Proceedings World Geothermal Congress 2015
Melbourne, Australia, 19-25 April 2015

Sulfides of the Modern Kamchatka Hydrothermal Systems

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Keywords: sulfides, modern hydrothermal systems, Kamchatka, pyrite

ABSTRACT

Sulfides pyrite, melnikovite-pyrite, marcasite, sphalerite, chalcopyrite, galena, cinnabar, coloradoite, metacinnabar are precipitating at the modern geothermal systems of Kamchatka: Kireunsky, Dvukhyurtochny and Apapel'sky in Central Kamchatka, Vilyuchinsky and Mutnovsky in Southern Kamchatka. Ore deposits are spatially associated with hydrothermal springs. Pyrite is the most common mineral precipitated at the discharge of hydrothermal style. It varies in mode of occurrence, size, inner structure, chemical composition and microstructure. Frequently pyrite occurs as framboids, idiomorphic crystals and their aggregates. By chemical composition, two varieties of pyrite are observed: homogeneous and heterogeneous. Heterogeneity of composition is due to impurities of As, Cu, Sb, Hg and Ag. Au as impurity in pyrite was relieved only in pyrite from Voinovsky hot springs in Southern Kamchatka. Cinnabar is the next most common occurring mineral at the modern hydrothermal systems in Kamchatka. Chalcopyrite, galena, sphalerite and gold are rare minerals.

The modern hydrothermal systems in Kamchatka provide the opportunity to study sulfide typomorphism and physico-chemical conditions of the deposition mechanism. We suppose that some of them are the elements of the long-life ore generating hydrothermal systems.

1. INTRODUCTION

The 2,200 km long Kurile-Kamchatsky volcanic arc consists of numerous of hot springs, which are associated with modern volcanic activity. The fields of hot springs are basically localized within active volcanic craters (for ex.: Mutnovsky volcano), surrounding the active volcanoes (for ex.: Uzon caldera), and at the extinct epithermal systems (for ex.: Rodnikovoe deposit). Kamchatka itself, with respect to the formation age, is divided into four roughly parallel volcanic belts, being active from Cretaceous to Present time. Most significant hot springs in term of heat resources and the chemical environment are situated in the Eastern active volcanic belt of Kamchatka, which is spatially associated with the subduction zone, generating on-going volcanic eruptions and fumorolic activities within the belt. A few hydrothermal springs are known in Central volcanic belt. Also present are the active volcanoes Ichinsky and Khangar (**Fig. 1**). Hydrothermal springs differ in water type, scale, temperature, precipitating materials and sorts of microorganism originated in the thermal water.

Approximately 200 fields of hot springs are recognized in Eastern and Central Kamchatka volcanic belts. However, only some hydrothermal systems of Uzon, Mutnovskaya, Nalychevo, and the most famous the Valley of Geysers, which are localized in the Eastern volcanic belt, are widely introduced to the international readers as the largest and unique ones, attracting tourists from all over the world. Therefore, there are plenty of other hydrothermal systems that can be considered as a source of energy, or important for medical purposes. The explorations by drillings have been taken place at a few hydrothermal systems, which are situated in the Southern Kamchatka. Others remain unstudied.

Some hydrothermal springs are located in the area surrounding the capital of Kamchatka Petropavlovsk-Kamchatsky city. These hot springs are used in healthcare. At many of them, the specialized clinics are built in the county of Petropavlovsk-Kamchatsky city (for. ex.: Paratunsky springs). Depending on thermal water types and concentration of specific elements, they are used to treat many diseases.

It is known that travertine and biomats originated at the hot springs (Saji et al., 2004), however, at some hot springs metals can be deposited (Simmons, et al., 2000). The high-temperature hydrothermal systems are considered to be the modern analogues of the epithermal gold-silver deposits (Mutnovsky modern hydrothermal system), providing a mechanism of metal-transport and deposition. Gold precipitation of 6 wt% and Ag 30 wt% was observed in the geothermal wells drilled at Broadlands-Ohaaki hydrothermal system in New Zealand. Tazaki, Okrugin with co-authors (Tazaki et al., 2004) has shown that gold, heavy metals and radioactive elements are precipitating at most of the Kamchatka hot springs. A little attention was paid to the study of biomineralization at the modern hydrothermal systems in Kamchatka, however, as it was proof by Tazaki and Okrugin that biomineralization may be related to the gold precipitating mechanism from the hot springs. Microbial mats composed of bacteria, cyanobacteria and algae in association with biominerals were found in almost all known hydrothermal systems in Kamchatka. Composition of water, mineralogy of precipitations and bacteria have been previously studied by Okrugin, Tazaki and et al. (Tazaki et al., 2004).

This study is focused on the origin of sulfides and native metals at the hot springs of Kamchatka. The water samples, travertine, silica and biomats have been collected at Apapel'sky, Kireunsky and Dvukhyurtochny hot springs in Central Kamchatka, Vilyuchinsky and Mutnovsky hot springs at Southern Kamchatka (**Fig. 1**). This paper presents the first results of mineralogical and geochemical studies of the thermal waters and precipitated sulfides, native metals.

The main investigations methods used in the research are EMPA, XRD, ICP and RFA.

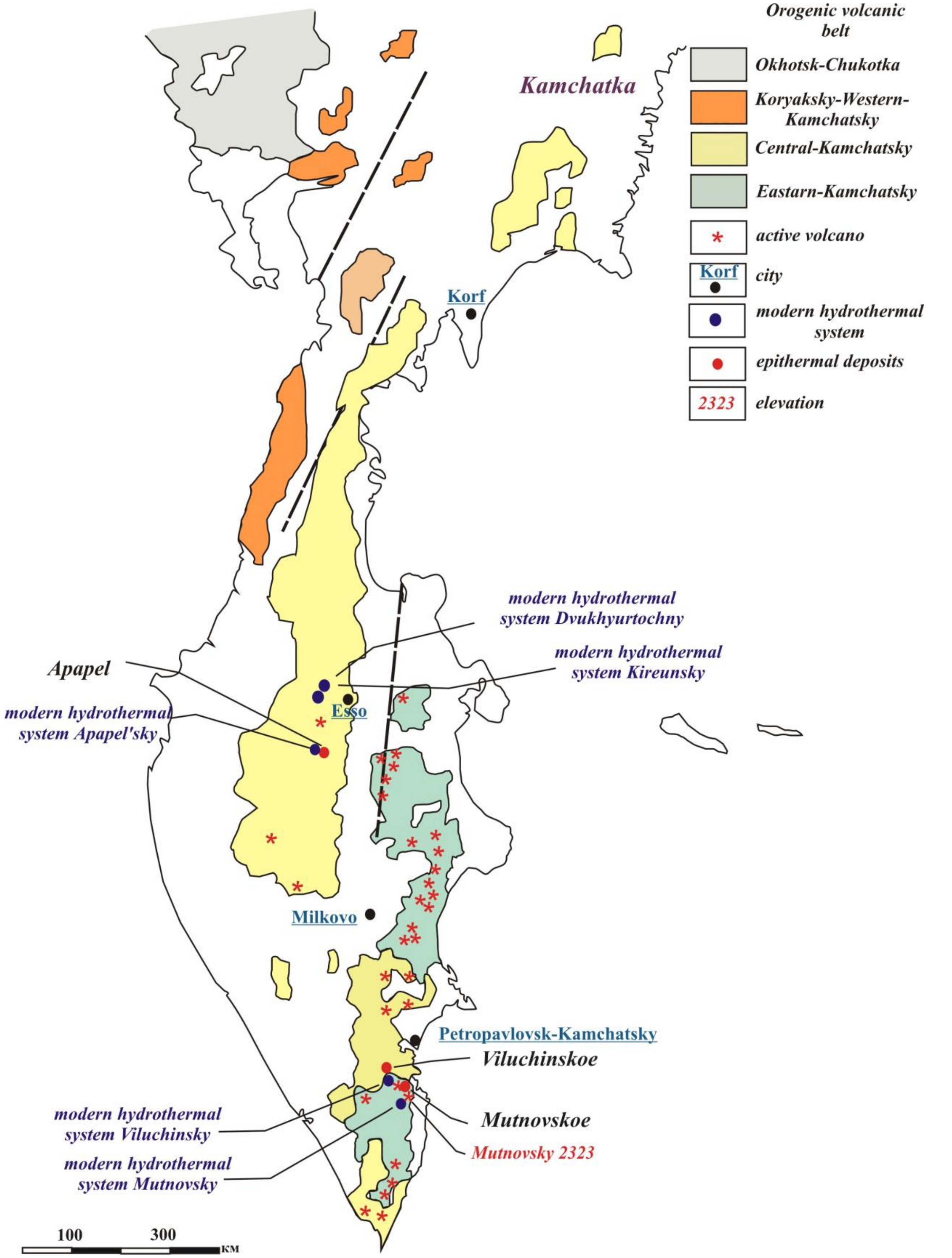

Figure 1: Localization of modern hydrothermal systems of Kamchatka.

2. HYDROTHERMAL SYSTEMS IN CENTRAL AND SOUTH KAMCHATKA

Despite four volcanic belts, the thermal springs are basically located within Central- and Eastern-Kamchatsky volcanic belts. Isotopic composition of the thermal waters has been concluded by a number of researchers (Kiryukhin, 2001, Pinea et al., 1999). These studies showed that the thermal waters of the most Kamchatka's springs are meteoric in origin. In appearance the hot springs are individual boiling springs, geysers, and hot pools. General characteristics of the hydrothermal systems and chemical compositions of the thermal waters, studied in this research, are listed in Table 2.1.

2.1.1 Central Kamchatka

Active volcanic eruptions has occurred in Central-Kamchatsky volcanic belt through Cretaceous to Quaternary time, with most intensive episode of igneous activity in Pleistocene to Quarterly. Most of volcanoes are extinct, whereas, fumarolic activity is still observed at Ichinsky and Khangar volcanoes (**Fig. 1**). Samples of the thermal waters and minerals were taken at the Apapel'sky, Kireunsky and Dvukhyurtochny thermal springs, occurring in southern part of the Central Kamchatka volcanic belt. This area is characterized by high mineralization of gold, silver, base metals, tellurium and mercury. Hydrothermal fields are located within or close by precious metals deposits.

Table 2.1 Characteristics of the hydrothermal systems

Hot springs	Temperature, °C	Discharge	pH	Type of water	Mineralogy
Central Kamchatka					
Kireunsky	18-40 up to 100	0.7 l/s up to 30 l/s	7.3	chloride, sulphate-chloride-sodium, siliceous (H_2SiO_3 - up to 109-232 ppm), boron (H_3BO_3 - to 104 - 155 ppm), arsenic (As - to 0.4-8.0 ppm), with a high content of lithium - to 2.56 ppm, rubidium - to 0.21 ppm, cesium - to 0.4 ppm.	pyrite, melnikovite-pyrite, marcasite
Dvukhyurtochny	20 up to 78	13 l/s up to 30 l/s	8.0	nitric sulphate-chloride-sodium, siliceous (H_2SiO_3 - 13.4-15.3 ppm), boric (H_3BO_3 - 84-196 ppm), arsenious (As - 0.25-3.8 to 8.5 ppm)	pyrite, marcasite
Apapel'sky	18-20 up to 98	0.3 l/s up to 44 l/s	7.6	sulphate-sodium bicarbonate, siliceous (H_2SiO_3 - up to 104-244 ppm), boron (H_3BO_3 - to 255-343 ppm), arsenic (As - to 1-3 ppm), with a high content of lithium - to 1.5-1.8 ppm, fluorine - to 1.9-6.0 ppm	cinnabar, coloradoite, metacinnabar (authors' data) opal, calcite, barite, realgar, metacinnabarite, mercury, psilomelane, orpiment, pyrite, marcasite, barite, pyrolusite, and goethite (Saji et al.)
South Kamchatka					
Vilyuchinsky	38 up to 90	up to 55 l/s	6.7 up to 12.3	hydrocarbonate-chloride, siliceous (H_2SiO_3 - up to 100-200 ppm), with content of lithium - to 1.2 ppm, manganese - to 0.326 ppm	pyrite, melnikovite-pyrite, marcasite, sphalerite, chalcopyrite, sphalerite, galena, native sulfur
Mutnovsky	up to 150 (about 230-280)		3.3 up to 7.2	chloride-sodium and carbonate- sulphate, siliceous (H_2SiO_3 - up to 50-1000 ppm), boron (H_3BO_3 - to 9-184 ppm), arsenic (As - up to 4-25 ppm)	pyrite, sphalerite, chalcopyrite, galena

Apapel'sky hot springs include Nizhne and Verkhne Apapel'sky groups of the hot springs, located in distance of 200-300 m apart at the elevation of 750-850 m (**Fig. 2**). Hot springs are located within the Apapel gold-silver-mercury ore occurrence with gold resource of 15 t. Verkhne Apapel'sky group of the hot springs is the largest one, uniting 14 boiling steam-water jets with temperature of 94-98 °C and total discharge of 5.5 l/sec. (Saji, et al, 2004). The waters are sulphate-sodium bicarbonate, siliceous in composition with high contents of lithium (1.8 ppm), arsenic (3 ppm), and fluorine (6 ppm, Table 2.1.). The waters have a neutral pH (Saji et al, 2004).

Figure 2: Apapel'sky of modern hydrothermal systems: Nizhne (a) and Verkhne Apapel'sky groups (b, c, d).

Discovery of the precipitation of cinnabar, native gold, galena, chalcopyrite, sphalerite, pyrite and barite from the hot spring waters was made by Zegalov and Vlasov in 1958. Distinct characteristics of Apaple springs compared to other Kamchatka springs are that travertines and гейзериты are not deposited there. Minerals are precipitated on the fragments of volcanics, metasomatities, quartzite, and vein quartz. Dried biomats show extremely high concentration of arsenic, marge, gold, silver, zinc, stibium, wolfram, mercury, and molybdenite.

Apapel' thermal waters are a favored environment for photosynthetic cyanobacteria and spherical cyanobacteria.

Kireunskie hot springs are the highest temperature springs of the Central volcanic belt. They are allocated into five groups in 20 km in the valley of Kirevna river. Most host springs are boiling, flowing up the water-steam jets.

Little is known on the chemical compositions of Kureunsky hydrothermal waters (Table 2.1).

Dvukhyurtochny hydrothermal system is located to the north-east from the Apapel and Kireuna springs at the Dvukhyurtochnoe lake at elevation of 900-1000 m. The system is located 85 km westward, far from the Klyuchevskoy active volcano. It houses three individual groups of hot springs, namely Western, Central, Eastern, and Southern. Dvukhyurtochye springs are represented by the hot pools (**Fig. 3**).

The waters are high temperature, slightly alakaline, nitric sulphate-chloride-sodium, siliceous. Their cationic and anionic composition is a result of interaction between water and volcanic rocks in the zones of leaching. The maximum temperature is 78 °C. Southern group springs are intensively aerated. Composition of gas is nitrogen. The Central group consists of 170 springs, with temperature ranging from 0 to 76 °C. The springs are distributed along the north-west coast of the Dvukhryurtichnoe lake. Southern springs are located at the western border of the lake. Springs are concentrated in the area of 20x40 m. The temperature of the springs is about 45.7 °C. Western springs are located in 2 km away to the north-west from Central springs. The temperature of the springs vary from 20 to 76 °C. The Eastern group of thermal springs is a hot pool of 120x20 m, showing periodic up steams. Temperature is up to 60 °C.

Figure 3: Dvukhyurtochnaya hydrothermal system: Central (a) and Eastern groups (b,c).

These are common infiltration therms with atmosphere origin. Precipitation of sulfides has been noted only at springs of Central and Western springs groups. Sulfides are deposited at the bottom of hot springs and coats the wooden fragments.

2.1.2 Southern Kamchatka

There are several hydrothermal hot springs fields, located in vicinity of active volcanoes and associated with precious metal mineralization. Generally hot springs are characterized by neutral pH, high mineralization and concentration of heavy metals such as As and Cd. Vilyuchinskaya and Mutnovskaya hydrothermal systems of South Kamchatka are most closely studied in terms of explorations, geochemical and mineralogical studies. These two systems occur in same complex volcanic-tectonic active area of the South Kamchatka (**Fig. 1**).

Mutnovskaya hydrothermal system is a part of Mutnovskaya geothermal area, which occurs in the Northern-Mutnovskaya volcanic-tectonic zone, formed by a series of submeridial faults. There are two active volcanoes, Mutnovsky and Gorely, gold-silver-polymetallic deposits with Au (Ag, Zn-Pb-In) resources up to the Mutnovskaya geothermal deposit are located (**Fig. 1**). Mutnovskaya hydrothermal system includes hot springs in the North crater and Active crater of the Mutnovsky volcano, Dachny, Perevalny hot springs. Temperature of water varies from 43 to 253-270^0 C (fumaroles max 509^0 C). The waters are from acid to neutral in pH.

The Mutnovskaya hydrothermal system is situated between two active volcanoes of the Southern Kamchatka. They are the Mutnovsky stratovolcano and Gorely shield volcano. Also, there are some paleovolcanoes preserving recognizable outlines. Some of them include epithermal mineral deposits, for instance, Mutnovskoe gold-silver-base metal deposits occur within the caldera of the Zhirovskoi paleovolcano. The hydrothermal system hosts by volcanic and volcanic-sedimentary rocks of the Ahomtenskaya, the Asachinskaya and the Alneyskaya Formations in regional scale. The age of igneous rocks was determined as Oligocene for andesite and andesitic dacite rocks of the Ahomtenskaya Formation, as Miocene for andesite, andesitic basalt and its tuffs of the Asachinskaya Formation and as Upper Miocene-Pliocene for volcanic rocks range composition from andesite to rhyodacite of lower unit of the Alneyskaya Formation. The upper unit of the Alneyskaya Formation consists of tuffs and from andesite to basalt lava flows of Pliocene. Quaternary deposits are exposed products of volcanoes, mainly consisting of basalt and olivine basalt, andesitic basalts on rare occasions.

In 1999-2002, two geothermal stations (Pilotnaya 12 MWt, Mutnovskaya 50 MWt, **Fig. 4**) with a total power of 62 MW, have been placed into service in order to provide electricity for Petropavlovsk-Kamchatsky and Elizovo cities. In this location is the Mutnovskoe gold-silver-base metal deposit, with estimated resource of gold 12 t and silver 520 t, and several hot springs spots (Dachny, Northern Mutnovsky, Western Mutnovsky, Voinovsky, Rudny and others) in the surrounding area of the Mutnovsky hydrothermal system. Another equally perspective gold-silver deposit is the Rodnikovoe one, located 15 km NNW and far away from the Mutnovskoe lode. The estimated reserves are 40 t of gold and 340 t of silver.

Figure 4: Mutnovskaya geothermal stations 50Mw (a) and new well 2and 3 (b).

Vilyuchinsky hydrothermal system is situated at the Eastern flank of the Rodnikovoe gold-silver deposit in 20 km to the south from the Mutnovskaya geothermal area. It consists of four groups of the hot springs with temperature ranging from lowest 55 to highest 78°C. Epithermal gold-silver veins occur in short distances from the hot springs. Chemical composition of water is similar to all of four groups of hot springs. The waters are chloride-sulfate-sodium, with pH neutral to alkaline (Tazaki et al., 2004). The waters of hot springs are enriched in As, Fe, Mn, Br and Sr. Travertine dome is a largest group of Vilyucha hot springs forms a big-scale travertine field. Traverite is presented by banded silica-carbonate veins with aragonite. Remarkably high concentrations of As (17-

2.525 ppm) have been measured in travertine (Okrugin et al., 2013). As shows a positive correlation with Sb. Additional travertines have a high Au content. In the Vilycuha hot springs, the reddish, brown, green and black microbial mats exist. Calcite and arogonite were detected in these mats with rare smectire, feldspar and siderite (Tazaki et al., 2004).

2.1.1 Central Kamchatka

Mineralogy of precipitations

Among other ore minerals were revealed sulfides - pyrite, melnikovite-pyrite, marcasite, sphalerite, chalcopyrite, galena, cinnabar, coloradoite, metacinnabar. Rarely arsenopyrite, alabandine, native gold were found at certain hydrothermal systems.

Pyrite is the most widespread (common) mineral. It varies in form, size, inner structure, features, chemical composition and microstructure. The most common forms of pyrite are framboids, idiomorphic crystals and their aggregates. Their size varies from 5-10 µm to 3-5 mm. According to the chemical composition and microstructure, they are divided into two groups: homogeneous and heterogeneous. Among the homogeneous, the zonal pyrite is widespread due to the alteration of “anomalous” zones enriched with arsenic, antimony, copper, mercury, silver and “normal” zones with stoichiometric composition. Pyrites with compound heterogeneous composition were also revealed. It is caused by the unequal (cloud-like, mosaic, subblock) separation of definite micro-zones usually enriched with silver, arsenic and sometimes gold.

Five-mode occurrence of pyrite has been recognized in the Mutnovskaya geothermal deposit. Pyrite varies in size from 0.01 to 0.75 and more mm. These are cubic and spear-like crystals, skeletal aggregates and framboidal shaped grains. In additional, pyrite was observed as veinlet filling up the small fractures. It is closely associated with titanomagnetite, chalcopyrite, galena, sphalerite, pyrrhotite, arsenopyrite, chalcosite, greenockite and native gold.

The chemical composition of pyrite was obtained by EPMA analysis in the ore genesis laboratory, Institution of Volcanology and Seismology, Kamchatka. The obtained data shows impurities of arsenic range from 0 to 5.07 wt. %. Among others were determined cobalt in 2.81 wt. %, antimony 2.41 wt. %, zinc 1.31 wt. %, lead 1.66 wt. %, cooper 13.22 wt. %, cadmium 14.65 wt. %, mercury 0.85 wt. % and gold 13.01 wt. %.

We also distinguished three types of pyrite in the Mutnovskaya hydrothermal system. The first type we named "empty"; that means pyrite doesn’t involve any tiny inclusions close to near-stoichiometric in composition. It formed, as rule, then pyrite replaced magnetite, titano-magnetite due to influence of hydrothermal process. The second type is pyrite, showing zonal structure made up of numerous impurities of arsenic principally (**Fig. 5**). The third type represents grains of pyrite, with a single micro-inclusion of native gold, greenokite, sphalerite, galena and chalcopyrite that is typical for epithermal gold-silver deposits.

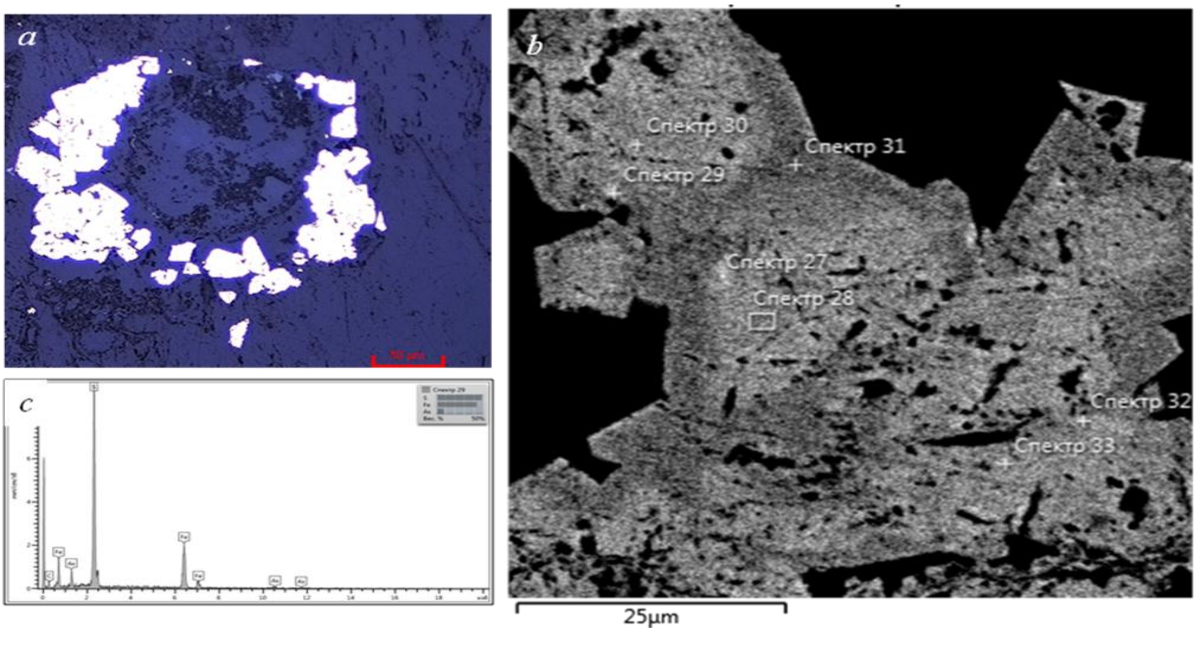

Figure 5: Multivendor pyrite due to arsenic, Mutnovskaya geothermal area: photo in reflected light (a), backscattered electron (b), spectrum (c).

Gold on the detection limit EMPA was revealed only in pyrites from Voinovsky hot spring deposits (the northern part of the Mutnovsky hydrothermal system and Mutnovsky gold-polymetallic deposit, Southern Kamchatka). Here were revealed pyrites with gold concentration 0.45-0.65% wt. in definite cloud-like separated microheterogeneities.

Arsenic is the most widespread admixture of pyrite. Its concentration may reaches 3-5% wt. in definite zonal crystals and framboids.

Antimony is another admixture of pyrite. It is also involved in structure of zonal crystals and framboids. Its concentration may reaches 2-3% wt.

Mercury is one of the most common impurities in pyrite. Along with arsenic and antimony it concentrates in form of definite microzonal strips inside the zonal crystals and framboids. Silver and copper are common admixtures of pyrite in carbon pipes and other deposits on slopes of submarine volcano named after Piip (NW of the Pacific Ocean).

The framboid pyrites from the Dvuhyurtochnaya hydrothermal system (Central Kamchatka) are the unique geological phenomena. This water causes deposition of various minerals and aggregates with anomalous concentrations of mercury (150-1000 ppm), arsenic (200-670 ppm) and antimony (100-230 ppm). Sulfide globulen - framboids with amazing zonal structure are of particular interest (**Fig. 6**). Such framboids are formed not only on the bottom of a thermal chamber around the pulsing streams of hot water. They deposit on the plant residues that are located on the hot ground within the “drying zone” around the thermal chamber. They are revealed in fine-dispersed black deposits along the brook running out of the spring. Their morphology resembles spherical sulfide formations from gold-bearing conglomerates Witwatersrand. In definite zones of such a framboids the concentration of mercury, arsenic and antimony may reach 18.5, 6.7 and 2.3% correspondingly. Sulphur of such a framboids belongs to the anomalously heavy type according to its isotope composition.

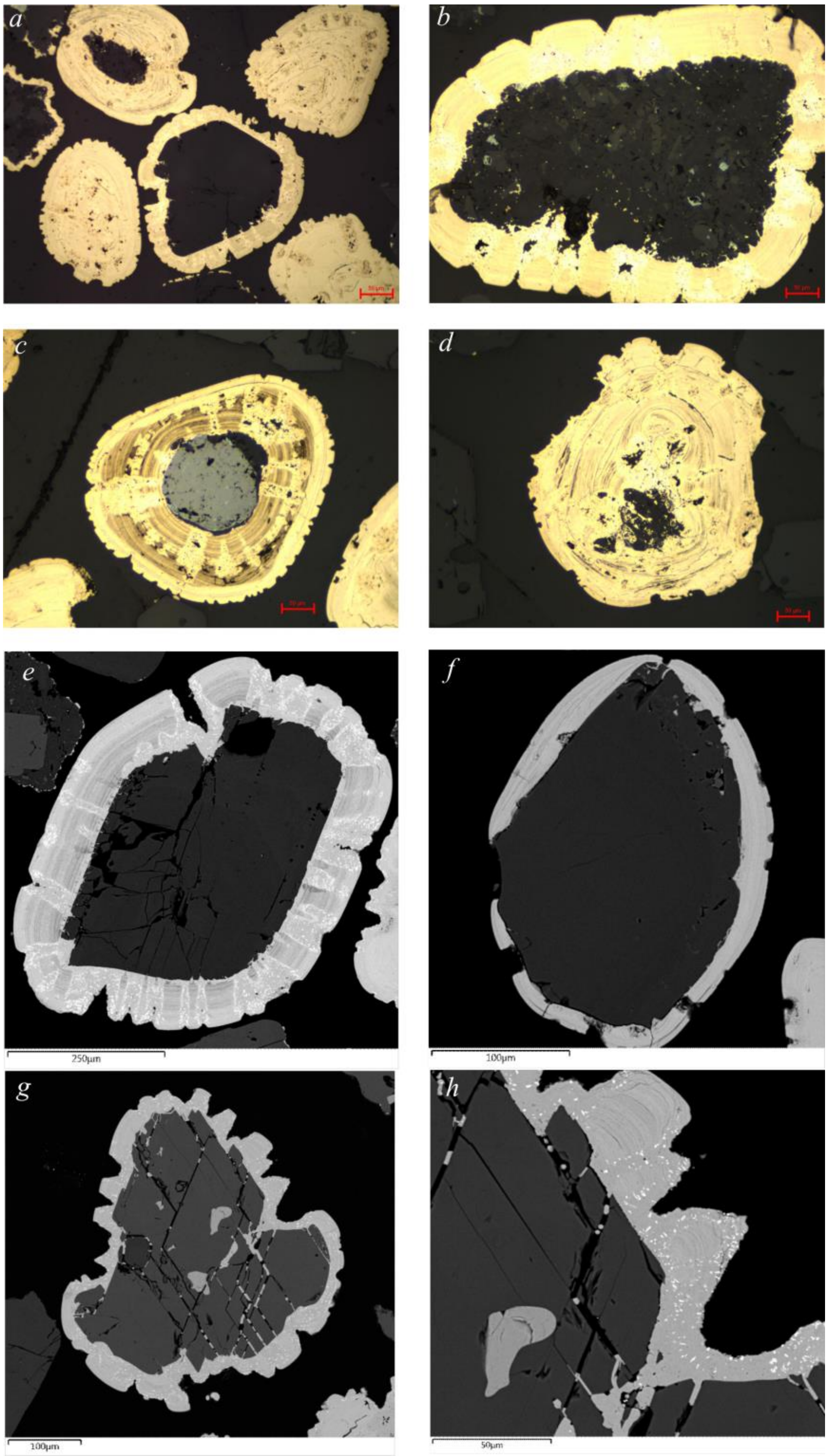

Figure 6: Spheroloides: forms of constitution (a,b,c,d), distribution of mercury (white) and arsenic (bright grey) in pyrite, which growths on rock, for ex. - Pl (dark grey, e,f,g,h).

Cinnabar has the second place for its distribution in the modern hydrothermal systems in Kamchatka. In association with coloradoite, metacinnabar is in the deposits of the Apapel'sky hydrothermal system (Central Kamchatka).

Chalcopyrite, galena, sphalerite are rare minerals. They were revealed in deposits from Mutnovskaya, Vilyuchinskaya hydrothermal systems.

CONCLUSION

The modern hydrothermal systems in Kamchatka provide an opportunity to study sulfide typomorphism and diversity of conditions for their formation. We may consider some of them as elemental long-term ore generating hydrothermal systems.

ACKNOWLEDGMENTS

This work has been carried out with a financial support from the Strategic development program of Vitus Bering State University (2012-2014 years) and Far-Eastern Division of the Russian Academy of Science.

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