

Geochemical Indication of Formation Water Influx to The Volcanic Hosted Hot Springs of Slamet Volcano, Indonesia

AGUNG HARIJOKO¹, SAEFUDIN JUHRI¹, SACHIHIRO TAGUCHI², KOTARO YONEZU³, and KOICHIRO WATANABE³

¹Department of Geological Engineering, Faculty of Engineering, Universitas Gadjah Mada, Jln. Grafika No. 2 Yogyakarta, Indonesia ²Department of Earth System Science, Faculty of Science, Fukuoka University, Fukuoka, Japan 8Chome-19-1 Nanakuma, Jonan Ward, Fukuoka, Fukuoka Prefecture 814-0180, Japan ³Department of Earth Resources Engineering, Faculty of Engineering, Kyushu University, Fukuoka, Japan 744 Motooka, Nishi Ward, Fukuoka, Fukuoka Prefecture 819-0395

> Corresponding author: aharijoko@ugm.ac.id Manuscript received: December, 15, 2018; revised: Pebruary, 7, 2018; approved: September, 18, 2019; available online: January, 17, 2020

Abstract - The Slamet Volcano is an active volcano lying above a sedimentary rock substratum with three complexes of geothermal manifestations: Baturaden, Guci, and Paguyangan. In order to understand the characteristic and origin of the geothermal fluid related to the Slamet volcanic system emphasizing the identification of formation water influx represented by sea water signature in the thermal fluid, the water chemistry has been analyzed including stable isotopes of the hot springs, cold springs, shallow groundwater, rainwater, and river water surrounding the Slamet Volcano. The temperature of manifestations is in the range of 42 - 72°C, while the chloride concentration of the geothermal water is ranging from 17 to 754 mg/L. Specifically, the manifestations in Baturaden are distinctively featured by a huge travertine deposit. The values of Cl/B ratio and non-equilibrium state of the reactive elements indicate the existence of two main geothermal fluid flows discharging as hot springs at Baturaden, Paguyangan, and Guci complexes. Guci hot spring complex shows a similar characteristic as fumarole condensate water from the summit of Slamet Volcano which has been diluted by meteoric water. On the other hand, Baturaden hot spring complex appears to be affected not only by fumarole condensate, but also by the contribution of formation water from marine sedimentary rock. Meanwhile, Paguyangan hot spring is more likely as the outflow of a geothermal reservoir which has also been interacting with marine sedimentary rock. Furthermore, the signature of stable isotope of δ^{18} O and δ^{2} H shows a significant portion of meteoric waters.

Keywords: Slamet Volcano, geochemistry, geothermal, fluid origin, formation water influx

© IJOG - 2020. All right reserved

How to cite this article:

Harijoko, A., Juhri, S., Taguchi, S., Yonezu, K., and Watanabe, K., 2020. Geochemical Indication of Formation Water Influx to The Volcanic Hosted Hot Springs of Slamet Volcano, Indonesia. *Indonesian Journal on Geoscience*, 7 (1), p.1-14. DOI: 10.17014/ijog.7.1.1-14

INTRODUCTION

There are several hot springs appearing adjacent to the Slamet Volcano, such as Guci (northern flank), Baturaden (southern flank), and Paguyangan (western flank). The government of Indonesia has already defined these places as geothermal working areas, and until now they are still in the exploration stages (Kementerian Energi dan Sumber Daya Mineral, 2017). The wall rocks of the hot springs in Guci and Baturaden are volcanic rock products of Slamet Volcano, while Paguyangan hot spring discharging on the sedimentary rocks is part of Rambatan Formation. The Rambatan Formation is a Miocene marine sedimentary rocks consisting of shale, marl, and calcareous sandstone. Those sedimentary rocks outcrop near and at the flank of the Slamet Volcano. Therefore, it may become the substratum rocks of Slamet Volcano (Kastowo, 1975; Djuri *et al.*, 1996; Mukti *et al.*, 2009).

Baturaden hot springs show a specific feature in comparison to Guci and Paguyangan hot springs due to the appearance of huge travertine deposit at Pancuran Pitu (Okumura et al., 2012). The deposition of travertine from geothermal fluid commonly occurs when the fluid is rich in bicarbonate that may be resulted by the condensation of volcanic gas (D'Alessandro et al., 2007) or the dissolution of calcareous rock at depth (Minissale, 2004). Furthermore, Harijoko and Juhri (2017), based on the Cl/B ratio, showed the difference of thermal water feeding the hot springs in Baturaden and Guci areas and interpreted the possibly of formation water contribution. These differences imply possible different water-rock interaction processes beneath the Slamet Volcano. The most possible mechanism is the involvement of marine sedimentary rocks beneath the Slamet Volcano in the water-rock interaction processes. Therefore, in this study the discussion is extended from Cl/B ratio in identifying the mixing of different water type through various methods, e.g. single-point diagram (Langelier and Ludwig, 1942), Na-K-Mg-Ca equilibrium diagram (Giggenbach, 1988), stable isotope analysis, and comparing the Cl/B ratio of the Java hot spring (Purnomo and Pichler (2014).

This study intends to determine chemical and stable isotope characteristics and types of geothermal water around the Slamet Volcano, and to reveal the origin of the thermal water emphasizing the detection of the water formation from marine sedimentary rock influence to the chemical composition of geothermal water in andesitic stratovolcano setting. Therefore, samples of hot spring water discharging were collected on volcanic rocks (Guci and Baturaden hot springs) as well as hot spring discharging on sedimentary rock (Paguyangan) in addition to the cold spring, river, and rainwater as a reference.

GEOLOGY OF THE RESEARCHED AREA

The Slamet Volcano is situated in Central Java and is part of Quaternary Sunda volcanic arc as a result of subduction of the Indo-Australia Plate beneath the Eurasia Plate (Hamilton, 1979). This volcano emerges in the boundary between two Miocene sedimentary basins of North Serayu Mountain and Bogor Zones. Those two sedimentary basins are uplifted forming east-west trending fold. This trend is more or less parallel to the trench that is situated in the southern part of Java. The Bogor Zone distributes from Slamet Volcano to the west, while the North Serayu Mountain spread out to the east of the Slamet Volcano.

Djuri et al. (1996) proposed that the substratum rocks of the Slamet Volcano were sedimentary rocks of Rambatan, and Halang Formation was part of North Serayu Mountain. Those sedimentary rock formations outcrop around the Slamet Volcano (Figure 1). Rambatan Formation was formed in an unstable back-arc basin flank (Husein et al., 2013), producing calcareous sandstone and conglomerate interbedded with shale, marl, and tuff (Djuri et al., 1996: Kastowo, 1975). During the sedimentation of Halang Formation, North Serayu region received supply sediment of volcanic product indicated by volcanic composition of Halang Formation such as andesitic sandstone, tuffaceous conglomerate, and marl with intercalations of sandstone (Djuri et al., 1996).

Sutawidjaja *et al.* (1985) divided the volcanism stages of the Slamet Volcano into two periods: the old and the young periods, which are distinguished by the morphology. The morphology of the old edifice is more dissected and rugged, while the eastern part is characterized by smoother surface. Furthermore, Vukadinovic and Sutawidjaja (1995) have divided the volcanism of

Geochemical Indication of Formation Water Influx to The Volcanic Hosted Hot Springs of Slamet Volcano, Indonesia (A. Harijoko *et al.*)



Figure 1. Regional geological map of Slamet Volcano and surrounding area. Guci and Baturaden hot springs are located on the border of Young and Old Slamet Products, while Paguyangan is located further west on sedimentary rocks of Rambatan Formation (modified from Kastowo, 1975; Sutawijaya *et al.*, 1985; and Djuri *et al.*, 1996).

The Slamet Volcano into three stages: Old, Lebaksiu, and Young stages. The Old Slamet sequence is dominantly composed of andesitic lava and pyroclastic deposit, the Young Slamet sequence comprises dominantly basaltic lava flow, while Lebaksiu sequence is a transition between Old and Young sequences. As of today, the Slamet Volcano is considered as an active volcano. The presently active eruption vent is Young Slamet Volcano in the eastern part of the Slamet Volcano. The last eruption was in 2011 and it is classified as a strombolian type of eruption.

Description of Thermal Manifestations and Hot Spring Clustering

The hot springs around Slamet Volcano occur in three areas: Guci, Baturaden, and Paguyangan. There are two main hot springs in Guci area: Pengasihan and Pancuran Tigabelas. This area is situated about 7.5 km from the Slamet cone to the northwest and at the elevation of about 1,200 m a.s.l. The temperatures of the hot springs are 40.5°C and 50.4°C at Pengasihan and Pancuran Tigabelas, respectively. Pengasihan hot spring has thin travertine deposit, while Pancuran Tigabelas has no significant deposit around it. On the southern flank, Baturaden area has two hot springs: Pancuran Telu and Pancuran Pitu, which are situated about 8 km from the summit and at the elevation of about 762 m a.s.l. (Table 1). The temperatures are 46°C and 50°C at Pancuran Pitu and Pancuran Telu respectively. Pancuran Pitu hot spring is characterized by thick brownish-yellow travertine deposit. Meanwhile, in Paguyangan area there is only one hot spring, named Paguyangan, that discharges at 25 km on the west of Slamet Volcano at the elevation of about 200 m a.s.l. The temperature is about 72°C, and travertine appears as thin reddish substances deposited around the hot spring. Furthermore, steam vents occur as solfatara in the summit of the Young Slamet.

Hot springs in Guci and Baturaden areas are discharged on the border of Young and Old Slamet products, while Paguyangan hot spring is discharged on the sedimentary rock of Rambatan Formation. Further west from Paguyangan, three cold springs are discharged on Rambatan and Halang Formations in Bantarkawung area (Figure 1).

Туре	Location	UTM C	oordinate	Elevation	Sample	Tem- perature	pН	Estimated distance from	Wall rock at discharge point	
		mE	mN	(m)	code	(°C)		Slamet summit (km)		
Hot spring	Baturaden, Pancuran Telu	304534	9191298	698	HP3	50	7	7.53	Basaltic lava	
	Baturaden, Pancuran Pitu	303810	9191933	762	HP7	46	6	7.66	Basaltic lava	
	Guci, Pengasihan	297197	9203712	1,236	HPN	40.5	8	7.39	Volcanic breccia	
	Guci, Pancuran Tigabelas	297559	9204082	1,200	HP13	50.4	8	7.35	Volcanic breccia	
	Paguyangan	280254	9190164	199	HPG	72	7	24.41	Calcareous sandstone	
Cold spring	Baturaden	304398	9191256	685	CSBR	21	6	8.10	Basaltic lava	
	Bantarkawung	272256	9196613	205	CSBK-1	26.9	7	30.82	Sandstone	
	Bantarkawung	270834	9197660	132	CSBK-2	27.4	8	34.25	Calcareous sandstone	
	Bantarkawung	271621	9195488	295	CSBK-3	26.2	7	35.33	Sandstone	
River water	Guci	297559	9204082	1,200	RWGC	22.4	7	7.35	Volcanic breccia	
	Bantarkawung	268536	9197370	146	RWBK-1	27.4	6	34.36	Calcareous sandstone	
	Bantarkawung	268264	9194662	481	RWBK-2	25.7	6	34.49	Calcareous sandstone	
Shallow ground- water	Bantarkawung	269326	9197971	118	GWBK-1	27.8	7	33.78	Calcareous sandstone	
	Bantarkawung	272652	9198184	74	GWBK-2	28.4	8	30.28	Calcareous sandstone	
Rainwater	Bantarkawung	269023	9196350	288	RNBK	28.1	5	34.00		

Table 1. Water Sample Types Used in this Study and the Types of Wall Rock Where the Springs Discharge (Some of which were presented in Harijoko and Juhri, 2017)

Methods

Samples and Sampling Method

Water samples used in this study are tabulated in Table 1, which consist of five hot spring samples taken from Guci, Baturaden, and Paguyangan areas. Aside from the hot spring samples, four cold spring samples were taken from the Bantarkawung and Baturaden to represent meteoric water, as well as three river samples from Bantarkawung and Guci, two shallow groundwaters, and one rainwater sample from Bantarkawung. The water samples were grouped based on its wall rock at discharge points: volcanic and sedimentary rocks. Guci and Baturaden hot springs are discharged on volcanic rock, while Paguyangan hot spring is discharged on sedimentary rock. Old water samples were also collected from cold springs and dug wells tapped at sedimentary rock in Bantarkawung area and volcanic rock in Baturaden. The river water samples were collected from sedimentary and volcanic rock riverbeds in Bantarkawung and Guci, respectively.

The sampling method refers to the procedure suggested by Nicholson (1993) by filtration using 0.45 µm filtrate membrane. Samples for cation and silica analyses were acidified using 0.1 M nitric acid (HNO₃) to eliminate the propensity of cations and silica to precipitate. Some 100 ml polyethylene bottles were used to preserve water for cation-anion analyses, while 25 ml clear glass bottles were used for δ^{18} O and δ^{2} H isotope analyses. Moreover, water temperature, pH, and flow rate (spring) were also measured with portable measurement tool (Table 1).

Laboratory Analysis Method

Major cations (Na, K, Mg, Ca, Li) and anions (F, Cl, SO₄, Br) were analyzed using ion chromatography (Dionex ICS-90 instrument), bicarbonate ion (HCO₃) was analyzed using titration method, while SiO₂, B, Fe, Al, Rb, and As were analyzed using inductive coupled plasma-atomic emission spectroscopy or ICP-AES (Optima 5300 DV series instrument). All analyses were conducted at the Department of Earth Resources Engineering, Kyushu University. The stable isotope analysis was conducted at Department of Earth System Science, Faculty of Science, Fukuoka University, using mass spectrometry.

RESULTS

As seen at Table 1, there is no significant differences on pH observed in both cold and hot water samples in which the cold water has pH range of 5 - 8, while the hot spring water possesses slightly higher pH range of 6 - 8. Meanwhile, Table 2 represents the chemical and stable isotope analysis result of water samples. Some of the chemical data had also been presented in the previous publication (Harijoko and Juhri, 2017). However, a deeper approach and more comprehensive discussion are presented in this article. A reliable result has been obtained for further analysis with ion balance of less than 5%.

Generally, the concentrations of Cl, Br, Li, Rb, B, and SiO, are higher in hot spring water than in cold water. Huge gap, about fifty times larger in hot water (17.30 to 754 mg/L) than in cold water (1.20 to 13.36 mg/L), are observed in Cl- concentration. Furthermore, small difference of Rb, B, and SiO, are detected. Rb in cold waters ranges from 0.13 to 0.21 mg/L and 0.20 to 1.27 mg/L in thermal waters. B concentration in cold water ranges from 0.28 to 0.93 mg/L, and from 2.84 to 6.87 mg/L in thermal water. Twice as much concentration is detected in SiO₂ content, 8.34 to 43.74 mg/L (cold water), and 26.96 to 79.07 mg/L (thermal water). Both Br and Li are found only in thermal water, where Br content ranges from 0.98 to 1.89 mg/L and Li ranges from 0.02 to 0.67 mg/L. Generally, hot springs from Baturaden have the highest concentration of Cl, Br, Li, SiO₂, and Rb, while the hot spring from Guci contains the highest concentration of B.

Table 2. Geochemical Data of Samples (Some of which were presented in Harijoko and Juhri, 2017)

aple code	Li	Na	к	Mg	Ca	F	CI	Br	HCO ₃	SO4	В	NH4	SiO ₂	Fe	Rb	As	Ionic balance	δ ¹⁸ O	δD
San								n	mg/L								‰ vs. SMOW		
RWBK-1	bdl	11.56	0.92	6.90	57.04	0.30	5.07	bdl	197.64	28.6	0.34	0.16	17.85	0.016	0.19	0.001	-1.0	-6.3	-39
RWBK-2	bdl	12.88	1.15	7.53	49.84	0.17	5.36	bdl	198.05	21.24	0.41	0.12	20.86	0.017	0.16	0.002	-2.5	-6.6	-39
RWGC	bdl	10.02	4.30	7.05	14.42	0.20	3.31	bdl	84.38	20.72	0.48	0.01	54.59	0.050	0.18	0.002	-1.8	-2.7	-6
RNBK	bdl	0.62	0.30	0.30	1.37	0.06	1.39	bdl	2.24	5.95	0.28	0.93	bdl	0.027	0.13	0.003	-12.4	-5.1	-32
GWBK-1	bdl	32.4	16.81	15.95	107.1	0.23	31.8	bdl	409.19	60.2	0.42	0.05	30.18	0.021	0.21	bdl	-2.4	-6.2	-38
GWBK-2	bdl	31.6	3.90	14.13	102.2	0.28	28.3	bdl	374.54	40.6	0.40	0.40	30.44	0.016	0.20	0.005	-2.4	-6.6	-40
CSBK-1	bdl	14	7.96	15.8	51.28	0.19	25.26	bdl	195.40	25.32	0.30	0.12	35.32	0.048	0.18	bdl	-1.6	-6.7	-40
CSBK-2	bdl	7.96	0.69	5.31	53.8	0.26	3.96	bdl	201.30	11.23	0.35	0.12	24.69	0.057	0.17	0.003	-2.5	-6.8	-41
CSBK-3	bdl	27.52	0.26	9.11	24.4	0.26	1.2	bdl	185.85	6.16	0.33	0.16	93.57	0.030	0.16	0.002	-1.6	-8.1	-50
CSBR	0.01	12.48	4.29	7.07	10.53	0.12	13.36	bdl	70.15	14.68	0.37	0.01	48.02	0.024	0.16	0.004	-2.3	-6.8	-38
HP3	0.67	389	76	185	193.5	0.15	754	1.89	687.27	609	4.40	0.67	169.14	0.088	1.30	0.023	-1.5	-9.0	-61
HP7	0.58	377	76.7	185	196.5	0.16	724	1.83	695.40	600	3.97	0.58	163.75	0.105	1.27	0.022	-10	-8.9	-60
HPN	0.02	57.3	24.35	29.8	28.9	0.14	17.3	bdl	345.67	32.5	2.84	0.02	121.33	0.028	0.39	0.013	0.6	-8.8	-56
HP13	0.06	129	36.3	46.1	40.1	0.21	44.2	bdl	549.00	89	6.87	0.06	134.83	0.264	0.46	0.019	0.7	-8.8	-60
HPG	0.16	193	2.92	0.23	63.4	0.53	414	0.98	20.33	8.51	3.72	0.16	57.67	0.022	0.20	0.002	-2.1	-5.3	-29

Note: bdl = below detection limit

The concentrations of Na, K, Mg, and Ca as reactive elements are higher in the hot spring samples. The concentrations of Na, K, and Mg in Guci and Baturaden hot spring samples are significantly higher than in the cold water samples. Na ranges from 57.3 to 389 mg/L, K ranges from 24.35 to 76.7 mg/L, and Mg ranges from 29.8 to 185 mg/L. On the other hand, Paguyangan hot springs contain low K and Mg compared to Guci and Baturaden (2.92 and 0.23 mg/L, respectively). Meanwhile, the concentrations of Ca in Guci and Paguyangan hot springs are similar to the cold water samples, and only Baturaden hot springs have higher concentration of Ca (193.5 to 196.5 mg/L). Furthermore, the bicarbonate and sulfate concentrations in Guci and Baturaden samples are generally higher than in the cold water samples (from 345.6 to 695.4 mg/L and 32.5 to 609 mg/L respectively), while Paguyangan hot spring contains lower bicarbonate and sulfate than most of the cold water samples.

Samples from Slamet geothermal area contain δ^{18} O ranging from -2.7‰ to -9.0‰ and δ^{2} H ranging from -6‰ to -61‰ compared to isotope content in seawater (SMOW). Rainwater from Bantarkawung has the heaviest δ^{18} O and δ D contents (-2.7‰ and -6‰, respectively), while Paguyangan hot spring has the heaviest δ^{18} O and δD contents (-5.3% and -29%, respectively) among the other thermal waters.

DISCUSSION

Chemistry and Types of Thermal Water

Understanding the chemical composition of the surface thermal water is important during the exploration stage. The chemical composition may help to understand the subsurface process and the hydrology of the thermal fluid. Although the characteristics of volcanic hosted deep geothermal fluid have been described by several researchers, e.g. White (1957), Ellis and Mahon (1977), and Nicholson (1993), understanding the thermal fluid discharging from geothermal manifestation should be conducted carefully. The deep fluid composition will be modified when it rises to the surface due to water-rock interaction and mixing with shallow ground water. Therefore, the composition of the geothermal manifestation fluid will be masked and is influenced by rock and water types involving in that processes.

In order to understand the chemical characteristics of the hot springs, the abundance and ratio of the elements were compared by using the Schoeller diagram as depicted in Figure 2. In general, hot spring samples show typical charac-



Figure 2. Plotting of geochemical data from the investigated area into Schoeller diagram. Samples with concentration of less than detection limit are not plotted. (Sample codes see in Table 1).

teristic of thermal water that is more concentrated than cold water, especially in the conservative elements (Cl, Br, B), mobile elements (Li, Rb), and As. However, samples from Guci have lowest content of those among the thermal waters. In term of reactive elements, Mg content in thermal water of Guci and Baturaden is anomalously higher than in cold spring followed by high Ca, Na, and K. This is likely due to rock leaching during neutralization (Nicholson, 1993). In contrast, Mg in Paguyangan water is lower than in cold water, resembling the more mature geothermal water discharged from reservoir (Giggenbach, 1991; Nicholson, 1993).

Halogen (Cl, Br, and F) content in thermal water is comparatively higher than in cold water, especially Baturaden and Paguyangan. Halogen content in thermal water can be contributed in rock-water interaction, in magmatic gas diffuse (HCl, HBr, and HF), or in mixing with sea water (Nicholson, 1993). The source of halogen in hot water from Baturaden and Guci is most probably of volcanic origin (magmatic gas), which is also characterized by the balanced content of reactive elements (Na, K, Ca, Mg) and high content of Rb, As, and SiO, from rock dissolution (Ellis and Mahon, 1964; Ballantyne and Moore, 1987; and Giggenbach, 1991). However, halogen content in Guci is lower than in Baturaden indicating a more intensive dilution by meteoric water. Meanwhile, an anomalously higher Br content in Baturaden and Paguyangan seems to be affected by the mixing of water with seawater characteristic, e.g. formation water or connate water in marine sedimentary rock (Nicholson, 1991).

Water types of hot springs were classified based on the composition of main anion components of Cl, SO_4 , and HCO_3 (Giggenbach, 1991) as presented in Figure 3. Baturaden hot spring samples can be classified as sulfate-chloridebicarbonate water since they have a similar content of sulfate, chloride, and bicarbonate. In geothermal areas, sulfate water is common as a result of steam-heated water due to the degassing of H_2S at depth. This kind of water has no or low Cl content, while high sulfate and chloride

concentrations may be the result of volcanic gas condensation. This condensate water may be flowing down slope and mixed with meteoric water. During its passage the water is neutralized by reacting with near surface rocks. This type of water is named advective flow by Hochstein and Sudarman (2015). Hot water from Baturaden may have been resulted from the similar process since it has almost balanced proportion of chloride, sulfate, and bicarbonate so called chloride-sulfatebicarbonate water. This balanced proportion was probably the result of chloride-sulfate water from volcanic gas condensate which was then diluted by bicarbonate-rich meteoric water during advective flow. Meanwhile, Guci hot spring is classified as bicarbonate water similar to the cold water collected from the adjacent of Slamet Volcano (Guci, Baturaden, and Bantarkawung). These hot waters have most probably been diluted by meteoric water in significant degree which is also supported by high Mg content. This implies that Guci hot spring is also the result of advective flow mixed with more proportion of meteoric water. Its chemical composition is therefore similar to the geothermal water.

Origins of Thermal Water

In this study, the origins of thermal water are discussed based on the chemical composition, including stable isotope of deuterium and oxygen-18 of the thermal and cold waters (Figures 2 - 7). Harijoko and Juhri (2017) reported that the hot springs around Slamet Volcano could be distinguished based on the Cl/B ratio into high and low *i.e.* Baturaden and Guci trends. Both trends have similar ratio value but different initial value. Baturaden trend is featured by higher initial Cl but lower initial B concentration compared to Guci trend. Baturaden trend includes Pancuran Telu and Pancuran Pitu of Baturaden area, Paguyangan hot spring, and cold spring from Baturaden. Guci trend includes Pancuran Tigabelas and Pengasihan of Guci area and river water form Guci. This implies that there are two distinctive thermal flows with different subsurface processes.



Figure 3. $Cl-HCO_3$ - SO_4 content in water samples from the studied area (symbols refer to Figure 2). Dotted line connecting Baturaden samples (black filled diamond) and cold water samples (all greyed colour) is indicating dilution of volcanic water by meteoric water (modified from Harijoko and Juhri, 2017). (Sample codes see in Table 1).



Figure 4. Cl/B ratio diagram of water samples from the studied area. Two oval areas indicate a different trend of Guci flow and Baturaden flow. A dashed line connecting fumarole condensate and ocean water is an estimation of parent fluid which the two flow systems is originated. Ocean water reflects formation water in marine sedimentary rock.

In order to understand the subsurface processes, the Cl/B ratio values of the Slamet waters (cold and thermal) were compared with sea water (Purnomo and Pichler, 2014), condensate water of Slamet Volcano (Surmayadi, 2014), and hot spring with sea water input (Purnomo *et al.*, 2016) as depicted in Figure 4. Guci trend represents a mixing line between meteoric water and condensate water of Slamet Volcano. As the value of Cl/B ratio is relatively constant during the mixing with the diluted meteoric water, it might be interpreted that the thermal water included in Guci trend is originally from the condensate water diluted by meteoric water. In contrast, the thermal water in Baturaden trend is a result of the mixing between meteoric water (represented by cold spring) and

Geochemical Indication of Formation Water Influx to The Volcanic Hosted Hot Springs of Slamet Volcano, Indonesia (A. Harijoko et al.)



Figure 5. The single-point diagram (Langelier and Ludwig, 1942) used to represent mixing process among waters in the studied area. (Sample codes see in Table 1, except: Fum. Cnd = Fumarole condensate of Slamet Volcano; Ind Oc = Indian Ocean).



Figure 6. Na-K-Mg-Ca diagram (Giggenbach, 1988) of geothermal waters from the studied area. Guci samples are plotted along fumarole condensate-basalt rock-cold water general trend, while Baturaden samples were plotted slightly deviated to ocean water. Dashed line indicates equilibrium of Na-K-Mg-Ca in different temperature by Giggenbach, 1988. (Sample codes see in Table 1, except: Fum. Cnd = Fumarole condensate of Slamet Volcano; Ind Oc = Indian Ocean; Br = Slamet basaltic rocks).

parental water that are enriched in Cl content but depleted in boron. Furthermore, the value of Cl/B is similar to the trend of hot water recognized as oceanic water origin such as Krakal and Parangtritis (Purnomo and Pichler, 2014). The parental fluid has the value of Cl/B ratio between sea



Figure 7. Stable isotope δ^{18} O vs. δ^{2} H (D) in determination of reservoir geothermal fluid origin. Dotted box indicates the range of δ^{18} O and δ^{2} H (D) composition in andesitic magma water according to Giggenbach, 1992 (Sample codes see in Table 1).

water and condensate water. Therefore, thermal water in Baturaden is interpreted to get influx from water having the composition similar to sea water *i.e.* formation water. Thus, the thermal water may intrude sedimentary rocks filled with formation water of Rambatan Formation and Halang Formation.

The single point diagram from Langelier and Ludwig (1942) gives an even more distinct mixing trend of advective flow from the summit of Slamet Volcano with oceanic (formation) water (Figure 5). A fine trend line is created between condensate sample with meteoric water from Guci and Baturaden resembling the mixing process during advective flow. Hot spring samples from Baturaden fall slightly deviated from the apparent mixture (A) of condensate water and meteoric water towards oceanic water, representing mixing process between apparent mixture products with oceanic water. Paguyangan hot spring water also falls near the oceanic water resembling a close relation with the water. However, since parent fluid of Paguyangan hot spring (deep geothermal water) is unknown, a mixing line cannot be created. On the other hand, Guci hot spring water falls further from the apparent mixture which can

be assumed as a result from other processes (*e.g.* rock-water interaction).

A further approach to understand the geochemical process can be obtained from Mg-Ca-Na-K equilibration from rock-water interaction proposed by Giggenbach (1988). Through this approach, rock-water interaction may be taken into account since mixing is unlikely to be the only process affecting chemical properties of thermal water. The comparison between cation content of geothermal water in the studied area and basaltic rock from Slamet volcanic product (Reubi et al., 2003) is presented in Figure 6. A common trend between condensate water, basalt rock sample, and meteoric water towards Mg-Ca-Na-K equilibrium line is given in the diagram. Water samples from Guci fall in condensate and rock area, resembling a close relation with condensate water from Slamet Volcano and rock interaction during advective flow. Meanwhile, water samples from Baturaden are slightly deviated towards oceanic water samples. On the other hand, sample from Paguyangan is plotted closer to the equilibrium line, resembling that this hot spring water is not directly related with advective flow, but more likely with deep lateral flow from geothermal reservoir.

Stable isotope diagram of δ^{18} O *vs.* δ^{2} H is commonly used to distinguish the type of water. The graph (Figure 7) shows that geothermal water samples from all manifestations are plotted close to global meteoric water line (Craig, 1961). Some water samples are even lighter than the groundwater, therefore the Local Meteoric Water Line (LMWL) is plotted which was proposed by Hendrasto (2005) in Prasetio *et al.* (2015). The rainwater collected from Bantarkawung suggests that local meteoric water line is more appropriate for further interpretation.

The geothermal water commonly has heavier isotope rather than meteoric water, especially the δ^{18} O that is enriched by water-rock interaction processes. When the geothermal water got influx of volcanic volatile, both isotope compositions of δ^{18} O and deuterium would be enriched (Giggenbach, 1992). In the case of hot water around Slamet Volcano, all the water samples are plotted near the LMWL. This indicates that the meteoric water is more dominant as the result of intensive mixing processes between meteoric water and geothermal water. The dominance of meteoric water therefore masks the initial composition of the thermal water. The plot distinguishes the isotope composition into three groups: heaviest, medium, and lightest. The hot waters from Guci and Baturaden are the lightest among the waters (hot and cold waters). The hot waters from Paguyangan and Bantarkawung are

the heaviest. While the cold water, *i.e.* representing meteoric water, is medium. In case of geothermal water, the composition of Guci and Baturaden is anomalous, where the isotope composition of hot water is lighter than the meteoric water from the same area. One possible explanation is that the initial isotope composition of hot water in Guci and Baturaden is light, and therefore they are originated from the highest elevation area. As both Guci and Baturaden are situated at the flank of the volcano, the possible source is the summit area or near the summit area. Moreover, this water is not enriched yet indicating that the water-rock interaction may occur within a short time. Possibly, the mechanism is the intensive mixing between meteoric water with condensate water in the summit. Then this water flows to the lower part forming Guci and Baturaden hot springs.

Hydrology of Hot Water

Figures 8a and 8b represent the discussion from the previous chapter. Magmatic fluid flowing upward to the summit of Slamet Volcano is mixed with the precipitated meteoric water on the summit, resulting in condensate water. The condensate water then flows downward due to the gravity force as advective flow, which is then discharged as Guci and Baturaden hot springs (Figure 8a). However, the advective flow towards Baturaden has passed through sedimentary rock of Rambatan and Ha-



Figure 8. Subsurface section of hydrogeological system along (a) Guci-Slamet Summit-Baturaden and (b) Slamet Summit-Paguyangan.

lang Formations which are estimated to appear at the elevation of 1,100 m a.s.l. (Sutawidjaja et al., 1985), higher than Baturaden at 762 m a.s.l., the interaction with marine sedimentary rocks gives a Cl/B signature of sea water and hot spring with sea water origin. Meanwhile, Paguyangan is located even further to the west and at the lower elevation of 100 m a.s.l. This hot spring is believed to be originated as the outflow discharge from the reservoir (Figure 8b) as shown by dominantly chloride content than bicarbonate and sulfate. The outflow from geothermal reservoir flows laterally to Paguyangan area, passing through sedimentary rock of Rambatan and Halang Formations. Therefore, the signature of Cl/B ratio of sea water and hot spring with sea water origin also appears in Paguyangan hot spring water.

CONCLUSIONS

Guci and Baturaden manifestations are certainly related and produced by volcanic activity of the Slamet Volcano based on its location, yet the origin and subsurface process get a little attention form researchers. Therefore, this study gives a comprehensive discussion in the origin of geothermal water and depict the subsurface process through geochemical approach. Both hot springs are evolved from the condensation of magmatic gas on the summit of the Slamet Volcano flowing downward as advective flow. On the other hand, water from Paguyangan is considered as Cl-rich geothermal water which resembles the outflow discharge of the geothermal reservoir.

Two flow systems are distinguished by Cl/B ratio, single-point diagram of Langelier and Ludwig (1942), and Ca-Mg-Na-K equilibrium diagram of Giggenbach (1988) which resembles the contribution of formation water from sedimentary rock in Baturaden hot spring. However, such signature was not found to appear in Guci hot spring. The signature of formation water also appears in Paguyangan hot spring as the result of outflow of the geothermal reservoir passing through sedimentary rock at depth.

ACKNOWLEDGEMENT

The authors would like to appreciate JASSO (Japan Student Service Organization) for their financial support to Saefudin Juhri during his Student Exchange at Kyushu University. The authors are grateful to Rie Yamashiro san and Ohashi san for their excellent assistance during laboratory analyses in Kyushu University. The authors thank Saefudin Juhri's family for their support during field data acquisition. The authors also acknowledge Dr. Himawan Tri Bayu Murti Petrus and Dr. Fiorenza Deon for their suggestion in English editing and Dr. Dasapta Erwin Irawan for the suggestions and discussion to improve this article.

References

- Ballantyne, J.M. and Moore, J.N., 1988. Arsenic Geochemistry in Geothermal System. *Geochimica et Cosmochimica Acta*, 52, p.475-483.
 DOI: 10.1016/0016-7037(88)90102-0
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science*, 133 (3465), p.1702-1703. DOI: 10.1126/science.133.3465.1702
- D'Alessandro, W., Giammanco, S., Bellomo, S., and Parello, F., 2007. Geochemistry and Mineralogy of Travertine Deposits of the SW Flank of Mt. Etna (Italy): Relationships with Past Volcanic and Degassing Activity. *Journal of Volcanology and Geothermal Research*, 165 (1-2), p.64-70. DOI: 10.1016/j. jvolgeores.2007.04.011
- Djuri, M., Samodra, H., Amin, T.C., and Gafoer, S., 1996. *Geological Map of the Purwokerto* and Tegal Quadrangle, Java, scale 1:100.000.
 Bandung: Geological Research and Development Centre.
- Ellis, A.J. and Mahon, W.A.J., 1964. Natural Hydrothermal Systems and Experimental Hot Water/Rock Interactions. *Geochimica et Cosmoehimica Acta*, 28, p.1323-1357. DOI: 10.1016/0016-7037(64)90132-2

Geochemical Indication of Formation Water Influx to The Volcanic Hosted Hot Springs of Slamet Volcano, Indonesia (A. Harijoko *et al.*)

- Ellis, A.J. and Mahon, W.A.J., 1977. *Chemistry* and Geothermal System. New York: Academic Press, 392pp.
- Giggenbach, W.F., 1988. Geothermal Solute Equilibria. Derivation of Na-K-Mg-Ca Geoindicators. *Geochemica et Cosmochimica Acta*, 52, p.2749-2765. DOI: 10.1016/0016-7037(88)90143-3
- Giggenbach, W.F., 1991. Chemical Techniques in Geothermal Exploration. *In*: D'Amore, F. (ed.), *Applications of Geochemistry in Geothermal Reservoir Development:* UNITAR/UNDP Centre on Small Energy Resources, Rome.
- Giggenbach, W.F., 1992. Isotopic Shifts in Geothermal Waters at Convergent Plate Boundaries. *Earth and Planetary Science Letters*, 113 (4), p.495-510. DOI: 10.1016/0012-821X(92)90127-H.
- Hamilton, W., 1979. Tectonics of the Indonesian region. USGS Professional Paper, 1078.
- Harijoko, A. and Juhri, S., 2017. Cl/B ratio of geothermal fluid around Slamet Volcano, Jawa Tengah, Indonesia. *IOP Conference Series: Earth and Environmental Science*, 103. DOI: 10.1088/1755-1315/103/1/012015
- Hochstein, M.P. and Sudarman, S., 2015. Indonesian Volcanic Geothermal Systems. Proceedings World Geothermal Congress 2015, Melbourne, Australia, 19 - 25 April 2015.
- Husein, S., Jyalita, J., and Nursecha, M.A.Q., 2013. Kendali Stratigrafi dan Struktur Gravitasi pada Rembesan Hidrokarbon Sijenggung, Cekungan Serayu Utara. *Prosiding Seminar Nasional Kebumian Ke-6 Teknik Geologi*, Universitas Gadjah Mada, Yogyakarta, Indonesia, 11 - 12 Desember 2013.
- Kastowo, 1975. *Geological Map of the Majenang Quadrangle, Java, scale 1:100.000*. Bandung: Geological Survey of Indonesia, Ministry of Mines.
- Kementerian Energi dan Sumber Daya Mineral, 2017. Potensi Panas Bumi Indonesia, Jilid I. http://igis.esdm.go.id/igis/img/Buku_Potensi Jilid 1.pdf [11 Nov 2018].
- Langelier, W.F. and Ludwig, H.F., 1942. Graphical method for indicating the mineral character

of natural waters. *Journal of the American-Waterworks Association*, 34, p.335-352. DOI: 10.1002/j.1551-8833.1942.tb19682.x

- Minissale, A., 2004. Origin, transport and discharge of CO₂ in central Italy. *Earth-Science Review*, 66 (1-2), p.89-141. DOI: /10.1016/j. earscirev.2003.09.001
- Mukti, M.M., Ito, M., and Armandita, C., 2009. Architectural Elements of a Longitudinal Turbidite System: the Upper Miocene Halang Formation Submarine-Fan System in the Bogor Trough, West Jawa. *Proceedings, Indonesian Petroleum Association, 33rd Annual Convention and Exhibition,* May 2009.
- Nicholson, K., 1993. *Geothermal Fluids: Chemistry and Exploration Techniques*. Berlin: Springer-Verlag.
- Okumura, T., Takashima, C., Shiraishi, F., Akmaluddin, and Kano, A., 2012. Textural Transition in an Aragonite Travertine Formed under Various Flow Conditions at Pancuran Pitu, Central Java, Indonesia. *Sedimentary Geology*, 265 - 266, p.195-209. DOI: 10.1016/j. sedgeo.2012.04.010
- Prasetio, R., Wiegand, B.A., Malik, D., and Sauter,
 M., 2015. Stable Isotopes Study of Wayang Windu Geothermal Field, Indonesia. *Proceedings of World Geothermal Congress 2015*, Melbourne, Australia, 19 - 25 April 2015.
- Purnomo, B.J. and Pichler, T., 2014. Geothermal Systems on the Island of Java, Indonesia. *Journal of Volcanology and Geothermal Research*, 285, p.47-59. DOI: 10.1016/j.jvolgeores.2014.08.004
- Purnomo, B.J., Pichler, T., and You, C.F., 2016. Boron Isotope Variations in Geothermal Systems on Java, Indonesia. *Journal of Volcanol*ogy and Geothermal Research, 311, p.1-8. DOI: 10.1016/j.jvolgeores.2015.12.014
- Reubi, O., Nicholls, I.A., and Kamenetsky, V.S., 2003. Early Mixing and Mingling In the Evolution of Basaltic Magmas: Evidence from Phenocryst Assemblages, Slamet Volcano, Java, Indonesia. *Journal of Volcanology and Geothermal Research*, 119 (1-4), p.255-274. DOI: 10.1016/S0377-0273(02)00357-8

- Surmayadi, M., 2014. Geokimia Panas Bumi Gunung Slamet Jawa Tengah. *Proceedings of Seminar Nasional Fakultas Teknik Geologi*, Bandung 24 May 2014, p.163-183.
- Sutawidjaja, I.S., Aswin, D., and Sitorus, K., 1985. Geological Map of Slamet Volcano, Central Java, scale 1:100.000. Bandung: Volcanological Survey of Indonesia.
- Vukadinovic, D. and Sutawidjaja, I., 1995. Geology, mineralogy and magma evolu-

tion of Slamet Volcano, Java, Indonesia. *Journal of Southeast Asian Earth Sciences*, 11 (2), p.135-164. DOI: 10.1016/0743-9547(94)00043-E.

White, D.E., 1957. Magmatic, Connate, and Metamorphic Waters. *Bulletin of the Geological Society America*, 68 (12), p.1659-1682. DOI: 10.1130/0016-7606(1957)68[1659:MCAM-W]2.0.CO;2.