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THE FORMATION OF HYDROTHERMAL-MAGMATIC SYSTEMS OF SKARN TYPE

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ABSTRACT

Accompanied by intensive CO_2 emission, submarine volcanic activity at equatorial latitudes of the globe creates the necessary conditions for the formation of coral reefs. In the process of its evolution, the coral head is getting compacted and turns into a water impermeable thickness (cap-rock), which plays a role of heat insulator. The big thickness of the cap rock (up to 2km) leads to the rise in temperature in the depths of hydrothermal-magmatic systems. Rocks with high content of silica can melt partially and form the chambers of acid magmatic melts in the Earth's crust as well as the secondary flows of volatile components. H₂O and CO₂ are the main volatile components.

The migration of CO_2 in the hydrothermal-magmatic system occurs in the form of diffusion and jet streams and is due to its weak chemical reaction activity in water and silicate melts. The migration of the gas phase of CO_2 in the water-bearing complex is controlled by the upper relative water impermeable horizon, the formation of which is conditioned by the processes of acid and propylite metamorphism. The bubbles of CO_2 rise along the border of the gas impermeable barrier which is usually tilted from the top of the volcanic edifice to its periphery. They combine into jets and stimulate the boil in a vertical column located above the apical part of the rock body at a depth of about 2km. Such uprising carbonated hydrothermal column acts as a gas lift pump. As a result of pumping of hydrothermal fluids, a hydraulic depression contacting with the igneous convective system appears in the water-bearing complex. Water vapor, which has high heat capacity, experiences tremendous heat losses in the magmatic convective column, immersed in the area of the thermal energy generation in the lower crust and upper mantle. The balance in favor of strengthening of the diffusion flux of CO₂ is caused by the increase of the thickness and decrease of the permeability of the upper water impermeable cover, which evolution is connected with the activities of the condensate water of the surface formation. Rise in temperature of the water,

caused by the evolution of the insulating properties of the cover, is accompanied by its vaporization, phreatic-magmatic phreatic degassing, and explosions. The connection between volcanic structures and limestone organic formations, including coral structures, is not random, but genetically determined. Such hydrothermal-magmatic systems are characterized by great heat capacity, which manifests itself in the surface thermal manifestations, in the places of exploitation of geothermal resources, and in the areas of the high intensity of minerals and ore deposits. The skarn type hydrothermal deposits are found in the depths of such systems.

This model describes, in particular, geological and hydrogeothermal situation which existed in the areas of Apennine Peninsula (Larderello Monte Amiata geothermal region) and California Cordillera (Geyzers-Clear Lake geothermal field).

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SKARNS

Terminology,localization,petrologic-mineralogical characteristics

Einaudi (1982) describes skarns and ore skarns. The first, which are distributed limitedly, were formed shale-limestone along contacts during metamorphism. The latter are skarns which contain the ore mineralization. They were formed as a result of the infiltration of the fluids produced by igneous intrusions. The classification of skarns may include the type of the rock as well as the mineral aggregates of substituted lithology. The terms of endo- and exoskarns relate to igneous rocks and carbonates, respectively. Einaudi (1982) subdivided exoskarns into Ca-skarns and Mg-skarns. Ca-skarns were formed as a result of the substitution of limestone.

They contain garnets (of andradite-grossularite series), clinopyroxenes (of diopside-hedenbergite series), wollastonite, scapolite, epidote and magnetite. Magnesian skarns are the result of the substitution of dolomites. They are presented by such minerals as diopside, forsterite, serpentine, magnetite, talc in the porous silica environments, and talc, tremolite-actinolite, in silicon-enriched environments. Silica-pyrite skarns are the third type of skarns. They relate to the ore formation stage associated with some porphyry deposits.

Ore skarns are classified according to the composition of the mineral aggregates. So there can be Fe-skarns, Au-skarns, W-skarns, Cu-skarns, Zn-Pb-skarns, Mo-skarns and Sn-skarns. In porphyritic systems, the hydrothermal changes and ore formation in carbonate rocks lead to the formation of the ore skarns which are economically important. The nature of the ore skarns in the conditions of the porphyritic systems depends mainly on the content of carbonates in the altered rocks, their permeability and structural characteristics. Carbonate rocks decompose in accordance with the reaction: CaCO₃ + 2H⁺ = Ca²⁺ + CO₂ + H₂O.

The type of the hydrothermal changes and ore formation also depends on the hydrothermal and metasomatic processes. They are responsible for the formation of the different types of skarns. Einaudi (1982) called them skarn hornstones, calcium skarns, magnesia skarns and silicon-pyrite skarns. Skarn hornstones are formed as a result of the decomposition of carbonates and dehydration of carbonate strata without input of additional components. They are presented by wollastonite and diopside hornstone. Formation of skarns is caused by the various processes and is associated with the final stage of the magmatic activization and hydrothermal phases of the magma intrusions into sedimentary rocks. Cooling of the plutonic masses is accompanied by the contact metamorphism and metasomatism of the enclosing rocks. Skarns are formed in the temperature range of 700 to 200°C and pressures of 0.3 to 3 kbars. Mineralization of the metasomatic fluids varies from 10 up to 45 weight % NaCl eq. The hydrothermal solutions came out of magma at an early stage and mingled with meteor waters in increasing amounts during cooling.

Tectonic position

Skarns occur in the areas of the manifestation of magmatism and the presence of carbonate rocks. Meinert et al. (2005) describes four main tectonic scenarios: 1- steep fall of the oceanic plate; 2-transitional low-angle subduction; 3- continental subduction and 4- continental rifting. Steep oceanic subduction leads to the formation of Fe-, Cu- and Au-skarns connected with diorite and granodiorite

plutons. Transitional low-angle subduction may be favorable for Mo- and W-Mo-skarns connected with monzonite and granitic plutons. Continental subduction relates to the tectonic positions for the majority of skarns which include Zn-Pb, Cu, Au, W, Mo deposits, usually associated with granodiorite and granite plutons. Continental rifting, associated with mantle plumes or upwelling asthenosphere, results in the intrusion of granitic plutons and Sn-W skarns.

PORPHYRY HYDROTHERMAL-MAGMATIC SYSTEMS

Burnham (1979) studied the hydrothermal-magmatic systems formed during the cooling of the granodiorite stocks containing 3 weight % of water. The intrusive body is formed in subvolcanic environments. It was supposed that at the initial stage of the cooling process the system was open. Which means that the volatile components evolve through the fractures located above the pluton. Burnham notes that at a later stage, when the hard shell forms from the cooling rocks, the intrusive body becomes a closed system. The maximum temperature inside the stock is 1025°C, and the 1000°C isotherm is located at a depth of 2.5 km. It limits the part of the body 90% of which is the melt. Above and to the other sides of 1000°C isotherm, the concentration of H₂O in the remaining melt increases to the area where the melt is saturated with H₂O up to 3.3 weight.%.

Using the experimental data, William-Jones and Heinrich (2005) consider that the phase of water vapor is an important agent in the transfer of metals in hydrothermal systems. The volatile phase is considered as a mineralized water fluid with the density less than critical. The fluid may be the brine (hypersaline) or water solution. Initially, it has a mineralization > 26 weight % NaCl eq., and later < 26 weight % NaCl eq. When the temperature is below the temperature of the critical point, the liquid is usually enriched with H₂O and salt. The fluid is a mobile phase containing volatile substances such as H₂O, CO₂, SO₂, H₂S, N₂ with a different quantity of the dissolved components, such as chloride salts.

The phase of the volatile components in the hydrothermal system becomes denser as the temperature and pressure increase. Coexisting liquid water increases in volume. At the critical point $(374^{\circ}C \text{ and } 225 \text{ bar})$, both phases become indistinguishable from the water. The volcanic sublimates around fumaroles indicate the role of the volatile components in the transfer of a significant number of metals. These sublimates show that, in addition to H₂O, other important components are CO₂, H₂S, HCl, CO and H₂.

The concentrations of the metal elements in the volatile volcanic components are variable and depend

on the composition and nature of the magmatic source. For example, basalt magma is enriched with Cu, Zn, Pb, Sb, Ag and Au. Andesitic magma is characterized by the high content of Cu, Pb, Zn, As, Mo and Hg. Felsitic (acid) magma has lower concentrations of these elements. It is characterized by the higher content of Sn and Mo. The active subaerial and submarine geothermal systems provide the data for the reconstruction of the physicochemical characteristics of the hydrothermal-magmatic systems.

The main agents which provide the activity of the hydrothermal-magmatic systems are the thermal energy, silicate melts, water in liquid and gaseous state and gases (H₂O, CO₂, H₂S, HCl, CO and H₂ etc.).

ACTIVE HYDROTHERMAL-MAGMATIC SYSTEMS

In the active hydrothermal-magmatic systems, the volatile components rise, discharge in the form of fumaroles or condense in the underground waters. The acid thermal waters are formed there. They determine the formation of the vast fields of the argillite hydrothermal changes. The study of the magmatic fluids in the active hydrothermal-magmatic systems may provide the additional material for the interpretation of the processes responsible for the formation of hydrothermal ore-magmatic fields.

Besides water, carbon dioxide is the most common volcanic component. Its mantle-magmatic origin is confirmed by the data on ¹³C, as well as by the mass balance estimation (Fischer, Marty, 2005).

Geochemical studies on volcanoes showed that a large amount of CO₂ was released not only in the form of jet flows (up to 380 000 t/day) from the active volcanic craters, but also in the form of the diffusion of soil emanations (up to 2 800 t/day) in the area of the volcanic structure (Notsu et al., 2005). CO₂ plays an important role in the formation of the hydrothermal solutions. Epithermal environments (up to the depth of 2.0km) deserve the special attention. The contrasting hydrothermal processes occur there. In the epithermal environments of the hydrothermalmagmatic systems, the poor mineralized chloride hydrothermal vents, enriched by silica, are responsible for the transportation and deposition of metals (Belousov, etc., 1998, 2008). Quantitatively, CO₂ prevails over chlorine and H₂S. Water, mainly meteoric, circulates to the depths of 5-10 km. It is heated by the igneous melt, subcritical fluids and anomalous heat flow in the specific geological conditions. The top water-impermeable horizon plays the role of a thermal insulator (cap-rock) there. As a result of the free and forced convection, the hydrothermal flows rise to the surface. They are exposed to boiling, cooling and mixing with cold meteoric waters of surface-related formation (Giggenbach, 1997)

Acid thermal waters of the surface-related (condensate) formation and deep neutral chloride hydrothermal fluids interact with the enclosing rocks. As the result, the minerals with other physical and chemical properties are formed. In particular, on the periphery of thermal flows, the shells with impermeable and heat-insulating properties are formed (Belousov, etc., 2008, Levers, Belousov, 2010). So the hydrothermal-magmatic systems become isolated from the surrounding meteoric waters. The deposition of the hydrothermal minerals on the periphery and in the apical part of the hydrothermal-magmatic system creates an almost impermeable shell for water and gases. It plays the role of the geochemical barrier (Giggenbach et al. 1989; Belousov, Rychagov, 2010). Under the influence of acid hydrothermal solutions, the volcanic rocks are getting transformed into argillites and opalites, and then they are neutralized. In the depths of hydrothermal-magmatic systems, the neutral chloride fluids are saturated with dissolved silica. During the horizontal migration, the hydrothermal solutions are cooling. In the site of discharge, the silicic acid polymerises, coagulates and becomes the negatively charged silica gel. The silica gel (lyophilic sol) and related colloid sulphides (lyophobic sol), also charged negatively, adsorb the cations of ore metals. They are deposited on the periphery of the hydrothermal-magmatic systems.

DYNAMICS OF CO₂ IN THE EPITHERMAL CONDITIONS OF THE HYDROTHERMAL-MAGMATIC SYSTEMS

Volcanoes emit much more CO₂ (in 10-100 times) than can be produced by the magmatic melts erupted by the volcanoes to the surface. It is believed that most of the CO_2 is released from the plutonic magma. Therefore, CO_2 can accumulate in the form of bubbles in the shallow magmatic chambers. The bubbles act as the transport phase for other volatile components (SO₂, H₂S, CO, HCl, HF and trace elements) and are characteristic for the fumarole phase in the active hydrothermal-magmatic systems. The discharge of CO₂ on volcanoes in the form of diffusion and plume flows is determined by its weak chemical reaction activity and evolution of the enclosing rocks. Plume flows are formed at the free gas phase in the flow of fluids of the hydrothermalmagmatic system (fig. 2). The migration of the CO_2 gas phase in the water-bearing complex is controlled by the gas-impermeable rocks which form the shell around the hydrothermal-magmatic system. CO₂ (gas phase) rises along the gas-impermeable barrier borders which are usually inclined from the top of the volcano to its periphery. The bubbles of CO_2 are

combined into the streams and stimulate the boiling of the hydrotherms in a vertical column above the apical part of the magmatic body. Such rising carbonated hydrothermal column acts as a pump. As a result of pumping of hydrothermal fluids, the hydraulic depression is formed in the water-bearing complex. It contacts with the igneous convective system.

The release of CO₂ stimulates the formation of water vapor characterized by a high heat capacity. This process is accompanied by large heat losses at the border of the hydrothermal and magmatic convective cells, where the thermal water has a critical temperature ($+374^{\circ}$ C). The temperature difference between the hydrothermal fluid and igneous melt increases the heat flow from the magma chamber to the roots of the hydrothermal circulation. Thereby, the flow of the trans-magmatic volatile components increases along the magmatic column. In addition to CO₂ and H₂O, volcanic gases contain gases capable of producing the detonating explosions (H₂, CH₄, CO and others.) and which are chemically active gases (HCl, HF, SO₂, etc.). HCl, HF and SO₂ form acidic solutions which, as was mentioned earlier, contribute to the formation of the local water- and gasimpermeable rocks. Detonating gases can accumulate under them. These gases explode when are mixed with air (Ohsawa et al., 2000). The authors believe that this mechanism can occur both in hydrothermal and magmatic cells (Rychagov et al., 2009a,b). Such process is possible at different levels of the hydrothermal-magmatic system, where detonating gases accumulate. Such processes are supposed to be characteristic for phreatic and phreatic-magmatic eruptions.

HYDROTHERMAL-MAGMATIC SYSTEMS OF SKARN TYPE

Coral reefs are widely distributed in tropical and subtropical waters in the band of about 30° S latitude up to 30° N latitude. The formation of coral reefs depends on the temperature and depth of the water. The best environment for the stony corals, or madrepores, is the depths up to 30 meters, and, with a sufficiently clear water, they can occur at the depths up to 40 meters. Below it, they quickly die off, forming the solid rock which serves as the basis for the continuing growth of the coral reef. Living madrepore corals are formed mostly in shallow waters along the east coast of the continents in the form of barrier reefs, as well as around the small islands and reefs in the form of crowns and atolls.

Charles Darwin was the first who noted that coral reefs are formed on volcanoes. He also came to the conclusion that in the recent past, large areas of the ocean floor were sinking. In 1947 the several boreholes were drilled at Bikini Atoll. One of them 779 m deep went exclusively through limestone. In 1954 at Enewetak Atoll (Marshall islands), two boreholes went through Eocene limestone (the age of about 50 million years) which at the depths of 1266 and 1405 m contacted with indigenous basalts (rocks of the volcanic origin). Considering the thickness of the limestone sediments, the formation of Funafuti and Nukufetau atolls can be explained by the gradual lowering of coral structure below the sea level (or by the significant fluctuations of the sea level).

Hydrothermal-magmatic systems with coral reefs

The foundation of Mururoa and Fangataufa atolls is formed by submarine and sub-aerial lava which are penetrated by volcanic rocks (Dudoignon, Proust D., 1997; Henry et al., 1996) (fig. 1).

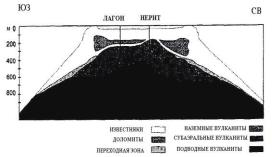


Fig. 1. The geological section of the atoll of Mururoa in Buigues et al. (1992).

Intrusion formed the zones of the altered rocks in the host basalts. At Mururoa, the rocks of the foundation have the K-Ar age of 10.7-11.8 million years, at Fangataufa - 10.7-11.8 million years. Lava of Fangataufa belongs to the alkaline series. The rocks with higher alkalinity are located in the upper part of the section. Fresh tholeiitic basalts have SiO₂ from 47 to 49% and Na₂O/K2O - 4.5-7.5. Sub-aerial volcanic rocks and volcanogenic-sedimentary formations are distributed to the periphery. In the internal part of the atoll structure (depth 270M), dolomites overlap submarine lava. Magnetic anomalies, fixed in the deep rift zones, are caused by magnetic bodies, presumably, plutones. Numerous dikes cross the thickness of the volcanic rocks. Lava is usually intensively altered. The average losses on ignition are 4.12% и 7.03% for Natice 1 and Mitre 1 boreholes of basalts-hawaiites, respectively. On the volcanic edifice of Mururoa, the intrusions produced the hydrothermal changes along the cracks and mass of the surrounding basalt. Calcite tells us that there is the dissolved magmatic CO_2 in the hydrotherms. At Fangataufa atoll, the zone of the hydrothermal changes is well-developed around the intrusions. In the depths interval 270-850m, the temperatures, calculated on isotopes, are 190 - 300° C.

<u>Hydrothermal-magmatic systems on the Apennine</u> <u>peninsula</u>

The centre and the South of Italy are characterized by a quaternary multi-channel volcanism. It is related with the geodynamic extension which is presented by the numerous active, dormant, and extinct volcanoes. They produced significant volumes of the alkaline rocks. The total volume of the pyroclastic deposits is 900 km³, distributed over an area of 6400 km². Four volcanic centers from the North to the South (Mts. Vulsini, Mt. Vico, Mts. Sabatini and Alban Hills) are characterized by multiple large calderas and ignimbrites eruptions connected with them. They are emplaced on a thick Mesozoic-Cenozoic carbonate sedimentary pile, identified at the depths between 1 and 8 km. Magma, united in Romanesque igneous province, is enriched with potassium. There are large fluctuations in the concentrations of silica in the products of volcanism.

In addition, this region is characterized by the intensive CO₂ emissions of deep origin (Gambardella et al., 2004). CO₂ is released both in area and in the form of gas plumes. It is assumed that, in the absence of the modern volcanic activity, CO₂ is generated through the processes of metamorphic decarbonation of limestone, magma and mantle degassing (Gambardella et al., 2004). The interaction between carbonate enclosing rocks and magma is confirmed by the presence of the high-temperature calcium skarn xenoliths in volcanic products. The composition of the isotopes of oxygen in the magmatic minerals indicates the large scale of this process (Marziano et al., 2007). It is assumed that the carbonate strata are formed in all hydrothermalmagmatic systems as a result of the accidental tectonic events (overthrust). This seems impossible.

The geothermal wells in the Larderello-Travale geothermal field penetrated the geological crosssection up to the depths of 3000-4000M below sea level. Top of section consists of neogene sediments (hydrothermal deposits), flysch facies (lower Cretaceous–Eocene), sandstones and limestones of the Tuscan Nappe (Upper Triassic–Lower Miocene) and metamorphic basement (Paleozoic). Bottom of the section is a metamorphic basement (phyllites and mica schists lower Paleozoic). Contact-metamorphic rocks (skarns and hornfels) in the lower part of the basement may represent the aureole formed around the underlying granitic intrusions. Figure 2 shows the schematic conceptual model of the geothermal region Larderello-Travale.

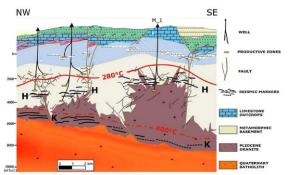


Fig. 2. Schematic conceptual model of the Travale area (Casini et al., 2010).

The hydrothermal-magmatic system of Geysers-Clear Lake in California (USA)

The system is often considered as an analog of the Larderello geothermal field in Italy. Both geothermal structures relate to the vapor-dominated geothermal systems characterized by a high heat capacity. Thereby, the interpretation of their origin and activities is of interest for geothermal geologists. There are no clear evidences that the Geysers-Clear Lake system refers to the skarn type system. However, a number of characteristics of these systems are similar.

Geysers-Clear Lake system is one of the few vapordominated systems in the world (Brikowski 2001). The system was intensively exploited and investigated. 780 deep wells were drilled there; many of them reached the underlying plutonic source of heat.

Geysers-Clear Lake system is located in Jurassic-Cretaceous rocks of the Franciscan Complex. The complex is presented by metagraywacke turbidite facies and argillites. Pleistocene intrusion of felsitic rocks provided the hydrothermal system with heat. The main body of the intrusion is located at a depth of 0.7км from the surface, in the area of south-west Geysers. According to the radiogenic data its age is 1.2 million years. The permeability of the overlying rocks of the intrusive was formed as a result of the hydrothermal dissolution of the more ancient metamorphic vein carbonates. The upper impermeable horizon (cap-rock) is presented by the non-dissolved metamorphic calcite and younger vein calcites. Their formation is connected with the modern hydrothermal system.

There are a large number of springs, fumaroles and gas plumes which emit a huge amount of CO_2 in the atmosphere in the area of Geysers-Clear Lake (Bergfeld et al., 2001). The regional gas analyses show that CO_2 , in particular, is formed from the relatively rich with ¹³C source, such as calcite veins. The increase in values of $\delta^{13}C$ -CO₂ could be a result of the inflow of CO₂ at the dissolution of marine

carbonate rocks. The geological mapping of the entire region showed that marine limestone is found in the Franciscan Complex, Grit Valley thickness and, in the form of exotic blocks, in the mélange and detrital serpentinite. The largest block of marine limestone (approximately 0.19 km²) is made of organogenic residues. It is established that CH₄ is not the main source for CO₂ in the region, that CO₂, most likely, was produced from calcite veins or C_{org}.

Modeling study of the hydrothermal-magmatic system of Geysers-Clear Lake, conducted by Stimac J.A. et al. (2001), showed that: 1- the intrusion of the numerous small and shallow acid magmatic bodies occurred in the area with high heat flow (about 750 km^2); 2- only a small fraction (much less than 10%) of the acidic magma, invaded in the upper part of the earth's crust, was erupted on the surface; 3- in some areas, the high conductive thermal gradients increased due to the heat coming along fault zones and 4- the major portion of the acidic magma presented in the upper crust became harden, or almost harden.

High concentrations of CO_2 dissolved in the liquid fluids of the hydrothermal-magmatic systems can also increase the thermal discharge. In the process of separation of CO_2 , these bicarbonate thermal waters stimulate the boiling of the water and large heat losses in the whole hydrothermal-magmatic system. It is expected that this process increases the flow of trans-magmatic volatiles along the magmatic column which supplies the magmatic heat source.

The thermal regime of the Geysers-Clear Lake hydrothermal-magmatic system is similar to the activity which is characteristic of porphyritic systems, including the Larderello skarn system.

DISCUSSION

The abovementioned data allow to draw a conclusion about the important role of CO_2 in the formation and activities of hydrothermal-magmatic systems. Most clearly, it is manifested in the systems of skarn type. The migration of CO_2 from the upper mantle to the surface of the Earth is a complex process. Near the Earth surface, it manifests itself in the form of dispersed flow, focused plumes and concentration of mineral formations of hydrothermal and organic origin. In the present work, we have paid attention to the formation and activities of hydrothermalmagmatic systems of skarn type in submarine environments of the equatorial belt, where coral reefs are developed. The description of the conceptual model of such systems is given below.

<u>The conceptual model of the hydrothermal-</u> magmatic system of skarn type

We believe that the formation of coral cover on the volcanic islands takes place due to the genetic hydrothermal and magmatic processes in the depths of the volcanic edifice.

Coral structures appear on them as the result of the organogenic reaction to the releasing of the magmatic CO_2 (Allard et al., 1992). As the coral structure (which thickness reaches >2 km (Buigues et al.,1992)) is forming, it gets compacted. It turns into an impermeable thickness (cap-rock). Under the caprock, the accumulation of the heat energy, emitted from different sources by the thermal channels system, takes place. This process leads to the increase of temperature in the depths of the hydrothermal-magmatic system.

It is well-known that in hydrotherms the dissolved silica is presented, which reaches saturation in the discharge and forms the colloidal system. The colloidal nature of silica and sulfides deposits on the thermal manifestations like "black smokers" shows that, in the discharge, hydrothermal solutions represent a complex system of hydrophilic and hydrophobic colloids (Nekrasov, 1973). Both colloids are negatively charged and are able to adsorb the positively charged particles. They also interact on coagulation. The hydrosols of silicic acid adsorb cations of the electrolyte (sea water) and coagulate. They do not precipitate, but continue to migrate in an aqueous solution to the site of discharge of the hydrothermal system. At the same time, they protect the hydrophobic sulfide colloids against coagulation and sedimentation (Belousov, etc., 2008).

In the hydrothermal convection cell, the process of leaching of silica and other components occurs. Then the components are being carried to the periphery of the hydrothermal-magmatic system, and a large number of basalt melt invades into the lower part of the earth's crust. The increase in the weight of this part of the earth's crust and heating take place. This process may cause a gradual sinking of the hydrothermal-magmatic system. In the tropics, where the biological communities with calcareous skeleton exist, the synchronous sinking and growth of coral reefs are possible.

The hydrothermal activity and modern volcanism on the Apennine peninsula are associated with carbonate sediments. They are closely related to maar-diatrem eruptions and formation of calderas (Giordano et al., 2006). The products of such volcanic activity are presented by ignimbrites, pumices and other types of pyroclastic rocks. These rocks are formed as a result of spontaneous and detonating degassing of acid melts. It is due to the pressure reduction when magma is moving to the surface or when acid magma in the earth's crust mixes with deep basalt melts (Grebennikov, 1998, Rychagov et al., 2009a,b). In the magmatic channel, the detonating explosions form the areas with very low pressure (less than atmospheric). This process is accompanied by the erosion of their walls and involvement of a large number of clastic materials into the eruption column. In the center of the explosion, very low pressure (much less than 1 atm) is accompanied by a strong compression of the melt particles and debris. The "plugs" of the pyroclastic material with a high density are formed. Under atmospheric pressure, such plugs are getting filled with air, expand rapidly and dissipate in the ash column. Later, ash columns partly collapse and are transported in the atmosphere to the basis of discharge (Sparks et al., 1978). We assume that this is how ignimbrites are being formed. The detonating explosions of the gases increase the spontaneous degassing of the melts in the magmatic convective cell. As the result of a gas lift, the rise of the melt occurs which is followed by melt's destruction from the place of its generation to the surface. On detonating explosions, the impact of degassing can reach the considerable depths, depending on the strength of the detonating explosion. This forced convection increases the speed of the trans-magmatic volatiles loaded with metals. We believe that this mechanism explains the big heat capacity of such active hydrothermal-magmatic systems, as well as the big resources of the skarn deposits.

In our opinion, potassium magmatism which is characteristic of the skarn hydrothermal-magmatic systems of the Apennine volcanic zone is the product of the heat exchange between the convective cells. Potassium is able to carry a large amount of heat to the upper part of the magmatic convective cell (Belousov, 1978; Rychagov, etc., 2008). In the zone of interaction between the hydrothermal and magmatic convective cells, the heat transfer agents change.

Thus, the formation and activities of the skarn hydrothermal-magmatic systems, as well as all porphyritic systems, is caused by the abnormal heat flows. In this process CO_2 plays an important role. Its regime is controlled by its thermodynamic parameters, as well as by its interaction with hydrosphere, atmosphere and biological processes.

CONCLUSION

The study of the skarn hydrothermal-magmatic systems gives us the possibility to understand the self-organization processes for geological systems. Formation and activity of such structures depend on the properties of the chemical compounds and their interactions in the upper mantle of the Earth's crust, hydrosphere, biosphere and atmosphere.

The hydrothermal-magmatic system is a selfdeveloping geological structure which serves as a mean for transference of the thermal energy from the upper mantle to the surface of the Earth. Convective heat transfer, dominating in such structures, is the main mechanism of heat transportation through the crust of the Earth. The mode of heat transportation is controlled 1) by a temperature difference at the ends of the hydrothermal-magmatic system, 2) by thermodynamic characteristics of the heat transfer agent and 3) by thermophysical properties of the enclosing rocks. Hydrothermal-magmatic convective system consists of two convection cells. Magmatic melt together with gases dissolved in it is the main heat transfer agent in the lower (magmatic) cell. Water together with gases dissolved in it is the main heat transfer agent in the upper (hydrothermal) cell.In the hydrothermal-magmatic system, heat transfer is provided by the preservation of heat and temperature conditions of the heat transfer agents and by the thermal self-isolation in this structure. Thermal isolation is caused by the formation of shell from the secondary minerals at the periphery of the system, which leads to the reduction of the convection there and to the transition to the molecular (conductive) method of heat transfer.

Basing on the chemical composition of carbonates $(CaCO_3)$, which participate in the skarn hydrothermal-magmatic systems, it can be said that CO_2 and Ca are required for its formation. CO_2 is a product of the redox reactions at the magmatic temperatures (combustion). Dissolved Ca is present in sea water. Thus, we can assume that refined carbonate can be formed on volcanoes in the seas and oceans. However, corals can exist in the warm seas, where the organisms with carbonate skeletons can live. So we came to the conclusion that the accumulation of refined carbonate is possible on volcanoes of the tropical zone. The accumulation of carbonates provides back reaction to the regime of hydrothermal-magmatic systems. The concentration of CO₂ can influence the intensification of the thermal energy and the processes of ore formation. This determines their large heat capacity and large mineral resources.

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