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Water-deposited sulfur of Golovnin and Mendeleev volcanoes (Kunashir Island, Southern Kuril Islands, Russia)*

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Abstract. It is generally believed that the sulfur of volcanic lakes is of exogenous origin and is formed as a result of the interaction of volcanic gases with each other and with atmospheric oxygen in the aquatic environment. This work contains descriptions the deposits of water-deposited sulfur, at clarifying the conditions and causes of their formation, and at assessing the importance of these deposits in the general genesis of sulfur in volcanic lakes. The conducted field, laboratory, and theoretical studies, taking into account the previously obtained results, do not confirm the exogenous origin of sulfur in volcanic lakes. Sulfur from hydrothermal springs on the surface and at the bottom of volcanic lakes, seas, and oceans is exclusively of endogenous (condensate) origin. Colloidal sulfur also has an endogenous (condensate) origin and does not precipitate in turbulent and convective water flows, gradually collapsing in sulfur disproportionation reactions. Aqueous deposits of fine crystalline sulfur occur under specific conditions of a saturated concentration of sulfur suspension. These deposits are the same local phenomenon as the formation of needle-shaped crystalline sulfur around gas outlets in terrestrial thermal fields.

Keywords: native sulfur, condensation, colloid, Golovnin volcano, Mendeleev volcano

Водно-осажденная сера вулканов Головнина и Менделеева (остров Кунашир, Южные Курильские острова, Россия)

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Резюме. Принято считать, что сера вулканических озер имеет экзогенное происхождение и образуется в результате взаимодействия вулканических газов друг с другом и с атмосферным кислородом в водной среде. Данная работа содержит описание отложений водно-осажденной серы, на выяснение условий и причин их образования, на оценку значения этих отложений в общем генезисе серы вулканических озер. Выполненные полевые, лабораторные, и теоретические исследования с учетом ранее полученных результатов не подтверждают экзогенное происхождение серы вулканических озер. Сера гидротермальных источников на поверхности, на дне вулканических озер, морей, и океанов имеет исключительно эндогенное (конденсатное) происхождение. Коллоидная серы также имеет эндогенное (конденсатное) происхождение и не осаждается в турбулентных и конвективных водных потоках, постепенно разрушаясь в реакциях диспропорционирования серы. Водные отложения мелкокристаллической серы возникают в специфических условиях пресыщенной концентрации серной суспензии и являются таким же локальным явлением, как и образование игольчатой кристаллической серы вокруг газовых выходов на наземных термальных полях.

Ключевые слова: самородная сера, конденсация, коллоид, вулкан Головнина, вулкан Менделеева

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Introduction

Sulfur is one of the main volatile substances providing magmatic activity (F.A. Perret: “Gas is the active agent, and magma is its vehicle!” [1, p. 36]). The critical temperature of sulfur is 1040 °C. The pressure of saturated sulfur vapor decreases with decreasing temperature. Therefore, a relative increase in its content in the composition of volcanic gases usually indicates the arrival of new portions of juvenile material and is used in predicting volcanic activity. The physicochemical properties of sulfur make it one of the key factors of ore formation [2], which provided humanity with reserves of sulfide and postsulfide oxide ores, as well as deposits of native sulfur itself.

Two points of view dominate the ideas about the formation of volcanogenic deposits of native sulfur. One point of view [3] considers sulfur as the end product of the hydrothermal ore-forming process. Another point of view [4, 5] proceeds from the natural sulfur cycle, in which the accumulation of its industrial concentrations occurs in the aquatic environment. Both points of view converge in relation to volcanic crater lakes. According to the researchers, sulfur here is of exogenous origin and is formed due to the interaction of volcanic gases with each other and with atmospheric oxygen in the aquatic environment.

Chemogenic sulfur occupies a central position in the concept of the sedimentary genesis of native sulfur in volcanic lakes [6–10]. S.I. Naboko [7, p. 100–103] wrote about the formation of sulfur in the volcanic lakes of Golovnin caldera: “Sulfur is probably formed as a result of the oxidation of hydrogen sulfide. It can also arise from sulfuric acid when it reacts with hydrogen sulfide. In all cases, colloidal sulfur is formed. In colloidal solutions, spherical aggregates formed around gas bubbles and solid silty particles, which were partially deposited on the bottom to form sulfur silts, and partially carried by gases to the surface in the form of sulfur foam.”

We did not find any deposits of colloidal sulfur in Golovnin caldera in previous studies [11] and concluded that the sulfur in the lakes of Golovnin caldera is predominantly endogenous condensate. We do not deny this conclusion, but we believe that studies of water-deposited sulfur at the previous stage of research remained incomplete. This work is aimed at eliminating the gap that has arisen. The purpose of the research is to determine the significance of water deposition of sulfur in the general genesis of its volcanogenic deposits, to confirm or deny the participation of colloidal sulfur in sedimentation and its chemogenic genesis. This allows for a more detailed and objective assessment of the importance of colloidal sulfur in the formation of deposits of volcanic lakes in Golovnin caldera. Since Naboko [7] cites deposits of thermal springs on Mendeleev volcano as an example of colloidal sulfur deposits, in this work we have geographically expanded the research to include these objects.

Methods

The work is based on field observations and research carried out mainly in September 2024 and partly in 2021–2023. In the course of the research, the deposits of water-deposited sulfur known from literature data and our own observations were examined, their distribution and sediment thickness were assessed, and attention was paid to the presence or absence of gas outlets and deposits of air-deposited sulfur in the vicinity of sulfur-depositing thermal springs. Samples of the water sediment were taken, as far as possible, without violating its integrity together with the water into airtight containers. The temperature measurements were carried out by a digital thermometer with a remote sensor with an operating measuring range from –20 to +300 °C and an accuracy of ±1 °C. pH measurements were performed with two pH meters (range 0.00–14.00 pH, accuracy ±0.01 pH) after cooling the water to a temperature of less than 60 °C.

The microstructure of bottom sediments was studied after prolonged (at least a month) sedimentation of selected sediment samples, draining of excess water and drying. The study was carried out using Tescan MIRA LANS scanning electron microscope with the prefixes EMF and DORE INCA Energy350X-Max50 and NordlysNano (Oxford Instruments). The sediment composition was determined using spectral scanning. In the presence of native sulfur, the size and morphology of its mineral aggregates were analyzed with control of the presence of colloidal particles in the sediment (dimension less than 1 μm).

The theoretical part of the discussion of the results uses molecular chemical modeling, which was discussed in detail in [10].

Volcanological settings

Mendeleev and Golovnin volcanoes (Fig. 1) are located in the southern part of Kunashir Island, the southernmost island of the Kuril island arc.

Mendeleev volcano

Mendeleev volcano (43.98 N, 145.73 E, height 896 m) has a complex structure. According to data from [12], it consists of three nested caldera-crater depressions (6 × 9; 3 × 3.5; 1 × 1 km) and an extrusive dome about 400 m high, filling the inner depression. The lavas of the dome have a dacitic composition. The rest of the volcano is composed of andesite and andesite-basalt lava flows. Volcanic Neogene structures are the foundation of the volcano.

The extrusive dome is about 2,600 years old according to radiocarbon dating [12]. The current activity of the volcano is confined to thermal fields located at a distance of 1–1.5 km from summit at an altitude of 300 to 500 m a.s.l. The North-Western field (Fig. 1, I) and the North-Eastern field (Fig. 1, II) are the most active. Occasional gas emissions and explosions occur here against the general background of calm fumarolic activity. Effusions of sulfur and sulfur-opal lavas also sometimes occur in the North-Western thermal field.

Several groups of thermal springs are known on the slopes of the volcano. We are interested in sulfur deposits in acidic hot springs located in the upper reaches of the Kedrovy (Cedar) Creek (Fig. 1 c, points 1 and 2) and in the middle reaches of the Kisly (Acid) Creek (Fig. 1 c, points 3–5). A detailed description of these and other hydrothermal vents of the volcano, as well as the hydrothermal system of Mendeleev volcano as a whole, is given in [13].

Golovnin volcano

Golovnin volcano (48.87 N, 145.50 E, maximum height 547 m) is a caldera that was originated ~38 thousand years ago [14] and has a diameter of about 6 km. In the post-caldera period, volcanic activity led to the formation of extrusive domes of andesite-dacite composition [15], one outside the caldera and four inside it. Two volcanic lakes are located in the caldera.

Kipyaschee (Boiling) Lake (135 m a.s.l., area 0.05 km^2) is located at the southern foot of the Central Eastern dome (Fig 1 d) and occupies part of the crater of the last strong volcanic eruption. The average water temperature on the lake surface is 35–37 °C. Kipyaschee Lake has a drain in Goryachee Lake by a stream about 400 m long. The total discharge from the lake is mainly provided by the hot springs upflowing from the lake bottom [13, 16]. The main gas-hydrothermal flow is confined to the deep-water part of the lake. The maximum depth of the

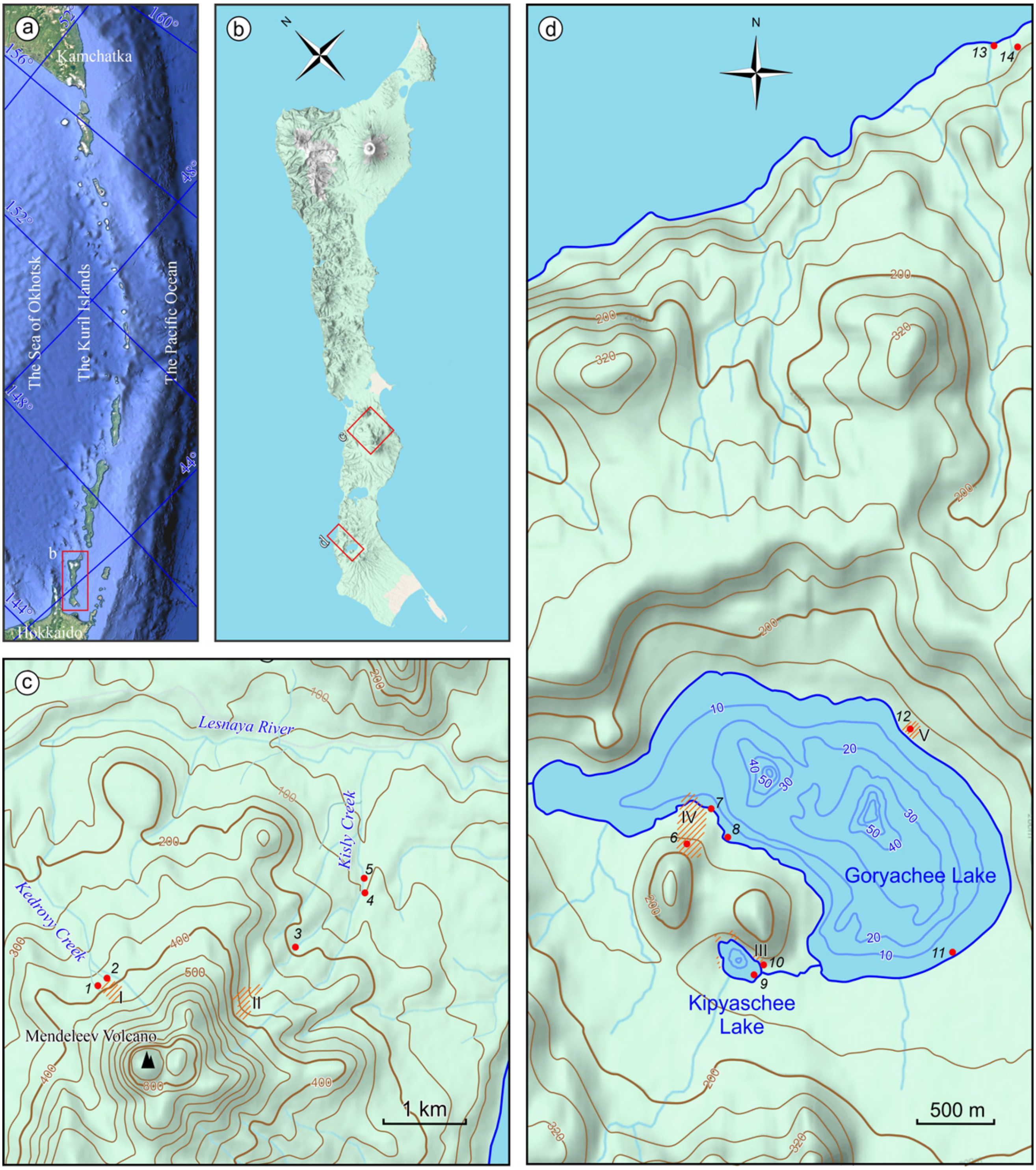

Fig. 1. (a) The Kuril Islands, (b) Kunashir Island, (c) Mendeleev volcano, (d) Golovnin caldera. I–V, thermal fields: North-Western field (I) and North-Eastern field (II) of Mendeleev volcano; Central East field (III), Central West field (IV), and Cherepakhovoe field (V) of Golovnin caldera. 1–14, observation points.

lake is 25 m [16]. There is evidence of the existence of sulfur melt at the bottom of the lake [11].

Goryachee (Hot) Lake (128 m a.s.l., area 2.94 km^2) is located in the northeastern part of the caldera (Fig 1 d). The surface water layer in the lake has a temperature of 17–18 °C in September. The average depth of the lake is 20 m. Two underwater craters are located in the western and eastern parts of the lake. The depth of the lake here reaches 60 m. Both craters exhibit gas-hydrothermal activity. The Ozernaya (Lacustre) River flows out of the lake in the west and after 2 km flows into the Sea of Okhotsk.

A last strong eruption occurred around 1300–1420 AD [17] at the southern foot of the Central Eastern dome. The volcano exhibits epidermal ($T < 400$ °C) volcanic activity currently. It localized mainly within the thermal fields and manifested in the form of fumaroles, hot springs and small mudpots. Central East field, Central West field, and Cherepakhovoe field (Fig. 1) are most active. Hot springs with water-deposited sulfur are also present on the outer slopes of the volcano from the Sea of Okhotsk. The volcano occasionally demonstrates epithermal effusive activity: three episodes of sulfur melt effusions occurred in August 1979 [18], the sulfur-opal flow and effusion of silicic acid gel were detected by us [19] in September 2022. There is indirect evidence of gas ejections: the forest died in the summer of 1980 in a strip more than 100 m wide, stretching for several kilometers from the coast of Goryachee Lake to the southwest [18].

Results

Water-deposited sulfur on Mendeleev volcano

The Kedrovy Creek deposits

The deposits of water-deposited sulfur in the upper reaches of the Kedrovy Creek (Fig. 1 c, points 1 and 2) are the most famous among researchers, locals and tourists. Hot springs with water-deposited sulfur are located in two ravines at the foot of the North-Western thermal field. According to [13], the springs belong to the sulfate type of thermal waters.

Water-deposited sulfur in the northwestern ravine (Fig. 1 c, point 1) is present at two sites. The upper site (Fig. 2 a–c) is located at an altitude of 391 m a.s.l. 40 m from the end of the opal and sulfur-opal rocks of the thermal field. The water sulfur deposits originate from two thermal springs in the northern side of the ravine. One of the hot springs (Fig. 2 b) has a temperature of 55 °C and a pH of 1.55, the second hot spring (Fig. 2 c) has a temperature of 56 °C and a pH of 1.21. The water in both sources is transparent, there are no gas outlets.

Water deposits of sulfur are insignificant at the outlet of thermal springs. Water streams from both hot springs merge into one stream 3–5 m from the sources. The thickness of the water sulfur deposits here is maximum – up to 1 cm on the surface of the rock fragments at the bottom of the stream and up to 10 cm in the voids between them. The sulfur deposits are white with a faint yellow tinge. They are loose, loosely bound, easily break down at the slightest touch and are carried away by the water stream in the form of whitish turbidity. The thickness of the sulfur deposits decreases rapidly downstream of the thermal stream, and the water sulfur deposits completely disappear at a distance of 13 m from the springs. The thermal water flow here has a temperature of 50 °C, pH = 1.38. The water stream flowing through the adjacent parallel channel and not depositing sulfur has a temperature of 36 °C and a pH of 1.76.

The lower section of water-deposited sulfur is located 35 m from the upper hot springs at an altitude of 377 m a.s.l. Water deposits of sulfur begin here with the outlet of thermal water in a depression at the bottom of one of the stream beds. There are no visible gas outlets. The thermal water of the bottom spring has a temperature of 51 °C, the water temperature in the stream in front of the source (upstream) is 40 °C. The pH values are approximately the same in the thermal spring and in the stream before the thermal outlet – 1.75 and 1.78, respectively.

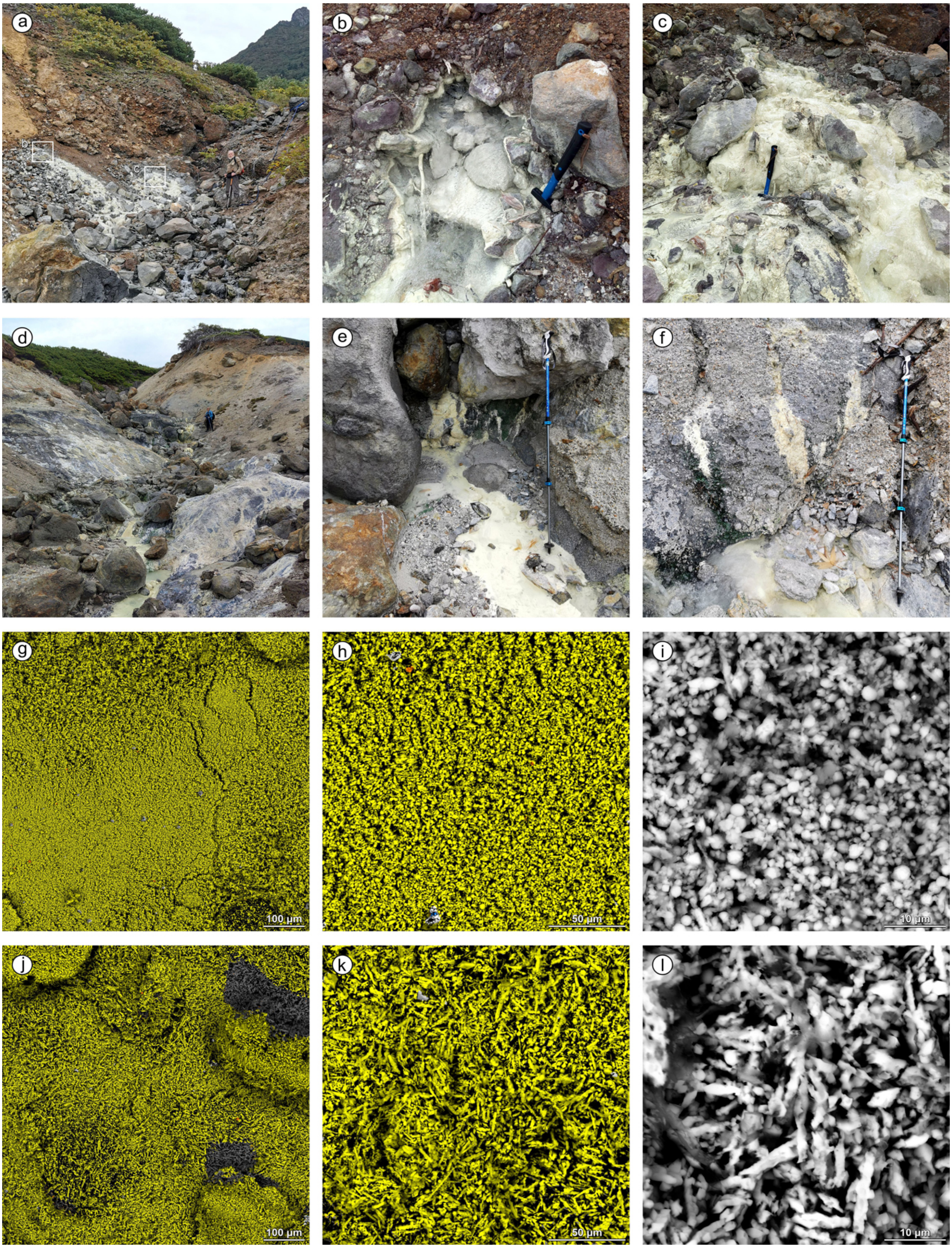

Fig. 2. Water-deposited sulfur in the upper reaches of the Kedrovy Creek on Mendeleev volcano (a–f) and its SEM-images (g–l). The conventional colors of spectral mapping for images g, h, j, k: yellow, native sulfur; orange, iron sulfide; light gray, silicon dioxide; dark gray to black, spectral shadows. See the text for explanations.

As in the upper section, water deposits of sulfur are minimal at the outlet of the thermal water, reach a maximum thickness of 4–5 mm at a distance of 3–5 m from the source, and completely disappear at a distance of 14.5 m.

The increased temperature of the thermal water causes its intense evaporation in a cool climate. The intensity of the odor (release of hydrogen sulfide) correlates with the thickness and surface area of water deposits of sulfur. The odor is insignificant in the area of the springs themselves, becomes strong in the fumes from the zones of maximum sulfur deposition, and then decreases downstream to the usual faint odor characteristic of sulfate thermal waters.

Water deposits of sulfur in the northern ravine (Fig. 1, point 2; Fig. 2 d) are also located at an altitude of 375–395 m a.s.l. The water-deposited sulfur is associated with numerous thermal springs at the bottom of the ravine (Fig. 2 e) and seeps of water in its sides (Fig. 2 f). The total length of the sulfur deposits at the bottom of the ravine is just over 50 m. The maximum extent of sulfur deposition from a single thermal spring does not exceed 15 m. Numerous seeps of water in the sides of the ravine form short (20–50 cm) plumes of water-deposited sulfur. Close-together groups of sources form a common plume of sulfur deposits at the bottom of the ravine and, together with isolated sources, create a dotted appearance of water sulfur deposits. The thickness of sulfur deposits is usually several millimeters, in rare cases reaching 1 cm.

The maximum flow rate of sources in the northern ravine is lower than the flow rate of sources in the upper section of the north-western ravine. The water temperature in the springs varies depending on the flow rate from 53 °C in large springs to 18 °C in small seeps of water in the sides of the ravine, pH = 1.2–1.8. There are no gas outlets. The smell of hydrogen sulfide in the vapors of thermal waters correlates with the thickness and area of water deposits of sulfur. There are no deposits of air-deposited sulfur on rocks and vegetation outside the water streams.

The particles of water-deposited sulfur (Fig. 2 g–l) are represented by low-temperature rhombic sulfur and sulfur balls. The crystalline forms of sulfur are spear-shaped skeletal crystals, truncated bipyramids, and prismatic crystals. Rare microparticles of opal and iron sulfides are present in addition to sulfur in water deposits. SEM images of sulfur from the lower (Fig. 2 g–i) and upper sections (Fig. 2 j–l) in the northwestern ravine (Fig. 1, point 1) are given as an example. Spear-shaped skeletal crystals up to 50 μm in size dominate the sulfur of the upper section. Sulfur spherules with a diameter of 1–3 μm dominate the water-deposited sulfur of the lower section, lance-shaped skeletal crystals are less common, and their longitudinal size does not exceed 15 μm. The minimum transverse particle size of the water-deposited sulfur is limited to about 1 μm in both cases. The microstructural characteristics of water-deposited sulfur in the northern ravine (Fig. 1, point 2) are similar and vary between these two examples – coarser-grained sulfur is typical for thermal springs with a higher flow rate and volume of water sulfur deposits.

The spatial position and volumes of water-deposited sulfur did not change during the entire 4-year period of our observations.

There are also several boiling springs with thermal streams flowing from them within the North-Western thermal field itself. The water in them is transparent, has a chloride-sulfate composition [13] at a temperature of 96–97 °C and pH = 1.9–2.1. There is no water-deposited sulfur in them, whereas air-deposited sulfur is quite common in rocks above boiling springs with gas outlets (Fig. 3).

The Kisly Creek deposits

The sources of the Kisly Creek are located in the North-Eastern thermal field (Fig. 1, II). Numerous streams flowing down from the slopes of Mendeleev volcano are grouped in two ravines here. The gas outlets (up to 98 °C) are located in opal-sulfur-sulfide rocks in the side slopes of these ravines. There are no thermal springs, water and mud boilers (and, accordingly, water-deposited sulfur) within the North-Eastern thermal field.

Upper Mendeleev thermal springs are located downstream of the Sour Creek about 800 m from the North-Eastern thermal field. Numerous gas outlets, water and mud boilers, and soaring opal-sulfur-sulfide rocks are located in the streambed and on its banks for 120 m. The springs have a sulfate composition of waters [13] with a pH < 2.5 and a temperature of up to 100 °C. There is no water-deposited sulfur in boiling springs, whereas air-deposited sulfur is quite common on the surface of rocks overhanging the sources (similar to Fig. 3). A strong smell of hydrogen sulfide accompanies all gas outlets.

Water-deposited sulfur is present in the lower part of the Upper Mendeleev springs (Fig. 1, point 3) in the cliff of the left bank of the Kisly Creek at an altitude of 178 m a.s.l. and 1–1.5 m above the water level in the stream. The deposits of aqueous sulfur are represented (Fig. 4) by small plumes in thermal water seeps, sulfur-opal stalactites, and sulfur deposits in a small puddle under the stalactites. A streamlet flows out of this puddle, in which sulfur deposits can be traced to a distance of about 1.5 m. The temperature of the water flowing in thin streams from the stalactites is 57 °C. The thermal seeps of water with deposited sulfur have temperatures from 52 to 71 °C. There are no gas outlets at the water sulfur deposition site, however, the water sulfur deposits themselves emit a strong odor of hydrogen sulfide.

Fig. 3. One of the boiling springs of the North-Western thermal field. Water-deposited sulfur is absent at the bottom of the spring, but air-deposited sulfur is present on the surface of the rocks overhanging the spring.

A small active mud boiler (Fig. 4 c) is located on the same bank of a Kisly Creek, 6 m from a cliff with sulfur-opal stalactites on top of a hill of thermal clays under a ledge of sulfur-opal rocks. The bubbling mud in the boiler has a temperature of 83 °C, the surface temperature of the surrounding thermal clays is 50 °C. A sample of mud from this boiler was used to control the presence and type of water-deposited sulfur in mud boilers.

Thermal water seeps with short (0.5–1.5 m) plumes of water-deposited sulfur were also found 80 m downstream of the Kisly Creek (168 m a.s.l.) at the base of the fresh avalanche of the left bank.

Microstructural analysis of water-deposited sulfur from seeps and sulfur-opal stalactites showed that it is dominated by spear-shaped or needle-shaped skeletal crystals of rhombic sulfur with elongated axis sizes up to 60 μm (Fig. 4 d, g). Bipyramids (up to 20 μm) and prismatic crystals are of subordinate importance. There are also particles of opal and iron sulfides. There are no particles with transverse dimensions less than 1 μm in the deposited material.

Sponge opal is the basis of sulfur-opal stalactites (Fig. 4 b, e, h). Clay aluminosilicates and rare inclusions of TiO_2 are present in it as an impurity. Needle-like sulfur crystals cover not only the outer, but also the inner surface of stalactites. A thin layer of sulfur at the boundary with spongy opal is enriched with microparticles of TiO_2 with sizes of 1–2 μm.

Clay aluminosilicates dominate in the mud boiler substance (Fig. 4 c, f, i). The second most common is opal with particle sizes up to 100 μm. Sulfur has a subordinate value and is represented by irregularly shaped molten particles with dimensions of 3–20 μm. Particles of iron sulfides, titanium dioxide, and silicate minerals from volcanic rocks are also present, and are of similar size but less abundant than sulfur.

The Lower Mendeleev springs are located at a distance of 1.3 km north-east of the Upper Mendeleev springs, have a chloride-sulfate water composition [13], and form two groups (according to the name of the largest source): the Povorotny (located on a bend) spring group (95–100 m a.s.l.) and the Kupal›ny (Bathing) spring group (84 m a.s.l.).

The Povorotny spring group is located in the floodplain of the Kisly Creek along its banks. There are small gas outlets in the shallows in the center of the riverbed. The Povorotny spring is located on the left bank of the stream and has a temperature of 42 °C and a pH = 1.9. There is no sulfur in its bottom sediments. A light coating of water-deposited sulfur was found within the Povorotny spring group only in one weak but most high-temperature (70 °C, pH = 1.7)

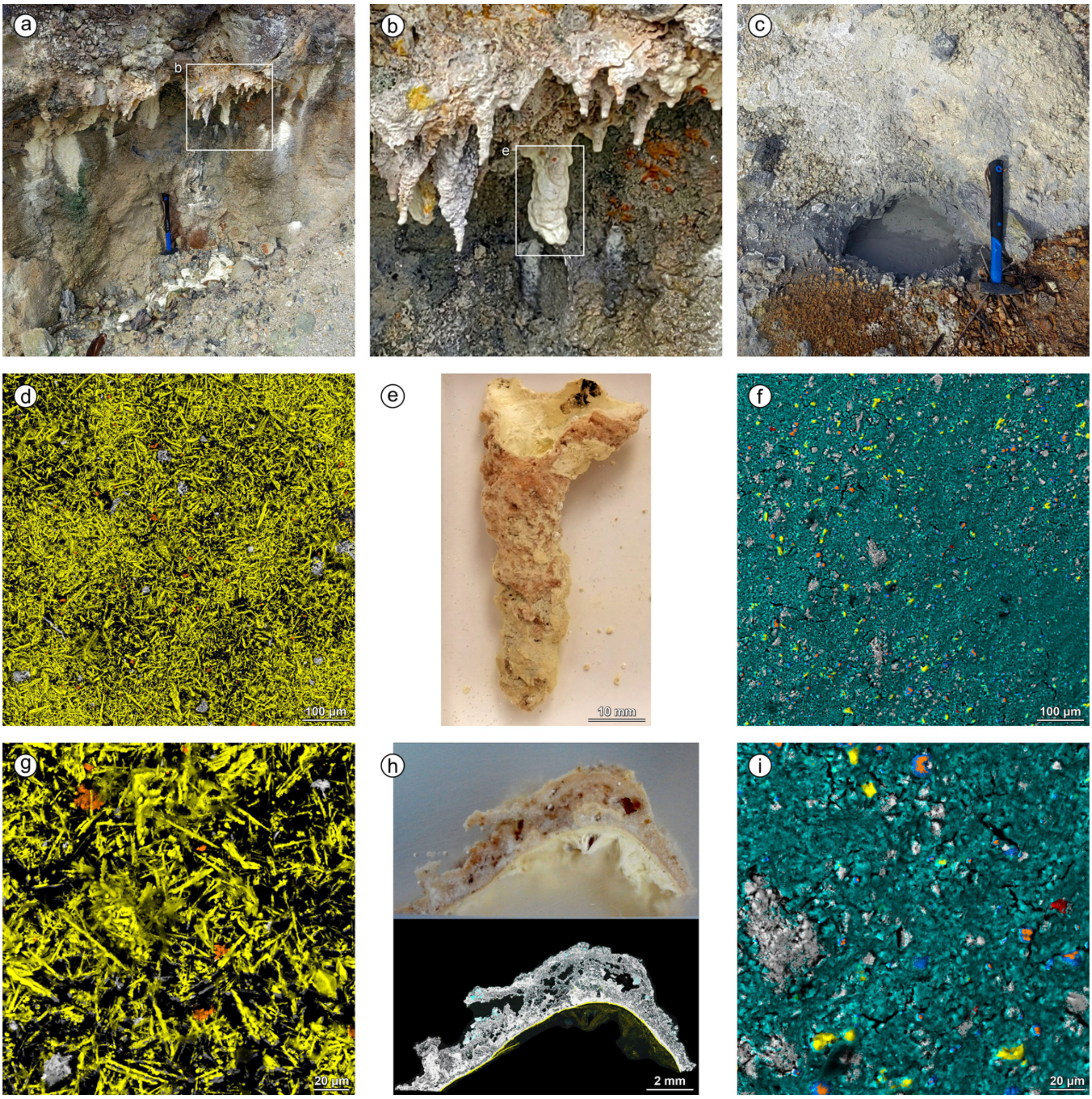

Fig. 4. Water-deposited sulfur of the Upper Mendeleev thermal springs. Conventional spectral mapping colors for images d, g, h (lower part), f, i: yellow, native sulfur; orange, iron sulfide; light gray, silicon dioxide; light blue, aluminosilicates (clay minerals); dark blue, silicates containing Fe, Mg, or Ca (particles of rock-forming minerals of volcanic rocks); red, titanium dioxide; dark gray to black, spectral shadows. The white rectangles with the letter designation here and below show the areas displayed with magnification on the part of the picture with the corresponding letter designation. See the text for explanations.

thermal spring near the right bank of the stream. A small puddle of thermal water with sulfur deposits is located here (Fig. 5 a). A small streamlet flows out of the puddle, in which a plume of water-deposited sulfur can be traced for a distance of about 3 m. There are no gas outlets, but the smell of hydrogen sulfide is present.

Opal dominates the bottom sediment of this thermal spring (Fig. 5 d–f). Sulfur is present in a smaller but comparable amount to opal. Sulfur is represented by relatively large (up to 0.25 mm) prismatic crystals and bipyramids. There are no sulfur particles with a size of less than a micron. Clay aluminosilicates and fragments of volcanic rock minerals are present in the bottom sediment in a subordinate amount.

The Kupal›ny spring group is located 200 m from the Povorotny spring on the ledge

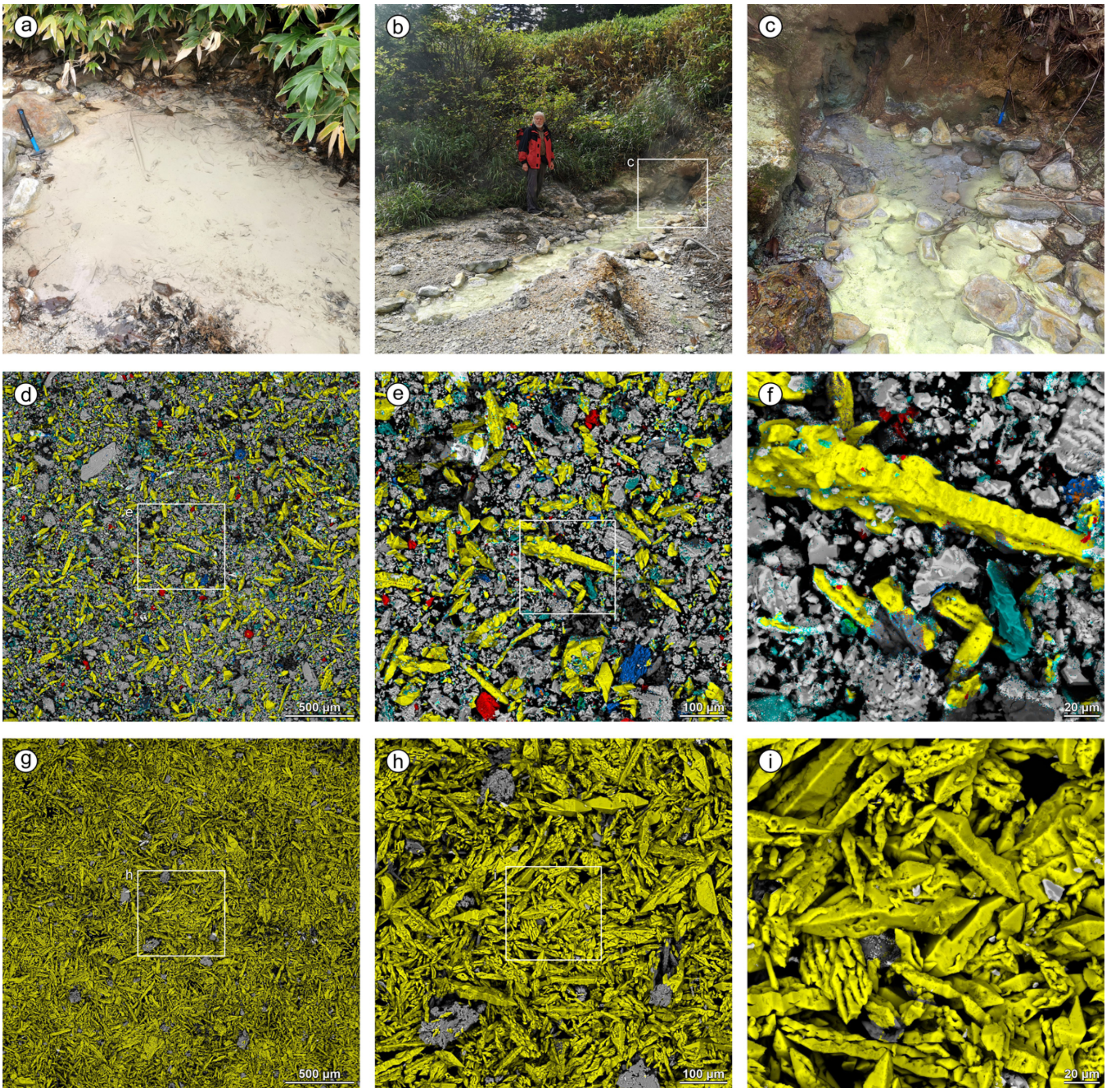

Fig. 5. Water-deposited sulfur of the Lower Mendeleev thermal springs. Conventional spectral mapping colors for images d–i: yellow, native sulfur; orange, iron sulfide; light gray, silicon dioxide; light blue, aluminosilicates (clay minerals); dark blue, silicates containing Fe, Mg, or Ca (particles of rock-forming minerals of volcanic rocks); red, titanomagnetite; dark gray to black, spectral shadows. See the text for explanations.

of the left bank of the Kisly Creek at an altitude of 1–1.5 m above the water›s edge. The Kupal’ny spring (81 °C, pH = 1.2; Fig. 5 b, c) is the largest of the thermal springs of the Kisly Creek. The thermal water of the spring flows out of an inclined 30-centimeter crack in the rock at the foot of the valley slope and springs from the bottom sediments adjacent to this crack.

Water deposits of sulfur are absent in thermal spring itself (Fig. 5 c), appear 30–40 cm from the water outlet, reach a maximum at a distance of 6–8 m, and completely disappear at a distance of 13 m from the outlet. White brushes of small gypsum crystals form along the water’s edge along the shores and on rocks protruding from the stream.

There are no gas outlets, but the thermal water is steaming intensively. The strong odor of hydrogen sulfide in the vapors is associated with the depositions of aqueous sulfur and correlates with its volume. Air-deposited sulfur is absent on the rocks and vegetation around the spring and on the shores of the thermal stream.

The water-deposited sulfur of the Kupal’ny spring is represented by crystalline aggregates of rhombic sulfur (Fig. 5 g–i). Spear-shaped skeletal crystals up to 200 μm in size dominate among the largest crystalline aggregates (Fig. 5 g). Bipyramids, prismatic crystals, and spear-shaped skeletal crystals make up the bulk of medium-sized crystalline aggregates (Fig. 5 h). Mostly bipyramidal shapes and their accretions are represented by the smallest particles of water-deposited sulfur (Fig. 5 i). A small amount of opal is also present in the water-deposited sulfur. There are no particles less than a micron in the sediment.

Water-deposited sulfur on Golovnin volcano

Bottom sediments of lakes in Golovnin caldera

We analyzed a number of sediment samples from caldera lakes in addition to previous studies [11]. A sample of the surface layer of bottom sediments of a Kipyaschee Lake (Fig. 1, point 9; Fig. 6 c, f, i, l) showed an opal-alunite-kaolinite composition. Sulfur is present in a subordinate amount in the form of fragments of sulfur spherules and small particles with molten shapes. Particles of iron and zinc sulfides, as well as titanium dioxide, are found in smaller quantities. As was shown earlier [11], the composition of the bottom sediments of Kipyaschee Lake is formed from alunite-kaolinite foam coming from bottom hydrothermal vents. The foam brings solidified droplets of bottom sulfur melt to the surface – sulfur and sulfur-sulfide spherules and their fragments.

The samples of bottom sediments of Goryachee Lake at points 8 and 11 (Fig. 1) showed a complete absence of native sulfur. They are represented by fine-grained, well-sorted sand, consisting of fragments of volcanic rock minerals and opal. The sand particles are 200–500 μm in size and are covered in places with a clay mineral (kaolinite) and gypsum from the surface. Sampling and sediment material at point 8 are shown in Fig. 6 g, j as an example.

Individual spots of bottom hydrothermal vents can be seen in clear water up to a depth of about 2 m near the Central West thermal field (Fig. 1, IV). They stand out with the turquoise color of the water and the white-yellow color of the bottom sediments. In some cases, the hydrothermal water is slightly turbid due to dispersed kaolinite. The white-yellow sediment spreads from the bottom hydrothermal vents to a distance of no more than 1.5–2 m. Multiple hydrothermal vents form a common plume of thin white-yellow sediment (mostly opal) along the coast near the Central West thermal field (Fig. 7). The sampling and composition of the material of these deposits at point 7 (Fig. 1) are shown in Fig. 6 b, e, h, k.

The maximum sediment thickness at point 7 does not exceed 2–3 mm. The sediment easily forms an aqueous suspension with careless movements. It is represented by almost pure fine-crystalline native sulfur (Fig. 6 e, h, k), similar to sediments the Kedrovy Creek (Fig. 2). The largest skeletal crystals of rhombic sulfur do not exceed 20 μm. A large magnification (Fig. 6 k) shows that among the crystalline forms

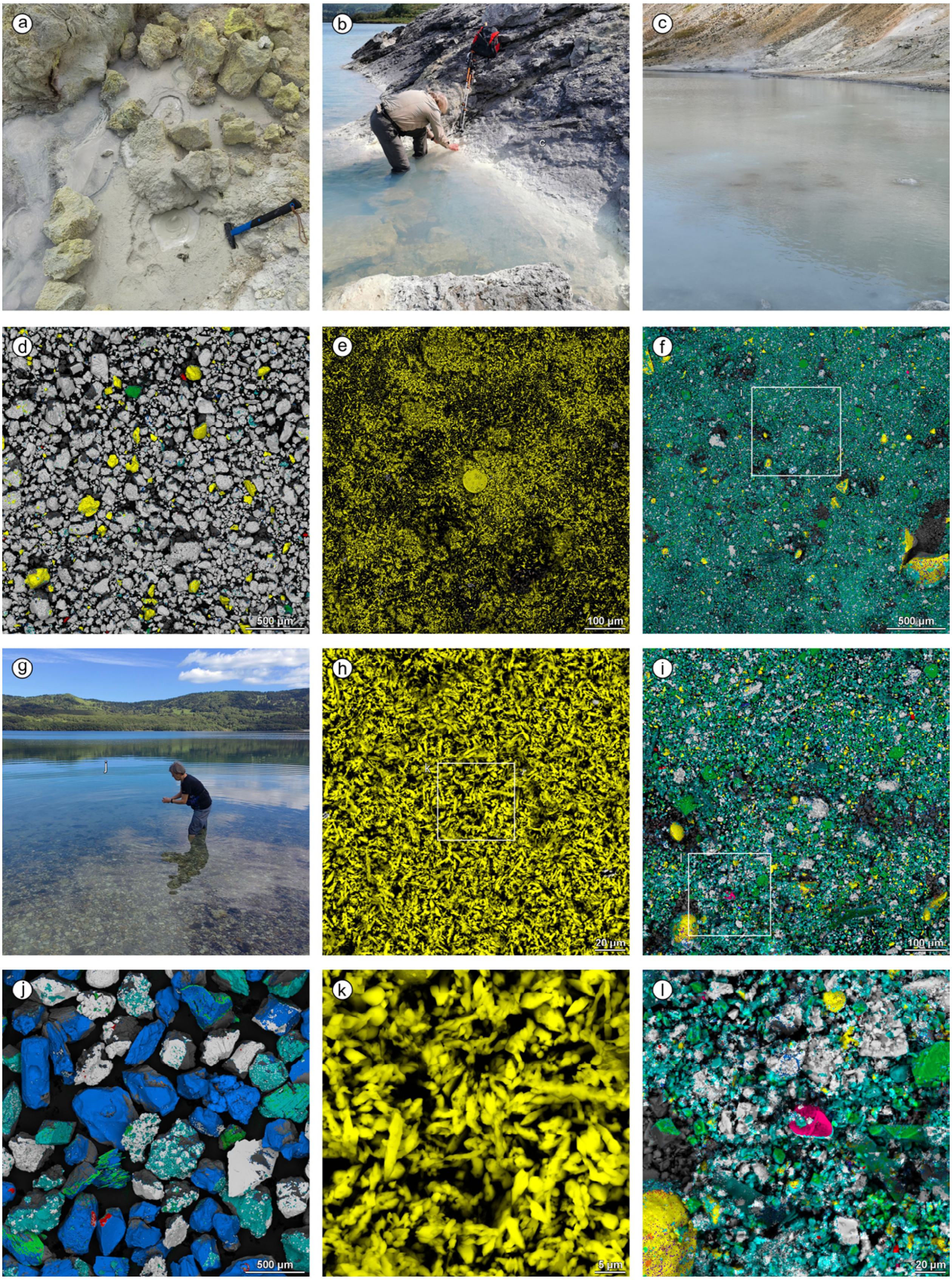

Fig. 6. Sulfur in the sediments of the mud (silica gel) boiler (a, d) and in the bottom sediments of the lakes of Golovnin caldera (other photos). Conventional spectral mapping colors for images d–f, h–l: yellow, native sulfur; orange, iron sulfide; magenta, zinc sulfide; light gray, silicon dioxide; light blue, aluminosilicates; dark blue, silicates containing Fe, Mg, or Ca; red, titan dioxide; green, sulfates; dark gray to black, spectral shadows. See the text for explanations.

of sulfur there are individual spherules of 2–3 μm in size. There are no particles smaller than a micron. A single large sulfur spherule measuring 50 μm was also found (Fig. 6 e, in the center). In addition to sulfur, there is a small amount of opal in the sediment.

Numerous bottom hydrothermal vents are present in shallow waters near the Cherepakhovoe thermal field (Fig. 1, V). The water in a small bay near the thermal field is cloudy due to dispersed kaolinite and has a turquoise hue (Fig. 8). Plentiful jets of gas bubbles are released from the bottom of the bay almost everywhere. The water temperature in the bay is 29–30 °C, whereas the usual water temperature in the lake is 17 °C. The temperature of the bottom water off the coast at a depth of 7 cm varies in places from 32 to 60 °C due to local thermal water outlets. The temperature rises to 97 °C when the thermometer is sunk into the ground by another 7 cm. The bottom sediment is represented by an opalitic gravel-sand mixture in an opal-kaolinite fine-grained material. Native sulfur is practically absent.

High-temperature springs and mud boilers in Golovnin caldera

Thermal springs with temperatures of 95–97 °C are usual on the territory of the Central East field, Central West field, and Cherepakhovoe field. As a rule, water-deposited sulfur is absent in their bottom sediments. A certain amount of native sulfur against the general background of the dominant opal appears in the sediment of hot water streams as a result of water erosion of fumarolic sulfur-opal hills through which hot streams flow to Goryachee Lake (Fig. 9).

The material of the mud boilers of the Central East thermal field (the coast of Kipyaschee Lake) consists mainly of an alunite-kaolinite mixture (Fig. 17 in [19]). It contains a small amount of pure native sulfur, as well as rare grains of opal, titanium dioxide and iron sulfide, sometimes with

Fig. 7. A plume of thin white-yellow sediment along the coast of Goryachee Lake near the Central West thermal field.

Fig. 8. Hydrothermal vents in shallow water near the Cherepakhovoe thermal field.

an admixture of arsenic sulfide. Opal dominates the small mud boilers of the Central West field. As an example, one of these boilers (Fig. 1, point 6; Fig. 6 a, d) has a diameter of only 20 cm. The white-yellow mud boiling in it resembles thick milk in consistency and has a temperature of 96 °C. Most likely, the watered silica gel is the binding mass of this mud. The silica gel completely coagulates and turns into opal after drying (Fig. 6 d). The pieces of sulfur with slightly melted shapes are of secondary importance. Alunite and kaolinite are present in insignificant amounts.

Low-temperature springs in Golovnin caldera

There are a number of terrestrial thermal springs with water-deposited sulfur in the Golovnin caldera. The volumes of water-deposited sulfur in them are extremely small. As a rule, crystalline forms of water-deposited sulfur coalesce into thin crusts here (Fig. 10).

A low-flow spring on the eastern shore of Kipyaschee Lake (Fig. 1, point 10; Fig. 10 a, d, g, j) has a maximum temperature of 63 °C of individual jets. The spring is covered with thin crusts (1–2 mm) of yellow-brown deposits forming an irregular spot about 1.5 m in size. The water temperature at the sampling point is 31 °C. Water-deposited sulfur is part of these crusts in the form of tracery coalescing of crystalline sulfur. The upper surface of sulfur is covered with small crystals and fibrous aggregates of calcium sulfate (gypsum).

There are two low-flow springs at the Cherepakhovoe thermal field (Fig. 1, point 12). Plumes of water-deposited sulfur spread over a distance of 12–13 m along small streams flowing out of them (Fig. 10 b). The water temperature in the areas of the greatest distribution of deposited sulfur is 26 °C in one stream, while in the other it is 23 °C (at an air temperature of 19 °C). Sulfur forms thin crusts (1–2 mm or less) of light-yellow color. Native sulfur dominates the composition

Fig. 9. Redeposition of sulfur and opal during erosion by a stream of hot water of fumarolic sulfur-opal hills on the Central West thermal field.

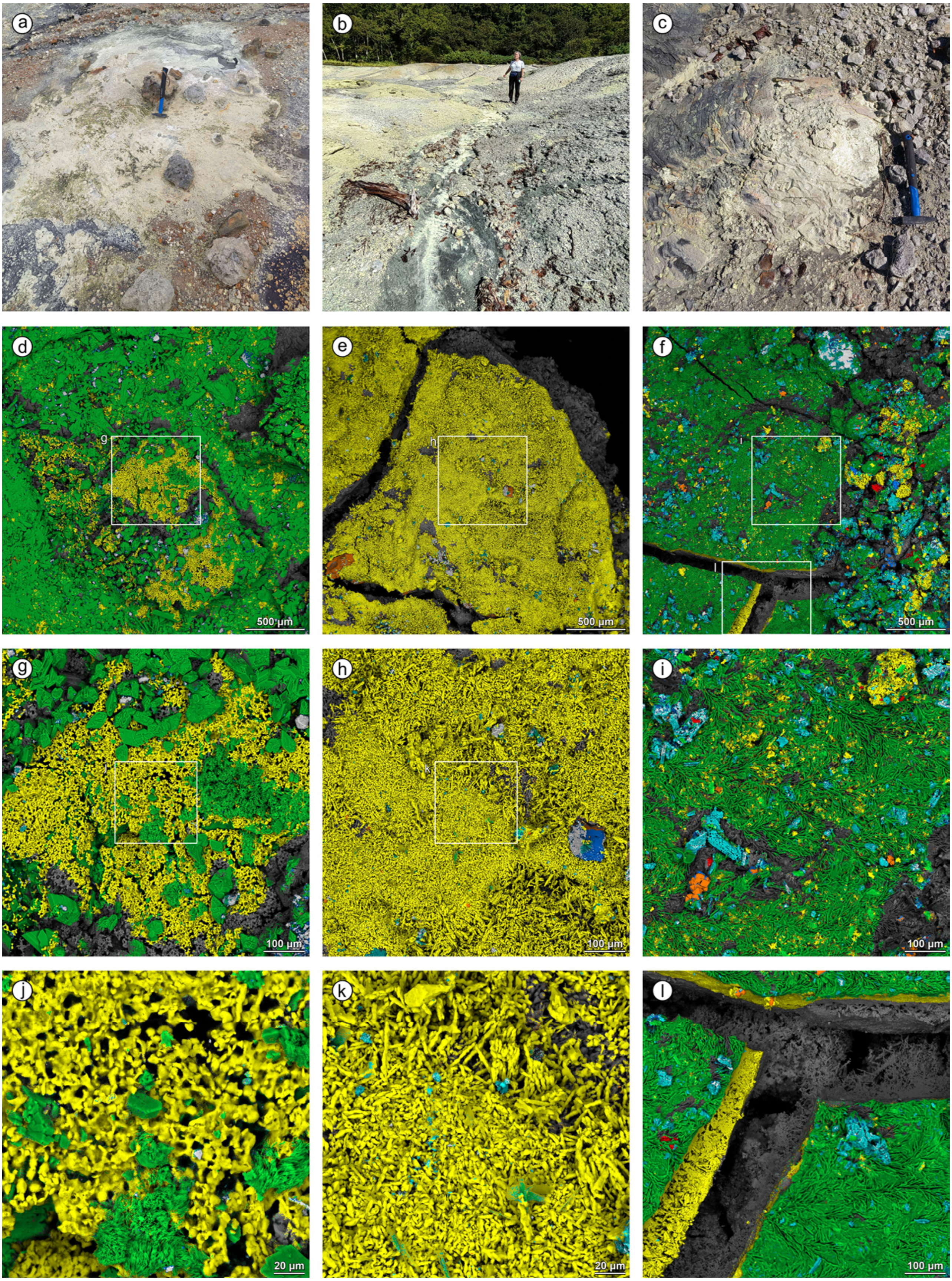

Fig. 10. Water-deposited sulfur from low-temperature springs in Golovnin caldera. Conventional spectral mapping colors for images d–l: yellow, native sulfur; orange, iron sulfide; light gray, silicon dioxide; light blue, aluminosilicates; dark blue, silicates containing Fe, Mg, or Ca; red, titan dioxide; green, sulfates; dark gray to black, spectral shadows. See the text for explanations.

of crusts (Fig. 10 e, h, k) in the form of crystalline aggregates (bipyramids, prismatic crystals, lance-shaped skeletal crystals). A small amount of opal, aluminum sulfates, iron sulfides, and particles of volcanic rock minerals are also present in the crusts.

A small seepage of thermal water with a temperature of 30 °C is located between two streams with water-deposited sulfur. A spot of layered water-deposited material with a diameter of about 70 cm surrounds this thermal spring (Fig. 10 c). A coalescing of lance-shaped skeletal crystals of native sulfur forms the inner base of these crusts (Fig. 10 f, j, l). The surface of the crusts is covered with a continuous layer of felt aluminum sulfate, which contains particles of opal, aluminosilicates, iron sulfides, and titanium dioxide.

The Alyokhinskie springs deposits

The Alyokhinskie thermal springs are located north of the Golovnin caldera on the outer slope of the volcano on the coast of the Sea of Okhotsk. We examined two of the largest thermal springs – the Orliny (Eagle) spring and the Zavalny (Blockage) spring (Fig. 11).

The Orliny spring (Fig. 1, point 14) consists of two sections – the upper (Fig. 11 a, b) and the lower (Fig. 11 d, e). The upper section is located at a distance of approximately 350 m from the coastline at a height of 23 m a.s.l. at the base of the cliff of the coastal cliff. Two thermal water sources are located here. The first source (Fig. 11 a) is located in a vertical crack 10–15 cm wide. The second source (Fig. 11 b) is located 3 meters to the left and 1.5 meters below the first one. It is a small grotto up to 0.5 m high and 1.2 m wide, from which flows a stream of thermal water about 30 cm wide. The thermal water in both sources has the same temperature of 53–54 °C and pH = 3.5.

There are no gas outlets in both sources and the surrounding rocks. Water deposits of sulfur are absent in the crack of the first source and decrease deep into the grotto of the second source. The volume of water-deposited sulfur is maximum at a distance of 3–4 m from thermal water sources. The band of sulfur deposits here reaches a width of about 2 m with a thickness of 2–3 cm on the surface of the stone fragments and 10–12 cm between them. The thickness of the sulfur deposits decreases further downstream. Water deposits of sulfur completely disappear at a distance of about 14 m from the outlet of thermal waters. After another 20 meters, the clean water of the upper section merges with the sulfur-depositing thermal water of the lower part of the Orliny spring. In Fig. 11 e, the transparent and free of sulfur sediment water of the upper section is in the lower left corner of the photo, the water of the lower section with deposited sulfur is on the right and in the center.

The source of the lower section is located at an altitude of 15 m a.s.l. and has three thermal water outlets (Fig. 11 d). The water of the weaker right outlet has a temperature of 48 °C, the central and left outlet – 52 °C, pH = 3.0–3.1. There are no gas outlets. The thickness of sulfur deposits is minimal in the deposits at the sources of thermal water and reaches a maximum of 3–5 mm at a distance of 3–4 m from the sources. Further, the thickness of the water-deposited sulfur gradually decreases. As a result, the water-deposited sulfur completely disappears at a distance of about 14 m from the thermal water outlets.

The evaporation of hot water in both sections has the smell of hydrogen sulfide. The intensity of the odor correlates with the volume of water-deposited sulfur. The wet surface of the stone fragments protruding from the water near the sulfur deposits is abundantly covered with fine crystalline gypsum (Fig. 11 i). The published data [20, Fig. 132–133] indicate that the volume and position of water-deposited sulfur here have remained unchanged for more than two decades.

The Zavalny spring (Fig. 1, point 13) is located at an altitude of 6 m a.s.l. 100 m west of the Orliny spring at a distance of several tens of meters from the coastline almost in the surf (Fig. 11 g, h). The spring has several dispersed weak outlets of thermal waters with a maximum temperature of 42 °C and pH = 3.2–3.4. The thickness of water-deposited sulfur does not exceed 1–2 mm, and their total length is about 15 m.

Two more groups of springs are located at a distance of 1.2 and 3 km from the Orliny spring to the southwest. All sources are located in the surf and heavily littered. Water-deposited sulfur is present in the sediments of the first group of sources, but it has a lower prevalence even compared to the sulfur deposits of the Zavalny source. Several vents of the second group of springs discharge boiling water on the sea shore [13]. Water-deposited sulfur is practically absent in them.

Microscopically, the water-deposited sulfur of the upper part of the Orliny spring (Fig. 11 c, f) is represented by the largest crystalline aggregates compared to all previously considered

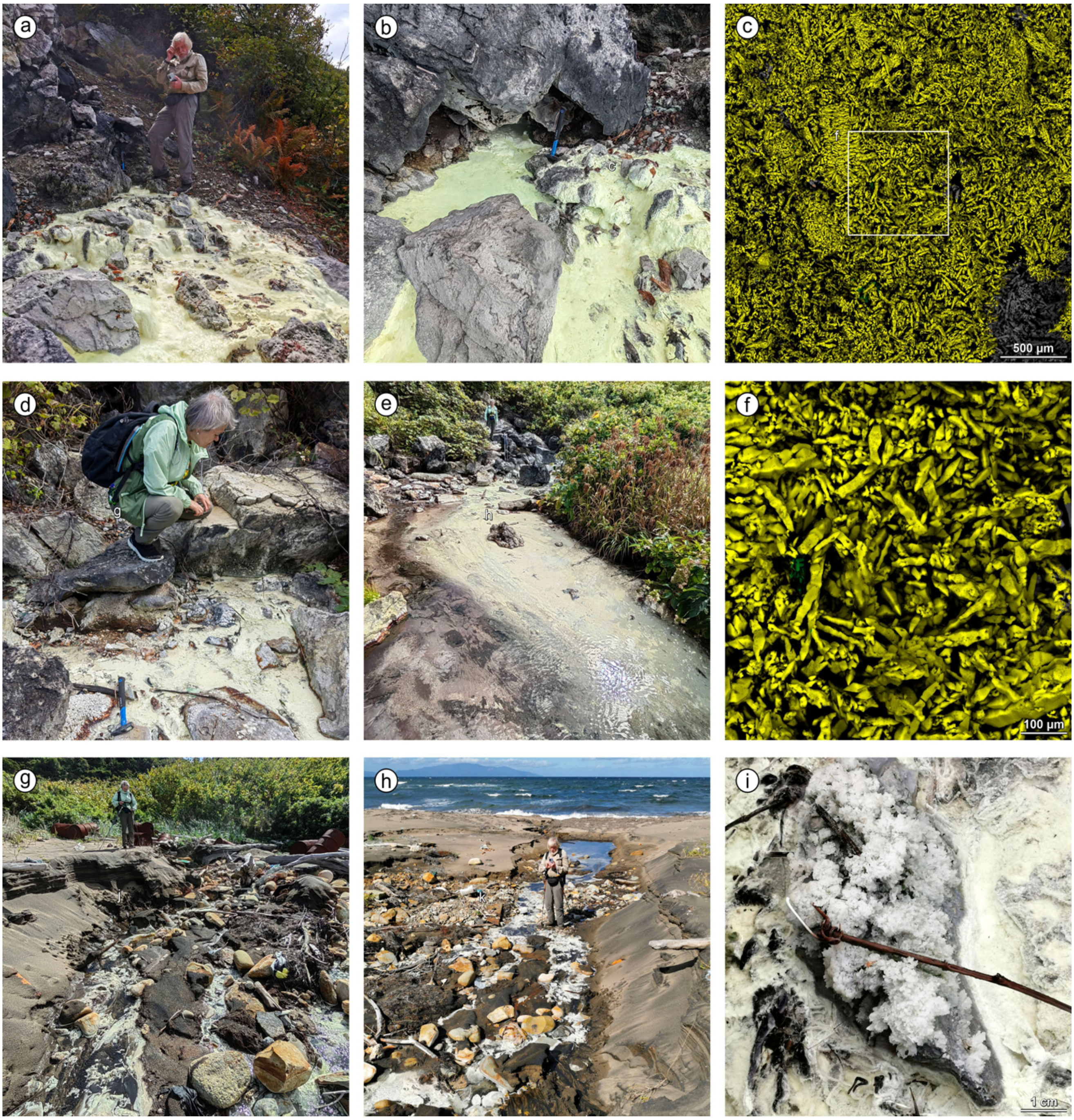

Fig. 11. Water-deposited sulfur of the Alyokhinskie thermal springs. Conventional spectral mapping colors for images c and f: yellow, native sulfur; green, calcium sulfate; dark gray to black, spectral shadows. See the text for explanations.

cases. Spear-shaped skeletal crystals, elongated accretions of bipyramids, and prismatic crystals often reach a length of 300 μm and are subparallel grouped into dense packages (Fig. 11 c). There are no sulfur particles less than a micron. A small amount of small gypsum particles is present in the sediment besides sulfur. The sulfur deposits of the lower part of the Orliny spring and Zavalny spring are similar to the sulfur deposits in the upper reaches of Kedrovy Creek.

Discussion

Generalization of observations

The particle size of the water-deposited sulfur in all the cases considered ranges from 1 to 300 μm. There are no sulfur particles less than a micron in size. According to the IUPAC definition*, the term 'colloidal' refers to a state of subdivision, implying that the particles dispersed in a medium have at least in one direction a dimension roughly between 1 μm and 1 μm. It follows that colloidal sulfur is not directly involved in the formation of aqueous sulfur sediment. Precipitation of colloidal sulfur particles per 1 cm in quiet water requires hours, days, or months, depending on the particle size. This makes the deposition of colloidal sulfur impossible under conditions of turbulent flow in water streams and convective mixing of water in thermal reservoirs. Nevertheless, it is obvious that colloidal or smaller (subcolloidal) molecular sulfur aggregates are actively involved in both the formation and destruction of water-deposited sulfur.

Water-deposited sulfur is mainly represented by crystalline rhombic sulfur. Sulfur spherules formed from droplets of molten sulfur under the influence of surface tension are extremely rare. The widespread occurrence of spear-shaped skeletal crystals indicates crystallization in conditions of high saturation, when the growth rate of individuals along the C axis prevails. At the same time, the volume and position of water-deposited sulfur at stable thermal springs often remain unchanged throughout the entire period of historical observations. There is no accumulation of water-deposited sulfur. Consequently, simultaneously with the crystallization of sulfur, its destruction occurs. The balance of crystallization and destruction determines the stability of the volume and profile of sulfur deposits.

The mechanical destruction of growing sulfur crystals occurs under the influence of a turbulent flow of thermal water. The chemical destruction of the deposited sulfur is possible as a result of the sulfur disproportionation reaction under the influence of thermal water:

$$3S_{(solid)} + 3H_2O_{(liquid)} \rightarrow 2H_2S_{(gas)}\uparrow + H_2SO_{3(solution)}$$

or

$$4S_{(solid)} + 4H_2O_{(liquid)} \rightarrow 3H_2S_{(gas)}\uparrow + H_2SO_{4(solution)}.$$

The direction of these reactions is determined by the possibility of hydrogen sulfide leaving the reaction zone.

The strong turbulent flow at the outlet of the terrestrial thermal springs prevents the deposition of sulfur. Therefore, water-deposited sulfur is absent here or its deposition thickness is minimal. The outflow of the stream onto the open surface and a decrease in its turbulence causes active crystallization and sedimentation of sulfur. In turn, the high concentration of sulfur causes its intense chemical destruction with the release of hydrogen sulfide. The peak concentration of deposited sulfur and its chemical destruction is usually found in thermal streams at a distance of 3–4 m from the source. Judging by the odor, the release of hydrogen sulfide is at its maximum. Further, the sulfur concentrations and the intensity of its destruction decrease. The sulfur sediment completely disappears at a distance of less than 15 meters from the thermal spring. The concentration of colloidal sulfur here becomes insufficient for crystallization. The background hydrogen sulfide odor of thermal water is provided by the gradual disproportionation

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* 'Colloidal' in IUPAC Compendium of Chemical Terminology. 5th ed. International Union of Pure and Ap-plied Chemistry; 2025. Online version 5.0.0, 2025. https://doi.org/10.1351/goldbook.C01172 (accessed 24 August 2025).

of residual colloidal sulfur in the water stream. In shallow-water thermal springs on the coast of Goryachee Lake near the Central West thermal field, the situation differs only in the absence of directional movement of bottom thermal water. Therefore, sulfur deposits usually form circular spots with a radius of 1.5–2 m around single thermal water outlets.

The possibility of formation of water-deposited sulfur due to the oxidation of hydrogen sulfide by atmospheric oxygen, as previously assumed (see, for example, [6–10]), can be excluded. Firstly, in most of the cases considered, there are no gas outlets in the thermal springs and surrounding rocks. Secondly, the source of the hydrogen sulfide odor is the water-deposited sulfur itself, and this odor persists for a long time after sampling. Thirdly, the intense release of hydrogen sulfide into the atmosphere by precipitated sulfur creates seemingly ideal conditions for the oxidation of hydrogen sulfide and the formation of sulfur deposited from air outside thermal watercourses. In reality, this is not observed, which indicates a minor role of atmospheric oxidation of hydrogen sulfide in the formation of sulfur in all the cases considered.

Theoretical aspects

The formation of colloidal sulfur during the condensation of gaseous sulfur is as natural as the formation of mist during the condensation of water. Therefore, the analysis of water and sulfur condensation conditions makes it possible to better understand and detail the formation of water-deposited sulfur. The difference in the molecular-chemical properties of solid and molten sulfur is also of great importance. The *TP* area of water condensation partially overlaps with the *TP* area of sulfur condensation (Fig. 12). The melting-solidification temperature of sulfur divides the *TP* areas into two more parts. As a result, 4 variants arise, differing in the conditions of formation and subsequent behavior of colloidal (and subcolloidal) sulfur.

The first variant is that sulfur condensation in *TP* area I (Fig. 12) occurs with the formation of colloidal sulfur in the form of an aerosol of liquid sulfur in endogenous gas flows. Low-temperature sulfur melt is chemically inactive, but is prone to polymerization and has high adhesion and cohesion due to the presence of open molecular chains with free bonds at the edges. Therefore, the resulting sulfur aerosol immediately loses its dispersion, as it is absorbed by the existing sulfur melt or forms new melt concentrations in the host rocks.

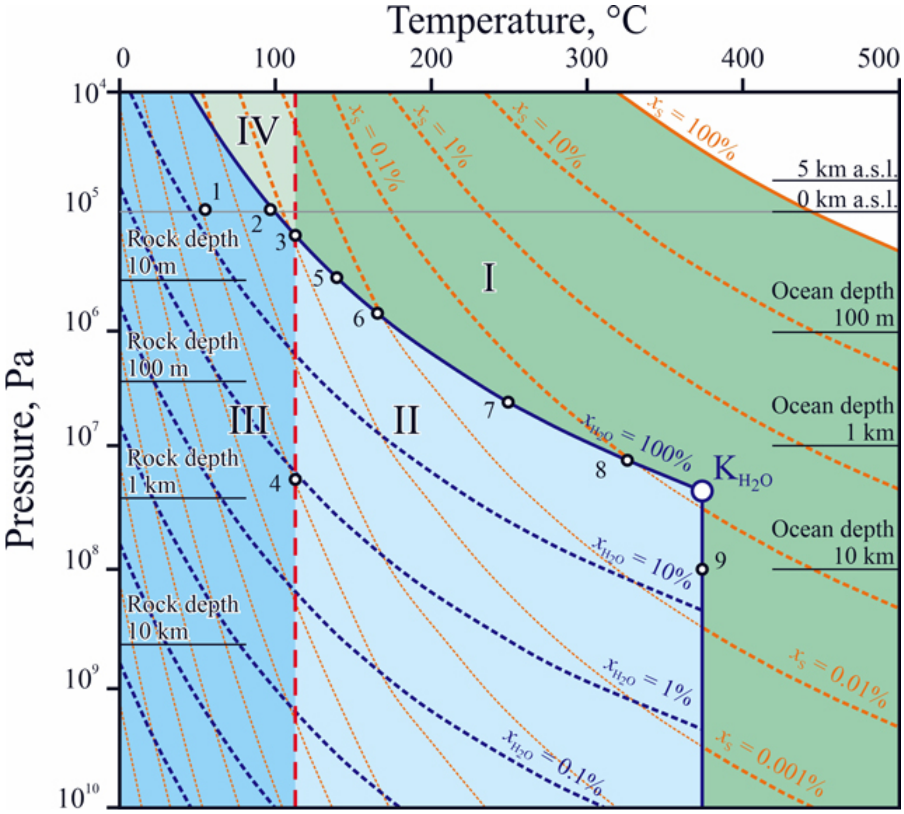

Fig. 12. *TP* diagram of condensation of sulfur and water. The vertical red dotted line corresponds to the melting–solidification temperature of sulfur. Rock depth and ocean depth are the lithostatic and hydrostatic pressure equivalent, taking into account atmospheric pressure. K_{H2O} is the position of the critical point of the water. x_S and x_{H2O} are the relative partial pressures (%) of saturated vapors of elemental sulfur and water, respectively. I–IV, *TP* areas, differing in the conditions of formation and subsequent behavior of colloidal sulfur. 1–9, calculation points (explanations are given in the text).

The second variant is that sulfur condensation in *TP* area II (Fig. 12) occurs with the formation of colloidal sulfur in the form of an emulsion of liquid sulfur in the water of hydrothermal flows. The situation is similar to the previous version in the limited space of the host rocks: the emulsion loses its dispersion and forms a melt of native sulfur; plasticity, high adhesion and cohesion prevent the mechanical destruction of the melt in turbulent flows; sulfur disproportionation reactions are blocked due to the inability to remove hydrogen sulfide from the reaction zone. The situation changes when a hydrothermal flow enters open water (hydrothermal vents at the bottom of lakes, seas and oceans). Firstly, disproportionation reactions become likely, as hydrogen sulfide gets the opportunity to leave the reaction zone. Secondly, the gradual dissipation of the resulting emulsion of sulfur condensate makes it difficult to form a sulfur melt. Thirdly, droplets of sulfur melt formed by the cohesion of emulsion particles settle to the bottom of a water basin under the influence of gravity.

The third variant: condensation of sulfur in *TP* area III (Fig. 12) leads to the formation of colloidal sulfur in the form of a suspension of solid sulfur in hydrothermal flows. The behavior of solid colloidal sulfur differs significantly from its liquid emulsion due to differences in the molecular structure.

The molecular structure of solid sulfur is represented by closed eight-atom sulfur molecules [21]. The most stable rhombic shape of the octasulfur has a crown-shaped shape with a size of 0.466 nm (in terms of the most distant atoms). The most stable rhombic shape of the octasulfur has a crown-shaped shape with a size of 0.466 nm between the most distant atoms. The angle between the two S–S bonds of each atom is 105°. This determines the crown-shaped shape of the molecule – the arrangement of adjacent atoms in two planes of 4 atoms each. The distance between the planes (crown height) is 0.099 nm.

With such a single molecule size, a cluster of about 100 molecules reaches the lower limit of a colloidal particle according to the existing IUPAC definition. However, in the context of this work, the lower bound of the colloidal particle size does not matter. All the described processes and phenomena are applicable to smaller molecular clusters, i.e., to subcolloidal particles.

Intermolecular electrostatic interaction (crystalline bonding) of sulfur molecules in the solid state is most stable when they are joined by corona planes, when 4 atoms of one molecule interact with 4 atoms of another at once. The absence of open molecular chains completely eliminates the possibility of polymerization, reduces the adhesion and cohesion of sulfur to negligible values. Sulfur loses its plasticity and becomes brittle.

Condensation of sulfur in a limited space of the host rocks: the strong turbulent flow of the hydrothermal flow prevents the crystallization of the colloidal suspension; the disproportionation reaction is blocked by the inability to remove hydrogen sulfide from the reaction zone. The condensation of sulfur under these conditions leads to the accumulation of colloidal particles without their crystallization and precipitation.

The crystallization of sulfur from the colloidal dispersion with simultaneous crystal destruction begins when the hydrothermal flow exits into the open space (thermal springs, hydrothermal vents at the bottom of reservoirs). The profile of the formed crystalline sulfur precipitate is determined by the balance of its accumulation and destruction. The relative stability of crystalline intermolecular bonds when corona-shaped sulfur molecules are joined to each other by corona planes ensures the predominant growth of crystals in the direction of the C axis and, accordingly, the needle-shaped and spear-shaped crystals.

The fourth variant. Condensation of sulfur in *TP* area IV (Fig. 12) leads to the formation of colloidal sulfur in the form of an aerosol of solid sulfur in gas streams. The features of sulfur formation and behavior are similar to the previous variant III and differ from it only in the gaseous dispersion medium. In particular, it is the solid sulfur aerosol formed in *TP* area IV that leads to needle-like crystal growth surround the gas vents on fumarole fields.

All our field observations of water-deposited sulfur were performed at altitudes of 0–400 m a.s.l. (pressure 0.096–0.101 MPa) at temperatures of thermal springs from 23 to 81 °C. As an example, the *TP* position of the Orliny thermal spring (54 °C, 0.101 MPa; Fig. 12, point 1) corresponds to the partial pressure of saturated sulfur vapor $x_S = 1.06 \cdot 10^{-5}$ %. The boiling–condensation point of water at atmospheric pressure (Fig. 12, point 2) corresponds to $x_S = 6.95 \cdot 10^{-4}$ %. As shown earlier in [11], magmas of medium acid composition, which are characteristic of the last eruptions of Golovnin volcano and Mendeleev volcano, are capable of generating fluid flows with a ratio of S/H_2O up to 0.03. The average number of atoms in sulfur vapor molecules varies little (N_S = 7.7–6.97) in the temperature range 100–374 °C. Therefore, the line of the beginning of sulfur condensation practically coincides with the isoline of the relative partial pressure of sulfur $x_S \approx 0.25$ % ($x_S = 0.236$ % at 100 °C, $x_S = 0.260$ % at 374 °C). This allows us to estimate the mass fraction of sulfur condensation m_S between arbitrary points on the *TP* diagram by changes in the relative partial pressure of sulfur as a first approximation. In particular, about 0.3 wt.% of total condensate potential ($x_{S(total)} \approx 0.25$ %) of sulfur condenses during cooling of the hydrothermal flow from point 2 ($x_{S(2)} = 6.95 \cdot 10^{-4}$ %) to point 1 ($x_{S(1)} = 1.06 \cdot 10^{-5}$ %): $m_{S(2\rightarrow1)} \approx (x_{S(2)} - x_{S(1)}) / x_{S(total)} = 0.00274$.

Sulfur does not deposit in boiling springs (Fig. 12, point 2). An aqueous suspension of sulfur at the boundary of *TP* area III has not yet formed, and an aerosol of solid sulfur from *TP* area IV passes through boiling water and participates in the formation of crystals of air-deposited sulfur above springs, as is often observed in boiling springs in Golovnin caldera and Mendeleev volcano (Fig. 3). The disproportionation of colloidal and residual gaseous sulfur in open thermal flows makes it impossible for colloidal dispersion to accumulate and water-deposited sulfur to appear in streams flowing from boiling springs.

On the contrary, the gradual cooling of the heat flow in closed thermal watercourses leads to the accumulation of colloidal suspension and the beginning of crystallization of water-deposited sulfur when the thermal water reaches the surface and turbulence decreases. The accumulation of colloidal suspension is maximal if the thermal water flow leaves the *TP* area of the sulfur melt under shallow conditions (Fig. 12, point 3) along closed watercourses: $m_{S(3\rightarrow1)} \approx 0.0046$. The accumulation of colloidal suspension in closed thermal watercourses decreases with increasing depth of the outlet of the thermal water stream from *TP* area II and completely stops at a certain depth. In particular, at point 4 (Fig. 12; the probable depth of point 4 according to the lithostatic pressure equivalent is 620 m), $x_{S(4)} = x_{S(1)}$ and, accordingly, $m_{S(4\rightarrow1)} = 0$. The significant feeding depth of many thermal springs determines the absence of water-deposited sulfur when they pour onto the surface.

The formation of water-deposited sulfur in underwater hydrothermal vents differs from terrestrial hydrothermal vents. The existence of crystalline water-deposited sulfur is possible only in shallow water (Fig. 6 b). The conditions for the formation of bottom sulfur melt appear at depths of more than 5 m.

Sulfur melt is formed in bottom crater craters in the lakes of the Golovnin caldera as a result of the cooling effect of lake waters on high-temperature fluid flows [11]. The pressure of the water column determines the partial pressure of saturated sulfur vapor at the beginning of water condensation: $x_{S(5)} = 3.90 \cdot 10^{-3}$ % in hydrothermal vents at a depth of 25 m in the bottom crater of Kipyaschee Lake (Fig. 12, point 5), $x_{S(7)} = 9.28 \cdot 10^{-3}$ % at a depth of 62 m in the bottom craters of Goryachee Lake (Fig. 12, point 6).

As it was shown earlier in [11], bottom sulfur melt in Kipyaschee Lake and Goryachee Lake is formed from 98.5 % and 96 % of the initial potential sulfur content, respectively. However, part of the gaseous sulfur (1.5 and 4 wt.%) is discharged into the aquatic environment. When cooled, this part of the sulfur forms a colloidal condensate, first in the form of an emulsion, and then in the form of a colloidal suspension. The particles of the sulfur emulsion, which manage to group into droplets of sulfur melt before entering the suspension state, are deposited on the bottom of the lake. Here they either combine with the melt in the bottom craters, or they settle as solid sulfur balls outside the bottom hydrothermal vents.

The colloidal suspension of solid sulfur is not involved in the formation of lake sediments due to convection. Dispersion, mechanical and chemical destruction prevent the participation of colloidal sulfur suspension in crystallization. As a result, this part of the sulfur is consumed in disproportionation reactions with the release of hydrogen sulfide and the formation of sulfates.

The outflow of gaseous sulfur into the aquatic environment increases with depth. Calculations show that $x_{S(7)}= 4.32\cdot10^{-2}$ % at a depth of 415 m (Fig. 12, point 7) in a small (~20 m × 14 m) depression on the northwestern slope Daikoku underwater volcano [22]. A small pond with molten sulfur is located here. The gaseous sulfur cools in a hydrothermal plume and forms a colloidal emulsion of liquid sulfur. The emulsion particles are actively involved in the formation of sulfur melt droplets, which settle to the bottom. As a result: “the apron surrounding the pond is conspicuous, formed as a sulfur-rich crust coated with a pavement of numerous spherules of sulfur, representing fallout of ‘lapilli’ from S-rich plumes” [22, p. 265].

Metal-bearing molten sulfur was discovered at a depth of 1700 m in a caldera in the northeast Lay Basin, southwestern part of Pacific Ocean [23]. The value of $x_{S(8)}$ increases to 0.118 % here (Fig. 12, point 8). The partial pressure of saturated sulfur vapor entering the aquatic environment increases to a maximum of $x_{S(K)} = 0.140$ % at a depth of 2245 m, where the hydrostatic pressure reaches the critical water pressure level of $2.212\cdot10^7$ Pa (Fig. 12, point K_{H2O}).

More than half of the total sulfur potential of medium acid magmas (56 %) enters the aquatic environment under these conditions. However, basalts dominate among the volcanic rocks of the ocean floor. The total sulfur potential of the mafic magmas corresponds to the ratio $S/H_2O = 0.12$–0.14 [2], which is higher than the potential of medium acid magmas. This determines the beginning of sulfur condensation by the partial pressure of saturated vapor $x_{S(total)} = 1$ % (0.925 % at 100 °C, 1.022 % at 374 °C). Therefore, sulfur condensation in bottom rocks is still dominant due to the higher total sulfur potential of mafic magmas. Only a smaller part of the total potential of gaseous sulfur is discharged into the aquatic environment ($m_S = x_{S(K)}/x_{S(total)} = 14$ %). Nevertheless, this amount of gaseous sulfur discharging is extremely high and ensures the appearance of the phenomenon of hydrothermal “black and white smokers” in the depth range of 2–4 km [24]. The formation of a colloidal sulfur emulsion during cooling of hydrothermal plumes leads here not only to the formation of droplets of sulfur melt as well as sulfates (“white smokers”), but also to the formation of a sulfide colloid due to sulfidization of the sulfur emulsion (“black smokers”).

The discharge of gaseous sulfur into the aquatic environment gradually decreases below the “critical” depth of 2245 m. The partial pressure of saturated sulfur vapor at the depth of the Mariana Trench is only $x_{S(9)} = 0.028$ % (Fig. 12, point 9), which is about five times less than the discharge of gaseous sulfur at the “critical” depth.

Conclusion

The colloidal suspension of sulfur has an endogenous (condensate) origin, does not precipitate in turbulent and convective water flows, and is gradually consumed in sulfur disproportionation reactions. Water deposits of fine crystalline sulfur occur under specific conditions of a saturated concentration of sulfur suspension and are the same local phenomenon as the formation of needle-shaped crystalline sulfur around gas outlets in terrestrial thermal fields. The field, laboratory, and theoretical studies performed, taking into account the previously obtained results [11], do not confirm the exogenous origin of sulfur in volcanic lakes as a result of the interaction of volcanic gases with each other and with atmospheric oxygen in the aquatic environment. Although these results were obtained based on the study of water-deposited sulfur from only two volcanoes on Kunashir Island, the theoretical analysis carried out in the work allows them to be extended to all volcanic objects and supplemented with the following conclusions: 1) the formation of fine-crystalline water-deposited sulfur is limited by shallow-water conditions, conditions for the formation of bottom sulfur melt appear at depths of more than 5 m; 2) the removal of sulfur into the aquatic environment increases with depth and reaches a maximum at a “critical” depth of 2245 m, which provides the phenomenon of “black and white smokers”, and then decreases again; 3) in deep-sea conditions, sulfur is deposited in the form of droplets of sulfur melt or participates in the formation of sulfides and sulfates in the “smokers’ fumes”.

The final conclusion is that the sulfur from hydrothermal vents on the surface and at the bottom of volcanic lakes, seas, and oceans is exclusively of endogenous (condensate) origin.

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