PGE in the Modern Hydrotherms of Kudryavy Volcano (Kuril Islands)

Vadim Distler, Marina Yudovskaya, Ilya Chaplygin and Vladimir Znamensky
Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM),
Russian Academy of Sciences
e-mail: maiya@igem.ru

Introduction

The behavior of platinum group elements (PGE) in the active volcanoes' hydrothermal systems was studied in the hydrothermal fields of Kudryavy volcano situated in the Iturup Island (the Kuril island Arc of the Russian Far East) (Fig.1). This research was carried out owing to an increased amount of the data on PGE mineralization in hydrothermal conditions. Previous research of Korzhinsky et al. (1996) as well as our preliminary data shows that PGE is present in some products of this volcano's fumarolic activity. The most significant fact established by the time was the detection of native platinum in the high-temperature fluid's sublimates precipitated in silica tubes with the high gradient. The specific field works were carried out in the fumarolic fields of Kudryavy volcano to expand actual database and to establish noble metal contents in different products of hydrothermal activity. We started our research hoping that it will be useful further understanding of traditional problems of platinum ore formation including those linked to stratified magmatic complexes.

Geological setting

There are more than 180 volcanoes including 39 active within the Kuril Island Arc. It is dated that the eruptive activity at Kudryavy volcano occurred in 1778-1779 and the last eruption took place in 1883. During the last 100 years the mostly fumarolic activity and degassing are observed interrupted by periodic phreatic explosions. Magmatic rocks of volcano are represented by andesite and andesite-basalts. They are a part of contrast basalt-andesite-dacite-rhyolite series. Initial magma is believed to correspond to mantle melt with composition similar to high-alumina picrobasalt.

The hydrothermal fields with high-temperature fluid degassing are located at the well-preserved eastern crater. They differ by fluid temperature and type of ore mineralization (Fig.2). The background high-temperature mineralization is developed within the limits of all fumarolic fields and represents by abundant pyrite, galena, sphalerite with accompanying silicates, barite, anhydrite, chlorides of sodium and potassium.

The Main Field, characterized by the highest temperature of fluid, is located in the center of the main volcano's crater. This summer the measured temperature was 870^{o}C whereas the maximal measured temperature was 940^{o}C. Specific mineralization of this Field consists of various lead-bismuth salfosalts. A basic peculiarity of the Rhenium Field is a wide spread occurrence of rhenium disulfide (ReS_2), Zn-Cd-In sulfides with increased Sn and Se contents and also lead-bismuth salfosalts. The maximal temperature of the ore-forming fluid is 500^{o}C. Typical gangue minerals are diopside, wollastonite, garnet and pyroxene.

The Molybdenum Field with gas temperature of up to 650^{o}C is characterized by molybdenite sulfide mineralization succeeded upwards on section by molybdates and molybdenum oxides. As for the Dome Field its most part is covered by thick crust of lithified native sulfur; high-temperature vents (up to 710^{o}C) are framed by drusy incrustations of chlorides associated with silicates, iron sulfides, Pb-Bi and Zn-Cd-In mineralization.

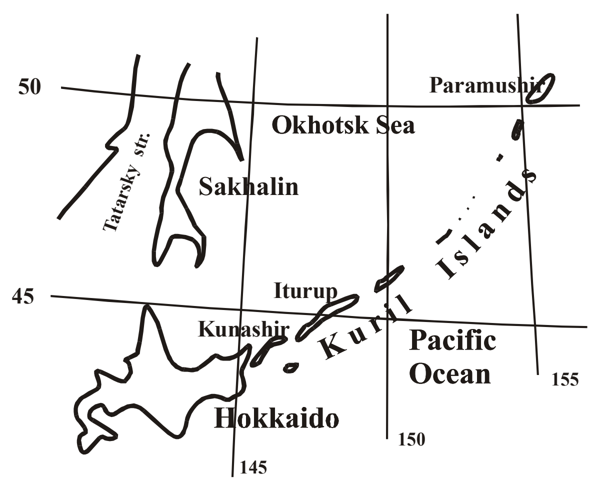

Figure1. *Geographic scheme of region.*

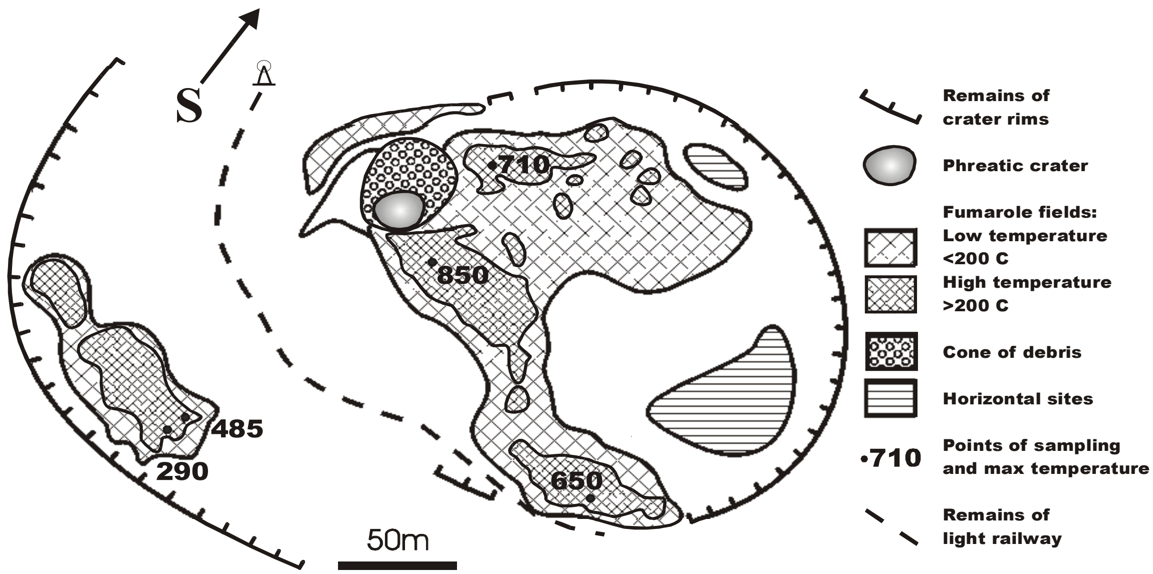

Figure 2. *Scheme of location of fumarolic fields*

Thus, the geochemical specialization of various ore components' distribution can be clearly seen in these fumarolic fields. So, there is no absolutely Re and Mo mineralization within the limits of the Main Field, and lead and bismuth are not distributed in the Molybdenum Field.

Methods

Temperature was measured by means of chromel-alumel thermocouples. Gas sampling was carried out from open fumarolic vents using pre-evacuated vacuum flasks with KOH and cadmium acetate solution by Giggenbach methods. Condensates were selected with cooling of gas by ice and water in the glass cooler from the same vents. For sampling of artificial sublimates we inserted silica tube of different diameter in open vents. The duration of mineral precipitation in them was up to 3 weeks. Natural mineral samples of fumarolic incrustation were collected from the depth of up to 50-70 centimeters under the surface.

All selected condensates were analyzed for Pt, Pd, Rh, Ir, Ru contents and for Os separately. Osmium determination was carried out in Vernadsky Institute of Geochemistry (Russian Academy of Science). It included autoclave leaching with the further osmium concentrating in a permeability cell. The subsequent analysis was carried out by AAS method with a detection limit of 10^{-6} % or by ICP-MS with a detection limit of 10^{-7} %. The rest of PGE determination was made by a chromatographic method with preliminary condensate concentrating up to solid phase. The detection limits (ppm) are: Pt - 0.02, Pd - 0.01, Rh - 0.001, Ir - 0.002. Some aliquots of acid decomposition were analyzed by ICP-MS in parallel.

Distribution of noble metals.

The presence of PGE was established in the mineralized rocks of the Main, Rhenium and Molybdenum Fields. The highest contents are determined in the Main and Rhenium Fields, and low - in the Molybdenum Field. Palladium prevails over platinum in all samples. The Pd/Pt ratio ranges from 1 up to 100 but the usual Pd/Pt ratio fits within an interval of 2 - 10. It was found that palladium content reaches hundreds ppb in a significant part of samples and two samples from the Rhenium and Main Fields contain about 1000 ppb of Pd. The highest PGE concentration (1000 ppb) was determined at a sulfide zone of the Main Field close to the most high-temperature vent with temperature of 920^{o}C. Gold content (Table 1) was analyzed in the same samples in addition to platinum metals.

The study of PGE distribution also was carried out in condensates of volcanic gas with gas temperature from 290 to 850 ^{o}C. The Pt and Pd content was measured in a dry residue after evaporation of condensate. According to analyses' results (Table 2) all the basic peculiarities of PGE fractionation in condensates are similar to those in mineralized rocks and incrustations. Palladium prevails over platinum and ratio of their concentration is close to 1:10. However, the solid of condensate is enriched in Pt and Pd with the sum of both metals up to 9000 ppb. The data on Os distribution is particularly interesting (Table 3). The Os increased content was detected at mineralized rocks. These content is quite high in comparison with any known ore mineralization of an earth's crust practically. The data presented in Table 3 shows that there is an irregular distribution of osmium in products characterized by different ore mineralization. So ReS_2 and MoS_2-bearing mineralized rocks is enriched in Os to high extent (1065 – 1670 ppb). Os content in samples with Pb-Bi mineralization is two times lower. The similar Os contents were found in artificial sublimates from silica tube inserted into vent with fluid temperature of 870 °C. Osmium content in gas condensates was determined also. It is established that all condensate samples display correlation of fluid temperature ranging from 290 to 850 ^{o}C with osmium content in solutions ranging from 60 to 400 ppb.

***Table 1**. Concentration (ppm) of Pt, Pd and Au in mineralized rock (Kudryavy volcano).*

Sample	**Field**	**Pt**	**Pd**	**Au**
1	**Molybdenum**	-	0.02	0.18
2	-“-	-	0.04	
3	Rhenium	0.02	0.9	0.2
4	-“-	-	0.04	0.4
5	-“-	-	0.1	0.4
6	-“-	-	0.4	0.07
7	-“-	0.01	0.1	0.16
8	-“-	0.16	0.02	
9	-“-	0.01	0.01	0.4
10	-“-	0.05	0.07	0.24
11	Main	-	0.14	
12	-“-	0.1	0.2	0.09
13	-“-	0.06	0.006	
14	-“-	0.05	0.02	
15	-“-	0.01	1.0	0.07
16	-“-	-	0.34	
17	-“-	0.015	0.1	0.05

***Table 2.** Pt and Pd concentrations in dry residue of gas condensate.*

Field	**Temperature of gas, ^{o}C**	**Content, ppm**	
		Pt	**Pd**
Main	850	0.5	7.5
Rhenium	290	0.5	6.0
	485	0.8	8.0
Molybdenum	650	0.8	4.0
Dome	710	0.6	7.0

***Table 3.** Os concentration (ppb) in mineralized rock and gas condensate.*

Field	**Os in gas con-densate**	**Tempera-ture of gas, ^{o}C**	**Os in miner. rock**
Main	380	850	844
Rhenium	60	290	437
	80	485	1670
Molybdenum	300	650	1065
Dome	400	710	950

Conditions of PGE migration and deposition

For the time being we don’t posses significant data on modes of PGE occurrences in natural hydrothermal environment. According to Korzhinsky et al. (1996) the native platinum containing the tenth of percentage point of iron is associated with various sulfides in high temperature mineral precipitations in silica tube. This is important especially as there are a lot of elements in a native (metallical) state in the same condensates. In addition to native platinum native aluminium, silicon, titanium, gold were found in a native state. It is typical, that deposition of native elements takes place in a hyperthermal part of the silica tube in the zone of sulfide and chloride precipitation.

Gas of Kudryavy volcano consists mainly of H_2O (93-98 mol%), CO_2 (0.5-2.8), H_2S (up to 1.25 mol%), SO_2 (up to 2.3 mol%). The high concentrations of hydrogen (up to 1.3), methane (up to 0.21 mol%), HCl (0.1-0.75 mol%), HF (0.06-0.01 mol%) have also been established (Korzhinsky et al., 1996). Main gas components are found in an oxidized state and oxygen fugacity of fluid is controlled by nickel-bunsenite and hematite-magnetite buffers transferred to the field of more reduced quartz-magnetite-fayalite buffer at extrapolation on temperature of about 1110-1200^{o}C. Noble metal mineralization can be precipitated from high-temperature oxidized fluid with insignificant contents as stability of their compounds is very sensitive to the variation of oxidation state of system (Taran et al., 2000, Gibert et al., 1998). It is possible that noble metals may form volatile complexes. Then their deposition in a native metallical state takes place most likely according to mechanism of disproportionation reactions, for example as

$$2PdCl_2 \rightarrow Pd + PdCl_4.$$

Possibility of such type of reactions has been discussed in analysis of ore-forming conditions on the PGE-bearing hydrothermal deposits (Sukhoi Log, Waterberg).

The study is supported by RFBR project N 01-05-64378.

References

Korzhinskii M.A., Tkachenko S.I., Bulgakov R.F., Shmulovich K.L., 1996, Condensate Compositions and native metals in sublimates of high-temperature gas streams of Kudryavy Volcano, Iturup Island, Kuril Islands: Geochemistry International, v.36, p.1175-1182.

Taran Yu.A., Bernard A., Gavilanes J.-C., Africano F., 2000, Native gold in mineral precipitates from high-temperature volcanic gases of Colima volcano, Mexico, Applied Geochemistry, v.15, pp.337-346.

Gibert F., Pascal M.-L., Pichavant H., 1998, Gold solubility and speciation in hydrothermal solutions: experimental study of the stability of hydrosulfide complex of gold ($AuHS^o$) at 350 to 450^{o}C and 500kbars, Geochim. et Cosmochim. Acta, v.62,p.2931-2947.