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Rare earth and major elements geochemistry of geothermal waters from Mutnovsky volcano, Kamchatka

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Abstract

The behaviour of major ions and rare earth elements (REE) was studied in the hot springs of the volcano Mutnovsky (Kamchatka). We found that the concentration of REE depended on the geochemical type of water, with maximum content of REE being in Ca-SO_4 waters. Overall, this study shows that the pH has a significant impact on the content and fractionation of REE.

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Keywords: geochemistry hot springs; rare earth elements; water-rock interaction

1. Introduction

Rare earth elements are widely studied in natural waters as the tracers of different hydrogeological and geochemical processes[1-8]. Eastern Kamchatka is not been well studies in respect to the REE. Few publications are available that show REEs in acidic hot springs of Kamchatka[3,6], however, thermal alkaline waters at the periphery of the Mutnovsky volcano were not well investigated to this data. The purpose of this work is to establish the levels of REE and their fractionation in the thermal waters at the volcano.

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2. Objects of study

The Mutnovsky geothermal area is located within the Eastern Kamchatka volcanic belt (EKVB), fig. 1. There, three groups of thermal manifestations could be distinguished: 1 − fumaroles within the crater itself; 2 − thermal waters of the North Mutnovskaya volcanic zone (North Mutnovsky and Dachny hot springs); 3 − volcano's peripheral thermal fields (Viluchinsky hot springs). Two groups were sampled in 2015: Dachny (samples K34, K35, K36) and Viluchinsky (samples K37, K39, K40). Detailed map is available on https://goo.gl/Es1tDb.

3. Methods

The aqueous filtrate was obtained using a standard 0.45µm pore size membrane filter. For the detection of REE was used HR-ICP-MS instrument. We then eliminated oxide and hydroxide interferences in analyzed samples with low concentration of REE using mathematical method, which was published[8].

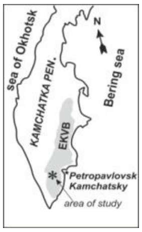

Fig. 1. Area of Study. EKVB-Eastern Kamchatka Volcanic Belt

4. Results and discussion

4.1. The main ions

The results of the hydrogeochemical studies of the Mutnovsky volcano were previously published in[2,3,6,9,10]. For the current study, the Dachny hot springs were tested in two places: at the foot of 'Skalisty" hill (sample K34), and hypsometrically below hot springs (sample K36), Table 1.

Table 1. Main ions (mg/L) and REEs (ppb) in the hot springs and surface waters of the Mutnovsky Volcano

	K34	K35	K36	K37	K39	K40	*
T°C	56	18	98	37	63	7.5	93.9
pH	3.34	5.95	5.74	7.19	6.81	7.27	2.34
TDS	348	34	290	1005	1110	25	2970
Ca	9.55	4.01	12.13	103	102.8	3.37	154
Mg	3.96	1.1	1.41	4.13	4.17	0.6	18.1
Na	2.96	1.25	32.35	156.5	191.4	2.66	10.1
K	2.45	0.4	7.57	11.28	12.97	0.47	1
HCO_3^-	0	6.79	17.7	305.09	383.65	20.44	0
Cl^-	0.7	0.7	0.7	149	208	3.78	0
SO_4^{2-}	115.2	12.8	134	172.8	182	4.28	610
La	0.4463	0.1196	0.0266	0.0135	0.0046	0.0055	1.2450
Ce	1.2755	0.2684	0.0760	0.0291	0.0064	0.0058	3.0075
Pr	0.2126	0.0386	0.0120	0.0040	0.0010	0.0017	0.6039
Nd	1.1503	0.1920	0.0635	0.0224	0.0044	0.0082	3.1450
Sm	0.3411	0.0411	0.0182	0.0081	0.0021	0.0023	1.8194
Eu	0.0999	0.0107	0.0062	0.0062	0.0052	0.0006	0.7599
Gd	0.4086	0.0525	0.0218	0.0142	0.0030	0.0024	3.8558
Tb	0.0660	0.0085	0.0032	0.0027	0.0004	0.0004	0.7624
Dy	0.4189	0.0494	0.0207	0.0206	0.0029	0.0024	6.6753
Ho	0.0908	0.0111	0.0047	0.0052	0.0007	0.0006	1.6309
Er	0.2730	0.0314	0.0152	0.0172	0.0020	0.0017	4.3694
Tm	0.0406	0.0044	0.0023	0.0023	0.0004	0.0002	0.8044
Yb	0.2720	0.0272	0.0143	0.0136	0.0019	0.0017	5.0223
Lu	0.0429	0.0043	0.0024	0.0024	0.0004	0.0003	0.7548

K34-hot spring, K35-acid stream, K36, K37 hot springs, K39-thermal water of borehole, K40-Vilucha River, *-boiling spring in crater of the Mutnovsky volcano[3], REEs in crater of Mutnovsky volcano are average (n=8)[9]

The stream (sample K35), showed extremely low salinity and a weakly acidic water (Table 1). The hot spring (sample K36), was slightly acidic, and had a TDS of 290 mg/L. Calcium and sulfate ions (sample K34) were predominant. In sample K36 sodium concentration was higher than calcium, and sulfate ion was dominant among anions. In stream water calcium and sulfate ions were predominant, but HCO_3 was also abundant (K35). The waters at the Viluchinsky hot spring was slightly alkaline with a TDS of 1000 mg/L (sample K37). In the well (170 m depth, sample K39), the pH was 6.81, and the TDS 1100 mg/L. The temperature of water in the well was higher than in hot spring and reached 63^{o}C. In these hot waters the sodium was a predominant cation. Within the crater of the volcano Mutnovsky, hot springs were characterized by low pH (2.34) and Ca-SO_4 composition. Overall, the composition of major ions and pH was different between crater of the Mutnovsky volcano and the hot springs at its periphery.

4.2. Rare earth elements

Results of REE in studied waters are presented in Table 1. The levels of REE were largely determined by its pH. There was almost a direct correlation between pH and the sum of REE under pH <6 (Figure 2). Figure 3 shows the normalized values of REE to the North American shale composite (NASC)[11].

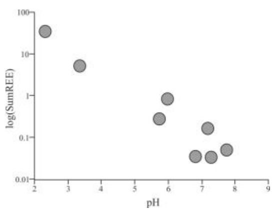

Fig. 2. Log (SumREE) vs pH for studied hot springs of the Mutnovsky volcano

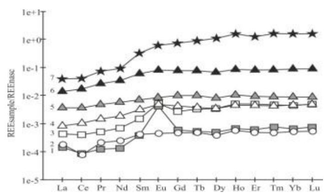

Fig. 3. Normalized REE water's samples of the Mutnovskaya area to NACS 1-K39; 2-K40; 3-4-K36,K37; 5-K35, 6-K34; 7- *average from 8 samples[9]

In acidic waters (pH = 2.3) of North-Mutnovsky thermal field (crater) we observed the enrichment predominantly by heavy REE. In less acidic waters (sample K34) the difference between heavy and light rare earth elements is less. With increasing pH of Viluchinsky hot springs we observed an appearance of a weak positive Eu anomaly, which was seen in the well (sample K39). The nature of the Eu positive anomaly is unclear. For example, in the high temperature hydrothermal systems (Italy, México, California and others) at a pH <7 a significant positive Eu anomaly is present, whereas for thermal waters with pH> 7, a clear negative Eu anomaly[7]. The appearance of positive Eu anomalies in alkaline thermal waters of the Taupo volcanic zone (New Zealand) was associated with the process of the hydrothermal formation of secondary minerals[5]. The host rocks at the Mutnovsky area are hydrothermally altered, and have probably secondary minerals as an additional source for Eu in alkaline thermal waters as well. The Vilucha River (sample K40) had a negative Ce anomaly. The occurrence of a Ce negative anomaly waters might be attributed to the oxidation of Ce^{3+} to Ce^{4+} in oxidizing conditions, and the decreased mobility of the oxidized form in an aqueous environment[1]. Similarly, a cerium negative anomaly was observed in most of rivers of the Eastern Sikhote-Alin, Primorye, Russia[4]. Speciation calculations of REE were performed using the computer program SELECTOR-Windows with the SPRONGS88 database of thermodynamic parameters[12]. The complexes modeled include REE^{3+}, $REE[CO_3]+$, $REE[HCO_3]2+$, $REE[OH_2]^+$, $REE[Cl]^{2+}$, $REE[F]^{2+}$, $REE[SO_4]^+$, $REE[O]^+$, $REE[O_2]^-$, $REE[O_2H]$*, Ce^{4+} and Eu^{2+}. The modeling results are shown in Table 2 for La, Eu, and Yb. The obtained data indicate that the solution complexation of REEs in thermal waters from the Mutnovsky volcano is mainly controlled by pH and temperature. In the acidic thermal waters (K34) up to78.3% of all REEs, occur as sulfate complexes. Other significant species in this sample was the free metal ion (REE^{3+}). In sample K39 with a pH of 6.8 $REE[CO_3]^+$ was important and predominant for Eu and Yb (Table 2). In the hot springs (K36) with pH 5.74 three REEs species are important: $REE[SO4]^+$, $REE[OH_2]^+$ and free metal ion, moreover Eu demonstrates the variable valence - Eu^{2+} (6%) and Eu^{3+} (7%). In the surface water (sample K40) REEs are mainly present as

$REE[CO_3]^+$. Contents of REE carbonate complex increased from LREE to HREE species. $REE[SO4]^+$ concentrations decreased from LREE to HREE (Table 2).

Table 2. Results of REEs speciation modeling, %

	La^{3+}	$LaSO_4^-$	$LaCO_3^+$	$LaOH_2^+$	Eu^{2+}	Eu^{3+}	$EuCO_3^+$	$EuOH_2^+$	$EuSO_4^+$	Yb^{3+}	$YbCO_3^+$	YbO^+	$YbOH_2^+$	$YbSO_4^+$
K34	23.4	76.6	-	-	21.7	-	-	-	78.3	25.5	-	-	-	74.5
K39	13.5	45.5	38.4	2.6	4.5	-	69.4	3.9	20.4	2.1	83.5	1.1	3.5	8.6
K36	10.9	81.6	-	7.3	7.6	6.8	0.1	20.2	60.2	6.6	0.1	12.7	26.5	47.8
K40	33.9	-	65.4	0.7	11.9	-	87.0	-	-	6.8	92.3	-	-	-

Thus, the study of REE in thermal waters of the Mutnovsky volcano showed that different geochemical water types are characterized by different concentration and behaviour of REE. The maximum concentrations of REE were in acid Ca-SO_4 hot springs. The normalized curves show the relative enrichment of heavy REE relative to the light REE, indicating heavy REE preferential accumulation in the solution. In peripheral Na-HCO_3 alkaline waters concentration of REE was much lower, and the difference in concentration between the light and heavy rare earth elements was not as pronounced.

5. Conclusions

The study of thermal waters of the Mutnovsky volcano showed that there is a geochemical zoning in their distribution. Geochemical water type and pH were different depending on its location. Ca-SO_4 acid hot springs were typical for the crater of the Mutnovsky volcano. The composition of hot springs water changes at the periphery of the Mutnovsky volcano, becoming neutral or weakly alkaline, with a Na-HCO_3 composition. The concentration of REE and their behaviour changes as well. The maximum concentrations of REE were observed in the acid Ca-SO_4 waters of the volcano crater, predominance of heavy REE accumulation comparing to the light REE. The peripheral Na-HCO_3 alkaline waters had REE levels two orders of magnitude lower values and were characterized by a positive Eu anomaly. The surrounding waters of the Vilyucha River had a negative Ce anomaly, indicating oxidizing condition.

6. Acknowledgements

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References

1. Sholkovitz E.R. The aquatic chemistry of rare earth elements in rivers and estuaries. *Aquat.Geochem*; 1995. V.1. p.1-34.

2. Chudaev O.V., Chudaeva V.A., Karpov G.A. Shand P., Edmunds M. *Hydrogeochemistry of geothermal territory of Kamchatka*. Vladivostok. Dalnauka. 2000. 160p.

3. Chudaev O.V. *Composition and origin of modern hydrothermal systems of the Far East Russia*. Vladivostok. Dalnauka. 2003. 216 p.

4. Chudaeva V.A. and Chudaev O.V. Accumulation and fractionation of Rare Earth Elements in the Surface Waters of the Russian Far East under the Conditions of Natural and Antropogenic Anomalies. *Geochemistry* 2011; 3. p.1-27.

5. Hannigan R. Rare earth, major and trace element geochemistry of surface and geothermal waters from Taupo volcanic zone, North Island New Zealand. // Netherlands: Springer. 2005. Ch.3. P. 161-186.

6. Karpov G.A.,Nikolaeva A.G.,Alekhin Yu.V. Contens and sourses of rear earth elements in modern hydrothermal systems of Kamchatka. *Petrology*. 2013; v.21., p.163-176

7. Michard A. Rare earth element systematics in hydrothermal fluids. *Geochim et Cosmochim. Acta.* 1989.V.53. pp.745-750.

8. Elovsky E.V. Mathematical elimination of spectral interferences at direct determination of rare earth elements in natural waters by inductively coupled plasma quadrupole mass spectrometry. *Mass spectrometry.* 2015. v.12. p.107-116.

9. Hydrotherms of active volcanoes from Kamchatka and Kuril Islands: composition, structure and origin. Ed. Gaskova O.L. and Manshtein A.K. 2012. Novosibirsk. SB RAS. 205p.

10. Vakin E.A., Kirsanova I.T., Kirsanova T.P. Thermal fields and hot springs of Mutnovsky volcanic territory. Hydrothermal systems and thermal fields of Kamchatka. Vladivostok. Dalnauka. 1976. P.85-114

11.Gromet P., Dymek R., Hoskin L., Krotev R. “The North American shale composite”. Its compilation, major and trace element characteristics. *Geochimica et Cosmochimica Acta.* 1984. V.48, pp. 2469-2482

12. Chudnenko K. V. and I. K. Karpov, “Selektor–Windows.A software for Calculation of Chemical Equilibria by Minimization of Thermodynamic Potentials. A Brief Guide (Irkutsk, 2003).