that more isometric pores are formed in the zones with the maximum intensity of leaching. The density successively decreases in accordance with the zones that were identified: 2.40 \rightarrow 2.23 \rightarrow 1.96 \rightarrow 1.65 \rightarrow 1.42 g/cm^3 . The porosity increases by a factor of five, from 10 to 49%. The open porosity is lower than the total porosity; its value increases from 6 to 39% (see Table 2). One cannot discern any progressive variation in the density of the solid particles, which is as it should be, and is consistent with the chemical composition of the rock concerned. We have ρ_s 2.65–2.68 g/cm^3 in zones I through III; the value increases to reach 2.76–2.78 g/cm^3 in zones IV and V due to ferruginization. The values of V_p decrease from 3.15 to 1.55 km/s in accordance with decreasing density and increasing porosity. The mineral and structural transformations of the rock make it much less strong, with the strength decreasing from 80 to 3–4 MPa. Magnetic susceptibility is low. Even in the central part of the sample, in the less affected patches, it does not exceed 4×10^{-3} SI.

RESULTS AND DISCUSSION

Thermal waters of acidic to ultra-acidic composition make the alluvial boulders and pebbles in Kipyachshaya Rechka Brook zonal in structure, whatever the original rock composition was. Macroscopically, the zones are identified by color variation, from darker tints (blackish grey to red–brown) in the central parts of the samples to lighter ones (beige, grey, rose, and white) in the edge zones, as well as from structural features. Three to five zones can be identified in each sample. The boundaries between zones are distinct. The zonal pattern is somewhat disturbed by microcracks, where more intensive reworking occurs and the rock acquires lighter colors, because the cracks are passageways for infiltrating thermal waters. The degree of hydrothermal reworking increases from the central part of a sample toward the outer zone and this is accompanied by significant changes in chemical and mineral composition, in porosity, density, and other petrophysical parameters of the rock.

The silica that is liberated as silicates are dissolved is deposited metasomatically where the primary minerals were, occasionally together with hydroxides of Fe and Al. The primary components (volcanic glass, plagioclase, and pyroxene) are leached out and replaced with various low-temperature polymorphic modifications of

silica, mostly cristobalite, but also low-temperature quartz, tridymite, and opal. The dissolution process usually prevails over precipitation, leaving leached-out cavities. The transformations first affect volcanic glass, which is transformed into an aggregate of opal and cryptocrystalline cristobalite. Volcanic glass is considerably affected, even in the inner parts of the samples.

The transformation of plagioclase and pyroxene phenocrysts starts along cracks and defects in crystals. The replacement front is generally clear cut. The primary minerals and volcanic glass in the edge zones of samples are completely replaced with siliceous minerals, but the original texture remains intact, i.e., a pseudomorph replacement. We did not detect any other secondary minerals in significant amounts. It is possible that occasional clayey material is mechanically removed by a running acidic solution.

The bulk chemical composition of the samples generally varies progressively from the center to the periphery (see Table 4 and Fig. 4). One notes increasing concentrations of SiO_2 , with CaO and MgO decreasing from the central zone toward the outer parts. The concentration of Al_2O_3 decreases in all samples, except V-6. However, the sets of samples discussed above have different patterns of the varying chemical composition (from the central parts to the outer parts).

Set I (S-2, B-8, L-1, A-4). (1) A significant increase in the concentration of SiO_2 from 54–60% to 71–89%; (2) decreasing concentration of Al_2O_3 , K_2O .

Set II (V-2, V-6). (1) An insignificant increase in the concentration of SiO_2 ; (2) Decreasing concentrations of CaO and MgO; (3) The concentrations of FeO and K_2O vary.

For all samples one notes increasing concentrations of TiO_2 . The amounts of the other components (MnO, P_2O_5 , and S) also vary, but the variation is not as great.

The increased concentration of TiO_2 can probably be of great interest in connection with the high activity of titanium (as reported previously) in hydrothermal metasomatic processes that are characterized by P–T and physico-chemical conditions (air pressure, temperature up to 100–105°C, and low pH) that are similar to those under discussion here. For example, Ti is contained (2 to 6%) in microstructures of hydrothermal clay, especially as amorphous phases become crystalline mineral phases [Rychagov et al., 2010]. We found the generation of titanium-bearing oxide–silicate mineral films on the surface of pyrite crystals formed on hydrothermal clay in the thermal fields of southern Kamchatka [Rychagov and Shchegol'kov, 2011].

Microscopic studies revealed the sequence of mineral transformations. The first occurrence consists in decomposition of the glassy basis of the effusive rock and replacement with siliceous minerals. The matrix contains 63–84% SiO_2 in the central parts of the samples, with the percentage increasing to reach 85–98% in the outer zone. The concentra-

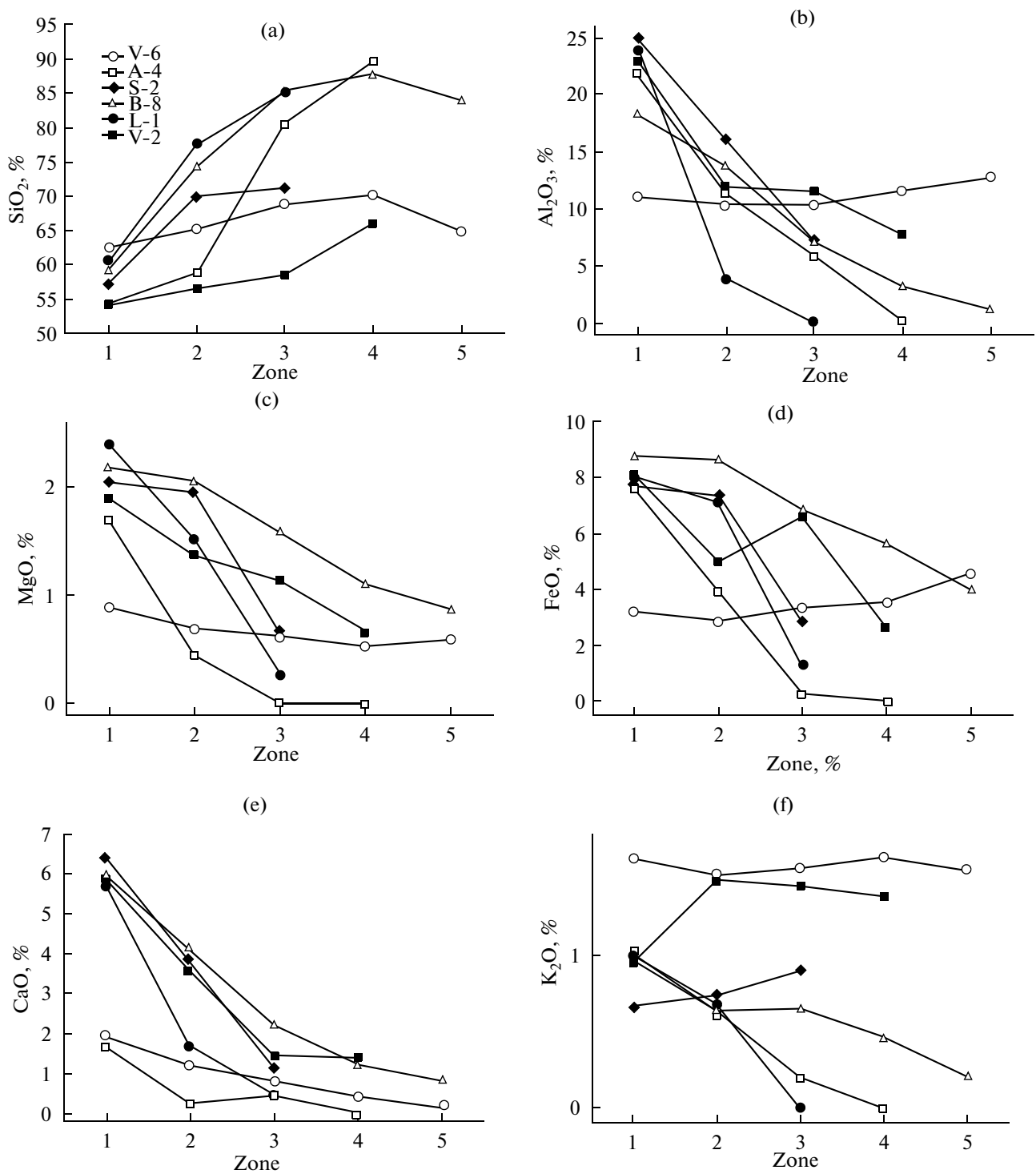


Fig. 4. Variation in the concentrations of main rock components, as revealed by bulk chemical analysis: a SiO_2 , b Al_2O_3 , c MgO , d FeO , e CaO , f K_2O .

tion of SiO_2 in the matrix is always higher than the total concentration of SiO_2 in the rock, indicating that the replacement of groundmass with silica occurred first. The high concentration of SiO_2

(84%) that was found in the central part of sample A-4 shows that this basaltic andesite had been subjected to reworking before it came into the brook, or else it has been in the brook for a long time.

The alteration affects both the matrix and the plagioclase and pyroxene phenocrysts. The concentrations of chemical components in the matrix and in the phenocrysts are considerably different after the generation of secondary minerals (see Table 3). Plagioclase is more stable than glass under alteration. The plagioclase (labradorite or andesine) phenocrysts found in the inner zones either have not been altered or only slightly replaced with silica along cracks. Active leaching and replacement in the central parts of crystals occur in the third zone. In the outer zone the plagioclase crystals have also been completely leached out and replaced with siliceous minerals as pseudomorphs. Pyroxene is the most stable mineral under the action of acidic thermal waters. The greatest alteration occurs in the last zones with rapidly increasing concentrations of SiO_2 and decreasing concentrations of oxides of Al, Fe, and Mg, although some amounts of fresh augite crystals were detected even in the outer zone, which has experienced the greatest reworking. One notes a well-defined boundary between primary silicate minerals and the siliceous minerals that develop there. The replacement front is a few tenths of a micron wide. The quantitative parameter that characterizes the transformation of pyroxene compared with that of plagioclase and the matrix can serve as a criterion to estimate the dynamics and time of action of flowing acidic (ultra-acidic) solutions on rocks.

The degrees of alteration found in the samples studied here differ, but the sequence of transformation is approximately the same for all samples. The transformation of chemical and mineral compositions gives rise to changes in the physical state of the rock. Hydrogen sulfate leaching gives rise to secondary porosity, that is, dissolution prevails over precipitation. The end result of leaching is an "open-work" porous frame formed by siliceous material. The porosity typically increases in a stepwise manner from the inner zones to the outer. In several cases one observes local compact patches at zone boundaries due to precipitation of siliceous material in the intercrystal space and micropores. Hydrogen sulfate leaching makes the pores larger (the average size increases from 20–30 μm to 75–80 μm), with the greatest increase occurring in the outer zone. Some samples contain pores as large as a few millimeters across in that zone.

Rock density is the main physical parameter that determines many other properties of the rock, in particular, its strength and strain behavior. The plot in Fig. 5 shows density variation as rock alteration proceeds. All samples show a well-defined progressive decrease in density from the center to the outer zone. The decrease is smooth within a zone, but at zone boundaries it experiences a jump; these steps or barriers characterize zone boundaries. The contrast in the decrease is

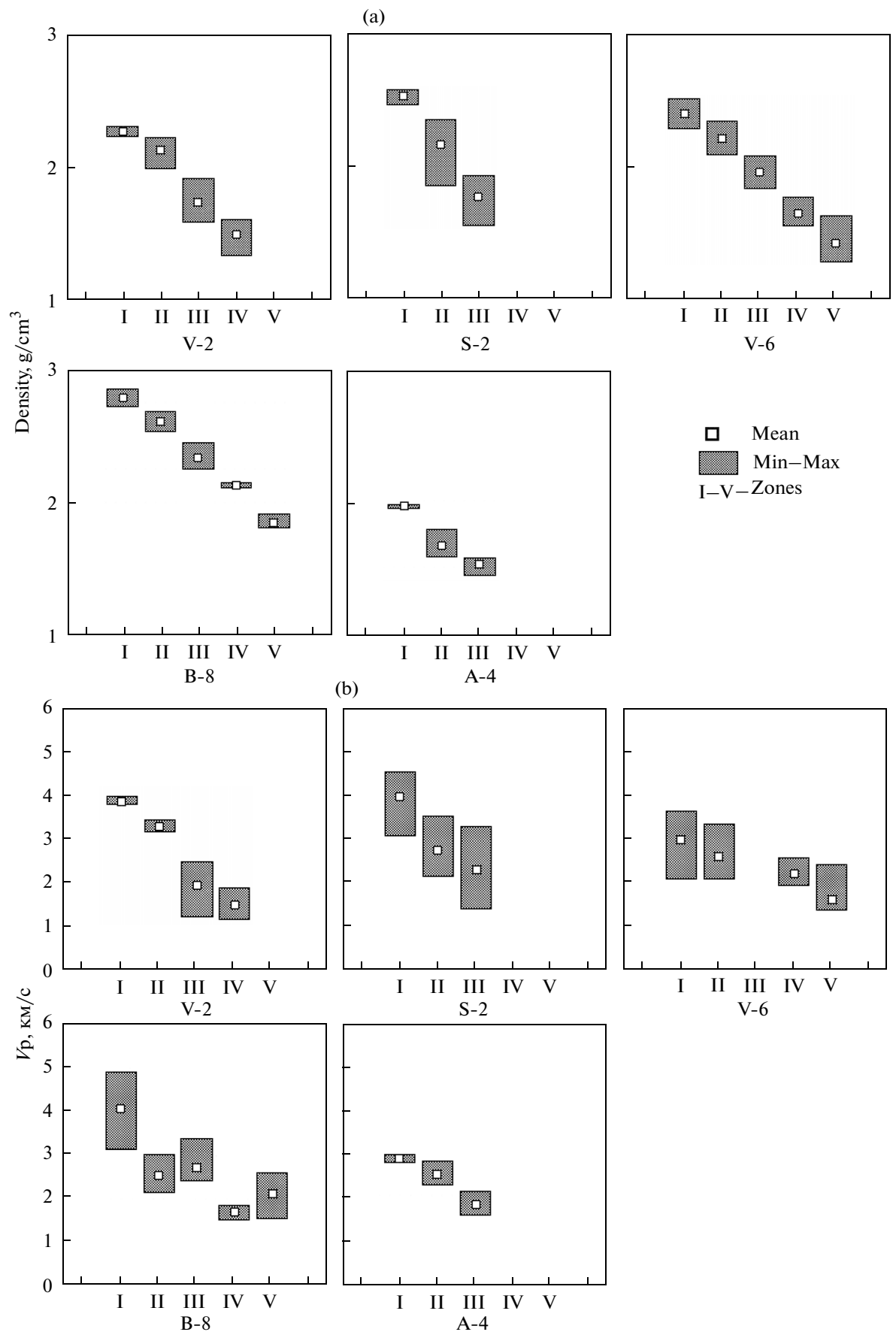
0.2–0.3 g/cm^3 (6–13%). Overall, the density decreases by 30–40% (from 2.5–2.8 to 1.35–1.5 g/cm^3). This density deficit is due to two factors: (1) the lower density of the solid particles (or mineral density), which reflects the chemical and mineral composition of the rock and (2) leaching and the generation of secondary porosity. The density of solid particles decreases from 2.85–2.96 g/cm^3 in the central parts to 2.26–2.51 g/cm^3 in the outer zones for most samples. This is caused by the decomposition of dense primary minerals and of volcanic glass and by the generation of lighter siliceous minerals whose densities are lower (2.2–2.3 g/cm^3). One exception is furnished by sample V-6, whose solid particles have a density that increases from 2.66–2.68 g/cm^3 to 2.76–2.78 g/cm^3 . This is due to iron being brought into the outer zones.

In all samples (except V-6), hygroscopic humidity increases with an increasing degree of reworking, from 0.3–1% in the central part to 2.8–4.3% in the edge zone. This is probably caused by the generation of opal, which contains numerous water molecules in its structure.

The other physical and mechanical parameters of the rock vary in accordance with decreasing density (see Fig. 5 and Table 2). The porosity increases in all samples as a result of leaching, by factors of 2 to 5 on average. Decreasing density and the generation of secondary porosity make for lower strength, which is lower by several times, from 200 to 40–60 MPa in some cases and from 100 MPa to a few MPa in others. The compressional velocity decreases from 3–4 km/s to 1.5–2.5 km/s. Thermal water makes igneous rocks lose their magnetic properties. Magnetic susceptibility generally decreases by 2 to 3 orders of magnitude, from $(20\text{--}40) \times 10^{-3}$ SI in the central zone to $n \times 10^{-5}$ SI in the outer. The central zones in some samples (S-2 and V-6) have largely been reworked, so that their magnetic susceptibility decreases to reach $(1\text{--}4) \times 10^{-3}$ SI. The character of magnetic susceptibility variation differs: in some cases (V-2 and A-4) this quantity already decreases in the first zone, while in others the variation occurs more smoothly and it is only in the outer zone that one observes a rapid decrease. The leading mechanism of variation for magnetic susceptibility consists in the dissolution of ferromagnetic minerals (magnetite and titanomagnetite) by acidic and ultra-acidic chloride sulfate waters that penetrate into rock fragments along systems of microcracks and pores. The outer zone is subject to the most dynamic leaching of the primary material that generates secondary porosity and cracking due to chemical and mechanical action on the part of the hydrothermal flow.

To sum up, the action of acidic flowing thermal waters on fragments of dacite andesitic and basaltic

Fig. 5. Variation in petrophysical properties of effusive rocks according to the zones that were identified: a rock density, b velocity of compressional waves, c magnetic susceptibility.



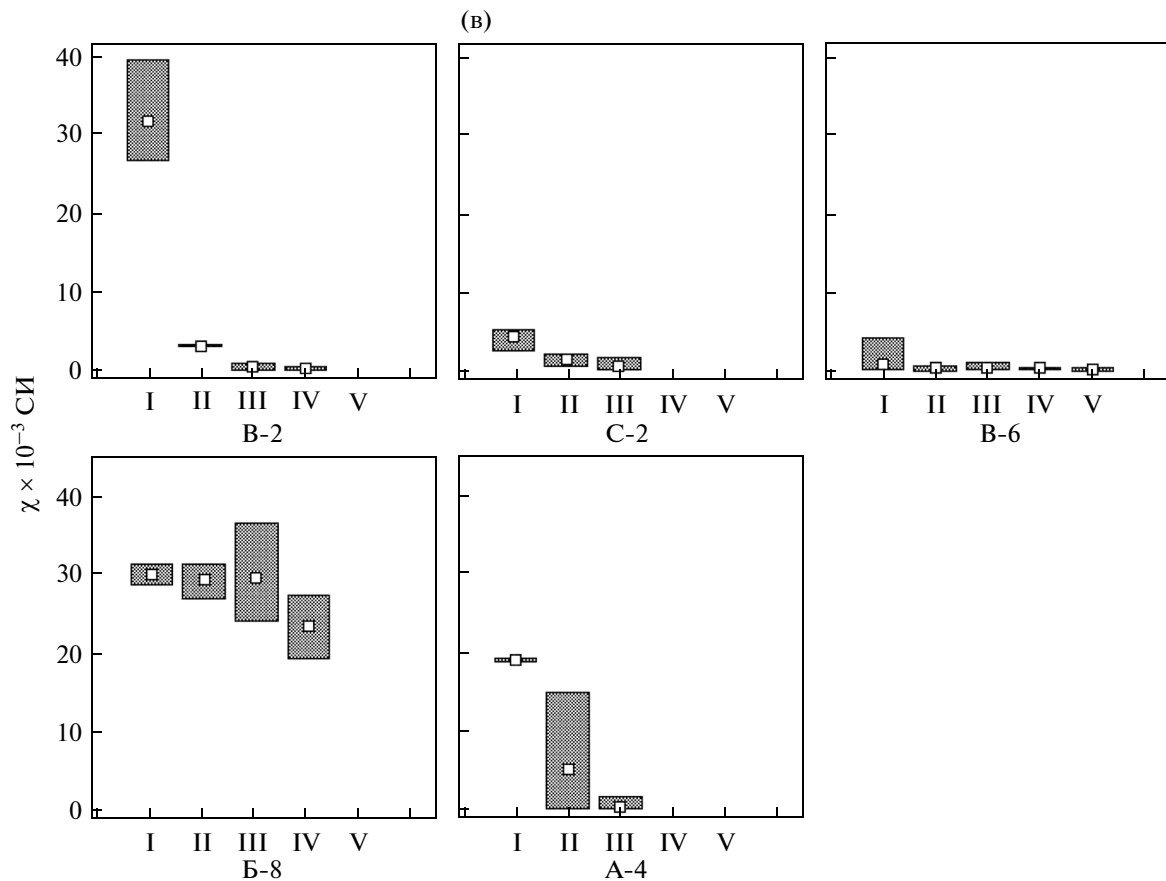


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andesitic lavas gave rise to a zonal texture in these fragments and a stepwise variation in their composition and properties. The leading mechanism that generates zone division consists in hydrogen sulfate leaching and metasomatic replacement of the groundmass and porphyric phenocrysts with siliceous minerals. Geochemical barriers are formed at zone boundaries; these barriers reflect changes in the physico-chemical parameters of the flowing water environment, causing dense cryptocrystalline silica to precipitate at the barriers. These locations can serve as a kind of (incomplete) isolation that impedes the reworking of the inner zones. Such barriers are probably important in the evolution of the zones and in the redistribution of the main rock components, including ore components.

The interaction of acidic near-surface thermal solutions with the host rocks, which converts them to opalites, was observed at many geothermal systems. A similar process seems to be occurring at depth in the zones of ascending thermal water flows charged with acidic volcanic gases. In particular, such a physico-chemical environment (but at higher temperatures) is typical in the apical parts of small gabbro–diorite intrusions on Baranskii Volcano, of diorites in the long-lived North Paramushir hydrothermal magmatic system, and

of diorite porphyrites in the Koshelev Volcanic massif, southern Kamchatka; above these thick zones of secondary quartzites and geochemical barriers with epithermal ore mineralization in the volcanogenic–sedimentary host rocks arise [Korobov, 1994; Rychagov et al., 2002]. To be specific, Korobov noted that greisen-like secondary quartzites are formed at depth in the Baranskii hydrothermal system with the active participation of halogens and sulfurous gases; these quartzites include a monoquartz, a garnet–quartz, and a muscovite–sericite–quartz facies (the temperatures of generation are 460–380°C). Sulfurous opalites form in the solfataras fields of this system with a composition that is consistent with secondary quartzites that combines the opal (mono-quartz) and the alunite–jarosite–opal facies (<200°C) [Korobov, 1993]. Free sulfuric and muriatic acids cause hydrogen sulfate leaching of the host rocks accompanied by the generation of secondary quartzites and mono-quartzites at depth (≥ 1200 m) and of mono-opalites with appropriate composition and conditions of generation in the hypergenesis zone of the geothermal system. These results are in agreement with those obtained by these authors, viz., metasomatites have been identified at depths of 800–1200 m and at the ground surface in the Baranskii system, with the soma-

tites being similar in composition, physico-mechanical properties, and the conditions of generation [Ladygin and Rychagov, 1995; Rychagov et al., 1993].

CONCLUSIONS

(1) The study of how boulders and pebbles consisting of effusive rocks are transformed under the action of acidic thermal water in a flowing stream showed that the reworking is zonal. The material within any particular zone is comparatively homogeneous in its composition and properties. At zone boundaries the composition and petrophysical properties experience stepwise changes.

(2) The degree of hydrothermal metasomatic reworking increases from the inner zones to the outer zones: primary minerals are replaced in a pseudomorph manner with various low-temperature polymorphic modifications of silica. The replacement front (primary minerals to secondary neogenic forms) is a few tenths of a micron.

(3) Sulfate and sulfate chloride thermal waters leach out most elements from the affected rock, except silicon, which is stable in an acidic environment. The removal of elements is accompanied by density deficit, the generation of secondary porosity, and a jump-like decrease of strength and strain parameters from zone to zone.

(4) Compactions frequently form at zone boundaries related to the precipitation of silica; the compaction can serve as a barrier for the precipitation of some mineral and ore compounds.

(5) Similar hydrothermal metasomatic processes (but at higher temperatures) seem to occur in the interiors of hydrothermal systems in the zones of ascending thermal water flows charged with acidic volcanic gases. For this reason, the study of the transformation of volcanic rocks in a flowing acidic environment at the ground surface provides new insight into the origin of metasomatic zonalities and the mechanisms and dynamics during the generation of secondary quartzites, mono-quartzites, and opalites, which play an important role in the evolution of present-day hydrothermal and long-lived mineralizing hydrothermal magmatic systems.

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SPELL: 1. metasomatic, 2. wairakite, 3. lomontine