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Research Article Geysers Valley CO₂ Cycling Geological Engine (Kamchatka, Russia)

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1941–2017 period of the Valley of Geysers monitoring (Kamchatka, Kronotsky Reserve) reveals a very dynamic geyser behavior under natural state conditions: significant changes of IBE (interval between eruptions) and power of eruptions, chloride and other chemical components, and preeruption bottom temperature. Nevertheless, the total deep thermal water discharge remains relatively stable; thus all of the changes are caused by redistribution of the thermal discharge due to giant landslide of June 3, 2007, mudflow of Jan. 3, 2014, and other events of geothermal caprock erosion and water injection into the geothermal reservoir. In some cases, water chemistry and isotope data point to local meteoric water influx into the geothermal reservoir and geysers conduits. TOUGHREACT V.3 modeling of Velikan geyser chemical history confirms 20% dilution of deep recharge water and CO₂ components after 2014. Temperature logging in geysers Velikan (1994, 2007, 2015, 2016, and 2017) and Bolshoy (2015, 2016, and 2017) conduits shows preeruption temperatures below boiling at corresponding hydrostatic pressure, which means partial pressure of CO₂ creates gas-lift upflow conditions in geyser conduits. Velikan geyser IBE history explained in terms of gradual CO₂ recharge decline (1941–2013), followed by CO₂ recharge significant dilution after the mudflow of Jan. 3, 2014, also reshaped geyser conduit and diminished its power.

1. Introduction

Geysers Valley is a unique site in Kamchatka where magnificent hydrothermal features are expressed in the form of numerous geysers, boiling springs, and mudpots with the total rate of ~250-300 kg/s of chloride thermal waters discharged in the Geysernaya river, mostly within the area of 1.0 km to 0.2 km along the Geysernaya river downstream basin. Discovered by T. Ustinova in 1941, this "kingdom of geysers" attracted a number of studies, which focused their work on different aspects of geysers functionality, geological setting, recharge/discharge hydrogeological conditions, heat sources, and geochemistry of hydrothermal system as a whole [1-8]. One of the significant results of these studies is the conclusion that cycling CO₂ recharge is the main driver of Velikan geyser activity [1]. A comprehensive review of geysers phenomena can be also found in the recent paper of Hurwitz and Manga [9].

In spite of a relatively calm period of 1941-2007, when geysers activity changed gradually, two catastrophic events (landslide on June 3, 2007, and clastic mudflow on January 3, 2014) significantly reordered discharge conditions (Figure 1). A number of important geysers were buried by clastic rocks (Pervenets, Troynoy) or sank in Podprudnoe Lake (Maly, Bolshoy, and Conus) after landslide on June 3, 2007. While some of them were lucky to reappear again (Bolshoy, Pervenets), the next disaster mudflow on Jan. 3, 2014, severely damaged Velikan geyser (this was the most impressive one in Geysers Valley). Velikan geyser conduit was completely filled by clastic rocks and although it released significant part of them by 2016, geysers functionality was not recovered in a full. This mudflow also created Podprudnoe Lake 2 upstream of the Geysernaya river, which might additionally recharge cold water in geyser hydrothermal system. It is worth noting that this natural story is much more dynamic as compared to industrial exploitation histories of



FIGURE 1: Schematic map of the Valley of Geysers. 1: alluvial and glacial deposits, Q_{3-4} ; 2: permeable units of rhyolite, dacite, and andesite extrusions ($\alpha\xi Q_3^{4}$); 3: basalt, andesite, and dacite lavas and pyroclastics (αQ_3^{1-2}); 4: low permeability units of caldera lake deposits (Q_3^{4}), which are complicated by a dyke complex (Q_3^{3} ust); 5: assumed thermal fluid-conducting faults; 6: Uzon-Geysernaya caldera boundary; 7: uplifted area that is associated with the contours of the active magma reservoir [10]; 8: geysers and hot springs (for numeration, see Table 6 in [1]); 9: Podprudnoe Lake and Podprudnoe Lake 2 dumb by mudflows; 10: catastrophic landslide-mudflow on 3.06.2007; 11: landslide-mudflow on 3.01.2014; 12: Geysernaya river flow rate measurement points: a: Podprudnoe Lake exit; b: Geysernaya river mouth. Grid scale: 500 m. AB: grey dotted line of cross section shown in Figure 19.

the Pauzhetsky (200–250 kg/s since 1966) and Mutnovsky (450–500 kg/s since 1999) geothermal fields in Kamchatka, where thermal losses accounted for two small geysers and one hot spring.

This paper aims to analyze cycling (IBE, interval between eruptions), chemistry, and available geysers conduit temperature logging data during the historical period of 1941–2017 to understand issues, which caused geysers functionality change.

2. Geological and Structural Setting of the Study Area

2.1. Geological Setting. In this section we followed the description of Kiryukhin, 2016. The age of the Uzon-Geysernaya caldera (Figure 1) was estimated to be 39,600 ± 1,000 years according to the radiocarbon dating of soil samples below the caldera-forming ignimbrites [6]. Uzon-Geysernaya pre-caldera deposits comprise dacite-andesite tuffs and lavas that are 40,000–140,000 years old (αQ_3^{1-2} , αQ_3^{-3} , and Q_3^{-3} ust). Initially, this caldera was an isolated hydrological basin, where volcanogenic and sedimentary lake deposits were formed (Q_3^{-4}). These deposits, which have thicknesses up to 400 m near the caldera rim, are represented by layered pumice tuffs and minor breccias and conglomerates. Caldera lake deposits are overlain by 15,000–20,000-year-old rhyolite-dacite lavas, which formed large domes and adjacent lava flows up to 100–150 m thick (ξQ_3^{-4} and $\alpha \xi Q_3^{-4}$).

Approximately 9,000 to 12,000 years ago, the southeastern wall of the caldera was eroded by the Shumnaya and

Cluster ##	Dip angle (deg)	Dip azimuth (deg)	X m	Y m	Z masl	Number of geysers	Area, km ²	Geysers production, kg/s
(1)	6.8	298.8	4055	2560	422	22	0.22	53.9
(2)	7.3	191.2	5767	1751	548	16	0.18	15.6

TABLE 1: Principal production zones, Lower Geysers (1) and Upper Geysers (2), of the geysers geothermal field are defined as 2D clusters of geysers discharge zones. *Note.* The total number of geysers is 51; X, Y, and Z are coordinates of the clusters centers.

Geysernaya Rivers, initiating the drainage of the hydrological basin. The ultimate lake below the Upper Geyser field was drained because of the Geysernaya river erosion that occurred approximately 5,000 to 6,000 years ago. Hence, a 400–500 m elevation drop in the discharge area occurred in the Geysernaya river basin. The absence of recent basaltic volcanism in the upper stream of the Geysernaya river may indicate the existence of shallow, partially melted magma bodies there, which trap emerging basaltic dykes.

2.2. Hydrogeological Stratification. The following hydrogeological units were identified in the Uzon-Geyzernaya caldera: 1: aquifers of alluvial and glacial deposits; 2: relatively low permeability units of caldera lake deposits (Q_3^4 grn, pmz, js, and col), including pumice tuffs, sandstones, and breccias; 3: permeable units of rhyolite, dacite, and andesite extrusions ($\alpha \xi Q_3^4$); 4: precaldera upper Pleistocene permeable units of lake tuffs and sedimentary deposits, which are complicated by a dyke complex (Q_3^3 ust), andesite lavas (αQ_3^3), pumice breccias (ξQ_3^3), and caldera rim dacite and rhyolite extrusions (ξQ_3^3); 5: aquifer of basalts, andesite, dacite lavas, and pyroclastics (αQ_3^{1-2}); 6: aquifer ($\alpha \beta Q_{1-2}$) basalt lavas; 7: aquifer of Pliocene tuffs, basalts, and sandstones; and 8: basement that is composed of tertiary sedimentary basins (Figure 1).

Figure 2 shows cold water discharge at the contact of relatively low permeability units of caldera lake deposits (unit 2, below) and permeable rhyolite-dacite extrusions of Geysernaya Mt (unit 3, above) (Lavovy creek, southern slope of Geysernaya Mt).

Geyser production reservoirs occur in shallow layer-type structures: Lower Geysers reservoir of 0.22 km^2 is inclined to NWW with a dip angle of 7°; Upper Geysers reservoir of 0.18 km^2 is inclined to the south with a dip angle of 7° (for details see Section 2.3).

2.3. Geysers Reservoir Production Properties. This study applies the program Frac-Digger 2 (Russian reg. #2017618050) in order to define discreet plane-oriented clusters of production feed zones (assumed to be points, where geysers appear on the surface) and the corresponding plane parameters (dip angle, dip azimuth, and fracture planar area), by using the top elevations of geysers (the total number is 51 (Table 6, [1])) as input data for this analysis. The method of 2D plane parameter estimation in Frac-Digger 2 is the same as that in Frac-Digger (see [13] for details of Frac-Digger), but the difference is in the cluster selection algorithm. The stochastic Monte-Carlo approach is used in Frac-Digger 2 to define the largest (the number of production zones included)



FIGURE 2: Permeability distributions feature. Cold water discharges at the contact (dotted line) of relatively low permeability units of caldera lake deposits (unit 2, below) and permeable rhyolite-dacite extrusions of Geysernaya Mt (unit 3, above) (Lavovy creek, southern slope of Geysernaya Mt.). Photo by A. V. Kiryukhin (Sept. 2017).

plane-oriented clusters. Several assumptions were also made as follows: (1) the maximum distance between the feed zone and the approximation plane is less than 10 m. (2) The maximum horizontal distance between feed zones in a 2D cluster is less than 1 km. Table 1 shows the 2D production zone parameters defined suchwise.

There are also some remarkable strike orientations in the Valley of Geysers, which are worth noting: (1) dacite dyke on the left bank of Podprudnoe Lake 1 (opposite to #31, Figure 1) submeridional strike, thickness 2-3 m, strongly silicified; (2) prominent dacite dyke ("Gates into Geysernaya") NW strike, 4-5 m thick, strongly silicified; (3) Velikan geyser pool long axis N15°E strike; (4) Bolshoy geyser pool long axis N30°E strike; (5) Vitrazh, a silicified wall which includes geysers ##14, 15, 19, 20, and 21 (Figure 1), which is characterized by N40°E striking. This data indicates active recharge faulting conditions of NNE and NE directions, while older hydrothermal veins are characterized by NW and submeridional orientation.

3. Available Data and Methodology

This paper analyzes almost all available hydrogeological data of the principal geysers monitoring since the discovery in 1941 until 2017. This data includes (1) geyser cycling (IBE) observations, based on visual records (since 1941), geysers discharge channels water level records (1968–1995), geysers discharge channels fluid conductivity records (1995–2003), and geysers discharge channels temperature loggers records (2007–2017); (2) geysers transient chemical and water isotope



FIGURE 3: Velikan geyser terminal eruptions in 1976, 1991, and 2011. The height of the stone on a right is 1 m. Photo by V. M. Sugrobov (1976, 1991) and A. V. Kiryukhin (2011).

composition (regular sampling since 1968); (3) thermal fluids total discharge in the Geysernaya river, estimated with regard to transient chloride rate and chloride normalized concentration of 900 ppm (since 1960); (4) bottomhole temperature records in Velikan and Bolshoy geysers (1995, 2008, 2016, and 2017); (5) topography maps 1:2000 and 1:10000 and geological map (Leonov, 2008, pers. com.) supplemented by hydrogeological information obtained using helicopter infrared surveys [8].

HOBO U12-015 temperature loggers were used to measure the interval between the eruptions (IBE) of the Velikan and Bolshoy geysers starting in July 2007. The loggers, which were installed in the channels of water discharge out of geysers, recorded the temperature of water outflow every 5 min. The eruption time of the geysers was estimated according to the time of the absolute maximum temperature prior to its absolute minimum (in a cycle). The same temperature loggers attached to iron tubes were used for temperature logging in geyser conduits.

The samples collected from geyser conduits were analyzed in Central Chemical Lab Institute of Volcanology and Seismology (for Na, K, Ca, and Mg analysis spectrometer SOLAAR M and for SiO₂ and NH₄ spectrophotometer UVmini-2140 were used; HCO₃ and CO₃ were analyzed using titration, standard pH meter "Анион," for pH determination). Geyser water isotope content (δ D, δ ¹⁸O) measurements were performed with a LGR IWA 35EP analyzer of water isotope composition in IVS FEB RAS since 2015.

Flow and chloride rates in Geysernaya river mouth measurements were conducted using standard hydrometric methods with water sampling for chloride determination. Since 2015 a Cl-tracer method for river flowrate determinations was also applied; for this purpose logger HOBO U24-001 (range 0–10,000 μ S/cm, the set recording interval of 10 s) was used. Since 2017 a portable Mainstream 400P flowmeter has been used too.



FIGURE 4: Velikan geyser terminal eruption in 2013. The height of the stone on a right is 1 m. Photo by A. V. Kiryukhin (2013). This is the latest photo of Velikan geyser full power eruption before harmless landslide of January, 3, 2014.

4. Historical Data of Geysers Activity, 1941–2016 (IBE)

4.1. Velikan Geyser. There are four historical periods of Velikan geyser (23, Figures 1, 3–6 and 7) cycling (IBE) monitoring (Figure 8(a)). During 1941–1968 Velikan geyser IBE was determined on the basis of visual observation; thus a very scarce row of observations was obtained. Since 1969 a water level instrument "Valdai" was put in the downstream channel from Velikan geyser conduit [3]; thus geyser eruptions were fairly recorded by water level rise. While these measurements were made regularly in the summer only, significantly more IBE data were obtained until 1990. Next monitoring system was designed by V. A. Droznin and was based on electric circuit switch, on/off, depending on geyser discharge conditions. This system successfully operated during 1993–2003 time period, mostly in the summer. The last monitoring

Geofluids



FIGURE 5: Velikan geyser. (a) Preplay event: height of eruption is 0.5–1.0 m; (b) terminal eruption with the height of erupted water of 15–20 m. Photo by A. Kiryukhin (2008, 2013).



FIGURE 6: Velikan geyser view after harmless mudflow of January 3, 2014: eruptions at 1.0–1.5 m height (a) and water level build-up after 2-3 m draw-down following eruption (b). Photos by A. V. Kiryukhin (April 2016).



FIGURE 7: Rise of the Geysernaya river level (+1.5 m) in a vicinity of Velikan geyser (#23) after mudflow of Jan. 3, 2014, is shown by blue dotted line. Horizontalny geyser (#26) is a river level marker (2014–2017). River water elevation coupled with erosion of river bottom (that served as a silica caprock for geysers reservoir) may cause cold water breakthrough into production geysers reservoir. Note also a small distance between river and Velikan geyser that is \approx 40 m. Photo by A. V. Kiryukhin (Sept. 2013).

deployment used HOBO U12-015 temperature loggers since 2007, which were put in a downstream channel from the Velikan geyser conduit [1, 8]. The IBE is easily estimated from temperature records as a time difference between

temperature absolute maximums. This method of monitoring yields a continuous information on Velikan geyser cycling.

Examining Velikan geyser IBE history plot (Figure 8(a)), we may clearly observe an almost linear trend of IBE increase from 1941 to 2007 (+200 min per 65 years, or +3 min/year). Then, after landslide of June 3, 2007, and Podprudnoe Lake pressure build-up, some IBE drop followed by stability at IBE ≈ 340 min was observed. All of the time 2007–2013 Velikan geyser eruption style was unchanged: a piston-like blow-out of ~20 tons of boiling water within 30-40 s at an elevation of 15-20 m. Conduit was empty after eruption end; then 1-1.5 hours were needed to refill conduit with water level gradual rise. That is followed by 4-4.5 hours of preplay (or intermediate boiling) events 20-25 min each (total number 7-12) preceding the terminal blow. The intrigue was that nobody knew if a preplay event would come over to the terminal eruption or would just remain with 1-1.5 m fountain of boiling water.

The mudflow of Jan. 3, 2014, brought rocks into Velikan geyser conduit, so its main 5.3 m top part was completely filled (E. Vlasov, pers. com. 2014). But by April 2014 the upper part of the conduit was released from clastic material, by Sept. 2015 the available depth was 1.95 m, and by Sept. 2016



(a) Interval between eruptions (IBE) versus time (years): Velikan geyser. 1941–1993 data from V. M. Sugrobov, 1995–2003 data from V. A. Droznin, and 2007–2016 data from A. V. Kiryukhin. Arrows with numbers 1 and 2 correspond to landslides-mudflows of June 03, 2007, and January 03, 2014



(b) Interval between eruptions (IBE) versus time (years): Bolshoy geyser. 1941–1993 data from V. M. Sugrobov, 1995–2003 data from V. A. Droznin, and 2007–2016 data from A. V. Kiryukhin. Arrows with numbers 1 and 2 correspond to landslides-mudflows of June 03, 2007, and January 03, 2014



(c) Interval between eruptions (IBE) versus time (DD-MMM-YY): Bolshoy geyser after mudflow on Jan. 3, 2014. Data from A. V. Kiryukhin



FIGURE 9: Bolshoy geyser terminal eruptions in 1966, 2014, and 2016. Photo by V. M. Sugrobov (1966) and A. V. Kiryukhin (2014, 2016).

it reached ~5.3 m. In 2016 a merely stable IBE of ~40 min was achieved, but the style of Velikan geyser eruptions completely changed from piston-type eruption to long-term chaotic boiling with rare 2-2.5 m fountain events followed by a water level drop-down.

4.2. Bolshoy Geyser (28, Figures 1 and 9). The methods of IBE monitoring of Bolshoy geyser were the same as for Velikan geyser, as described above. There is no clear trend in Bolshoy geyser IBE plot (Figure 8(b)); it ranges from 60 to 140 min in the time period of 1967–1989, later on in a more narrow range from 85 to 115 min during 1991–2007. Landslide on June 3, 2007, created Podprudnoe Lake, which put Bolshoy under water for a few months, but in Sept. 2007 Bolshoy geyser appeared on the surface and started to cycle again. Bolshoy geyser functionality strictly depended on the water level in Podprudnoe Lake: in flood time the geyser disappears below water and its conduit was used as cold water injector, while in low water seasons Bolshoy was regularly cycling with IBE range of 50–70 min (that is 1.5 times shorter, as compared to IBE before June 3, 2007).

Mudflow on Jan. 3, 2014, brought some mud in Bolshoy geyser conduit, but the geyser was recovered to previous IBE soon. In recent years a tendency of IBE splitting with some "missed" (or less powerful) eruptions was observed (Figure 8(c)).

5. Chemical History of Geysers Activity in 1969–2016

Fluid samples from main geysers and boiling springs in Geysers Valley were regularly taken by the Institute of Volcanology & Seismology, Far East Branch, Russia Academy of Sciences (IVS FEB RAS) since 1969. Those samples were analyzed in Central Chemical Lab of the Chemistry of IVS FEB RAS for major elements. Tables 2(a) and 2(b) give an example of chemical analysis of the samples collected in 2015 and 2016 correspondingly; more older chemical analysis data 2010–2014 is available in [1]. Table 2(c) gives gas chemical and isotopic (δ^{13} C) composition, which characterized feeding reservoir of Velikan geyser in 2013. This table shows magmatic origin of CO₂ and thermogenic origin of CH₄, correspondingly. Figures 10(a), 10(b) and 10(c) reflect transient changes in chloride, HCO₃, and Na-K geothermometer estimates in the three key geysers: Velikan (23), Bolshoy (28), and Pervenets (3) (numbers correspond to Figure 1; see also Figures 3–9 and 11). We do not use silica geothermometer for this analysis, since liquid samples from geyser conduits are oversaturated in silica due to steam phase separation into the atmosphere (thus silica temperatures are 40–50°C greater as compared to Na-K temperatures in samples collected from geysers).

Chloride concentration trend slowly decreased in Velikan geyser (-1.1 ppm/year), was almost stable in Bolshoy geyser (-0.2 ppm/year), and was somewhat growing in Pervenets geyser (+0.8 ppm/year) during 1969–2003. Giant landslide of June 3, 2007, induced chloride drop in Bolshoy geyser (-60 ppm) and chloride rise in Pervenets geyser (+40 ppm) when they appeared on the surface again in 2010. After 2007, chloride started to decline faster in Velikan geyser (-5.7 ppm/year), while showing some trend of rise in Bolshoy geyser (+2.8 ppm/year) (Figure 10(a)).

 HCO_3 concentration sensitively follows pH conditions and it seems to slowly decline in Pervenets geyser and Bolshoy geyser (-0.1 ppm/year) and slowly rise in Velikan geyser (+0.2 ppm/year) during 1969–2003. Then, after giant landslide on June 3, 2007, we see a drastic drop of HCO_3 in Velikan geyser to zero values; this zero level was achieved immediately after mudflow on Jan. 3, 2014 (Figure 10(b)). Giant landslide also induced the decline of HCO_3 by half in Bolshoy geyser, but there is some trend of recovering after 2010 (2.6 ppm/year). Pervenets geyser shows +1.1 ppm/year rise of HCO_3 during 2010–2016 period of recovering.

 $T_{\text{Na-K}}$ geothermometer [14] shows slow decline in Velikan, Bolshoy, and Pervenets geysers from -0.3 to -0.9°C/year

TABLE 2

(a) Chemical composition (in ppm) of hot springs and geysers in 2015. The samples collected by A. V. Kiryukhin directly from geyser conduits were analyzed in Central Chemical Laboratory of Institute of Volcanology and Seismology. Geyser and spring numbers (##) correspond to Table 6 [1]

Data	##	pН	HCO3	CO3	Cl	SO4	Na	Κ	Ca	Mg	NH4	H3BO3	SiO2 t
27.07.2015	23A	9.3	23	17	837	173	587	81	3		0.9	124	566
27.07.2015	28	6.7	77		802	163	555	39	31	0.3	0.7	103	417
27.07.2015	20	8.80	29	8	709	173	502	58	5		2.0	97	404
27.07.2015	23	6.7	53		808	178	530	73	28		2.5	133	335
27.07.2015	SH	6.3	38		837	158	491	47	37	4.0	35.0	228	286
01.09.2015	23	8.9	49	8	748	192	517	69	20	0.6	0.6	108	
02.09.2015	28	8.6	46	6	610	192	447	37	22		0.7	80	
02.09.2015	28	8.9	33	13	709	192	495	41	24	2.4	0.8	102	
02.09.2015	28	8.9	33	10	709	192	522	41	22		0.9	96	
02.09.2015	21	9.2	34	20	709	172	500	66	22	2.4	0.7	117	
02.09.2015	20	8.9	46	10	709	204	517	52	22		1.0	96	
02.09.2015	3	9.1	48	10	472	204	364	32	22	0.2	0.4	59	
02.09.2015	G-Rv	7.4	23		76	67	55	6	15	3.3		9	
03.09.2015	45	9.6	104	10	134	134	178	10	4	0.0	0.5	193	
03.09.2015	G-Lake2	6.8	22		1	38	5	1	15	3.6			
03.09.2015	50	5.9	6		404	231	321	15	18	16.0			
03.09.2015	47	9.2	18	15	560	222	436	30	22			100	
03.09.2015	46	7.0	44		128	288	181	16	16		1.2		

Notes. (1) G-Rv: Geysernaya river mouth; G-Lake2: Podprudnoe Lake 2 exit (Figure 1); SH: Shaman geyser (Uzon); (2) SIO2 t: total concentration of SiO2 (in colloidal form and solution).

(b) Chemical composition (in ppm) of hot springs and geysers in 2016. The samples collected by A. V. Kiryukhin directly from geyser conduits were analyzed in Central Chemical Lab of Institute of Volcanology and Seismology. Geyser/spring ## corresponds to Table 6 [1]

Data	##	pН	HCO3	CO3	Cl	SO4	Na	Κ	Ca	Mg	NH4	H3BO3	SiO2 t
23.04.2016	3	7.5	55		479	125	364	26	13	0.3	1.3	56	366
23.04.2016	23	7.8	61		740	154	546	75	12	0.3	1.3	95	440
23.04.2016	28	8.20	55		650	154	463	47	13	0.1	1.3	84	387
31.08.2016	3	8.5	56	5	444	125	336	34	8	0.1	1.0	62	398
01.09.2016	23	9.1	67	3	724	144	517	59	3	0.1	1.3	93	588
01.09.2016	23A	9.2	37	24	749	154	536	69	5		0.7	88	420
01.09.2016	21	9.1	40	19	750	144	520	56	0		0.6	99	416
01.09.2016	28	8.9	38	13	664	144	472	40	1	0.1	1.0	70	399
01.09.2016	20	8.8	49	9	666	144	469	48	4		0.7	82	451
01.09.2016	N37	8.1	62		479	115	340	30	0	0.3	1.3	71	357
02.09.2016	23	8.8	54	9	721	163	516	60	3	0.1	0.9	82	535
02.09.2016	28	8.9	53	11	646	144	487	41	1	0.1	1.0	71	398

(c) Chemical composition of free gas (vol. %), which characterized feeding reservoir of Velikan geyser. Sampling was performed by A. V. Kiryukhin in Sept. 2013 from hot degassing pool located 8 m from Velikan geyser. Sample (1) was analyzed by V. I. Guseva in IVS FEB RAS; sample (2) was analyzed by V. Y. Lavrushin in GIN RAS. Isotopic analyses (δ^{13} C) were performed by B. G. Pokrovsky

##	H ₂	Ar	O ₂	N ₂	CO ₂	СО	CH_4	H_2S	δ^{13} C (CH ₄)‰	δ^{13} C (CO ₂)‰
(1)		0.9	6.6	48.9	32.7	0.3	9.2	0.03		
(2)	0.45		0.02	32.1	61.5	0.003	5.8		-28.3	-4.95

(Figure 10(c)) during 1969–2003. After giant landslide on June of 3, 2007, the positive trend was observed in all of the abovementioned geysers (from 4.2 to 5.0° C/year). Currently the range from 180 to 230°C of $T_{\text{Na-K}}$ geothermometer values was achieved in Velikan geyser, while in 1969–2003 the range was from 165 to 185°C.

6. Temperature Measurements in Velikan and Bolshoy Geysers Conduits

In Aug. 1994 temperature measurements in the conduit of Velikan geyser were performed by V. A. Droznin by using an original device, which was made in the Institute



(a) Cl versus time (years) (Velikan, Bolshoy, and Pervenets). 1969–1993 data is provided by V. M. Sugrobov, 1995–2003 data is provided by O. P. Bataeva (pers. com., 2017), and 2007–2016 data is provided by A. V. Kiryukhin



(b) HCO₃ versus time (years) (Velikan, Bolshoy, and Pervenets). 1969–1993 data is provided by V. M. Sugrobov, 1995–2003 data is provided by O. P. Bataeva (pers. com., 2017), and 2007–2016 data is provided by A. V. Kiryukhin



(c) $T_{\rm Na-K}$ versus time (years) (Velikan, Bolshoy, and Pervenets). 1969–1993 data is provided by V. M. Sugrobov, 1995–2003 data is provided by O. P. Bataeva (pers. com., 2017), and 2007–2016 data is provided by A. V. Kiryukhin

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Data	Depth, m	Hydrostatic pressure, bars	Preeruption temperature, °C	Saturation pressure (bars) at given temperature	$P_{\rm CO2}$ bars
Aug. 6, 1994	5.0	1.43	99.5	0.99	0.44
July 27, 2007	4.65	1.39	105.5	1.23	0.14
Sept. 1, 2016	4.65	1.39	106.0	1.25	0.12
Sept. 1, 2017	4.30	1.36	104.0	1.17	0.19

TABLE 3: Preeruption temperatures recorded in the bottom of Velikan geyser conduit and partial CO_2 pressure estimates at hydrostatic pressure distribution (*Patm* = 0.956 bar) preceding the eruption.



FIGURE 11: Pervenets geyser terminal eruptions with the height of erupted water of 5–7 m (1990) and 1.5–2.0 m (2016). Photo by V. M. Sugrobov (1990) and by A. V. Kiryukhin (2016). *Notes*. (1) Pervenets (Firstborn) geyser was the first one which T. Ustinova saw on April 14, 1941, when Geysers Valley was discovered. (2) On June 3, 2007, this geyser was buried by 3 m thick clastic mudflow but was recovered in 2015.

of Volcanology and included thermistor MMT-3, controller KR1006VI1, memory chips 537RU10, and motherboard of ser. # 561. Accuracy of measurements of this device was anticipated at 0.5°C. Maximum depth of measurements in Velikan geyser conduit was 5 m [11]. Temperature records (1 record in 30 s) during one full cycle of geyser activity were obtained at that depth (Figure 12(a)).

Since 2007, temperature measurements in geysers conduits were performed by using temperature loggers HOBO U12-015. In the case of geyser Velikan two T-loggers were installed on a 6 m drilling rod in the positions, corresponding to depth 4.65 from maximum elevation of water level in geyser conduit. Temperature measurements were performed on July 27, 2007, and on Sept. 1, 2016. Depth of 4.65 m (near bottom conditions) corresponds to pressure of 1.39 bar, if hydrostatic pressure distribution refers to water at boiling conditions and atmospheric pressure of 0.956 bar on the top. Figure 12(b) shows temperature records observed.

Temperature records on July 27, 2007, in Velikan geyser show eight cycles of eruptions with eruption temperature of 98.5°C at bottom depth of 4.65 m (Figure 12(b)). Maximum temperature before eruption was 105.5°C that is significantly lower (-4.5°C) than saturation temperatures at the given depth. Thus, saturation pressures at recorded preeruption temperatures are lower than hydrostatic pressures, and the difference is attributed to partial CO₂ pressures [1], which is estimated at 0.14 bar (Table 3). It is also worth noting that "preplay" events (10–12) before terminal eruptions, which expressed as intermediate boiling in geyser conduit, are synchronized with cyclic 1°C temperature drops (P_{CO2} positive changes up to 0.04 bar) (cycle 6 example in Figure 12(b)). These preplay events (or small eruptions) of cycling activity were characterized at this time by IBE2 = 21 min.

As mentioned above, Velikan geyser conduit was filled by mudflow debris on Jan. 3, 2014. Gradually, Velikan geyser pulled out clastic material; thus temperature logging on Sept. 1, 2016, revealed a possibility of reaching the former bottom of the Velikan geyser conduit (~5.3 m depth). At this time Velikan geyser gained a rather regular temperature cycling mode (IBE = 39 min) in the conduit and showed preeruption temperatures of 106.1°C at the depth of 4.65 m (Figure 12(c)). This corresponds to partial CO_2 pressures of 0.12 bar. Repeated temperature logging in Velikan geyser on Aug. 30-Sept. 1, 2017, reveals preeruption temperature of 104.0°C at 4.3 m depth in the hottest part of the conduit that corresponds to partial CO_2 pressures of 0.19 bar (Table 3), but we also found a cold spot at the temperature of 22°C in the bottom (at depth of 5.1 m) of the Velikan geyser. The latest records indicate cold water entry into the Velikan geyser conduit.

Temperature logging in Bolshoy geyser was performed in 2015, 2016, and 2017. Temperature records in Bolshoy geyser





(a) Temperature records in the conduit of Velikan geyser observed in 1994 at the depth of 5 m below maximum water level elevation (one cycle) (data digitized from [11])

(b) Temperature records in the conduit of Velikan geyser observed in 2007 at the depth of 4.65 m below maximum water level elevation (one cycle). Time unit format on *x*-axis is M/DD/YY HH:MM



(c) Temperature records in the conduit of Velikan geyser observed in 2016 at the depth of 4.65 m below maximum water level elevation. Time unit format on *x*-axis is M/DD/YY HH:MM

Figure 12



FIGURE 13: Temperature records in the conduit of Bolshoy geyser observed in 2016 at the depth of 3.15 m below maximum water level elevation. Time unit format on *x*-axis is M/DD/YY HH:MM.

conduit obtained on Sept. 28, 2016, at 3.15 m depth revealed eruption temperature of 97.2° C (Figure 13), which corresponds to 0.37 bar partial CO₂ pressure. At this time regular temperature cycling was observed. Temperature logging in Bolshoy geyser on Aug. 31, 2017, reveals similar conditions as in 2016 (Table 4).

7. Thermal-Hydrodynamic-Chemical Modeling of Velikan Geyser

TOUGHREACT-ECO2N [15, 16] and TOUGH2-EOS1 + tracer [17] modeling were used to explain the chemical history of Velikan geyser in 1969–2016 focused on chloride decline, HCO_3 disappearance in 2014, and bottom temperature rise in 2016 as compared to 2007. In order to do this, a two-element lumped parameter model representing the Velikan conduit of 20 m³ was set up (Figure 14).

Model flow conditions were specified in the following way. The deep thermal fluid recharge source was assigned as follows: (1) time dependent deep water mass flow (1 kg/s before 2014, 0.8 kg/s since 2014) with enthalpy of 457 kJ/kg or 109°C; (2) time dependent CO_2 mass flow, 0.010 kg/s during 1941–2013, and then drop to 0.008 kg/s. The river water recharge source was assigned to be active since 2014 with mass flow rate of 0.2 kg/s and an enthalpy of 457 kJ/kg or 109°C (heated to reservoir temperature). Velikan geyser discharge was assigned in the model in terms well on deliverability (PI = 10^{-9} m³, Pb = 1.39 bar) which corresponds to hydrostatic pressure bottom hole conditions in a geyser conduit; this approximation seems to be reasonable since 80% of Velikan geyser time cycle was spent in self discharge conditions

Data	Depth, m	Hydrostatic pressure, bars	Preeruption temperature, °C	Saturation pressure (bars) at given temperature	P _{CO2} bars
Sept. 28, 2016	3.15	1.25	99.4	0.91	0.34
Aug. 31, 2017	3.15	1.25	99.5	0.94	0.31

TABLE 4: Preeruption temperatures recorded in Bolshoy geyser conduit and partial CO_2 pressure estimates at hydrostatic pressure distributions (*P*atm = 0.956 bar) before the eruption.

TABLE 5: Chemical properties of deep and river waters, assigned in the TOUGHREACT-ECO2N model.

Chemical species	Deep water, ppm	Deep water, mole/kg H2O	River water, ppm	River water, mole/kg H2O
h+		1e - 7		3.16e – 12
na+	605	2.64e - 2	55	2.39e – 3
k+	47	1.2e - 3	6	1.53e - 4
ca+2	22	5.5e - 4	15	3.74e - 4
mg+2	0	1e - 7	3	1.23e - 4
Cl-	872	2.46e - 2	76	2.14 <i>e</i> – 3
hco3–	68	1.12 <i>e</i> – 3	23	3.77e - 4
so4-2	161	1.68e - 3	67	6.98e - 4
alo2–		1e - 8		1e - 8
sio2(aq)	289	4.82e - 3	55	9.16 <i>e</i> – 4



FIGURE 14: Two-element lumped parameter model of the Velikan geyser.

before terminal eruption (Figures 12(a) and 12(b)). Rock porosity 0.5 was assigned to activate water/rock interaction and modeling time 2000 years preceding the time interval of interest (1941–2017) was assigned in this model too.

Chemical properties of recharged fluids were assigned according to chemical analysis of samples taken from Velikan geyser (representing deep water) before 2007 and samples taken from Geysernaya river (representing river water) (Table 5). The only corrections were applied to pH values in deep water (we used in the model pH = 7, instead of 8.4 measured in a sample, to account for degassing of samples) and in river water (we used in the model pH = 11.3, instead of 8.4 measured in a sample, since we envision a two-step process whereby river water having a pH of 8.4 reacts with volcanic glass to form secondary minerals before entering the geyser,

causing the pH to rise to 11.3). Note that this possibility of pH rise in river water was confirmed using TOUGHREACT-ECO2N one-element lumped parameter modeling too.

The initial mineral composition was assigned as glass 3, and possible secondary minerals include calcite, gypsum, quartz, sio2(am), cristobalite-a, and mordenite (we also used a kaolinite for testing river water pH rise). Calcite and gypsum were assigned at equilibrium, while other minerals were assigned using kinetic rate law conditions.

Figure 15 shows the results of TOUGHREACT-ECO2N runs and comparison with Velikan geyser observational Cl, HCO_3 , and preeruption bottom temperature data. The model reasonably matches observational data; thus it explains deep water component (Cl) decline and HCO_3 disappearing after 2014 (Figures 15(a) and 15(b)) as a result of high pH river water influx, following geyser bottom hole temperature rise (Figure 15(c)) due to partial pressure of CO_2 drop. Of note, we used a TOUGH2-EOS1 + tracer model to get a better match between modeling and observations for chloride Cl; in this case Cl component was assigned in the deep water source as a time dependent linear decreasing function with chloride drop rate of 1.7 ppm/year during 1969–2014 and then 5.6 ppm/year after 2014 (Figure 15(a)).

8. Discussion/Conclusions

(i) TOUGHREACT-ECO2N modeling of Velikan geyser thermal-chemical history of 1969–2016 clearly explains the observed chloride component decrease, HCO_3 drop after 2014, and preeruption bottom temperature rise as a result of mixing of the deep thermal water (80%) and Geysernaya river water (20% of which reacted with volcanic glass to form secondary minerals before entering the geyser, causing the pH to rise).

(ii) Geysers water isotope content ((δD , $\delta^{18}O$) measurements were performed by P. O. Voronin with a LGR IWA



(a) Comparison of modeling and the observed Velikan geyser chloride Cl data. Time unit format on x-axis in years

Model C2_0 TREACT V5

(b) Comparison of modeling and the observed Velikan geyser HCO_3 data. Time unit format on x-axis in years

(c) Comparison of modeling and the observed Velikan geyser bottom hole preeruption temperature data. Time unit format on x-axis in years. *Note.* We did not use for this matches the data obtained in 1994, since the accuracy of measurements at this time was not sufficient

FIGURE 16: Water isotope data of Velikan geyser (red circles, year of sampling) and Bolshoy geyser (grey circles, year of sampling) during 2011–2016 time period versus Geysernaya river waters (GR-*, where * indicates elevation, masl) and Kronotskoye lake (blue circles). Samples from geysers and rivers were taken by A. V. Kiryukhin; samples from Kronotskoye lake were taken by G. Markevich (2014). Analysis was performed by P. O. Voronin using LGR IWA 35EP in the IVS FEB RAS.

35EP analyzer of water isotope composition in IVS FEB RAS (for data of 2010 see [18]; for data of 2011-2014 see [19]) which is close to local meteoric water, and there is no significant difference in water isotope composition along the Geysernaya river up to Podprudnoe Lake 2. Hence, δD and $\delta^{18}O$ data is difficult to use to identify which part of Geysernaya river valley acts as injection area into geothermal reservoir (Figure 7) or if this water came from Podprudnoe Lake 2 (created in 2014 after mudflow dam Geysernaya river 2.5 km upstream) (Figure 16).

(iii) Giggenbach geoindicators tool [12] clearly shows events of immaturation of thermal waters of Velikan geyser after 2010 and Bolshoy geyser after 2007, which possibly reflects the influx of river waters into geysers conduits (Figure 17).

(iv) There is no sign of the total deep water component discharge decrease during 1961–2017 (Figure 18). That means chloride and CO_2 (deep magmatic components) changes are attributed mostly to mixing processes (due to river/meteoric waters influx into geothermal reservoir) and redistribution of discharge due to the change in surface conditions (giant landslide 2007 shapes, Podprudnoe Lake 1, Geysernaya river and Podprudnoe Lake 2 cold water injections events, self-sealing processes, etc.).

(v) Temperature logging in geysers Velikan (1994, 2007, 2015, 2016, and 2017) and Bolshoy (2015, 2016, and 2017) conduits shows preeruption conditions under temperatures below boiling at corresponding hydrostatic pressure that means partial pressure of CO_2 lowers boiling temperatures

FIGURE 17: Giggenbach [12] geoindicator plot (Velikan geyser). Grey circles: data before 2007; red circles with numbers (years): data after 2007.

and creates gas-lift upflow conditions. $P_{\rm CO2}$ estimated in Velikan and Bolshoy geysers are based on 2007, 2015, 2016, and 2017 temperature logs ranges from 0.12 to 0.31 bar.

(vi) Velikan geyser IBE history 1941-2007 with an almost linear trend of IBE increase (+200 min per 65 years or +3 min/year, Figure 8(a)) and with almost unchanged conduit and shallow pool geometry conditions may be interpreted as a result of gradual CO₂ recharge decline, which should follow chloride decline (Figure 10(a)), as both are a deep magmatic components. Some shortage of IBE during 2007-2013 is explained by recharge rate increase due to reservoir pressure build-up after Podprudnoe Lake 1 entrance (caused by giant landslide of June 3, 2007). Once Velikan geyser conduit eroded on the top and was partially buried (as a result of Jan. 3, 2014, mudflow) and CO₂ recharge was by 20% diluted, then the power of its eruption significantly decreased. The open question is why its CO_2 influx cycles frequency increased twofold from ~20 min to ~40 min (cf. Figure 12(b) and Figure 12(c)).

(vii) 1941–2016 period of monitoring in the Valley of Geysers (Kamchatka, Kronotsky Reserve) reveals a very dynamic geysers behavior in natural state conditions, in which a deep upflow CO_2 recharge plays a major role in geysers sustainability. Velikan geyser and Bolshoy geyser examples show that cycling CO_2 flux triggered gas-lifted geysers eruptions, while the power of eruptions is defined by partial CO_2 pressure. Deep magmatic CO_2 flux redistribution in geysers geothermal reservoir and local meteoric inflows were found to be crucial for geysers functionality (Figure 19). The next page in the geysers history significantly depends on future thermal hydrodynamic impact of the Podprudnoe Lake 2, created upstream of the Geysernaya river on Jan. 3, 2014.

FIGURE 18: Estimate of the total discharge of deep thermal water component of the Geysernaya river (kg/s) by using chloride normalized concentration of 900 ppm. Blue circles: measurements just above Shumnaya river joint; red circles: measurements at the exit from Podprudnoe Lake (see Figure 1). 1961–1994 data provided by V. M. Sugroboy; 2007–2017 data provided by A. V. Kiryukhin.

FIGURE 19: Geological cross section along line AB (see Figure 1) of the Geysers Valley. 1: upflows of deep geothermal fluids; 2: inflows of meteoric waters; 3: geysers (for numeration, see Table 6 in [1]).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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