

Hydrothermally Altered Hyaloclastites at the Earth's Surface in the Rift Zone of Iceland: Problem of the Biochemogenic Accumulation of Trace Elements

A. R. Geptner, T. A. Ivanovskaya, E. V. Pokrovskaya, S. M. Lyapunov,
A. T. Savichev, A. V. Gorbunov, and N. V. Gor'kova

Geological Institute, Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 119017 Russia

e-mail: heptner@mail.ru

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Abstract—Results of the mineral and chemical study of surface-altered hyaloclastites from the Theistareykir and Nāmafjall geothermal zones, the North Iceland rift, are considered. The paper scrutinizes the composition of hydrothermally altered rocks mainly consisting of clay minerals related to the transformation of bedrock hyaloclastites. The clay minerals also make up slope talus or proluvial deltas around highlands. The major clay minerals in areas of the present-day fumarole activity are kaolinite and smectite, while the redeposited talus–proluvial sediments are mainly composed of smectites. The studied rocks contain framboids, globules, rods, and other structures with morphology and size similar to those of mineralized bacteria. The local concentration of Ag in proluvial deposits is attributed to the intense bacterial activity. It is supposed that elevated contents of some trace elements could be related to an intense microbiotic influence.

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INTRODUCTION

The tectonic position of Iceland at the strike of the Mid-Atlantic Ridge offers a unique opportunity to study the subaerial hydrothermal alteration of basaltic material in the present-day rift setting. Specific features of this process can be used for the comparison with ancient rocks accumulated in the continental rift zones.

An important problem in the study of hydrothermal alterations is the estimation of scales of migration, redistribution, and local accumulation of chemical elements. It is difficult to estimate the effect of hydrothermal activity by the comparison of altered and unaltered rocks of the same age within a limited space. This problem can successfully be solved by studying hydrothermal process at the Earth's surface. The spotty and mosaic distribution of geothermal zones reflect specifics of the geological structure and anisotropic distribution of permeable zones and pathways of groundwaters and provides the unique possibility to compare the adjacent hydrothermally altered and unaltered rocks.

It can now be considered a proven fact that thermal waters of Iceland are fed by rain and glacial meltwaters heated in areas with high geothermal gradient. The only exception is the coastal areas, where marine water takes part in the composition of groundwaters (Árnason, 1976).

Heated waters ascend to the surface through faults zones and fissure–dike swarms. Three main zones of

basaltic alteration, which reflect progressive increase in temperature, can be distinguished in the vertical section of high-temperature hydrothermal manifestations: smectite–zeolite zone, zone of mixed-layer minerals and prehnite, and chlorite–epidote zone (Kristmannsdóttir, 1982).

According to Walker (1960) and other researchers, the composition of secondary minerals significantly depends on the composition of host rocks interacting with heated groundwaters and rocks. This viewpoint rules out a long-range migration of petrogenic elements with heated groundwaters and implies that hydrothermal alteration of basalts is an isochemical process.

However, the study of composition and distribution of hydrothermal minerals in the basaltoid sequence led to a different conclusion. It was established that the formation of smectites, celadonite, zeolites, siliceous, and other minerals (for example, apophyllite) in the flood basalt sequence is related to the redistribution of petrogenic elements by heated groundwaters (Geptner and Sokolova, 1989; Geptner and Petrova, 1989; Kurnosov et al., 2004).

As to hydrothermal process at the Earth's surface, the interaction of heated waters or vapor with rock at solfataras and fumarole sites is a very slow process characterized by the volumetrically insignificant lateral migration of liquid phase, with no percolation typical of groundwaters. Rocks in fumarole areas are transformed under the influence of high temperature and

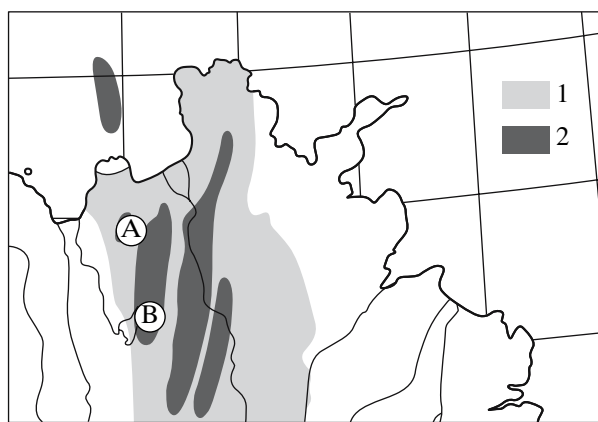


Fig. 1. Volcanic and geothermal systems of the rift zone of Iceland (modified after Einarsson, 1994). (A) Theistareykir, (B) Námafjall. (1) Belt of active volcanic manifestation; (2) fissure swarms and local volcanic systems.

ascending vapor and gas. The alteration could span a limited area in groundwater highstand areas.

The study of present-day hydrothermalites and hydrothermally altered Holocene sediments in the southwestern rift zone of Iceland revealed a significant influence of microbiota (metabolism of bacteria and fungi) on the redistribution and accumulation of trace elements (Geptner et al., 2005, 2006).

Material for the present investigation was taken from high-temperature geothermal fields located in the present-day northern rift zone of Iceland. Special attention was given to the major and trace-element composition of the rocks containing remains of mineralized microbiota.

METHODS

Interrelations between differently altered rocks were studied during field works. Then, the main types of clayey rocks were distinguished based on their color, position in the geothermal field, compositional homogeneity, and relations with weakly altered or unaltered hyaloclastites.

After the petrographic study in laboratory, fractions from <5 to <50 μm in size were elutriated from the main types of clayey rocks.

Fresh and altered hyaloclastites, as well as clay fractions, were analyzed using the complete silicate, XRF, and INAA analyses.

Micro- and nanostructures of individual minerals were studied on a CamScan MV-2300 scanning electron microscope, while the composition of samples was analyzed with an INCA-200 energy-dispersive system. Microprobe was equipped with 0.5- μm -thick input mylar window, which allowed us to determine elements up to oxygen and carbon. The scan area was 1 μm . The software package of quantitative analysis provides measurements with an accuracy of no less than cate-

gory 4, according to requirements of the Scientific Council. The analytical accuracy was controlled by standard samples.

Analysis of hydrous samples is rather difficult, because microprobe does not detect hydrogen and the microprobe software package recalculates all results to 100%. The absence of data on the hydrogen content leads to the overestimation of concentrations of other elements, which is insignificant for weight percentages but can be considerable for atomic percentages. Therefore, the analysis of hydrous samples must be qualified as semiquantitative one.

GEOLOGICAL POSITION OF THE STUDIED OBJECTS

The rift zone of Iceland is characterized by active volcanism and high heat flows. Intense hydrothermal activity is mainly related to the fault zones. The alteration zones spatially associated with the largest faults and fumarole fields are strongly heated and steamed in some places. This fact indicates a continuing hydrothermal activity, which embraces not only Pleistocene hyaloclastite sequences, but also Holocene lavas and scoria cones. The continuous formation of new fissures and the renewal of old fissures are responsible for changes in pathways of groundwaters and compositions of mineral complexes.

The distribution and composition of hydrothermally altered rocks at present-day high-temperature geothermal areas were studied in the northern rift zone of Iceland in 2005. Samples of rocks and minerals characterize the hydrothermally altered hyaloclastites of the Theistareykir and Námafjall geothermal zones (Fig. 1). The samples were taken from fumarole sites, heated hyaloclastites in situ, and redeposited hydrothermally altered hyaloclastites.

The Theistareykir geothermal zone. The study area is located on the northern slope of the Baejarfjall Pleistocene subglacial volcano (table mountain) and the adjacent plain. Hydrothermal activity is restricted to two fault zones. The first zone intersects the northern slope of the mountain, whereas the second zone is traced westward in the Holocene lava field. Solfataric mud pots, fumaroles, and heated areas are developed on the slope and the adjacent lowland. At the earlier stages, the fumarole activity and hydrothermal alteration spanned larger areas. This is indicated by chains of round holes left after the extinction of solfatara mud pots on slopes covered at present by thick turf. Slopes within the hydrothermal occurrences are characterized by smooth gentle outlines. The loose sedimentary cover in such areas contains abundant clay material.

Intense moistening of soils and clayey rocks promotes of intense strong solifluction processes, which are atypical of talus and rudaceous slope deposits of Iceland (Geptner, 2005). The friable material transported downslope along small depressions (striated and

fine-groove washout) and ravines is accumulated in the low slope and adjacent plain to form deluvial-proluvial deposits. In the zone of present-day solfatara and fumarole activity, deposits of the proluvial fan are subjected to repeated pulses of hydrothermal alteration.

The **Námafjall geothermal zone**. Hydrothermally altered hyaloclastites (Pleistocene) were studied within the S- to N-trending Dalfjall range in the field of Holocene lava flows. The hyaloclastites were produced by subglacial fissure eruptions of the submeridional direction. The lava cover is also related to the NS-trending fissure eruptions in this area in the historical time (1728) and Late Holocene. At present, the Holocene lavas and hyaloclastites are crosscut by fractures, as well as small S- to N-trending grabens and fissures extending parallel to the general strike of the volcanic system in this area (Fig. 1). Numerous fumaroles and steaming sites at the surface of hyaloclastite sequences are distributed as chains along faults and large fissures in the craters of Holocene fissure eruptions and large scoria cones. The hyaloclastites are crosscut by subvertical gypsum veins (20–40 cm thick). Native sulfur accumulations are developed in the most intensely altered hyaloclastites.

GENERAL CHARACTERISTICS OF THE ROCKS

Based on grain-size (fine- or coarse-grained) composition and color, the rocks are subdivided into three complexes: (1) highly altered bedrock hyaloclastites; (2) slope talus deposits, and (3) proluvial-deltaic deposits in the periphery of uplands.

Secondary mineral assemblages in the periphery of zones of intense hydrothermal alteration typically include palagonite and smectite developed after glass, as well as siliceous minerals in the groundmass. In this zone, the major part of mineral components of igneous rocks and the central part of large glass fragments remain unchanged (Kurnosov et al., 2004).

Regardless of grain-size composition of constituent clasts, the coarse-grained hyaloclastites in the studied zone of intense alteration are completely replaced by secondary minerals mainly composed of clay minerals and iron hydroxides, which impart an uneven ochreous yellow and red-brown color to the hydrothermally altered zones. Hydrothermally altered hyaloclastites are crosscut by large vertical gypsum veins characterized by brown and red-brown color in the marginal part due to the presence of iron hydroxides. Gypsum veins and variegated (red, yellow, and white) bands and spots of variably altered rocks mark the fault and fissure zones at the Earth's surface.

Bedrock and proluvial deposits were studied in the **Theistareykjir geothermal site**. On the slope of Mt. Baejarfjall, bedrock samples were taken in the zone of

present-day fumarole activity along the W–E profile beneath the thick talus.

Light beige clumpy rocks with a great amount of yellow sulfur aggregates (sample 0514) were sampled in the intensely steaming area ($T = 43.1^{\circ}\text{C}$). White homogeneous compact (plastic when wet) clayey rock with scarce light yellow spots was taken 10–15 m west of the talus (sample 0515, 19.8°C). Sample 0516 (23.1°C) taken nearby also consists of white homogeneous (plastic when wet) clayey rock. Sample 0517 (24.4°C) taken 20 m west is spotty reddish brown (in places, crimson) clayey rock with accumulations of iron hydroxides and spots of creamy clayey matter. Brown clumpy clayey rock with light beige and white spots was recovered in a small hole (15–20 cm thick) in the westernmost point of the studied profile. They are proximal products of downslope transported and hydrothermally altered rocks (sample 0518, 13.5°C ; sample 0519, 10.9°C).

Sampling of proluvial deposits from vertical clearings on the slope of ravine allowed us to trace some horizons (H1–H5) along the strike and to determine the formation sequence of rocks of different colors (Fig. 2). The proluvial deposits are heterogeneous in grain-size composition and consist of clay, clayey siltstones, and lenses and beds of gravelly conglomerates.

The coarse-grained composition of the proluvial sediments indicates that the material was repeatedly transported by intense water streams from uplands. Traces of buried soils found in proluvium indicate an intermittent formation of these deposits. The main part of proluvial deposits has a brown and red-brown color. The hydrothermal activity in the fault activation zone is superimposed on the lower part of proluvial deposits. This is indicated by intense steaming, elevated temperature (up to 30°C), and variegated color of this part of deposits.

The zone of active hydrothermal activity represented by variegated clayey rock was recovered during cleaning in the lower part of the small ravine slope (Fig. 2, point 3). Downslope, the brown and red-brown proluvium sequentially grade into light green and variegated sediments with yellow, white, violet, and bluish spots (samples 0511, 0512, 0513).

Rocks with similar color gradation were recovered several tens of meters down the slope (Fig. 2, point 9). The lower part of this exposure (horizon H1) consists of sandy (blue-gray when wet) clayey rock (Fig. 2, points 8, sample 0523, 18.7°C) with yellow-brown and white interbeds and spots. White clayey matter includes numerous tiny pyrite crystals. The overlying horizon H₂ (sample 0524) is composed of light green sandy clayey rock with yellow spots. At the same level, downslope the ravine, these rocks give way to the brown compact (plastic when wet) laminated clayey sediments (horizon H2, Fig. 2, point 9, sample 0524a, 19.7°C). When dry, the rock is brown spotty (with numerous light beige spots) and is penetrated by extended and branching cav-

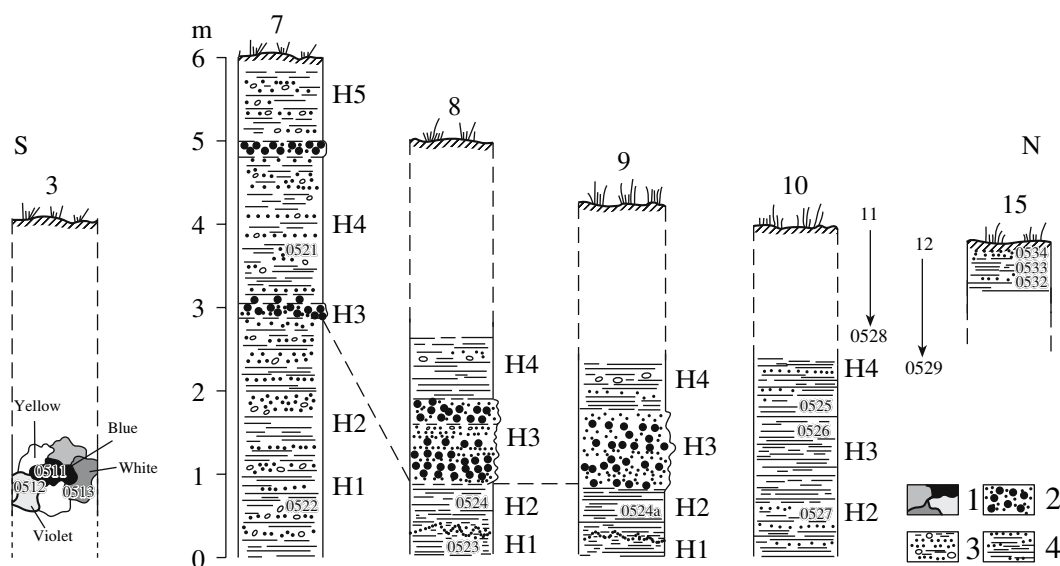


Fig. 2. Sections across the proluvial delta. Numbers above columns are observation points; H1, H2 and others are the studied horizons; numbers inside the column are sample numbers. (1) Variegated rocks; (2, 3) coarse-grained rocks: (2) gravel-pebble, (3) sandy-silty rocks with rare pebble; (4) clayey rocks with interbeds and lenses of sandy-silty material.

ities 0.1 mm in diameter. The walls of cavities are incrustated by light beige clayey matter. Judging from their shape and distribution, the cavities can be interpreted as root holes. This horizon is extended further southward along the strike and grades into light brown thin-bedded clayey rocks (Fig. 2, point 10, sample 0527, 18.8°C). Upsection, this horizon is replaced by massive (plastic when wet) brown clayey rock with numerous extended cavities presumably left from the root system (horizon H3, sample 0526). These cavities are surrounded by abundant iron hydroxides and incrustated by a black substance. Upward, this horizon gives way to the brown compact (plastic when wet) clayey rock (horizon H4, sample 0525). Further along the strike, the ravine slope is composed of brown (Fig. 2, point 11, sample 0528, 14.6°C) and red clayey rock consisting of tiny white particles and clumps and sparse coarse (sandy silt size) dissemination of hydrothermally altered hyaloclastites (Fig. 2, point 12, sample 0529, 13.6°C, stream water 17.4°C).

Distribution of rocks with different colors and temperatures over the study area suggests that the proluvial deposits mainly composed of redeposition products of hydrothermally altered hyaloclastites are intensely affected by hot steam and groundwaters at points 3 and 8 at present. The hydrothermal alteration of the already formed proluvial deposits is supported by the appearance of rocks (with green and blue color when wet) in the lower part of the section.

In the **Námafjall hydrothermal area**, the hyaloclastites are confined to a large fracture with prominent graben morphology. The white, red, and yellow bands distinctly seen on the talus-covered (10–25 cm thick) slopes of the Dalfjall range reflect the distribution of

hydrothermally altered rocks of diverse composition. Samples taken from this area (samples 0543, 0544, 0551, 0552, 0554, 0556, 0561, 0562, 0562) comprise variably altered bedrock hyaloclastites.

The strongly altered rocks have brown, red-brown, and yellow (with variable tint) color. The domain of white rocks coincides with that of the most intense fumarole activity and strongest alteration of hyaloclastites. Accumulations of native sulfur are often found in such places. Sample 0544 was taken from S-free white rocks.

White clumpy clayey rocks with spots, films, and veins of black and dark brown iron hydroxides are represented by samples 0554 and 0556. Large sharply outlined fragments are completely replaced by clayey material and characterized by blue-gray, yellow, red, and brown color. White rocks traced along the strike (samples 0561, 0562, 0563) contain a layer with rootlets (sample 0562).

Talus at the eastern foothill of the Dalfjall Range consists of fine-grained rocks with a great amount of clayey matter. These deposits are located in the zone of present-day solfatara activity. Samples were taken from different parts of the talus cover (samples 83119f, 83119h–83119j).

CHEMICAL COMPOSITION OF HYDROTHERMALLY ALTERED HYALOCLASTITES

Complete silicate analysis was carried out for the altered rocks taken from the Theistareykir and Námafjall geothermal areas, as well as from adjacent territories from the following zones: (1) volcanic rocks (lavas

and hyaloclastites) unaffected by hydrothermal alteration; (2) bedrocks from the zone of present-day hydrothermal (fumarolic) activity; (3) redeposited hydrothermally altered hyaloclastites that compose talus and proluvial deposits.

Content and Distribution of Petrogenic Elements

According to available (Gerasimovskii et al., 1978) and original (sample 0531) data, the unaltered lavas and hyaloclastites in the Theistareykir geothermal area have the following major element composition (wt %): SiO₂ 44–49, TiO₂ 0.8–2, Al₂O₃ 13–17, Fe₂O₃ 1–4, FeO 5–9, MgO 6–8, CaO 8–13 (Table 1, nos. 1–6). Rocks from the Námafjall geothermal zone show within the following compositional range (%): SiO₂ 48–50, TiO₂ 1–2, Al₂O₃ 12–15, Fe₂O₃ 1–5, FeO 8–14, MgO 5–7, CaO 8–13 (Table 1, nos. 25–30).

Unlike the unaltered rocks, the altered hyaloclastites have significantly wider compositional variations. In the Theistareykir area (Table 1, nos. 7–13), the variation is as follows (wt %): SiO₂ 38–67, TiO₂ 0.2–3, Al₂O₃ 3–30, Fe₂O₃ 2–15, FeO 0.1–0.5, MgO 0.5–5, CaO 0.1–2. In the Námafjall geothermal area (Table 1, nos. 31–40), the variation is as follows: SiO₂ 43–86, TiO₂ 1–7, Al₂O₃ 1–33, Fe₂O₃ 0.2–16, FeO 0.2–2, MgO 0.2–5, CaO 0.2–6.

Sediments from the hydrothermally altered zones on slopes (talus) and adjacent lowlands (proluvial deposits) also differ from the unaltered volcanic rocks in the major element composition.

Relative to the unaltered volcanic rocks, the hydrothermally altered hyaloclastites and talus–proluvial deposits have higher contents of Fe₂O₃ and lower contents of CaO, MgO, Na₂O, and K₂O (Table 1, nos. 15–24, 41–44).

The white rocks are sharply enriched in Al₂O₃ (30.5–33.7%) (samples 0516, 0544, 0554) or SiO₂ (54–87%) (samples 0501, 0561–0563) and depleted in Fe₂O₃ (Table 1, nos. 10, 32, 35).

Insignificant variations in the TiO₂ concentration recorded in both unaltered and altered volcanic rocks are presumably related to the inert behavior of Ti. It should be noted that the abundance of petrogenic elements in hydrothermalites presently formed in the solfataric pots (samples 0501, 0520) is almost identical to that in the hydrothermally altered hyaloclastites (Table 1, nos. 37, 14).

Content and Distribution of Trace Elements

Data on the trace element composition of volcanics in Iceland are scanty. The distribution and composition of trace elements in different alteration zones of the Miocene lavas and volcanoclastic rocks of eastern Iceland are given in (Gibson et al., 1982; Schmincke et al., 1982). Lavas have the following compositional varia-

tions (ppm): Cr 4–250, Cu 15–215, Ni 3–160, Sc 24–48, V 75–480, and Zn 73–179. It was shown that Zr, Nb, and Y behave as immobile or low-mobile elements during the hydrothermal alteration of lavas up to the epidote formation zone. However, proportions of these elements in the studied hydrothermally altered hyaloclastites attest to the mobile behavior of Y.

Pleistocene and Holocene lavas in the northern part of the rift, including the studied areas, show the following variations in trace elements (ppm): Pb 3–4, Zn 110–180, Mo 2.0–2.5, Ag 0.05–0.06, B 8–9, Hg 0.05–1.30, Zr 45–70, Nb 2.0–5.2 (Gerasimovskii et al., 1978).

The trace element composition of rocks was determined by the XRF and INAA methods (Tables 2, 3). Significant trace element variations were recorded in the altered hyaloclastites and their redeposited products. However, these variations are within the ranges known for unaltered volcanic rocks. These values exceed the known maximum values only for some elements. For instance, two samples from the modern fumarole site have the maximum contents of the following elements (ppm): V 1700 (sample 0516), As 100, Ag 22, Se 390, Sb 2.9, I 8.3, Au 12, Ag 22 (sample 0514) (Tables 2, 3).

No significant differences were found between contents of trace elements in the bedrock hyaloclastites (sample 0552), cross-cutting veins (sample 0551), and modern analogues of these veins at the surface represented by sediments from high-temperature solfataric pots (samples 0501, 0520) (Tables 2, 3).

MINERAL AND CHEMICAL COMPOSITIONS OF CLAY MINERALS

The mineral and chemical compositions of clay minerals (Tables 4, 5) were determined using X-ray and chemical characteristics of clay fractions (from <5 to 50 µm) extracted from the hydrothermally altered hyaloclastites and products of their proximal redeposition (proluvium).

X-Ray Data

Minerals were identified in the studied fractions on the basis of diffraction patterns recorded in oriented and unoriented samples.

Kaolinite occurs as the major clayey component in sample 0544 (fraction <10 µm). Diffractograms of oriented natural and saturated specimens are characterized by reflections with $d(001) \sim 7.20$ and 3.58 Å. Diffractogram of unoriented specimen shows the reflection 1.491 Å in the 060 region. Hence, $b = 8.95$ Å. Kaolinite as subordinate component or traces is also observed in samples 0511, 0524, 0524a, 0518, 0552, 0523 (Table 4).

Smectites are present in the clay fraction of samples 0518, 0552, 0523, 0524, 0524a and have the following diffraction features.

Table 1. Chemical composition of basalts and hydrothermally altered hyaloclastic rocks (wt %)

Theistareykir geothermal zone													
No.	Sample no.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I.
Basalts unaffected by hydrothermal alteration; (0531, 11913) hyaloclastites; (11910 and others) lavas													
Σ													
H ₂ O ⁻													
H ₂ O ⁺													
CO ₂													
Stot													
SO ₃													
1	0531*	44.17	2.02	15.03	4.45	9.17	0.21	6.29	8.50	1.80	0.31	0.24	7.20
2	11910**	48.62	1.02	14.7	1.2	8.92	0.18	0.1	13.9	1.98	0.22	0.05	n.a.
3	11913**	48.08	1.57	13.43	3.18	9.61	0.21	6.35	10.95	2.13	0.31	0.11	n.a.
4	11904**	48.50	0.83	15.88	2.08	7.93	0.2	8.35	13.29	1.82	0.07	absent	n.a.
5	11896**	48.48	1.18	16.82	1.49	9.65	0.18	6.72	12.2	2.02	0.19	0.08	n.a.
6	11907**	49.6	0.86	17.8	4.21	5.89	0.16	7.03	12.7	1.84	0.14	0.08	n.a.
Hyaloclastites in the zone of intense influence of hot steam and gas (fumarole and solfatara activity)													
7	0511	44.32	2.35	19.22	10.85	0.29	0.04	1.01	0.22	0.02	0.02	0.11	19.84
8	0513	67.84	3.51	9.16	4.67	0.11	0.01	0.52	0.34	0.06	0.02	0.13	12.92
9	0514	48.84	0.26	3.68	2.56	<0.1	0.04	2.12	0.73	0.86	0.16	0.15	n.a.
10	0516	48.92	1.94	30.51	0.68	0.11	0.07	3.51	0.17	0.06	0.02	0.07	13.46
11	0517	40.90	1.34	12.19	15.72	0.11	0.14	5.17	1.40	0.04	0.03	0.20	22.40
12	0504	47.10	1.46	12.07	11.25	<0.1	0.11	4.65	2.18	0.07	0.05	0.12	20.52
13	0523	38.66	2.55	16.77	12.57	0.43	0.04	1.01	0.45	0.03	0.03	0.09	23.00
14	0520	41.60	1.57	11.02	13.30	0.50	0.13	5.17	1.51	0.09	0.04	0.15	22.38
Redeposited hydrothermally altered hyaloclastites, proluvial delta sediments													
15	0518	42.34	1.43	12.24	14.88	0.18	0.18	4.48	2.58	0.09	0.08	0.13	20.86
16	0524	45.74	2.02	18.91	9.70	0.25	0.03	2.75	0.45	0.07	0.04	0.11	19.60
17	0524a	41.90	2.33	19.23	13.57	0.29	0.07	2.46	0.45	0.06	0.05	0.23	18.94
18	0526+	42.82	1.82	14.48	14.04	0.29	0.09	3.96	2.07	0.12	0.06	0.14	19.86
19	0528	43.74	1.92	15.24	11.70	0.11	0.18	4.36	1.90	0.08	0.05	0.13	19.92
20	0529	42.61	2.01	15.49	12.03	0.13	0.14	4.41	2.42	0.05	0.05	0.14	20.32
21	0530	43.63	2.89	19.87	7.64	1.98	0.05	2.11	1.86	0.32	0.12	0.19	18.64
22	0532	42.37	1.74	13.82	12.15	1.71	0.14	5.80	3.29	0.17	0.08	0.18	17.90
23	0533	43.43	2.11	16.26	9.63	1.37	0.16	4.07	2.80	0.30	0.11	0.20	18.94
24	0534	42.93	1.94	15.35	10.65	2.19	0.18	5.47	3.66	0.33	0.12	0.19	16.43

Table 1. (Contd.)

Námafjall geothermal zone																			
No.	Sample no.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I.	Σ	H ₂ O ⁻	H ₂ O ⁺	CO ₂	Stot	SO ₃
Basaltoids unaffected by hydrothermal influence, lava samples																			
25	11876**	48.10	2.00	14.30	5.39	11.75	0.25	5.41	9.90	2.16	0.24	0.20	n.a.	100.04	absent	0.12	n.a.	n.a.	n.a.
26	12754**	48.74	1.52	15.24	1.75	9.26	0.17	7.55	13.55	2.50	0.25	0.11	n.a.	100.68	absent	0.04	n.a.	n.a.	n.a.
27	12746**	49.39	2.07	14.34	1.89	9.75	0.21	7.07	12.37	2.34	0.40	0.14	n.a.	100.13	0.14	0.02	n.a.	n.a.	n.a.
28	11945**	50.80	2.20	13.40	3.85	11.00	0.22	5.04	9.90	2.75	0.38	0.41	n.a.	100.01	0.03	0.03	n.a.	n.a.	n.a.
29	11834**	49.10	2.15	12.50	3.62	14.76	0.15	5.20	8.85	2.65	0.32	0.23	n.a.	99.88	0.10	0.35	n.a.	n.a.	n.a.
30	11842**	49.00	1.43	15.30	2.99	8.48	0.22	7.01	12.23	2.07	0.15	absent	n.a.	99.12	0.24	absent	n.a.	n.a.	n.a.
Hyaloclastites in the zone of intense influence of hot steam and gases (fumarole and solfatara activity)																			
31	0543	43.20	1.15	12.44	10.88	1.35	0.42	5.92	6.33	0.29	0.23	0.09	17.35	99.65	9.37	7.94	<0.2	<0.1	<0.1
32	0544	48.94	2.81	33.73	0.55	<0.1	0.01	0.28	0.38	0.04	0.02	0.02	13.09	99.87	1.05	12.06	<0.2	<0.1	<0.1
33	0551	45.98	1.75	17.97	11.29	<0.1	0.04	2.09	0.79	0.05	0.04	0.30	19.50	99.80	11.12	8.80	<0.2	<0.1	<0.1
34	0552	40.12	2.23	16.58	16.96	<0.1	0.24	3.65	1.00	0.03	0.03	0.29	18.93	100.06	10.18	9.06	<0.2	<0.1	<0.1
35	0554	41.10	2.41	30.31	9.11	<0.1	0.20	0.95	0.25	0.05	<0.01	0.06	15.19	99.63	3.05	11.86	<0.2	<0.1	0.23
36	0556	40.93	2.37	18.51	15.96	<0.1	0.08	2.36	1.58	0.04	<0.01	0.08	17.44	99.35	11.91	5.22	<0.2	<0.1	<0.1
37	0501	54.23	2.96	10.07	10.57	0.56	0.02	0.71	0.74	0.15	0.08	0.17	16.70	96.96	4.99	6.71	<0.2	7.56	2.96
38	0561	87.52	3.32	2.01	0.28	0.25	0.01	0.28	0.26	0.03	0.01	0.05	5.80	99.82	2.74	2.84	<0.2	0.10	<0.1
39	0562	86.83	7.91	1.14	0.20	<0.1	0.01	0.39	0.27	0.04	<0.01	0.03	3.00	99.82	1.42	1.11	<0.2	0.28	0.16
40	0563	58.38	3.16	11.07	8.76	2.47	0.13	2.42	3.06	0.49	0.13	0.15	9.50	99.72	5.03	4.39	<0.2	0.34	0.13
Redeposited hydrothermally altered hyaloclastites, talus at the foothill																			
41	83119f	38.41	1.84	17.38	1.17	0.14	0.01	<0.1	10.13	0.15	0.09	0.09	15.76	85.17	7.44	6.74	<0.2	6.05	14.58
42	83119h	29.27	1.28	10.09	28.03	0.14	0.01	<0.1	7.01	0.17	0.12	0.18	14.04	90.34	5.51	5.03	<0.2	4.48	9.89
43	83119i	42.29	2.61	11.19	17.84	0.13	0.05	2.84	1.36	0.08	0.07	0.26	20.55	99.27	11.37	9.03	<0.2	<0.1	0.18
44	83119j	29.37	2.80	21.29	31.27	<0.1	0.02	0.45	0.25	0.05	0.03	0.25	12.98	98.76	2.14	9.63	<0.2	0.27	0.58

Note: * Hyaloclastites unaffected by hydrothermal alteration (the author's materials); ** volcanic rocks unaffected by hydrothermal alteration (Gerasimovskii et al., 1978). Sample numbers: (0531, 11913) hyaloclastites, (11910 and others) lavas; (0501) clayey sediments of the solfatara hot pot, Námafjall; (0520) clayey sediments of the solfatara hot pot, Theistareykir; (n.a.) not analyzed.

Table 2. Results of the XRF analysis (ppm)

Theistareykir geothermal zone																				
No.	Sample no.	V	Cr	Ni	Cu	Zn	Ga	Ge	Rb	Sr	Y	Hf	Zr	Ta	Nb	Mo	Sn	Ba	Pb	U
Hyaloclastites unaffected by hydrothermal influence																				
1	0531	310	340	140	140	120	15	1.9	9.1	160	34	3.9	160	1.1	17	<1	3.9	180	4.4	<1
Hyaloclastites in the zone of intense influence of hot steam and gas (fumarole and solfatara activity)																				
2	0504	460	180	160	190	180	20	0.8	2.3	89	21	2.8	90	0.8	10	2.8	2.8	140	4.2	<1
3	0511	250	230	90	160	36	22	1.2	1.4	8.0	1.0	4.4	140	1.1	18	<1	2.3	130	2.0	<1
4	0513	400	270	18	<1	13	68	0.6	1.7	24	2.6	6.5	240	2.1	31	<1	0.9	37	<1	1.3
5	0514	40	45	36	140	27	5.6	3.2	9.9	22	4.4	0.50	20	0.1	5.8	12	1.5	46	5.3	1.6
6	0516	1700	540	12	<1	7.0	24	<0.5	<1	99	2.3	2.8	110	0.7	15	1.6	1.6	50	<1	<1
7	0517	200	170	440	120	240	16	<0.5	2.6	34	22	2.5	75	0.4	10	<1	0.7	71	<1	<1
8	0518	210	180	200	120	100	12	<0.5	3.7	92	21	2.1	81	0.6	11	2.4	1.0	99	<1	<1
9	0520	260	260	130	18	91	13	<0.5	3.1	120	25	2.4	92	0.6	11	2.5	1.1	140	1.2	3.2
10	0523	340	230	150	350	66	23	1.7	1.9	54	1.7	4.3	150	1.0	20	2.4	4.2	95	2.9	2.7
Redeposited hydrothermally altered hyaloclastites, sediments of proluvial delta																				
11	0524	330	260	98	100	78	20	0.6	3.4	70	2.5	4.1	120	1.2	17	<1	0.7	78	<1	<1
12	0524a	400	230	100	100	92	23	1.3	3.6	64	8.4	2.8	140	1.2	19	2.8	2.6	140	1.7	<1
13	0526+	360	230	140	180	100	19	0.8	3.5	83	29	2.5	110	0.5	13	1.7	3.1	110	<1	<1
14	0528	350	240	140	140	150	20	<0.5	2.9	82	24	2.7	110	0.8	13	2.5	2.1	110	<1	<1
15	0529	330	220	130	140	95	21	0.9	3.3	89	24	2.5	110	0.8	14	1.3	2.7	79	1.9	<1
16	0530	440	200	54	72	62	28	1.2	6.4	71	20	5.6	200	1.1	25	3.8	2.4	120	7.9	3.6
17	0532	310	230	98	160	110	16	0.8	3.9	99	23	3.1	100	0.6	13	1.1	1.1	120	2.4	<1
18	0533	350	200	120	120	90	21	1.0	4.5	91	25	3.8	140	0.7	17	1.9	3.1	96	1.7	<1
19	0534	340	280	120	140	110	19	2.5	4.8	110	27	2.6	120	1.1	15	<1	2.0	130	1.3	<1
Námafjall geothermal zone																				
Hyaloclastites in the zone of intense influence of hot steam and gases (fumarole and solfatara activity)																				
20	0501	410	99	45	120	51	21	1.8	2.9	120	5.2	4.5	170	1.2	24	3.9	3.6	140	1.9	6.2
21	0543	200	240	76	170	81	7.6	<0.5	8.1	120	20	1.6	55	0.4	6.9	1.9	0.8	53	3.9	<1
22	0544	670	360	8.5	<1	3.5	15	0.7	<1	25	1.0	5.1	180	1.3	22	<1	<0.5	<1	1.4	<1
23	0551	400	260	33	56	110	36	<0.5	1.5	40	4.0	2.7	95	0.7	13	1.3	1.7	100	<1	<1
24	0552	400	150	80	220	230	24	<0.5	2.2	31	21	3.1	120	0.7	15	1.3	4.2	110	3.3	<1
25	0554	690	380	32	22	17	17	1.2	<1	25	3.4	3.7	120	0.9	15	1.6	0.5	20	5.1	<1
26	0556	350	220	64	160	97	27	<0.5	1.2	19	4.3	2.8	140	0.9	17	2.1	1.5	16	<1	<1
27	0561	250	170	12	35	12	25	<0.5	1.3	<1	1.9	5.4	170	1.1	22	1.9	<0.5	19	<1	<1
28	0562	770	190	16	<1	8.6	3.4	1.4	1.4	<1	<1	11	320	2.7	49	5.9	2.5	4.5	<1	8.0
29	0563	350	160	53	140	95	2.5	0.8	4.3	72	17	5.3	160	1.6	22	2.5	2.0	110	<1	<1
Redeposited hydrothermally altered hyaloclastites, talus cover at the foothill																				
30	83119i	530	140	29	72	77	16	1.1	2.5	50	4.5	3.9	130	0.8	18	2.0	2.8	170	<1	<1
31	83119j	790	99	43	37	36	20	2.3	<1	190	1.8	5.7	150	0.9	18	2.9	5.2	120	2.9	<1
32	83119f	220	200	15	<1	60	27	1.5	1.3	96	3.5	2.3	100	0.6	15	2.6	2.2	65	<1	8.5
33	83119h	490	150	27	7.5	16	18	<0.5	1.6	140	3.3	1.9	69	0.4	9.7	2.7	1.1	110	1.2	4.1

Note: (Sample 0544) rock; (0501) clayey sediments of the solfatara hot pot, Námafjall; (0520) clayey sediments of the solfatara pot, Theistareykir.

Table 3. Results of the INAA analysis (ppm)

Theistareykjir geothermal zone																			
No.	Sample no.	Sc	Co	As	Se	Br	Ag	Sb	I	Cs	La	Sm	Eu	Yb	W	Ir	Au	Hg	Th
Hyaloclastites unaffected by hydrothermal alteration																			
1	0531	49	60	<0.05	<0.5	28	4.1	0.29	0.9	0.4	14	6.4	2.6	4.4	1.6	0.003	0.029	<0.2	1.3
Hyaloclastites in the zone of intense influence of hot steam and gases (fumarole and solfatara activity)																			
2	0504	39	190	7.7	<0.5	1.2	0.8	1.8	0.4	0.3	5.0	2.6	1.3	2.5	0.6	<0.001	0.052	0.2	0.3
3	0511	48	41	0.09	0.6	0.7	<0.5	0.02	0.4	<0.1	3.2	0.48	0.11	0.12	0.5	0.005	0.002	<0.2	1.0
4	0513	27	4.7	0.27	0.8	1.3	<0.5	0.12	<0.1	0.5	5.1	0.87	0.39	0.63	0.9	0.006	0.008	<0.2	1.1
5	0514	7.7	8.9	100	390	2.1	22	2.9	8.3	0.6	1.9	0.83	0.33	0.24	1.0	0.001	12	<0.5	0.1
6	0516	13	1.1	0.07	2.3	1.0	<0.5	0.06	0.2	<0.1	2.9	5.3	1.9	0.07	0.7	0.001	0.022	0.2	0.2
7	0517	42	190	0.13	<0.5	1.4	6.7	<0.05	0.2	0.7	5.8	3.5	1.4	2.3	0.2	0.003	0.009	0.2	0.5
8	0518	41	81	<0.05	<0.5	1.4	<0.5	0.07	1.1	<0.1	5.8	3.1	1.2	2.5	0.2	0.001	0.011	<0.2	0.2
9	0520	39	46	0.10	2.8	0.2	<0.5	0.05	0.5	0.4	6.3	3.4	1.6	2.7	<0.2	0.002	0.017	<0.2	0.3
10	0523	59	87	0.29	0.8	6.8	1.5	0.15	0.6	0.1	11	1.9	0.34	0.63	1.8	0.002	0.005	<0.2	0.6
Redeposited hydrothermally altered hyaloclastites (sediments of proluvial delta)																			
11	0524	66	30	0.13	1.7	0.6	1.5	0.06	0.2	0.2	3.3	0.63	0.39	0.55	1.5	0.009	0.009	0.4	0.4
12	0524a	48	28	<0.05	<0.5	1.7	1.4	<0.05	<0.1	0.2	7.4	1.7	0.39	1.1	0.2	0.001	0.003	<0.2	0.7
13	0526+	45	40	<0.05	<0.5	0.9	1.0	<0.05	0.2	0.4	7.3	3.9	1.9	3.2	<0.2	0.003	0.007	<0.2	0.1
14	0528	45	49	<0.05	2.2	4.5	0.9	<0.05	0.5	0.5	7.5	3.6	1.5	2.8	<0.2	<0.001	0.006	<0.2	0.5
15	0529	49	52	0.28	<0.5	1.8	<0.5	0.15	0.2	0.2	7.6	4.1	1.9	3.1	0.5	<0.001	0.004	<0.2	0.3
16	0530	51	21	0.36	3.1	11	0.9	0.12	<0.1	0.9	13	3.7	1.5	2.2	0.3	0.009	0.009	<0.2	0.9
17	0532	45	49	<0.05	0.8	4.4	1.2	0.05	0.2	0.4	6.3	3.4	1.6	2.6	0.2	0.002	0.005	<0.2	0.6
18	0533	39	42	<0.05	4.8	11	0.6	0.11	0.2	0.4	8.2	3.7	1.6	2.9	<0.2	<0.001	0.008	0.2	0.7
19	0534	42	53	<0.05	0.8	3.9	1.6	0.06	0.2	0.2	7.8	3.9	1.8	2.9	0.5	0.001	0.021	0.2	0.7
Námafjall geothermal zone																			
Hyaloclastites in the zone of intense influence of hot steam and gases (fumarole and solfatara activity)																			
20	0501	27	25	0.54	<0.5	0.9	0.6	0.09	0.4	0.2	8.2	2.7	1.1	0.41	0.5	<0.001	0.009	0.4	0.9
21	0543	49	51	0.28	<0.5	1.5	1.2	0.07	0.2	<0.1	4.9	2.9	1.4	2.2	0.9	0.002	0.006	<0.2	0.1
22	0544	14	0.6	0.15	<0.5	1.4	<0.5	0.05	<0.1	0.1	1.5	0.25	0.10	0.03	<0.2	0.006	0.076	0.2	0.2
23	0551	66	8.1	<0.05	2.1	1.4	2.5	<0.05	<0.1	0.2	6.9	0.68	0.38	0.51	<0.2	0.002	0.001	<0.2	0.2
24	0552	68	76	<0.05	2.4	1.9	0.5	<0.05	0.2	0.8	6.3	3.2	1.1	2.9	<0.2	0.002	0.028	<0.2	0.4
25	0554	39	3.2	<0.05	3.7	1.4	1.5	0.07	0.3	0.6	9.5	1.1	0.27	0.13	0.4	0.009	0.014	0.3	0.5
26	0556	56	23	0.32	<0.5	1.4	1.4	0.15	0.5	0.5	1.3	0.57	0.46	0.51	1.1	<0.001	0.005	<0.2	0.4
27	0561	4.9	1.2	0.37	2.5	1.8	<0.5	0.05	0.2	0.2	0.3	0.23	0.18	0.57	<0.2	<0.001	0.005	<0.2	0.1
28	0562	9.2	0.5	0.05	<0.5	2.6	0.5	0.21	0.2	0.2	0.2	0.01	0.14	0.05	0.2	<0.001	0.016	<0.2	0.1
29	0563	35	38	0.97	<0.5	1.9	<0.5	0.11	<0.1	0.6	7.1	3.1	1.5	1.9	<0.2	<0.001	0.004	0.2	7.4
Redeposited hydrothermally altered hyaloclastites, talus at the foothill																			
30	83119f	22	0.9	<0.05	<0.5	1.1	<0.5	0.08	0.4	0.3	8.6	2.6	0.83	0.41	<0.2	<0.001	0.018	<0.2	0.4
31	83119h	23	1.9	0.63	1.9	2.8	2.1	0.08	<0.1	<0.1	8.3	2.3	0.61	0.38	0.2	<0.001	0.012	<0.2	0.6
32	83119i	45	23	0.34	2.7	2.5	0.8	<0.05	0.4	<0.1	2.7	0.99	0.60	0.68	0.4	0.003	0.002	<0.2	0.5
33	83119j	15	15	0.11	4.4	0.9	1.4	<0.05	0.2	0.1	18	2.1	0.56	0.57	0.5	0.002	0.008	<0.2	0.5

Note: (Sample 0544) rock; (0501) clayey sediments of the solfatara hot pot, Námafjall; (0520) clayey sediments of the solfatara hot pot, Theistareykjir.

Table 4. Mineral composition of clay fractions of the studied samples (X-ray data)

Geothermal zone	Rock type	Color	Sample no.	Fraction, μm	Mineral components			
					major	subordinate	$d(06)$, Å	parameter b , Å
Theistareykir	Bedrock	Brown	10518	<50	smectite	traces of kaolinite, anatase	1.513	9.08
	Proluvium in the zone of fumarole activity	Blue	10511	<5	pyrite	smectite, kaolinite, anatase	1.491 (?)	8.95
	Proluvium in the zone of fumarole activity	Blue	10523	<50	smectite	traces of kaolinite, pyrite, anatase, zeolites	1.490	8.94
	Proluvium	Brown	10524	<50	smectite	kaolinite, zeolites, pyrite	1.494	8.96
	Proluvium	Brown	10524a	<50	smectite	kaolinite, zeolites, pyrite, anatase	1.491	8.95
Námafjall	Bedrock	White	10544	<10	kaolinite	traces of anatase	1.491	8.95
	Bedrock	Brown	10552	<50	smectite	zeolites	1.496	8.98

Smectite is the major component in sample 0518 (fraction <50 μm). Diffractogram of natural specimen demonstrates reflection with $d(001) \sim 14.85$, which increases to 17.159 Å in ethylene glycol-saturated samples and decreases to 9.72 Å at their heating up to 550°C (Fig. 3a). Given the fact that the difference between calculated and true values of $d(001)$ decreases significantly as the order of reflection l increases (Drits and Sakharov, 1976), the value of true interplanar spacing $d(001)$ in saturated state is $d(001) = 5 \times d(005) = 16.86$ Å. It is seen that the basal reflection (001) is shifted toward the low-angle region. Diffractogram of unoriented sample 0518 shows reflection 1.513 Å in the region $d(06)$ ($b = 9.08$ Å).

Other smectite-bearing samples (samples 0552, 0523, 0524, 0524a) are characterized by higher values of first basal reflections in natural and saturated specimens (from 15.78 to 16.21 Å and from 17.85 to 18.60 Å, respectively).

Let us calculate the value of true interplanar spacing $d(001)$ for natural sample 0552. It is seen that values of the first basal reflection reach up to 15.92 Å in natural oriented sample and increase to ~ 17.50 Å in saturated sample (Fig. 3b). Here, $d(001) = 2 \times d(002) = 15.06$ Å. In this case, the basal reflection (001) is also shifted toward small angles.

Parameter b in samples 0552, 0523, 0524, and 0524a varies from 8.94 to 8.98 Å ($d(06) = 1.490$ –1.496 Å).

It is known that mixed-layer and other clay minerals are composed of fine-dispersed particles of variable size. If particles are small, the basal reflection (001) is shifted toward the low-angle region. Hence, the calculated interplanar spacings can differ from interplanar spacings in the studied mineral (Drits and Sakharov, 1976).

Precisely this pattern, i.e., shift of basal reflection (001) toward the low-angle region, is observed in the diffractograms recorded from oriented specimens of the studied clay fractions. Hence, such a shift can be explained by small thickness of smectite particles. It should be noted that the coarser-grained smectites have $d(001)$ no more than 15–15.4 Å in natural samples (X-ray..., 1965; X-ray Diffractometry..., 1983).

Thus, smectites in the studied samples belong to the dioctahedral variety ($b = 8.94$ – 9.08 Å) and their particles are characterized by small sizes. The most dispersed smectites were found in samples 0523, 0524, 0524a, and 0552.

In addition to clay admixtures, some fractions contain zeolites (samples 0524, 0542a, 0523, 0552), anatase (samples 0511, 0518, 0544, 0524a, 0523), and pyrite (samples 0523, 0524, 0524a) (Tables 4; Figs. 3a, 3b). Pyrite is the predominant component in sample 0511, while smectite and kaolinite occur in subordinate amounts.

Chemical Composition

Table 5 presents results of the complete silicate analysis for bulk rock and extracted clay fraction (Table 5). In addition to components typical of clay minerals (smectite and kaolinite), the bulk rocks and fractions contain TiO_2 , CO_2 , P_2O_5 and S_{tot} . Together with X-ray data, the above fact testifies to the presence of fine-dispersed mechanical admixture of anatase, gypsum, phosphate (?), pyrite, and native sulfur.

The chemical composition of kaolinite in sample 0544 (fraction <10 μm) (Table 5) is close to its theoretical composition (Mineralogy..., 1992). It is difficult to determine the composition of smectites in the analyzed clay fractions, because they contain an admixture of kaolinite (samples 0524, 0524a), pyrite (samples 0511,

0523) and, possibly, weakly crystallized Mg-bearing silicates (sample 0518), which cannot be determined by the X-ray analysis (Kristmannsdóttir et al., 1999). For instance, the latter sample contains a minimum amount of admixture, but the formula of smectite could not be calculated because of the presence of excess MgO.

Based on the complete silicate analysis (in the absence of X-ray data), the studied clayey rocks in two samples (samples 0554, 0156) are mainly composed of kaolinite, while other samples are dominated by smectite (Table 1).

Clay fractions show wide variations in trace elements (Tables 2, 3). Figure 4 demonstrates variations of As, Se, Br, Ag, and Sb contents in the hydrothermally altered hyaloclastites, proluvial deposits (Fig. 4a), and clay fractions extracted from these rocks (Fig. 4b). Both rocks and clay fractions in all the studied rocks show unsystematic variations in concentrations of trace elements.

INVESTIGATION BASED ON ELECTRON MICROSCOPE EQUIPPED WITH MICROPROBE

To reveal microtextural–structural features and composition of rocks, which are widespread in the geothermal field, we analyzed the following rock varieties using scanning electron microscope equipped with microprobe: (1) white and light beige soft rock with a great amount of bright yellow sulfur crystals (sample 0514) from well-heated zone (43°C) and active fumarole activity; (2) rock formed during the intense leaching of hyaloclastite layer and its replacement by white soft matter (sample 0561); (3) red-brown clayey rock from the periphery of the fumarole zone (sample 0517, 24.4°C); (4) red-brown clayey rock from proluvial deposits related to the redeposition of hydrothermally altered hyaloclastites (sample 0529); (5) red-brown clayey rocks from a buried soil bed in the proluvial deposits (sample 0524a); and (6) blue-gray clayey rock formed in the course of the present-day fumarole reworking (18.7°C) of proluvial red-brown deposits (sample 0523).

1. White and light beige rocks (Table 1, no. 9, sample 0514) with abundant crystals of light yellow sulfur were taken at the Theistareykir geothermal field. They mark the zones of intense fumarole activity. The clastic structure of the rock is well discernible at large magnifications (Fig. 5a). All clasts identified as fragments of volcanic glass are embedded in the porous microglobular groundmass (Figs. 5b, 5c). Microglobules of similar size (0.2–0.5 μm) make up short chains and irregular aggregates, which cover the clasts and whole space between them. In some places, the microglobular groundmass includes prominent rounded and oval structures (globules) up to 0.1–2.5 μm in size. Cavities are clearly seen inside such solitary or coalesced globules. The globules are coalesced in the rock to form gradually bending zones (Fig. 5d).

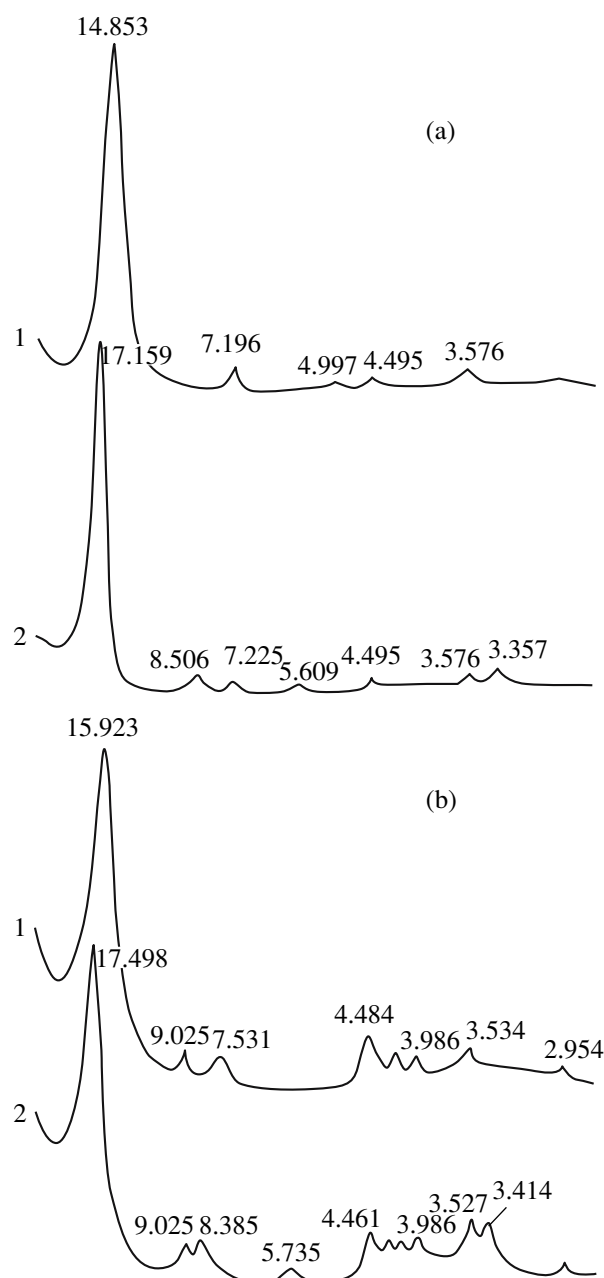


Fig. 3. Diffractograms of oriented specimens of fractions <0.01 and <0.05 mm. Samples: (1) air-dry, (2) ethyleneglycol-saturated; (a) sample 0518, (b) sample 0552.

Judging from microprobe data, the microglobular groundmass consists of silica with an admixture of Ti, and occasionally, Al and Mg. The globules are typically enriched in TiO_2 (18–38%) (Table 6).

2. White rock (Table 1, no. 38, sample 0561) was formed during the fumarole activity and intense alteration of hyaloclastites in the Námafjall geothermal field. It consists of variably shaped fragments of volcanic glass, which was partially or completely replaced by a homogenous ultrafine matter (Fig. 6a). This matter

Table 5. Silicate analyses of the bulk rocks and clay fractions (wt %)

Sample no.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I.	Total	H ₂ O ⁻	H ₂ O ⁺	CO ₂	Stot	SO ₃
0511	44.32	2.35	19.22	10.85	0.29	0.04	1.01	0.22	0.02	0.02	0.11	19.84	98.29	8.94	7.53	<0.2	5.90	1.11
0518	42.34	1.43	12.24	14.88	0.18	0.18	4.48	2.58	0.09	0.08	0.13	20.86	99.47	13.67	7.48	<0.2	0.22	<0.1
10518	42.81	1.77	14.54	12.42	<0.1	0.13	4.98	2.18	0.03	0.05	0.10	20.63	99.64	13.84	7.00	<0.2	<0.1	<0.1
0523	38.66	2.55	16.77	12.57	0.43	0.04	1.01	0.45	0.03	0.03	0.09	23.00	95.63	9.39	8.18	<0.2	6.87	4.53
10523	41.58	2.93	20.00	11.76	0.39	0.09	1.25	<0.1	0.03	0.03	0.10	17.80	95.96	6.12	8.41	<0.2	6.08	1.63
0524	45.74	2.02	18.91	9.70	0.25	0.03	2.75	0.45	0.07	0.04	0.11	19.60	99.67	12.03	7.81	<0.2	0.20	<0.1
10524	46.10	2.43	22.00	8.61	0.09	0.04	1.77	<0.1	0.03	0.03	0.11	18.00	99.21	8.88	8.11	<0.2	<0.1	<0.1
0524a	41.90	2.33	19.23	13.57	0.29	0.07	2.46	0.45	0.06	0.05	0.23	18.94	99.58	10.44	8.65	<0.2	0.11	<0.1
10524a	42.13	2.67	21.09	12.74	0.12	0.12	2.52	0.26	0.04	0.04	0.22	17.52	99.47	7.76	8.89	<0.2	<0.1	<0.1
0544	48.94	2.81	33.73	0.55	<0.1	0.01	0.28	0.38	0.04	0.02	0.02	13.09	99.87	1.05	12.06	<0.2	<0.1	<0.1
10544	46.94	2.06	35.96	0.20	<0.1	0.01	0.29	0.13	0.02	0.02	0.01	14.10	99.74	0.85	13.13	0.25	<0.1	<0.1
0552	40.12	2.23	16.58	16.96	<0.1	0.24	3.65	1.00	0.03	0.03	0.29	18.93	100.06	10.18	9.06	<0.2	<0.1	<0.1
10552	40.65	2.49	17.14	15.39	<0.1	0.16	3.68	0.93	0.04	0.02	0.26	19.00	99.76	10.85	8.95	<0.2	<0.1	<0.1

Note: (Sample nos. 0511, 0518 and others) rocks, (10544, 10552, and others) clay fraction.

Table 6. Elemental composition of microglobular light beige soft rock with fragments of globular microtextures, sample 0514 (%)

Elements	Microglobular rock			Globular microtextures		
Si	45.00	43.41	46.39	19.81	17.08	32.38
Ti	1.91	4.28	0.45	34.55	38.05	18.42
O	52.80	52.31	53.16	45.64	44.87	49.20
Total	100.00	100.00	100.00	100.00	100.00	100.00

is composed of tiny globules $\sim 0.1\text{--}0.2\ \mu\text{m}$ in size (Fig. 6b). The coarser-grained globules ($3\text{--}5\ \mu\text{m}$) were found in the pore space and at the surface of volcanic clasts.

Silica is the major ore-forming element (Table 7). Titanium found at each point can probably be considered an element related to basaltic glass and retained in siliceous groundmass after the dissolution of glass. Together with silica, Ti is incorporated in the neogenic microglobular matter.

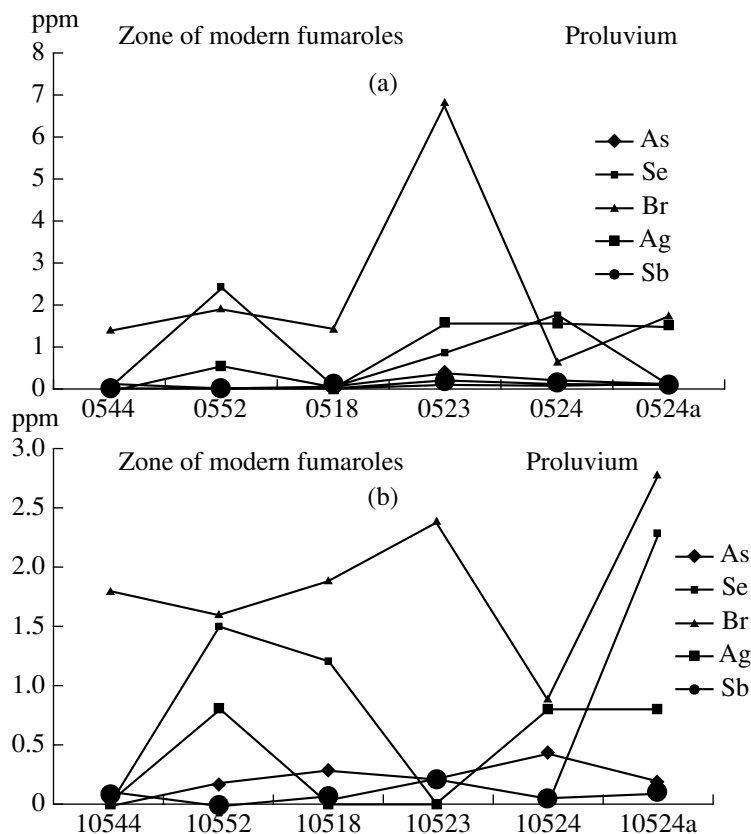
3. Red-brown rock (Table 1, no. 11, sample 0517) is widespread at the periphery of the fumarole zone of the Theistareykir geothermal site. Its major component

Table 7. Elemental composition of white rock formed during the intense leaching of hyaloclastites, sample 0561 (%)

Element	Groundmass of the rock					
Al	0.23	0.65	0.30	0.14	0.39	0.38
Si	44.53	44.92	44.85	44.56	40.67	43.24
Ti	2.58	1.60	2.09	2.64	7.35	4.07
O	52.66	52.83	52.76	52.66	51.59	52.32
Total	100.00	100.00	100.00	100.00	100.00	100.00

is clayey matter. The rock includes a compact homogeneous (structureless) matrix with volcanic fragments partially or completely replaced by clay minerals (Fig. 7a). The clay minerals contain Si, Al, Fe, Mg, Ti, and Ca. The rock also contains the Ti-free framework pseudomorphs of microlites and phenocrysts partially or completely replaced by clay minerals (Fig. 7b).

Of special interest are rounded and oval particles and their chains distributed in the pore space of clay matrix. The particles range from 0.2 to $10\ \mu\text{m}$ in size. Large globules and their chains consist of the finer coalesced globules (Figs. 7c, 7d). Their surface is covered

**Fig. 4.** Comparison of trace element abundance in the rocks and clay fractions extracted from them (zones of the recent hydrothermal alteration and redeposited hydrothermal sediments, i.e., proluvium). (a) Rock, (b) clay minerals.

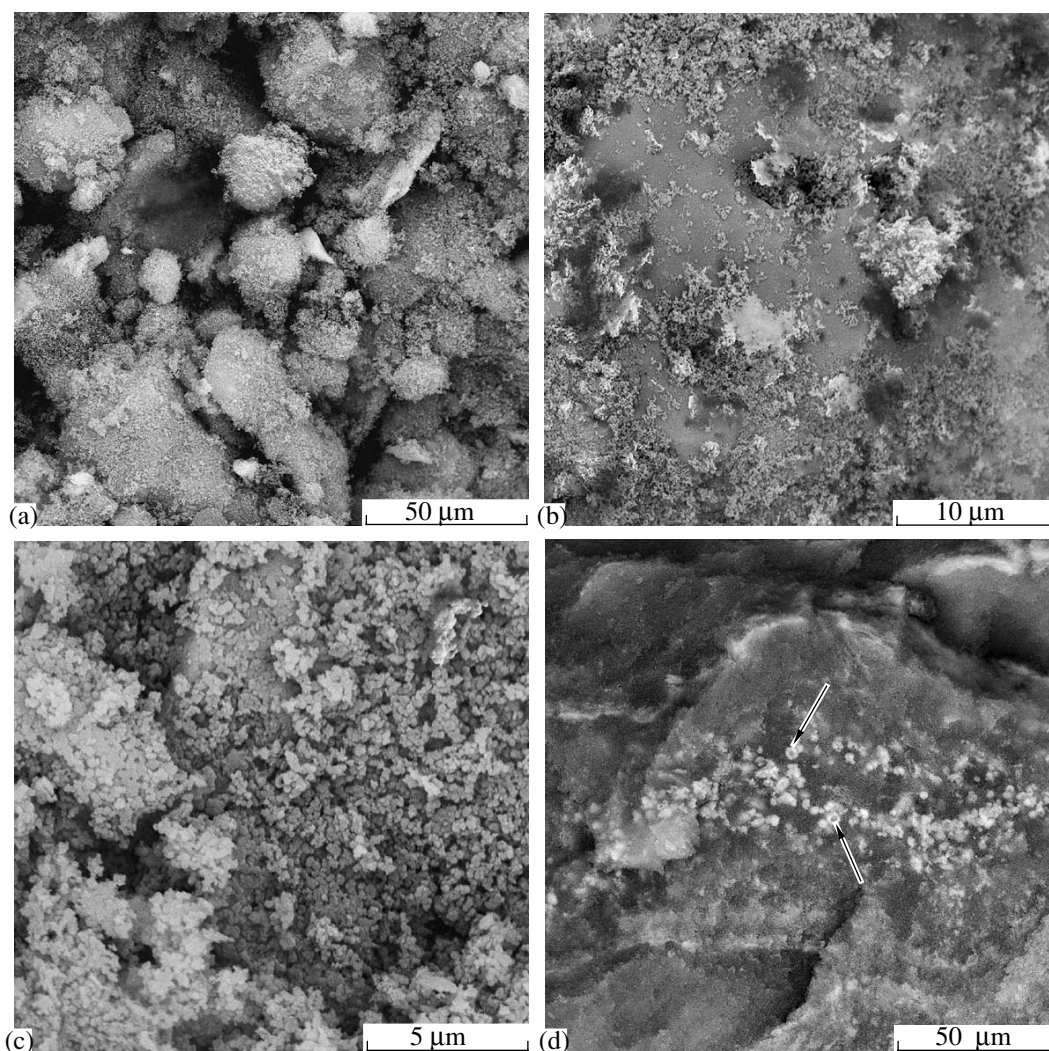


Fig. 5. Microstructure of white and light beige rocks with numerous bright yellow sulfur crystals (Theistareykir geothermal field). (a) Clastic texture of the rock; (b) fragments of volcanic rocks; (c) microglobular porous matrix; (d) globules within microglobular matrix (arrows).

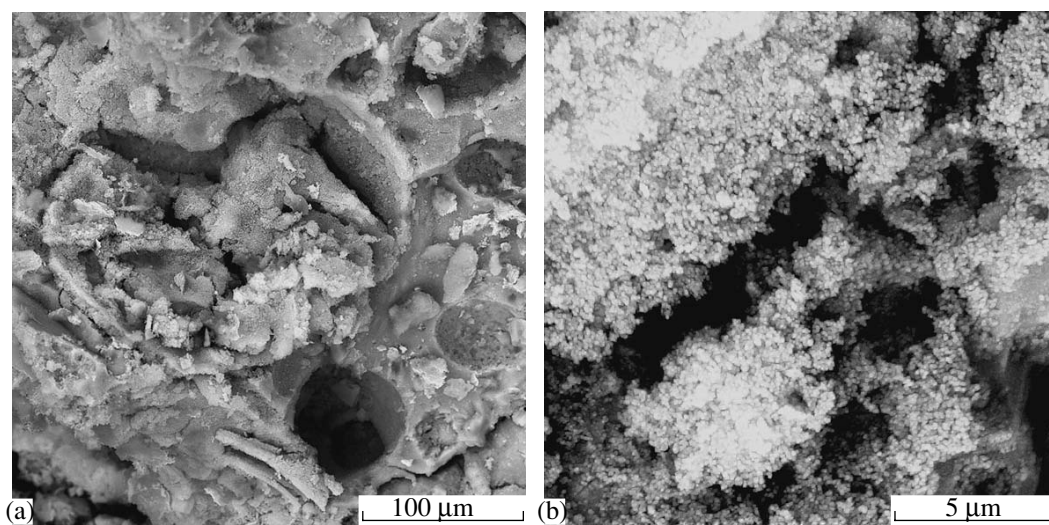


Fig. 6. Microstructure of white rock (zone of the present-day fumarole activity, Námafjall geothermal field). (a) Fragments of volcanic glass partially replaced by the fine-grained material; (b) groundmass.

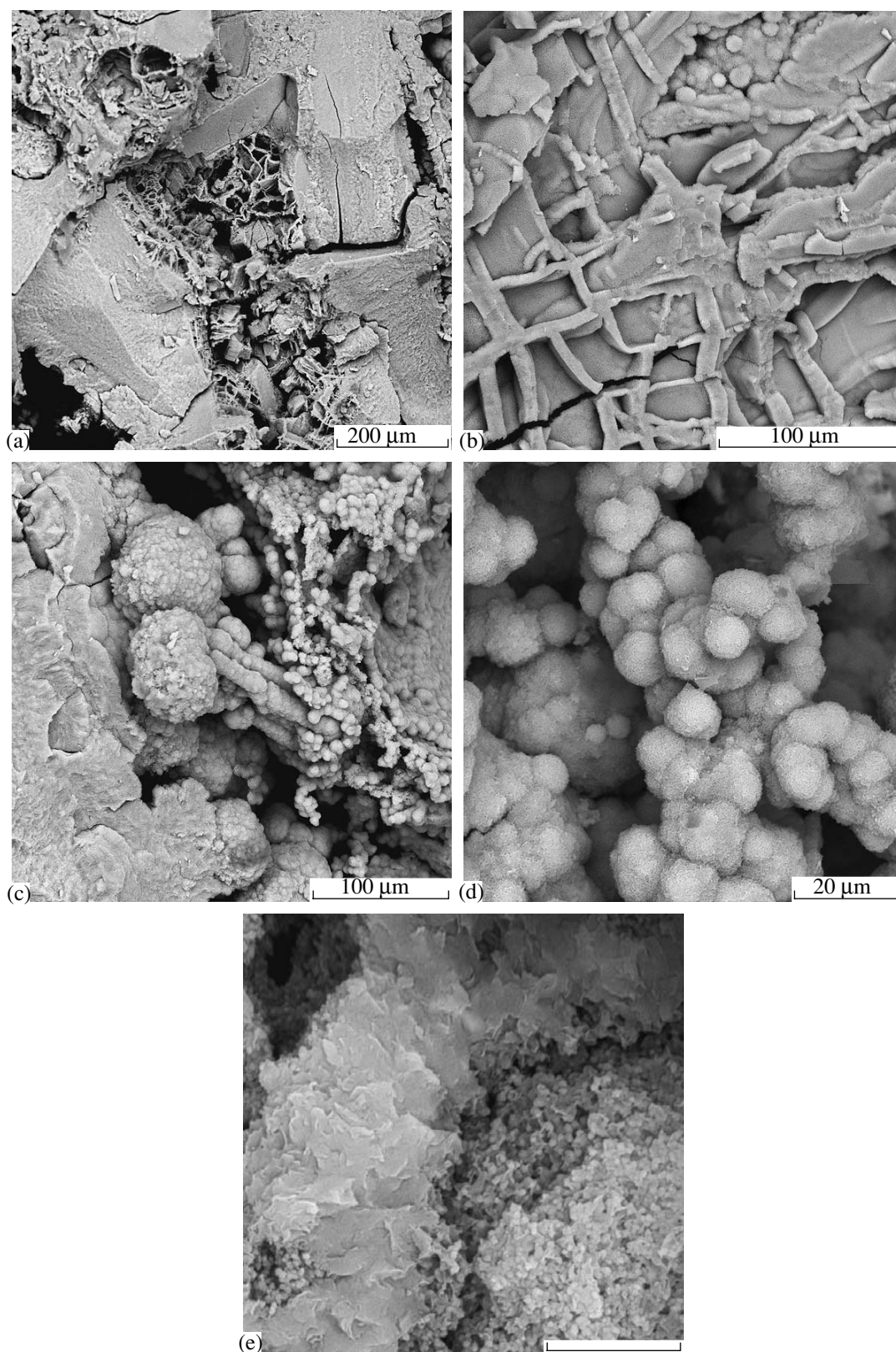


Fig. 7. Microstructure of red-brown rock (periphery of fumarole zone, the Theistareykir geothermal field). (a) Homogenous uniform matrix with fragments of volcanic rocks replaced by clay minerals; (b) framework pseudomorphs related to the replacement of completely dissolved crystalline fragments by clay minerals; (c) rounded and oval formations, as well as chains of globules in the pore space of clayey rock; (d) single large globules and chains of small coalesced globules with characteristic cellular microtexture at the surface; (e) incrustated rim of clay minerals at the surface of a large globule.

Table 8. Elemental composition of red-brown rock, sample 0517 (%)

Elements	Groundmass	Skeletal segregation of dissolved crystal	Globule	Globule	Crustification rim of the globule
Mg	2.47	2.74	0.71	0.24	2.21
Al	11.05	8.16	4.07	1.16	11.84
Si	26.93	25.79	11.07	3.62	28.82
Fe	5.31	18.00	17.07	4.56	7.74
O	52.24	43.87	37.05	56.49	47.56
Ca	0.90	1.44	1.32	–	1.04
Ti	1.11	–	28.71	33.93	0.80
Total	100.00	100.00	100.00	100.00	100.00

Note: (–) Not found (Tables 8–11).

Table 9. Elemental composition of red-brown rock, sample 0529 (%)

Element	Clay matrix of the rock			Mineralized bacteria	Biomorphic textures associated with mineralized plant organics		
					accumulations of small globules	individual globules	
Al	13.30	4.35	7.35	9.15	3.77	1.55	1.02
Si	26.31	5.85	10.24	24.33	36.45	33.10	30.93
Ca	0.71	0.59	1.00	1.18	–	–	–
Fe	3.31	5.23	8.87	14.01	9.10	20.42	2.74
Mg	0.54	–	–	1.88	0.48	–	–
Ti	7.45	18.35	30.81	3.63	1.44	–	–
C	–	–	–	–	–	–	7.74
Ag	–	–	–	1.72	–	–	–
O	48.37	65.61	41.73	44.12	48.76	44.93	57.56
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

by clay minerals with the typical cellular microtexture. Their composition corresponds to smectite (see below).

We studied the inner and outer zones of globular aggregates of various sizes. Small globules with a vague rim are characterized by a very high Ti content (up to 28–33%). Large globules are compositionally heterogeneous. Their inner zone contains the following elements (%): Si 11–15, Al 4–6, Fe 5–17, Mg up to 2, Ti 15–28, and Ca 1. the outer shell contains the following elements: Si 23–28, Al 11, Fe 3–7, Mg 2, Ti up to 1, and Ca 1. These data indicate that the inner zones of the globules are enriched in Ti relative to their outer shells (Table 8).

Clay minerals make up crustification rims around individual large globules and their accumulations (Fig. 7e). The crustification rims with Si, Al, Fe, Mg, Ti, and Ca as major components are compositionally close to groundmass (Table 8).

4. Red-brown rock (Table 1, no. 20, sample 0529) compose the proluvial deposits resulted from the redeposition of hydrothermally altered hyaloclastites of the same color. The rock contains tiny clumps and particles

of white matter and fragments of variably altered basaltic material.

The heterogeneous rock includes fragments of variably altered rock and glass embedded in the flaky clay matrix. All clastic fragments are coated with clay flakes, which mark the framework dissolution textures (Figs. 8a–8c) and fill the pore space (Fig. 8d).

Clay minerals are often associated with diverse biomorphic structures, which are represented by elongated particles with rounded ends and distinguished from the clay matrix by bright luminescence under electron microscope. With respect to shape and size (1.5 × 4.5 μm), they could be identified as mineralized bacterial rods (Fig. 8e).

Structures similar to coccoidal bacteria in size (0.5–5.5 μm) and shape are preserved at the surface and in pores of mineralized plant organics (Fig. 8f, 8g). The remains of mineralized coccoidal bacteria (5.0–5.5 μm) were also found at the surface of the partially dissolved volcanic glass fragment (Fig. 8h).

The clay matrix contains Si, Al, and Fe as the major components, Mg and Ca as subordinate components,

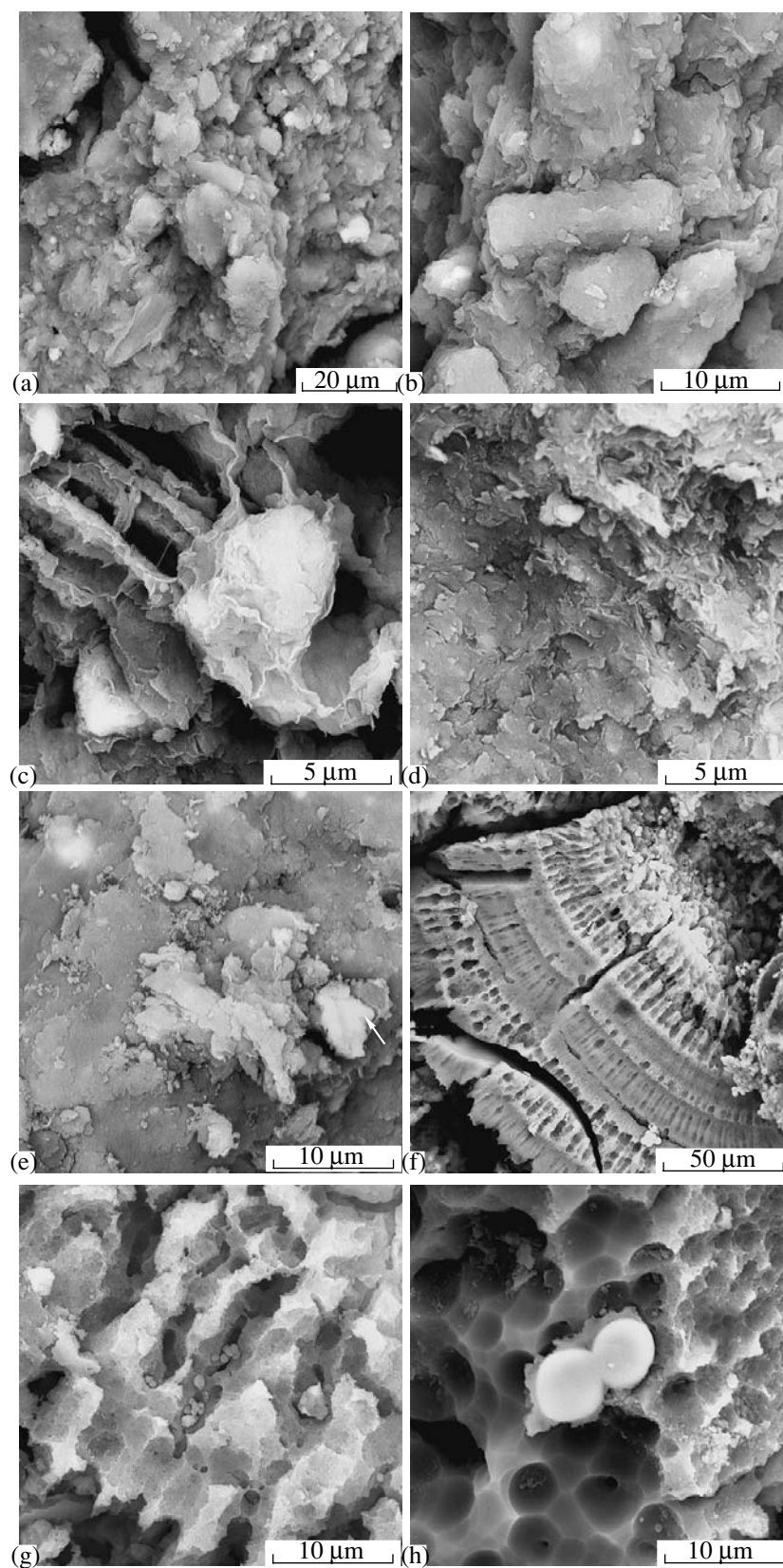


Fig. 8. Microstructure of red-brown rock (proluvial deposits). (a) Fragments of differently altered rock and glass in a flaky clay matrix; (b) flakes of clay minerals as coating of clastic fragments; (c) clay minerals fixing the framework dissolution textures; (d) clay matter with flaky microtexture in the pore space of rock; (e) mineralized aggregates with rounded terminations identified as mineralized bacterial rods (arrows); (f) silicified fragments of plant organics; (g) structures morphologically similar to coccoidal bacteria in pore space of plant remnants; (h) mineralized coccoidal bacteria at the surface of a fragment of partially dissolved volcanic glass.

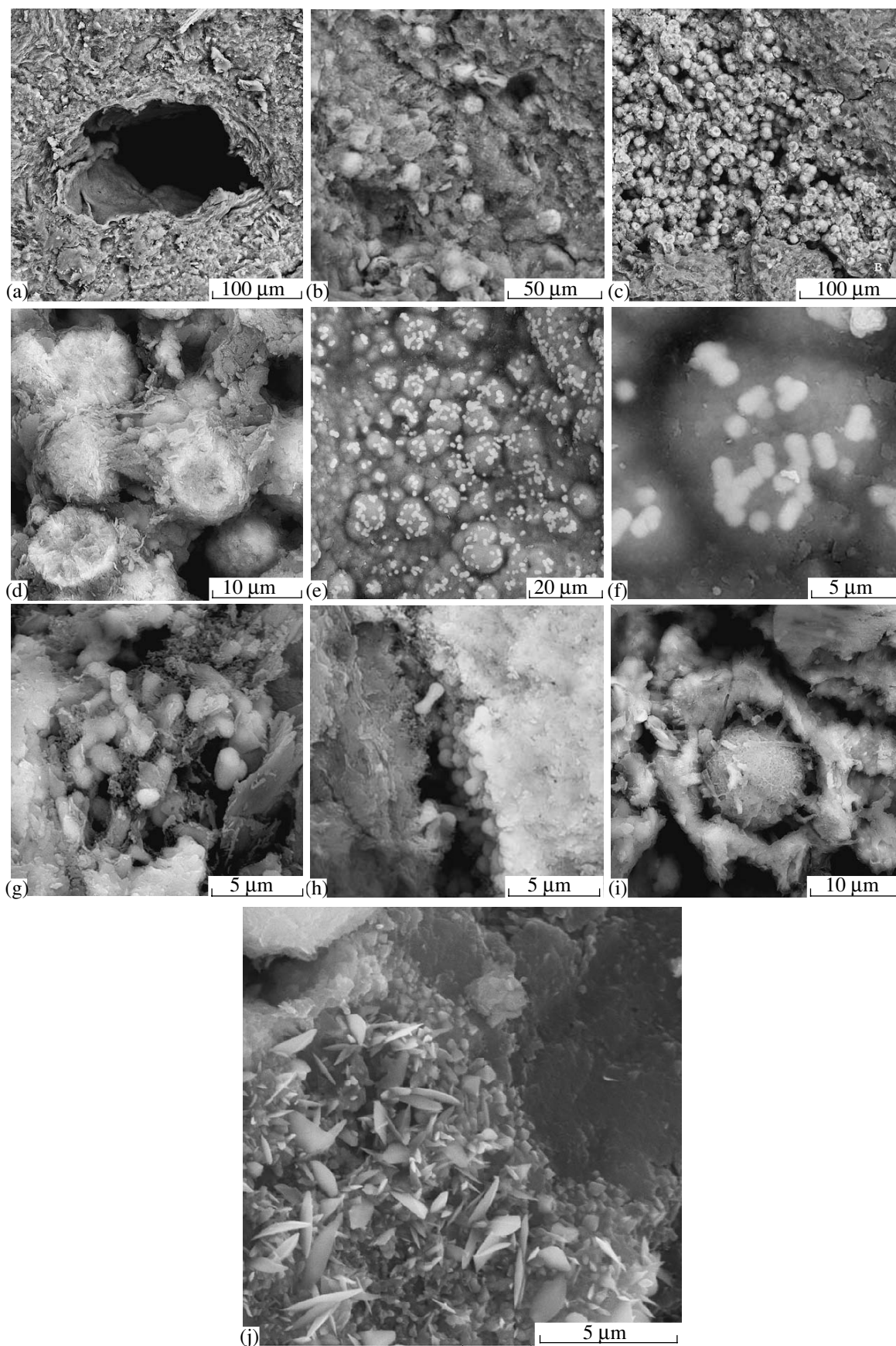


Fig. 9. Microstructure of the rock with a great amount of iron hydroxides (proluvial deposits with traces of buried soil horizons). (a) Subparallel clay flakes coating the walls of oval cavities; (b) globules scattered over the clay matrix; (c) globules in the field of iron hydroxides and ferruginous crusts; (d) concentric and radial microtextures of the globules; (e–f) biomorphic microtextures: (e) accumulation of single and paired mineralized bacterial rods at the globule surface; (f) mineralized breccia with characteristic sectional structure and rounded ends; (g) accumulations of mineralized bacterial rods in the pore space of rock; (h) accumulation of mineralized bacterial structures with a distinct dumbbell shape; (i) association of globule with filaments; (j) microcrystals of octahedral and rhombohedral argentine

and Ti (7–30%) as a significantly variable component (Table 9). Based on composition, the matrix consists of smectites closely associated with partially or completely altered components of basalts and hyaloclastic glass. The high Ti content indicates that the clay matrix was formed in situ from the volcanic material.

In addition to common elements, the bacterial rods (Fig. 8e) located in the clay matrix contain Ag (~1.7%). Numerous biomorphic structures (globules) are enclosed in the pores of silicified plant organics (Fig. 8f) and contain silica (30–36%), Al, Fe, and occasional Mg, Ti, and C (7.74%).

5. Rocks with high content of iron hydroxides (Table 1, no. 17, sample 0524a) were taken from proluvial deposits with traces of buried soil horizons. The iron hydroxides compose isomorphic aggregates and crusts. The clay matrix contains numerous extended cavities, and their walls are covered by subparallel clay flakes having a sharp contact with the clay matrix (Fig. 9a).

The clay matrix contains abundant dissemination of globules, which are mainly confined to zones of iron hydroxides and ferruginous crusts (Figs. 9b, 9c). The globules are closely intergrown with clayey flakes that envelop and penetrate them. They are characterized by similar sizes (no more than 10 μm). Some structures suggest the splitting of globules into two parts. At the shear fracture, the globules demonstrate concentric and radial structures (Fig. 9d).

The globule surface locally contains accumulation of single or paired biomorphic structures, which

approximate mineralized bacterial rods (1.0 $\times$ 2.0 μm) with characteristic sectional structure and rounded ends (Figs. 9e–9g). In some cases, the rods have a distinct dumbbell structure (Fig. 9h). The association of globules with filiform structures has a distinct biogenic nature (Fig. 9i).

The major components of flakes (Si, Al, Fe, and Mg) indicate their smectite composition. Ti and C (6–8%) are also recorded in the majority of analyzed points (Table 10).

The analysis of mineralized microbiota showed that the inner parts of the globules have higher Fe content (67–72%) than the outer parts (7–39%).

The inner and outer parts of the globules also differ in the silica content (1–3 and 7–19.5%, respectively). Similar relations are observed for Al (0–2 and 4–11%, respectively). Carbon was found in the outer part of the globules and at their surface.

Silver was found in some Fe-rich and C-bearing globules. Abundant Ag associated with S was found in the accumulation zone of mineralized biomorphic structures resembling coccoidal bacteria (Table 9).

Silver was also found locally in ferruginous crust that contains numerous globules occasionally merging into a solid matrix (Figs. 9b, 9c). The correlation of Ag with S suggests the presence of argentite.

The rock locally contains intergrowths of octahedral and rhombohedral microcrystals containing Ag (41–75%) and S (7–10%) (Table 10, Fig. 10j). Accumulations of mineralized bacteria (rods and dumbbells)

Table 10. Elemental composition of proluvial deposits, sample 0524a (%)

Elements	Clay matrix			Mineralized bacterial colonies, globules			Mineralized coccoidal bacteria		Accumulation of crystals at the surface and near globular textures	
Al	12.22	10.80	11.49	4.89	1.59	1.08	5.04	3.97	3.71	0.67
Si	20.21	19.25	19.45	5.49	1.96	1.17	10.05	7.39	5.37	1.50
Fe	4.87	4.63	7.84	44.30	51.97	73.01	1.40	1.75	5.61	1.64
Mg	0.66	0.61	0.63	–	–	–	0.38	–	–	–
Ti	0.20	1.04	2.22	0.79	–	–	1.03	1.00	–	–
C	7.09	8.11	5.96	5.09	5.91	–	8.01	5.15	3.69	–
Ag	–	–	–	1.88	2.86	1.43	22.66	38.17	40.84	74.87
S	–	–	–	–	–	–	4.47	5.17	6.77	10.41
O	54.75	55.56	52.41	37.55	35.03	23.31	46.97	37.40	34.01	10.92
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100	100

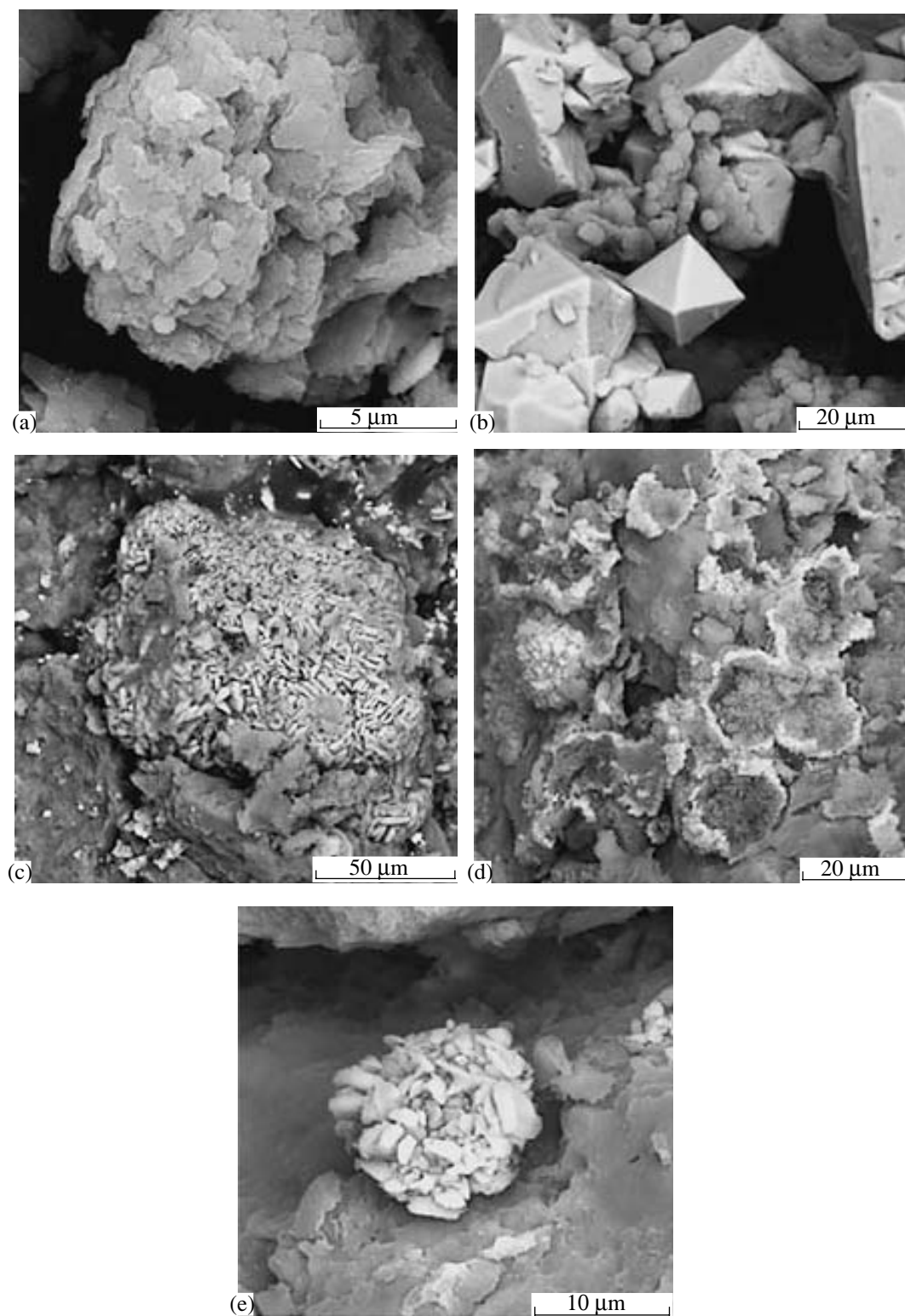


Fig. 10. Microstructure of blue-gray clayey rock (zone of the fumarole reworking of proluvial deposits). (a) Clayey rock consisting of closely packed flakes, (b) relations between single globules, their chains covered by the cellular clay material, and octahedral pyrite crystals; (c) framboids consisting of platy marcasite crystals; (d, e) relations between framboids and clay matrix: (d) clay minerals coating the marcasite framboids; (e) clay matrix in the internal space of framboids.

Table 11. Elemental composition of the rock with framboidal pyrite, sample 0523 (%)

Elements	Clay minerals from groundmass, individual globules, and chains of globules				Porous aggregate		Pyrite rim around the aggregate	Pyrite crystal
Al	12.87	10.07	12.22	9.96	8.25	7.12	2.07	1.32
Si	22.20	21.33	21.15	18.17	13.08	11.86	1.95	1.58
Fe	5.80	9.14	3.00	15.22	13.65	12.95	32.72	28.88
Mg	—	—	0.58	—	—	0.63	—	—
Ti	2.41	5.51	0.81	3.90	1.06	1.26	—	—
S	3.91	4.67	2.85	9.53	15.53	16.14	43.73	31.89
O	52.80	49.28	59.39	43.22	48.42	50.04	19.52	36.34
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

(Fig. 9h) mainly consist of Ag, S, and C with insignificant admixture of Si, Al, Fe, and Mg, indicating the possible presence of smectite.

6. Variegated rocks produced by the fumarole reworking of proluvial deposits differ from enclosing rocks in bright color and mosaic distribution of white, green, red-brown, violet, and blue spots (Table 1, no. 13, sample 0523).

Blue-gray clayey rock, a product of the present-day fumarole reworking of red-brown proluvial deposits, consists of closely packed clayey flakes with rounded ends (Fig. 10a). The clayey groundmass of the blue-gray rock consists of smectite and traces of kaolinite (Tables 1, 4, 5, 11). The hydrothermal clay matrix contains random dissemination of abundant pyrite crystals and framboids with a very thin coating of clay minerals. The octahedral pyrite is separated by single globules or their chains with a cellular clayey coating (Fig. 10b).

The framboids consist of well-developed octahedral pyrite and platy marcasite crystals (Figs. 10c, 10d).

Oval and rounded particles (16–19 μm across) morphologically similar to framboids are covered by pyrite crystals. Their inner parts include a porous aggregate of thin reticular filaments that are merged into uninterrupted films (Fig. 10e). The inner parts of these structures contain Fe (12–13%) and S (15–16%) likely incorporated in sulfides. In addition, they also include Si, Al, and Ti, which are the major components of clay minerals (Table 11).

The study of thin sections showed that violet color is related to the rearrangement of rounded particles of iron hydroxides ($\sim 5 \mu\text{m}$) into branching filaments and uninterrupted fields in the clay matrix (sample 0512, Fig. 11a).

DISCUSSION

Local migration of chemical elements related to the hydrothermal activity results in the mosaic distribution of rocks of different colors and compositions. Intensity of this process is controlled by the appearance and renewal of fissures during rifting.

The microscopic study showed that the clay minerals (for example, kaolinite) are crosscut by a system of microfissures formed during the replacement of hyaloclastites. One can see under cross nicols that the weakly polarizing clay matrix has a distinct block structure: the system of intersecting fissures splits the rock into closely packed angular blocks. The fissure-filling clay

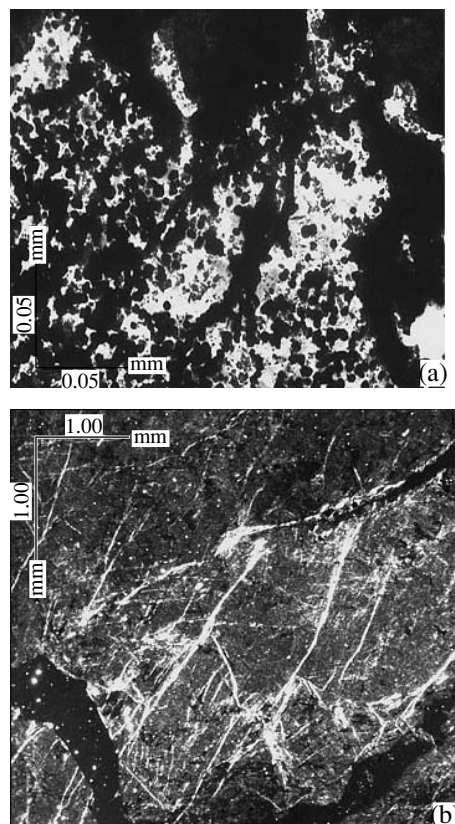


Fig. 11. Characteristic microstructural features of rocks composed of iron hydroxides and kaolinite. (a) Tiny rounded aggregates, which are merged into branching filaments, and continuous fields of iron hydroxides; (b) weakly polarizing clay matrix of block structure and kaolinite composition.

minerals differ from the fine-dispersed matrix in oriented extinction and high birefringence. The shape of blocks and character of the fissure system suggest that clay particles were displaced, oriented, and amalgamated along fissures (Fig. 11b).

Rock alteration in the discharge area of high-temperature hydrothermal systems was mainly controlled by the ascending flows of vapors and gases, while lateral flows of hydrothermal solutions at the Earth's surface played a subordinate role. Redistribution and local accumulation of chemical elements were revealed by the comparison of altered and unaltered basaltoids of the same age. Results of this study are presented in this paper.

As was mentioned above, the chemical compositions of unaltered basalts and hyaloclastites for comparison were taken from monograph (Gerasimovskii et al., 1978), in which petrogenic, trace, and ore element data on more than 600 samples of unaltered volcanic rocks are summarized. The unaltered basalts from two study areas (Theistareykir and Námafjall) have similar average contents of major elements, while compositional variations for individual samples are within the variation range for individual flows and hyaloclastites. This fact indicates the compositional similarity of primary basaltoids within the study areas.

Rocks formed at the solfatara and fumarole sites are mainly composed of clay and siliceous minerals, native sulfur, sulfides, and iron hydroxides. The majority of altered rocks contain iron hydroxides and smectites as the major secondary minerals. They are enriched in Fe_2O_3 (due to the oxidation of FeO) and depleted in MgO , CaO , and Na_2O as compared to unaltered basaltoids (Table 1). In particular, fresh and altered rocks from the Theistareykir geothermal field have the following average contents of petrogenic elements, respectively (in %): MgO 5.8 and 2.9, CaO 11.9 and 2.1, Na_2O 1.9 and 0.1. In the Námafjall geothermal field, the respective contents are as follows: MgO 6.2 and 1.2, CaO 11.1 and 4.6, Na_2O 2.4 and 0.1. One can see even more notable differences in the petrogenic element composition for hyaloclastites completely or significantly replaced by kaolinite (Table 1, nos. 10, 32, 34) or siliceous matter (nos. 8, 38, 39), indicating intense redistribution of petrogenic elements in fumarole activity zone.

At the same time, the rocks contain immobile or weakly mobile elements, such as the petrogenic Ti and trace elements Nb and Zr, which stay inert even in the course of intense alteration of basalts leading to the formation of abundant secondary epidote (Kurnosov et al., 2004; Gibson et al., 1982).

Ti is typically considered a weakly mobile element. The average TiO_2 contents are similar in the fresh volcanic rocks and hyaloclastites replaced by clay minerals. The higher TiO_2 contents (3–7%) are found in some altered samples, in particular, in rocks replaced by siliceous minerals (samples 0513, 0561, 0562, 0563) and

characterized by the loss of the most part of petrogenic elements. The apparent enrichment in Ti indicates its weak mobility even in extreme conditions of hydrothermal reworking.

The microprobe study revealed high contents of Ti in rocks almost completely composed of silica in the zone of intense fumarole activity (sample 0514, Table 6) and in the red-brown deposits from its periphery (sample 0517, Table 8). High-Ti zones of different sizes and internal structures (globules, isometric accumulations, and bands) were found in samples 0514 (Fig. 5d) and 0517 (Fig. 7c, 7d). The highest Ti contents (up to 33%) were found in the inner parts of the globules, whereas their outer parts and groundmass of the rocks have similar low Ti contents (1–2%). The reason for this distribution and formation of Ti-rich microscopic nodules is unclear. Such nodules could form during the decomposition of glass and the formation of silicagel at extremely low pH values. This is supported, for instance, by the great amount of S in sample 0514 (Table 1, no. 9). These conditions could favor the existence of colloidal TiO_2 and its coagulation into local aggregates. One cannot also rule out the influence of bacterial activity on TiO_2 accumulation at the microlevel. This is supported by the presence of diverse mineral accumulations in some places. The abundance of anatase in association with mineralized bacteria and plant organics was found in the clay deposits in the zone of modern hydrothermal activity (Geptner et al., 2006).

The presence of numerous pyrite and marcasite framboids in the proluvial deposits in the zone of modern fumarole activity (sample 0523) indicates that bacterial activity played an important role in the studied rocks. Close relations of all forms of pyrite and clay minerals indicate their simultaneous formation. This is emphasized by the formation of framboids with clayey matter in the inner part. Single globules and their aggregates in the form of filaments are confined to the accumulation zone of pyrite crystals. The cellular structure at the globule surface makes them similar to the coccoidal bacteria covered by mineralized glycocalix (Zhegallo et al., 2000).

Similar relations between clay minerals and sulfides were produced by the hydrothermal reworking of the already formed proluvial clay deposits. This process resulted in the formation and close intergrowth of crystals and framboids of pyrite and marcasite with clay minerals.

The examination of trace element contents highlights the migration of chemical elements in the fumarole activity zone. This can be exemplified by the distribution of Ag. The average Ag content in the unaltered volcanic rocks of this area is 0.05–0.06 ppm (Gerasimovskii et al., 1978). Distribution of this element over the studied thermal fields is extremely uneven: 0–22 ppm in the Theistareykir field and 0–2.5 in the Námafjall field. The comparison of average values

showed that the altered hyaloclastites from the Theistareykir field have the higher Ag content (7.75 ppm) than the same rocks from the Námafjall area (1.25 ppm). In the Theistareykir field, the distribution of Ag is also unsystematic (0–1.6 ppm) in proluvial deposits consisting of the redeposited altered hyaloclastites. It should be emphasized that the Ag content in the sample from proluvial deposits is almost two times higher (1.5 ppm) than that in the clay fraction (0.8 ppm). This fact indicates that Ag was likely related to the coarse-grained component rather than the fine-grained pelites extracted for the analysis of clay minerals.

Let us emphasize once more that the clay minerals (smectites and kaolinite) compose significant, even predominant part of the hydrothermally altered hyaloclastites and proluvial deposits. The major clay mineral is smectite.

Other important components of the studied rocks are represented by diverse framboids, globules, and rods, which are similar to the described mineralized bacteria in morphology and size (*Baktrial'naya paleontologiya*, 2002; Zhegallo et al., 2000). The proluvial deposits contain globules and rods mainly consisting of smectites and/or iron hydroxides. In some cases, the rods have a distinct dumbbell shape (Fig. 9h). Biogenic nature is also inferred for the association of globules with filaments (Fig. 9i). Diverse globules with a coating of single or paired bacterial rods with the characteristic sectional structure and rounded ends also have bacterial origin (Figs. 9e–9g).

Flakes of clay minerals (smectite) envelop globules and diverse fragments and crystals of volcanic rocks. They are incorporated in very large aggregates (for example, framboidal aggregates). Such relations of clay minerals with clastic fragments and biomorphic aggregates indicate their simultaneous or temporally close formation.

Based on available data, Ag often associates with iron hydroxides, which compose crusts and take part in the fossilization of microbiota.

Microdruses of crystals were found in the ferruginous crust (as aggregates of tiny globules in some places) and clay matrix. In the latter case, they grow together with clay flakes. In composition, they are close to argentite (Ag 40–74%, S 6–10%).

Accumulation of Ag and S due to the microbiological activity is confirmed by microprobe data on the aggregates of mineralized bacteria (dumbbells and rods) embedded in the clay matrix of proluvial deposits (Ag 22–38%, S 4–5%). Almost all local Ag accumulations in both clayey groundmass and mineralized bacteria contain C (3–8%). This fact can be considered an argument in favor of microbiological activity during the formation of biomorphic structures (globules, rods, and dumbbells) and the involvement of microbiota in the local Ag accumulation.

Significant variations in contents of As, Se, Sb, Br, I, Au, Ag, and some other trace elements in the considered deposits are hardly be related to uneven distribution of these elements in unaltered hyaloclastites. Significant difference in the trace element composition between closely spaced hyaloclastites seems improbable. Rocks with a low content of water are also unfavorable for the long-range migration of chemical elements. In addition, no correlation was found between typomorphic elements of fumarole deposits (As, Se, Sb, Br, I).

The concentration of trace elements (Au, As, Se, Sb) was recorded in hydrothermally altered clayey sediments at the present-day hydrothermal site in the southwestern rift zone of Iceland. This is attributed to metabolic activity of bacteria and fungi (Geptner et al., 2006). The uneven distribution of Ag and other trace elements, which are typical of volcanic gas emanations, can also be related to their local accumulation during bacterial activity.

CONCLUSIONS

Oxidation of FeO and migration of Mg, Ca, and Na in the surface zone of high-temperature hydrothermal activity produce rocks with different colors and compositions of secondary mineral components.

The studied thermal fields include the following rock types: (1) white rocks mainly consisting of kaolinite or silica; (2) red-brown rocks with smectites and iron hydroxides as major components; and (3) bright blue and green rocks formed during the repeated thermal reworking of red-brown rocks. The newly formed rocks inherit the composition of clayey matter (smectites), but contain a great amount of sulfides (pyrite and marcasite). The clayey matter is redistributed to form biomorphic microstructures (individual globules and their chains) and microglobular aggregates of iron hydroxides.

Significant variations in trace element contents in the hydrothermally altered deposits can be related not only to the water–rock interaction, but also to the bacterial metabolism and local biochemogenic enrichment in elements, such as As, Se, Sb, Br, I, Au, and Ag. This is confirmed by the association of Ag, C, and mineralized bacteria in smectites and iron hydroxides.

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REFERENCES

- Árnason, B., *Groundwater Systems in Iceland Traced by Deuterium* Reykjavik: Societas Scientiarum Islandica, 1976, vol. 42.
- Bakterial'naya paleontologiya (Bacterial Paleontology), Rozanov, A.Yu., Ed., Moscow: Paleontol. Inst. Ross. Akad. Nauk, 2002.
- Drits, V.A and Sakharov, B.A., *Rentgenostrukturnyi analiz smeshanosloinykh mineralov* (X-Ray Structure Analysis of Mixed-Layer Minerals), Moscow: Nauka, 1976.
- Einarsson, Th., *Geology of Iceland. Rocks and Landscape*, Reykjavik: Mal og Menning, 1994.
- Geptner, A.R., Specific Features of Structure and Genetic Types of Volcanosedimentary Slope Sediments in Iceland, *Byull. Komis. Izuch. Chetvertich. Perioda*, 2005, no. 66, pp. 22–32.
- Geptner, A.R. and Sokolova, T.N., Migration of Petrogenic Elements during the Formation of Zeolites in Basalts of Iceland, *Litol. Polezn. Iskop.*, 1989, vol. 24, no. 1, pp. 3–14.
- Geptner, A.R. and Petrova, V.V., Apophyllite and Gyrolite as Indicators of Low-Temperature Hydrothermal Alteration of Basaltoids, *Litol. Polezn. Iskop.*, 1989, vol. 24, no. 6, pp. 100–115.
- Geptner, A.R., Kristmannsdóttir, H., and Selezneva, M.A., Secondary Minerals of Basaltoids Altered by Hydrothermal Brine on the Reykjanes Peninsula (Iceland), *Litol. Polezn. Iskop.*, 1987, vol. 22, no. 2, pp. 25–41.
- Geptner, A.R., Ivanovskaya, T.A., and Pokrovskaya, E.V., Hydrothermal Fossilization of Microorganisms at the Earth's Surface in Iceland, *Litol. Polezn. Iskop.*, 2005, vol. 40, no. 6, pp. 1–19 [*Lithol. Miner. Resour.* (Engl. Transl.), 2005, vol. 40, no. 6, pp. 505–520].
- Geptner, A.R., Ivanovskaya, T.A., and Pokrovskaya, E.V., Hydrothermally Altered Clayey Sediments in the Rift Zone of Iceland (Influence of Microbiota on Accumulation of Minor Elements), *Litol. Polezn. Iskop.*, 2006, vol. 41, no. 4, pp. 1–14 [*Lithol. Miner. Resour.* (Engl. Transl.), 2006, vol. 41, no. 4, pp. 332–343].
- Gerasimovskii, V.I., Polyakov, A.I., Durasova, N.A., et al., *Islandiya i sredinno-okeanicheskie khrebet. Geokhimiya* (Iceland and the Mid-Atlantic Ridge: Geochemistry), Moscow: Nauka, 1978.
- Gibson, I.L., Kirpatrick, R.J., Emmerman, R., et al., The Trace Element Composition of the Lavas and Dikes from a 3-km Vertical Section Through the Lava Pile of Eastern Iceland, *J. Geoph. Res.*, 1982, vol. 87, no. B8, pp. 6532–6546.
- Kristmannsdóttir, H., Alteration in the IRDR Drill Hole Compared with Other Drill Holes in Iceland, *J. Geophys. Res.*, 1982, vol. 87, no. B8, pp. 6525–6531.
- Kristmannsdóttir, H., Ildefons, Ph., Bertaux, J., and Flank, A.M., Crystal-Chemistry of Mg–Si and Al–Si Scales in Geothermal Waters, Iceland, in Abstract of Papers, *Proc. of the 5th Int. Symp. on Geochemistry of the Earth's Surface*, Reykjavik, 1999, pp. 519–522.
- Kurnosov, V.B., Geptner, A.R., and Petrova, V.V., Hydrothermal Lithogenesis, in *Osadochnye basseiny: metodika izucheniya, stroenie i evolyutsiya* (Sedimentary Basins: Investigation Methods, Structure, and Evolution), Leonov, Yu.G. and Volozh, Yu.A., Eds., Moscow: Nauchnyi Mir, 2004, pp. 272–306.
- Mineraly. Spravochnik* (Minerals: Reference Book), Moscow: Nauka, 1992, vol. 4, no. 2.
- Rentgenografiya osnovnykh tipov porodoobrazuyushchikh mineralov (sloistye i karkasnye silikaty)* (X-Ray Diffraction Analysis of the Main Types of Rock-Forming Minerals: Phyllosilicates and Tectosilicates), Leningrad: Nedra, 1983.
- Rentgenovskie metody isucheniya i struktura glinistyykh mineralov* (X-Ray Analysis Techniques and Structure of Clay Minerals), Braun, G., Ed., Moscow, Mir, 1965.
- Schmincke, H.-U., Lothar, G.V., Brendon, J.G., and Pritchard, R.G. Volcaniclastic Rocks of the Reydarfjörður Drill Hole, Eastern Iceland, 1. Primary Features, *J. Geophys. Res.*, 1982, vol. 87, no. B8, pp. 6437–6458.
- Walker, G.P.L., Zeolite Zones and Dyke Distribution in Relation to the Structure of the Basalts in Eastern Iceland, *J. Geol.*, 1960, vol. 68, pp. 515–525.
- Zhegallo, E.A., Rozanov, A.Yu., Ushatinskaya, G.T., et al., *Atlas of Microorganisms from Ancient Phosphorites of Khubsugul (Mongolia)*, Huntsville, Alabama, USA, 2000.