Hydrothermal Ore Minerals: Composition, Distribution and Formation Conditions in A Conductive Geothermal Environment

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Keywords: modern volcanism, hydrothermal-magmatic systems, ore minerals, geothermal deposits

Synopsis

Ore and silicate mineral formations in the shape of globules and other shapes identified within central parts of modern high temperature hydrothermal-magmatic systems (in geothermal deposits) of the Kuril-Kamchatka island arc were described in detail. Native iron, magnetite globules and zonal ones with iron center and magnetite-iozite rim, as well as more complex ones were identified by means of mineralogical, spectral, microprobe, x-ray phase and other analyses. Globules have traces of Ni, Mn, Ti, Cu etc. – up to 5%, and mark 1.5 km deep opened heat-conducting zones of tectonic faults within horst structures, located above heat (ore) feeding sources of geothermal deposits. It is assumed that these minerals are formed by means of injection of "dry" recovered fluid having a temperature not less than 500-600^{0}C into metasomatites from a depth ≥ 1.5 – 2.0 km. It was established that pyrite disseminated in altered rocks contains traces of numerous ore and non-ore elements in an amount of 3.2%. The fluid injects traces of Fe, Mg, Mn, Ti, Cr, Cu, Pb, Au, Ag, As, Al, Si, K, Na, Ca and others into host rocks. On the whole, these and other element concentrations sustainably increase from early geothermal deposit development phases to the later. Silica, contained in hydrothermae in the form of silica gel, acts as a selective sorbing agent which impacts the ore-bearing properties of hydrothermal solutions, differentiates sorbed metals and transports them. Consideration of geological-geochemical aspects of ore mineral formation and metal-bearing fluids in modern hydrothermal-magmatic systems and geothermal deposits is of principal importance for the development of valuable chemical component extraction technologies to be used in a conductive geothermal environment. The study was supported by the Russian Foundation for Basic Research (project 06-05-64689a), Presidium of Far East Division RAS (projects 06-III-A-08-332 and 06-III-B-08-371), Russian Association of Geothermal Energy Society and International Geothermal Association.

Introduction

In recent years, hydrothermal-magmatic systems in modern volcanism areas have been in focus of researches as ore-generating structures. It is assumed that there is relation between geothermal and epithermal ore deposits (Hedenquist et al., 1996). However, ore formation in the interior of modern hydrothermal-magmatic systems is either declared on the basis of indirect data (study of metal bearing properties of volcanic gases and hydrothermal solutions), or mineral ore formation processes are researched near and on the daylight surface (Giggenbach et al., 1990). The authors of this paper showed that processes of mineral ore formation evolved in the interior of modern hydrothermal-magmatic systems of an island arc during transition from progressive to regressive development stage (Rychagov et al., 2000). Resolution of an ore matter source issue usually depends on a knowledge level about specific mineralization. In our opinion this problem can be principally resolved using another approach, namely, study of initial stages of hydrothermal (geothermal) mineral ore formation by example of modern high temperature hydrothermal-magmatic systems.

Present-day mineralization

Heavy concentrate and mineralogical sampling were used to isolate globular mineral formations (globules) and particles in the form of irregular-shaped grains from core samples and drill cuttings from wells drilled in the central blocks of Baransky, North-Paramushir and partly Mutnovsky hydrothermal-magmatic systems. Grain sizes are from 0.01 mm to 1.7 mm with fine grains being dominant. Most frequently, they are regular globules, less frequently oval, drop-shaped, flattened from both sides etc. All globules are magnetic in various degrees. Many grains are hollow with one or more outlets. Globules are homogenous and have either one or several nucleuses distinguished by high reflecting capacity. Composition of minerals was determined using x-ray micro analyzer "Camebax" and x-ray phase analyses with DRON-2 (survey conditions: Co-emission, 30 kv, 30 mA) (Rychagov et al., 1997). The following minerals were identified: 1) native iron; 2) magnetite; 3) schorlomite garnet - Fe-Ti-Mn-silicate globules; 4) zonal with native iron core with traces of Ti, Mg, Ni, Mn, Cu, Cr and other elements constituting up to 5%, and with magnetite and iozite rim. Porous and highly porous grains prevail (typical for schorlomite), less frequently homogenous massive ones occur (typical for native metals and intermetallic compounds). Besides, *native Ni* in the form of independent phases, iron-nickel phases, in concretion with native iron and quartz; *native Cu, Pb, Zn, Ag; system compounds Cu-Zn, Pb-Sn, Fe-Cr, Fe-C, Cu-Pb-Sn, Cu-Zn-Sn-Pb* (solid solutions and alloys?)*; native graphite* in the form of hexagonal tabular plates < 0.5 mm in size; *moisannite; corundum* were identified in rocks from the section of hydrothermal-magmatic systems of Baransky, North-Paramushir and Mutnovsky (to a lesser degree). The study of ore mineral distribution demonstrated that they were indicative for zones of ascending flow of hydrothermal fluid – horsts, their marginal and axial parts (Rychagov et al., 2002). The interval of brecciated and highly permeable tuffs and tuffites within the reference geological section of the North-Paramushir hydrothermal-magmatic system is enriched with native metals and intermetallic compounds; vein-impregnated sulfide mineralization is developed lower (Rychagov, Belousov et at., 2002).

Ore minerals (pyrite) as indicators of structure, fluid and geochemical regimes in the interior of hydrothermal-magmatic systems

Pyrite in modern hydrothermal systems is deposited in metasomatites throughout all development stages, that is why researches often consider it low informative. The authors' research established that morphology peculiarities, composition of inclusions and pyrite distribution reflected alteration of thermodynamic parameters and composition of endogenic fluid, as well as structural setting in the interior of present-day hydrothermal-magmatic systems of the Kuril-Kamchatka island arc. Pyrite was identified in all three types of rocks and hydrothermal new formations: high-, mid- and low-temperature propylites, argillized metasomatites, thermal clays and ore sediments from mud pots. Pyrite from hydrothermal-magmatic systems being both at progressive stage (Baransky) and at regressive stage (Pauzhetsky) contains traces of many ore elements (Au, Ag, As, Sb, Hg, Pb, Ca, Mg, Mn, Mo, V, Co, Ni, Zr, Si, Al et al.) in quantities up to 3.2% which conforms to composition of solutions (Structura…, 1993). Totally, contents of trace ingredients in Pauzhetsky system's pyrite is by an order higher than in Baransky system. Trace ingredients "infest" hydrothermal-metasomatic pyrite scattered by the whole system **(Fig. 1, 2)**. Au was traced in pyrite within an interval of 0-400 meters from the daylight

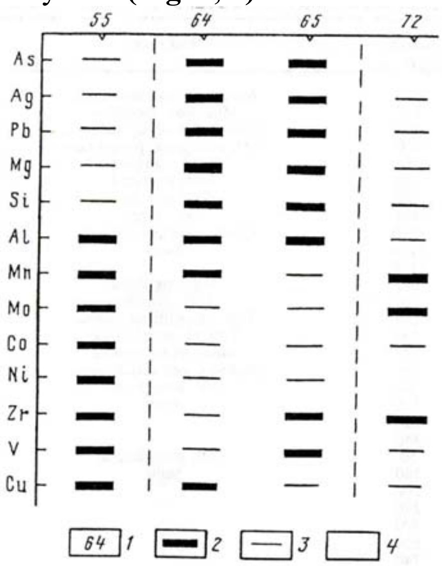

Fig 1. Trace element distribution in pyrite from metasomatites in the Baransky hydrothermal-magmatic system, based on spectrochemical data: 1 – well №; 2,3 – relatively high and relatively low concentrations, respectively; 4 – not found. The vertical dashed lines separate geologic sequences of different blocks.

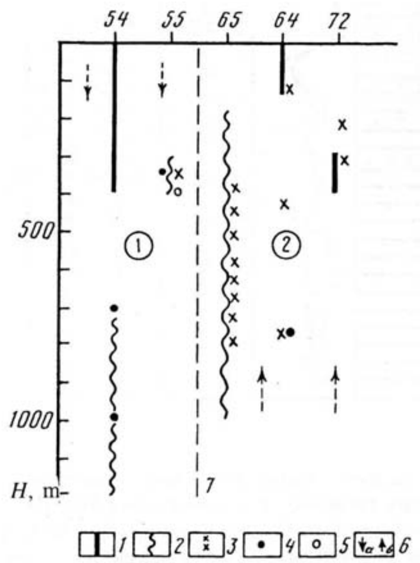

Fig. 2. Trace element distribution in pyrite …, based on microprobe data: 1-5 – Distribution of Au (1), Pb (2), As (3), Cu (4), Zn (5); 6 – dominant water flow direction (a- downward, b – upward); the numbers in circles denote downthrown block (Wells 54 and 55) (1) and horst (Well 64, 65, and 72) (2).

surface, As is typical for middle horizons (400-800 m), Pb forms stable contents in the whole section of geological blocks in the zone of ascending flow of hydrothermae and in the lower part of blocks located within hydrothermal feeding zone (Rychagov et al., 1999). Pyrite is enriched with Hg by the whole geological section of progressive hydrothermal-magmatic system with a noticeable trend of contents increase towards lower horizons; pyrite essentially lacks Hg in deep horizons of cooling system. Such pattern of host rocks enrichment with many pyrite trace ingredients within present-day hydrothermal-magmatic systems during transition from progressive stage to regressive one was confirmed by microprobe and spectral analysis of pyrite from low temperature (temperature of solutions ≤ 110^0C) Paratunsky hydrothermal system on Kamchatka. Besides significantly higher contents of Au, As, Co, Hg and other elements (by one order higher than in Pauzhetsky), it should be noted that pyrite is uniformly enriched with trace ingredients throughout deep parts of sections (distribution of chemical elements in pyrite was studied to a depth of 2, 500 m) and trace gradients are distributed evenly within grains. Metasomatite pyrite grains from Pauzhetsky and especially Baransky systems are enriched with trace ingredients on margins. This confirms the conclusion that minerals-concentrators (sulfides) are saturated sustainably and gradually (?) with many ore elements.

Absorption properties of silicic acid and silica

Hydrothermal solutions in high temperature hydrothermal-magmatic systems of modern volcanism areas are saturated and often oversaturated owing to alteration of P-T conditions when hydrothermae are overflowing to different hypsometric levels and from certain hydrogeological structures to others. It was established that hydrothermal solutions containing significant amounts of silicic acid possessed high adsorption capacity with regards to various metals cations, especially heavy ones (Eitel, 1962; White et al., 1992). Properties of silicic acid hydrosols differ significantly from those of common sols. After compounding with metal cations they do not coagulate but form gel as temperature of hydrothermae decreases during heat dissipation into surrounding rocks, during steam formation and mixing of solutions with cold waters. Efficient deposition of silica in the form of cryptocrystalline quartz and chalcedony takes place when hydrothermae saturated with silicic acid mix with seawater. Interaction of silicic acid colloids and sulfides in hydrothermal solutions occurs in "black smokers": amorphous silica, sulfides of copper, iron, anhydrite and iron oxides are precipitated here. Our works demonstrated that high temperature hydrothermae in modern volcanism regions were silica aqueous solutions which ceaselessly, as long as a hydrothermal system lived, reproduced silica gels. Silica gels interact both with metal cations and with other colloid particles having positive electrostatic charge whereby new compounds form. In this manner, compounding of silica gel particles with Al hydroxide leads to formation of mixed-layer argillic minerals of the montmorillonite group (Eitel, 1962). Similar interaction with colloid formations of Fe promotes the formation of chlorite minerals, etc. Thus, many mineral complexes in hydrothermal systems of modern volcanism regions are formed based on silica gel or with their indirect participation (Chukhrov, 1955; Petit et al., 1989). Hydrothermae contain dissolved carbon dioxide which retains Ca ions in hydrothermal solution. Therefore, silica gel is present in such hydrothermal solutions as Ca-silica gel, whose sorption capacity is by 1.5-2 orders higher as compared to silica gels produced by hydrothermae with low contents of carbon dioxide. Such systems are Pauzhetsky system and Valley of Geysers on Kamchatka, North-Paramushir and Baransky in the Kuril islands, Vairakei in New Zealand etc., where contents of carbon dioxide in discharge centers are measured in tens of mg/kg^{-1}. This circumstance indicates that high temperature hydrothermae connected with island arc andesite volcanism may have elevated ore content.

Conclusion

Exploration of transition zone between the proper hydrothermal and magmatic conditions by means of deep drilling demonstrated that native metal ore elements, intermetallic compounds, solid solution and metal alloys were deposited in this very zone **(Fig. 3)**. Within this zone hydrothermae circulate and they contain elevated concentrations of chemical elements, primarily, Au, Ag, As, Fe, Mg, Mn, Ti, Cr, Hg, Pb, Zn, Cu, Sn, Si, B, K, Na, Li, Rb, Cs, and others., and their compounds. Circulation of geothermal ore-generating solutions occurs inside the complex system of permeable tectonic ruptures and aquifers. Formation of thick vapor zones (over 300-500 meters), whose boundaries are geochemical barriers for Au, Ag, As, Fe, Pb, Cu, Zn, Hg, B, K, Si and other elements occurs in strictly distinct structures (as a rule in axial parts and on the boundaries of upstanding tectonic blocks). During the long evolution of hydrothermal-magmatic system from progressive to regressive stage, host rocks are profoundly altered due to interaction with high-, mid-, low-temperature hydrothermal solutions of different compositions and different pH. Thick layers of propylitized rocks n x 100 km^3 in size are formed within the limits of one hydrothermal-magmatic system. Argillized propylites and products of sulfur- and carbon-dioxide leaching the sizes of which are comparable with propylitized rocks play an important role as pre-ore and ore-associated metasomatites. The role of these rocks in hydrothermal gold ore formations and formation of gold-silver, gold-polymetallic and copper-porphyry type mineralizations has been indicated by many researchers. Precisely in the zone of argillized propylites and argillizites alkaline rare-earth and ore elements are actively leached from host rocks and many chemical components are precipitated at geochemical barriers. An important role in transport and precipitation of ore elements and their compounds in the structure of

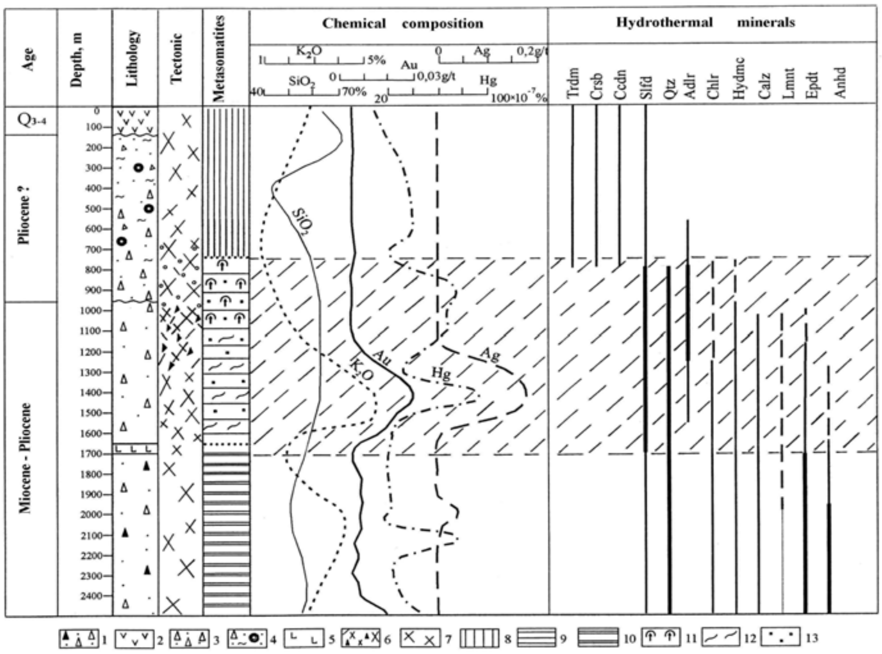

Fig. 3. Geological and mineral-geochemical section of North-Paramushir hydrothermal-magmatic system (Well GP-3) (Rychagov, Belousov et al., 2002). 1 – Intrusive tuffs. 2 – Andesitic lavas. 3 – Andesitic tuffs. 4 – Tuffites. 5 – Andesitic-basaltic lavas (dykes). 6 – Tectonic breccia. 7 – Cracks. 8 – Opal-cristobalite-tridimite-chalcedony mineralization. 9 – Quartz-adular metasomatites. 10 – Middle-temperature propylites. 11 – Boiling thermal water zone. 12 – Quartz-chalcedony veinlets with ore minerals. 13 – Ore mineralization.

hydrothermal-magmatic systems is assigned to solutions of silicic acid and silica gel being formed in liquid-vapor transition zones and at other temperature barriers. Long evolution of liquid-vapor transition zones results in formation of thick (up to 1,500 m) zones of silicification–adularization of rocks which accommodate ore mineralization. Hydrothermae, as well as siliceous earth, argillizites and other depositions, are of significant interest for the development of valuable components extraction technologies.

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