

## Reservoir Temperatures by Means of Mineralogic-Geochemical Geothermometers

A.D. Korobov<sup>1</sup>, S.N. Rychagov<sup>2</sup>, S.F. Glavatskikh<sup>2</sup> and S.P. Goncharenko<sup>1</sup>

<sup>1</sup>Saratov State University, 161 Moskovskaya st., Saratov, 410750, Russia

<sup>2</sup>Volcanology Institute, FED of RAS, 9 Piipa Blvd., Petropavlovsk-Kamchatsky, 683006, Russia

rychsn@kcs.iks.ru

**Keywords:** hydrothermal reservoirs, temperatures, correlation of metasomatic zones

### ABSTRACT

The evolution of hydrothermal process (high-temperature haloid-sulphur-carbon dioxide stage → sulphur-carbon dioxide → low-temperature-carbon dioxide stage) reflects the series of reducing heat capacity of fractured and layer-fractured geothermal fields: solfatara thermals as steam (Nizhnekoshelevskiye, Okeanskiye, Geizers) → solfatara thermals with steam near the surface and fluid at the depth (Mutnovskiye) → chloride geyser thermals (Pauzhetka, the Taupo Zone in New Zealand) → non-chloride geyser thermals (Bolshe-Bannyie). The results from the universal character of the compositional changes in magmatic emanations during the processes of silicate melt cooling and water temperature reduction.

When volcanic-plutonic phenomena control the hydrothermal process, the change of haloid-sulphur-carbon dioxide stage with the sulphur-carbon dioxide and later on by the carbon dioxide one proper, lowers the contrasts among the compounds forming volcanic (fumarole) and magmatogene (hypogene) solutions. In such cases, compositions of two types of synchronously originating hydrothermals gradually become more similar, and the general vertical metasomatic zonality reduces to the products of carbon dioxide (hydrocarbonate) metasomatosis. Taken separately, the zones of the general metasomatic column constitute a single system with no isolated degradation of concrete zones possible. This provides the grounds of the correlation principle for metasomatic zones; according to this principle, availability of certain alteration zones in thermal fields always suggests the presence of concrete alteration zones with characteristic temperatures in the entrails of hydrothermal system. Zeolite and smectite (zeolite-smectite, smectite-zeolite) facies of hydrothermal argillites, making a kind of "basis" for hydrothermal activity, are the exceptions. Proceeding from the correlation principle and detailed study of the mineral compositions of surface metasomatites in active thermal manifestations, one can make rather accurate estimations of hydrothermal reservoir temperatures, acidity and alkalinity of the environment, reveal the changes in dynamics and physical and chemical parameters of hypogene fluids with time, and consequently, to reconstruct the evolution of hydrothermal system.

### 1. INTRODUCTION

Much attention is paid throughout the world to the problem of studying and practical development of geothermal resources. Forecasting, search, exploration and geologic-economic evaluation of the fields of natural heat-carriers are important problems of geoenergetics. Besides the conventional geologic-hydrogeologic and geothermal methods, highly informative research methods, such as the

mineralogic-geochemical ones, become progressively more wide-spread. One of the most important mineralogic and geochemical problems associated with the development of geothermal resources, consists in acquiring more reliable reservoir temperatures by means of mineralogic geothermometers. Interaction of hot circulating solutions and host rocks results in hydrothermal-metasomatic processes accompanied by the changes in both, the solutions and the rocks. Some rock-forming components pass over to the hot heated waters from the solid state, the process becoming more active with rising temperatures. The fluid temperatures are believed to reduce as they move towards the surface, but the mineral load remains essentially the same. According to the majority of specialists, the mineral load is determined, in particular, by the contents of alkali and alkaline-earth metals and silica. This was taken as the basis for the Na-K, Na-K-Ca and Si-geothermometry developed due to the research by G.S. Bodvarsson (1961), A.J. Ellis (1963), A.H. Truesdell et.al. (1979) and other scientists. Temperature dependence should be controlled by dynamic equilibrium (or some approximation) in the water-rock system. In the zones of ascending flows, however, thermal solutions mix (sometimes repeatedly) with cool near-surface waters. This brings about changes in the physical-chemical properties of the solutions, in their solvency, etc., which result in alterations (often radical) of the initial Si, K, Na, Ca water concentrations and cause substantial errors in geochemical thermometry. That is why occasional hydrogeochemical studies at the beginning of explorational-assessing works produce but rough estimates of the regional hydrogeochemistry. This is especially true for the regions of active volcanism. In such cases, complex, long-term observations of the thermal-water regime are necessary, which require much time and additional expenses. This reduces the efficiency of the conventional approaches to evaluation of heat anomalies from geochemical properties.

These complications can be overcome if hydrothermal metasomatites proper are studied: the products of interaction between heated waters and hosting rocks. The durations of metasomatite formation are comparable to the periods of existence of geothermal systems themselves (tens – many thousands of years). An assumption seems to be logical, that in such cases, the heated waters and the rocks in the reservoir achieve chemical equilibrium (at certain stages of the system development), which allows to use metasomatites as geochemical (mineralogic-geochemical) thermometers for assessing temperatures at the depths of geothermal fields. The origin and the structure of metasomatic zonality in the regions of terrestrial volcanism are the matters open to discussion. The research in the region of various tectonic-magmatic activities (Korobov, 1999), has revealed new regularities in the evolution of hydrothermal systems and arising metasomatites in subvolcanic and surface conditions. The present paper offers a principally new scheme for the zone

correlation in the process of formation of a single metasomatic column. Using these correlations, a tentative evaluation of the heat regime in the interiors of geothermal fields may be made from the mineral compositions of the surface metasomatites originating in active thermal manifestations. No well drilling is involved.

Silicate melts contain diverse volatile components that effervesce from magma, ascending to the Earth's surface, and may join hydrothermal solutions. Volatile isolation occurs at various depths, i.e. under various thermobaric conditions corresponding to subvolcanic (intrusive) or volcanic (effusive) processes. Magmatogenic hydrothermals originate in the former case, and magmatic proper (volcanic) or fumarole ones – in the latter case (Naboko, 1974; Ivanov, Kononov, 1977). Both contribute simultaneously to formation of hydrothermal systems, since such systems are thermodynamically open. Maximum mantle degassing takes place during volcanic eruptions in island arcs (Polyak et al., 1987), the Kurils-Kamchatka region being a typical example. A most vast set of magmatic emanations is observed to participate in hydrothermal process there (Cl, F, H, SO<sub>2</sub>, S, H<sub>2</sub>O, CO<sub>2</sub>, CO, H<sub>2</sub>S, etc.) as well as the highest temperatures of mineral formation in the deep zones of the system and in fumarole fields.

In the island-arc regions, hydrothermal mineral-forming processes develop within two kinds of settings (Naboko, 1980): 1) in volcanoes in hydrothermal stages of activity, and 2) in the zones of hydrothermal system unloading. All the processes proceed synchronously in time and space; they are genetically related by a single magmatic (volcanic-plutonic according to E.K. Ustiyev) feeding source for solutions. In such cases, crystallization of silicate melts and loss of volatile components from intrusives occur synchronously with volcanic and post-volcanic process. The direct relationship of hydrothermal systems and volcanic-plutonic complexes, determines the maximum influence of the hypogene factors on the hydrothermal process development, which is confirmed by isotope studies. Thus, high-temperature sulphate-chloride [some-times, almost purely chloride (Arsanova, 1974)] solutions, formed at the contacts of active intrusive bodies and host rocks, contain the greatest amounts of juvenile components. The portion of meteoric components in hydrothermal solution increases rapidly with the distance from such contacts (Ellis, 1963; Sakai, Matsubaya, 1977; Rusinov, 1989). Similar tendency is observed in fumarole fields controlling the structures of thermal discharge from eruptive centres. High-temperature gas condensates (HCl, SO<sub>2</sub>, etc.) are more “hypogene” there; they may also be of chloride and/or sulphate compositions (Vetshtain et al., 1971; Baskov et al., 1973).

## 2. RESULTS

### 2.1 Volcanoes In Hydrothermal Stage Of Activity

According to theoretic views of A.A. Shpak and co-authors (1992) and S.I. Naboko (1980), solfatara thermals in the form of steam along the whole of the well-shaft, or in the form of steam close to the surface and of fluid in the depth, are genetically related to such eruptive centers. Baranskiy volcano (the island of Iturup in the Kurile Chain) is a typical example. The Kipyaschaya caldera in its southwestern slope holds the Okeanskaya hydrothermal system. The tuffaceous material of the caldera hosts ground waters heated with abnormally high heat flow related to a shallow-lying (2 km) intrusive body. Heated hydrothermals emanate along the faults. Fumarole fields are localized in the heat-conductive structures of the volcano (fault zones) and in the

areas of effusive magmatic bodies. They are associated with the most heated areas and indicate the ascending gas-hydrothermal flow. This accounts for the fact that the Kipyaschaya caldera contains the broadest set of volatile components involved in hydrothermal activity (haloids, sulphurous gases, carbon dioxide, etc.), and the mineral-forming processes proceed at the highest temperatures: over 350°C in the deep zones of the field and up to 250°C in fumarole fields (Rychagov et al., 1993).

The significant role of hypogene factors determines characteristic features of the vertical zonality and the mineralogic-geochemical features of metasomatites. In the Okeanskaya hydrothermal system, high-temperature (460-380°C) greisen-like secondary quartzites are formed, comprising monoquartz and quartz-muscovite (quartz-sericite) facies. These are associated with the exocontact zones of intrusive bodies (diorites, granodiorites). The metasomatites mentioned associate with medium-temperature (380-200°C) propylites. In the fumarole fields, indicating the thermal-discharge structures of the volcano, a high-temperature (250-200°C) formation of sulphureous opalites (solfatara secondary quartzites) develops alongside with the near-contact secondary quartzites; the formation combines mono-opal and alunite-opal (jarosite-opal) facies, associated with kaolinite-opal (kaolinite-quartz) rocks (200-150°C). High temperatures and free HCl and H<sub>2</sub>SO<sub>4</sub>, involved in the hydrothermal process, account for the poor development of low-temperature (290-200°C) propylites in the deep zones and opal-kaolinite and kaolinite proper metasomatites in fumarole fields. The formation of hydrothermal argillites is represented by argillized propylites (200-150°C) and hydrothermal smectite clays (150-100°C).

In such settings, high activity of the “deepest” ingredients of magmatic emanation is observed: haloids (primarily Cl) and sulphureous compounds (mainly SO<sub>2</sub>); in the Okeanskoye field this is confirmed by the development of secondary quartzites, formation of sulphates and accumulation of alkalis.

Pressure is established to determine the forms of haloid separation and hydrolysis, which control alkalinity-acidity of the fluids. In the entrails of hydrothermal system, with the beginning of intrusive process, alkali-metal chloride fluid leaves the cooling magmatic centre; the fluid contains alkali and iron chlorides as well as subordinate amounts of alkali fluorides (Fig.1). The solution initiates high-temperature chloride-sodium-potassium waters with the Na/K ratio of 1. Partial alkali hydrolysis produces (in small amounts) HCl and HF, causing near-contact leaching. Simultaneously, HCl and HF enter fumarole fields and form ultra-acid thermals, as well as limited amounts of alkali and iron chlorides (White, Waring, 1963; Arsanova, 1974; Ryabchikov, 1975; Naboko, 1980). There are no principle differences in the forms of separation of sulphureous gases from magmatic melts in the course of intrusive and volcanic (effusive) processes. In aeration zone (in solfatara fields and thermal sites), the H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>S ratios are controlled by temperatures, redox potentials and biogenic activity of microorganisms; in the hypogene zones of hydrothermal systems – mainly by temperatures (Holland, 1970; Ovchinnikov, 1976). The presence of “near-contact” and solfatara monoquartzites limiting the single vertical metasomatic column of the hydrothermal system (see Fig.1), is indicative of ultra-acid leaching of the rocks, called forth by free HCl and H<sub>2</sub>SO<sub>4</sub> both, in the hypogene zone of the hydrothermal system, and in fumarole fields.

High activity of  $\text{SO}_2$  and magmatogene solutions from the Okeanskoye field provides formation of sulphates: anhydrite, barite, jarosite. Substantial portion of sulphur enters the hydrothermal system in oxidized state ( $\text{SO}_2$ ) and subsequently evolves, producing sulphate and sulphite radicals. This results in formation and deposition of sulphates at high temperatures, and later on, at lower temperatures – of the bulk of sulphides. That is why the amounts of pyrite in propylites increases and the content of anhydrite reduces with growing distances from intrusive bodies, compared to the near-contact secondary quartzites. This is also promoted by increasing solubility of anhydrite with solution cooling.

Na and K accumulation associated with arrival of alkali-metal chloride fluid, is limited by solubilities of micas and carcass aluminosilicates. Higher hydration energy for Na than for K accounts for potassium participation in formation of micas, hydromicas and mixed-layer illite-smectites. Na is accumulated in liquid phase and promotes formation of sodium-chloride compositions of hydrothermals most widely occurring in the region of recent arc volcanism. One may suppose with confidence, that alunite and jarosite form from alkalis and iron entering fumarole fields in limited amounts as chlorides (see Fig. 1).

While alkalis (mostly potassium) in sericite quartzites (hypogene zones of the fields) are contained only in micas, in alunite opalites (fumarole fields), K and Na are concentrated only in alunite (jarosite). Micas and alunite (jarosite) have much in common in terms of localization conditions and interrelations with surrounding minerals. In particular, both are later (superimposed) compounds relative to silica minerals.

Thus, high temperature halo-sulphur-carbon dioxide stage of hydrothermal process is characteristic of hydrothermal systems genetically related with island-arc volcanic-plutonic activity and going through the progressive stage in their development. Under the influence of the same volatile components (haloids and sulphur gases), both, in subvolcanic conditions and in fumarole fields, monoquartz and monoopal zones form, associated with two types of hydrothermalites: respectively, quartz-muscovite (quartz sericite) and alunite-opal (jarosite-opal) ones. Their origins are related with fixation of alkalis. Consequently, taken in pairs, these facies, as well as medium-temperature propylites (entrails) and kaolinite-opal (fumarole fields) rocks, common for such fields, should be regarded as independent ones (see Fig. 1).

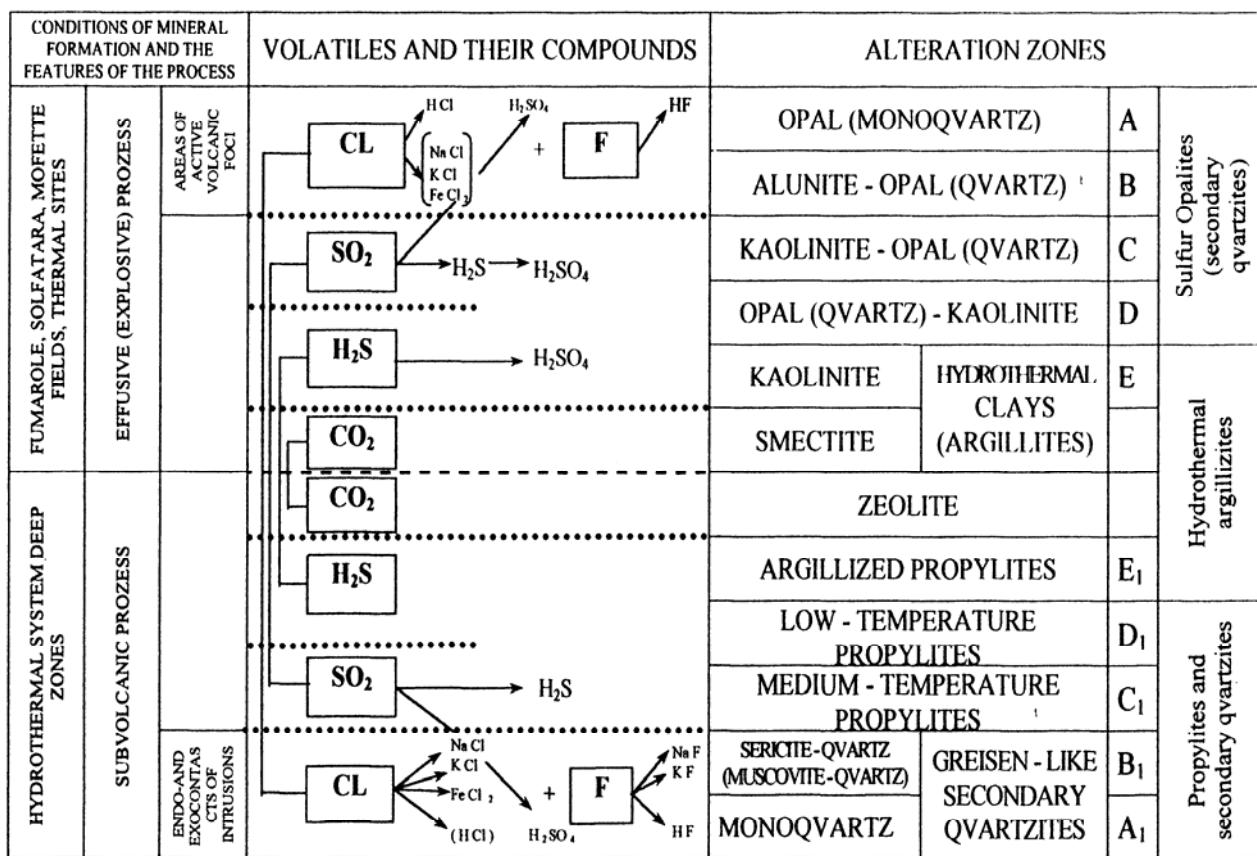


Fig. 1. Role of magmatic emanations in formation of interdependent metasomatic zones.

## 2.2 Zones Of Hydrothermal System Unloading

A.A. Shpak and co-authors (1992) and S.I. Naboko (1980) believe that chloride geyser thermals dominate in such regions. These zones are peculiar for the surface outlets for thermal fluids being spatially removed from the site of heating. The Pauzhetka hot-water field (South Kamchatka) is a typical example. Volcanic apparatus in the Kambalny eruptive centre serve as heat-feeders for this system. Ground waters at the watersheds and slopes of the Kambalny Ridge make a single aquifer. Hot-solution outlets are more than 10 km removed from generation sites (Averyev, Belousov, 1965). This is the evidence of the reduced influence of the internal factors (magmatic centre and separating high-temperature emanations) on the hydrothermal system formation.

The facts above account for the limited set of volatile components involved in hydrothermal activity [H<sub>2</sub>S, (SO<sub>2</sub>), CO<sub>2</sub>, H<sub>2</sub>O] and for the lower temperatures of mineral formation. In the Pra-Pauzhetka [the Pauzhetka field at the end of the Pleistocene – beginning of Holocene (Kiryukhin, Sugrobov, 1987)], they rarely exceeded 300°C in the internal zones of the system and were as high as 150°C at the thermal sites. The present temperatures in the field are, respectively, less than 200 and less than 100°C. This determines the specifics of vertical zonality and mineralogic-geochemical features of metasomatites.

Thus, in the Pra-Pauzhetka internal zones of the system, medium-temperature (from 330 to 300-280°C) propylites were in the embryonic state, while low-temperature (290-200°C) propylites dominated. In thermal sites, alongside with propylites, kaolinite-opal (sporadically) and opal-kaolinite (frequently observed) rocks (150-100°C) of sulphur opalite facies were formed. A formation of hydrothermal argillites occupies an intermediate position in the section: between propylites and sulphur opalites. This is represented (from the bottom upwards) by: argillized propylites (200-150°C) → high-siliceous zeolites (170-110°C) → hydrothermal clays (150-80°C); the latter ones are composed of smectites replaced by kaolinite at the very surface. The lack of typical secondary quartzites (“near-contact” and solfatara ones) shows, that haloids did not participate in hydrothermal activity, and the role of SO<sub>2</sub> was limited. The hydrothermal process in the Pra-Pauzhetka was in its sulphur-carbon dioxide stage, which corresponded to the progressive stage in the field development.

Recent mineral formation in the field reflects regressive trend of the process, which, according to D.S. Korzhinsky, is especially characteristic of hydrothermal activity and manifests itself in the low-temperature mineral associations superposing the higher-temperature ones. At present, propylite formation in the depths of the Pauzhetka field has stopped, as well as origination of secondary quartzites on the surface. In the interior of the system, argillized propylites (200-150°C) become widely developed; kaolinite and kaolinite-smectite hydrothermal clays are formed synchronously in the thermal sites. A zone of high-siliceous zeolites (clinoptilolite, heulandite, mordenite) and amectite clays (150-80°C) occupies the intermediate position in the section. This is associated with sharp reduction of the H<sub>2</sub>S role in the hydrothermal process during the transition of propylitization to the stage of hydrothermal argillization, with growing converting role of CO<sub>2</sub> and the surface waters rich in atmospheric oxygen. At present, the Pauzhetka hydrothermal system is in the boundary state between the sulphur-carbon dioxide stage of mineral formation and the carbon-dioxide stage proper.

Thus, in the settings with reduced influence of volcanic-plutonic magmatism on the hydrothermal process (regions of unloading of hot solutions): one observes reduction of the set of magmatic emanations [H<sub>2</sub>S, (SO<sub>2</sub>), CO<sub>2</sub>] involved in formation of thermals, and lower temperatures of mineral formation. The hydrothermal systems are in the sulphur-carbon dioxide stage of development. Completion of this stage is manifested in successive “dying off” of some propylite facies (embryonically developed medium-temperature → widely represented lower-temperature ones) in the interior of the system and the corresponding facies of sulphur opalites (embryonically developed kaolinite-opal → commonly occurring opal-kaolinite) in thermal sites. Consequently, these facies, as well as commonly occurring argillized propylites (entrails) and kaolinite clays (thermal sites) taken in pairs, should be regarded as interdependent ones.

In the region of subsiding or relatively weak volcanic activity, the hydrothermal systems may be in the carbon-dioxide stage of mineral formation. CO<sub>2</sub> is the dominant gas component in hot solutions. In such settings, non-chloride geyser thermals originate (Shpak et al., 1992; Naboko, 1980). The low-temperature (below 150°C) rock alterations are referred to carbon-dioxide (hydrocarbonate) metasomatism. Zeolite and smectite (zeolite-smectite, smectite-zeolite) metasomatites form in such cases. Compositions of the rocks being converted, determine zeolite formation. Acid vitreous volcanites are substituted with mordenite and clinoptilolite. Natrolite, mesolite, stilbite, chabasite, low-temperature analcime develop in the increased-basicity rocks. Dioctahedral smectites dominate among clay minerals. The minerals mentioned, superimpose on the higher-temperature zones of the previous development stages (propylites, secondary quartzites) and form spatial co-occurrences. This, in particular, is observed in the Bolshe-Bannoje and Paratunskoye hot-water fields with the solution temperatures less or equal to 165 and 104°C, respectively.

Thus, zeolite-smectite (smectite-zeolite) hydrothermalites devoid of any interdependent metasomatic zones form in geothermal systems which are in the low-temperature carbon-dioxide stage of development.

## 3. DISCUSSION

It is established (Frolov, 1991; Shpak et al., 1992), that productive zones of hydrothermal systems are characterized by increased rock permeability determining the development of steaming sites, solfatara and fumarole fields at the very surface of the earth. These thermal manifestations constitute direct exploratory features in the fields of natural heat-carriers.

The facts cited in the present paper, show that in island-arc settings, under the influence of the same magmatic emanations, metasomatic zones of various mineral compositions may be generated simultaneously at the earth surface and in the interior of hydrothermal systems. Since each of these zones are initiated by certain sets of specific volatile components, the zones, taken in pairs, should be regarded as interdependent ones (Fig. 2 and see Fig. 1, A1-A, B1-B, C1-C, D1-D, E1-E). Substitution of the haloid-sulphur-carbon dioxide stage (Kipyascheye field) by the sulphur-carbon dioxide one (Pra-Pauzhetka) is accompanied by disappearance of monoquartz (A1) and quartz-sericite (B1) metasomatites, as well as medium-temperature propylites (C1) (subvolcanic conditions), on the one hand, and monoopal (A), alunite-opal (B) and kaolinite-opal (C) rocks (fumarole fields) – on the other. I.e. the changes manifest themselves in successive

disappearance of the extreme correlational members of the general vertical metasomatic zonality. As the result, two new facies are specified: zeolite and kaolinite ones; this is evident in the case of Pra-Pauzhetka and testifies to the direction of the process towards argillization. The transition to the stage of hydrothermal argillization proper (the present state of the Pauzhetka field) is associated with complete "extinction" of propylites in the depth [embryonic medium-temperature (C1) → low temperature (D1)] and sulphur opalites in thermal sites [embryonic kaolinite-opal (C) → opal-kaolinite (D)]. The character of mineral formation changes alongside with disappearance of the extreme interdependent members of the vertical zonality and is directed towards smectite formation.

The case of the Paratunsky field shows, that the further development of hydrothermal argillization (carbon-dioxide stage) leads to disappearance of argillized propylites (E1) and kaolinite clays (E), sharp reduction of the amount of mixed-layer minerals and wide distribution of smectite-zeolite (zeolite-smectite) metasomatites. The tendency is still preserved of losing the extreme correlational members of vertical metasomatic zonality with simultaneous volume increase of smectitized rocks and smectite clays.

The above comparisons show that the transition of one member of the series to the other one is associated with regular loss of the extreme interdependent members of metasomatic zones. This occurs alongside with increasing hydrothermal argillization as the reflection of the universal character of composition changes in magmatic emanations and reduction of water temperatures (see Fig. 2). The evolution of hydrothermal process (high-temperature haloid-sulphur-carbon dioxide stage → sulphur-carbon

dioxide → low-temperature carbon dioxide stage) reflects the series (revealed by A.A. Shpak et al., 1992) of decreasing thermal capacity of fractured and formation-fractured fields: solfatara thermals as steam (Nizhnekoshelevskiye, Okeanskiye, Geysers) → solfatara thermals with steam close to the surface and fluid in the depth (Mutnovskiye) → chloride geyser thermals (Pauzhetka, the thermals in the Taupo Zone, New Zealand) → non-chloride geyser thermals (Bolshe-Bannye). The above tendencies of the evolving hydrothermal process and of the resulting successive series of hydrothermal fields, are associated with decreasing contrast ranges of the compounds responsible for volcanic and magmatogene solutions. In such cases, gradual composition convergence is observed in two types of synchronously originating hydrothermals and reduction of the general vertical metasomatic zonality to the products of carbon-dioxide (hydrocarbonate) metasomatosis. Taken separately, the zones of the general metasomatic column make a single system in which no isolated degeneration of definite zones is possible. This makes the basis for the principle of metasomatic zone correlation (Korobov, 1999). According to the principle, certain zones of alteration of active thermal manifestations on the very surface of the earth, always presuppose the existence of concrete alteration zones with characteristic temperatures in the entrails of the hydrothermal system. Zeolite and smectite (zeolite-smectite, smectite-zeolite) facies of hydrothermal argillites, representing a kind of the "basis" for hydrothermal activity, are regarded as the exceptions. This is especially true as far as smectites are concerned, since they represent the final crystalline phase that terminates the development of a series of rock-forming minerals in a regressive hydrothermal process.

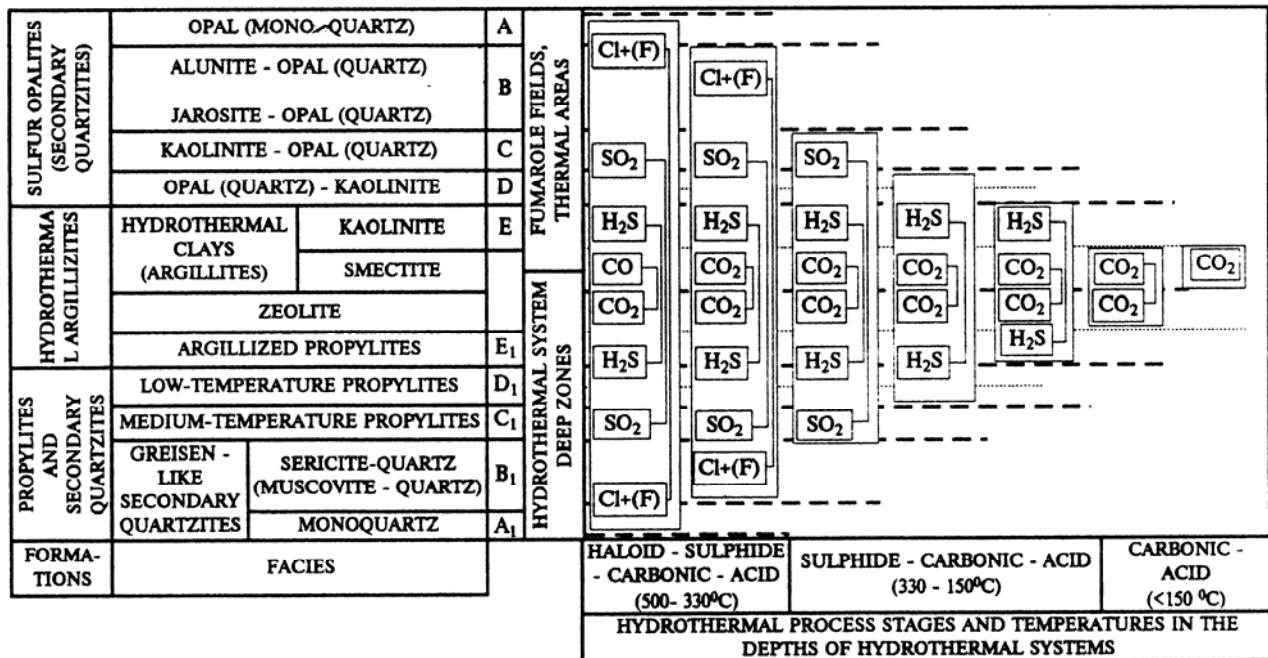


Fig. 2. Principal scheme of interdependent metasomatic zones behaviour as the hydrothermal process evolution and the change of depth temperatures in hydrothermal deposits.

## CONCLUSION

Thus, for island-arc hydrothermal systems, a general tendency is established in origination of vertical metasomatic zonality as an index of stages in the hydrothermal process and the interrelated heat capacities of the fields. Proceeding from the principle of metasomatic zone correlation, detail study of mineral compositions of the surface metasomatites from active thermal manifestations allows reliable assessment of reservoir temperatures, various physical-chemical parameters and dynamics of hypogene fluids, i.e. makes it possible to reconstruct the evolution of the hydrothermal system. That is why relatively cheap mineralogic-geochemical studies of the surface metasomatites at the stage of exploration may provide the grounds for tentative assessment of hydrothermal resources in the fields of natural heat-carriers. This may also reduce the risks of expensive drilling later on.

## ACKNOWLEDGEMENTS

The authors are indebted to Ya.A. Rikhter, N.S. Zhatnuev, V.M. Ladygin, N.M. Ulzutuev and G.P. Koroleva for assistance in field work,

and material interpretation. We would like to thank S.I. Soldatkin for the review and critical remarks and E.V. Serebryakova and E.B. Rakitina for translation and computer make up.

The research was financially supported by the Russian Foundation for Fundamental Research (project 03-05-64044a) and by the "Russian Universities" Programme.

## REFERENCES

Arsanova, G.I. (1974). Alkaline elements in the Uzon hydrothermals. In: Volcanism, hydrothermal process and ore formation, S.I. Naboko (Ed.), Nedra, Moscow, pp. 195-210. In Russian.

Averev, V.V., and Belousov, V.I. (1965). Geologic study of the region In: Pauzhetka hot solutions from Kamchatka, B.I. Pipp (Ed.), Nauka, Moscow, pp.8-22. In Russian.

Baskov, E.A., Vetshtain, V.E., Surikov, S.N., Tolstikhin, I.N., Malyuk, G.A. and Mishina T.A. (1973). Isotopic compositions of H, O, C, Ar, He in thermal waters and gases from the Kuriles-Kamchatka volcanic region as the indices of their formation. Geokhimiya, Vol. 2, pp. 180-189. In Russian.

Bodvarsson G.S. (1961). Physical characteristics of natural heat resources in Iceland. Proc.Un.Conf. New Sources Energy. Rome (Italy), Vol. 2, pp. 62-69.

Ellis, A.J. (1963). The effect of temperature of ionization of hydrofluoric acid. Jnl. Chem. Soc., Vol. 9, pp. 4300-4304.

Frolov, N.M. (1991). Fundamentals of hydrogeothermy. Nedra, Moscow. 336 pp. In Russian.

Holland, G.D. (1970). Vein minerals in hydrothermal fields. In: Geochemistry of hydrothermal ore fields. H. Barns (Ed.), Mir, Moscow, pp. 325-366. In Russian.

Ivanov, V.V. and Kononov, V.I. (1977). The problem of thermals genesis in the regions of active volcanism. Izvestiya AN SSSR, geology series, Vol. 11, pp. 131-143. In Russian.

Kiryukhin, A.V. and Sugrobov, V.M. (1987). Heat-transfer models for the hydrothermal systems from Kamchatka. Nauka, Moscow. 152 pp. In Russian.

Korobov, A.D. (1999). Metasomatite homologous series as the indices of the ratio of plutonic and volcanic phenomena in hydrothermal processes. In: The problems of biosphere studies, G.I. Khudyakov (Ed.), Gos.UNC "College" Publ., Saratov, pp.167-180. In Russian.

Naboko, S.I. (1974). Chemical types of volcanic rocks. In: Hydrothermal mineral-forming fluid from the regions of active volcanism, S.I. Naboko (Ed.), Nauka, Novosibirsk, pp.8-14. In Russian.

Naboko, S.I. (1980). Metal contents in modern hydrothermals from the regions of tectonomagmatic activity. Nauka, Moscow. 200 pp.

Ovchinnikov, L.N. (1976). On the role of SO<sub>2</sub> in hydrothermal ore-formation. Doklady AN SSSR, Vol. 227 (3), pp. 680-683. In Russian.

Polyak, B.G., Kononov, V.I., and Gavrilina, G.B. (1984). Interrelations of modern hydrothermal and tectonic activities over the USSR. In: Modern tectonic activity over the USSR, Yu.G. Leonov and V.E. Khain (Eds.), Nauka, Moscow, pp. 66-73. In Russian.

Rusinov, V.L. (1989). Metasomatic processes within volcanic sequences. Nauka, Moscow. 213 pp. In Russian.

Ryabchikov, I.D. (1975). Thermodynamics of the fluid phase from granitoid magmas. Nauka, Moscow. 232 pp. In Russian.

Rychagov, S.N., Glavatskikh, S.F., Goncharenko, O.P., Zhatnuyev, N.S., and Korobov, A.D. (1993). Temperature and mineralogic-geochemical characteristics of the Okeanskoye geothermal field. In: Geologiya rudnykh mestorozhdenij, Vol. 35 (5), pp. 405-418. In Russian.

Sakai, H. and Matsubaya, O. (1976). Table isotope studies of Japanese geothermal systems. Geothermics, Vol. 5, pp. 97-124.

Shpak, A.A., Melkanivitsky, I.M., and Seryozhnikov, A.I. (1992). Methods for studying and assessing geothermal resources. Nedra, Moscow. 316 pp. In Russian.

Truesdell A.H., Mahon A., Limenez M.E. (1979). Geochemical evidence of drowdown in the Cerro-Prietto geothermal field. Geothermics, Vol. 8 (3/ 4), pp. 257-267.

Vetshtain, V.E., Baskov, E.A., Klimov, G.I., Malyuk G.A., and Surikov, S.N. (1971). New data on the contents of oxygen-18 in some volcanic thermal mineral waters from the Kuriles, Kamchatka and the Trans-Baikal region. Sovietskaya geologiya, Vol. 9, pp. 98-108. In Russian.

White, D.E. and Waring, G.A. (1963). Volcanic emanations. US Geol. Surv. Profess. Paper. N 1-4, 440-kvi., 29pp.