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Chemical and microbiological investigations of hot spring deposits found at the hydrothermal systems of Kamchatka Peninsula, Russia

Ichiro SAJI[1], Osamu NISHIKAWA[2], Natalia BELKOVA[1], Viktor OKRUGIN[3] and Kazue TAZAKI[2]

1 Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa, 920-1192 Japan

2 Department of Earth Sciences, Faculty of Science, Kanazawa University, Kakuma, Kanazawa, 920-1192 Japan

3 Institute of Volcanology of Far Eastern Division of Russian Academy of Sciences, 9 st. Piip, Petropavlovsk-Kamchatskii 683006 Russia

Abstract : Chemical and biological characteristics of hot spring water, travertines and microbial mats collected from seven hydrothermal systems of the Kamchatka Peninsula, Russia are described. Water quality of the Vilyuchinskie hot springs was almost the same as those of Tazaki et al. (2003). Elemental concentration of hot spring waters was mainly composed of Na, K, Ca, and Mg with high contents of Fe, As, and Sr. The structure and elemental composition of travertine and biomats were studied with optical microscopy, ED-XRF, XRD, and EPMA. High content of As (43.88 wt%) was found in the deposits and biomats of the Nalychevskie hot springs. Extremely high concentration of Cd of 9.56 wt% was detected in the deposits of the Paratunskie hot springs. Traces of mercury (0.57 wt%) were found in the soft parts of biomats from the Apapelskie-1 hot springs. Optical microscopic observation of thin section of Oksinskie, Apapelskie, and Vilyuchinskie biomats revealed laminated structures. Soft parts of biomats mainly consist of cyanobacteria *Anabaena* spp. and green algae. A calcareous travertine of the Vilyuchinskie hot springs recorded the evidences of a long-term transition of water chemistry and periodic changes of environmental conditions such as water flux from the well and rainfall. Intensive hydrothermal alteration was observed in the Dachnye hot springs. Optical microscopic observation of microbial mats revealed diversity of microorganisms both in free-living forms and in association with mineral particles. Metabolically active cells were detected in the microbial mats indicating the impact of bacteria to the geochemical processes in the surroundings environments.

Keywords : hydrothermal system, hot spring water, biomats, travertine, cyanobacteria, algae, calcium carbonate, Kamchatka.

1. Introduction

The Kamchatka Peninsula is the only example of modern volcanic activity in Russia. The volcanic activity has been started from Cretaceous (130～140 m.y.) and still continues (Okrugin, 1995). As a result, four roughly parallel, N-S oriented, volcanic mountain chains were formed (Lattanzi et al., 1995). Hot springs as well as geothermal systems in volcanic regions are not only the source of geothermal energy, but also the sources of many kinds of metal resources and the habitat of microorganisms (Kiryukhin, 2002). However, only little is known about biogeochemical interactions in these modern geothermal systems (Okrugin et al., 2002 ; Tazaki et al., 2003).

Tazaki et al. (2003) have reported hot springs at the Southern Kamchatskaya geothermal provinces from a view of biomineralization and concentration of heavy metals and radioactive materials. The microscopic and chemical analyses of microbial mats as well as ambient γ-ray analysis revealed various ecosystems and diversity of microorganisms at the high and low temperature hydrothermal systems.

The travertines and biomats are formed around hot springs. Travertine is one of hardened hydrothermal products of calcium carbonate, whereas, biomats relatively soft sediments that consist of microorganism assemblages. It has been known that distinct laminated structures develop both in the deposits and biomats around hot springs. Their patterns reflect a periodic change of phenomena that occurs in the microenvironment. Investigation of these structures could be an effective way for understanding daily and seasonal variation effects of mineral deposition in the hot springs. On the other hand, microbial mats of different color grow in the pools of hot spring water. The formation process of biomats that mainly consists of calcium carbonate involved the activity of microorganisms (e.g. Tazaki, 2000). To know the mechanism and process of concentration of hot spring elements, we need to inspect both deposits and microorganisms. But the detail relationships between travertine and microbial mats have been known little because chemical and biological factors are complexly intertwined.

Biological fixation of CO_2 in carbonates is carried out by some bacteria and fungi as well as by photosynthetic cyanobacteria and algae. Bacteria, including cyanobacteria, form calcium carbonate extracellular through aerobic and anaerobic oxidation of organic matter and due to cyanobacteria photosynthesis (Ehrlich, 1995 ; Tazaki et al., 2001). In the microbial mats hot spring water flows through the microchannels and interstitial voids of mats and biofilms, which enhances the direct interaction of microbes with water chemistry (Pierson et al., 1999). The photosynthetic microorganisms create a microenvironment in which the pH and the oxygen concentration are higher than that in surrounding environments due to photosynthetic activity. The entrapment and agglutination processes of calcium carbonate deposition can be induced on their cell walls. Travertine is formed from rapid calcium carbonate precipitation due to cyanobacterial photosynthesis in waterwalls and streambeds of fast-flowing rivers, which tend to bury the cyanobacteria (Ehrlich, 1995 ; Tazaki, 2000).

We have visited seven hydrothermal systems of Southern and Central Kamchatskaya geothermal provinces in 2003 from September 25th to October 1st. In this study, we describe the relationship between microbial mats, travertines, and hot spring waters under high and low temperature hydrothermal systems in Kamchatka, showing chemistry and structures of modern hot spring deposits and diversity of microorganisms.

2. Geological setting

We visited seven hydrothermal systems : Nalychevskie hot springs, Bystrinskie (Thermal springs at the 47th km), Oksinskie, and Apapelskie hot springs in Anavgaiskii geothermal field, Paratunskie hot springs in Paratunskoe geothermal field, Dachnye hot springs in Mutnovskii geothermal field and Vilyuchinskie hot springs of Vilyuchiskii geothermal field.

2.1. Nalychevskie hot springs

Nalychevskaya geothermal system is localized within Avachinsko-Zhupanovskaya part of graben-synclinal of Eastern Kamchatka. In late-Pliocene-Early-Pleistocene here took place strong volcanic activity due to which basaltic lava plate-plateau and shield volcanoes were formed. During Middle Pleistocene-Holocene volcanoes of Avachinsko-Koryakskaya and Zhupanovskaya groups were formed. Nalychevskii horst is located between these volcanic groups. It is formed by rocks of Oligocene-Lower-Miocene age. Nalychevskaya geothermal system consists of Nalychevskie, Zhyoltorechenskie, Goryacherechenskie, Kraevedcheskie, Talovskie, and Shaibnye hot springs. They are located along thermal rift. Its axis goes through crater lakes of Gorelyi (SW) and Malyi Semyachik (SE) volcanoes. Discharge of some springs is from 0.27 up to 10 l/sec, total visible discharge is 57.5 l/sec. Total discharge is 140-149 l/sec. Temperatures vary from 17 up to 77°C. Nalychevskie hot springs form a series of pots and gryphons along the left bank of the Goryachaya River. They formed a travertine ground 150×200 m large here. Travertine cone is up to 2.5-3 m high. This part of Nalychevskie hot springs is called Kotyol. Earlier here were numerous small geothermal craters out of which flew thermal waters. In 1959-1960 at Nalychevskoe deposit of thermo-mineral waters 4 boreholes for geological-structural study were drilled (max depth was 217 m). The boreholes opened thermal reservoirs at depth of 25-117 m in the zone of contact of Pliocene-Pleistocene vulcanite with subvolcanic diorite. Boreholes are self-flowing ; their discharge is 1.4-6.5 l/sec (specific discharge is 6.8-8.3 l/sec, height of the thermal jet above bore-holes varies from 2.1-7.2 m, temperature varied from 58 to 75°C). In the place of the deepest borehole there formed a gryphon (Ivanov's gryphon) with temperature 75.6°C. This is a small thermal lake 5×6 m large, out of which a creek flows. On shores of the lake and along the creek there takes place siliceous-carbonate precipitation. For 33 years this precipitation formed a travertine ground of yellow-brown colour more than 5000 m^2 large. At the same time, activity of Kotyol hot springs sharply decreased. As early as in 1996 we were able to take thermal water samples from the crater of the central part of the travertine dome. Presently, thermal water level became lower. Thermal waters are sulfate-chloride nitric and calcium-nitric with mineralization of 1.8-9.2 g/l, siliceous (H_2SiO_3 67-270 mg/l), boron (H_3BO_3 230-504 mg/l), carbonic (CO_2-36-275 mg/l), arsenic (As-0.3-13.5 mg/l) with anomalous contents of Li (5.1-10.5 mg /l), Mn (0.7-1.2 mg/l), Fe (0.9-12 mg/l), Br (4.5-17 mg/l), I (0.8-28.mg/l) Rb (0,4-1.35 mg/ l), Cs (0.15-0.9 mg/l), Sb (0.06-0,15mg/l), F (5-10.9 mg/l), Ge, Tl, W, Mo, and Zn. Gas composition is mainly CO_2, rare nitrous-carbonic or nitrous. According to the properties waters are balneological, slightly arsenian, boron siliceous. They belong to one specific water type called Nalychevskii balneological water type. Thermal waters are the area of modern arsenic and iron mineral formation. Mineralogical composition of travertine is calcite, quartz, opal, scorodite manganocalcite, aragonite, rivermandite, jarosite, limonite, and goethite.

2.2. Anavgaiskii geothermal region

Anavgaiskii geothermal region includes six main hydrothermal systems such as Bystrinskie (synonymic name is the Thermal springs at the 47th km), Anavgaiskie, Uksichanskie, Oksinskie, Apapelskie, and Krerukskie. Anavgaiskaya geothermal area belongs to the Central-Kamchatskii mountain-ore region that is the most promising one in Kamchatka. Numerous deposits and ore manifestations of gold and silver, base metals, copper, cobalt and nickel, antimony, mercury, sulfur, thermal and mineral waters are located in its territory. Anavgaiskaya geothermal area is located within Bystrinskii ore knot that is structurally localized within Alneisko-Kozyrevskii volcanogenic-ore centre. In geological terms the area is formed by (upwards direction) : Neogene vulcanite of medium and medium-acid composition intruded by subvolcanic bodies (from diorite and andesite to liparite-dacite). Quaternary basic vulcanite overlaps the greater part of the territory. Host rocks are volcanogenic and subvolcanic rocks of Upper-Miocene-Pliocene. Ore specialization of the area is due to two types of ore formations, namely : antimony-mercury (quartz-dikkite-nacrite-kaolinite-cinnabar) and epithermal Au-Ag. Main ore objects of the ore knot are Chempurinskoe deposit of mercury, Apapelskoe, Aglikichskoe, and Krerukskoe gold-silver ore manifestations. All these objects are localized in the development (concentration) zone of subvolcanic bodies of diorite, porphyrite, and andesites of general (typical) NE strike. The typical feature of Bystrinskii knot is a large number of various thermal springs that belong to Anavgaiskaya, Bystrinskaya (Uksichanskaya), Oksinskaya, and Apapelskaya hydrothermal systems.

2.2.1. Bystrinskie hot springs

Bystrinskie hydrothermal springs are also known as the Thermal springs at the 47th km. They are located 10 km south-east of the settlement Anavgay on the left bank of the Bystraya River flowing the Kamchatka River. In hydrogeological terms Bystrinskie springs are located within artesian volcanogenic basin of the Bystraya River valley. Water-bearing horizons lie inside of volcanogenic-sedimentary Miocene rocks. Rocks are greatly dislocated and altered by hydrothermal processes. On the surface at the foothill of the mountain Koluman there are two groups of springs with temperatures of 30°C and 52°C and total discharge of 3.8 l/sec. Two bore-holes opened thermal reservoirs at the depths of 346 and 810 m. Discharge of self-flowing bore-holes is 11.6 and 13.3 l/sec, and temperature at the river mouth are 46.3°C and 43.8°C, respectively. These are chloride-sulfate calcium-sodium slightly alkaline waters with mineralization from 2.1 up to 2.9 g/l. They contain high contents of boron and arsenic. In mouth parts of the boreholes halite have been identified among sublimates.

2.2.2. Oksinskie hot springs

Oksinsko-Apapelskoe deposit of thermo-mineral waters unites Oksinskie, Apapelskie (Nizhne-and Verkhne-Apapelskie (Lower and Upper Apapelskie), Opalskie, and Aglikichskie hot springs that occupy the area of about 20 km^2. This deposit belongs to volcanogenic basin formed by Pliocene vulcanite of basic, medium and acid composition. Oksinskie hot springs are located in the middle stream of the Anavgay River 35 km north-east of the settlement Anavgay. There are three groups of hot springs located on the left bank of the Anavgay River 7 km north of the mercury deposit Chempura. They occupy the area about 0.5 hectares. For the first time the springs were described in all details by P.T. Novograblenov who visited the place in 1929 (Novograblenov, 1932). We visited two groups of isolated springs that located 300-400 m apart. Due to activity of the first group of springs a large travertine field (area about 60-100 m) with travertine dome in the central part was formed. The travertine dome is 2-3 m high. The thickness of the travertine varies from 1 to 4 m. At the present time, the discharge of these springs is insignificant (less than 1 l/min) and temperature is rather low (30-40°C). The second group of springs is characterized by relatively high discharge (more than 3 l/sec) and high water temperature about 67°C. Waters are characterized by high contents of boron, arsenic, etc. Mineral composition of travertine is calcite (60-90 %), quartz, clay minerals, pyrite, marcasite, pyrolusite, and goethite.

2.2.3. Apapelskie hot springs

Apapelskie springs (Verchne-Arnautskie, and Apapelskie hot springs by Novograblenov (1932) and Piip (1937)) consist of two groups, namely Nizhne-and Verkhne-Apapelskie that left located about 700 m apart. They are located in the valley of the creek flowing to the Anavgay River. Verkhne-Apapelskie springs are the largest ones. They unite 14 boiling steam-water jets with water temperature of 96-98°C and total discharge of 5.5 l/sec. These springs are localized within the vein zone of Pliocene epithermal gold-silver deposit. The largest springs are located at the foothill of a small picturesque cliff (fragment of the vein zone) called Idol ("Apapel" by koryak language). Due to functioning of these springs modern precipitation of mercury minerals such as cinnabar, metacinnabar, native mercury takes place. I.I. Tscheglov first discovered cinnabar in 1958 (Tscheglov, 1962). Waters are characterized by high contents of arsenic, antimony, molybdenum, lithium, and thallium. Classical travertine can be hardly found here. Springs are warm bog where the precipitation of compound amorphic mineral aggregates takes place on fragments of the quartz vein. High content of mercury, selenium, arsenic, and bismuth is typical for them. Mineral composition of these aggregates is opal, calcite, cinnabar, metacinnabar, realgar, orpiment, pyrite, marcasite, barite, pyrolusite, and goethite. Multi-layered biomats are distinguished by increased content of mercury, arsenic, bismuth, gold, and silver are formed in these springs (Vasilevskii et al., 1977).

2.3. Paratunskie hot springs

Paratunskaya hydrothermal system belongs to the Paratunskaya hydrothermal area, which also includes the Bolshebannaye and Karymshinskaya hydrothermal systems and some thermal fields and occurs in the southern Nachikinskaya fold-block zone. This geothermal system is located 20-45 km south-west of the town Petropavlovsk-Kamchatskii and is presented by a large group of hot springs that stretch along the left bank of the Paratunka River for the distance of 20 km up to the watershed of the Paratunka and Vilyucha Rivers. Paratunskie hot springs first described by Ditmar in 1854 have been repeatedly studied as a power supply since 1958. The Kamchatka regional geological survey performed hydrogeological mapping of the Paratunka River basin at a scale of 1 : 50 000, has done seismic, magnetic and gravity surveys, and drilled more that 55 000 m of exploration holes. This resulted in a rather detailed interpretation of the origin and structure of the hydrothermal system. Wells, drilled in the discharge areas of the Northern, Nizhne-Paratunskie, Sredne-Paratunskie, and Karymshinskie hot springs penetrated thermal water of the same composition as in corresponding hot springs. Sredne-Paratunskie hot springs are sulfate-bearing, and Nizhne-Paratunskie and Northern hot springs are chloride-sulfate-sulfate-bearing. At the periphery of the geothermal system, individual wells drilled carbonate-, hydrocarbonate-to carbonate-, and sulfate-carbonate-bearing waters. The temperature of waters at the main water-bearing levels varied from 70 to 90°C, only in few wells of the Nizhne-Paratunskii sector were the temperatures as high as 100 to 106°C recorded. The geothermal profile of the Paratunskaya hydrothermal system shows a steep-like dip of high temperatures from the Sredne-Paratunskii sector to the north. The temperature 80°C is at a depths of 150-200 m at the Sredne-Paratunskii sector, plunges to 350-400 m at the Nizhne-Paratunskii sector, and reaches 750 m at the Northern sector. Economic reserves of the Paratunskaya hydrothermal system calculated for the average temperature of 77°C from wells are estimated as 314.6 l/sec, including 166.5 l/sec in the Sredn-Paratunskii, 69.9 l/sec in the Nizhne-Paratunskii, and 78.2 l/sec in the Northern sector. Natural reserves of hot springs in the same sector (including the Verkhne-Paratunskii sector) are 780 l/sec. The total heat capacity of the hydrothermal system is estimated as 18 200 kcal/sec. The age of the Paratunskaya hydrothermal system is estimated as 0.25 My. The analysis of hydrothermal mineralization and alteration rock showed three stages of the hydrothermal system and the associated metasomatic processes. The first and the earliest stages of progressive metasomatism and the hydrothermal system evolution is conventionally limited to temperatures below 180°C. The second stage is the most intensive, reaching maximum heat capacity and maximum temperature of 220°C. Cooling of the system marks the third, regressive stage. Major altered minerals are albite, epidote, chlorite, and K-feldspars. Vesicles and fractures are filled with epidote, chlorite, laumontite, stilbite, clinoptilolite, heulandite, chabasite, wairakite, quartz, calcite, and more uncommonly prehnite, pyrite, galena, chalcopyrite, and cinnobar. We took water samples and carried out the research in the Northern sector. A borehole 200 m deep was drilled here.

2.4. Dachnye hot springs

Dachnye thermal springs are the largest ones in the structure of Mutnovskaya geothermal system. They are located 9 km north of the Mutnovskii volcano between Holocene volcanoes called Skalistyi and Dvugorbaya. They are localized on the ignimbrite plateau that crossed by numerous ravines and valleys of small rivers. The relief is mountainous, steep slopes of some ravines are interchanged by small hollows with flat bottom. Absolute heights are 850-950 m. Hot springs and thermo-manifestations form five groups traced for about 1 km in sublatitudinal direction. These groups are Active group (Kotyol or Yuzhnaya), Kholodnaya, Utrennaya, Utinaya, and Medvezhya. They are typical vapour-water steams, boiling mud pots, warm lakes and thermal swamps. As some of them are located in depressions, they are flooded with subsoil waters. Thus, chemical composition of such hot springs is the result of mixing of geothermal fluid and subsoil waters. Host rock is tuffobreccia of medium composition, dacite, liparite, pumice tuff and ignimbrite. This year we visited the thermal plot named Utinaya group or Utinye hot springs. This group is located at the foothills of Skalistyi volcano (acid extrusion). Thermal lakes and swamps with small hot springs are situated in the depression that is lower than the level of subsoil waters. On the highland there are boiling pots, dry vapour-waters jets. Across the thermal field there flow numerous creeks and streams that join into one large watercourse with water discharge of 20 l/sec and temperature about 6-8°C.

2.5. Vilyuchinskie hot springs

Vilyuchinskaya geothermal system consists of three groups of sources with total discharge 55 l/sec and water temperature high ranging from 38 to 90°C. Host rocks are Neogene subvolcanic diorite and volcanogenic-sedimentary rock of Oligocene-Miocene age. The system was studied with boreholes and adits (Vakin et al., 1977). In gabbro-diorite in the interval of 31.5-243 m borehole No 2 (295 m deep) opened thermal reservoirs with temperature about 76°C. The borehole is the self-flowing one with discharge of 50 l/sec. Waters are hydrocarbon-chloride and chloride-hydrocarbonate with mineralization of 1.0-1.2 g/l, siliceous with high content of Li, Mn, Fe, As, and B. Gas composition is carbonic-nitrous.

3. Analytical Methods

3.1 Sampling and field measurements of water quality

Sampling of deposits, biomats, and hot spring waters and field measurement of water quality were performed at seven hydrothermal fields of Central and South Kamchatka, namely Nalychevskie, Thermal springs at 47th km, Oksinskie, Apapelskie, Paratunskie, Dachnye, and Vilyuchinskie hot springs from 25rd of September to 1st of October, 2003 (Fig. 1). Water samples were bottled quickly in the centrifuged tube after nitric acid treatment. Measurements of chemical characteristics of hot spring waters (pH, EC : Electrical conductivity, WT : Water temperature) were done in the field by the same methods with Tazaki et al. (2003). Eh was measured by Eh-meter (Horiba) and recalculated as Electrode potential versus the standard hydrogen electrode (Table 1).

Table 1. Characteristics of hot spring waters measured in the field in Kamchatka, Russia

locations	pH	EC (mS/cm)	Eh (mV)	WT (°C)	Comments
Nalychevskie	6.3	6.28	-10	64.0	Hot spring source, Fig. 2A
Nalychevskie	7.1	6.30	40	59.0	100 m downstream
47th km	8.2	3.60	–	41.0	Bath
47th km	8.4	3.79	350	40.0	Pump, Fig. 4
Oksinskie-1	6.9	3.71	120	54.0	Fig. 5A
Oksinskie-2	6.8	3.77	130	53.0	Fig. 5B
Apapelskie-1	7.8	2.38	330	36.0	Fig. 7A
Apapelskie-2	7.4	2.00	–	91.0	Fig. 9
Paratunskie	8.3	2.45	30	53.0	Fig. 11
Dachnye-lower	7.2	0.27	-180	83.0	Black biomats, Fig. 12D
Dachnye-middle	6.0	0.50	-100	61.0	White biomats, Fig. 12E
Dachnye-upper	3.3	0.65	90	81.0	
Dachnye-mud	5.4	0.23	-40	71.0	Clays, Fig. 12B
Vilyuchinskie (V2)	6.6	1.71	70	66.0	Fig. 14A
Vilyuchinskie (V3)	6.7	1.66	50	43.0	Bottom of well, Fig. 15A
Vilyuchinskie (V3)	12.3	6.92	-210	29.0	Top of well, Fig. 15A, blue arrow
Vilyuchinskie (V5)	6.5	2.06	150	52.0	Fig. 16A

–; not detected

3.2 Chemical composition of water, travertine, and biomats in hot springs

3.2.1 Chemical compositions of hot spring waters

Chemical composition of hot spring waters was measured by the methods of collometry and photometry listed in Table 2A combined with inductively coupled plasma-mass spectroscopy and inductively coupled plasma-atomic emission spectrometry (ICP-MS, ICP-AES) in Central Chemical Laboratory of the Institute of Volcanology Far-Eastern Division of Russian Academy of Sciences (FED RAS), Petropavlovsk-Kamchatkii and in the Analytical Laboratory of the Institute of Problem Microelectronic Technology of Russian Academy of Sciences (RAS), Chernogolovka.

Major elements such as Na, K, Mg, Ca, Mn, and Fe were also analyzed by an atomic absorption spectrophotometer (AAS : SEIKO SAS-727). Na and K contents were measured by flame emission spectrometry (Analytical length ; Na : 589.0nm, K : 767.3nm).

Concentrations of Mg, Ca, Mn, and Fe were measured by flame atomic absorption spectrometry (Analytical length ; Mg : 285.4nm, Ca : 423.0nm, Mn : 280nm, Fe : 248.5nm).

3.2.2 X-ray powder diffraction analysis (XRD)

The powder material was mounted onto slide glasses to fit the diffractometer sample-holder. The analyses were done for bulk untreated and ethylene glycol-treated specimens by X-ray diffractometer (Rigaku RINT1200) with Cu Kα radiation, generated at 40 kV and 30 mA and scan speed of 2 ° /min.

3.2.3 Energy dispersive X-ray fluorescence analysis (ED-XRF)

Travertines and fresh biomats were air-dried up at room temperature and ground to fine powder for ED-XRF analysis. The powder samples were pressed to make pellet and mounted on the Mylar film. Analysis was carried out by an energy dispersive X-ray fluorescence spectrometer (JEOL JSX-3201), using Rh Kα, which operated at an accelerating voltage of 30 kV under a vacuum condition.

A travertine sample was cut and polished for elemental content mapping. Analysis was carried out by an ED-XRF with equipment for X-ray probe scanning system (JEOL JSX-3600), using Rh Kα, which operated at an accelerating voltage of 30 kV under the vacuum condition.

3.2.4 Elemental content mapping by an electron probe microanalyzer (EPMA)

Polished thin sections of the samples coated with carbon or gold were made for EPMA analysis. Fine-scale (sub-mm) mappings of element contents were carried out with an electron probe microanalyzer (EPMA, JEOL JXA-8800R). The analyses were carried out at the accelerating voltage of 15 kV, with prove current of 1.0×10^{-7} A.

3.2.5 Transmission electron microscopy (STEM/EDX)

Nano-scale observations and elemental distribution analyses of hot spring deposits were performed with a transmission electron microscope (JEOL JEM-2010FEF), equipped with a scanning TEM image generator (EM-Z90471) and an energy dispersive X-ray spectrometer (EX-34025JGT).

3. 3 Optical microscopy of biomats and travertine

3.3.1 Sample collection and preservation

The samples of microbial mats were preserved by diluting 1 : 50 (v/v) in filtrated (0.22 μm pore size) fixative solution (10 mM $NaPO_4$ [pH 7.2], 120 mM NaCl, 10 mM sodium pyrophosphate, 4% (w/v) paraformaldehyde) to final concentration of 3% paraformaldehyde. Paraformaldehyde solution was made fresh daily. Preserved samples were stored at 10°C.

3.3.2 Dissociation of cells from sediments

Filter-sterilized hot spring water was used for resuspension, dilution, and subsequent filtration of sediment preparations. Sediment samples were suspended in 10 ml filter-sterilized water and vortexed vigorously for 2 min before sonication on ice for 30 sec. The final dilution and ultrasonic treatment time for each experiment were varied. One milliliter of diluted sample was placed in a ultrasonic bath to dislodge bacteria from solid particles and distribute the sample evenly on the filters. Samples were then analyzed by optical microscopy.

3.3.3 Cell staining and microscopic slide preparation

Final dilutions (1 : 1000 to 1 : 3000) were made by adding 1 ml DAPI (4',6-diamidino-2-phenylindol) solution for a final concentration of 5 μg/ml DAPI and the samples were stained in the dark for a minimum of 15 min. The resulting 2 ml solution was filtrated through a 0.2 μm black membrane 25 mm diameter filter with a backing filter. Two milliliters of pre-filtered (0.22 μm pore size) rinse water were filtered to remove the excess DAPI from the filter. The filter was wet mounted on microscopic slide with non-fluorescing immersion oil, and stored in the dark at 4°C until observation at Nikon EFD-3 epifluorescence microscope by using appropriate optical filter sets and 100×Plan objective.

3.3.4 Number of active bacteria

The metabolic activity of the free-living and attached bacteria was determined using the tetrazolium redox dye CTC (5-cyano-2,3-ditolyltetrazolium chloride) and cell viability indicator CFDA (5-carboxyfluorecein diacetate). CTC assay was performed using a procedure modified from Rodriguez et al. (1992), in which samples were diluted 1 : 2 with R2A medium. The 5 mM CTC (final concentration) was added to each sample followed by a 20-h incubation with shaking at room temperature in the dark. CFDA was added to the samples to a final concentration of 0.01 mM (Porter et al., 1995). Samples were incubated statically for 20 min in the dark. After incubation samples were filtered through a 0.22 μm black membrane filter with a backing filter. The filters were wet mounted onto a slide with immersion oil. Negative control comprised samples, which were fixed with 1% (final concentration) glutaraldehyde solution.

4. Results and Discussion

The chemical analyses and microbiological observations of hot spring waters, biomats, travertines, and sediments collected from each hydrothermal systems are described as follows.

4.1 Nalychevskie hot springs

Nalychevskie hot springs are located in the valley of the Nalycheya River (Fig. 1). Soils in this area show dark-red color, suggesting high concentration of heavy metals such as As and Fe (Fig. 2A, B). Around the hot spring source, calcareous travertine mounds are formed (Fig. 2C).

Water qualities of this hot springs have been measured at the pool of source and 100 m downstream (Table 1). 6.3-7.1 of pH were obtained there. The values of EC at both measurement points are of 6.3 mS/cm and are in good correlation with the high content of total cations and anions (Table 2B). Moreover, the highest concentration of Na (859.9 ppm) is detected in this hot spring water by AAS analyses (Table 2D). Eh values varied

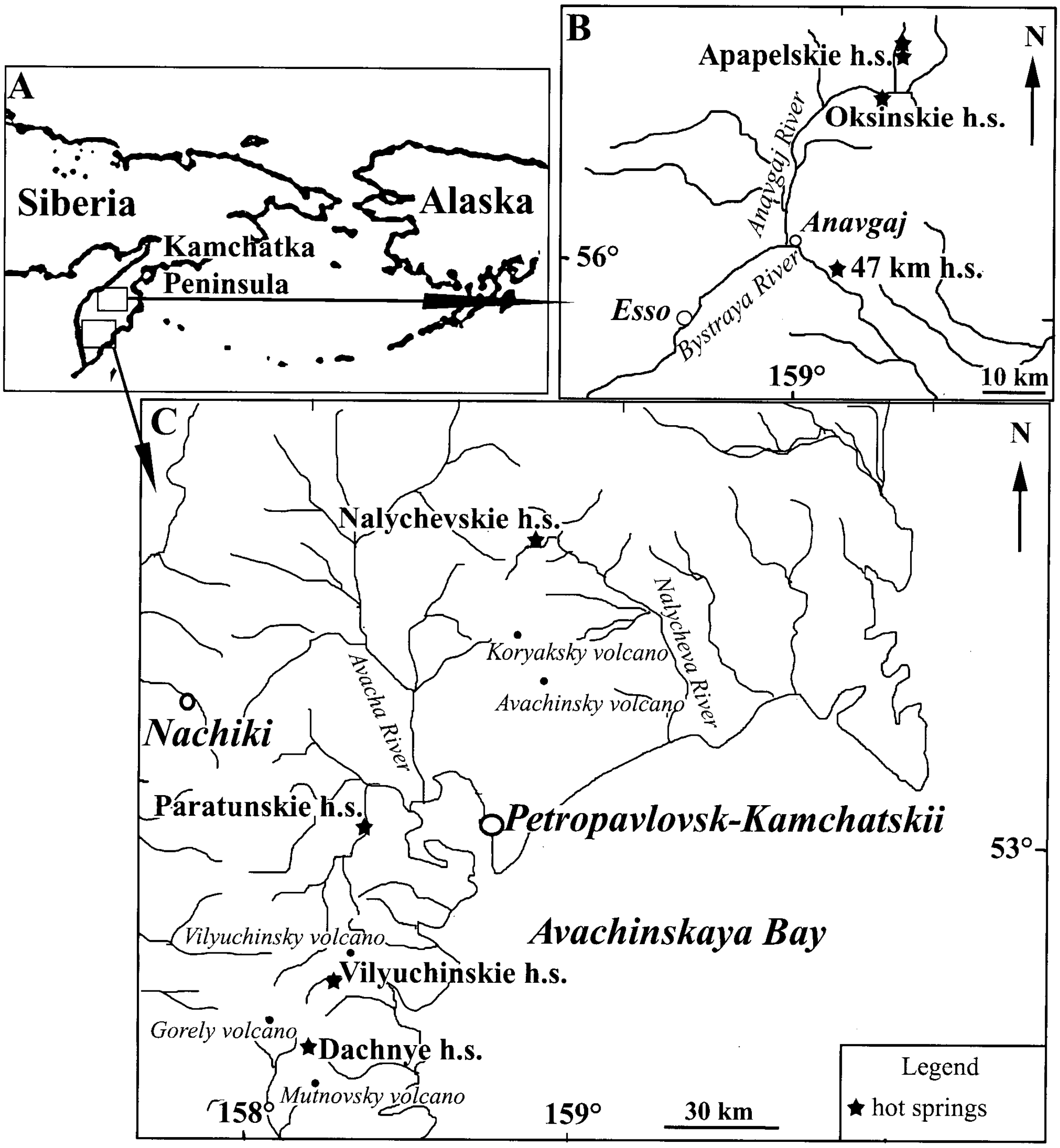

Fig. 1. Locality maps of the study area (A) in Central (B) and Southern (C) parts of Kamchatka, Russia.

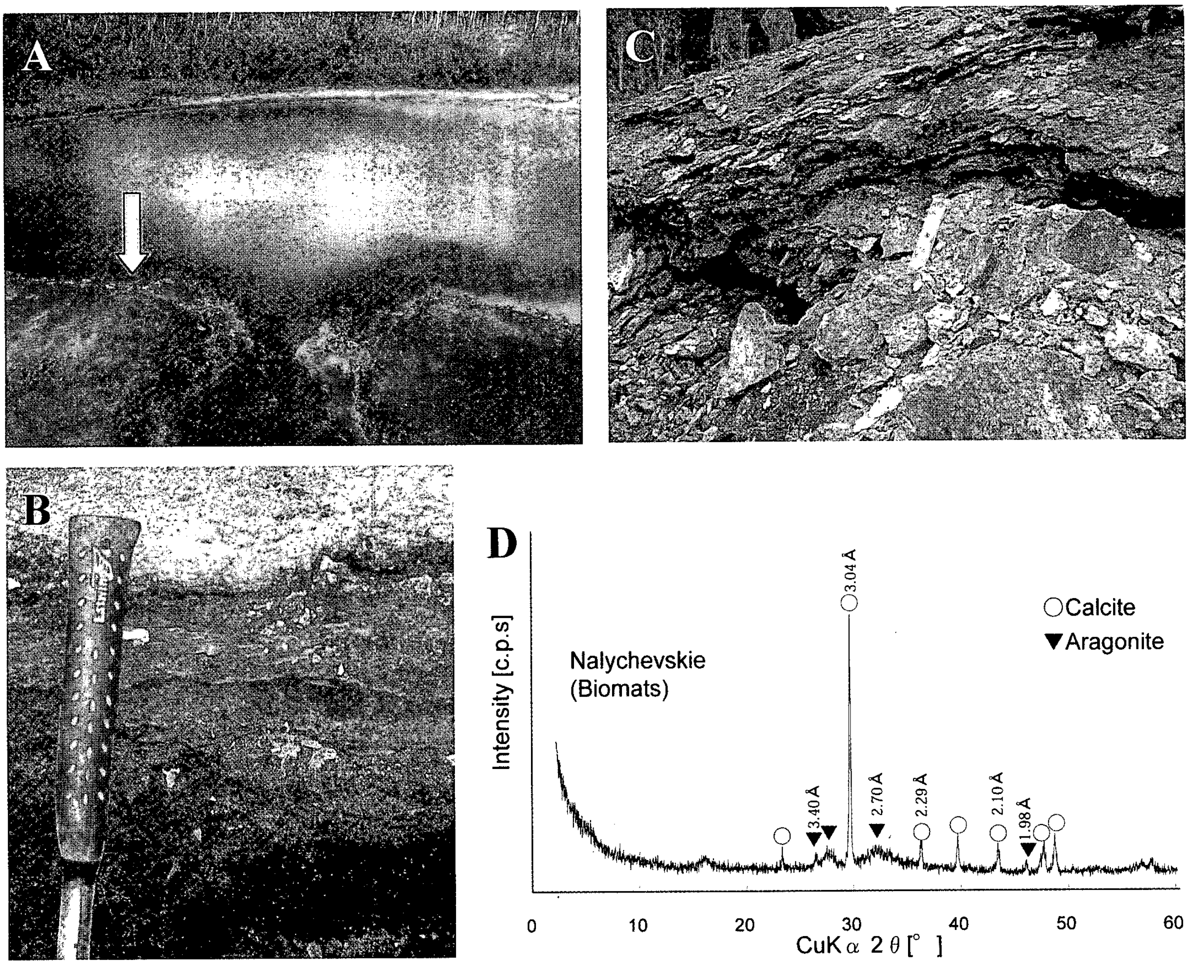

Fig. 2. Field views of Nalychevskie hot springs in Southern Kamchatka. Reddish-brown gelled deposits formed near the source of hot springs. Sampling point is marked by an arrow (A). White, black, and reddish-brown layers are formed in the travertine (B). Large travertine dome develops which alteration of reddish-brown calcareous beds. (C). XRD pattern of the deposits (A) identified calcite and aragonite (D).

from -10 to 40 mV, indicating reductive effect of hot spring water in the pool (source of the hot spring water) and occurrence of oxidation process in downstream. Note that As (6.4 mg/l) and H_3BO_3 (400.5mg/l) contents are significantly high in this water (Table 2B, C).

Reddish-brown deposits that develop in the pool with thermal water are physically loose and collapse easily in the air. Optical micrographs of the deposits showed brown mineral aggregates that were mainly composed of spherical particles (Fig. 3A). Using TEM, these particles are found as aggregations of fine tissue-like minerals (Fig. 3D). The deposit contains extremely high level of As (43.9wt%) and Fe (37.6w%) (Table 3). STEM/EDX analysis revealed that As has similar distribution as Ca and Fe, and not associated with C (Fig. 3D) suggesting inorganic materials. Calcite and aragonite are detected by XRD analysis (Fig. 2D). Epifluorescence micrographs revealed low density of attached bacterial population (Fig. 3B). Short rods and cocci were observed in both types of attached mineral

Table 2A. The list of methods used for analyses of anions and cations in the water samples

Components	Methods	Units	Error range
NH_4^+	Method of straight colorimetric evaluation with Nessler reagent, all-Union State Standard 23268.10-78	mg/l mg-eqv/l	± 5%
Na^+	Method of photometry of flame on spectrophotometer SP-2900, management directive RD 52.24.391-95, all-Union State Standard 23268.6-78	mg/l mg-eqv/l	1-50 mg/l ±15%, > 50 mg/l ±10%
K^+	Method of photometry of flame on spectrophotometer SP-2900, management directive RD 52.24.391-95, all-Union State Standard 23268.7-78	mg/l mg-eqv/l	1-5 mg/l ±20%, > 5 mg/l ±15%
Ca^{2+}	Chelatometry method, management directive 52.24.403-95, PNDF 14.1:2.95-97	mg/l mg-eqv/l	0.5-50 mg/l ± 10%, > 50 mg/l ± 5%
Mg^{2+}	Chelatometry method amount for Ca^{2+} and Mg^{2+}, calculation, PNDF 14.1:2.98-97	mg/l mg-eqv/l	0.5-50 mg/l ± 10%, > 50 mg/l ± 5%
Fe^{2+}	Express colorimetric definition of thiocyanate method, Chelatometry method, all-Union State Standard 23268.11-78	mg/l mg-eqv/l	± 5%
Fe^{3+}	Express colorimetric definition of thiocyanate method, Chelatometry method, all-Union State Standard 23268.11-78	mg/l mg-eqv/l	± 5%
HCO_3^-	Potentiometric definition on universal ion meter EV-74, PNDF 14.2.99-97	mg/l mg-eqv/l	10-90 mg/l ± 10%, > 90 mg/l ± 5%
Cl^-	Volumetrical argentometry method with thiocyanate, PNDF 14.1:2.96-97	mg/l mg-eqv/l	1-10 mg/l ± 25%, 10-500 mg/l ± 10%, >500 mg/l ± 5%
SO_4^{2-}	Volumetrical method with nitromazo, all-Union State Standard 23268.4-78	mg/l mg-eqv/l	± 2.5%
F^-	Potentiometric definition on universal ion meter I-130 with ioncelective electrode, all-Union State Standard 23268.18-78	mg/l mg-eqv/l	± 8%
H_3BO_3	Potentiometric definition on universal ion meter EV-74 with mannitol	mg/l	< 0.3 mg/l ± 30%, 0.3-0.7 mg/l ± 15%, > 0.7 mg/l ±10%
H_4SiO_4 soluted and colloidal	Colorimetrical method attenuated ortho- silicates and all forms attenuated silicates on photocolorimeter KFK-3 with ammonium molibdate ($(NH_4)_6Mo_7O_{24}$), management directive 52.24.433-95	mg/l	0.01-0.3 mg/l ± 50%, 0.3-1.0 mg/l ± 25%, > 1.0 mg/l ± 15%

aggregates and free-living forms, whereas, filaments from 5 to 15 μm in length were visualized only as free-living organisms. Mostly filaments were detected as enzymatically active cells by CFDA treatment (Fig. 3C).

4.2 Thermal springs at the 47th km

A natural hot springs have been utilized for bath at the 47th km. Water quality of this springs is pH 8.2-8.4 and EC 3.6-3.8 mS/cm (Table 1). Drilled borehole opened thermal reservoirs at the depths of 346 m, and the hot springs are self-flowing with discharge about 11.6 l/sec (Fig. 4). The values of pH, EC and Eh of this hot spring water are 8.4, 3.79 mS/

Table 2B. Chemical composition of water samples collected from Southern and Central Kamchatskaya geothermal areas

Localities/ Components(mg/l)	Nalychevskie	47th km/bath	47th km/pump	Oksinskie-1	Oksinskie-2	Apapelskie-2
NH_4^+	0.2	<0.1	<0.1	0.1	<0.1	< 0.1
Na^+	937.2	500.0	540.0	768.2	761.3	357.1
K^+	149.0	1.8	1.9	21.3	22.7	13.9
Ca^{2+}	232.5	264.5	270.5	43.3	44.1	14.0
Mg^{2+}	36.5	<0.2	1.2	23.3	19.0	1.8
Fe^{2+}	0.3	–	–	< 0.3	<0.3	<0.3
Fe^{3+}	0.7	–	–	< 0.3	<0.3	<0.3
total cations	1356.3	766.3	813.6	856.2	847.1	386.8
HCO_3^-	497.9	35.4	30.5	1235.0	1200.8	228.2
Cl^-	1453.9	588.6	617.0	187.9	187.9	138.3
SO_4^{2-}	456.3	845.3	922.2	552.3	571.6	408.3
F^-	1.0	2.0	2.1	2.2	2.3	6.1
total anions	2409.1	1471.3	1571.8	1977.4	1962.6	780.9
H_3BO_3	400.5	89.0	90.3	108.8	113.7	63.7
$H_4SiO_{4\ soluted}$	232.0	33.0	32.1	231.0	200.0	300.0
$H_4SiO_{4\ colloidal}$	156.0	17.1	14.8	89.0	223.0	385.0

–; Not Detected

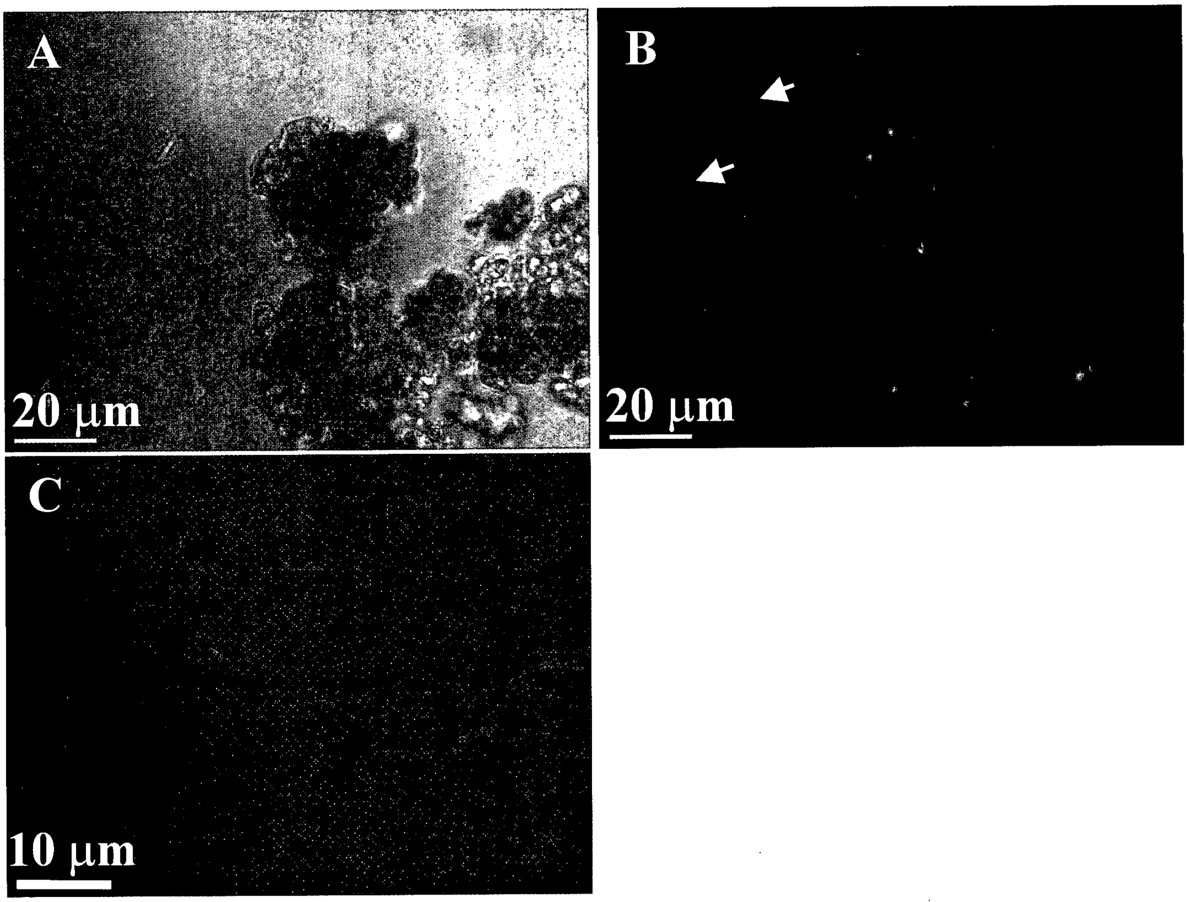

Fig. 3. Micrographs of brown colored microbial mats at the Nalychevskie hot springs. Optical light (A) and epifluorescence (B) micrographs show the small number of microorganisms such as spherical and rods-shaped bacteria that are attached to the mineral particles. White arrows point free-living bacteria. Filamentous bacteria are observed as active free-living bacteria and are visualized by CFDA staining (C). STEM/EDX maps of C, Ca, Si, Fe, and As contents in the hot spring deposits collected from Nalychevskie hot springs (D). BF : Bright field image.

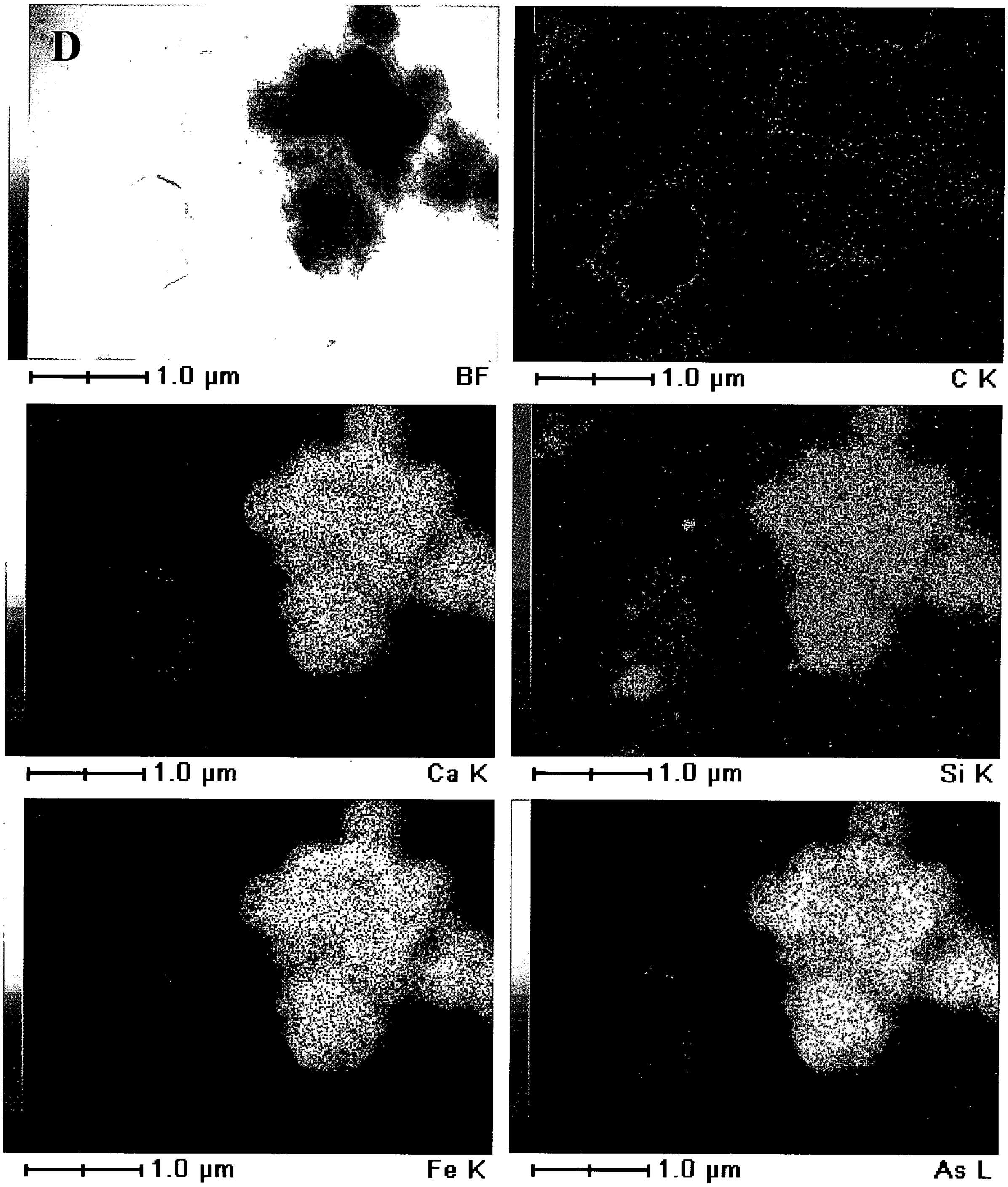
D
1.0 µm
BF
1.0 µm
C K
1.0 µm
Ca K
1.0 µm
Si K
1.0 µm
Fe K
1.0 µm
As L

Table 2C. Chemical compositions of hot spring waters measured by ICP-MS and ICP-AES

Localities/ Components	Detection Limits (DL, μg/l)	Nalychevskie	47th km/bath	47th km/pump	Oksinskie-1	Apapelskie-2	Dachnye	Vilyuchinskie-2	Vilyuchinskie-3	Vilyuchinskie-5 (mg/l)
Li	0.08	4.2	0.1	0.1	0.9	0.8	2.0*	0.7	0.7	0.6
Be	0.01	0.28*	0.1	-	0.091*	0.082*	0.16*	0.081*	0.12*	0.15*
Al	3	-	-	-	-	0.7	4.1	39.2*	33.3*	0.4
P	48	-	-	-	-	0.1	0.4	-	-	-
V	0.5	-	-	-	5.5*	-	35.1*	5.3*	4.9*	<1
Mn	0.4	0.6	-	-	0.1	0.1	65.5*	0.4	0.4	0.5
Fe	7	0.9	-	-	1.6	-	7.7	25.4	3.6	1.3
Co	0.04	0.40*	1.8*	0.27*	0.17*	0.073*	4.2*	0.24*	0.24*	0.29*
Cu	1	-	0.01*	-	-	-	35.6*	-	-	-
Zn	2	-	2.5*	-	-	-	33.6*	4.0*	19.0*	12.7*
Ge	0.08	-	7.6*	15.5*	-	-	<0.4	11.8*	12.1*	10.6*
As	0.3	6.4	0.5	0.5	2.4	1.4	73.7*	0.6	0.7	0.6
Se	0.6	<3*	-	-	-	-	-	-	-	-
Br	26	4.6	1.4	1.6	0.5	0.3	53.6*	0.4	0.5	0.4
Rb	0.09	0.8	8.9*	9.4*	-	-	41.3*	77.5*	77.1*	72.1*
Sr	0.5	2.3	1.0	1.0	1.3	0.2	0.4	1.1	1.2	1
Y	0.01	0.28*	-	-	0.079*	-	6.1*	0.077*	0.3*	0.76*
Mo	0.05	9.9*	46.1*	50.4*	-	-	0.7*	3.0*	2.0*	1.8*
Cd	0.02	-	0.67*	0.25*	0.33*	0.11*	0.3*	-	0.68*	0.074*
Sn	0.08	0.77*	-	-	-	-	-	-	-	-
Sb	0.01	0.1	0.33*	0.37*	-	0.2	0.61*	0.09*	8.1*	5.3*
Cs	0.002	0.8	2.0	2.7	-	0.1	1.4*	67.5*	68.3*	56.8*
Ba	0.1	0.1	8.9	8.0	-	0.1	0.2	69.8*	65.6*	57.9*
Ce	0.006	-	3.1*	3.7*	-	0.024*	5.1*	0.0088*	0.034*	0.08
W	0.09	1.5*	1.6*	1.7*	0.83*	-	-	5.4*	6.0*	3.6*
Tl	0.003	0.013*	0.055*	0.024*	0.097*	0.22*	0.37*	-	0.013*	-
Pb*	0.1	-	2.0*	0.43*	1.3*	0.60*	9.5*	0.17*	0.56*	1.4*
Bi	0.01	-	0.1	-	-	-	0.7*	-	-	-
Th	0.005	-	-	-	-	-	0.91*	-	-	-
U*	0.002	-	0.045*	-	0.039*	0.0071*	0.67*	0.0028*	-	0.0039*

*: μg/l, -: less than detection limits

Table 2D. Chemical compositions of hot spring waters measured by Atomic absorption spectrophotometer

Samples	Na	K	Ca	Mg	Fe	Mn (ppm)
Nalychevskie	859.886	121.467	191.256	25.736	0.233	0.327
47th km	488.763	3.431	203.770	0.206	-	-
Oksinskie-1	457.350	37.103	6.663	9.770	-	-
Oksinskie-2	-	15.213	23.660	7.846	0.380	0.028
Apapelskie-2	598.130	9.965	1.107	0.137	-	0.055
Dachnye-middle	24.264	13.382	19.064	9.848	0.642	0.026
Dachnye-lower	44.266	4.533	0.395	0.030	0.436	0.021
Dachnye-mud	23.422	7.580	0.899	1.006	0.162	0.114
Vilyuchinskie-2	207.737	15.937	70.737	43.187	0.099	0.215
Vilyuchinskie-3 bottom	174.081	15.053	67.417	3.967	0.116	0.249
Vilyuchinskie-3 cup	-	26.912	290.747	-	0.060	-
Vilyuchinskie-5	193.968	13.435	68.938	3.648	0.450	0.280

-: Not detected

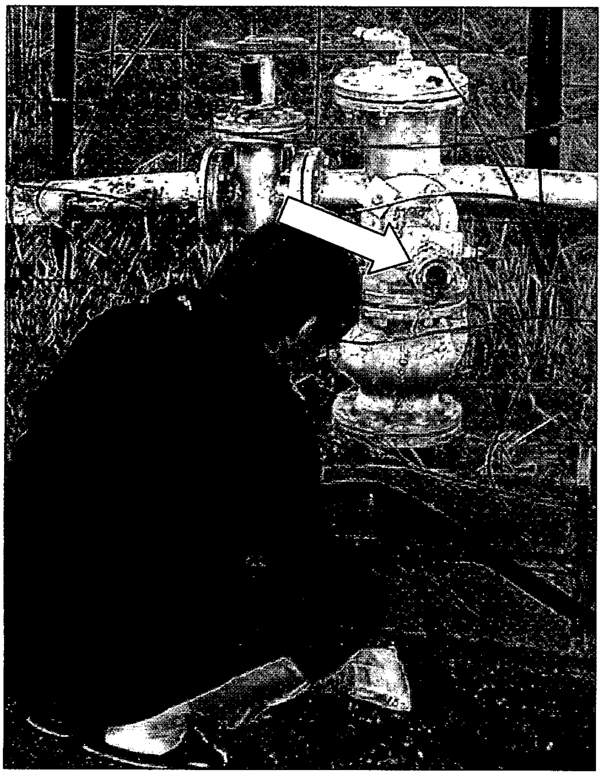

Fig. 4. Field view of sampling and measuring points (an arrow) at the thermal springs at 47th km in Central Kamchatka.

cm and 350 mV, respectively (Table 1). White deposits are attached on the water pump. This deposit contains Ca (65.3w %) and S (31.28wt%) with the traces of Al, Si, Fe, Zn, As, and Sr (Table 3).

4.3 Oksinskie hot springs

There are two hot springs (Oksinskie-1 and Oksinskie-2) in Oksinskaya hydrothermal system (Fig. 5). Products of hot spring activity have thickly deposited around this area. Particularly, a large travertine mound develops at the Oksinskie-2 hot springs (Fig. 5 B, C).

Water qualities are similar in Oksinskie-1 and Oksinskie-2 hot springs, such as neutral pH, EC 3.7-3.8 mS/cm and Eh 120-130 mV (Table 1). Characteristics of these hot spring waters are Na -HCO_3-type and high concentration of As (2.4mg/l) and Sr (1.3mg/l) (Table 2B, C).

Around sources of both of hot springs, green and reddish-brown colored microbial mats develop (Fig. 5A, C). Surface of the biomats collected from Oksinskie-1 is consisted of filamentous cyanobacteria (Fig. 5D). Compositional layering develops in the biomats depending on the density of the fiber of algae. Ferrihydolite deposit, which forms reddish brown layer is abundant in the biomats. Fragments of black organic matters are found at

Table 3. Energy dispersive X-ray fluorescence (ED−XRF) analyses of travertines, biomats, and clays collected from hot springs in Kamchatka

	ED-XRF (wt%)																
Sampling points	Materials	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe	Zn	As	Sr	Zr	Cd	Hg
Nalychevskie-1	D	-	-	-	2.58	-	-	0.44	14.85	-	0.70	37.56	-	43.88	-	-	-	-
Nalychevskie-2	B	-	-	-	2.30	-	0.49	0.39	32.13	-	0.76	33.01	-	30.92	-	-	-	-
47th km	T	-	-	0.94	1.64	-	31.28	-	65.30	-	-	0.29	0.25	0.10	0.21	-	-	-
Oksinskie-1	B	-	2.63	0.35	18.31	-	1.55	0.47	43.76	-	0.48	31.10	-	0.59	0.76	-	-	-
Apapelskie-1	T	-	0.98	0.50	28.30	-	1.16	0.62	63.93	0.35	0.17	3.41	-	0.10	0.47	-	-	-
Apapelskie-1	B	-	1.03	1.28	15.76	0.29	1.84	0.81	71.08	0.58	0.23	6.11	-	-	0.45	-	-	0.57
Apapelskie-2	T	-	-	0.77	64.61	-	1.00	0.84	26.66	0.35	1.11	4.19	-	0.15	0.22	-	-	-
Paratunskie	T	14.63	-	-	-	-	62.68	0.71	2.34	-	0.50	9.00	-	-	-	-	9.56	-
Dachnye	C	-	-	9.38	42.10	-	7.81	5.36	6.13	4.38	0.54	23.67	-	-	0.36	0.21	-	-
Vilychinskie-2	T	-	-	-	8.12	-	0.84	-	74.07	-	0.59	13.85	-	1.61	0.92	-	-	-
Vilychinskie-3	T	-	-	-	0.34	-	-	-	97.81	-	-	0.90	-	-	0.94	-	-	-
Vilychinskie-5	B	-	-	0.37	4.45	-	-	-	78.56	-	3.74	11.30	-	1.55	-	-	-	-
Vilychinskie-5	T	-	-	-	0.71	-	0.24	-	94.67	-	2.24	1.67	-	0.22	0.25	-	-	-

D: Gelled Deposits, T: Travertine, B: Biomats, C: Clays. -: Not detected

the bottom of the biomats. The result of ED-XRF analysis of biomats shows concentration of Si (18.31wt%), Ca (43.76wt%), Fe (31.1wt%), and Mg (2.63wt%) with the traces of Al, S, K, Mn, As, and Sr (Table 3).

Rust microbial mats were mainly composed by variety of filamentous organisms (Fig. 6A, C, E). Most of them were covered with brown colored mineral sheath or capsule (Fig. 6C, E). They were filamentous algae, cyanobacteria, and bacteria. Blue fluorescence of DAPI staining and red fluorescence of chlorophyll were detected only from sheathless organisms (Fig. 6D, F). The density of filamentous bacterial population was quite high, that some of mineral particles could not be observed inside the microbial mats by epifluorescence microscopy (Fig. 6B). Variety of respiring-active spherical and rods-shaped bacteria was visualized by CTC treatment (Fig. 6H, G).

4.4 Apapelskie hot springs

We visited two hot springs (Apapelskie-1 and Apapelskie-2) in this area. The waters of Apapelskie hot springs show neutral pH. EC varies from 2.00 to 2.38 mS/cm and Eh is about 330 mV (Table 1).

Green microbial mats are formed around the source of the Apapelskie-1 hot springs (Fig. 7A). In the biomats collected from Apapelskie-1, calcareous thin layers

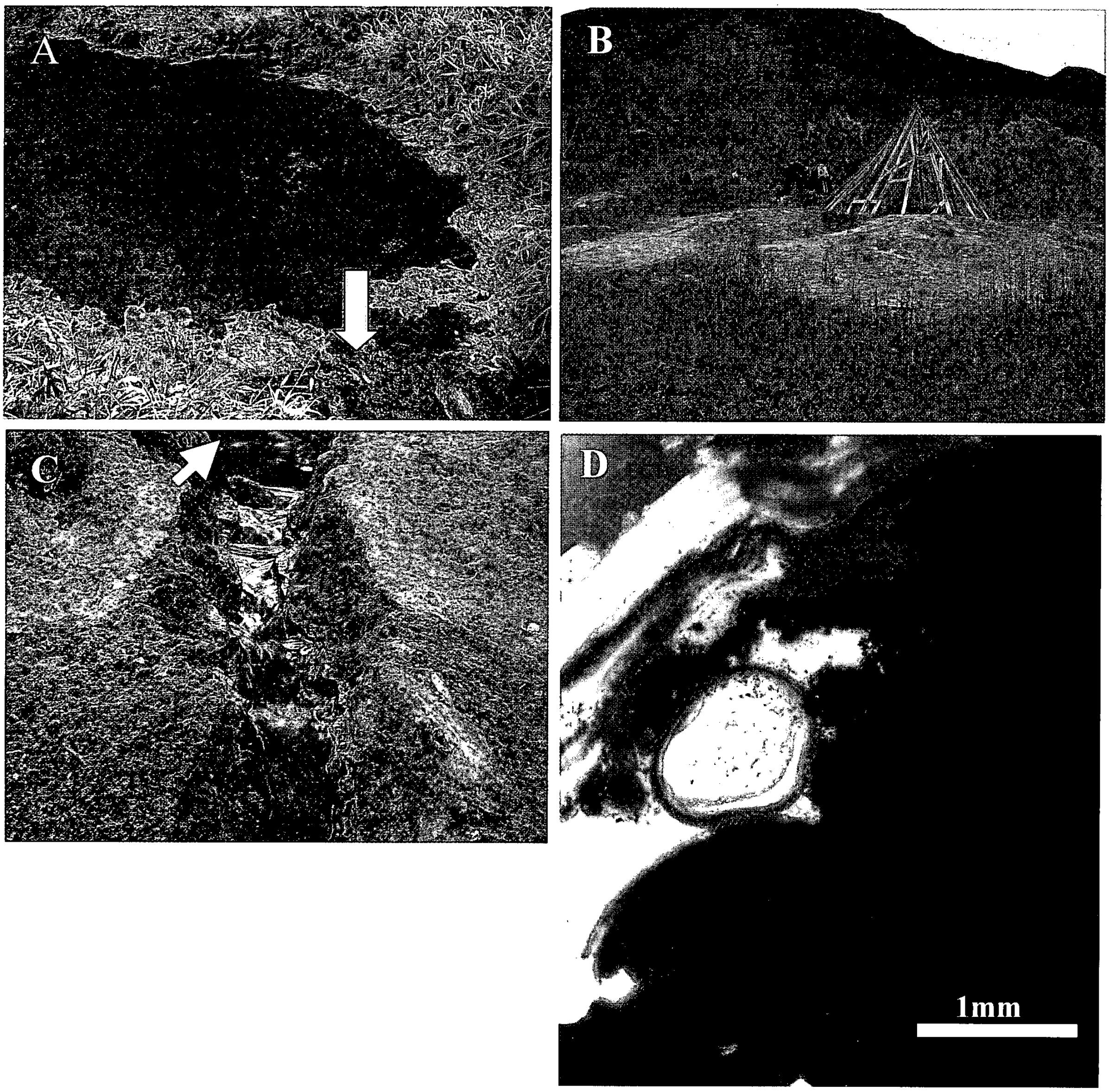

Fig. 5. Source of hot springs in Oksinskie-1 Central Kamchatka (A). Green and reddish-brown biomats (an arrow) dominantly develop. Travertine mound formed around Oksinskie-2 hot springs (B). Stream of hot spring water flowing down from source (pointed by an arrow) of Oksinskie-2 hot springs. Green and reddish-brown biomats develop in the stream (C). Optical light micrograph of thin section of agar embedded green biomats collected from Oksinskie-1 hot springs (D).

develop covering on the surface. They are interlaid with soft layers (Fig. 7B). Calcareous layers are 1-3 mm in thickness and quite fragile. Main component of the layer is anhedral calcite grain, which is irregular in size and shape (Fig. 7C). The calcareous layer contains Ca (63.93wt%), Si (28.3wt%), Fe (3.41wt%), and Mg (0.98wt%) with the traces of Al, S, K, Ti, Mn, As, and Sr (Table 3, Fig. 7D). The thickness of soft layers is about 2-8 mm. Soft parts of biomats are mainly consisted of long filamentous algae and cyanobacteria. Even under the calcite layer, photosynthetic organisms keep alive. Soft layer also have

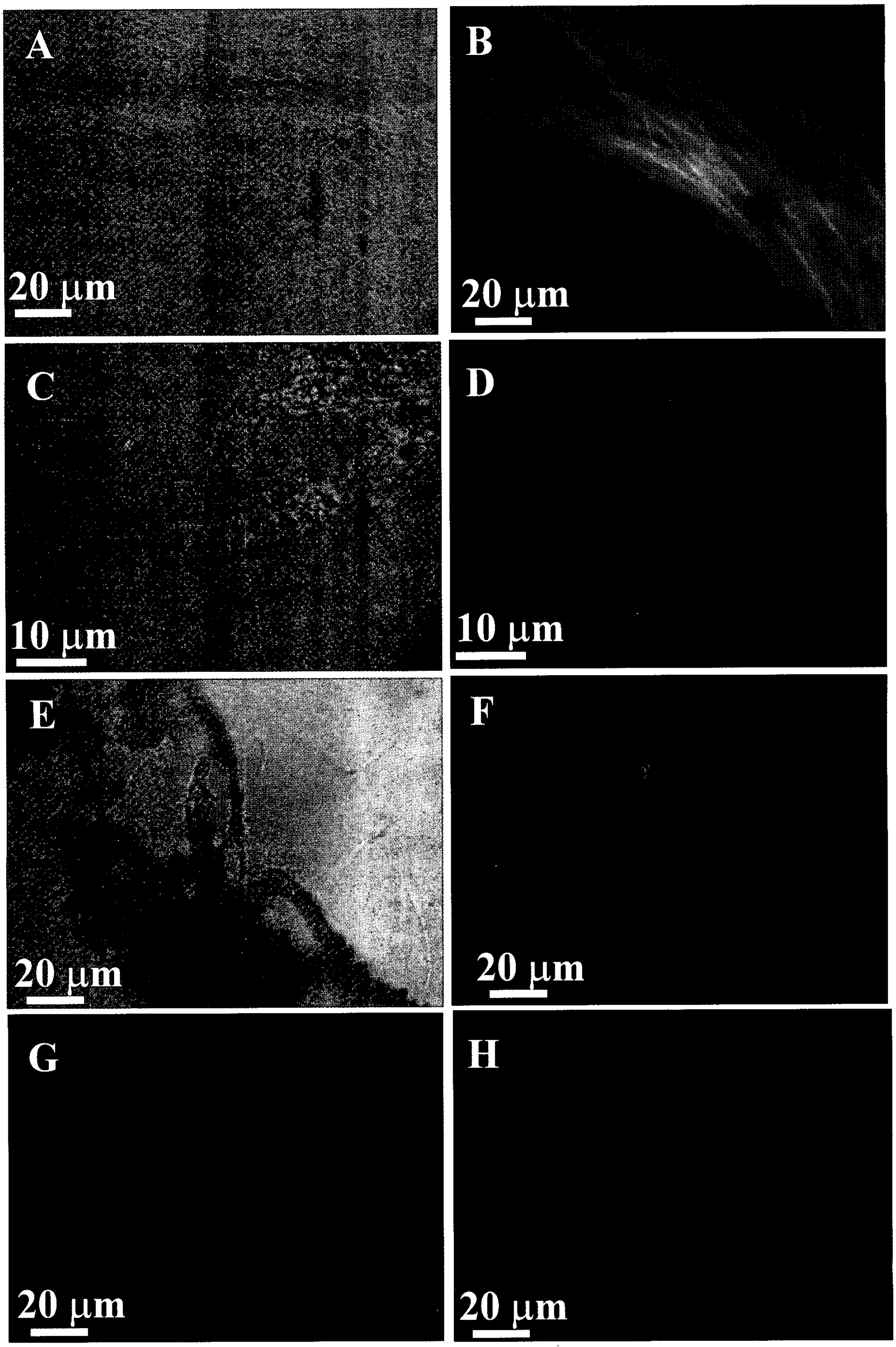

Fig. 6. Micrographs of reddish-brown colored microbial mats collected from the Oksinskie-1 hot springs. Optical light micrographs show filamentous (A) and chained (C, E) organisms that are abundant in the biomats. Epifluorescence micrographs revealed high density of filamentous bacteria population (B) and blue and red fluorescence of sheathless chained microorganisms (D, F). Epifluorescence micrographs of respiring bacteria (G, H) show strong red fluorescence of microorganisms that are associated with mineral particles.

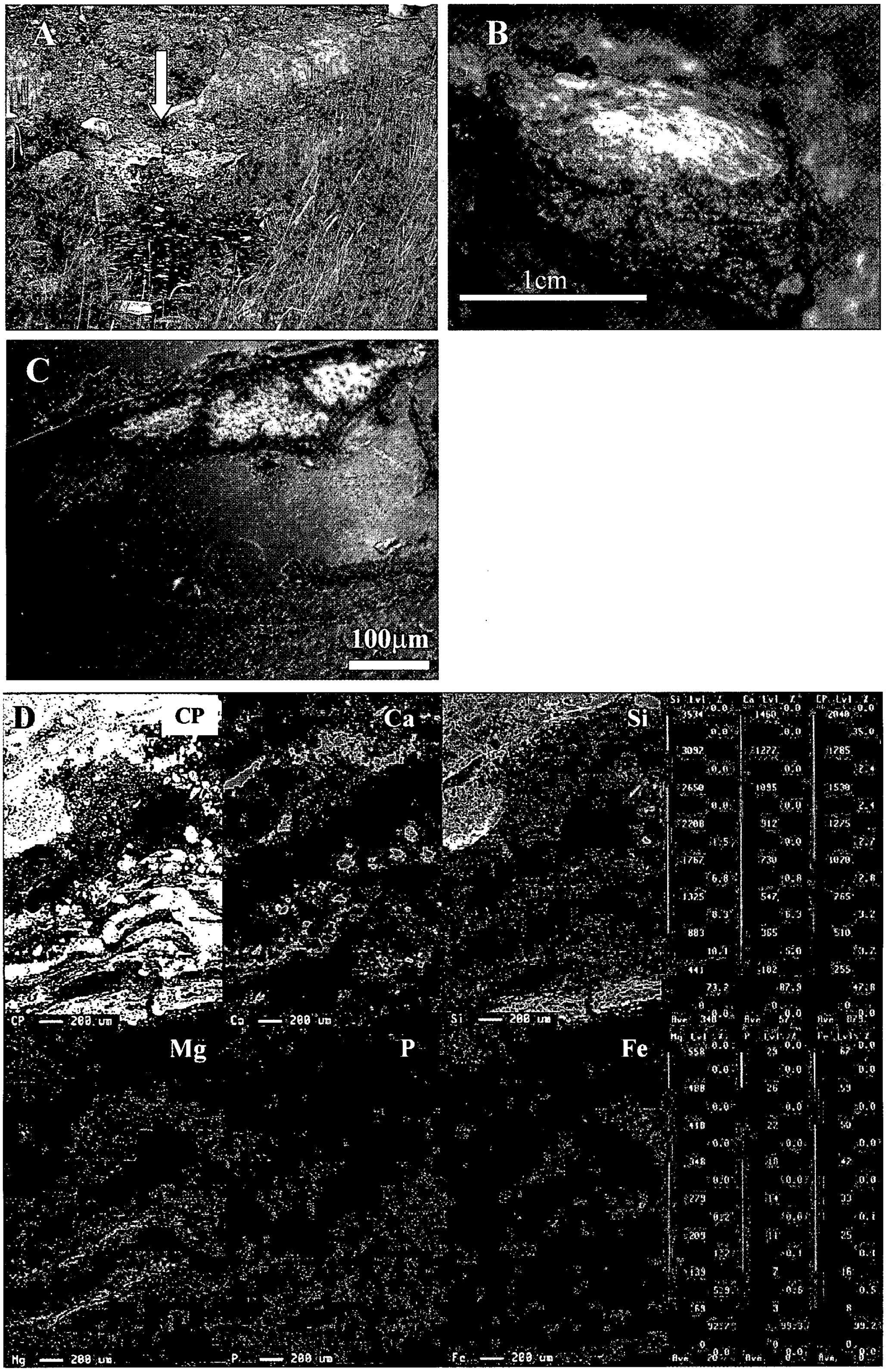

Fig. 7. Field views of the source of spring water (an arrow) of the Apapelskie-1 hot springs in Central Kamchatka (A). Green biomats in which soft parts interbeding with calcareous sheets (B). Thin section of biomats collected from Apapelskie-1 hot springs (C). A calcareous sheet covers on the surface of green biomats. EPMA chemical composition maps of the biomats of (B) (D).

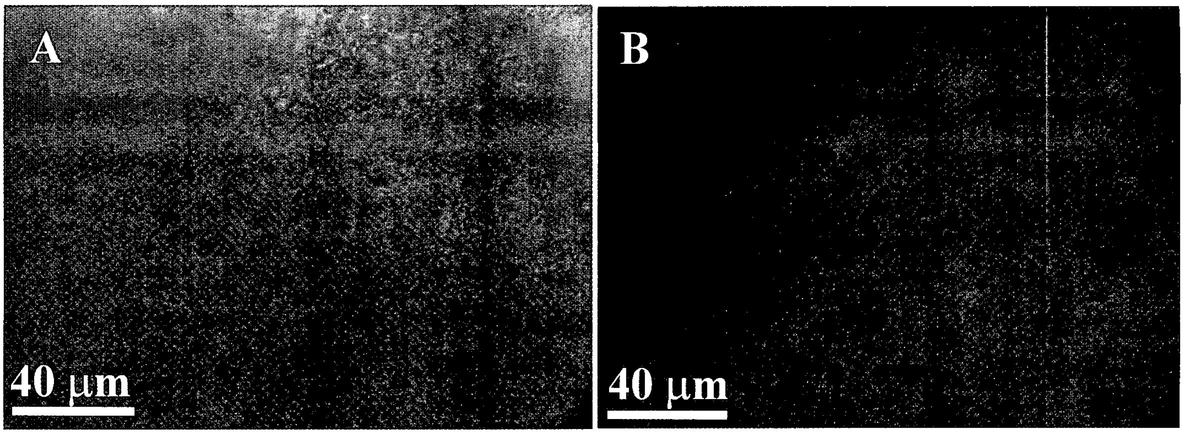

Fig. 8. Optical light (A) and epifluorescence (B) micrographs of green microbial mats collected from the Apapelskie-1 hot springs showing brown colored mineral particles associated with chained photosynthetic cyanobacteria (*Anabaena* spp.).

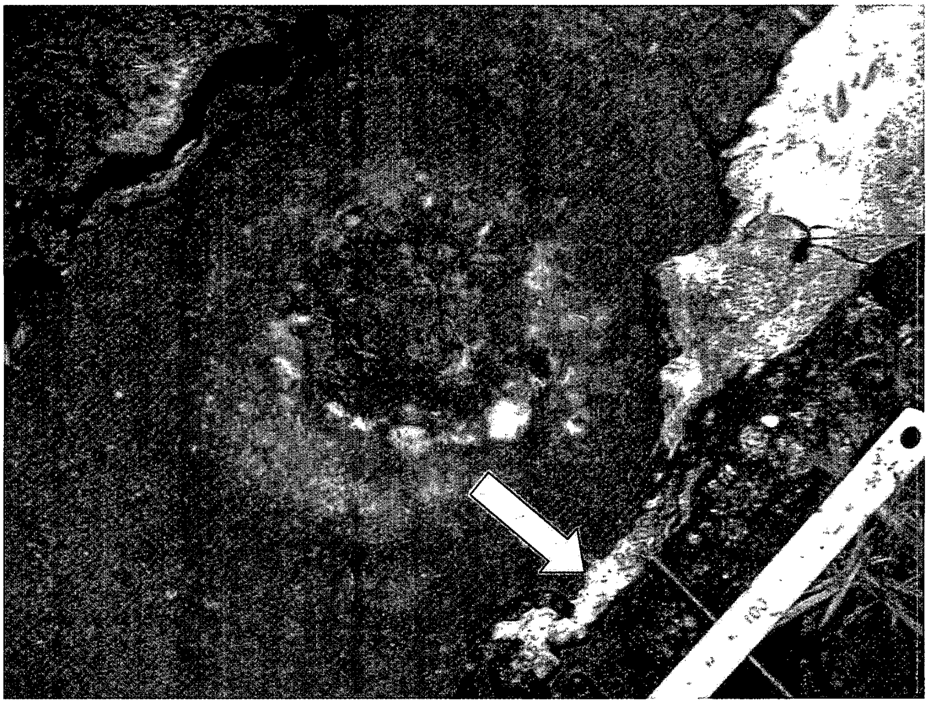

Fig. 9. Source of hot spring water at 91°C in Apapelskie-2. Green biomats formed around the source of hot springs are sandwiched by calcareous sheets (an arrow).

similar elemental composition to calcareous layer. However, 0.57 wt% of Hg concentration is detected only in the soft part of biomats (Table 3). Optical micrographs of Apapelskie-1 green microbial mats showed the presence of brown mineral aggregates and photosynthetic cyanobacteria (*Anabaena* spp.) (Fig. 8A). The dead spherical sheaths were found mainly in the mineral aggregates. On the other hand, strong red fluorescence of chained microorganisms was observed by epifluorescence microscopy (Fig. 8B).

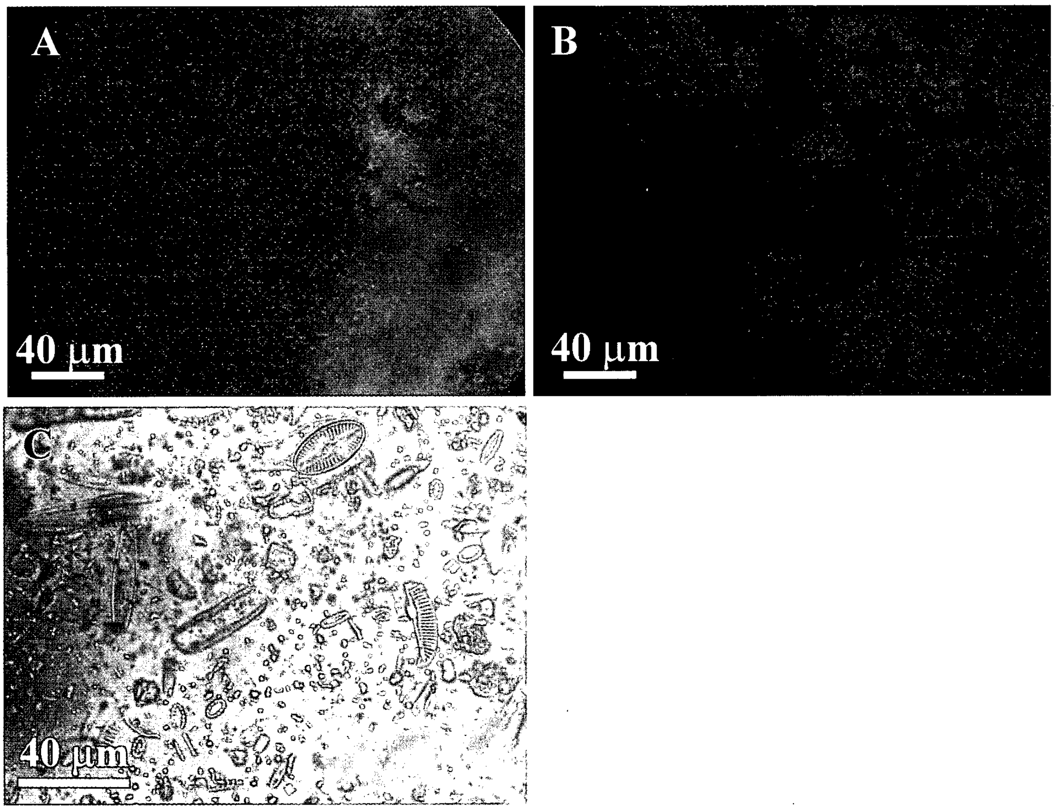

Fig. 10. Optical light (A, C) and epifluorescence (B) micrographs of green microbial mats collected from the Apapelskie-2 hot springs. Cyanobacteria (*Anabaena* spp.) and diatoms are dominant in the mats.

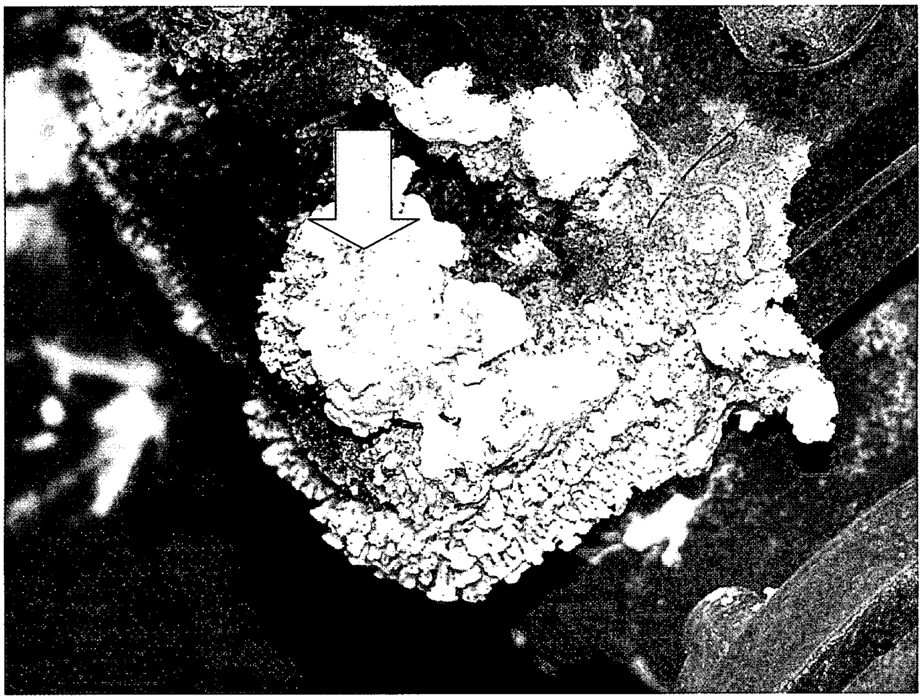

Fig. 11. View of white deposits attached on the water pump (an arrow) of Paratunskie hot springs in Southern Kamchatka. The ED-XRF analysis of this deposits showed the high concentration of Cd (9.56wt%).

The hot spring water with temperature of 91°C gashes out at Apapelskie-2 (Fig. 9). The biomats in Apapelskie-2 have similar structure to those in Apapelskie-1 that the soft layers are sandwiched by calcareous thin layers. Calcite grains in isolated form (i.e., calcite ball) are rarely found in the biomats. Major constituents of soft parts of the biomats are algae and organic matters, such as decayed stems and leaves of plants. Apapelskie-2 biomats showed concentration of Si (64.61wt%), Ca (26.66wt%), Fe (4.19wt%), Mn (1.11wt%), and S (1.00wt%) with the traces of Al, K, Ti, As, and Sr (Table 3). Both fine fibrous and spherical algae, which have bright green color are observed in the biomats. Apapelskie-2 microbial mats showed a high density of diatom population and photosynthetic chained spherical cyanobacteria that were mainly found in aggregation with mineral particles (Fig. 10). The diatoms varied in size and shape. High Si content of biomats could be considered as a contribution of dense diatom population. On the other hand, low number of bacterial cells was observed both in free-living and in attached forms.

4. 5 Paratunskie hot springs

Water of Paratunskie hot springs is pumped up from 1080 m depth, and utilized for bath in sanatorium. Water quality was measured at the pump. The values of pH 8.3, EC 2.45 mS/cm and Eh 30 mV were obtained for this hot spring water (Table 1). White deposits are attached on the water pump (Fig. 11). Chemical analysis of the deposits revealed presence of S (62.68wt%), Na (14.63wt%), Cd (9.56wt%), Fe (9.00wt%), and Ca (2.34wt %) with the traces of K and Mn (Table 3).

4. 6 Dachnye hot springs

Studied area of Mutnovskie geothermal field is approximately 50,000 m^2 placed inside the geothermal electric power station (Fig. 12A). There are a large number of gushes of vapor and hot water in this area. Hot spring waters are neutral to acidic pH up to 3.3. The redox potential is high ranging from -180 to 90 mV (Table 1). On the other hand, EC shows the lowest values in comparison with other hot spring waters and varies from 0.23 to 0.65 mS/cm. Moreover, remarkably low concentrations of Na (23.4-44.3 ppm), K (4.5-13.4 ppm), and Ca (0.4-19.1 ppm) are detected by AAS analysis (Table 2D).

Argillization of volcanic rocks and volcanoclastic materials is significantly proceeded, which may be caused by intense hydrothermal alteration in this area (Fig. 12B). Minerals found in the clays are kaolinite, smectite, pyrite, and small amount of silica minerals (Fig. 12F). The clays show concentration of Si (42.10wt%), Fe (23.67wt%), Al (9.38wt%), S (7.81wt%), K (5.36wt%), Ca (6.13wt%), and Ti (4.38wt%) with the traces of Mn, Sr, and Zr (Table 3).

Thin crusts, which consist of hydrothermal deposits and algae, are found around gushes (Fig. 12C). They show irregular pachy pattern combination of sulfur-rich dark-yellow parts, Fe-rich brown parts and parts of green biomass of photosynthetic organisms. Jarosite and kaolinite are identified in this biomats (Fig. 12F).

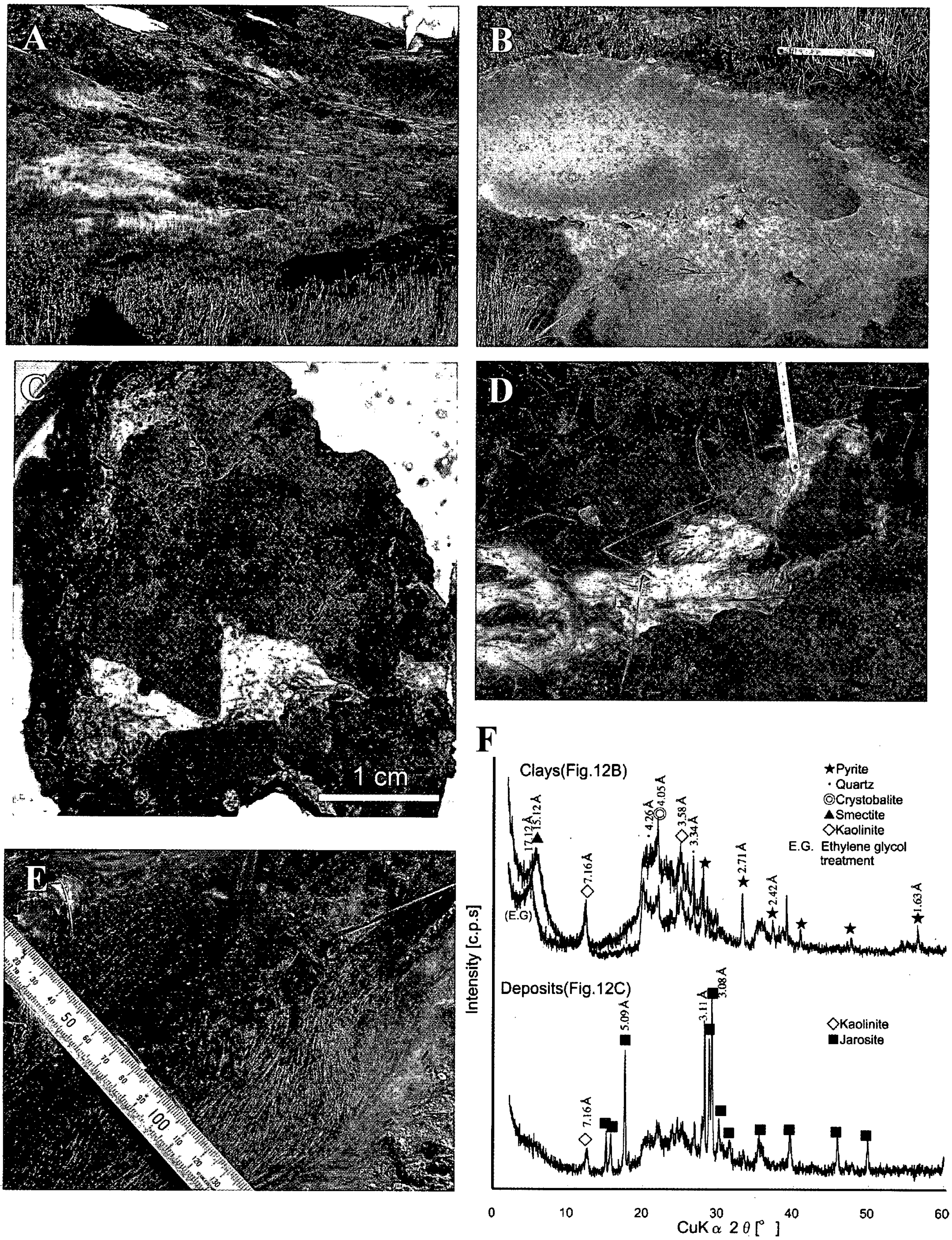

Fig. 12. Field views of studied area of Dachnye hot springs in Southern Kamchatka (A). Clay deposits around a hot water gash (B). Thin crust made by hydrothermal deposits and green algae collected from Dachnye hot springs (C). White (D) and black (E) filamentous microbial mats formed around the gashes of hot spring water. XRD patterns of the clays indicated kaolinite, smectite, pyrite, and small amount of silicate minerals, and the deposits identified jarosite and kaolinite (F).

White and black colored microbial mats were found in the hot spring water. They have filamentous shape and are streaming in the water (Fig. 12D, E). Optical microscopy revealed the presence of elongated rod-shaped bacteria in both mats (Fig. 13). Free-living rods were mainly found in white microbial mats (Fig. 13A), whereas, they formed filamentous structures with mineral particles and were attached to the filaments in the black mats (Fig. 13B, C, D). It is found that the white mats tend to grow under the acidic and lower temperature condition. On the other hand, the black microbial mats grow under the neutral and high temperature condition (Table 1).

4.7 Vilyuchinskie hot springs

Wide variety of water quality, chemical compositions, feature of biomats have been found in Vilyuchinskaya hydrothermal system (e.g. Tazaki, et al., 2003). This year we investigated three hot springs (V2, V3 and V5 in Tazaki et al. (2003)), specially focusing on the annual changes of their properties, structures, and material distributions of biomats and travertines.

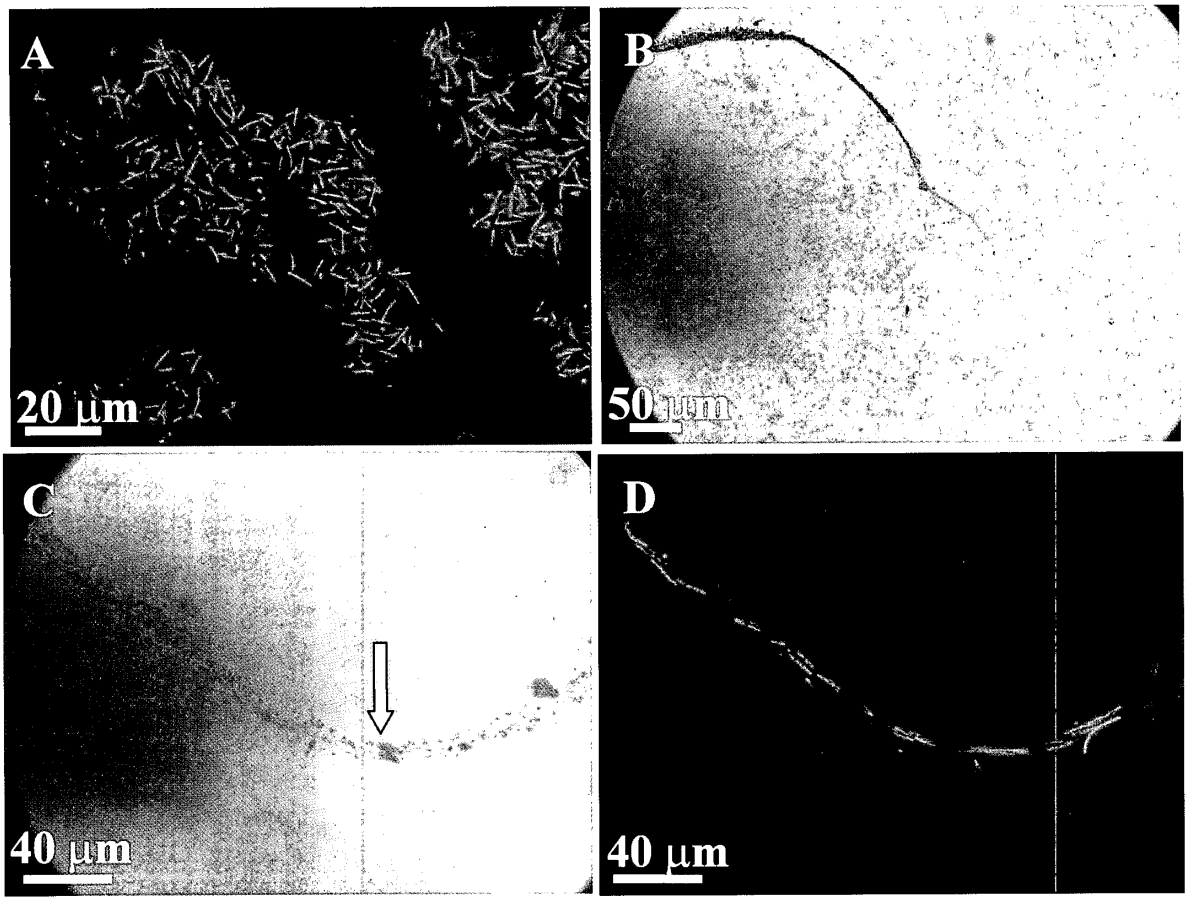

Fig. 13. Optical micrographs of white (A) and black (B, C and D) microbial mats collected from the Dachnye hot springs. Epifluorescence micrograph (A) shows long rods-shaped bacteria that are dominant in white bacterial mats. Optical images of the black filament (B, C and D) showing bacteria associated with mineral particles (an arrow).

4.7.1 Spot V2

Measurement of water qualities and sampling were performed at a hot water pool formed around a pump (Fig. 14A). The water quality of V2 is almost the same with those reported in Tazaki et al. (2003) (Table 1).

Calcareous travertine, ironic brown deposits, red-brown and green microbial mats were found in the pool (Fig. 14A). Calcareous travertine has a laminated texture, an alternation of porous and dense laminae (Fig. 14B). The dense laminae are generally thicker than porous ones, approximately 0.2 mm for former and 0.5-1 mm for latter. Kano et al. (2003) reported similar texture in tufa and discussed the lamination rhythms in relation

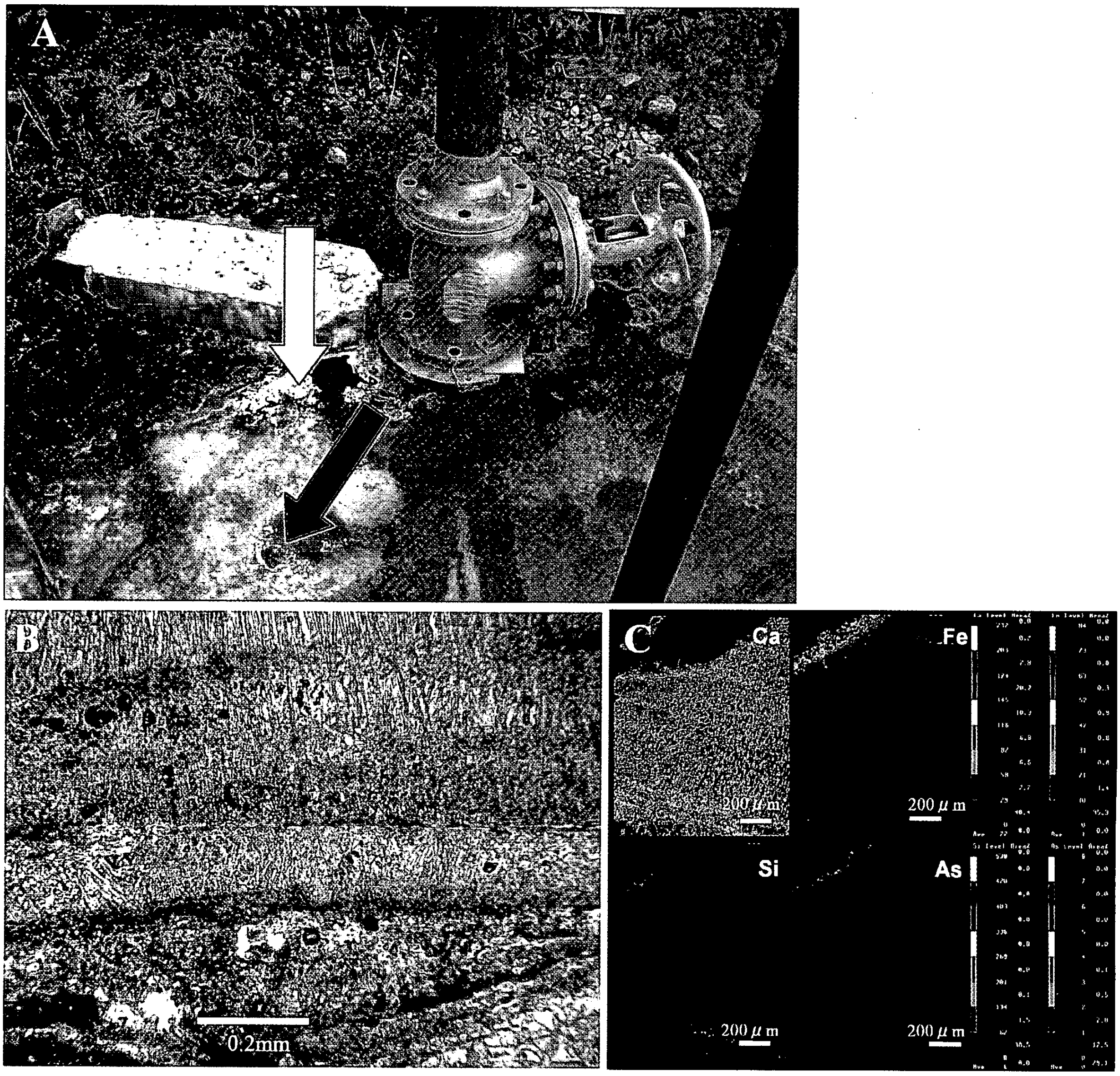

Fig. 14. Field view of water pump in Vilyuchinskie-2 hot springs in Southern Kamchatka (A). Travertine (blue an arrow) and calcite films (red an arrow) are formed. Micrograph of thin section of travertine collected from the point indicated by blue an arrow in A (B). EPMA chemical composition maps of the travertine (blue an arrow) showed concentration of Fe, As, and Si on the surface of travertine (C).

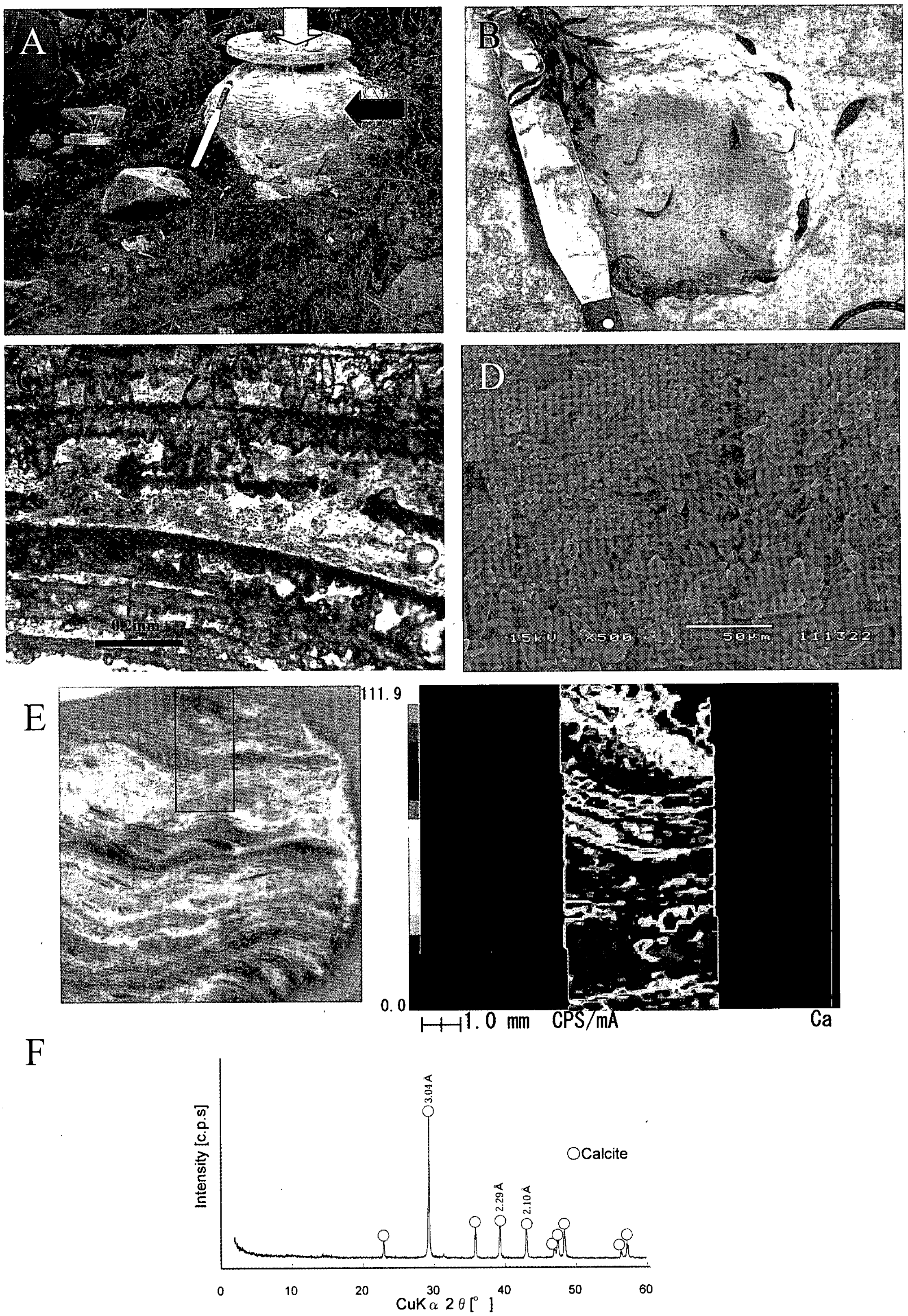

Fig. 15. Field views of source of well in Vilyuchinskie-3 hot springs in Southern Kamchatka (A). Micrograph of thin section of travertine collected at the middle part of the well (pointed by red an arrow in A) (B). Calcite thin film formed on the pit of well (pointed by blue an arrow in A) (C). SEM image of the calcite thin films (D). ED-XRF elemental map showing layered Ca distribution in the travertine shown in B (E). Analyzed area is indicated by red box in the photograph left side of the elemental map (E). XRD patterns of the calcite thin films identified pure calcite (F).

with seasonal changes of rainfall, water temperature and activities of cyanobacteria. They found a tendency that high dense lamina is formed in the season with high temperature and heavy rain fall. Change of water flux from the well and rainfall may be particularly important controlling factors for laminae formation in travertine at hot springs. The major elements of Ca (74.07wt%), Fe (13.85wt%), Si (8.12wt%), and As (1.61wt%) associated with the traces of S, Mn, and Sr were detected in the Vilyuchinskie travertine (Table 3).

Thin calcite films (approximately 20-30 μm in thick) are found floating on the surface of the pool, growing outward from the center of the films (Fig. 14A). At the center part, green biomats are formed around small insects. The films show the ellipsoidal shape with 1 -2 cm in diameter. Optical microscopy revealed that calcite films are formed by gathering of calcite ball with 50 to 100 μm in size.

4.7.2 Spot V3

Hot water of V3 springs was sampled from the top and the bottom of the well (Fig. 15 A). Water quality at the bottom of the well is almost the same as those of Tazaki et al. (2003) (neutral pH and EC of 1.66 mS/cm) except for Eh showing 50 mV (Table 1). On the other hand, the pit at the top of the well has a distinctive water quality ; namely extremely high alkaline condition (pH 12), reductive effect of Eh (-210 mV) and EC valve of 6.92 mS/cm.

The well is coated with thick white travertine, suggesting that hot spring water which has been spilled out and flown down from the pit at the top of the well. The travertine has a laminated structure, which could be caused by periodic intermission of water spill (Fig. 15 B). The thickness of laminae is almost same and very thin (0.05 mm). This travertine has different compositions between outer and inner parts. Outer part of the travertine mostly consists of calcite (Fig. 15F). The concentration of Ca with the traces of Si, Fe, and Sr are detected by ED-XRF (Table 3, Fig. 15E). While inner part deeper than 3 cm from surface, iron-rich reddish-brown laminae develop as well as calcite laminae. It could be considered that this vertical change of chemical composition in the travertine records the history of chemical change of water, namely Ca and Fe-rich water to Ca-rich one.

Optical microscopy of outer part of travertine revealed that each laminae sheet consists of euhedral calcite grains growing to the surface from the same bottom plane of the layer where small grains are aggregated (Fig. 15B). Dark materials are often observed around the bottom of each layer as inclusions of calcite grains. Any metallic elements were hardly detected from there, suggesting organic matter-rich.

A calcite sheet thinner than 20 μm forms on the hot water in the pit (Fig. 15C). Under the microscope, euhedral calcite grains grow with their long axis distributing radially around fine grains, which seem like a gathering of flowers (Fig. 15D).

4.7.3 Spot V5

A large travertine dome is developed at V5 hot springs. "Side part" of V5 hot springs

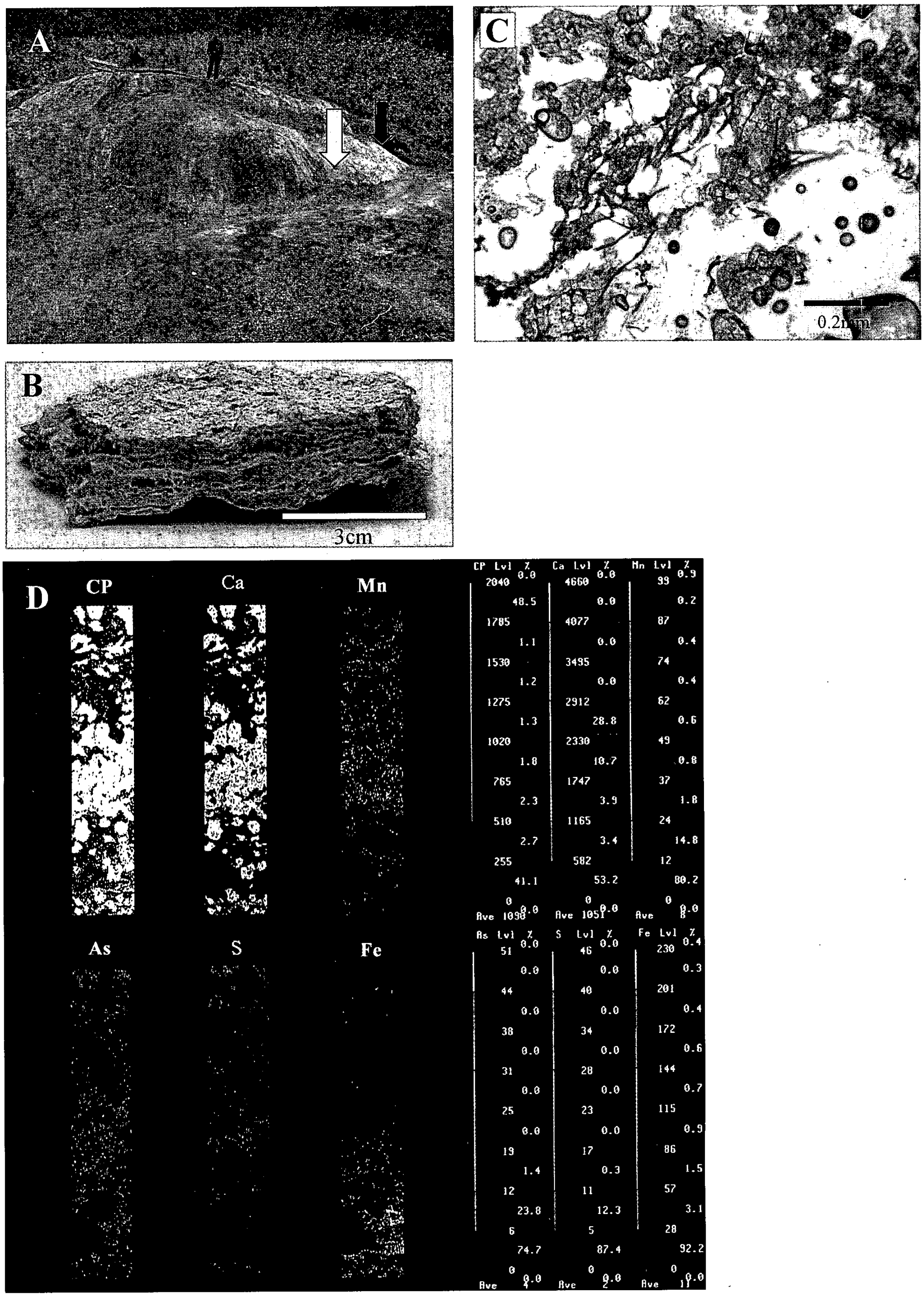

Fig. 16. Field view of travertine dome at Vilyuchinskie-5 hot springs (A). Studied hot springs "V5-side" in Tazaki et al. (2003) is indicated by red an arrow. Analyzed travertine sample collected from the middle part of the dome (marked by blue an arrow at A) (B). White, dark-gray, and brown colored laminae are formed in the travertine. Micrograph of a brown lamina in which iron bacteria assemblage are observed (C). EPMA chemical composition maps showing distribution of Ca, As, S, Mn, and Fe (D). Concentration of Mn and Fe are observed in dark-grey and brown laminae, respectively.

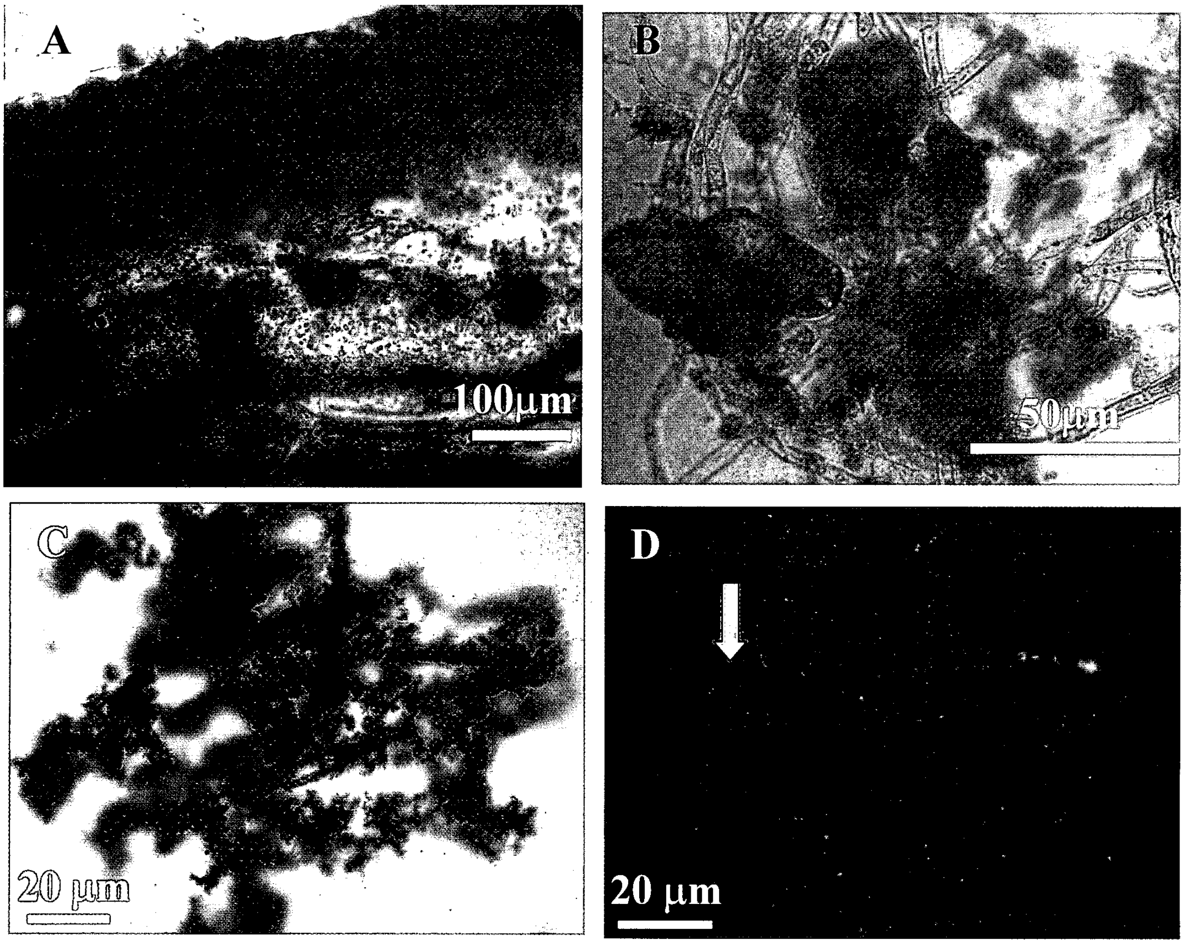

Fig. 17. Micrographs of green biomats collected from V5 hot springs. Thin section of green biomats (A). Calcite balls array parallel to the layering of biomats. Calcite balls attached on fibrous algae in the biomats (B). Optical micrograph of brown microbial mats at the Vilyuchinskie hot springs showing the filamentous mineral particles (C). Variety of bacteria associated with the minerals (an arrow) is inferred by intense green luminescence under epifluorescence mode (D).

(Tazaki et al., 2003) and travertine dome was investigated in this study (Fig. 16A). Water quality of V5 is almost the same as Tazaki et al. (2003) (Table 1).

White-grey colored travertine (Fig. 16A) and green and orange colored biomats are observed in this spot. A travertine collected from the middle part of the dome shows alteration of laminae with white, dark-grey and brown in colors, depending on the amount of calcite (Fig. 16B). Each lamina has a rough surface and low continuity. Assemblages of filamentous iron bacteria cemented by calcite are found in the travertine (Fig. 16C). The travertine is composed of Ca (78.56wt%), Mn (3.74wt%), and Fe (11.30wt%) with the traces of Si, S, As, and Sr according to ED-XRF analysis. EPMA elemental maps show that Fe is concentrated in brown parts of laminae (Fig. 16D).

Compositional layers are developed in the biomats. Major constituent of green biomats is algae, which show fibrous and spherical shapes. Both cyanobacteria and *Chlorophyta* are found in the microbial mats. The alive algae are found even 2-3 mm under the surface. Calcite balls which have a short columnar shape and 5 to 50 μm in size grow in the biomats (Fig. 17A). It is often observed that calcite balls are attached to the fiber of algae, which could provide abundant nucleation site for these calcite grains (Fig. 17B). The shape, size and environment around calcite balls are similar to those described by Yasuda et al. (2000). Calcite balls are not only randomly distributed in the biomats, but also array with black organic matters in a plane which defines the bottom of macro scale layers developed in biomats (Fig. 17A).

Optical micrographs of microbial mats showed the presence of filamentous bacteria and brown mineral particles (Fig. 17C, D). The density of bacterial population was low. In the green microbial mats, concentration of Ca, Fe, Si, Mn, and As with traces of Al are detected (Table 3).

5. Conclusions

Analysis of reproducible field data, laboratory analytical and microscopic data from hot spring waters, travertine and biomats of hydrothermal systems of Southern and Central Kamchatka allow us to make conclusions as follows :

1. The water quality of the Vilyuchinskie hot springs (spots V2, V3 and V5) was almost the same as those of Tazaki et al. (2003) varying within the limits of the seasonal variation except for redox potential for spot V3, where oxidative conditions were detected by Eh value of 50 mV.
2. The acidic pH values were detected in the hot spring waters of the Dachnye-upper hot springs, whereas alkaline conditions were found in the waters of the thermal springs at the 47th km, Paratunskie and V3-top in Vilyuchinskie. The EC values varied from 0.23-0.65 mS/cm in the water of Dachnye to 6.28-6.30 mS/cm in the water of Nalychevskie hot springs. The values of Eh showed the reductive effect of the hot springs waters of Dachnye and Nalychevskie and the oxidative effect of that of all others springs.
3. According to the content of main cations and anions, Nalychevskie hot spring waters are Na-Cl-type, the 47th km springs are Na-SO_4-Cl-type, and Oksinskie are Na-HCO_3-type and Apapelskie waters are Na-SO_4-type. Elemental concentration of hot spring waters is mainly composed of Na, K, Ca, and Mg with high contents of Fe, Mn, As, and Sr.
4. Elemental concentration of hot spring deposits, biomats, and travertines varied significantly. Arsenic, iron, and calcium were detected in high concentration in the gelled deposits and biomats of the Nalychevskie hot springs. Traces of mercury (0.57 wt%) were found in the biomats from the Apapelskie hot springs. Extremely high concentration of Cd of 9.56 wt% was detected in the deposits of Paratunskie hot springs.
5. Chemical analyses of white deposits that were attached to the water pump of Paratunskie and thermal springs at the 47th km revealed concentrations of S, Na and Fe in Paratunskie and high contents of Ca and S in the deposits of the 47th km.
6. Optical microscopic observation of green, brown, white and black colored microbial mats revealed diversity of bacteria, cyanobacteria, and algae both in free-living forms

and in association with mineral particles. Metabolically active microorganisms were detected in the microbial mats indicating the impact of bacteria on the geochemical processes in the surroundings environments.

7. Optical microscopic observation of thin section of biomats from Oksinskie, Apapelskie, and Vilyuchinskie hot springs revealed a laminated structure. Soft part of biomats mainly consists of fibrous cyanobacteria *Anabaena* spp. and green algae.
8. Calcareous travertine of the Vilyuchinskie hot springs showed vertical variation of compositions from Ca and Fe-rich laminae to Ca-rich laminae, which indicates a long-term transition of water chemistry. Changes of environmental conditions such as water flux from the well and rainfall would be recorded in the periodic laminated structure of travertine.
9. Intensive hydrothermal alteration was observed in the Dachnye hot springs. Modern hydrothermal deposits found around gushes showed irregular pachy pattern combination of sulfur-rich dark-yellow parts, Fe-rich brown parts, and green colored parts composed of photosynthetic microorganisms.

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