Processes Responsible of Variations in the $\delta^{18}\text{O}$ – δD values of Thermal Waters from the Kuril Islands (Russia)

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Abstract. Many active and dormant volcanoes of the Kuril Islands host hydrothermal systems which discharge acid to ultra-acid $\text{SO}_4\text{-Cl}$ (Cl-SO_4) and SO_4 waters. On some island, hot near-neutral Na-Cl waters can be found discharging in coastal hot springs. Four main different isotopic shifts relative to the local meteoric water line can be observed in the corresponding δD vs. $\delta^{18}\text{O}$ diagram. For the acid Cl-SO_4 waters discharging within thermal fields on volcano slopes, there is a clear mixing trend between meteoric water and volcanic vapor. Steam-heated SO_4 waters demonstrate trends indicating kinetic fractionation at temperatures close to the boiling-point. For the coastal springs, the trend is apparently a mixing line between meteoric and seawater. The $\delta^{18}\text{O}$ -shift for deep thermal waters is related to isotopic exchange with host rock but there is also a clear latitude effect in the isotopic composition of the meteoric endmember.

1 Introduction

The Kuril Island arc (fig. 1) stretches for more than 1200 km from the Kamchatka Peninsula to Hokkaido Island. This area hosts active Pleistocene to Quaternary volcanism with more 30 active volcanoes. At least one hydrothermal system associated with

Fig. 1. The Kuril island arc. Hydrothermal systems associated with volcanoes: 1- Ebeko, 2 - Sinarka, 3- Kuntomintar, 4- Rasshua, 5- Ushishir, 6-Ketoy, 7- Berg, 8- Baransky, 9- Mendelev, 10-Golovnin.

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volcanic structures can be found on each island. Differences in volcanic evolution, hydrological and geological conditions have led to differences in the conditions of formation and discharge of hydrothermal systems of the region.

Three major hydrochemical types of thermal waters discharging on the islands can be distinguished (fig. 2):

(1) Acid sulfate waters (steam-heated waters) with temperatures up to 95°C and TDS up to 5 g/L generated at near-surface levels of thermal fields.

(2) Acid ($1 < \text{pH} < 4$) chloride-sulfate (sulfate-chloride) waters showing temperatures of 30-90°C with TDS up to 14 g/L. These waters are formed by absorption of magmatic gases (SO_2 and HCl) by ground waters, and discharge mostly through the weakened zones from beneath extrusive domes. Ebeko volcanic complex (Paramushir Island) hosts the most powerful hydrothermal system with a high discharge rate of hot $\text{SO}_4\text{-Cl}$ acidic water (Yurievskie springs).

(3) Near-neutral ($6.2 < \text{pH} < 7.4$) chloride-sodium waters with temperatures up to 100°C and TDS from 3 to 15 g/l. These waters discharge along the shores of the Shiashkotan, Rasshua, Iturup, Kunashir Islands and are also tapped by the wells drilled at thermal fields of big islands (Paramushir, Iturup, Kunashir).

This paper reports original data on the isotope composition of thermal and surface waters of seven Kuril Islands (Paramushir, Shiashkotan, Rasshua, Ushishir, Ketoy, Urup and Kunashir; fig. 1) acquired during the 2015-2017 field campaigns. Data for Iturup Island are from [6]. The distribution patterns of δD and $\delta^{18}\text{O}$ in various types of waters are presented and discussed, the possible causes of isotopic shifts for different types of waters will be considered.

The water samples were analyzed for their oxygen and hydrogen isotopic composition, using “Los Gatos” Liquid Water Isotope Analyzer in the Institute of Volcanology and Seismology, Kamchatka, Russia. The isotope ratios are expressed in permil vs. V-SMOW. The uncertainties are $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1\text{‰}$ for δD (one standard deviation).

2 Results and Discussion

Globally, variations of isotope composition of atmospheric precipitates and surface waters are distributed quite regularly and can be described by the Craig equation [2] named as a global meteoric water line (GMWL), $\delta\text{D} = 8 \cdot \delta^{18}\text{O} + (10)$. For the Kuril-Kamchatka region, Cheshko and Esicov [1] estimated a local meteoric water line (LMWL) described by the equation $\delta\text{D} = 8 \cdot \delta^{18}\text{O} + (15 \pm 1)$ (fig. 3).

The isotopic composition of the studied cold surface waters show linear trends on the δD vs. $\delta^{18}\text{O}$ plot and located on the local meteoric water line (Fig. 3). The latitude effect is controlled by the geographic position of the islands. On the average, surface waters of the northern Paramushir Island show lower values of deuterium (by 20 ‰) and ^{18}O (by 3 ‰) when compared to those reported for the southern Kunashir Island. Surface waters of the central islands (Shiashkotan, Ketoy, Rasshua and Urup) show similar values and their compositions occupy intermediate positions in the Fig. 3.

2.1 Steam-heated waters

Most of the points for the steam-heated waters group close to or located on the local meteoric water line (LMWL; Fig. 3). Boiling springs and drainless and low-discharge pools show a trend towards isotopically heavier values of δD and $\delta^{18}\text{O}$ relative to the LMWL. Such a shift could be caused by a partial contribution of magmatic water. However, increased supply of magmatic water to thermal waters is accompanied by the increase of chloride-ion concentrations [7], whereas waters of the studied boiling pools are almost free

Fig. 2. Anions composition of thermal waters. Numbers of volcanoes as in Fig.1.

Fig. 3. Isotopic composition of the meteoric and steam-heated waters.

of chloride-ion. The slope of this trend is between 3 and 3.5, which is likely due to kinetic fractionation during the surface boiling [4]. It should be noted that in spite of the similar slopes of the isotope shifts reported for different islands, their datapoints form individual trends in the Fig. 3 due to the latitude effect. For example, δD of thermal waters from Ketoy and Shishkotan Islands are by 10 ‰ lower than those observed in similar waters from Kunashir Island.

2.2 Acid chloride-sulfate waters

Along with the data of thermal waters, the δD vs. $\delta^{18}O$ diagram (Fig. 4 a) shows data obtained for the volcanic gas condensates from some Kurilian volcanoes [8]. Most of the datapoints for springs start from the meteoric water line forming, together with the condensates, a common trend towards the compositions of andesitic waters (A), representing magmatic waters of subduction zones [3, 5].

Fig. 4. a) Isotopic composition of acid Cl-SO₄ waters from Kuril Islands and volcanic vapours (see text). Inserted is the δD vs. $\delta^{18}O$ plot for the Yuryevskie springs on Paramushir Island. b) δD vs. $\delta^{18}O$ diagram for the Yuryevskie springs. Numbers of volcanoes as in Fig.1.

Contribution of magmatic water to acid Cl-SO₄ waters is determined by their Cl content and by a difference in the δD between magmatic and meteoric waters and is estimated as 15-20%. Boiling thermal waters of the Ushishir Island form a separate group in the diagram. They are mainly related to the mixing of volcanic emanations with seawater, which is reflected by the locations of their datapoints in the δD vs. $\delta^{18}O$ diagram.

Changes in the isotopic composition of these waters in the periods of the volcano activity are well expressed in the case of Yuryevskie springs at Ebeko volcano (Paramushir Island) that were sampled in 2014, 2016 and 2017. Eruptive activity of Ebeko volcano began in October 2016 and continues to the present. In the δD vs. $\delta^{18}O$ plot (Fig. 4 a), isotope compositions of the Yuryevskie springs (data from 2014) are plotted close to the meteoric water line, showing, however, a distinct positive shift of both $\delta^{18}O$ and δD . The compositions of the 2016 and 2017 samples form an extension of this trend, which is accompanied also by the increasing concentrations of chloride-ions in the composition of thermal waters (fig. 4 b). Thus, the Ebeko volcano eruption triggered changes in the isotope and chemical composition of the Yuryevskie springs.

2.3 Sodium-Chloride near-neutral thermal waters

Positive shifts of δD and $\delta^{18}O$ are typical of the studied thermal waters. Coastal springs of Shishkotan and Rasshua Islands show a trend extending from the local meteoric water line towards seawater, which is also evidenced by the δD vs. Cl trend (Fig. 5 a, b) showing mixing with seawater. Isotopic composition of waters discharged by the coastal springs at the flanks of the Mendelev volcano (Kunashir Island) shows much lower values if compared to that of meteoric water at the sea level, which is probably related to the higher altitude of the catchment basin.

Fig. 5. Isotopic composition of sodium-chloride near-neutral waters: a) δD vs. $\delta^{18}O$, b) δD vs. Cl.

An horizontal oxygen shift is observed for both deep thermal waters sampled from the geothermal wells and for boiling springs located at the outer slope of the Golovnin volcano, Kunashir Island. Values of the $\delta^{18}O$ are significantly heavier in thermal waters if compared to cold groundwater. Only this type of waters shows the oxygen shift caused by the water-rock interaction at depth.

3 Conclusions

- The hydrothermal activity of the Kuril Island arc is mainly manifested by acid sulfate and chloride-sulfate springs at volcano slopes. Neutral Cl-Na thermal waters are subordinate and discharge mainly as coastal springs or tapped by geothermal wells on big islands.
- The isotopic composition of the steam-heated SO₄ waters is controlled by the surface boiling and kinetic fractionation with a characteristic slope of 3.5 on the δD vs. $\delta^{18}O$ diagram.
- The isotopic composition of acid Cl-SO₄ and SO₄-Cl waters is controlled by mixing between meteoric water and magmatic vapor with the maximum magmatic contribution of ~ 20%.
- Near neutral Cl-Na coastal springs form their isotopic composition by mixing with seawater. Hot water from geothermal wells and some boiling springs show an oxygen shift due to the water-rock isotopic exchange.
- All waters show a latitude effect on the meteoric water endmember.

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References

1. A.L. Cheshko, A.D. Esicov, *Water Res.*, **6**, 12 (1990)
2. H. Graig, *Science*, **133**, 1702 (1961)
3. W.F. Giggenbach, *Earth Planet. Sci. Lett.*, **113**, 495 (1992)
4. W.F. Giggenbach, M.K. Stewart, *Geochem. Int.*, **11**, 71 (1982)
5. Y.A.Taran, B.G. Pokrovsky, Y.M. Doubik, 1989, *Dokl. EarthSci.*, **304**, 1191 (1989)
6. Y.A. Taran, V.S. Znamenskiy, L.M. Yurova, *J. Volcanol. Seismol.*, **17**, 471, (1996)
7. Y. Taran, M. Zelenski, *In: The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas.* (Geol. Soc. L. Sp. Pub. 410, 2014)
8. Y. Taran, et al., *Geochim.Geoph.Geos.*, **19**, 1859 (2018)