Colloids in the hydrothermal-magmatic systems of Kamchatka and the Kuril Islands

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ABSTRACT
Metacolloids in active hydrothermal systems began to be investigated in the 1960s. Currently, several hydrothermal-magmatic systems associated with stratovolcanoes have been explored in Kamchatka and the Kuril Islands. The water-volcanic reaction leads to the formation of silicate and sulphide colloids. Silicate colloids are a geological and geochemical factor that changes the permeability of host rocks, the temperature regime, the chemical properties of thermal waters and affects the formation of ore deposits. The accumulation of heat and non-reactive gases under impermeable layers leads to an increase in temperature and is accompanied by partial melting of siliceous rocks with the formation of ignimbrites and foci of acid magmas.

1. INTRODUCTION
High-temperature hydrothermal systems are the subsurface convective cells of meteoric water circulating in the Earth's crust to a depth of 5-10 km (Belousov, 1978). The lower part of such cells is overlapped by the crust-mantle convective cell in which the heat and mass transfer is performed by magmatic melts, and the source of thermal energy generation is the upper mantle.

According to the data of geological survey, all of the selected geochemical types of thermal waters are interconnected and originate from high-temperature chloride waters. The study of the rocks of aquifer complexes and impermeable horizons in high-temperature hydrothermal systems showed that they interact with hydrothermal solutions (Naboko, 1963). Primary minerals and igneous volcanic glass are converted into minerals of almost the same chemical composition, but with different crystal-chemical structure adapted to the new P-T conditions. In the composition of high-temperature chloride thermal waters there is always orthosilicic acid which plays an important role in the formation of hydrothermal minerals. Chloride thermal waters are often supersaturated with silica, and therefore silicate colloid is formed, which is genetically related to sulfide colloids (Large, 1969). The latter are formed as a result of the interaction of metals, leached by acidic hydrothermal solutions from water-bearing rocks, and magmatic hydrogen sulfide (H2S). Many researchers of the ore genesis consider the role of colloids in the transportation and formation of ores to be very insignificant.

Our article describes the physical and chemical properties of colloidal systems. They determine the role of colloids in the active hydrothermal-magmatic systems and affect the change in their geological and structural conditions, migration of hydrothermal solutions, heat accumulation and the formation of ores.

2. HISTORICAL REVIEW
Chukhrov V.F. (1955) gives an overview of the colloids in the Earth in which he describes their role in the formation of hydrothermal deposits. The composition of hydrothermal solutions is studied by fluid inclusions. It is believed that the waters of hydrothermal-magmatic systems are diluted ionic solutions (Pauzhetsky hot waters, 1965). It should be noted that this problem is debatable. Chukhrov V.F. (1955) suggested that the studies of active hydrothermal systems in the areas of modern volcanism could solve this problem.

The geysers characteristic feature is the deposition of siliceous amorphous rocks on the surface around griffins, known as “geyserites” (Fig. 1). It is composed of opal by almost 100%. The pearl brightness of fresh geyserite is caused by the presence of a thin film of silica sol on it. During the boiling before an eruption the water in the large vents of geysers is blue, and this is caused also by the presence of silica sols in water (Fig. 2).

Fig. 1. The Geyserites of Troynoy geyser. Kamchatka
In 1961 on Pauzhetsky geothermal field, Sugrobov V.M. gathered from the snow surface silica gel which was ejected by a steam-water jet of a geothermal well (Fig. 3). He also investigated the deposition of a white powder on vegetation surrounding the wells. Vegetation died. The monograph by L.M. Lebedev (1967) “Metacolloids in endogenous deposits which describes silica gel of active hydrothermal-magmatic systems is widely known.

The operation of geothermal wells entails cooling and degassing. These changes favor the formation of opal deposits in a well, on pipelines and in streams. The pumping of separated geothermal waters through injection wells back into the reservoir is an integral part of the geothermal field management or ecological requirements. As waste geothermal water is introduced, silica may precipitate causing a gradual or dramatic decrease in the rate of injection. This problem motivates experiments investigating the deposition rates of various types of silica, which are due to the regime of silica gels in the hydrothermal-magmatic systems. Intensive studies of colloidal silica are associated with its industrial extraction, the cultivation of precious opal and development of methods for obtaining three-dimensional nanocomposites at the Mutnovsky geothermal field (Potapov, Kamashev, 2006).

External signs of the active hydrothermal-magmatic systems are boiling springs, steam jets and steamy grounds. In the discharge sites of thermal waters and in the structural traps along the path of superheated water flow, their boiling up and separation of the vapor phase with gases dissolved in water occurs. Near the Earth’s surface or on it, condensation of a cooling vapor phase occurs in which significant quantities of gas components dissolve. As a result of this process, acidic solutions are formed characterized by high aggressiveness with respect to host rocks. Under their influence, there is an almost complete regeneration of host rocks with the decomposition of primary minerals of magmatic origin (plagioclase, augite, olivine, volcanic glass) and the formation of new mineral complexes mainly consisting of clay minerals (kaolinite, montmorillonite), opal, alunite, hydrohematite and pyrite. This process is described from various positions by many researchers.

Naboko S.I. (1963) identified this process as the secondary acid leaching exhibited in volcanic structures. It is expressed in the formation of vast fields of opal rocks with a full change in the composition of aluminosilicate rocks of igneous origin. Their study leads to the conclusion about the significant role of surface and subsurface acid leaching processes in the formation of high-temperature hydrothermal systems on stratovolcanoes (Belousov, 1978).

Opal rocks are characterized by an amorphous structure, and that suggests their connection with the formation of colloidal solutions in the upper part of the ascending hydrothermal jets in stratovolcanoes. The formation of opals in the volcanoes of Kamchatka and the Kuril Islands was studied in detail by Naboko S.I. (1965). The transformation of volcanogenic rocks of an acidic and intermediate composition into opals occurs under the influence of sulphate-chloride and sulphate solutions with pH less than 2. This process is manifested in the leaching of almost all metals from silicate minerals and volcanic glass of rocks containing SiO₂ more than 55% (Naboko, 1963, Esin and Held, 1966) and in the formation of siliceous residues containing minor amounts of titanium. Opal rocks retain the structure of the original rocks and have a high porosity (up to 50%) and low volumetric weight (up to 1.2).

The first stage of formation of such rocks is characterized by the destruction of plagioclases, pyroxenes and olivines with full preservation of the primary rock structure. Phenocrysts of plagioclase transform into opal with retention of zoning. Usually, the process begins with zones rich in an anortite molecule, until the complete transformation into opal. Pyroxene is replaced by opal, starting with cracks. The glassy bulk of lava and tuff cement are replaced with opal, first also near cracks and pores, then the rest of them. Opal is colorless and monolithic. The resulting mineral-opal is isotropic and has a texture in the form of jets and spherulites. The rock contains cristobalite, tridymite, and quartz.
Simultaneously with opals, gelatinous silica gel is observed which can move and fill cracks. It is assumed that silica gel transforms into dense opal in the form of veinlets and lenses in porous opal rock and hydrothermal clays. The formation of silica gel was observed in the areas of evaporation and formation of hydrochloric and sulfuric acids, composed of lake sediments. These poorly cemented rocks turned into white masses of opal appearance. In some areas under the opal fine crust there was hot plastic silica gel which, on cooling, formed a dry white powder. It contained 52% water. The ratio of SiO₂ : H₂O is 1:3.8. Most of the water was released from the opal at the temperatures below 80°C - 46.95%, at the temperature 105°C - 1.57% and at the temperature 120°C - 0.42%. X-ray silica gel is amorphous. When cooled, it becomes hard, when dehydrated it transforms into opal, with aging of opals it transforms into quartz with cristobalite. The silica gel released during acid leaching of rocks goes into the solution and migrates to deep levels of hydrothermal-magmatic systems to propilitic zones. These changes are made by alkaline high-temperature waters with pH = ~ 7.

3. HYDROTHERMAL-MAGMATIC SYSTEMS OF KAMCHATKA AND KURIL ISLANDS

Hydrothermal-magmatic systems of Kamchatka (Mutnovskaya, Pauzhetskaya) and the Kuril Islands (North Paramushirskaya, Paramushir Island; Okeanskaya, Iturup Island; Mendeleevskaya, Kunashir Island) have been studied in detail by drilling geothermal wells. The Kikhpinych hydrothermal-magmatic system, genetically related to the Valley of Geysers and the Uzon Caldera, is also well studied. The drilling in this system was not carried out, due to the fact that it is located in the Kronotsky Nature Reserve. However, good exposure in it made it possible to conduct detailed geological and geothermal studies. The results of these researches were published in our report for the geothermal seminar at Stanford University (Belousov, Belousova, 2018).

One of the conclusions in this article is the assumption that the magma chamber of the Kikhpinych hydrothermal-magmatic system is formed due to partial melting of siliceous metamorphic rocks. They are formed as a result of the transformation of volcanic rocks interacting with hydrothermal colloidal systems. Since these conclusions were obtained on circumstantial evidence due to the lack of geological and mineralogical data for deep levels of the Kikhpinych hydrothermal-magmatic system, we use data from the studies of the above-mentioned systems in Kamchatka and the Kuril Islands.

3.1. Pauzhetsky hydrothermal-magmatic system.

Belousov V.I. has been studying Pauzhetsky hydrothermal-magmatic system from the 1950s to the present (Belousov, 1978). During many years of research of the Pauzhetsky geothermal area, a large amount of geological material was collected, mainly at the Pauzhetsky thermal water deposit (Fig. 4).

![Fig. 4. Satellite image of the Pauzhetsky geothermal area.](image)

The discharge chamber of the system, located on the north-western slope of the Kambalny Range, has been thoroughly studied (Fig. 4, 5). As a result of these studies, complexes of rocks composing the Pauzhetsky geothermal area, their age interrelations, regional and local structures were established. The theory of Southern Kamchatka evolution was proposed (Belousov, 1978). The analysis of the material obtained during the drilling of wells at the Pauzhetsky geothermal area, the determination of the time of some rock complexes formation made it possible to clarify the evolution of the geological structures in the area.

![Fig. 5. Pauzhetsky hydrothermal-magmatic system. Geothermal wells and acidic extrusion. Right - the remnant of a volcano Termalny.](image)

The rocks of the area are of volcanic and volcanogenic-sedimentary origin. The volcanogenic-sedimentary complex is permeated by numerous wells. The maximum depth of GK-1 is 1,150 m deep. Several wells intersected the horizon of litho-crystalline tuffs (Fig. 6).
Fig. 6. Geological-hydrological section of the Pauzhetsky field of thermal waters. 1 - piezometric level of thermal waters; 2 - exploration wells; 3 - geosoterms; 4 - tectonic faults: established and assumed; 5 - alluvium; 6 - lava and lava-breccia of andesite-dacites; tuffs of dacites; 8 - pumice tuffs of dacites; 9 - tuff-breccia of andesites; 12 - litocrystalline silicified tuffs of dacites (“ignimbrite in situ”); 13 - basalt tuffs and tuff-breccias; 14 - sandstone.

The first researchers (Pauzhetskaya hot water, 1965) defined them as analogues of ignimbrite of the Wairakei hydrothermal system in New Zealand (Fig. 7).

Fig. 7. Cross-section through wells in the west of Wairakei including the Te Mihi area, highlighting spatial relationships of rhyolite lavas in the Waiora Formation and ignimbrites (Rosenberg et al., 2009).

Belousov V.I. (1978) showed that lithoclastic tuffs were cemented by amorphous methacolloid silica, zeolites, and hydromica of hydrothermal origin. The primary texture of the rock of this horizon was porous due to the size of the fragments of basalt lavas of pyroclastic and sedimentary deposits on the slope of the Termalny stratovolcano (Fig. 4). In this horizon, a stream of high-thermal waters of the underwater hydrothermal-magmatic system was localized. The mixing of these waters containing silica gel with seawater (cold, containing Mg) was accompanied by the formation of amorphous silica and other hydrothermal minerals in the pore space (Iler, 1979). The rock became monolithic, impermeable to water, with an increased amount of SiO₂ (average content - about 60%). This process led to the geochemical isolation of the hydrothermal-magmatic system of the Termalny volcano (Belousov et al. 1999).

Extrusions. At the Termalny volcano and its periphery, the young extrusive formations of rhyolite and andesito-dacitic composition are widely developed. They date from the Upper Pleistocene and Holocene and occupy a significant part of the area. Their dimensions range from 0.01 to 8 km². Small extrusions have the shape of domes. They are usually surrounded by tuff deposits which fall to the sides of the dome and are disturbed by faults with small displacements (Fig. 8).
Subsidence of thermal water filtration in impermeable horizons leads to the formation of pumiceous rhyodacitic tuffs. At various depths, the thickness of interlayers is from 0.5 to 2.0 m. When plagioclases are heated in crystalline glassy inclusions at a temperature of 950–1015°C, gas bubbles were released. As the temperature increased, they united. At a temperature of 1340°C gas bubbles turned into barely noticeable points. Small drop-shaped glassy inclusions homogenized at a temperature of 1334°C. The temperatures obtained indicate the crystallization of plagioclase phenocrystals at a considerable depth from water-poor magmas.

Average chemical analyzes confirm the existence of two phases of effusion. The first phase has a dacitic composition and forms the base of the dome and the lower lava flow. The second phase forms the dome itself and the upper lava flow and corresponds in composition to liparite-dacite. The lower stream is characterized by a lower content of SiO₂ and K₂O compared to the upper lava flow. The chemical composition of the liparite-dacite of the dome and the upper lava flow does not have significant differences, which indicates the proximity of the formation processes of the dome and the upper lava flow in time.

The presence of two phases of introduction differing in the composition, one after another without a significant interruption, indicates differentiation in the supply channel. At the same time, the low SiO₂ content in the first portions of lava can be explained by hybridization, capture and melting in the crown of the magma chamber of the host rocks. Thus, the Ploskaya extrusion is a multi-act formation. At the early stage of its development a melt eruption occurred, resulting in the formation of the basal part of dome and the lower lava flow. Subsequently, the dome increased due to more acidic lavas of rhyolitic and liparite-dacitic composition. As it grew, new portions of lava squeezed out the previous ones, as a result of this process the dome rose upwards. Viscous material flowed through a relatively narrow channel and that contributed to the formation of concentric flow lines.

In the deep incisions of the south-western extrusion, the onion structure of the dome is observed. Flattening of the top of the dome could occur due to the subsidence of cooling lava and to partial retraction of erupted material back into the channel. Complex interrelationships of tuff-sedimentary rocks and extruding bodies of acidic and basic composition, varying in volume and penetrating not simultaneously, lead to the conclusion that Termalny volcano structure (Fig.4) is a complex volcanic-tectonic uplift.

Hydrothermal changes in water-bearing rocks. The main trajectory of the movement of hydrothermal solutions in the depths of the Pauzhetskaya system at the stage of low-temperature propitization is characterized by the development of lomontite. A sharp decrease in the rate of thermal water filtration in impermeable horizons leads to the paragenesis of lomontite and calcite-hydromica. Of particular interest is the formation of quartz-adular, wairakit-prenit-epidote-quartz-adular and epidote-quartz-adular associations. Quartz areas are composed of fine-crystalline chaledony and mosaic-quartz aggregates. In the intervals of 25–80 m and 125–150 m, complete silicification is observed. Also there is a wide development of quartz-adular metasomatites at various depths. The thickness of zones is from tens of meters to centimeters.

Acid changes. The rhyoliths of the extrusion apical part in the center of the volcano Termalny caldera are altered to opals with a small amount of alunite (Fig. 9).

Fig. 8. Geological map of the Pauzhetskaya geothermal field (Belousov, 1978). 1 - alluvial deposits; 2 - pumice; 3 - tuffs; 4 - lava rhyodacites; 5 - extrusive domes of rhyodacites; 6 - basalts; 7 - wells; 8 - East-Pauzhetskaya thermal field; 9 - faults.
Fig. 9. Opal rocks of the Termalny volcano. In the background is the Kambalny volcano.

The modified rocks compose the southern, most elevated part of the extrusion. In some places, it is possible to observe the initial morphology of extrusion which, in the upper part, is represented as a fan of pillars. Opal rocks form the slopes of the upper streams gully discharging into the south-western part of the Kurile Lake (Fig. 4). The upper part of the section was processed into argillites, in which kaolinite makes up a large proportion. They are colored brown with iron hydroxides. The thickness of the sections is measured by the first meters. The lower horizons of rocks are characterized by a lesser degree of argillization, and gradually pass into brown massive opalits with an admixture of clay minerals and alunite. Deeper, they are replaced by basalts subjected to low-temperature propilization. In the deepest incisions, unchanged basalts are observed. The maximum thickness of the modified rocks is 30-40 m. The volume of the rocks treated with these solutions is significant and covers not only extrusion, but also the host rocks. The extensive section of hydrothermal rocks suggests that acid leaching occurred at a distance of two to three kilometers from the source of solution generation. In this regard, we believe that the hydrothermal solutions were formed at the extrusion site and formed a ground stream that was filtered along the eastern slope of volcano Kambalny ridge, where the glacier moraine is located. The glacier feeding area was located at the top of the dome. Morena covers pumice deposits that are 8,000 years old. There are no fragments of altered rocks in the moraine. Currently, the top of the moraine is above the bottom of the circus. It is assumed that this is due to the rapid erosion of hydrothermally modified rocks by the system of the river Levi Etamynk (Fig. 4).

Hydrogeothermy. Alluvial boulder-pebble deposits contain groundwater flow. Low-permeable tuffs under them are the upper impermeable horizon. Below is the main artesian aquifer. Litocrystalklasic tuffs underlying the aquifer complex play the role of its values, and α-argillization caused the rocks that make up this ridge. Three geothermal wells were drilled at the foot of the Ebeko volcano (Fig. 10). The geological section of the GP-3 well was studied by Rychagov and others (Rychagov et al., 2002). The upper part of the section is composed of almost fresh lavas of andesites and andesite basalts. Hydrothermal minerals are found in thin cracks and voids. Hydrothermal changes of rocks in the section of the well GP-3 are characterized by a zonal structure.

3.2. Other hydrothermal-magmatic systems of Kamchatka and the Kuril Islands

3.2.1. Mutnovsky hydrothermal-magmatic systems

Mutnovsky hydrothermal-magmatic systems are located 70 km to the south of Petropavlovsk-Kamchatsky. They are associated with the Mutnovsko-Gorelovskaya group of volcanoes, in which two volcanoes are active - Mutnovsky and Gorely and two are inactive – Dvugorby and Zhirovska. Zhirovska volcano is strongly eroded. One of these hydrothermal-magmatic systems, associated with the Dvugorby volcano, is currently explored by geothermal wells. Here there are fields of hydrothermal altered rocks, formed as a result of acidic waters influence on volcanogenic rocks (Belousov Belousova, 1985). It is assumed that on the volcano Dvugorby there was a glacier, which tongues descended along the river valleys. The eruption of the last portions of acidic viscous melts led to the melting of the glacier and the formation of a groundwater flow of acidic waters directed to the north-east. Filtration of those solutions with pH ≤ 2 along the pores and cracks of lavas and tuffs masses which make up volcanoes caused the primary rocks transformation to opals and alunites. Partly neutralized by interaction with rocks, thermal waters with a pH ≥ 3-4 contributed to the formation of clays, which filled cracks and pores and formed “cap-rock”. The deep flow of high-temperature chloride waters of this hydrothermal-magmatic system is characterized by the deposition of quartz minerals. Quartz is formed at the depths from 50 m in the central part of the field to 500-600 m on its periphery. It is represented by chalcedony and amorphous quartz minerals. These minerals confirm the presence of silica gel in the high-temperature waters of the Mutnovskaya system.

The problem of extracting this product in industrial quantities is currently being studied (Potapov, 2002). Opal and α-cristabolite are developed in the subaerial conditions up to temperatures of 110 - 120°C. Opal is also developed in the montmorillonite-zeolite zone (up to depths of 500 m) in pores and cracks.

3.2.2. North Paramushir hydrothermal-magmatic system

The North Paramushir hydrothermal-magmatic system is located in the northern part of the Vernadsky Range (Paramushir Island, the Great Kuril volcanic arc) (Fig. 10) (Belousov and others, 2002).

The geology of this system is due to the activities of the volcanoes that make up this ridge. Three geothermal wells were drilled at the foot of the Ebeko volcano (Fig. 10). The geological section of the GP-3 well was studied by Rychagov and others (Rychagov et al., 2002). The upper part of the section is composed of almost fresh lavas of andesites and andesite basalts. Hydrothermal minerals are found in thin cracks and voids. Hydrothermal changes of rocks in the section of the well GP-3 are characterized by a zonal structure.
In the interval ~ 100-1650 m the main mineral is siliceous cement of volcanic-sedimentary rocks. SiO$_2$ content is ~ 60%. Cement is represented by opal, cristobalite, tridymite, quartz and chalcedony. Quartz and chalcedony predominate. Rocks are cap-rock. They are also insulators of heat. From a depth of ~550 m, adularis, quartz, chlorite and epidote are found. Also present is organic material substituted with silica and sulphides. According to the researches of fluid inclusions, the temperatures of the formation of minerals range from 130-150 to 220-250°C. They are typical for the boiling zones (up to 130-180°C).

In the interval of 1650-2500 m, the hydrothermal mineralization is represented by the quartz-chlorite-epidote-muscovite association. The temperatures of formation of these minerals are 180-300°C. Deeper than 2000 m, muscovite, sericite are anhydrite are found along with quartz minerals.

3.2.3. The hydrothermal-magmatic system of the Baransky volcano

The hydrothermal-magmatic system of the Baransky volcano is controlled by its structure. It is located in the north-eastern part of the Grozny range on the Iturup Island (the Kuril volcanic arc). The Grozny ridge is characterized by a cluster of active volcanoes, on which there are several large craters and domes. Numerous sources of acidic thermal waters are associated with them. In the valley of the Sernaya River, the thermal manifestations of the Ocean field are located. On this thermal field, several productive wells have been drilled, which supply a geothermal power station with steam. The geological sections of these wells are described by Rychagov and others (1993). They are characterized by the zonation of hydrothermal changes. In the range of 0–100 m, such acid-altered minerals as opal, kaolinite, and alunite predominate. In the range of 100–300 m, minerals characteristic of low-temperature propylites are present, such as montmorillonite, calcite, zeolites, chlorite, smectites, and hydromica. Deeper than 300 m, in cores, high-temperature (250-300°C) minerals of the quartz, epidote group and sulfides prevail.

3.2.4. Mendeleevskaya hydrothermal-magmatic system

The basic structure of the Mendeleevsky hydrothermal-magmatic structure is the Mendeleeva stratovolcano on the Kunashir Island. He has two sommas (Gorshkov, 1967). The first one is composed of andesites and andesite-basalts, and the second – of andesite-basalts and basalts. In the second cone there is a dacite dome.

On the border of the second somma and the dome, the Western, North-Western, North-Eastern and South-Eastern thermal fields are located at the altitude of 300-400m above sea level. Thermal manifestations of the Northeast and Southeast fields are located in aexplosive craters and are represented by sulfur fumaroles, mud pots and heated soils. A lot of thermal springs emerge at the foot of the volcano. On the coast of the Pacific Ocean, 8 km to the south from Yuzhno-Kurilsk, the Goryachi Plyazh deposit has been explored (Fig. 11). On the site Preobrajenski of the deposit (its area is of 1 x 0.5 km) nine wells were drilled in 1964-67. One of them has a depth of 759.4 m.

The site of the deposit is mainly composed of Neogene and Quaternary volcanogenic sequences. Quaternary deposits are represented by volcanicogenic and volcanic-sedimentary rocks of the Upper Pleistocene and Holocene. The igneous rocks include extrusive dacites of the modern volcanic summit, as well as Pliocene acidic extrusions and coastal zone intrusions. It is assumed that the thermal channels of Goryachi Plyazh are localized in the fractures around the extrusion of Goryachi Miis.
Wells were drilled through tuffs modified by high-temperature waters. The processes of the formation of various types of quartz and zeolites predominate. The number of quartz and zeolites increases significantly down the section. The chemical composition of the thermal waters of the Goryachi Plyazh is similar to chemical composition of the waters of the Pauzhetskaya hydrothermal system, but they have increased mineralization (up to 7-8 g/l). In the lower fractured zone, deep boreholes revealed the water with a salinity of ~ 25 g/l, which suggests a local income of sea water into the hydrothermal system.

4. DISCUSSION
The model of a hydrothermal-magmatic system is represented as a structure linking various hydrothermal manifestations and products of magma activity (Fig. 12).

Fig. 12. Model of the hydrothermal-magmatic system in areas of modern volcanism (Hedenquist & Lowenstern, 1994).

The main process that forms the chemical composition of hydrothermal solutions is the interaction of thermal waters saturated with igneous emanations and volcanic rocks. The above data indicate that hydrothermal solutions of the active hydrothermal-magmatic systems of Kamchatka and the Kuril volcanic arc are a colloidal silicate system. Silica colloids are formed in aquifer complexes composed of volcanogenic and volcanogenic-sedimentary aluminosilicate rocks, along the migration routes of meteoric water from the upward flow of igneous fluids to the sites of discharge. The behaviour of colloidal silica is determined by the chemical properties and temperature of hydrothermal solutions. Potapov V.V. and Kamashev D.M. (2006) believe that the formation of colloidal silica in a hydrothermal solution occurs as a result of the nucleation and polycondensation of orthosilicic acid molecules.

The hydrolysis reactions of aluminosilicate minerals and volcanic glasses, which form the water-bearing and impermeable complexes of high-temperature hydrothermal systems, began to be studied in the 1930s (Belousov and others, 1999). Two models of such reactions are known: one is based on diffusion-controlled kinetics and the other is based on kinetics controlled by surface reactions. Recently, most research has focused on modeling reactions controlled by the water-rock contact surface. These studies have shown that leached layers are formed on the surface of aluminosilicate minerals and volcanic glasses. When interacting with acidic solutions, mainly alkaline and alkaline-earth elements and aluminum are extracted from them. The thickness of the leached layers depends on the pH of the solution. Aluminum is leached to a depth greater than alkali metals, except when hydrothermal solutions are neutral. Diffusion of reactive compounds and reaction products through these layers does not affect the rate of these reactions. These phenomena make it possible to explain the natural processes of leaching, chemical weathering and metamorphism that are widespread in the Earth’s crust. In the process of continuous interaction of thermal waters with aluminosilicate minerals and volcanic glasses, hydroxysilicate chains and layers are peeled off, and in the form of micelles (sols) are transferred to hydrothermal solutions, saturating them with silica (Yanagisawa et al., 1995). Silica is constantly undergoing the processes of dissolution and precipitation. The studies of hydrothermal-magmatic systems have established a link between hydrothermal changes and the temperature regime of thermal waters (Fig. 13).

Fig.13. Graph of solubility of various polymorphic differences of silica in water depending on temperature (White et al., 1992).
The silica concentration in meteoric water ranges from 5-35 mg/kg. The silica content in seawater ranges from 2 to 14 mg/kg. Manganese and magnesium can precipitate dissolved silica, reducing its concentration in seawater to 0.3 mg/kg. During coagulation, the settlement of silica from the solution occurs through the interaction of colloidal particles and with other particles charged with an opposite electrostatic charge. In acidic, neutral and alkaline solutions, silica solutions always retain their negative charges. Only a very high concentration of acid (pH <2) can change the charge (Eitel, 1962 p. 255). Neutral and positive charges of silica solutions can explain the formation of residual silica in the interaction of rocks with ultra-acidic hydrothermal solutions. The result of this interaction is the almost complete leaching of metal cations (with the exception of Ti), which also have a positive charge. Neutralization of the hydrothermal acid solution leads to a negative charge of the sol. This contributes to the joining of silica solutions with positively charged AlO2 particles and the formation of clay minerals near opal rocks (Eitel, 1962). A further increase in the pH of hydrothermal solutions and a negative charge of the silica sol is accompanied by interaction with cations of alkalis and alkaline-earth elements and the formation of mineral complexes such as propylitization.

As it is known from the work of Eytel V. (1962), the properties of silica hydrosols are somewhat different from ordinary sols. At the beginning of the process of the connection with the metal cation, they do not coagulate, but form a gel as the temperature decreases when the hydrothermal solutions evaporate or when mixed with cold water. The most effective deposition of silica in the form of chalcedony occurs when hydrothermal solutions (silica gel) mix with sea water, which contains magnesium.

4.1. Sintered tuff in situ

The formation of impermeable horizons in the strata of volcanic-sedimentary rocks can be explained by the influence of sea water magnesia on the silica gel of temperature waters. As noted earlier, in the volcanic-sedimentary strata of the Pauzhetskaya hydrothermal-magmatic system and as well as other systems in Kamchatka and the Kuril arc, horizons of welded tuffs are described, which we interpret as siliceous volcanogenic-sedimentary rocks. In the Pauzhetskaya hydrothermal-magmatic system, such a horizon, relatively impermeable to water and gases, separates two aquifers. The lower complex of carbon dioxide waters, composed of volcanic sandstones of basaltic composition and mudstones with marine fauna, is covered with tuff breccia and basalt tuffs cemented by amorphous silica (“in situ ignimbrites”). It is assumed that this horizon was formed as a result of silica deposits in the thickness of clastic rocks on the slope of andesite-basalt subaerial volcano as a result of the interaction of hydrothermal solutions with sea water. The sections of the aquifer complexes and impermeable horizons in the Mutnovsky, North-Paramushirsky, Baran and Mendeleevsky hydrothermal-magmatic systems also have a volcanogenic-sedimentary origin and contain horizons of dense, “welded and baked” tuffs and tuff breccias similar to Pauzhetka’s “ignimbrites in situ”. The average chemical composition of these rocks is characterized by a higher content of SiO2 compared with the composition of basalt and andesitic debris.

Silicic acid hydrosols possess the properties of lyophilic sols which are capable of stabilizing lyophobic sols (similar to metal and sulphide suspensions), the latter are highly sensitive to the coagulating action of cations. Therefore, the lyophilic suspensions of silicic acids of this type act as protective colloids. In the best way, the protective property of silica sols is manifested at the time of simultaneous precipitation with lyophilic particles.

A natural object of the interaction processes of colloids of silicic acid and sulphides in hydrothermal solutions are “black smokers” at the bottom of the oceans. According to deepwater drilling, a surface hydrothermal construction has “roots” to a depth of 125 m (Fig. 14) (Bogdanov, 1997). Similar processes can occur in the places where opals and clays are formed. The interaction of ultra-acidic and acidic hydrothermal solutions with aluminosilicates leads to the formation of positively charged silica gel. This leads to almost complete leaching of metal cations and their migration into the zone of ascending jets of magmatic fluids containing H2S and other sulfur compounds. The formation of sulphides and they aggregate with the formation of negatively charged sols, which, together with the negatively charged silica gel, migrate at depth to the places of discharge of hydrothermal solutions. Here, coagulation and precipitation of a mixture of both colloids occurs as a result of a drop in temperature or mixing with seawater.

Fig. 14. The structure of active hydrothermal construction from drilling data (Bogdanov, 1997). 1 — pyritic breccia; 2 pyrite-anhydrite breccia; 3 - pyrite-siliceous-anhydrite breccia; 4 - pyrite-siliceous breccia; 5 - siliceous basalts breccia; 6 - breccia of chlorinated basalts; 7 - basalts.

Pokrovsky and others (2015) dispute the modern model of formation and distribution of gold deposits, according to which hydrogen sulfide and chloride are ligands responsible for the mobilization of gold and its precipitation by hydrothermal solutions in the lithosphere. They propose a model based on the fact that sulfur radicals, such as the trisulfan ion S3-, form very stable and soluble complexes with Au+ in aqueous solution at elevated temperatures (> 250°C) and pressures (> 100 bar). These compounds make it possible to extract, transport, and focus gold deposition by sulphurous fluids 10–100 times more efficient than only by
sulphides and chlorides. In our opinion, the colloidal concept of transfer and accumulation of polymetals and noble metals is less controversial. The role of CO₂ in hydrothermal-magmatic systems forming gold deposits is not explained in these models.

Studies of the sorption nature of silica gels showed that under terrestrial conditions there are several types of them. The most common form is hydrogen silica gel. The magnitude of the cations sorption of such silica gel is strictly dependent on the pH of the solution, and is also very small not only in acidic, but also in neutral medium. Ca-silica gel has a significantly greater exchange capacity (50-100 times) compared with H-silica gel, even in the acidic pH range. It differs from most other salt forms in that the Ca²⁺ ion, which does not have any appreciable specific adsorbability, is relatively easily and reversibly exchanged for other cations (Belousov and others 1999). The presence of Ca-silica gel in hydrothermal solutions with elevated CO₂ contents (up to 29-30%) is demonstrated by the high contents of Ca-silicate minerals of the zeolite group (lomonite-Ca(Si₄Al)O₂•4H₂O). In this regard, it is assumed that metals, preferably with large atomic radii, are transported by carbonated hydrothermal solutions. Since CO₂ begins to be released from boiling hydrothermal solutions, the change of Ca-silica gel to another type of silica gel with less adsorption capacity occurs. This process is associated with the apical parts of magma chambers in the upper part of hydrothermal-magmatic systems, where phreatic and phreato-magmatic eruptions are generated (Belousov, Belousova, 2016). This is the way pay ores can be formed.

5. COLLOID MODEL OF HYDROTHERMAL-MAGMATIC SYSTEM

The composition of hydrothermal solutions obtained as a result of laboratory analyzes is represented in the ion-molecular form. This fact apparently is a prerequisite for creating models of the formation of ore deposits by true solutions. However, researches of these minerals properties led to a different understanding of hydrothermal processes. The ideas were proposed of other chemical processes which can be described by the laws of colloid chemistry. There are evidences that hydrothermal solutions of high-temperature systems are the complex colloidal systems formed as a result of the interaction between water and igneous rocks. They are involved in the formation of the hydrothermal-magmatic system structure, including magma chambers in the Earth's crust, and affect their activity and formation of ore deposits.

5.1. The formation and activity of acidic magma chambers hydrothermal-magmatic systems of Kamchatka and the Kuril volcanic arc

The embryonic phase of evolution of the Kamchatka and Kuril volcanic arc hydrothermal-magmatic systems can be compared with underwater high-temperature hydrothermal systems of mid-oceanic ridges. They are formed as a result of infiltration of ocean water into the lithosphere at depths of up to 10-11 km into the zone of interaction between magma chambers and sea water. Due to the heat flow associated with the generation of igneous systems in the upper mantle and oceanic crust, porous rocks saturated with water are heated (Belousov et al., 2017). In these rocks, hydrothermal solutions are formed, containing silica gel and sulphide colloids. Silica deposition occurs on their migration paths, and this leads to the isolation of hydrothermal water draining the anomalous heat flow.

The described hydrothermal-magmatic systems of Kamchatka and Kuril volcanic arc are in a transition step from the subaerial stage to continental stage. It is characterized by a gradual decrease of the interaction between the hydrothermal-magmatic system and seawater.

The evolution of the colloidal model of hydrothermal-magmatic systems under conditions of the island volcanic arc regime is shown on an example of Tersmalny volcano. The early stage of its evolution is represented by tuff and coarse clastic deposits of basalts and andesites, in the upper part of which there was a stream of thermal waters with silica gel. The coagulation of silica gel and silica deposits, caused by the interaction of hydrothermal solutions with seawater, has led to the appearance of an impermeable horizon with a high content of SiO₂. The temperature rises beneath it, and gases (CO₂, CO, CH₄, H₂, etc.) are accumulated, which leads to the formation of an upward flow of higher-temperature hydrothermal solutions with high concentrations of silica gel. Thickness of the siliceous horizon increases as a result of the boiling of these solutions and intensive precipitation of amorphous silica in the apical part of the volcanic edifice. Accumulation of the additional amount of heat causes the increase of the temperature to the point of partial and complete melting. This process of granite formation is discussed in the monograph of Guo-Neng Chen and Grapes R. (2007). The accumulation of CO₂ and detonation gases leads to phreatic and phreatomagmatic eruptions, the formation of caldera, deposition of ignimbrites (with fiamme) and elevation of the resistive dome of rhyodacites. The most high-temperature melts of rhyodacite composition erupted in the form of flows, several meters thick, on the western slope of this volcano. Pumice and ash tuffs were deposited on the north-western slope and at its foot in the subglacial lake, where the upper complex of chloride waters of the Pauzhetsky hydrothermal-magmatic system was formed. Under the influence of the load of eruption products and thick glacier, as well as injections of mantle basalt melts, low-temperature acid melts were squeezed into a dome and viscous flows. The migration of the flows was limited to the preserved parts of the volcano edifice and glaciers. The introduction of a resurgent dome has distorted the encompassing strata formed by previous eruptions. The interaction of glaciers and the dome, evolving HCl, SO₂ and H₂S, was accompanied by the formation of acidic and ultra-acid hydrothermal solutions with pH <2.

It is noted that the magma chambers of modern or recently operating hydrothermal-magmatic systems in the Earth's crust are formed at a shallow depth (first kilometers), and volcanogenic rocks modified by hydrothermal solutions are involved in these processes which is confirmed by the studies of halitum isotopes in zircons (Simakin, Bindeman, 2014).

5.2. Heat generation in an acid magma chamber

Leached metals, both from the rocks of the resurgent dome and the host rocks of the volcano, can penetrate to a considerable depth with ultra-acidic and acidic solutions. These solutions, interacting with the surrounding rocks, became neutral. The main gas components in the formation of such solutions are hydrogen chloride (HCl), sulfur dioxide (SO₂) and hydrogen sulfide (H₂S). Shinoara and Kazakhaya (1991) propose the concept of the influence of a magma chamber in the Earth's crust on the generation of acid gas HCl which is involved in the formation of silica gel. The origin of hydrogen chloride is connected with the mineralization of deep seated thermal springs, which include chloride compounds of alkali and alkaline-earth elements in the ionized state. It is
assumed that seawater may infiltrate into the zone of influence of a magma chamber in the Earth's crust, which contains chlorine. Also, the source of chlorides is magmatic hydrogen chloride, caused by infiltration of chloride-sulphate water of surface formation along deep faults. In this case, gases with hydrogen chloride, previously separated from the magma of the hydrothermal-magmatic system, return to the bowels of this system. Chlorine, in the above mentioned sources, is in the form of salts. Experiments conducted by Kazakhaya and Shinohara (1991) show that as a result of hydrolysis, HCl will be generated in the NaCl-H$_2$O system at high temperature which is characteristic for all the above mentioned sources of NaCl (Fig. 15).

**Fig. 15. Diagram of a simple model of the flow system used for the migration of HCl in the vapor phase (Kazakhaya K., Shinohara H., 1991)**

Ultra-acidic and acidic solutions in the hydrothermal-magmatic system are encountered with ascending streams of sulfur dioxide. As a result, constantly replenished deposits of sulphide minerals are formed, pyrite and pyrrhotite dominate in them. During phreatic and phreatomagmatic eruptions, meteoric water saturated with oxygen and atmospheric air (Ohsawa et al., 2000) enter these levels (up to a depth of 2 km). As a result of redox reactions, heat is generated. It is possible that the introduction of basalt melts, the temperature of which is more than 1000°C, causes the burning of sulphides with the release of large quantities of heat. These processes are confirmed by excessive degassing of sulfur gases by volcanoes with magma chambers in the crust (Shinohara, 2008). Thus, acidic magma chambers in the structure of hydrothermal-magmatic systems are the generators of thermal energy that maintains this system in working condition, and largely provides thermal power to hydrothermal flows. It is assumed that an intensive meteoric and atmospheric air circuit enhances the processes of heat transfer, both in the crust and in the mantle (Belousov, Belousova, 2016).

6. CONCLUSION

Studies of the active hydrothermal-magmatic systems in the areas of modern volcanism show:

- in the long-lived volcanic centers, the transfer of anomalous heat fluxes in the Earth's crust occurs by basalt melts and magma fluids;
- interaction of mantle heat-transfer agents with host rocks and meteoric waters contained in them is accompanied by the formation of a colloidal system consisting of a lyophilic colloid of silica and lyophobic colloids of sulphides;
- the colloidal system participates in the creation of acidic magma chambers in the upper part of the Earth's crust in the mode of self-organization and associated hydrothermal systems;
- changes in the thermodynamic parameters of the colloidal system near the Earth’s surface lead to the formation of ore deposits;
- the interaction of sulphides with injections of basaltic melts leads to intensive redox processes with excessive heat generation, which keeps the hydrothermal-magmatic system in operation.

REFERENCES


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