

Hydrothermally Altered Clayey Sediments in the Rift Zone of Iceland (Influence of Microbiota on Accumulation of Minor Elements)

A. R. Geptner, T. A. Ivanovskaya, and E. V. Pokrovskaya

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

e-mail: remheptner@mtu-net.ru

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Abstract—Results of the first detailed study of mineral and chemical compositions in the rift zone of Iceland near the town of Hveragerði are presented. The major clayey components represented by dioctahedral smectites (mainly, montmorillonite with variable Fe contents) are associated with the subordinate kaolinite. The geological setting, timing, and composition of metasomatic clay minerals and their synthesized counterparts precipitated from solution in the course of interaction of hot groundwaters with basaltic volcanics and sedimentary clayey rocks are considered. Based on textural–structural features and (or) compositions, the sediments are divided into three types: (1) massive unsorted sediments with abundant fine-grained sand to silt-sized clay pellets, (2) horizontally laminated clayey sediments, and (3) organogenic sediments. The massive unsorted sediments enclose remnants of microorganisms replaced by smectite, while laminated clayey sediments host a siliceous layer with abundant mineralized remains of filamentous microorganisms. Clayey rocks of hydrothermally altered hyaloclastites and sediments related to their redeposition are similar in the composition of petrogenic elements. However, they differ notably from each other in the contents of some minor elements (Au, As, Se, Sb, and Hg). Increase in the share of minor elements in sediments is explained by the active influence of bacteria and fungi on their accumulation. The data obtained shed light on some specific features in the composition of clayey rocks, which can be used for mud cure of arthritis and rheumatism in the Health and Rehabilitation Clinic of the Nature Health Association of Iceland, Hveragerði.

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Thermal waters of Iceland (except some coastal areas where seawater prevails in the thermal system) are formed during the penetration of basaltic sequences by meteoric and melted glacier waters in areas with high geothermal gradient. Clayey minerals are widespread in areas of hydrothermal activity. They mark three major zones of basalt alteration: (1) smectite–zeolite, (2) mixed-layer silicates—prehnite, and (3) chlorite–epidote (Kristmannsdóttir, 1977, 1978, 1982). In terms of the formation mechanism, secondary components of the smectite–zeolite zone can be divided into metasomatic minerals and minerals precipitated from solutions or produced by gel crystallization. Minerals precipitated from solutions are deposited in various cavities, caverns, and interstices.

It was previously shown that some secondary minerals in the smectite–zeolite zone are related to the redistribution of various petrogenic minerals by heated waters (Geptner and Sokolova, 1989; Geptner and Petrova, 1989, 1996). However, the study of hydrothermal minerals reveals that migration of petrogenic elements is often not so obvious, particularly, in the case of compositionally similar minerals, such as smectites, which formed in different periods and settings.

The purpose of this work was to study the composition of clayey sediments used for mud cure of arthritis and rheumatism in the Health and Rehabilitation Clinic of Hveragerði and to reveal their specific features, which provide the beneficial therapeutic effect of mud cure.

OBJECTS AND METHODS

The study objects are located within the high-temperature geothermal fields at the southern margin of the large Hengill volcanic system in the southwestern sector of the present-day rift zone of Iceland. Near the town of Hveragerði, horizontally bedded sediments are exposed in the terrace (altitude 80–90 m) resting against the slope of the volcanic massif at upper reaches of the Varmá River. The massif is composed of Pleistocene hydrothermally altered volcanics largely represented by hyaloclastites and pillow basalts of subglacial eruptions. Subaerial lava flows are subordinate. The volcanics include olivine basalts, porphyritic basalts with phenocrysts of basic plagioclases, picritic basalts with olivine phenocrysts, and tholeiites (Saemundsson, 1967, 1979).

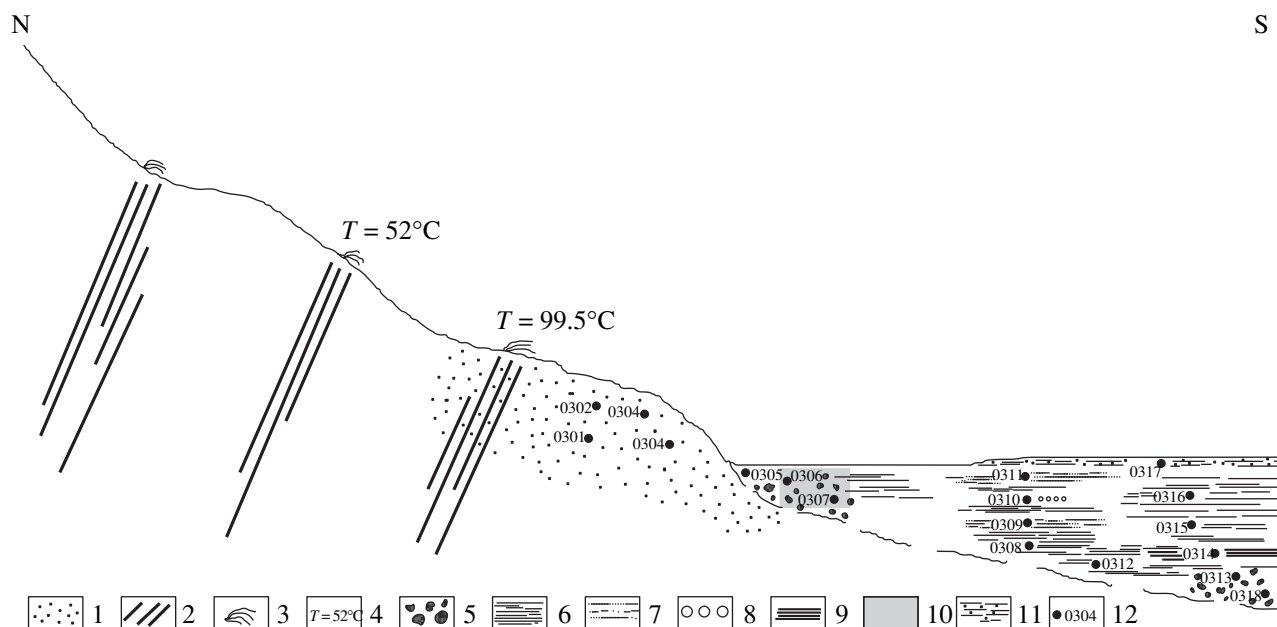


Fig. 1. Schematic section and location of samples in examined outcrops.

(1–4) Bedrocks: (1) hydrothermally altered hyaloclastites, (2) zone of fissure swarms and faults, (3) hot springs, (4) water temperature in springs; (5–11) terrace sediments: (5) massive unsorted clayey sediments with abundant fine-grained sand- to silt-sized clay pellets, (6) horizontally laminated compact clayey, (7) horizontally laminated clayey sediments with fine-grained sand- to silt-sized clay pellets, (8) bed composed of loose nonswelling material of largely silica composition, (9) bed of coalified plant detritus, (10) section interval, where clay is mined for therapeutic mud bath, (11) compact siliceous rocks locally armoring the terrace surface; (12) sample numbers.

Numerous hot springs and solfataras mark the SW- to NE-trending systems of fissure swarms, faults, and grabens that crosscut lavas and hyaloclastites of the Hengill volcanic massif. The volcanic rocks are variably altered: slightly altered rocks alternate with hyaloclastites partly or entirely replaced by clay minerals.

The studied sediments are related to the redeposition of hydrothermally altered hyaloclastites mainly composed of smectites. This is shown in the map of zones of hydrothermal rock alteration (Saemundsson, 1995).

The samples for investigation were taken by A.R. Geptner in 2002 and 2003 from bedrocks, which represent hydrothermally altered groundwater-saturated hyaloclastites (samples 0301, 0303), and from the overlying talus saturated with the hot spring water (sample 03104). Compact siliceous rocks locally envelop the slope, overlie the talus, or the surface of the terrace leaning against the bedrock slope (sample 0317). They are products of present-day active hot springs and solfataras exposed in some areas.

Wet plastic clays were sampled from the ~5-m-thick section exposed in the terrace (Hver-11, 0305, 0306, 0312–0314, 0316). It should be emphasized that mud used for cure of arthritis and rheumatism in the Health and Rehabilitation Clinic of Hveragerði is taken from this section.

The section encloses a bed composed of clayey material enriched in siliceous matter (sample 0310). The lower part of the study section includes a bed of coalified plant detritus (sample 0314).

The sampled material characterizes different (in age and formation mechanism) rocks and sediments. Pleistocene volcanic rocks (hyaloclastites) formed during subglacial basaltic eruptions and underwent the impact of hydrothermal solutions long before the accumulation of the adjacent Holocene sediments. The Holocene sediments, located in the present-day intense activity zone of hot groundwaters, also experienced hydrothermal alteration. Figure 1 demonstrates the section structure and location of examined samples.

Microtextural features of clayey rocks and enclosed organic remains and fossilized microbiota were studied with a scanning electron microscope by A.R. Geptner together with N.V. Gor'kova at the Geological Institute of the Russian Academy of Sciences. Microstructural features and qualitative chemical composition of mineral components were studied using a LINK-860 microprobe at the Paleontological Institute, Russian Academy of Sciences (L.T. Protasevich, analyst).

The complete silicate analysis of rocks and clay fractions (<1 and <5 μm) and determination of minor elements were performed at the Chemical Laboratory

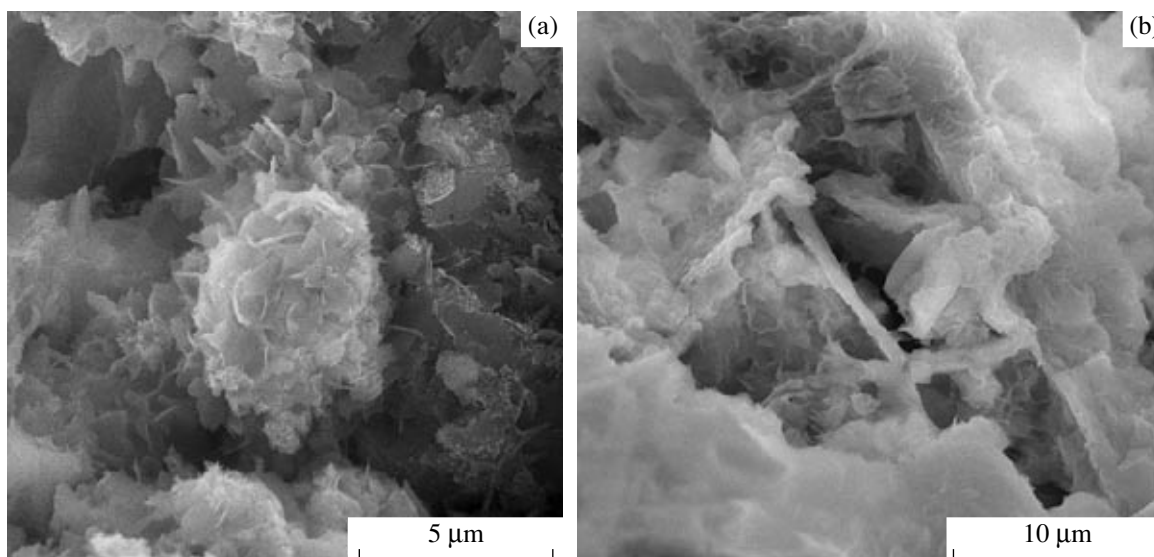


Fig. 2. Clay minerals replacing hydrothermally altered hyaloclastites. (a) Reticular microtexture; (b) compact matrix replacing the dissolved mineral phenocryst.

of the Geological Institute, Russian Academy of Sciences (T.N. Tsepkova and A.V. Gorbunov, analysts).

RESULTS

Bedrock Hyaloclastites

The natural outcrop demonstrates that hyaloclastites at the terrace/bedrock contact are entirely replaced by clay minerals. The hyaloclastites represent variegated (white, vinous, violet, and red-brown) water-saturated soft rocks with irregularly distributed variegated spots and bands. The study of samples under a binocular microscope revealed that red-brown patches are related to irregular distribution of iron oxides and hydroxides, which probably emphasize the older zones of maximal permeability. Bedding or other structural features of the primary distribution of hyaloclastite fragments are absent.

The microtextural analysis of bedrock hyaloclastite samples 0301 and 0303 under a scanning electron microscope shows that the primary rock primarily consisted of angular volcanic glass fragments now entirely replaced by clay minerals associated with well-developed pyrite crystals.

Clay minerals are represented by flakes (0.5–1.15 μm), which form a distinct reticular microtexture in some areas and are chaotically arranged in other areas. In some places, one can see their accumulations (up to 5–6 μm) among the reticular groundmass (Fig. 2a). Clay minerals also constitute a compact matrix with vague flakes, which locally form a framework of crosscutting elongate bodies (Fig. 2b). Such microtextures probably resulted from the partial dissolution of glass and enclosed mineral phenocrysts with their subsequent replacement.

Sedimentary Rocks

Based on textural–structural features and (or) composition revealed in the course of field and microscopic investigations, the studied sedimentary rocks can be divided into three types.

The bedrocks are overlain by massive and unsorted bluish gray clayey rocks with abundant fine-grained sand- to silt-sized clay pellets, coalified remains of plant tissue, and fragments of differently shaped siliceous aggregates (first type). Along the strike, the massive rocks grade into horizontally laminated clayey sediments with alternating gray, white, light brown, and brown laminae (second type). The lower part of the section includes a coalified plant detritus layer (third type).

The SEM study revealed some microtextural features of these rocks, distribution of authigenic minerals in them, and presence of mineralized microbiota.

Massive unsorted clayey rocks (samples 0305, 0306, 0307, and Hver-11) are composed of well-rounded fine-grained sand- and silt-sized pellets consisting of hyaloclastite fragments entirely replaced by clay minerals. Clastic material is unsorted, and rock fragments vary from 10 to 150 μm in size. The fragments have the following types of surface: (a) even and smooth surface; (b) surface with distinct dissolution structures; and (c) surface with a thin coating of reticular clayey flakes. One can often see fragments with rectangular (square) caverns (2 to 4 μm across) at the surface. Sometimes, they are filled with small pyrite cubes that are abundant in clayey bedrocks of the slope. Some pellets are crosscut by dehydration cracks (Figs. 3a–3c).

Interstices between fragments are often free. Rounded fragments within the clayey matrix have a clayey coating with locally discernible reticular flakes.

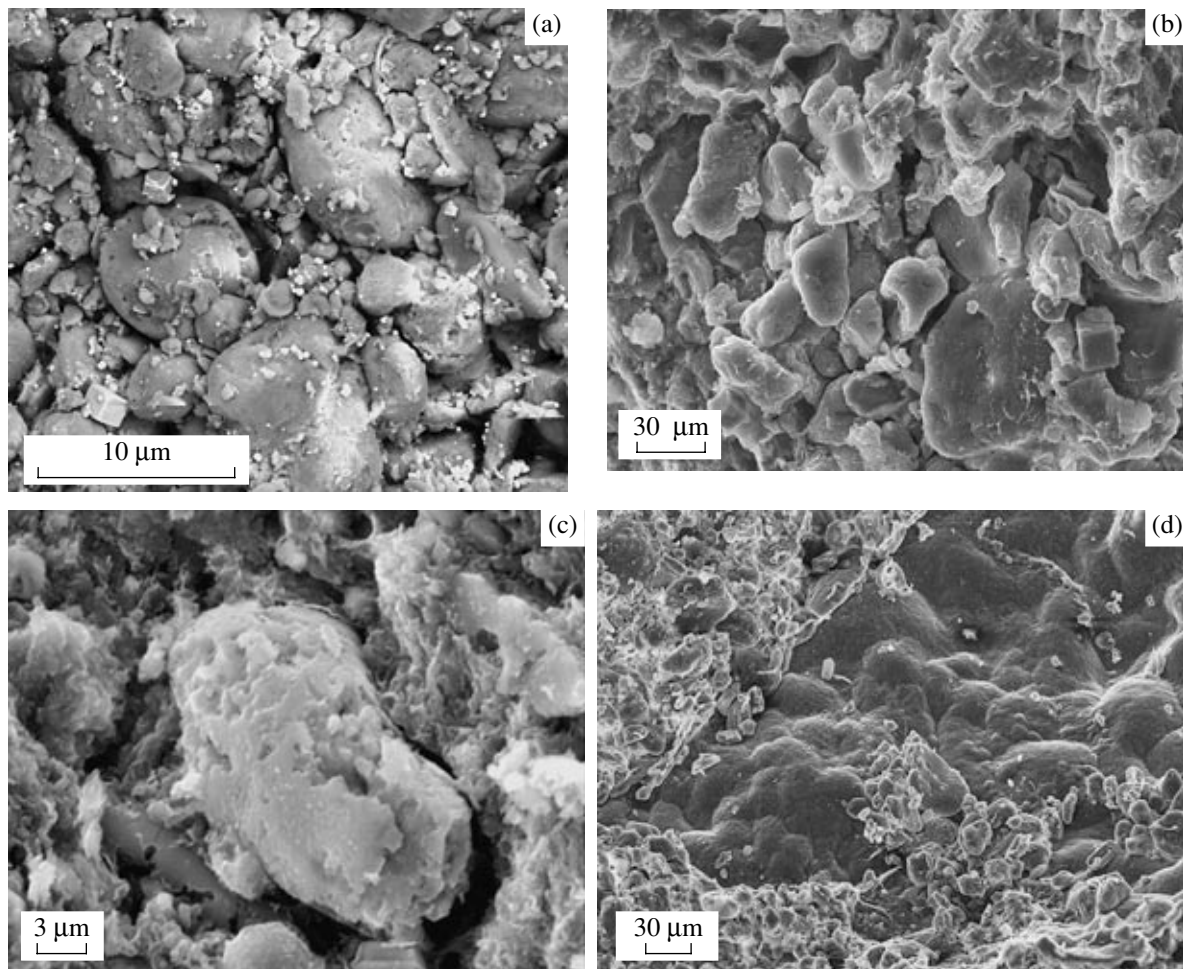


Fig. 3. Well-rounded fine-grained sand- to silt-sized pellets composed of hyaloclastite fragments entirely replaced by clayey material. (a) General view of clay pellets; (b) pellets with a thin coating of authigenic clay minerals; (c) pellets with distinct dissolution marks at the smooth surface; (d) contact between the lamina of unsorted clay pellets and underlying compact clayey crust.

The clayey matrix contains random dissemination of pyrite crystals and framboids, gypsum druses, and acicular phosphate and anatase crystals. In some places, clay pellets enclose microgranular silica aggregates with distinct boundaries. It should be emphasized that laminae of unsorted rounded clay pellets have distinct (conformable) contact with the underlying compact clayey crust (Fig. 3d).

Coalified plant remains are irregularly scattered in sediments. Their surface has a coating of clay minerals. Sometimes, plant remains occur together with globular silica aggregates and anatase crystals (Fig. 4).

Horizontally laminated clayey rocks (samples 0310, 0312–0314, 0316). In these rocks, terrigenous material is represented by poorly sorted fine-grained sand- and silt-sized clay pellets. The sandy fraction includes fragments with typical shapes of volcanic glass and vesicles entirely filled with clay minerals.

Fine lamination of clayey sediments is related to alternation of laminae of different colors (white, beige, gray, brown, and others) and grain-size compositions.

The base and roof of laminae (minimal thickness 70–80 µm) are well seen at the fresh fracture of rocks. The surface of some distinct laminae has a coating of compact uniform matter up to 12–25 µm thick.

These laminae are composed of an aggregate of silt-sized clayey particles. At different levels of the section, they enclose numerous cavities (interstices) up to 1–2 mm across. Sometimes, the laminae make up a chain extended along the bedding surface. The largest cavities are encountered in specific areas where the clayey groundmass includes laminae with abundant clayey fragments and sand-sized pellets.

White laminae (sample 0312), which are readily distinguishable in the section, consist of uniform nonswelling pelitic rocks containing rare fine silt-sized particles with elongate pores. In terms of shape and porosity, these particles resemble ash material.

The light beige bed (sample 0310) is composed of loose nonswelling material (approximately 5–8 cm thick) mainly consisting of silica and traces of smectite.

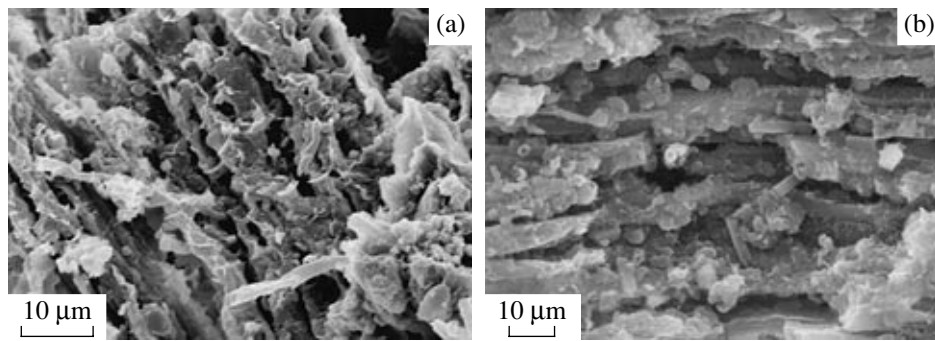


Fig. 4. Coalified plant remains. (a) With a coating of clay minerals; (b) incrustated by globular silica aggregates and anatase crystals.

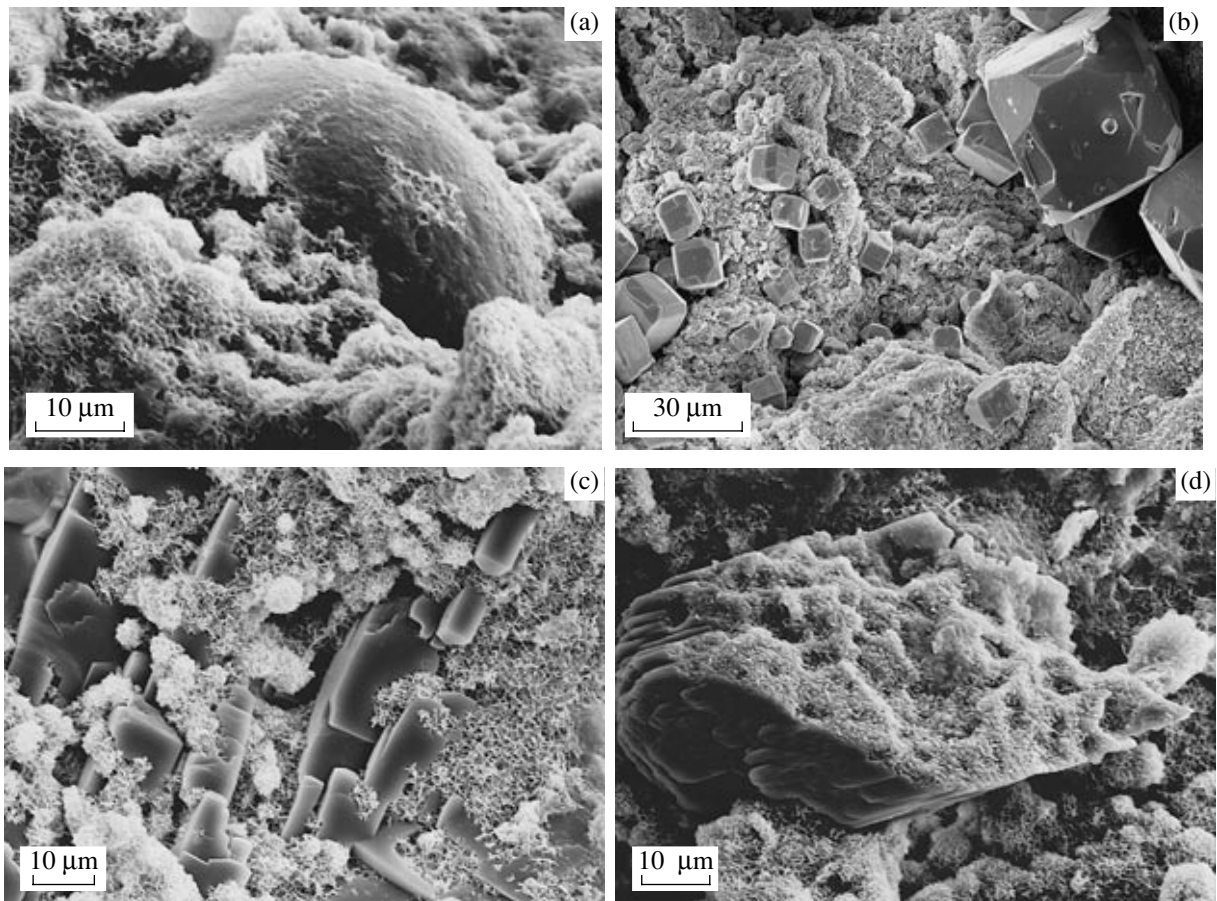


Fig. 5. Authigenic clay minerals. (a) At the surface and in interstices between clay pellets; (b) enclosing and enveloping pyrite crystals; (c) corroding and replacing plagioclase crystal; (d) corroding and replacing gypsum crystal.

Coalified and fossilized plant remains occur as isolated fragments in the entire section. They are also abundant (but mostly replaced by silica) in the previous layer. The light beige bed includes variably preserved diatom frustules.

The lower part of the examined section is characterized by coarser bedding. It encloses beds of poorly sorted rounded sand- to silt-sized clay pellets. Inter-

stices between them contain aggregates of clay minerals with distinct reticular microtextures (Fig. 5a).

Regardless of their grain-size composition, massive and bedded sediments of the entire section contain dispersed isolated crystals and small accumulations of pyrite and gypsum. The pyrite crystals are developed on walls of microcavities and cracks that crosscut bedding planes. Clay minerals with the distinct reticular texture include and envelop the pyrite crystals (Fig. 5b). Pla-

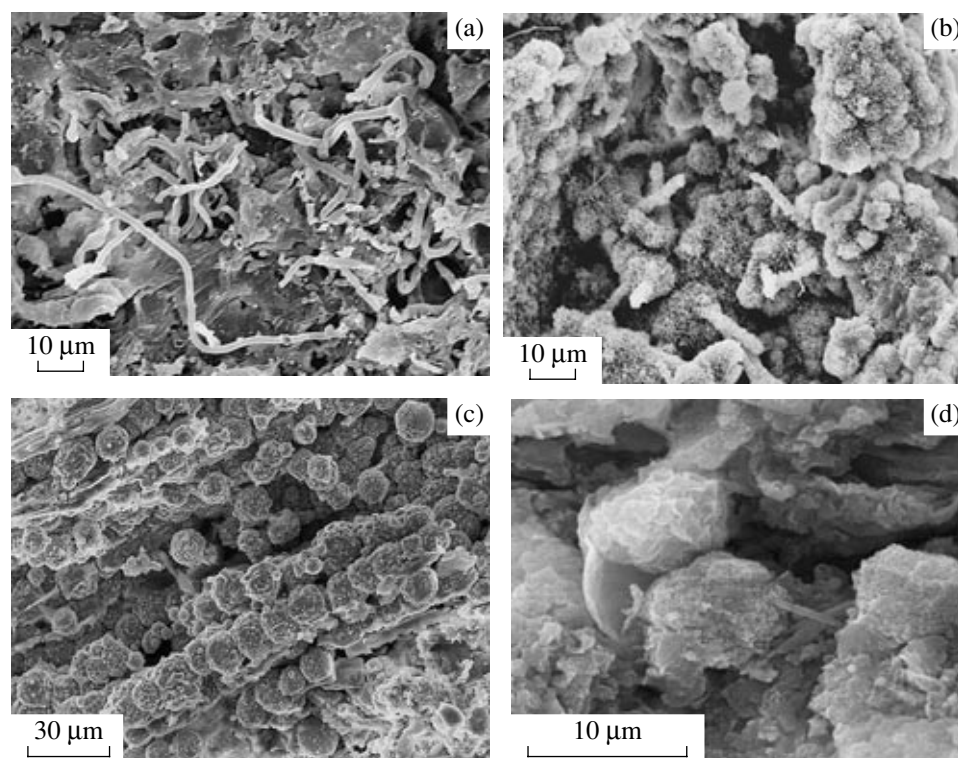


Fig. 6. Mineralized microfossils. (a) Nonmineralized filaments in the layer of coalified plant remains; (b) rod-shaped bodies with clay minerals in the clayey matrix with the typical reticular microtexture; (c) plant remains incrustated by pyrite framboids; (d) pyrite framboids and clay pellet in laminated clayey sediments.

gioclase crystals are intensely corroded and replaced by clay minerals that form irregular and globular accumulations (Fig. 5c). Some gypsum crystals in the clayey matrix are corroded and partly replaced by clay minerals (Fig. 5d).

The surface of dried clay samples is covered with numerous gypsum crystals that make up small druses and thin films. It should be noted that gypsum crystals differ in morphology at the surface of drying samples and inside them. In the first case, the crystals are characterized by flat apex and elongate cavities. In the second case, the elongate cavities and perfect crystallographic shape are absent. Pyrite and gypsum are often closely associated in space, but signs of pyrite dissolution and corrosion (oxidation) are absent.

Organogenic sediments. One can see a black bed (~10 cm thick) among the gray and brown clayey laminated rocks occurring in the lower part of the outcrop (sample 0314). The bed is composed of coalified plant debris associated with spores and hyphae of fungi of the family Polypodiaceae (genera *Cystopteris*, *Dryopteris*, and *Athyrium*), pollen of dicotyledon herbaceous-shrubby plants¹ diatom frustules, pyrite and gypsum crystals, and insignificant quantity of clayey matter.

¹ Palynological study of one sample was performed by N. Yu. Filipova at the Geological Institute, Russian Academy of Sciences in 2004.

Fragments of plants retain well-preserved cellular structure.

The surface of plant remains is even and smooth with distinct tubular structure and hollow elongate cavities. The irregularly distributed clayey material fills up pores between plant remains. Plant fragments are covered with a film of clayey flakes and rare globular silica aggregates (0.5–3.0 μm). Well-developed anatase crystals are also common (Fig. 4b).

Mineralized microbiota. Fossilized remains of microorganisms are found in the massive unsorted sediments. They are particularly abundant at different levels of the laminated section. Differently fossilized filamentous structures are commonly associated with plant remains. Long branching filaments (up to 3 μm in diameter) penetrate the porous plant remains and the clayey matrix. The filaments have a smooth surface, which is locally covered with clay minerals. The filaments and rod-shaped structures in the clayey matrix are coated with clayey flakes with a specific reticular microtexture (Figs. 6a, 6b).

Some plant fragments are incrustated with pyrite framboids. In the clayey matrix, framboids associate with isometric pyrite crystals and rounded particles. It is remarkable that both framboids and rounded clayey particles have similar sizes (8–9 μm across) (Figs. 6c, 6d).

Table 1. Mineral composition of examined samples based on X-ray data

Sample no.	Fraction, μm	Components	
		major	subordinate
0301	<5	Smectite	Kaolinite, quartz
0303	<5	Smectite	Kaolinite (traces), quartz, pyrite
0305	<5	Smectite	Pyrite, anatase, gypsum
0306	<5	Smectite	Pyrite
Hver-11	<1	Smectite	Clinoptilolite, pyrite, anatase
Hver-11	<5	Smectite	
0316	<5	Smectite	
0313	<5	Smectite	Pyrite, anatase
0310	<5	Cristobalite	Smectites (traces)
0312a	<5	Smectite	Kaolinite, pyrite

Note: Sample 0312a is represented by fraction <5 μm extracted from sample 0312 (rock).

Variably fossilized filamentous structures are abundant in the siliceous layer with subordinate clayey material (sample 0310). The entirely fossilized fila-

ments are up to 10 μm in diameter, while the thinnest unfossilized filaments are approximately 1 μm across.

X-ray Data

Clayey fractions (<1, <5 μm) extracted from hydrothermally altered hyaloclastites (samples 0301, 0303) and different sedimentary rocks (samples Hver-11, 0305, 0306, 0312, 0313, 0316) were subjected to the X-ray analysis (Table 1). Diffractograms of oriented preparations of clayey fractions in the natural state show basal reflections with $d(001) \sim 14.16\text{--}15.78 \text{ \AA}$. Values of the first basal reflection increases to 16.86–17.49 \AA in ethylene glycol-saturated preparations and decreases to 9.77–10.2 \AA upon their heating to 550°C. Figure 7 shows diffractograms obtained for oriented preparations of fraction <5 μm (sample Hver-11).

Diffractograms of unoriented preparations show reflections with $d = 1.489\text{--}1.506 \text{ \AA}$ ($b = 8.93\text{--}9.04 \text{ \AA}$) near the $d(060)$ region.

All the above-mentioned characteristics indicate that dioctahedral smectites are the major clayey component of examined fractions (Table 1, Fig. 7).

Kaolinite occurs as a subordinate clayey component in samples 0301, 0303, and 0312 and as traces in sample 0302. Diffractograms of oriented natural and saturated preparations are characterized by reflections with $d(001) \sim 7.22\text{--}7.28 \text{ \AA}$ and 3.55–3.56 \AA , respectively,

Table 2. Chemical composition of clayey fraction <5 μm , wt %

	0301	0303	Hver-11	0306	0312	0312a	0313	0316
SiO ₂	46.95	37.46	50.70	44.60	45.76	48.16	47.04	48.76
TiO ₂	5.45	4.01	1.87	2.57	1.40	1.50	2.68	1.91
Al ₂ O ₃	19.66	16.09	12.54	14.26	20.83	19.53	14.60	14.69
Fe ₂ O ₃	11.68	19.17	12.05	11.68	10.48	8.72	10.58	11.61
FeO	0.72	2.48	0.25	0.86	0.21	0.21	2.00	0.64
MnO	0.19	0.22	0.07	0.15	0.10	0.08	0.05	0.05
MgO	1.45	1.86	3.31	3.33	2.10	2.83	3.15	2.67
CaO	0.89	0.90	1.51	1.68	1.57	1.01	2.69	2.80
Na ₂ O	0.06	0.04	0.05	0.03	0.05	0.05	0.16	0.31
K ₂ O	0.03	0.03	0.10	0.07	0.04	0.06	0.13	0.12
P ₂ O ₅	0.22	0.20	0.09	0.16	0.12	0.11	0.24	0.11
CO ₂	0.33	<0.2	<0.2	0.22	0.33	0.42	0.32	0.34
H ₂ O ⁻	5.94	6.73	8.67	11.39	8.69	9.67	11.48	11.77
H ₂ O ⁺	6.09	7.79	4.93	5.98	5.98	6.16	3.90	3.93
S _{tot}	<0.1	4.24	4.00	4.71	4.41	1.97	1.60	0.29
Σ	99.76	101.02	100.14	101.69	101.90	100.48	100.66	100.00

Note: (Sample 0312) rock; (sample 0312a) fraction <5 μm .

which disappear upon heating. Parameter b of minerals is 8.95 and 8.93 Å, respectively ($d(060) = 1.492$ and 1.488 Å, respectively).

In addition to layered silicates, the studied fractions contain admixtures (sometimes, significant) of the following minerals: clinoptilolite (sample Hver-11), gypsum (sample 0305), quartz (samples 0301, 0303), anatase (samples 0305, Hver-11, 0313), and pyrite (samples 0303, 0306, Hver-11, 0312, 0313) (Fig. 7, Table 1).

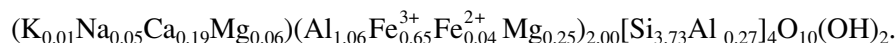
In sample 0310, cristobalite is a major component, while smectite occurs as traces.

Chemical Composition

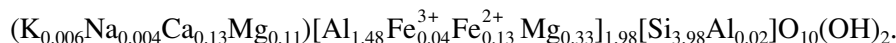
The complete silicate analysis, including the determination of S_{tot} , was conducted for bulk rock (sample 0312) and clayey fractions $<5 \mu\text{m}$ (samples 0301, 0303, Hver-11, 0306, 0312a, and 0316). Table 2 shows that nearly all of the examined samples contain not only dioctahedral smectites, but also TiO_2 , CO_2 , P_2O_5 , and S_{tot} , indicating the presence of mechanical admixtures of anatase, calcite, phosphate, and pyrite in clayey fractions.

Classification of minerals of the smectite group according to (Drits and Kossovskaya, 1990) is based on their iron index (Z), i.e., the Fe^{3+} content in dioctahedral positions and ratios between octahedral and tetrahedral charges in 2 : 1 layers.²

Calculation of crystallochemical formulas of dioctahedral smectites was based on the following assumption: the anionic framework of one-half of the cell of 2 : 1 layers is characterized by an integral negative valence of 22. The formulas were calculated for samples 0316, 0313, 0306, and 0303 that do not virtually contain admixtures of layered silicates (kaolinite) and zeolites (heulandite). The formula obtained for sample 0303 appeared to be doubtful owing to the slightly overestimated F_2O_3 content, underestimated SiO_2 content, and low sum total of exchange cations K, Na, Ca, and Mg (Table 2).



According to the classification (Drits and Kossovskaya, 1990), dioctahedral smectite in sample 0316 is represented by Fe^{3+} -Al montmorillonite ($Z = 0.65$). The octahedral charge (0.29 v.u.) is slightly higher relative to the tetrahedral charge (0.27 v.u.). Smectite in sample 0313 also belongs to the Fe^{3+} -Al montmorillo-



²In dioctahedral Al-rich smectites, the octahedral negative charge exceeds the value of the uncompensated tetrahedral charge. Beidellites include Al-bearing smectites with the tetrahedral charge exceeding the octahedral one (Drits and Kossovskaya, 1990).

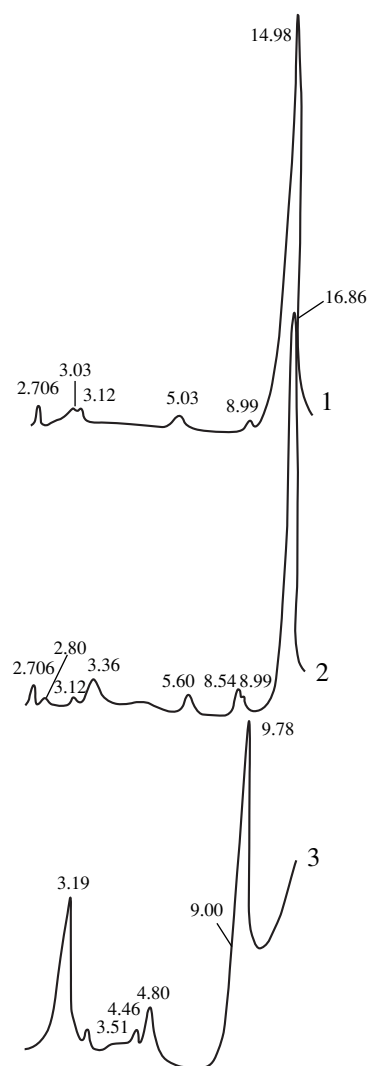


Fig. 7. Diffractograms obtained for oriented preparations of fraction $<5 \mu\text{m}$ (sample Hver-11). (1) Air-dry; (2) saturated with ethylene glycol; (3) heated.

The idealized averaged formula obtained for sample 0316 is as follows:

nite variety ($Z = 0.51$). Its octahedral charge (0.38 v.u.) exceeds the tetrahedral one (0.27 v.u.).

Sample 0306 contains Al-smectite (or montmorillonite) ($Z = 0.04$). The charge is mainly localized in octahedrons. This is evident from the following formula:

Table 3. Contents of minor elements and REEs in hydrothermally altered hyaloclastites (samples 0301 and 03003) and sedimentary rocks (samples 0306, 0312, 0312a, 0313, 0316), ppm

	Au	As	Sb	Se	Hg	Br	Sc	Co	Cr
0301	0.012	<0.1	<0.05	3.2	0.04	0.5	55.7	18	44
0303	<0.005	<0.1	0.24	4.2	0.17	<0.2	50.5	67	51
0306	0.557	9.6	1.84	8.6	0.12	0.5	46.9	50	91
0312	1.08	1.5	1.12	9.2	0.13	0.6	13.7	25	68
0312a	0.488	1.1	0.96	3.1	0.34	0.4	15.9	22	64
0313	0.061	8.1	2.41	8.2	0.09	0.4	49.5	58	89
0316	0.302	0.9	0.72	29.0	0.08	<0.2	41.7	34	104
	La	Ce	Sm	Eu	Yb	Lu	Hf	Ta	Th
0301	30	59	11	3.6	4.4	0.9	3.9	3.1	1.8
0303	37	72	17	5.4	6.9	0.8	2.8	1.7	1.2
0306	18	34	9.1	2.6	4.1	0.4	2.5	1.0	1.1
0312	14	22	3.8	1.1	1.3	0.3	1.5	0.4	0.9
0312a	16	28	4.5	1.8	1.3	0.3	1.5	0.5	0.7
0313	15	28	6.5	2.5	3.2	0.5	2.6	0.6	0.8
0316	13	25	6.1	2.3	2.9	0.5	1.2	0.8	0.7

Note: Samples 0313 and 0316 are represented by fraction <5 μm .

Table 4. Contents of minor elements and REEs in clayey sediments from “boiling” pots in solfatara fields, ppm

Locality	Au	As	Sb	Se	Hg	Br	Sc	Co	Cr
Reykjanes	<0.005	7.3	0.07	1.4	20.0	6.6	61.1	69	305
Krafla	0.029	10	0.26	11	4.10	1.5	24.4	25	320
Nämafjall	<0.005	<0.1	0.09	<0.5	1.4	<0.2	44.5	28	155
	La	Ce	Sm	Eu	Yb	Lu	Hf	Ta	Th
Reykjanes	5.6	11	2.6	1.5	0.9	0.1	2.5	0.9	0.5
Krafla	4.9	9	1.1	0.3	0.4	0.1	1.9	0.3	0.7
Nämafjall	13	22	3.8	1.3	0.4	0.1	2.4	1	0.8

When comparing the results of chemical analysis of the bulk sample and fraction <5 μm (sample 0312a), we should keep in mind that differences mainly concern contents of Fe_2O_3 (10.48 vs. 8.72%) and S_{tot} (4.41 vs. 1.97%) (Table 2). This is naturally explained by higher pyrite concentrations in the rock.

Due to the admixture of kaolinite and pyrite, compositions of smectite in samples 0312 and 0312a and clay minerals in samples 0301 and 0303 are unclear. One can only assume that, like in samples 0316, 0313, and 0306, smectites in both these samples belong to montmorillonites with different iron indices.

Table 3 and 4 present contents of some minor elements in the rock and fractions <5 μm . Table 3 shows substantial variations in contents of Au, As, Se, Sb, and Hg at different levels of the sedimentary section (0.012–1.08, <0.1–8.1, 3.1–29.0, <0.05–2.41, and 0.04–0.34 ppm, respectively).

The spectrum of minor elements in clayey sediments of “boiling” mud pots (Table 4) suggests their specific compositions in different geothermal areas.

DISCUSSION

The timing of horizontally laminated clayey rocks in the terrace can be judged from radiocarbon dating of the plant remains performed in the Laboratory of Isotope Geochemistry and Geochronology (Geological Institute, Russian Academy of Sciences) in 2004. Sample 0314 from this layer yielded the total carbon date of 4220 ± 100 yr (GIN-12717).

In Iceland, this Holocene period, the Late Birch Period (Einarsson, 1994), was relatively warm and characterized by the development of arboreal, shrubby, and herbaceous vegetation over significant areas. The sealevel at that time was higher as compared with the

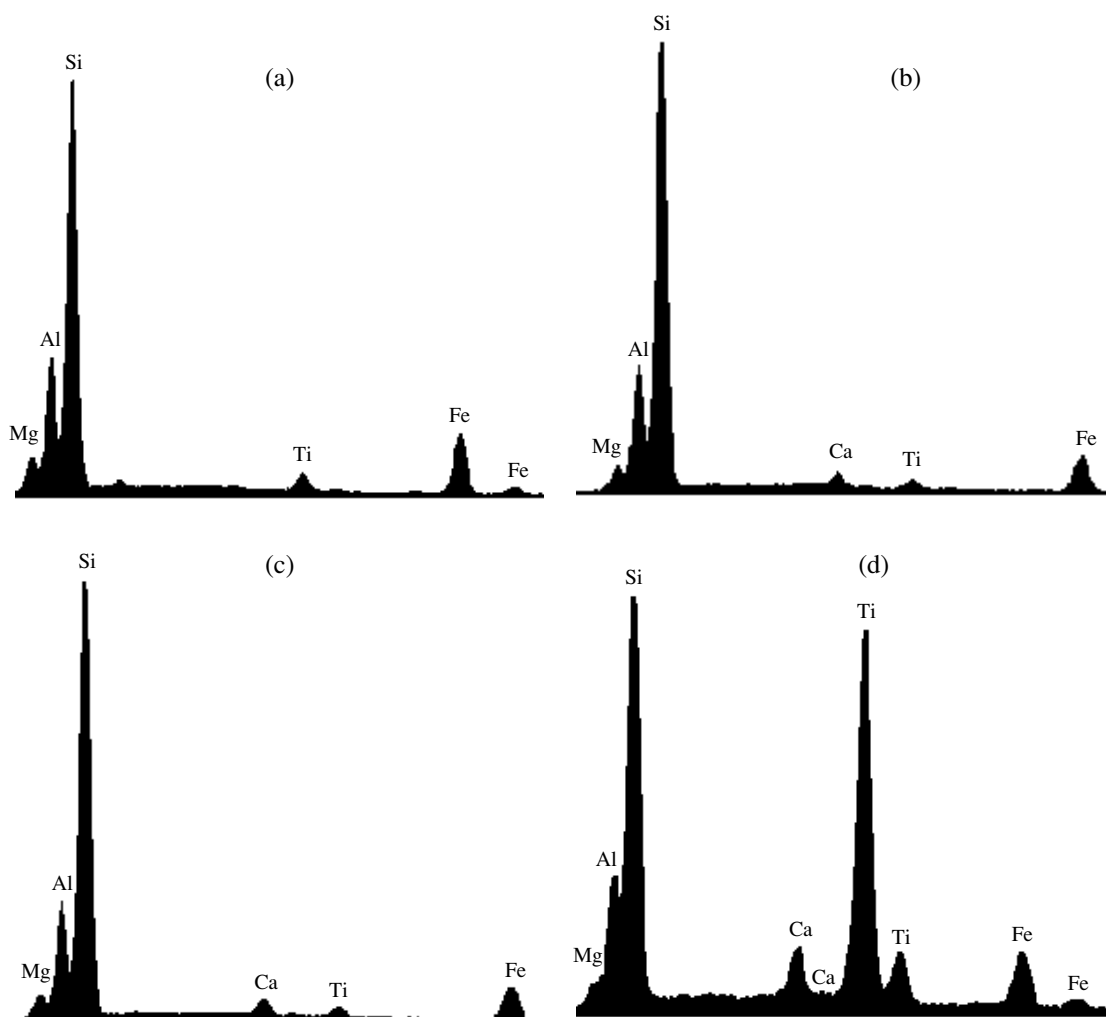


Fig. 8. Microprobe data on clay minerals (a, b) redeposited from altered hyaloclastites and (c, d) formed after the sediment deposition. (a) Composition of clay pellets; (b) composition of the terrigenous matrix of clayey sediments; (c) authigenic clayey material at the surface of plant remains; (d) mineralized plant detritus.

present-day one, and sediments in the studied terrace (altitudes 80–100 m), probably, accumulated in the coastal part of the sea basin.

Unsorted massive sediments (clay pellets, plant detritus, and clayey material) were related to the erosion of altered hyaloclastites, the subsequent reworking of clastic material by waves, and its deposition near the seashore. The laminated clayey sediments, which enclose ash beds (white laminae) and plant detritus bed (sample 0314), accumulated at some distance from the shore in a quiet hydrodynamic environment (probably, a shallow area of the basin). During the sealevel fall, this area could include subaerial settings favorable for the deposition of siliceous matter (sample 0310) from discharges of hot springs at the surface.

The reticular clayey material covers walls of microcavities and forms films at the surface of plant fragments. Its rounded and oval accumulations fill interstices in the entire sedimentary section (Fig. 2a). One

can judge about the timing of this clayey material from its relationships with authigenic pyrite and gypsum crystals related to the transformation of sediments. The pyrite crystals are enveloped by clay minerals. Some gypsum crystals are corroded and replaced by clay minerals, suggesting that clay minerals formed at the last stage of the hydrothermal alteration of sediments (Fig. 5).

Hence, two types of clay minerals can be defined based on their timing: (i) minerals related to the redeposition of altered hyaloclastites and (ii) epigenetic minerals. Let us remind that dioctahedral smectites with different iron indices are the dominant component among the examined clay minerals.

It is noteworthy that authigenic crusts and druses of gypsum rapidly cover the surface of drying clayey rock. This phenomenon indicates a high mineralization degree of interstitial solutions, which could partly inherit the groundwater signature of the earlier hydro-

thermal stage. It should be emphasized that the formation of gypsum due to the oxidation of pyrite seems unlikely in the considered case. Gypsum crystals are generally associated with perfect pyrite crystals without traces of oxidation.

Silica is deposited at the surface as a result of the evaporation of solutions discharging above and below the examined sedimentary section at the present-day hot springs.

Although chemical compositions of clayey fractions are very similar, the TiO_2 content is higher in fractions from bedrock hyaloclastites (samples 0301 and 0303) (Table 2).

The relative increase in the TiO_2 content in the course of the alteration of sideromelanitic glass (major component of basaltic hyaloclastites) and its replacement latter with palagonite has been noted in many works (Hay and Iijima, 1968; Jakobsson, 1979; Geptner, 2001; and others). In the course of further alteration of hyaloclastites and formation of clay minerals, Ti remains in primary rocks as a low-mobile chemical element (Geptner et al., 1987). The lower TiO_2 content in sedimentary rocks is related to the fact that the rocks contain not only terrigenous minerals, but also in situ clay minerals. Therefore, the Ti concentration decreases in the sedimentary rocks. This assumption is supported by the universal presence of synthesized clay minerals (smectites) as isometric accumulations, films, and incrustations at the surfaces of clay pellets, pyrite crystals, and plant remains.

The microprobe analysis revealed the principle similarity between chemical compositions of clay minerals related to the redeposition of altered hyaloclastites (Figs. 8a, 8b; type 1) and the epigenetic minerals (Figs. 8c, 8d; type 2). The redeposited clay minerals, which make up pellets and silt-sized clayey matrix, contain Si, Al, Fe, and Mg as major components accompanied by the subordinate Ti and Ca. The mineralized plant remains are characterized by high Ti contents, probably, related to anatase admixture. Clayey matter of rims and isometric accumulations on walls of microcavities and the surface of plant remains universally contain S and Ca, probably, related to the presence of gypsum. The composition of clayey matter developed after volcanic ash is appreciably different. According to the microprobe (area and point analysis) data, Si and Al are dominant in the ash layer (sample 0312), while Ca, Ti, and Fe concentrations are at the analysis accuracy level.

In terms of redistribution ability in the course of water-rock interaction, minor elements can be divided in the inert and mobile groups. It is believed that, during the low-temperature hydrothermal transformation, inert elements (La, Ce, Sm, Eu, Yb, Lu, Hf, Ta, and Th in the considered case) stay in the altered rock, while mobile elements (Cr, Co, Au, As, Sc, Se, Sb, Br, and Hg) migrate with thermal solutions (Gibson et al., 1982). One can see such a behavior of minor elements by com-

paring data on bedrocks (samples 0301 and 0303) and sediments related to the redeposition of hydrothermally altered hyaloclastites (samples 0306, 0312, 0312a, 0313, and 0316). Noteworthy are substantial variations in contents of some mobile elements (for example, Au, As, Se, Sb, and Hg) at different levels of the sedimentary section (Table 3).

It is well known that clay minerals have good sorption properties. In the Reykjanes, Krafla, and Námafjall hydrothermal fields, they play a significant role in the composition of present-day solfatara deposits. The spectrum of minor elements in clayey sediments from the "boiling" mud pots of these hydrothermal fields testifies to their specific chemical composition.

Table 3 demonstrates the enrichment of some clayey sediments (samples 0306, 0312, 0313, 0316) with minor elements (Au, As, Se, Sb, and Cr) as compared with neighboring bedrocks (samples 0301 and 0303). This is difficult to explain by zoned patterns of hydrothermal springs or progressive accumulation of some elements in the course of slow washout of low-permeable clayey rocks by heated groundwaters. Such a process also seems unlikely because of negligible contents of some elements, such as As, Sb, Cr, and others in present-day thermal solutions of Iceland (Kononov, 1983).

The chemical composition of hydrothermally altered clayey sediments (mainly, smectites) could also be affected by bacteria and fungi (their fossilized remains are described above). Smectites can absorb toxins, bacteria, and viruses from solutions and suspension (Carretaro, 2002). Depending on the chemical composition, clay minerals can stimulate or suppress the development of bacterial communities (Williams et al., 2004). Smectites from the study area appeared to be a favorable substrate for the habitat and intense development of microbiota communities. In the course of metabolism, bacteria and fungi could oxidize or reduce some chemical elements (for example, As, Sb, Se, Hg) and, thus, stimulate their sorption by clay minerals and accumulation in sediments (Ehrlich, 1995). It should be emphasized that contents of elements mentioned above are not increased in altered hyaloclastites of bedrocks lacking the mineralized microbiota.

CONCLUSIONS

In the examined rocks from the rift zone of Iceland (Hveragerði area), clay minerals are mainly represented by dioctahedral smectites (montmorillonites with different iron indices). Kaolinite occurs as an insignificant admixture.

The studied sediments are characterized by similar distribution patterns of the major petrogenic components. However, hydrothermally altered clayey sediments are enriched in minor elements (Au, As, Se, Sb, and Cr) as compared with the parental bedrocks. The difference in the minor element signatures of these

rocks is difficult to explain by specifics of hydrothermal activity in this area. It is assumed that their formation could be significantly governed by bacteria and fungi communities.

The examined clayey sediments are being successfully used for a long period for the mud cure of arthritis and rheumatism in the Health and Rehabilitation Clinic of Hveragerði, Iceland. Specific features of the composition of these sediments were not studied so far. We believe that the data presented above fill up this gap. They can be used to decipher therapeutic properties of clay minerals from not only the study region, but also other areas with present-day hydrothermal activity.

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