Rare Earth Elements Vapor Transport By Fumaroles In The Post Caldera Complex Of Weh Island Submarine Volcano, Aceh Province Northern Sumatra

Transportasi Uap Unsur Tanah Jarang oleh Fumarola dalam Kompleks Post Kaldera Gunungapi Bawah Laut Pulau Weh, Provinsi Aceh Sumatera Utara

Hananto Kurnio and Ediar Usman

Marine Geological Institute (MGI), Jl. Junjunan 236, Bandung 40174 INDONESIA

Corresponding author : hanantokurniosalamun@gmail.com

(Received 09 May 2016; in revised from 17 June 2016; accepted 24 November 2016)

ABSTRACT: Research found out that fumaroles and solfataras are rare earth element (REE) vapor transport agents in Weh Island submarine volcano – Aceh. Shallow high resolution single channel seismic was used to map the distribution of seafloor fumaroles surrounding the submarine volcano. Samples of REE depositions were taken from Jaboi geothermal field, and mineralization zone at Pria Laot coast; as well as seafloor surrounding active fumaroles by divers. Rare earth elements (REE) were analysed using ICP – MS (inductively coupled plasma – mass spectrometry) with detection limits ranged from 0.05 to 0.1 ppm (part per million).

The central part of Weh submarine volcano is the most active REE deposition. This area is build by normal faults and grabens oriented north – south of open character which acted as channel for hydrothermal fluids reaching seafloor surface.

Some REE abundances such as La, Ce, Pr, and Nd due to its location in the central of hydrothermal activity. This proximity explains such abundances of this andesitic component sample of agglomerate.

Keywords: REE, vapor transport, fumaroles, Weh Island, Aceh.

ABSTRAK: *Penelitian mendapatkan bahwa fumarole dan solfatara adalah sebagai agen transportasi uap Logam Tanah Jarang (LTJ) di gunungapi bawah laut Pulau Weh – Aceh, Provinsi Nanggroe Aceh Darussalam (NAD). Seismik saluran tunggal dangkal resolusi tinggi digunakan untuk memetakan fumarole dasarlaut di sekitar gunungapi bawah laut tersebut.*

Bagian tengah gunungapi bawah laut Pulau Weh merupakan area paling aktif pengendapan LTJ. Bagian ini dibangun oleh sesar-sesar normal dan graben berorientasi utara – selatan dengan karakter terbuka sebagai saluran untuk fluida hidrotermal mencapai permukaan dasar laut.

Kelimpahan unsur tanah jarang La, Ce, Pr dan Nd dikarenakan posisinya pada pusat aktivitas hidrotermal. Kedekatan dengan pusat hidrotermal ini menjelaskan kelimpahan REE dari contoh komponen andesitic yang diambil dari aglomerat ini.

Kata kunci: *UTJ (Unsur Tanah Jarang), transportasi uap, fumarol, PulauWeh, Aceh.*

INTRODUCTION

The idea that vapor phase as a possible agent of metal transport in ore-forming hydrothermal systems was only recently known (Gilbert and Williams-Jones, 2008 and Pokrovski et al, 2013). This idea was supported by fluid inclusion analyses (Heinrich et al., 1999) and experiments on solvation and complexation reactions that lead to concentrations of metals in water vapor (William-Jones et al., 2002). The analyses and experiments found out that mass of vapor can exceed that of the liquid which further support the idea of some magmatic hydrothermal deposits possibly have shaped as a result of metals transport in vapor (Gilbert and Williams-Jones, 2008).

The first observation on the formation of crust (encrustation) in the surface volcanism activities was reported by Keller and Krafft (1990) where after one or two days of lava extrusion was observed cover of white sometime greenish and yellow crusts on the lava flow. More recent encrustations were reported by Zaitsev and Keller (2006) which also found similar description of crust formations. Agreements among scientists that the encrustations were resulted from vapor sublimates derived from lava extrusion over a meteoric-water saturated substrate and alteration of lavas by vapors (Genge et al., 2001; Zaitsev and Keller, 2006). According to Mitchell (2006) encrustations are composed of aggregates which is unstable under normal atmospheric conditions.

The study area Weh Island is a submarine volcano in the northwest of Sumatra Island (Figure 1). The island is currently in the state of post caldera complex characterized by reduced volcanism activities (Gasparon, 2005). The reduce activities take the form of mostly fumarole and solfatars observed in seafloor and coastal areas (Kurnio et al, 2015a and Kurnio et al, 2015b). On the other hand, the submarine volcano Weh Island is the part of Sunda volcanic arc extended along the islands of Sumatra, Java and Lesser Sunda Islands. The study area is an arc that consisted of active volcanoes such as Bur Ni Telong and Peuet Sague in Aceh mainland. These active volcanoes are acted as backbone of these islands; where some of them occurred in the sea (Figure 1). Geology regional of the study area belongs to Andaman Sea terrain (Metcalfe, 2006). This terrain is a Neogene to Quaternary extension basin with basement composed of oceanic crust; and consisted of short spreading rifts and transform fault in the middle of Andaman Sea (Curray et al., 1979).

The study area is flourished with post-caldera surface volcano activities. Calderas in Weh Island were formed after catastrophic eruption occurred approximately in Lower Pleistocene which nowadays took the form of bays in the north-northwestern and south-southeastern. Nowadays activities are largely took the form of fumaroles and solfataras. Fumaroles are any gases produced by volcanic activities from the vent which are mostly consists of water vapor; while solfataras if it only produce sulphur deposited surround the vent or crater (Klaus et al., 2005).Fumaroles are indication of reduced volcanic activities (Gasparon, 2005). According to Kilburn and McGuire (2001) solfataras are usually found at shallow crater associated with a dormant or inactive volcano. At Jaboi geothermal surface manifestation, it occurrs as solfataras field.

Fumarole gas composition (unit in % mol) taken from geothermal manifestation Jaboi at the south of Weh Island is consisted of CO_2 (6.79-8.23), H_2S (0.24-0.23), SO_2 (0.12-0.24), NH_3 (0.25-0.37), CH_4 (0.04), HCl (0.05) and H_2O (90.39-91.58) (Kusnadi et al., 2005). Jaboi fumarole gas composition in general indicates its relation with hydrothermal system (Giggenbach, 1980; Arnorsson, 1985; Taran, 1986 and Chiodini, 1989). Surface geothermal activities in this area take the forms of fumarole, sulphur sublimation, hot ground and hot spring. Hot spring type is sulfate acid.

There is a possibility that geothermal hot fluids in the beginning interact with subsurface rocks before becoming hot spring in the surface, especially when relate with ground water and sea water. Hot spring formations in shallow seas and coastal zones of Serui and Pria Laot – in the middle of Weh Island are of choride fluid type (Kusnadi et al., 2005).

It seems that fumaroles in the study area were the agent of metal transport as revealed from geochemical analyses of samples taken closed to the fumarole points which shown

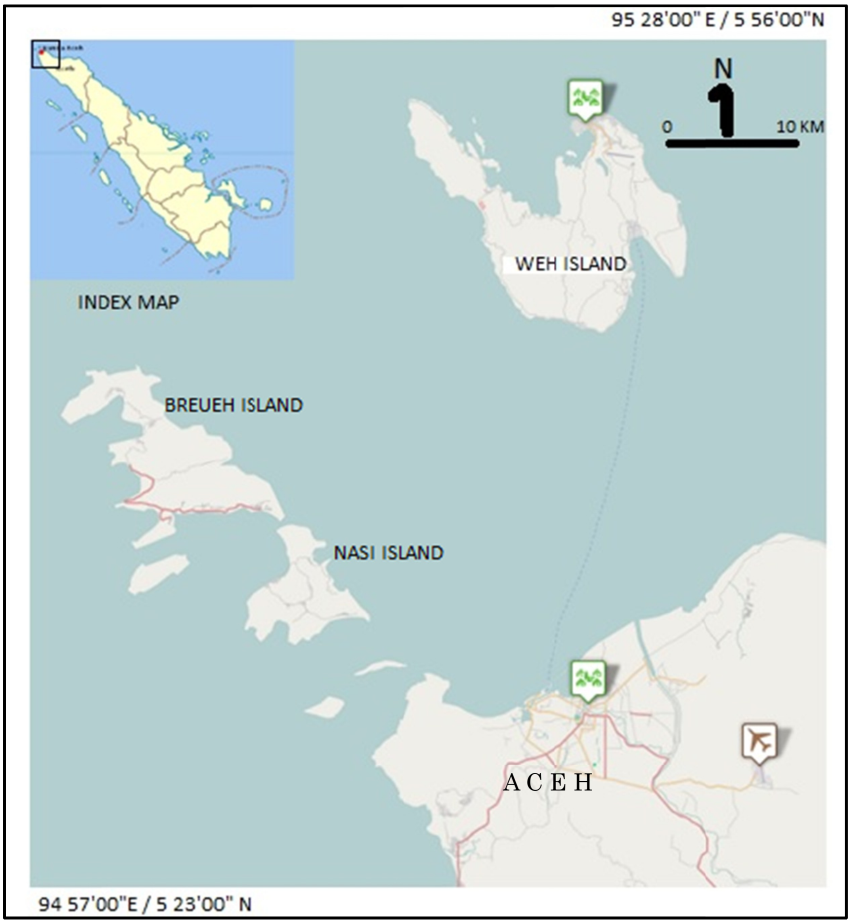


Figure 1. Study area, Weh Island, is located in Northern Sumatra.

quite abundances of rare earth elements.According to Fiske et al. (2001) at the end of volcanism, fumarole activites were the dominant process which produced polymetalic deposits in the vicinities of fumarole points.

Previous study of volcanism in Weh Island had been conducted by Kusnadi et al. (2005). The study was related to geothermal energy for electricity in Jaboi geothermal manifestation area at the south of the Weh Island. One method which have been used was resistivity measurements. Measurements revealed low anomaly less than 10 ohm-m with its southwestern elongation to Keuneukai hot spring and southeastern continuation to Jaboi coastal area hot spring complex (Figure 2A). At deeper resistivity penetration the affected area is resemble with the shallower one but wider (Figure 2B).It indicates the existence of altered subsurface rocks enriched in clay minerals resulted from hydrothermal alteration in acid environment.

METHODS

Samples of encrustations were taken from Jaboi geothermal field, and mineralization zone at Pria Laot coast; as well as seafloor surrounding active fumaroles by divers. At mineralization zone, the samples analysed for microscopic examination as well as geochemical analyses were taken from agglomerate andesitic component. Due to high LOI of the mentioned samples (> 5%), REE contents were also compared with the lava taken from coastal zone surrounding the island. Lava has LOI contents less than 5%. List of samples are presented in Table 1.

All samples were analysed by PT Intertek Utama Services Jakarta, an international laboratory services with main office in London UK. Rare earth elements (REE) were analysed using ICP – MS (inductively coupled plasma – mass spectrometry) with detection limits ranged from 0.05 to 0.1 ppm (part per million). The instruments employed argon plasma as the ionization source and mass spectrometer to determine ions produced.

Microscopic observation of petrography analyses were conducted to describe some features relate to encrustation proccesses, as well as its textures. Optic mineralogy informations such as forms and colours were collected to identify microscopically observed minerals.

Temperature was also measured in the field using Water Resistant Digital Probe Thermometer Model BG 363 Blue Gizmo with accuracy +/- 1^{o}C, range -10 to 200^{o}C and resolution 0.1^{o}C. Temperature measurements were conducted at the very active surface volcanism in the coastal zone of middle Weh Island.

The survey was carried out throughout marine area surrounding Weh Island which took approximately 150 kilolines of seismic and bathymetry and to sea depths below 100 meters for safety reason. Samples for REE geochemical examinations were taken in seafloor in the vicinity of active vents that still emits fumaroles appear as gas bubbles in sea water column with strong sulphur

Table 1. General description of samples used and analysed

NO	SAMPLE CODES	LOCATION	DESCRIPTION	GEOCHEMICAL ANALYSES
1	KPW7	Coast	Andesitic lava	REE
2	KPW8	Coast	Gravelly sand	REE
3	KPW9	Coast	Andesitic lava	REE
4	KPW10	Coast	Andesitic lava	REE
5	KPW11	Coast	Andesitic lava	REE
6	KPW12	Coast	Andesitic lava	REE
7	M01B	Coast	Agglomerate	REE
8	JABOI SOLFATARA	Jaboi geothermal	Sulphur deposit in the rim of solfatar crater	REE
9	JABOI 244/60	Jaboi	Rhyolite	REE
10	SERUI–A–5 M (DIVING)	Seafloor	Andesitic lava	REE
11	SERUI–A 10 M (DIVING) (S)	Sea floor	Sand dominant andesite fragments	REE
12	SERUI-B-10 M (DIVING)	Seafloor	Altered (kaolinization?) andesitic lava	REE
13	SERUI-B-15 M (DIVING) (S)	Seafloor	Sand dominant andesitic fragments and mafic	REE
14	SERUI-C-23 M (DIVING) (S)	Seafloor	Sand dominant andesite fragments	REE
15	SERUI-D(DIVING)	Seafloor	Altered lava	REE
16	SERUI-E-(DIVING)	Seafloor	Limestone	REE

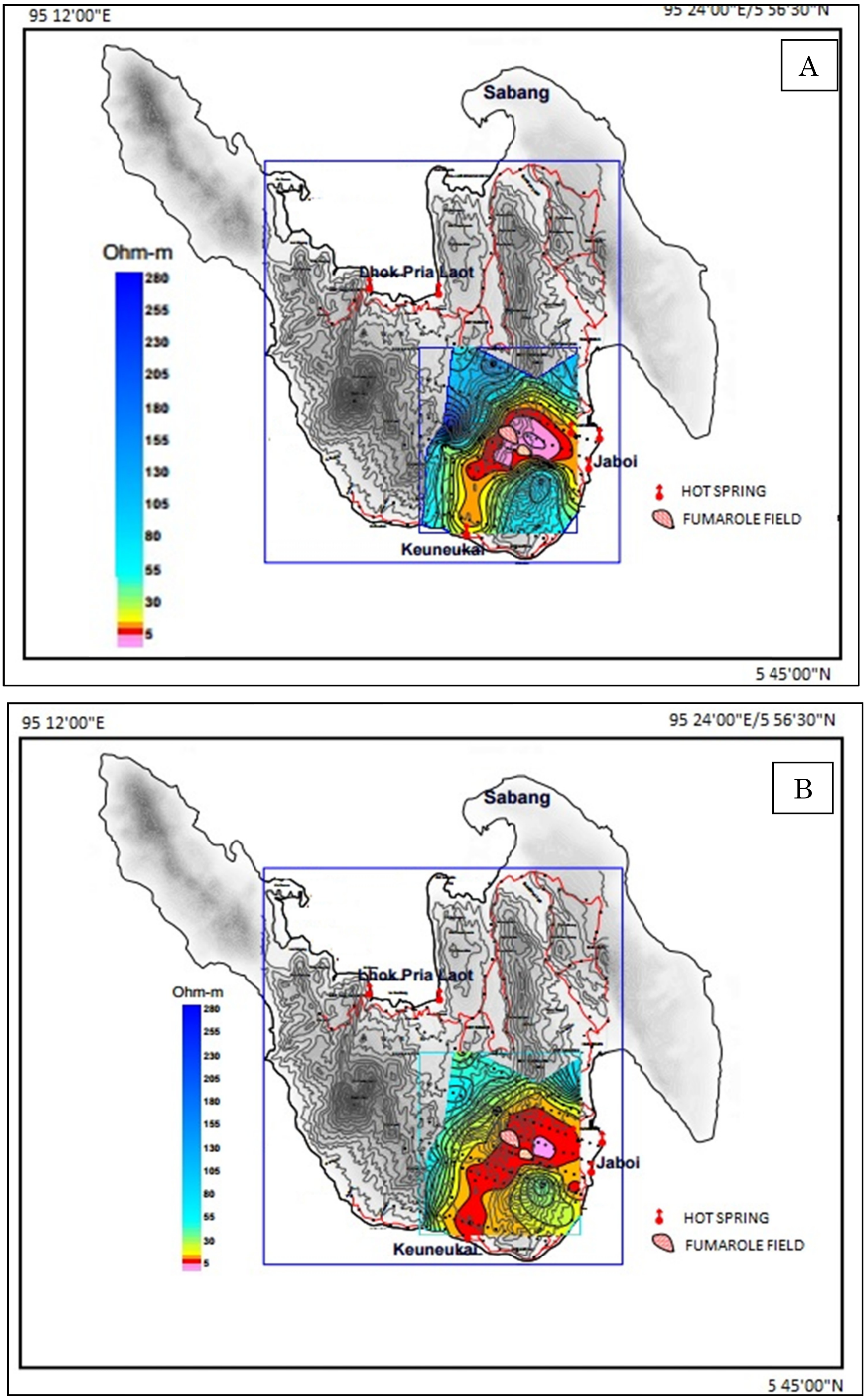


Figure 2. Resistivity surrounding geothermal manifestation Jaboi at the central of Weh Island; shallow (500 m, 2a) and deeper (750 m, 2b) (Source: Kusnadi et al., 2005). The shallow and deeper resistivity demonstrates development to southwest and southeast and possibly offshore (Koesnadi et al, 2005).

odour observed in the sea surface. The samples were collected by divers, and surround the active seafloor vents could be observed encrustations of rare earths (Kurnio et al, 2016).

RESULTS

The fumaroles are mostly taken place in the middle of Weh Island. This area is consisted of normal faults and grabens of relatively oriented north – south. The faults of this part are differ from general direction of Sumatra Fault which oriented northwest – southeast and are also of different character; where the former is dilatational and the latter compressive.

Surface volcanism activities are listed in Table 2. These activities could be seen either at seafloor or coastal zone especially at Serui and Pria Laot in the middle of study area. Figure 3 shows sample locations for this vapour transport study.

After geochemical analyzes, seafloor samples taken in the surrounding of active fumaroles by divers in Serui (sample code SERUI-) reveal its rare earth element contents. For the purpose of rare earth elements vapour transport study, these samples were also compared to REE values of lava taken from coastal zone around Weh Island (KPW-); as well as agglomerate (M01B) from mineralization zone in Pria Laot beach (Table 3). From the Table reveals that some REE such as La, Ce, Pr, and Nd are the most abundance in agglomerate sample (M01B) compared to other sample types. The sample analysed was taken from agglomerate andesitic component, and its location is in the central of hydrothermal activity in Pria Laot coast (see also Figure 6 for sample M01B location). This proximity to hydrothermal activity explains some REE content abundances of this sample.

The formation of crust surrounding active fumaroles (encrustations) also produce native sulphur crystals as observed in the solfataras field in hydrothermal surface manifestation of Jaboi (Figure 4). According to Zaitsev and Keller (2006) native sulphurs were sublimates precipitates from volcanic gases.

Figure 5 demonstrates microscopic encrustation formation in the study area. The encrustations take place as white color rim surrounding existing minerals such as quartz and metal minerals. The cracks are also filled with metal mineral which possibly brought by hydrothermal fluids. Area of influence was done relate to surface hydrothermal activities in Pria Laot beach (Figure 6).

DISCUSSION

Rare earth elements are not known until recently that its accumulation could be facilitated by vapour transport relate to either active or inactive volcanism (Genge et al, 2001; Williams-Jones et al, 2002 and Gilbert and Williams-Jones, 2008). This discovery could revolutionize exploration of REE not just in the geological scheme of old deposits but it could also be found in the vicinities of active or inactive volcanism. In Indonesia, active volcanic belts are distributed along western coastal areas of Sumatra, south of Java and to the east of Lesser Sunda Islands; on the other hand, inactive volcanic belts are distributed a little bit westward of Recent volcanoes of Sumatra and southward of Java and Lesser Sunda Islands.

CONCLUSIONS

It could be concluded that fumaroles and solfataras are REE vapor transport agents in submarine volcano of Weh Island – Aceh Province. Distribution of fumaroles

Table 2. Volcanism activities as observed at Serui Beach middle of Weh Island (no sample collected, field work only temperature measurements)

NO	VOLCANISM ACTIVITIES	TEMPERATURE	NOTES
1	Mud pool	1. 42,4º 2. 66,0° 3. 69,2º 4. 77,7° 5. 79,4º	Temperature measurements were carried out using digital thermometer of capacity 200ºC, in the middle and periphery of mud pool
2	Hot spring	1. 88,3º 2. 85,0º 3. 95,3º 4. 85,6º 5. 58,1º	The activities were occurred at nearby points
3	Fumaroles / solfatars	1. 46,1º 2. 47,6º	Sulphur deposits were found in the vicinity of solfataravents
4	Hot spring	1. 92,2º 2. 71,0º	Measurements were separated about 50 meters

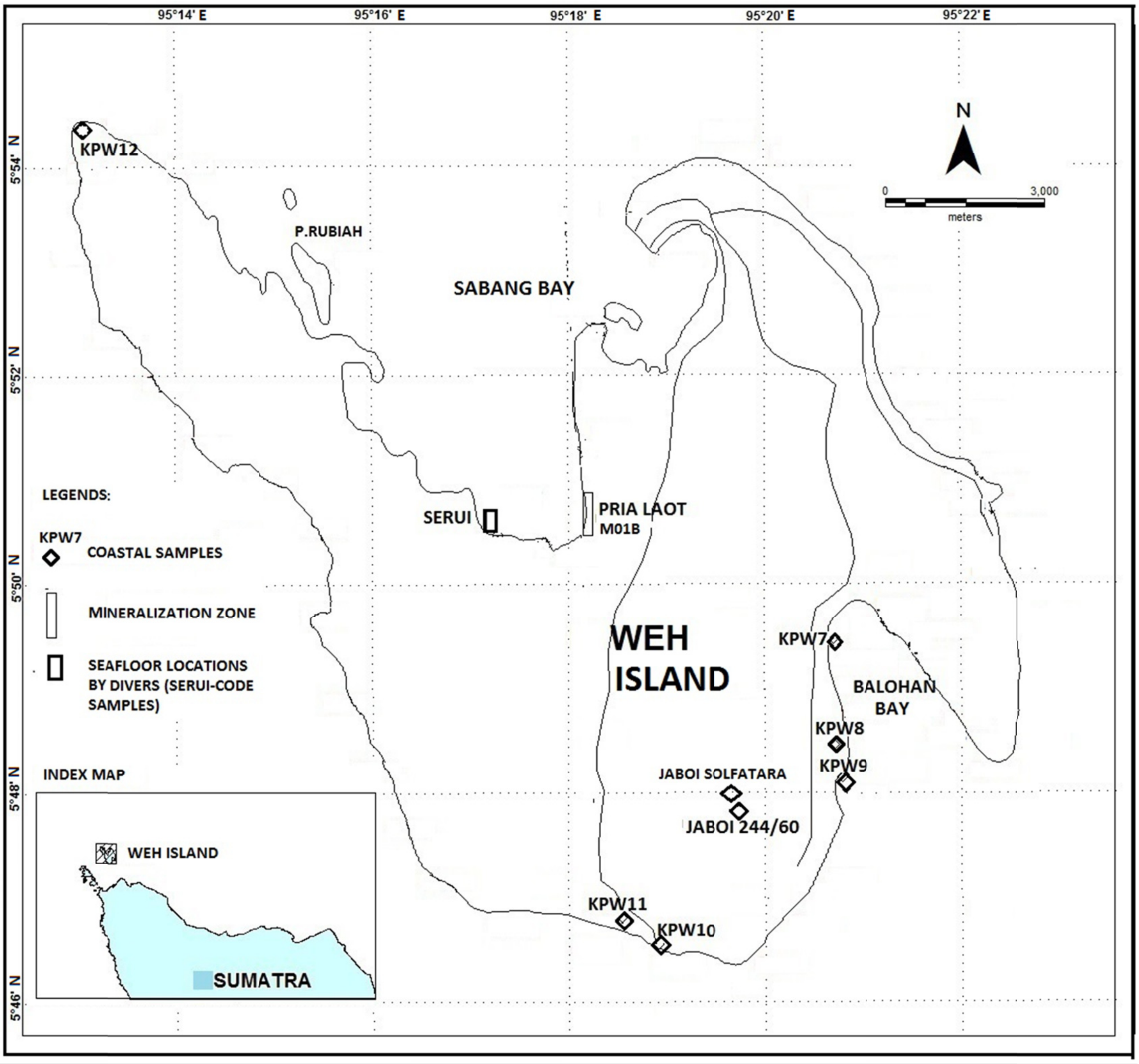


Figure 3. Map shows selected sample locations surrounding Weh Island.

Table 3. Rare earth element (REE) contents in lava (KPW-), encrustations (JABOI- and SERUI-) and agglomerate (M01B).

ppm	KPW 07	KPW 08	KPW 09	KPW 10	KPW 11	KPW 12	M01B	JABOI SOLF.	JABOI 244/60	SERUI-A-5 M (DIV.)	SERUI-A-10 M (DIV.)(S)	SERUI-B-10M (DIV.)	SERUI-B-15 M (DIV.)(S)	SERUI-C-10M (DIV.)	SERUI-C-23M (DIV.)(S)	SERUI-D- (DIV.)	SERUI-E- (DIV.)
La	21	19.7	22.9	10.7	20.8	17.1	25.7	0.2	0.6	17.4	13.7	14.3	20.2	13.9	15.5	17.7	0.6
Ce	50.3	46.4	48.1	25.3	43.9	41	56	0.4	1.4	37.6	30	30.8	42	35.2	35.2	39	1.5
Pr	5.2	5.43	6.13	3.02	5.04	4.37	6.5	0.025	0.17	5.14	3.56	4.4	4.58	4.78	4.05	4.78	0.17
Nd	19.2	20.7	23.2	12.2	18.8	16.9	24.8	0.2	0.6	20.4	14.5	18.3	18.6	21.8	17.2	21.8	0.7
Sm	4.1	4.7	4.6	2.9	4	3.9	3.7	0.05	0.1	5	2.9	4.9	3.7	5.5	4.2	5.3	0.1
Eu	1	1.1	1	0.8	0.9	1	0.6	0.05	0.05	1	0.6	1	0.8	0.9	0.8	0.9	0.05
Gd	4.2	4.2	4.1	2.9	4	3.5	3	0.05	0.1	4.2	2.7	4.7	4	5.2	4.2	5.3	0.2
Tb	0.53	0.56	0.52	0.46	0.48	0.55	0.27	0.025	0.025	0.63	0.38	0.75	0.49	0.73	0.55	0.69	0.025
Dy	3.3	3.6	3.2	3.1	3.1	3.1	1.1	0.05	0.2	4.4	2.4	4.1	3.1	5	3.4	4.8	0.1
Ho	0.6	0.7	0.6	0.7	0.6	0.7	0.2	0.05	0.05	0.9	0.5	0.9	0.6	1	0.7	1	0.05
Er	1.7	2.1	1.8	1.8	1.6	2.1	0.4	0.05	0.05	2.3	1.4	2.6	1.8	2.7	1.9	2.6	0.05
Tm	0.3	0.3	0.3	0.3	0.3	0.3	0.05	0.05	0.05	0.4	0.2	0.4	0.2	0.4	0.3	0.4	0.05
Yb	1.8	2	1.8	1.9	1.7	1.9	0.4	0.05	0.1	2.2	1.4	2.5	1.7	2.6	1.8	2.5	0.1
Lu	0.28	0.32	0.32	0.3	0.28	0.31	0.07	0.025	0.025	0.83	0.21	0.41	0.28	0.42	0.29	0.37	0.025

Notes: KPW-, JABOI-, SERUI- and M01B are sample codes for REE analyses. (DIV) is andesitic lava sample code taken by divers and (S) for sediment

Figure 4. Jaboi solfataras field. It is observed that in the crater rim was deposited native sulphur (red square).

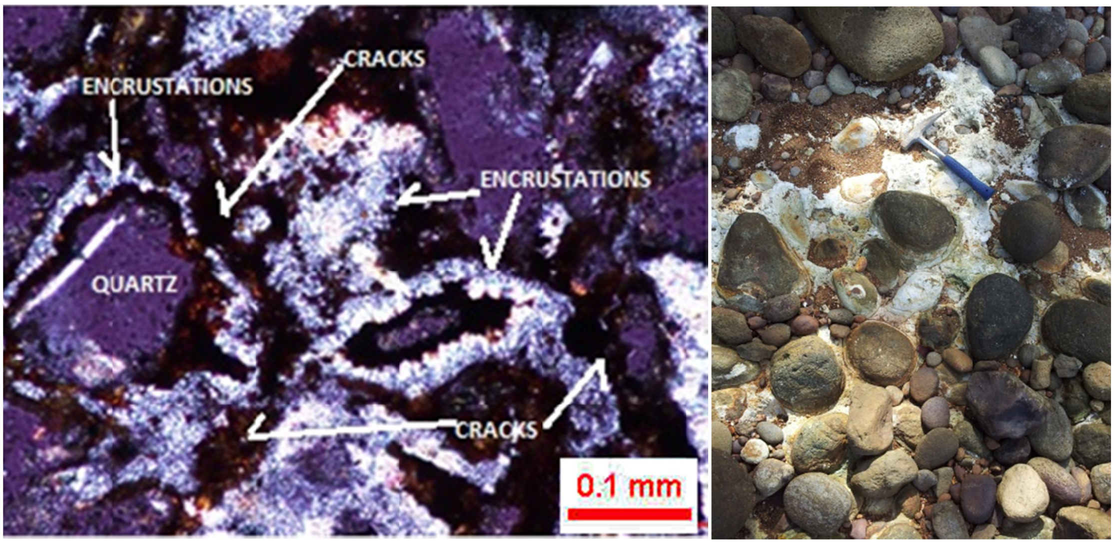
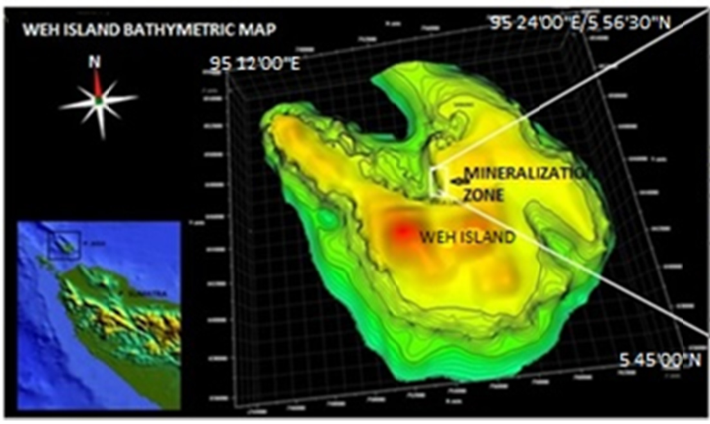


Figure 5. Microscopic thin section of agglomerate andesitic component demonstrates encrustations around the cracks (left, cross nicol). Agglomerate outcrop (right) shows white colour encrustation at groundmass surrounding andesitic components. The sample was taken at Pria Laot beach in the middle of Weh Island.



AREA OF HYDROTHERMAL INFLUENCE

NO	DISTANCE (M)	LITHOLOGY	NOTES
0	START OF MEASURED SECTION	AGGLOME-RATE	WHITE ENCRUST. AMONG AGG. COMPONENTS (MS01B)
1	0-30	AGGLOM.	
2	33	AGGLOM.	HOT SPRING
3	37.5	AGGLOM.	ALTERED
4	120	ANDESITE LAVA	ALTERED & STRONG SILICIFICATION
5	180	LIMESTONE	FORMATION OF RHODOCHROSITE (MnCO3),Mn 1.74%
6	187	LIMESTONE	RHODOCHROSITE

Figure 6. Area of hydrothermal influence activities in Pria Laot beach (right) and its location (left).

in the seafloor were mapped through shallow high resolution single channel seismic.

The most active rare earth elements (REE) deposition takes place at the central of Weh Island submarine volcano which is constructed by normal faults and grabens which are oriented approximately north – south and of tensional or open character and acted as channel for hydrothermal fluids reaching seafloor surface.

It reveals that some REE such as La, Ce, Pr, and Nd are the most abundance in andesitic component sample of agglomerate compared to other sample types and its location is in the central of hydrothermal activity in Pria Laot coast. This proximity to hydrothermal activity explains some REE content abundances of this andesitic component.

ACKNOWLEDGEMENT

We would like to thank to the management of Marine Geological Institute for providing us with budget, personnel and equipment to conduct research on submarine volcano in Weh Island Aceh. Thanks are also for team members for their great contributions especially in field works. We would like also to thank to the local government and people of Sabang that facilitated us on doing this research, that could not be mentioned one by one.

REFERENCES

Arnorsson, S., 1983, New gas geothermometers for geothermal exploration calibration and application, GeochimicaetCosmochimicaActa Vol. 49, pp 1307-1325

Chiodini,G., 1989, Gas geobarometry for hydrothermal systems and its application to some Italian geothermal areas, Applied geochemistry, Vol . 4, pp 465-472

Fiske, R.S., Naka, J., Iizasa, K., Yuasa, M. And Klaus, A., 2001. Submarine silicic caldera at the front of the Izu-Bonin arc, Japan: Voluminous seafloor eruptions of rhyolite pumice. The Geological Society of America Bulletin, v.113 no.7 p. 813-824.

Fournier,1981, Application of WaterGeochemistry Geothermal Exploration and Reservoir Engineering, “Geothermal System: Principles and case Histories”. JohnWilley&Sons, New York.

Gasparon, M., 2005. Chapter 9. *Quarternary volcanicity.* Eds. Geological Society, London, Memoirs 2005; v.31; p. 10.1144/GSL. MEM. 2005.031.01.19.

Genge, M.J., Balme, M., Jones, A.P., 2001. Salt-bearing fumarole deposits in the summit crater of OldoinyoLengai, Northern Tanzania: interactions between natrocarbonatite lava and meteoric water. Journal of Volcanology and Geothermal Research 106, 111–122.

Giggenbach, dkk, 1988, Methods for tthe collection and analysis of geothermal and volcanic water and gas samples, Petone New Zealand

Gilbert, C.D. and Williams-Jones, A.E., 2008.Vapour transport of rare earth elements (REE) in volcanic gas: Evidence from encrustations at OldoinyoLengai. Journal of Volcanology and Geothermal Research 176 (2008) 519-528.

Heinrich, C.A., Gunther, D., Audetat, A., Ulrich, T., Frischnecht, R., 1999.Metal fractionation between magmatic brine and vapour, determined by microanalyses of fluid inclusions. Geology 27 (8), 255-258.

Keller, J., Krafft, M., 1990.Effusive natrocarbonatite activity of OldoinyoLengai, June 1988. Bulletin of Volcanology 52, 629–645.

Klaus K. E. (2005). Jackson, Julia A.; Mehl, James P.; Neuendorf, Klaus K. E., eds. Glossary of Geology.Springer Science & Business Media.p. 257. ISBN 9780922152766.Retrieved 2015-06-06. fumarole field[:] A group of cool fumaroles.

Kooten, 1987, Geothermal Exploration Using Surface Mercury Geochemistry, Journal of volcanology and Geothermal Research , 31, 269-280.

Kurnio, H., Syafri, I., Sudradjat, A., Rosana, M.F. and Muslim, D., 2015a. Seafloor Faulting and its Relation to Submarine Volcanic Activities Based on Sub Bottom Profiling (SBP) Analyses in Weh Island Waters and its Surrounding, Nanggroe Aceh Darussalam Province. Bulletin of the Marine Geology, Vol. 30, No. 1, pp. 1 to 10.

Kurnio, H., Lubis, S. and Widi, H.C., 2015b. Submarine Volcano Characteristics in Sabang Waters. Bulletin of the Marine Geology, Vol. 30, No. 2, pp. 85 to 96.

Kurnio, H., Syafri, I., Sudradjat, A. and Rosana, M.F., 2016. Sabang Submarine Volcano Aceh, Indonesia: Review of Some Trace and Rare Earth Elements Abundances Produced by Seafloor Fumarole Activities. Indonesian Journal on Geoscience Vol.3 No.3 December 2016: 173-182.

Kusnadi, D., Supeno and Purwoto, E., 2005. Penyelidikan geokimia panas bumi Daerah

Jaboi, Sabang, Nanggroe Aceh Darussalam. Pemaparan Hasil Kegiatan Survei Panas Bumi 2005. Pusat Sumber Daya Geologi (In Bahasa Indonesia).

Pokrovski,G.S., Borisova, A.Y. and Bychkov, A.Y., 2013. Speciation and Transport of Metals and Metalloids in Geological Vapors.Reviews in Mineralogy and Geochemistry, Vol. 76. No.1, p. 165-218.

Scher, S., 2012. Fumarolic Activity, Acid-Sulfate Alteration and High-Sulfidation Epithermal Precious Metal Mineralization in the Crater of Kawah Ijen Volcano (Java, Indonesia). A thesis submitted to McGill University in fulfillment of the requirements of the degree of Master of Science. Department of Earth & Planetary Sciences McGill University Montreal, Quebec, Canada.

Taran, 1986, Gas Geothermometers for hydrothermal Systems, Geochemistry International Vol. 23 No.7, 111-126

Williams-Jones, A.E., Migdisov, A.A., Archibald, S.M., Xiao, Z., 2002. Vapour transport of ore metals. In: Hellman, R., Wood, S.A. (Eds.), Water-Rock Interactions, Ore Deposits, and Environmental Geochemistry: A Tribute to David A Crerar. Special Publication, vol. 7. The Geochemical Society, pp. 279-305.

Zaitsev, A.N., Keller, J., 2006. Mineralogical transformations of Oldoinyo Lengainatro carbonatites, Tanzania. Lithos 91, 191–207.