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Mercury as an Indicator of Temperature and Geochemical Barriers in Hypergenesis Zone of Geothermal Deposits (Kamchatka)

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SYNOPSIS

The distribution of mercury in all types of solid deposits presented in the hypogene zone of the South Kamchatka geothermal fields is demonstrated: in rocks, in hydrothermally-altered rocks, in soils and soil-pyroclastic cover, in bottom sediments, in hydrothermal clays, in siliceous sinter deposits and in iron sulfides (Rychagov et al., 2009). Mercury content ranges from background for the Kuril-Kamchatka region (1.0 – 1.5 x 10^{-6} %) in non-altered rocks to high and outstanding content (n x 10^{-2} %) in hydrothermal clays and monomineral pyrite samples. Data on sources, migration conditions and concentration mechanisms were acquired. Mercury is transported to the surface as a constituent of a deep-earth hydrothermal fluid and is concentrated at thermodynamic barriers in hydrothermal clays, in siliceous sinters (silica gel) and in soils with elevated salinity due to earth silicon, sulfates and other compounds precipitated from the steam-water mixture. Newly-formed iron sulfides (pyrite), silicate gel and peat, which is found on surface of deposits and derived from plants that decayed under siliceous sinters, are good sorbents of mercury in geothermal conditions under atmospheric pressure and temperatures varying from 20°C to 150°C. Mercury concentration levels in solid deposits and its distribution character in hypogene zone of geothermal deposits indicate the thickness and probable depth of occurrence of a heat source.

1. INTRODUCTION

In recent years, attention to mercury behavior in the geological environment has significantly increased because of the wide distribution of this element in the lithosphere, hydrosphere and atmosphere and because of identification of new qualities in mercury (Hg) migration, primarily in the geodynamically active regions of the world. For example, the connection of anomalous variations of Hg content in water of active faults with present-day seismic activity of the Baikal Rift Zone has been demonstrated (Koval et al., 2003). Lithochemical haloes of Hg dispersion in marine quaternary deposits localized along fluid-conducting faulting are used to detect and map sources of hydrocarbon resources (Astakhov et al., 2007). The study of Hg behavior in geothermal deposits is traditionally associated with search tasks: identification and tracking of permeable zones, delineation of thermal anomalies, etc. (Trukhin et al., 1986). It is thought that, under the influence of an anomalously high convective heat flow, practically all of the Hg from host rocks is distilled off from depth and is accumulated in the thin near-surface layer of argillized rocks. We demonstrate that during the high temperature phase of a hydrothermal-magmatic system's development Hg may form anomalously high concentrations in fracture-breccia zones throughout the whole geological cross-section to a depth of 1.0 – 1.5 kilometer and as the system evolves the main body of Hg is gradually (?) transported to the surface (Rychagov and Stepanov, 1994). Mercury migration zones are localized in the central parts of systems and deposits and at the same time the connection between hydrothermal Hg flow and deep-earth (magmatic?) Hg sources is lost. Such a behavior of Hg in present-day geothermal conditions, as well as the correlation of Hg distribution with Au, Ag, Pb, Cu, Zn and other elements in certain sections of the structure of hydrothermal-magmatic systems, makes Hg a possible indicator of formation mechanisms for temperature and geochemical barriers in the hypogene zone of geothermal deposits.

2. RESULTS

Sampling, sample preparation and analytical investigation were implemented using standard techniques (Rychagov and Stepanov, 1994) to study of the South Kamchatka best-known geothermal deposits – Mutnovsky, Pauzhetsky, Paratunsky and Nizhne(Lower)-Koshelevsky, and the thermal fields of the Kambalny volcanic ridge **(**Figure 1). A "baseline" site was selected on the flank of Paratunsky geothermal deposit – a part of the geological structure where effects of anomalous heat flow are not observed. Initial bedding rocks, hydrothermally-altered rocks, argillites (hydrothermal clays), iron sulfides (pyrite) formed in hydrothermal clays, soil-pyroclastic deposits, siliceous sediments and travertines, salt exudates and bottom sediments were studied. All the materials are observed to have non-homogenous distributions of Hg that depend on the type of solid deposits and their confinement to a certain geothermal deposit (Table 1).

Study of the Hg distribution in geological reference sections (wells) of the Okeansky geothermal deposit, which is located on the slope of the active Baransky volcano (the Iturup island, the Greater Kuril Ridge), demonstrated that Hg created elevated concentration anomalies not only in near-surface zones but also at different depths (Rychagov and Stepanov, 1994). Rocks, on the whole, are enriched with Hg – an order higher than baseline values for the region (Leonova, 1979). At the same time, the Hg distribution is irregular from section to section. Relatively down thrown blocks, where rocks get cooled due to downward seepage of meteoric and mixed thermal waters, are observed to have alternating sections with low and high concentrations of Hg **(Figure 2*a*)**. Anomalously high Hg content correlates with zones of excessive rock fissuring and porosity, with decompaction zones at boundaries of lithological horizons and sulfidation zones. Accumulation of Hg is also observed in loose clastic rocks emplaced between lava flows and andesite sills. Lava flows and subhorizontally bedded sills

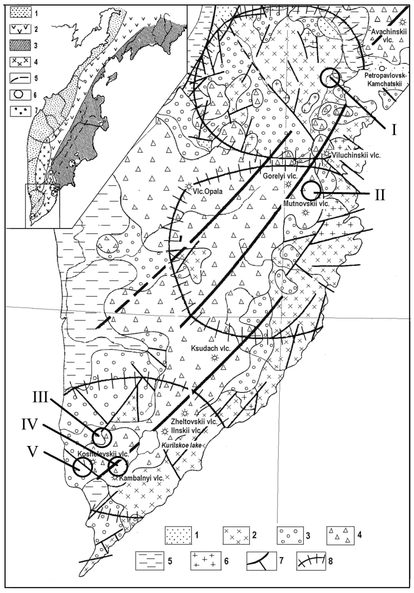

Figure 1. Geothermal Regions of South Kamchatka: the Structural Plan (Rychagov et al., 2006_1). <u>Inset map:</u> main structural areas of Kamchatka in Paleogene-Neogene time (made by G.M.Vlasov and V.V. Yarmolyuk in 1964): 1 – West-Kamchatka, 2 – Central Kamchatka, 3 – East-Kamchatka; 4 – Sredinny massif (Sredinny Ridge); 5 – boundary of the East-Kamchatka volcanic zone; 6 – geothermal regions; 7 – geothermal systems. <u>Main map:</u> 1 – Pre-Island-Arc-Stage rocks (Pre-Oligocene); 2 – Lower structural stage (Oligocene (?) – Middle Miocene); 3 – Middle stage (Middle Miocene–Pliocene); 4 – Upper stage – Quaternary volcanites; 5 – Quaternary and Pliocene - Quaternary (?) sedimentation masses of the upper structural stage of the internal area of the island arc; 6 – Large bodies of the quartz diorite complex; 7 – Faults; 8 – Boundary of geothermal areas, from North to South: Paratunsky, Mutnovsky-Zhirovsky and Pauzhetsky-Kabalny-Koshelevsky. Roman numbers indicate geothermal fields: I – Paratunsky, II – Mutnovsky, III – Pauzhetsky, V – Lower-Koshelevsky; and thermal manifestations of Kambalny Ridge (IV).

and dykes, noted for low permeability for steam-hydrothermae and gases, apparently act as screens for a fluid saturated with mercury vapor. On the other hand, Hg concentrations in liquid-vapor transition zones are usually not higher than baseline values. Probably, in the conditions of boiling zone thermodynamic barriers, Hg easily migrates across the section. Sections are virtually barren in the upstanding blocks of rocks (Figure 2*b*), where only minute Hg concentration anomalies are measured. The high temperature of rocks in such blocks (up to 380-470^{0}C at a depth of 800-1000 meters) governs fluxes of an ascending high-temperature fluid and causes migration of Hg from fracture-interstitial space and minerals' crystal lattice towards the surface. Thus, within the structure of the Baransky system, hydrothermal-magmatic conditions determine mechanisms of mercury accumulation and redistribution in various parameters of geothermal environment.

It has been demonstrated earlier that the high Hg contents of hydrothermal clays are mainly caused by its accumulation in clay minerals at the temperature barrier (Stepanov et al., 1982). In addition, pyrite is a proficient concentrator of Hg in hydrothermal zones. This point is confirmed by studies of hydrothermal clays from the Nizhne(Lower)-Koshelevsky thermal anomaly and the Verkhne(Upper)-Pauzhetsky geothermal field. The latter has high Hg concentrations associated with a near-surface horizon of blue clay (up to $\geq 2 \times 10^{-4}$ %), where pyrite may amount to 90 % by volume. Monomineralic pyrite samples yield Hg concentrations higher by 1-2 orders of magnitude. Hydrothermal clays in sections of the Nizhne(Lower)-Koshelevsky thermal anomaly are characterized by generally higher content and by relatively even distribution of pyrite in layers (up to 30-40 volume %). Concentrations of Hg in bulk clay samples amount to $n \times 10^{-3}$ % and $n \times 10^{-2}$ % in pyrite monofractions. Thus, pyrite is a good concentrator of Hg, as well as Au, semimetals and other elements, which was demonstrated not only for epithermal ore deposits but also for the present-day geothermal conditions (Structura, 1993).

Siliceous sinter deposits of the Pauzhetsky geothermal field contain, on the average, $1\text{-}3 \times 10^{-6}$ % Hg, which corresponds to baseline values for solid deposits that have experienced hydrothermal processes. Siliceous sinters deposited by a thermal spring may be noted by Hg concentrations higher by one order of magnitude than the baseline values. There is also a trend for Hg concentrations to decrease from the upper layer of deposits to the lower one and from the beginning of a "coat" formation down along the strike. The represented data are indicative of the fact that Hg occurs in deep-earth hydrothermal fluids (the exploited water-bearing horizon in this section of Pauzhetsky deposit is, on average, located within a depth range of 600-800 m) and is concentrated together with colloid silica acid at the first thermodynamic barrier, which is the well top. Probably, the silica gel is a good Hg sorbent, as is the vegetation substrate. As silica gel ages and silicon minerals form, Hg residing here in the atomic form can easily escape from the lattice or from defective mineral structures and so migrate towards the foundation of the section along with the flux.

The high Hg concentrations in soils in the central parts of geothermal deposits are caused by the following: 1) intense emanation of mercury from the host rocks (deep-earth source?) under the conditions of anomalously high temperature in an ascending heat flow, which was detected for the Nizhne(Lower)-Koshelevsky and Mutnovsky deposits and 2) mercury accumulation in near-surface rocks at the temperature barrier. At the progressive development stage of a hydrothermal system, mercury is an indicator of higher permeability zones, temperature conditions and, apparently, ore geochemical barriers, including ones at depths of over 500-1,000 meters.

Table 1. Average values of concentration of mercury in various types of sediments on geothermal deposits of Southern Kamchatka

Type of sediments	Hg, 10^{-7} %			
	Geothermal deposits			
	Pauzhetsky	Nizhne-Koshelevsky	Mutnovsky	Paratunsky
Rocks	**16** / 220	**16** / 220	**136** / 13	**29** / 42
Metasomatites	**75** / 220	**75** / 220	**1184** / 5	**217** / 22
Soils	**523** / 50	**2010** / 62	**510** / 38	**106** / 34
Bottom sediments	**102** / 42	-	**977** / 56	-
Siliceous deposits	**19** / 34	-	-	-
Hydrothermal clays	**2727** / 250	**15350** / 48	**5000** / 32	-
Pyrite	**7280** / 57	-	-	-

The note. Definitions are executed in Institute of Volcanology and Seismology FED RAS by atom-fluorescent method. Analysts I.I. Stepanov, N.I. Chebrova, N.I. Svinuhova and V.P. Korosteleva. In numerator – average values of concentration of mercury in tests, in a denominator – quantity of definitions.

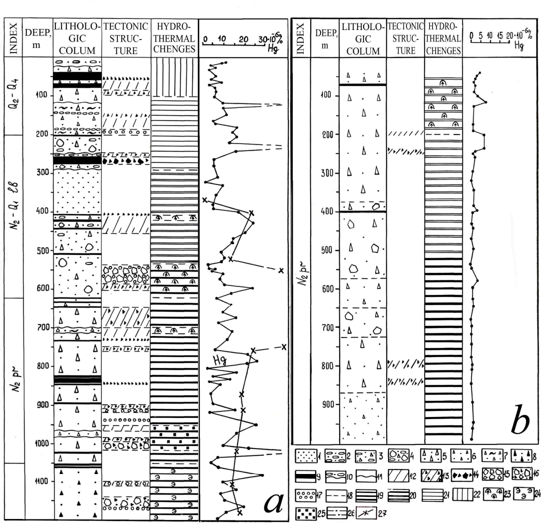

Figure 2. Geological cross-sections of the Baransky system (Rychagov, Stepanov, 1994), *a* – downthrown block (well 54), *b* – upstanding block (well 65). 1 – tuffites; 2 – gravel; 3 – tuff gravel; 4 – tuff conglomerates; 5 – psephitic tuffs of andesite-dacitic composition; 6 – same psammitic; 7 – ignimbrites and pumice tuffs; 8 – intrusive breccias; 9 – effisives, dykes and sills of andesite-basalt composition; 10 – diluvium; 11 – stratigraphical boundaries; 12 – fissure zones; 13 – tectonic breccias; 14 – near-contact breccias; 15 – hydrothermal breccias; 16 – polymictic combined breccias; 17 – areas of higher porosity rocks; 18 – boundaries of tectonic zones and metasomatites facies; 19 – mid-temperature, 20 – low-mid-temperature, 21 – low-temperature propylites; 22 – rocks of sulfuric leaching zones; 23 – hydrothermalites of boiling zones; 24 – elevated content of epidote; 25 – same of sulfides; 26 – boundaries of geochemical anomalies; 27 – content of mercury in pyrite monofractions.

The study of Hg distribution in the hypogene zone of South Kamchatka geothermal deposits demonstrated that the behavior of this element is ambiguous and depends on the temperature and physical-chemical conditions of formation and on the alteration of various geological sediments. For the most part, rocks occurring at the surface have Hg concentrations that are low and baseline for the Kuril-Kamchatka region (Leonova, 1979). However, the Mutnovsky geothermal deposit is notable for having high average Hg concentrations in non-altered rocks of various origin (lavas, tuffs, ignimbrites, breccias), and in other solid sediments, including metasomatites, soils, and clays (Figure 3). In our opinion, this is primarily because the Mutnovsky deposit and the Mutnovsky hydrothermal-magmatic system are different from the other studied sites with respect to a number of general parameters. The Mutnovsky deposit has a high installed and forecasted capacity (62 and >300 MW_e, respectively); is a long-lasting system (was active during the whole quaternary period) that is associated with hydrothermal-metasomatic alteration of a huge rock mass (≥ n x 100 km^3); has a large exposure of argillizite sequence on the surface (≥ n x 10 km^2); and has a large, long-lived heat and ore feed source in the interior of the hydrothermal-magmatic system. Hydrothermally altered rocks, as well as considerable soil-pyroclastic deposits all the way through the hypogene zone, have Hg concentrations higher by 1-2 orders of magnitude than baseline values.

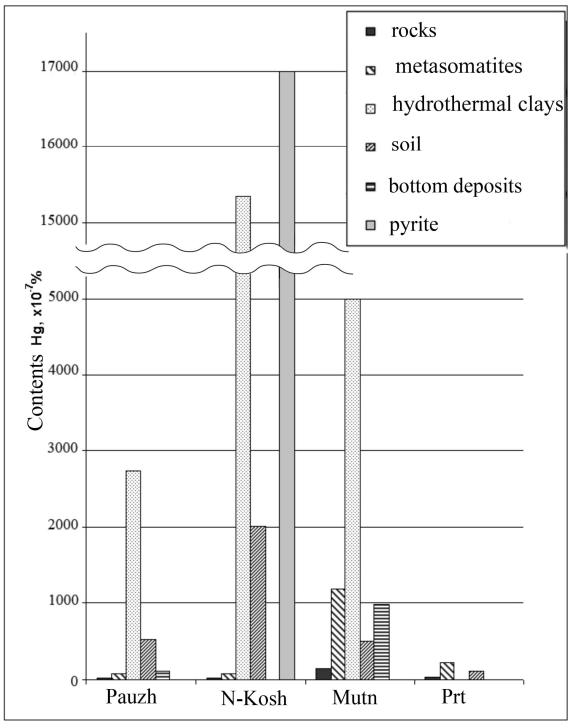

Figure 3. Content of Hg in various types of solid deposits at Pauzhetsky (Pauzh), Nizhne(lower)-Koshelevsky (N-Kosh), Mutnovsky (Mutn) and Paratunsky (Prt) geothermal fields.

The same is observed in bottom sediments studied in detail at two geothermal deposits – Pauzhetsky and Mutnovsky. Accumulation of mercury in the indicated formations is associated with present-day hydrothermal processes and the presence of rock-forming and secondary Hg-concentrating minerals in metasomatites, soils and bottom sediments. To some extent, studies of hydrothermal clay strata and artificial siliceous sinter deposits may explain thermodynamic and geochemical barriers in the foundation of soil profiles, namely barriers due to precipitation of a variety of salts (sulfates, cryptocrystalline silicon earth from silica gel, etc.), which can be Hg sorbents. Peat buried under modern siliceous sinters deposited by thermal waters of Pauzhetsky deposit (Figure 4) can be also considered a good Hg sorbent. Sorption properties of the peat bed are probably influenced by the open nature of the "siliceous sinter/ vegetative substrate" system where there is active and ongoing thermal water circulation and by the intensive processing of buried vegetation in an elevated temperature environment.

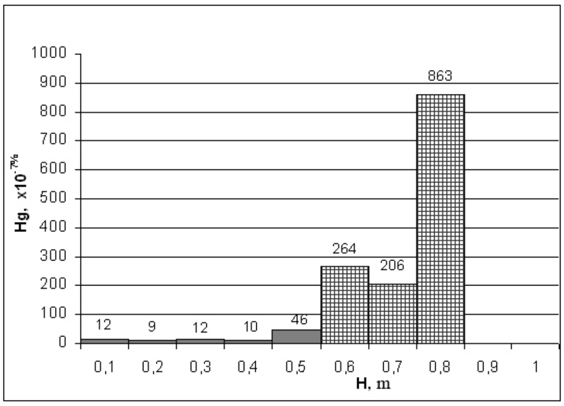

Figure 4. Distribution of mercury concentrations by layers of vertical section of mass of siliceous sinter deposits in the point 30 meters away from top of well R-120. Three lower layers are composed of peat formed during 25-27 years due to conservation and transformation of plant remains under the layer of siliceous deposits under the conditions of constant elevated temperatures (75-90^{0}C); intermediary layer (0.5 – 0.6 m) is composed of thin mud precipitation.

3. CONCLUSION

To sum up, we have received new data on sources, migration conditions and mechanisms of Hg concentration within geothermal systems. Based on continued studies, the distribution of Hg in all the types of solid precipitations manifested in hypogene zone of the South Kamchatka geothermal deposits is demonstrated, including in rocks, in hydrothermally-altered rocks, in soils and soil-pyroclastic cover, in bottom sediments, in hydrothermal clays, in siliceous sediments and in iron sulfides (Rychagov et al., 2009). Mercury content ranges from background in the Kuril-Kamchatka region (1.0 – 1.5 x 10^{-6} %) in non-altered rocks to anomalously high values (n x 10^{-2} %) in hydrothermal clays and monomineral pyrite samples. Data on sources, migration conditions and concentration mechanisms were acquired. Mercury is transported to the surface as a constituent of a deep-earth hydrothermal fluid and concentrates in thermodynamic barriers in hydrothermal clays, in siliceous sediments (silica gel), in travertines (calcic gel), and in soils with elevated salinity due to silicon, sulfates and other compounds precipitated from steam-water mixture. Newly-formed iron sulfides (pyrite), silicate gel and peat, found on surface of deposits and derived from plants that decayed under siliceous sinters, are good sorbents of mercury in geothermal conditions under atmospheric pressure and temperatures varying from 20^{0}C to 150^{0}C. Mercury concentration levels in solid precipitates and its distribution character in the hypogene zone of geothermal deposits indicate thickness and probable occurrence depth of the heat source.

4. ACKNOWLEDGEMENTS

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