Proceedings World Geothermal Congress 2000
Kyushu - Tohoku, Japan, May 28 - June 10, 2000

ISOTOPIC GEOCHEMISTRY OF ACID LAKES IN THE UZON-GEYSERNY AND KARYMSKY GEOTHERMAL AREAS (KAMCHATKA).

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Key Words: volcano, caldera, geothermal system, water isotopes

ABSTRACT

Conditions of formation and long existence of acid caldera lakes in areas of active volcanism are examined on the basis of study of saline and hydroisotopic composition of different water manifestations in the Uzon-Geyserny and Karymsky geothermal areas of Kamchatka. A wide spectrum of hydrochemical types of solutions with pH varying from neutral up to acid values is observed in both areas. But recent volcanic activity in caldera structures of these areas differs in degree of intensity. A short-term but powerful phreatic-magmatic eruption occurred in the Karymsky geothermal area in the Akademii Nauk caldera where the Karymskoe Lake, which until 1996 was a fresh-water one, was located. Enormous quantity of erupted material was ejected. Practically instantly the lake water got acid reaction (pH = 3,2) which has already been keeping for 4 years in spite of constant inflow of fresh sub-neutral water owing to atmospheric precipitation. In this lake processes of extraction of water-soluble sulphate-chloride complexes from newly erupted rocks mainly maintain water acid reaction. Possibly, endogenic fluids are still supplying from the bottom of the lake. In the Uzon caldera (the Uzon-Geyserny geothermal area) the Fumarolnoe and Bannoe Lakes also have acid reaction (pH = 3,5-5,0) for a long time, but owing to processes of oxidation of sulfur-containing compounds in surrounding hydrothermally-changed rocks. It has been concluded that endogenic factor intensity is determinative in acidification of water mass in caldera structures in areas of recent volcanism and acid lake existence duration depends on time of exhaustion of resources of sulfur-containing components in enclosing rocks.

1. INTRODUCTION

There are acid lakes in Japan, Indonesia, New Zealand, Kuril Islands, Kamchatka and other regions of active volcanism of the Earth (Eroschev-Shak, V.A. et al (1985), Giggenbach, W. (1974), Karpov, G.A. et al (1966), Markhinin, E.K. (1957), Sydorov, S.S. (1966), Skripko, K.A. et al (1966), Takano, B. et al (1994), Zelenov, K.K. and Kanakina, M.A. (1962), and Zelenov, K.K. (1972)). They occur in places of volcanic gases' discharged (solphatares) in the craters of active volcanoes and exist for a while in the interparoxyzmal stage of their activity. Acidity of water in these lakes is caused by condensation of steam-gaseous volcanic emanations, containing acid gases HCl, HF,SO_2, H_2S. Dimensions of such lakes vary in wide range – from first metres up to hundreds metres. Usually crater lakes have no drainage or discharge of the outflowing steams is very little. During the paroxyzmal stage of the volcano activity the eruption often happens in the lake itself, and then cases of crater's walls breaks happen and big quantities of acid waters outflow into the environment. The last is connected with disasters (Markhinin, E.K. (1957), Zelenov, K.K. and Kanakina, M.A. (1962), and Zelenov, K.K. (1972)). Among the types of acid lakes of active volcanism the special place is occupied by caldera acid lakes. They exist for a long time, being characterised by wide variations of common mineralization, non-constant chemical composition of water mass and changing acidity. These lakes arise in the caldera basins and fix zones of tectonic faults, along which also high-temperature fluids from not deep magmatic centres and apical parts of subterranean magmatic bodies – roots of andesite-dacitic extrusions, dikes, sills also come (Eroschev-Shak, V.A. et al (1985) and Karpov, G.A. et al (1966)). On the borders of these calderas usually active volcanoes exist. In the calderas themselves large high-temperature hydrothermal systems are localised (Esikov, A.D. et al (1990) and Esikov, A.D. et al (1991)). Saline composition of water in the acid caldera lakes is mainly a mixture of salts of sulphuricacid and muriatic - as products of deep haloid-sulphurous emanations' transformations and their reactions with rocks (Eroschev-Shak, V.A. et al (1985), Giggenbach, W. (1974), Karpov, G.A. et al (1998), and Takano, B. et al (1994)).

Owing to the peculiarities of caldera structures, appearing on the final stage of the activity of strato volcanoes, on the background of usual solphatare activity, magmatic eruptions happen in them very rarely. But sometimes and for a very short time phreatic and even more rare phreatic-magmatic eruptions are observed. It is in these cases sudden acidification of lake water up to pH 5,0 – 2,5 (Karpov, G.A. et al (1966), Karpov, G.A. et al (1996), Karpov, G.A. (1998, 1999), Markhinin, E.K. (1957), Sydorov, S.S. (1966), Takano, B. et al (1994), and Zelenov, K.K. and Kanakina, M.A. (1962)) happens. Descriptive examples of such acid lakes are the lakes Bannoe, Fumarolnoe in the Uzon caldera (Esikov, A.D. et al (1990), Esikov, A.D. et al (1991), Karpov, G.A. et al (1966), and Karpov, G.A. et al (1998)), and the Karymskoe lake in the Akademii Nauk caldera in Kamchatka (Karpov, G.A. et al (1996) and Vergasova, L.P. et al (1998)).

2. BASIC REGULARITIES OF HYDRO-CHEMISTRY AND ISOTOPIC COMPOSITION OF WATER COMPOSITION OF THE UZON-GEYSERNY AND KARYMSKY GEOTHERMAL AREAS

The authors studied for a long time the features of chemical composition and hydroisotopic characteristics of many thermal springs and lakes of the Uzon caldera (Esikov, A.D. et al (1990), Esikov, A.D. et al (1991), Karpov, G.A. (1966), and Karpov, G.A. et al (1998)). Since 1996 analogous research has being conducted in the Akademii Nauk caldera, where, as the result of short, but mighty phreato-magmatic underwater eruption fresh-water Karymskoe became acid (pH = 2,5-3,4) practically in one moment with chloride-sulphate-calcium-natrium composition and mineralization up to 1 g/l (Table 1), and on the borders of the lake new nearly neutral and even alcaline springs mainly of chloride-natrium composition appeared (Karpov, G.A. et al (1996) and Vergasova, L.P. et al (1998)). This phenomenon made us consider the questions of reasons and mechanisms of salinity of caldera lakes in volcanic areas.

Explanation of genetic characteristics of waters in thermal springs and lakes in both calderas gave us opportunity to find the following laws, reflected in triple diagrams of solution composition (Figure 1 A, B).
The wide spectrum of hydrochemical types of solutions with variations of pH from nearly neutral up to acid is observed in both calderas.

Exact grouping on chemical composition of waters is noted: all thermal springs (including drilling holes up to 16 m deep) and waters of thermal lakes Fumarolnoe and Chloridnoe in the Uzon caldera lie in the narrow field of chloride-natrium composition (field 1). All the thermal spring of the Akademii Nauk caldera, despise of similar chemical composition have their specific field on the diagram SO_4–Cl-HCO_3 (field II in Fig.1, A).Variation field of water composition in the Karymskoe lake (and river Karymskaya), having changed (acidified) after the eruption of 1996 tends to sulphate part of the diagram, with tendency of potassium component prevalence (field III). It is interesting that in the same field points of water composition of the weekly-acid Bannoe Lake in the Uzon caldera exist.

Precipitation (field IV) and fresh cold waters of streams and snow water trend towards the right corner of the diagram (fields IV and V).

Even more descriptive picture is drawn on the diagram $\delta^{18}O$-δD for thermal and cold waters of the same objects (Fig.2). Non-changing precipitation, freshwaters, both cold and snow, from the Uzon caldera and the Akademii Nauk caldera are placed along Creig's line. Points, representing the lakes Bannoe, Karymskoe and river Karymskaya join to this line. This fact enables to conclude that isotope water composition of these objects had very little changed under the influence of hydrothermal processes. Chemical composition of these waters points to the admixture of endogenous fluid (high in sulphur content, caused rising of acidity)

At the same time isolated position of the points corresponding to the Fumarolnoe Lake water and mud cauldrons on the diagram $\delta_{18}O$- δD (points 1 and 3 in Fig.2) enables to conclude that water masses of these objects contain significant quantities of deep fluids, which were under the influence of hydrothermal processes.

3. CONCLUSIONS

According to the complex of data the authors came to the conclusion that acidification of the Karymskoe Lake waters is connected with inflow in its basin and drainage system of significant mass of eruption products of andesite-dacite ash of Karymsky volcano and different (from basalts to dacites) materials of underwater eruption in 1996, from which as the result of interaction "solution-water" interaction water-dissolved chloride-sulphate-natrium-potassium complexes are washed out. After acid components are over, lake's water will begin becoming fresh. The process of fresh-water restoration of such a large lake as the Karymskoe may last for several decades.

Acidity of the Fumarolnoe Lake in the Uzon caldera is caused both by continuing income of endogenous emanations of sulphur-chloride composition along the fracture zones and cyclic exchanging "water-solution" reactions (with participation of early dissolved sulphur and sulphide minerals) in the lake basin itself.

ACKNOWLEDGEMENTS

The authors are indebted to their colleagues Marynov, V.K. and Cergeev, S.V. for qualified conducting hydrochemical analyses and also to Charvyakova, G.P. – the staff member of Puschino meteostation – for conducting routine sampling of atmospheric precipitation. In the whole, this work has been carried out owing to finansial support and Scientific Report 9828/Ro-RI concluded with IAEA.

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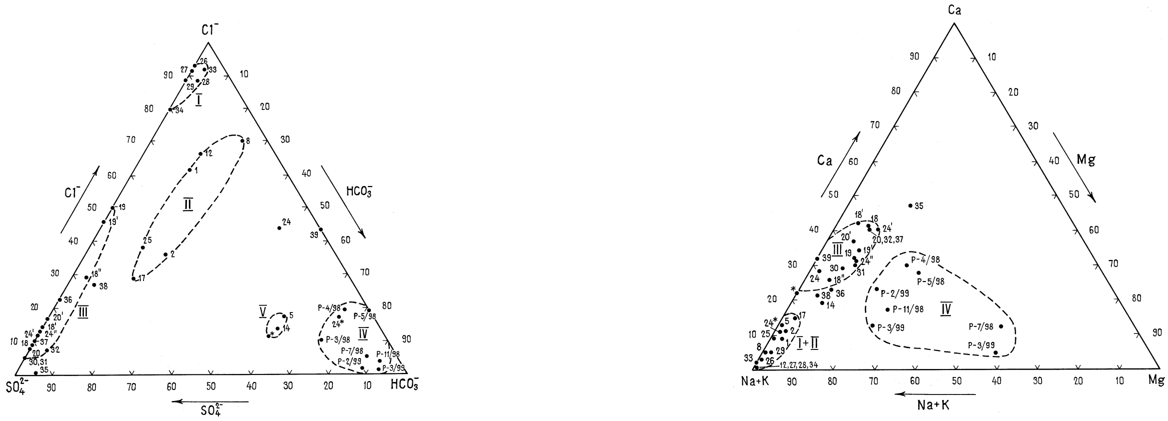
Table 1. Results of regime measurements of hydrochemical parameters of the Karymskoe Lake basin (contents of components - mg/l)

Date of sampling	To C	pH	Na	K	Ca	Mg	Cl	SO_4	$HCO_3 + CO_3$	M, mg/l
1. The Karymsky Lake water area, centre										
11.02.96	19,0	3,2	75,0	7,3	66,0	14,4	35,5	379,0	-	921,7
19.07.97	14,0	4,1	46,0	5,2	34,0	6,7	35,5	168,0	-	412,9
17.09.99	10,8	4,0	64,8	7,1	40,1	9,7	44,0	220,9	-	552,1
2. The crater of subaqueous eruption 1996, centre										
11.02.96	20,0	3,7	74,3	7,6	64,0	7,2	57,8	317,0	-	695,3
07.02.98	15,5	3,7	65,0	8,5	42,0	9,7	246,7	249,6	-	795,2
19.09.99	11,2	4,0	64,0	7,7	40,1	10,9	46,2	220,9	-	552,3
3. The Karymskaya river effluent										
09.10.96	10,0	3,7	69,2	7,1	62,0	10,9	49,3	317,0	-	676,3
03.01.97	3,0	3,4	62,0	7,0	58,0	14,5	42,6	307,0	-	688,7
28.05.98	4,5	3,7	74,9	9,1	46,1	14,6	41,9	249,8	-	-
28.08.99	12,0	4,0	60,0	7,8	40,1	8,5	44,0	220,0	-	529,0
4. Seepage of hot water in the beach area of the lake northen sector										
03.01.97	18,1	7,3	255,0	24,0	48,0	9,7	282,0	240,0	152,0	1417
02.07.98	71,0	7,6	225,0	20,0	50,0	4,9	175,7	336,0	98,9	1199
28.08.99	72,0	7,6	280,0	30,2	38,1	3,6	176,1	393,8	92,8	1313
5. The thermal spring on the left bank of the Goryachaya river										
03.01.97	86,0	6,7	547,0	64,5	96,0	29,0	824,0	345,0	162,0	2502
28.05.98	78,0	6,8	532,0	32,2	60,1	17,0	688,7	288,2	154,0	2235
29.08.99	82,0	7,4	440,0	56,6	50,1	10,9	507,7	345,8	98,9	1856

Notes: analyses were carried out in the central chemical laboratory of the Institute of Volcanology FED RAS by analysts Sergeeva, S.V. and Marynova, V.K.



A B

Figure 1. Triple diagrams of ion composition of the solutions in the Uzon caldera and the Akademii Nauk caldera.

A. Diagram of SO_4 –Cl-HCO_3 composition
B. Diagram of Na + K –Ca – Mg composition

I-V – variation fields:
I – of chemical composition of thermal sources' waters (including drilling holes) and water of the Fumarolnoe and Chloridnoe Lake in the Uzon caldera.
II - of chemical composition of thermal sources in the Akademii Nauk caldera.
III - of water composition in the Karymskoe Lake, river Karymskaya and Bannoe Lake (in the Uzon caldera).
IV - of precipitation composition (on data of hydrometeostation Puschino).
V - of composition of cold freshwater springs and snow water in the region of the Karymskoe Lake.

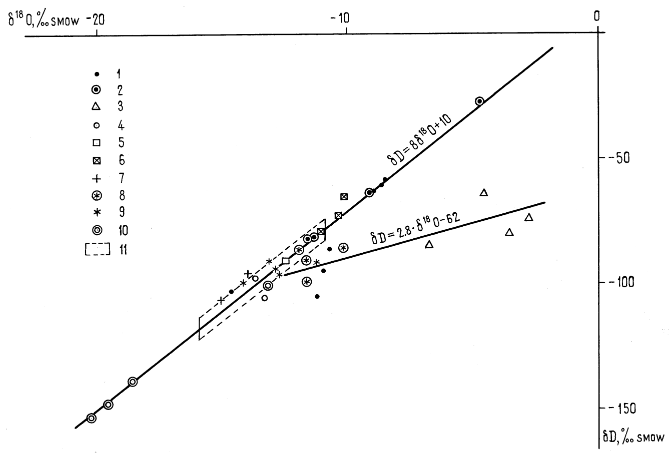


Figure 2. Characteristics of isotope composition of thermal and cold waters of the Uzon caldera and the Karymsky geothermal area.

Designations.
1. Thermal sources and waters of the Fumarolnoe Lake in the Uzon caldera.
2. Thermal sources in the Akademii Nauk caldera (area of the Karymskoe Lake).
3. Waters of mud cauldrons in the Uzon caldera
4. Waters of the thermal lake Bannoe in the Uzon caldera
5. Fresh cold waters in the Akademii Nauk caldera springs, flowing in the Karymskoe lake.
6. Snow water from the Karymskoe lake area.
7. Fresh cold waters of the Uzon caldera.

8. Waters of the Karymskaya river.
9. Waters of the Karymskoe lake.
10. Precipitation of the hydrometeostation Puschino.
11. Variations field of isotope composition of Kamchatka precipitation on references data.