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Deducing Geothermal Boiling Zone from Rare Earth Elements on Early-Stage Geothermal Exploration

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ABSTRACT

An integration of REEs analysis, oxygen and hydrogen isotope ratios and normalized-to-host rocks REEs series from eight acidic hot spring waters were investigated. The REEs concentrations in both types of sulfate and bicarbonate water introduced large variations with 3σ of background level (BGD), with some undetected values. The varying distribution patterns in the light REEs presumably resulted from either due to shorter water-rock interaction times, which refers to dilution with meteoric water, or the presence of boiling zone. Two distinctive sulfate hot springs came up as the signature representatives of boiling zones in geothermal system. Boiling zones were predicted from hot spring with positive Eu anomaly and enriched oxygen isotope. Meanwhile, positive Ce anomaly could bring a hint of fully developed stage of water-rock interaction process in a geothermal system. Reversely, negative Ce anomaly gives a prediction of mixing geothermal fluid with surface water. Analyses of the REEs integrated with isotopes and chemistry analyses can provide an assistance to support geochemistry approaches for identifying geothermal flow paths and boiling zones in a preliminary stage of geothermal exploration.

1. INTRODUCTION

Concentrations and geochemistry of rare earth elements (REEs) especially in acid-sulfate geothermal springs and volcanic rocks may provide important indications to the nature of water–rock interaction and the process of mineralization in geothermal systems (Wood, 2006). REEs are often utilized by geochemists as stamps of different rock types, because their composition resembles those of the primary rocks sources during fluid migration. In many studies, REEs fractionation has been focused on acidic waters and their water-rock interaction relationships. Acid-sulfate features and alteration may identify areas overlying a permeable boiling zone, even though some caution in interpreting it is necessary, as impermeable zones always present as a barrier zone. Thus, under such circumstances, the presence of acid discharge features may also point out to thinning horizontal impermeable zones (clay caps). As geothermal manifestations have a range of pH with their specific origins, few have paid particular attentions to analyze possible boiling process in a geothermal field by using the REEs. Thus, an integration of REEs analysis, oxygen and hydrogen isotopes are implemented in this paper in order to track the process of boiling process, providing a supplemental assistance to enrich hydrogeological analyses in geothermal exploration phase.

2. GEOLOGICAL SETTING

The study area selected, Wayang Windu Geothermal Field (WWGF), is located in 48S UTM 784,000 to 796,000 mE and 9,212,000-9,202,000 mN 40 km southern part of the West Java's capital city, Bandung. WWGF and the accompanying Karaha-Bodas (southeastern) and Tangkuban (southwestern) are examples of volcano-hosted liquid-vapor-dominated reservoirs in West Java, Indonesia. Twenty years ago, WWGF was a juvenile geothermal field. But now it has been recognized as a notably transitional geothermal system which generating a total of 227 MWe from two units with a single turbine generator. Even though now the physical and chemical properties of surface manifestations in WWGF might be slightly changed due to production activities, we assume they still represent the characteristics of subsurface activities for the REEs analysis.

Many geothermal manifestations in WWGF are located in multifarious elevations (1,400 to 1,900 masl). The hot springs have pH vary between 2.9 to 8.9, with temperatures ranging from ambient to 64°C. Fumaroles have temperatures of 93°C, with local boiling point and are associated with acid sulfate hot springs as well as mud pools and altered grounds. In this study, only hot springs are the main focus (Fig. 1). MBA, Wayang, and Cibolang hot springs are located in higher altitudes, close to fumaroles in each area. The rest of them are located in relatively plain terrain, and their presences are probably related to the surface faults (both conjectured or exposed faults). Compiled from Soestrisno (1983) and Riyadi (2007), there are six types of aquifers govern the hydrological flow (Fig. 1).

3. MATERIAL AND METHODS

In this study, eight samples from hot spring were collected on August 2016 (Fig. 1 and Table 1). Physicochemical parameters of sample fluids, such as temperature, pH, and electrical conductivity (EC), were measured in-situ using a portable Horiba multimeter. The amount of 250mL of samples from each location were filtered through 0.45 μm pore-sized filter papers into HDPE bottles for anions and silica analysis, and 50mL were also filtered and collected for cations and trace elements analysis. Some of them were prepared unfiltered and acidified for bicarbonate analysis. The bottles were previously washed thoroughly with dilute nitric acid and then with distilled water in the laboratory. Each bottle was washed three-times with sample water before final sampling. The samples were brought to Japan from Indonesia inside Pelican boxes to be analyzed in Kyoto University laboratory. Concentrations of major geothermal elements, bicarbonate, major anion-cation, and water isotopes were measured by using standard titration, Shimadzu ion chromatograph, and Picarro water isotope analyzer, respectively.

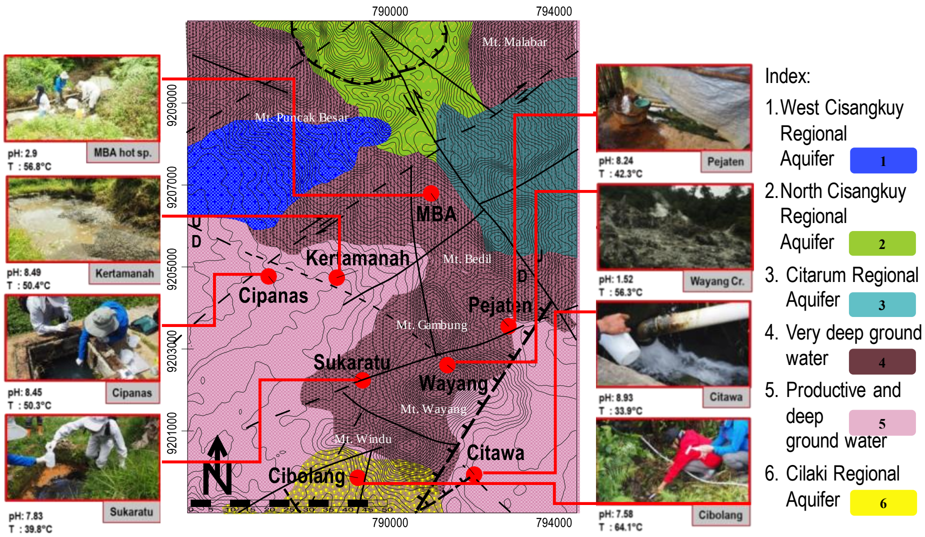

Figure 1: Eight hot springs were visited on August 2016 in Wayang Windu geothermal field. There are six types of aquifers govern the hydrological flow. Mostly hot springs are located in the productive and deep groundwater (Index #5 and #6).

4. RESULTS AND DISCUSSIONS

4.1 Major composition for determining type of fluids

The results for major elements from water samples are shown in Table 1, presenting MBA and Wayang are typical acid-sulfate geothermal springs, Citawa is a typical of sulfate-bicarbonate, and the rest are bicarbonate waters. Wayang and MBA hot springs are derived from steam-heated water, where steam from the possible boiling zones rises to near surface and contact with shallow groundwater. Owing to the fact that hydrogen sulfide present in the steam tends to be oxidized at the surface by atmospheric oxygen. Formation of sulfuric acid in this way may cause steam heated surface water to attain low pH around 1-2 and potentially alter soil and rock to produce surficial zones of acid leaching. Then acid steam-heated pools and mud-pools are developed like those in Wayang and MBA-Burung fumaroles. This is a common preliminary premise of deducing a boiling zone on thinning impermeable zones in an early-stage of geothermal exploration.

Table 1. Field measurements, major ions and selected trace elements concentration of hot spring samples.

No	Location	pH	T (°C)	EC (µS/cm)	Al (mg/l)	Ba (µg/l)	Fe (mg/l)	Si (mg/l)	Sr (mg/l)	K^+ (mg/l)	Na^+ (mg/l)	Mg^{2+} (mg/l)	Ca^{2+} (mg/l)	SO_4^{2-} (mg/l)	F^- (mg/l)	Cl^- (mg/l)	HCO_3^- (mg/l)
1	Cibolang	6.30	64.1	0.99	0.02	55.91	0.03	101.04	0.28	22.45	54.12	36.77	63.36	14.61	0.01	1.36	420.00
2	Cipanas	6.40	50.3	n. a	0.01	58.95	0.52	91.32	0.11	29.63	54.94	20.58	37.77	15.03	0.06	0.34	275.00
3	Kertamanah	6.65	50.4	0.90	0.03	15.94	0.19	86.81	0.27	11.27	41.18	24.67	76.42	7.97	0.02	0.25	406.00
4	MBA	2.72	56.8	n. a	0.01	88.48	0.52	113.85	0.20	27.05	80.42	27.79	45.35	12.40	0.03	0.17	0.00
5	Pejaten	6.00	42.3	0.34	9.61	3.02	2.83	53.66	0.01	2.12	4.73	2.81	4.97	6.29	0.03	0.16	94.60
6	Sukaratu	6.60	39.8	n. a	0.02	29.51	1.14	94.81	0.09	8.90	15.68	9.53	24.58	10.08	0.02	0.45	548.00
7	Wayang	1.30	56.3	12.70	0.02	72.00	1.22	80.21	0.32	15.67	92.11	43.65	60.04	31.55	0.00	0.10	n. a
8	Citawa	6.20	33.9	0.86	101.04	94.83	11.26	196.59	0.42	24.24	8.15	2.77	6.73	145.37	0.07	0.63	73.82

n.a — not analyzed

Unlike sulfate waters, bicarbonate hot springs are typical outflow zone (Nicholson, 1993). Steam-heated CO_2 waters form marginal high-temperature aquifer generally bring low H_2S content. Hot springs with high mean concentrations of SO_4^{2-} and Ca along with lower concentrations of HCO_3^- that are Wayang and MBA (Table 1) may indicate a deep circulation for the thermal springs. This finding corresponds with their positions in the productive and deep groundwater of Index #5 in Fig. 1. Thus, Wayang and MBA springs may be considered as deep volcanic water derived of oxidized sulfur gas phase from a boiling zone.

4.2 Oxygen and hydrogen isotopes

Local meteoric water line in Fig. 2 was obtained by Hendrasto (2005). All of hot springs were derived from meteoric waters, some of hot springs either encountered contact with hot vapor from the depth resulting steam-heating fluid or had water-rock interaction process (in case of Wayang hot spring). Its enriched value of oxygen isotope ratio denotes that the sample probably has interacted with rocks, which gives greater enrichment in oxygen isotope value. As Wayang and MBA are located in the similar elevation (around 1,900 masl), the values of their isotopes should have shown significant depletion, if we assume their source is from meteoric water at higher elevation. But in this case, Wayang shows different pattern. It can lead to another assumption that meteoric water from lower elevation have experienced water-rock interaction and steam-heating processes before appear as Wayang hot spring. MBA has probably undergone dilution of steam-condensate with an aquifer near to surface since its position is apparently adjacent to the local meteoric water line.

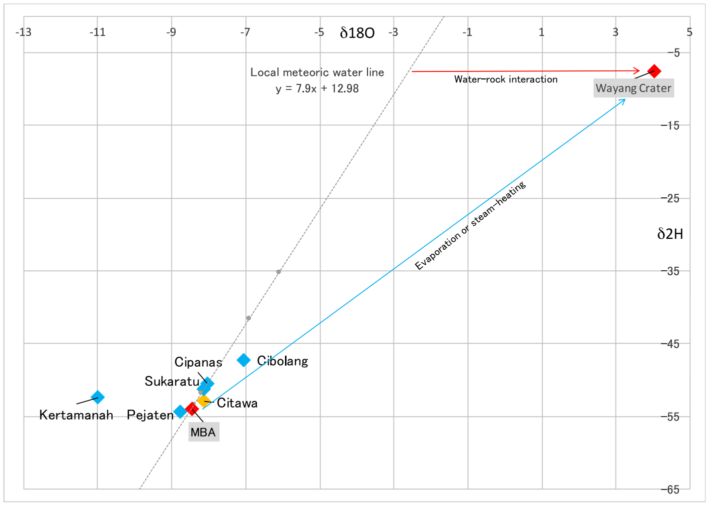

Figure 2: Isotopic trends of hot springs in WWGF.

Citawa either has undergone a little bit of water-rock interaction process as well as mixing with meteoric water, or surface evaporation and steam-heating process. This explains its type of water as sulfate-bicarbonate. Based on major cations and oxygen isotope analysis, Cibolang hot spring is typical marginal high-temperature from deeper regional fluid derived from meteoric aquifer. Cipanas, Pejaten and Sukaratu are typical of marginal fluid from lower-temperature. An exceptional example is spotted in Kertamanah hot spring that is probably resulted from the reaction of meteoric water and rocks/formation waters at low to medium temperature.

4.3 Rare earth elements in Wayang Windu host rocks

The REEs of host rock samples from each volcano in WWGF (data from Bogie et al., 1998, Table 2) were normalized to chondrite from Boynton (1984). If samples were not normalized, they appear in an Oddo-Harkins pattern (Fig. 3A). Chondrite-normalized host rocks values show similar patterns of enrichment in LREE, and positive anomalies in Eu (Fig. 3B). Due to high distribution coefficient, Eu tends to be in feldspar, especially plagioclase (Schnetzler and Philpotts, 1970; Paster and Schauwecker, 1974). Positive anomaly of Eu in average WW host-rock pattern confirmed the amount of Eu that was more leached out from plagioclase in a higher temperature condition. Positive Eu anomaly in hydrothermal fluids may also reflect maintenance of a high temperature during flow to the surface. Moller (2000) found significant positive anomalies of Eu always occur at temperature above 250°C. Eu is leached out less than other REEs during rock alteration processes. These patterns are commonly found as the result of differential leaching of minerals from the geothermal reservoir wall-rocks. Negative Ce/Ce* or Eu/Eu* ratios indicate a short water rock interaction process in lower temperature condition with oxygen rich water. Slope values of Eu/Eu* and Ce/Ce* of average WW host rocks are portrayed in Fig. 4B: all samples have similar patterns of positive Eu/Eu* and Ce/Ce* in chondrite-normalized plot.

Table 2. REEs of host rocks Bogie et al. (1998). All of the values were normalized to chondrite.

No	Host Rock (HR)	HR Code	LREE (ppm)					HREE (ppm)									∑REE
			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
1	Puncak Besar	PB	56.96	122.36	14.77	63.29	16.46	18.99	18.99	2.95	16.88	3.38	9.28	1.69	8.02	1.69	355.70
2	Malabar	MA	54.85	116.03	14.77	61.18	17.30	18.99	5.06	3.38	18.14	3.38	10.55	1.69	10.13	1.69	337.13
3	Gambung	GB	61.18	130.80	15.61	63.29	17.72	18.14	5.06	2.95	16.03	2.95	9.70	1.69	8.86	1.69	355.70
4	Bedil	BD	50.63	118.14	13.50	54.85	16.88	15.61	5.06	2.53	14.77	2.95	8.02	1.27	8.02	1.27	313.50
5	Wayang	WYG	86.50	168.78	23.63	94.94	23.63	27.00	6.75	4.22	21.94	4.22	12.24	1.69	10.97	1.69	488.19
6	Windu	WIN	54.85	118.14	13.08	54.85	14.77	14.35	4.64	2.53	13.08	2.53	7.59	1.27	7.59	1.27	310.55

4.4 Rare earth elements in Wayang Windu hot springs

REEs contents in WWGF hot springs range over many orders of magnitude from below detection limit (10^{-7} times chondrite) up to 10^{-2} chondrite. Only Pejaten and Citawa hot springs have some identified REEs. The rest of REEs concentrations were either lower than detection limit (3σ of BGD) or undetected on the ICP-MS. Data results from ICP-MS are presented in Table 3. Some studies pointed out to direct linear relationship of pH and ΣREE. For example, Wood (2006) found that the highest REE contents coincidence with lowest pH water, higher concentration of sulfate, and high TDS content. But in WWGF hot springs, those terms are invalid. Instead of Wayang, Citawa which has pH 6,2 appears to have the largest REEs concentration amongst all. Shortfalls of Eu will exhibit negative anomalies (log Eu/Eu* -0.06 from Table 4), as we can see in Pejaten, introducing a consequence of rock dissolution of secondary mineral phases at a quite in lower temperature. On the contrary, Citawa shows positive Eu anomaly, appointing to high temperature during flow to the surface. Positive anomalies in Ce recorded in Pejaten hot spring, indicate its neutral pH to slightly oxidizing fluid type. Citawa does not inherit the characteristics of the average host-rocks in Wayang Windu volcanic complex, its nearly horizontal pattern generally is a consequence of dissolution of rock by sulfate complex (Fig. 4B). Hence, this statement supports the genesis of bicarbonate-sulfate Citawa hot spring from anion-cation analysis.

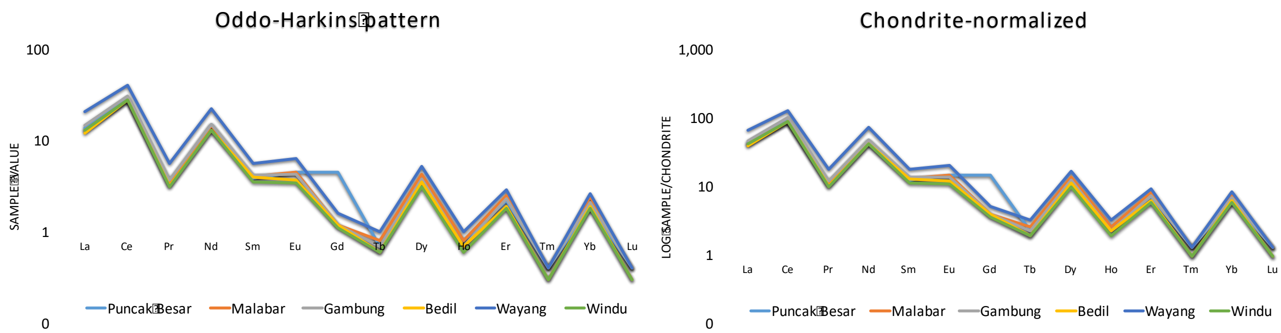

Figure 3: A) Enrichment in even atomic numbers are seen in a pattern called Oddo-Harkins pattern. B) Chondrite-normalized host rocks values show similar patterns of positive anomalies in Eu and negative anomalies in Gd.

Table 3. REEs of hot spring samples before they were normalized to chondrite.

No	Location	pH	LREE (ppb)					HREE (ppb)									∑REE
			Ce	Ce	Pr	Nd	Sm	Gd	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
1	Wayang	1.30	0.02	n.d	n.d	<0.12	n.d	n.d	<0.13	<0.058	0.01	n.d	<0.085	<0.045	<0.34	n.d	0.03
2	MBA	2.72	0.02	<0.039	n.d	n.d	n.d	n.d	<0.13	<0.058	0.02	n.d	<0.085	<0.045	<0.34	n.d	0.04
3	Pejaten	6.00	0.04	0.09	<0.038	<0.12	<0.24	0.04	0.27	<0.057	0.39	0.03	0.3	0.047	<0.34	<0.081	1.2
4	Citawa	6.20	23	41	4.2	14	2.3	0.7	2.2	0.3	1.7	0.3	1.0	0.1	0.8	0.1	92
5	Cibolang	6.30	0.00	<0.039	n.d	n.d	<0.24	n.d	n.d	n.d	0.06	n.d	<0.085	<0.045	n.d	n.d	0.06
6	Cipanas	6.40	0.02	<0.039	<0.038	<0.12	n.d	n.d	n.d	<0.058	0.02	n.d	<0.085	<0.045	n.d	<0.082	0.04
7	Sukaratu	6.60	<0.015	<0.039	n.d	n.d	n.d	n.d		n.d	0.05	n.d	<0.086	<0.045	n.d	n.d	0.05
8	Kertamanah	6.65	0.03	<0.039	n.d	<0.12	<0.23	n.d	<0.13	n.d	0.05	n.d	<0.084	<0.045	n.d	n.d	0.08

<value — below detection limit; n.d —not detected

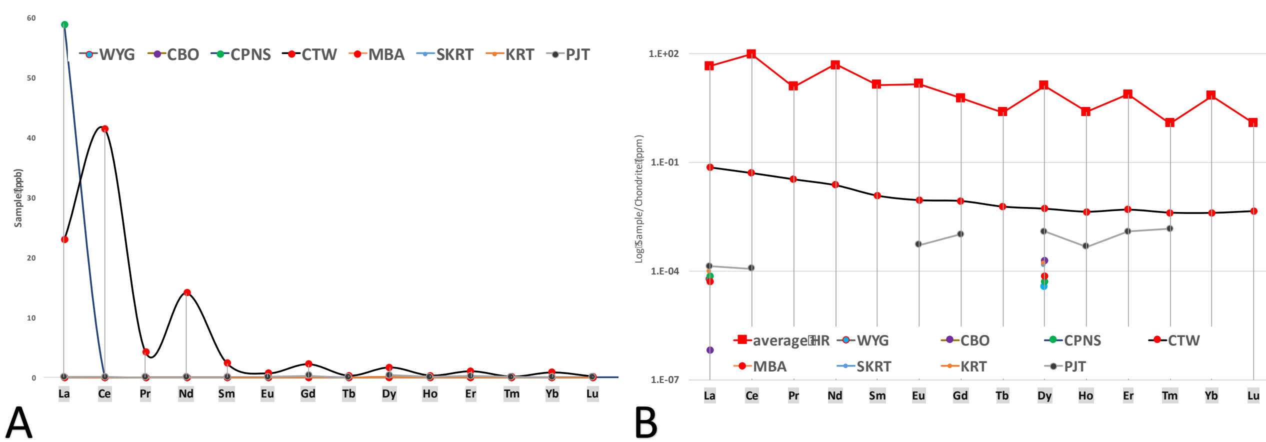

Figure 4: A) Ordo-Harkins patterns for hot spring samples. B) Samples were normalized to chondrite.

Even though theoretically pH is the dominant control on REEs concentrations, pH in WWGF hot springs clearly do not correlate with the amount of REEs values. Several possibilities to answer why the value of the REEs in acidic hot spring can be lessening: 1) shorter water-rock interaction times; 2) loss of REE to scale as thermal waters separate into liquid and vapor phases on ascent to the surface after boiling process; 3) the absence of precipitation of native sulfur (Wood and Shannon, 2002). It is still at loss to explain why only La and Dy were detected in all the hot spring samples. The absences of the rest of lanthanide values halt the further REEs analyses in this study.

5. CONCLUSIONS

In case of WWGF, after all of the samples were normalized to the average host rocks, we can see it clearly that Citawa hot spring does not resemble the pattern of WW host rocks. It implies that REEs in this hot spring doe not inherit its characteristic from WWGF volcanic host rocks. Citawa has different host rock aquifer during migration of its fluid from zone with higher temperature. REEs in Pejaten are derived from rocks dissolution of secondary minerals in lower temperature. Among three processes affecting the REEs concentrations: shorter water-rock interaction, dilution with meteoric water, and the presence of boiling zone in the deep, the later one is the primary reason of the absences of the REEs other than La and Dy in almost all of the hot springs. It is also suggested that their locations near exposed faults are responsible to the shorter time of water-rock interaction process and mixing process with a large amount of meteoric water that could possibly wash the REEs away.

Table 4. Ratio of LREE/HREE of hot springs and WWGF host-rocks, both are normalized to chondrite.

No	Hot spring	pH	Ratio of $LREE/HREE_{CN}$	Log Eu/Eu*	Log Ce/Ce*	No	Bulk host rock	Ratio of $LREE/HREE_{CN}$	Log Eu/Eu*	Log Ce/Ce*
1	Wayang	1.30	0.42	-	-	1	Puncak Besar	0.95	0.52	0.00
2	MBA	2.72	0.19	-	-	2	Malabar	0.96	0.68	-0.02
3	Pejaten	6.00	0.03	0.01	0.23	3	Gambung	1.12	0.65	0.00
4	Citawa	6.20	3.35	-0.06	-0.02	4	Bedil	1.13	0.60	0.03
5	Cibolang	6.30	0.00	-	-	5	Wayang	1.17	0.70	-0.05
6	Cipanas	6.40	0.34	-	-	6	Windu	1.21	0.62	0.01
7	Sukaratu	6.60	0.00	-	-		Eu/Eu*: $(La_N + Pr_N)/2Ce_N$			
8	Kertamanah	6.65	0.15	-	-		Ce/Ce*: $(Sm_N + Gd_N)/2Eu_N$			

An integration of REEs, isotopes and chemistry data show three types of fluid in WWGF: sulfate waters (MBA and Wayang) that overlie in the boiling zone of the system; bicarbonate waters (Cibolang, Citawa) in the margin of the boiling zone; and diluted bicarbonate waters (Pejaten, Sukaratu, Kertamanah, Cipanas) from mixing of meteoric water and lateral steam outside the boiling zone. In a ballpark, enriched oxygen isotope and positive Eu anomaly could denote boiling zones; negative Eu anomaly and depleted oxygen isotope may infer short water rock interaction process in lower temperature or mixing with meteoric water.

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REFERENCES

Bogie, I., and MacKenzie, K.M.: The application of a volcanic facies model to an andesitic stratovolcano hosted geothermal system at Wayang Windu, Java, Indonesia. *Proceedings*, 20th NZ Geothermal Workshop, New Zealand (1998).

Bogie, I., Kusumah, Y.I. and Wisnandary, M.C.: Overview of the Wayang Windu geothermal field, West Java, Indonesia. *Geothermics* **37**, (2008), 347-365.

Boynton, W.V.: Cosmochemistry of the rare earth elements: meteorite studies. *Rare Earth Element Geochemistry*. Ed. P. Henderson, Elsevier, Oxford-Amsterdam, (1985), 115 – 11522.

Hendrasto, F.:Recharge Area Determination of Geothermal System of Wayang-Windu Volcano West Java, *Geology of Institute of Technology Bandung*, (2005). [Unpublised Master Theses]

Moller, P.: Rare Earth Elements and Yttrium as Geochemical Indicators of the Source of Mineral and Thermal Waters. Stober, I., Bucher, K. (Eds.), *Hydrogeology of Crystalline Rocks*, Kluwer Academic Publishing, Dodrecht, Netherlands, (2000), 227–246.

Nicholson, K.: Geothermal Fluids, Chemistry and Exploration Techniques, Springer-Verlag, Berlin Heidelberg, (1993).

Paster, T.P., and Schauwecker, D.S.: The Behavior of Some Trace Elements during Solidification of the Skaergaard Layered Series. *Geochim. Cosmochim. Acta*, **38**, (1974), 1549–1577.

Rabiet, M., Brissaud, F., Seidel, J.L., Pister, S., and Elbaz, F.: Positive Gadolinium Anomalies in Wastewater Treatment Plant Effluents and Aquatic Environment in The Hérault Watershed (South France), *Chemosphere 75,* (2009), 1057–1064.

Schnetzler, C.C., and Philpotts, J.A.: Partition Coefficients of Rare-Earth Elements between Igneous Matrix Material and Rock-Forming Mineral Phenocrysts II. *Geochim. Cosmochim. Acta,* **34**, (1970), 331–340.

Riyadi, D.: Informasi Geologi Lingkungan dalam Menunjang Pengembangan Panas Bumi Wayang Windu Di Kec. Pangalengan, Kab. Bandung [Information on Geological Environmental in Supporting Wayang Windu Geothermal Development], Laporan Pusat Geologi Lingkungan, Badan Geologi (2007). [In Bahasa Indonesia]

Soestrisno, S.: Peta Hidrogeologi Lembar Bandung, Skala 1:25.000 [Hydrogeology of Bandung, Scale 1:25.000], Direktorat Geologi Tata Lingkungan, Bandung (1983). [In Bahasa Indonesia]

Wood, S.A., and Shannon, W. M: Rare-earth elements in geothermal waters from Oregon, Nevada, and California. *J. Solid State Chem*. **171**, (2003), 246-253.

Wood, S.A.: Rare earth element systematics of acidic geothermal waters from the Taupo Volcanic Zone, New Zealand. *J. Geochem. Explor*. **89**, (2006), 424–427.