Transport and Concentration of Ore Chemical Compounds in the Geothermal Environments

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Abstract

Behavior of ore chemical elements at deep-seated, subsurface and aquatic geochemical barriers in hydrothermal systems is discussed. Intense water-rock interaction processes occur within the confines of thick (≥ 100-300 m) zones of boiling hydrotherms: here, within the interstitial-breccia interior, quartz-adularia (quartz-adularia-prehnite-wairakite) metasomatites are enriched with alkaline, ore and rare chemical elements, or contrariwise (when physical-chemical parameters of the system are altered) – the leaching and concentration of these elements occur in hydrothermal fluid. Hydro- and lithochemical anomalies of ore and alkaline elements are formed within the confines of moving tectonic structures, which bring the hydrothermal fluid to near-surface levels. Structure of metal-bearing fluid localization areas is demonstrated. Hypergenesis zones of geothermal deposits (at aquatic and subaquatic barriers) produce geochemical anomalies in kaolinite-montmorillonite clays and siliceous sinters. Structurally, the anomalies are confined to the boundaries or axial zones of elevated blocks. Peculiarities of metal-bearing fluid composition within different geological blocks of deposits are indicated. The most probable forms of transport and concentration of Au, Ag, As etc. by water fluids in the near-surface environment of high-temperature hydrothermal systems are established.

Evolution of steam dominant zones within hydrothermal systems is discussed in detail by example of Pauzhetsky geothermal deposit (the South Kamchatka). Thermodynamic and geological-structural conditions of the emergence of steam zones within the confines of cooling magmatic bodies and above-intrusive areas at different depths are shown. A numerical model study for zones' evolution in space and time at various starting and boundary temperature and host rocks permeability parameters is conducted. The influence of geochemical fluid-steam barrier on processes of mass transfer, namely, on deposition or leaching of gold and silver from the siliceous matrix, and on alteration of composition and properties of hydrothermal fluid and steam is experimentally studied. It is also demonstrated that composition and properties of a liquid phase are profoundly changed during the boiling of saline solutions and repeated expansion and compression of a steam phase. Factual thermodynamic and physical-chemical parameters of the "steam hydrotherm – rock" system are the base for the development of extraction technologies applied to take useful chemical components from saline solutions, siliceous deposits or other mineral media. The work has been done with a financial support of the Russian Fund of Fundamental Research (project 06-05-64689a) and Russian Association of Geothermal Energy Society.

Introduction

The availability of many facts derived from studies of distribution of Au, Ag, As, Pb, Hg and other elements in hypergenesis zone and in near-surface and deep-seated geochemical barriers in modern hydrothermal-magmatic systems and geothermal deposits of Kamchatka (Pauzhetsky, Mutnovsky, Uzon-Geyzerny) and the Kuril islands (Baransky – the Iturup island, North-Paramushir – the Paramushir island) enables us to conduct a distribution analysis, formation conditions and ore elements source probability within structure of long-existing ore-bearing hydrothermal-magmatic system. Pauzhetsky (the South Kamchatka) and Baransky (the Iturup island) hydrothermal-magmatic systems are the most studied and along with other sites are used as models to deal with geochemistry issues of Au and some other elements.

Ore elements in hypergenesis zone

Based on study of argillizites of Pauzhetsky geothermal deposit, elevated contents of Au in kaolinite-montmorillonite clays restricted to sulfuric-acid leaching zone are identified. Sulfide-containing blue and gray clays occurring at a depth of 20-60 cm to 1.5 m and outcropping brown clays contain Au up to 20 mg/t. Certain samples contain elevated grades of Ag (up to 500 mg/t), Sb (up to 60 g/t) and As (up to 300 g/t). Up to 100 mg/t of Au was identified in sulfides sampled from blue clay horizons. Upper boundary of sulfide-containing clay horizon conforms to alteration of reduction-oxidation potential. Pore solutions in the horizon are sulfate-chloride acid aqueous solutions (pH=0,97-3) with high concentrations of Mn (up to 12 mg/l), Fe (10-580 mg/l), Zn (4-340 mg/l), Cu (0,4-33 mg/l) and Au (0,39-1,4 mkg/l) (Pampura, Khlebnikova, 1987). Broadlands geothermal field rocks near surface are enriched with Sb, Au and Tl, at a depth – with Pb, Zn, Ag, Cu and other elements (Ewers, Keays, 1977). Authors came to a conclusion that precipitation of gold from hot springs in near-surface conditions was in the first place determined by decreasing contents of H_2S in aqueous solutions due to solutions boiling when pH (about 5) was destabilized by bisulfide complexes and As and Sb sulfides were precipitated. Colloid arsenic and antimony sulfides act as effective concentrators of Au and other metals.

Despite contents of Au and its associated elements in modern hydrothermae are low (Structura …, 1993), they concentrate at surface (aqueous) geochemical barrier in geyserites, saline exudations and other neocrystallisations. For instance, based on data from 63 geyserite samples taken from deposits on operational well mouths and around natural hydrothermae outlets, an average content of Au is 33.5 mg/t at a maximum of 420 mg/t; Ag – 242 mg/t (up to 20 g/t); As and Sb – 20 g/t at a maximum of 600 g/t. Saline exudations, mainly K and AL sulfates, are developed at sites with active fumaroles. Average contents of Au and associated elements in exudations are comparable with their concentrations in geyserites (Koroleva et al., 1993). On the whole, aqueous geochemical barrier is typical for hydrothermal-magmatic systems of Pacific volcanic belt, where siliceous deposits with high contents of Au, Ag, As, Sb and other elements have been found. Such are geothermal fields of New Zealand and Japan: back in 1937 J. Grage established contents of Au above 20 g/t and Ag – up to 500 g/t in siliceous new formations (New Zealand) (Structure …, 1993).

Ore elements in hydro- and lithochemical flux leakage

Behavior of ore elements in hydro- and lithochemical flux leakage, relationship of their anomalous concentrations with geological structure was studied in detail on Okeansky vapor-hydrothermae deposit (Rychagov et al., 2002). Base drainage level of hydrothermal solutions is confined to middle current of the main stream flow where main discharge of deep-seated chloride-sodium sub-alkaline thermae occurs. Hydrochemical anomalies of Au, confined to the riverbed, are most probably conditioned by hydroxyl- and chlorine-containing gold complexes. Small by size and grade Au anomalies were identified in bottom sediments in relatively downthrown block area and on the boundary of tectonic-magmatic elevation. Geochemical barrier is formed here owing to abrupt change of physical-chemical conditions during ultra-acid hot thermae discharge. The geochemical barrier forms depositions of sulfur, opal, jarosite, barite, acicular iron ore, pyrite, silica gel which act as collectors of electrically neutral particles of gold (Structura…, 1993). Higher grade of silver (up to 0.5 g/t) in bottom sediments of the relatively downthrown block as compared to other sections allows to state the formation of such hardly soluble compounds as kerargyrite (AgCl) and argentite (Ag_2S) taking into consideration their formation conditions (pH < 4, presence of Cl^- and barbotage of H_2S). Weak anomalies of silver in surface waters are restricted to discharge areas of weakly acid and neutral thermae where thiosulfate complex may occur $Ag(S_2O_3)_2^{3-}$. Weakly-contrasting anomalies of Sb in waters are also restricted to downthrown section and conditioned by migration of compounds H_2AsO_4 and H_2AsO_3. Lithochemical anomalies of As in near-wellhead section are formed as a result of precipitation of As_2S_3 (Rychagov et al., 2002). The anion diversity in local hydrothermae creates potential for existence of many forms of Pb both in complexes and in hardly soluble salts. Pb anomalies are confined to acid thermae discharge zones where probably formation of complex compounds of $PbCl^+$ и $PbCl_3^-$ with low solubility takes place. Simultaneously, lithochemical anomalies created by hardly soluble compounds $PbSO_4^o$, $Pb(OH)_2^o$ are formed within these zones and these anomalies are more contrasting than hydrochemical ones. On the whole, Au, Ag, As, Pb and Hg distribution anomalies in the hypergenesis zone have more distinct structural confinedness. Lithochemical anomalies are concentrated within horst structures or on the boundaries of geological blocks and in zones of intersection of present-day tectonic faults conducting hot mineralized waters to the daylight surface. Bottom sediments within ore matter concentration areas are a mixture of fine particles of opal, alunite, jarosite, goethite, pyrite and other sulfides which corresponds to mineralogical composition of host rocks locally decomposed by waters – argillisites of acid leaching zone. These rocks, as well as geyserites, have a high sorption capacity with respect to ore compounds and form a 50-225 m thick stratum at the most part of the system.

Hg distribution and behavior features

It was observed that Hg was distributed unusually for geothermal manifestations – rocks, in general, are enriched with Hg by an order higher than background values in the region: (5-25) x 10^{-6} % against (1-2,2) x 10^{-6} % (background values, by L.L. Leonova, 1977). At the same time, Hg distribution is not homogenous from section to section and depends on geological setting of rock blocks and temperature of a hydrothermal fluid. High and low Hg grade rocks are observed to alternate ***in the relatively downthrown blocks*** by the whole cross-section down to bottom. Anomalously high contents of Hg correlate with zones of higher fracturing and rock porosity, decompaction areas on boundaries of lithological horizons and sulfidization in metasomatites **(Fig. 1)**.

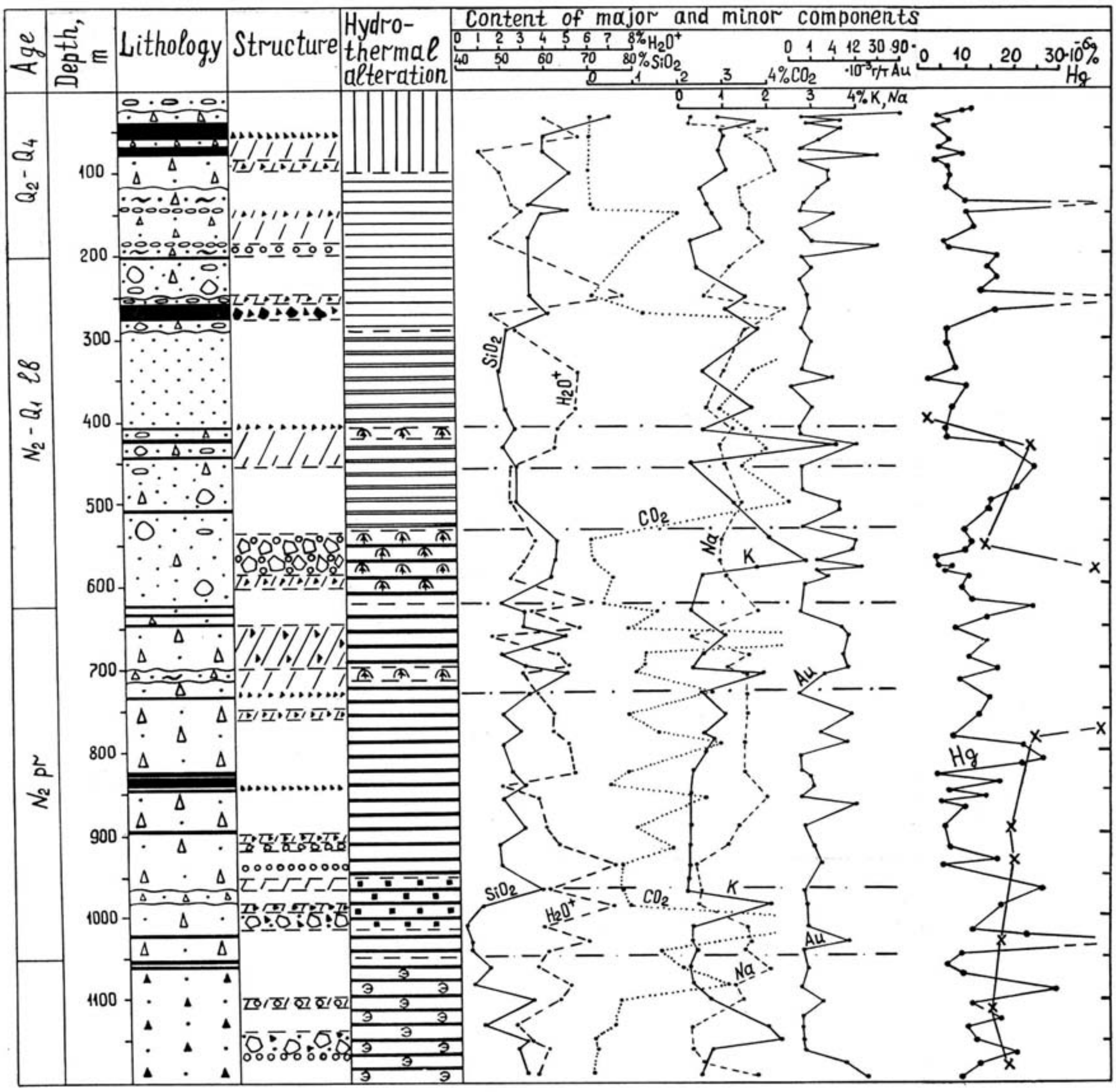
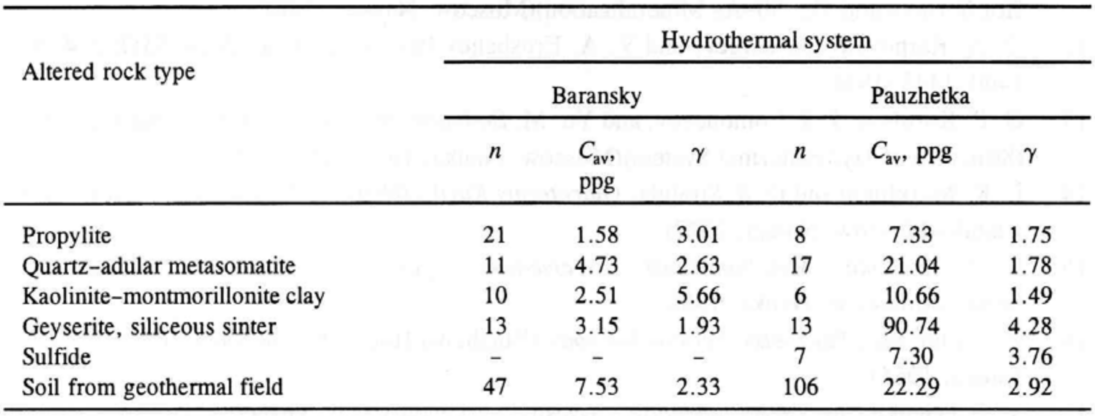


Fig. 1. Distribution of some petrological, mineralogical and geochemical characteristics of rocks in Well № 54 (Baransky hydrothermal-magmatic system)

It is observed that Hg accumulates in loose clastic rocks situated under and between lava flows or andesite-basalt sills. Hg contents distribution is not observed to correlate with various types of metasomatites, but a decline of Hg contents down to background values is identified within liquid-vapor transition zones. High open porosity of liquid-vapor transition zones (to 50 %) is provided by macropores being formed due to loose cement leaching and mechanical wash-out of fragments and serving as conduits which enable mercury to migrate easily by the section. A content of Hg in monomineral pyrite samples is even higher than in rocks. Apparently, Hg is localized not only on the surface and in microfissures of pyrite crystals but also is included as an isomorphic ingredient to mineral structure whereupon complete precipitation occurs only at lattice melting temperatures (above 450-500^{0}C). ***In cross-section of tectonic-magmatic elevations*** a larger part of Hg grades in rocks is close to those of the background. Identified anomalies exhibit the same trends of confinedness to crushing zones, lithological and metasomatic boundaries. Distribution of Hg contents in ***horst rocks*** is nonuniform from section to section. This feature of mercury behavior in horst sections is apparently associated with their being highly subdivided by various thickness block-lamination with numerous open tectonic ruptures through which thermal and cold meteoric waters actively circulate; with non-uniformity of present-day temperature field and rise of local heat flow fronts close to the daylight surface. This results in run-down of Hg from the most heated sections and accumulation of Hg in cooling zones.

Discussion of results

Elevated concentrations of Au, Ag, As, Pb and other ore elements in the hypergenesis zone are associated with discharge of deep-seated sub-alkaline chloride-sodium solutions at the daylight surface. Concentrating of electrically neutral particles of Au and hardly soluble chorine- and sulfur-containing compounds of Ag, As and Pb in bottom sediments is caused by abrupt decline of pH and temperature of solutions in near-surface zone of mixture of deep-seated sub-alkaline chloride-sodium waters with acid vapor-heated waters, or at the daylight surface during the mixing of acid sulfate (sulfate-chloride) ones with meteoric waters. Hydro- and lithochemical anomalies of ore elements in the hypergenesis zone are localized within horst structures, contact zones of tectonic-magmatic elevations with relatively downthrown blocks and intersection areas of tectonic faults opened to a depth of 1.5-2.0 km. Sulfides, intermetallic compounds, native Au, Ag, Cu and other metals, their alloys and solid solutions are precipitated in the area of intensive mixing of near-surface acid and deep-seated sub-alkaline waters on the boundaries of steam-dominant zones in quartz-adularia metasomatites and quartz-epidosites, and also in partially argillized propylites. Probably, ore mineralization of copper-porphyry type is originated in near-contact zones of intrusions at a temperature over 400-500°C. This is evidenced by data from studies of distribution of native metals, their alloys and intermetallic compounds in the deep section of the North-Paramushir hydrothermal-magmatic system (Rychagov et al., 2002). Notably, there is also a tendency that accompanying element concentrations in sulfides and various rocks become higher from a high-temperature system to a cooling one **(Table 1)**. Thickness of geochemical ore barriers being formed during a long evolution of modern hydrothermal-magmatic system reaches 300-500 m and more. Concentrations of ore elements are up to n x 10 g/t.



Altered rock type	Hydrothermal system					
	Baransky			Pauzhetka		
	n	C_{av}, ppg	γ	n	C_{av}, ppg	γ
Propylite	21	1.58	3.01	8	7.33	1.75
Quartz–adular metasomatite	11	4.73	2.63	17	21.04	1.78
Kaolinite–montmorillonite clay	10	2.51	5.66	6	10.66	1.49
Geyserite, siliceous sinter	13	3.15	1.93	13	90.74	4.28
Sulfide	–	–	–	7	7.30	3.76
Soil from geothermal field	47	7.53	2.33	106	22.29	2.92

Table 1. Main characteristics (average geometric concentration C_{av} and standart factor γ) of Au distribution in metasomatic rocks (n – number of measurements).

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