

Boron isotope variations in geothermal systems on Java, Indonesia



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ABSTRACT

This paper presents $\delta^{11}\text{B}$ data for hot springs, hot acid crater lakes, geothermal brines and a steam vent from Java, Indonesia. The processes that produce a large range of the $\delta^{11}\text{B}$ values were investigated, including the possible input of seawater as well as the contrast $\delta^{11}\text{B}$ compositions of acid sulfate and acid chloride crater lakes. The $\delta^{11}\text{B}$ values of hot springs ranged from -2.4 to $+28.7\%$ and acid crater lakes ranged from $+0.6$ to $+34.9\%$. The $\delta^{11}\text{B}$ and Cl/B values in waters from the Parangtritis and Krakal geothermal systems confirmed seawater input. The $\delta^{11}\text{B}$ values of acid sulfate crater lakes ranged from $+5.5$ to $+34.9\%$ and were higher than the $\delta^{11}\text{B}$ of $+0.6\%$ of the acid chloride crater lake. The heavier $\delta^{11}\text{B}$ in the acid sulfate crater lakes was caused by a combination of vapor phase addition and further enrichment due to evaporation and B adsorption onto clay minerals. In contrast, the light $\delta^{11}\text{B}$ of the acid chloride crater lake was a result of acid water-rocks interaction. The correlations of $\delta^{11}\text{B}$ composition with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ indicated that the B isotope corresponded to their groundwater mixing sources, but not for J21 (Segaran) and J48 (Cikundul) that underwent ^{11}B isotope enrichment by B adsorption into minerals.

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1. Introduction

Geothermal waters are known to have a large range of $\delta^{11}\text{B}$, from -9.3 to $+44\%$ (Musashi et al., 1988; Leeman et al., 1990; Palmer and Sturchio, 1990; Aggarwal et al., 1992; Barth, 1993; Vengosh et al., 1994; Aggarwal et al., 2000). That range is caused by the $\delta^{11}\text{B}$ composition of the host-rocks, seawater input, groundwater mixing and B isotope fractionation. For example, different types of host rocks were identified to produce different $\delta^{11}\text{B}$ values in the geothermal fluids on the Argentine Puna Plateau (Kasemann et al., 2004). The heavy $\delta^{11}\text{B}$ of seawater, $+39.6\%$ (Foster et al., 2010), was successfully used to identify seawater components in geothermal waters on Iceland (the Reykjanes and Svartsengi geothermal fields), in Japan (the Izu–Bonin arc, Kusatsu–Shirane area, and Kagoshima) and in Italy (Vulcano island) (Nomura et al., 1982; Kakihana et al., 1987; Musashi et al., 1988; Oi et al., 1993; Aggarwal and Palmer, 1995; Oi et al., 1996; Aggarwal et al., 2000; Leeman et al., 2005; Millot et al., 2009). Shallow groundwater dilution also changes the $\delta^{11}\text{B}$ composition of thermal waters due to a wide range in values (Palmer and Sturchio, 1990; Barth, 1993; Rose et al., 2000a; Chetelat et al., 2005; Yuan et al., 2014). Fractionation of B isotopes in thermal waters by adsorption/incorporation of B onto clay minerals and iron oxide is caused by the transformation of mineral coordination from trigonal in the liquid phase to tetrahedral in the solid phase (Schwarcz et al., 1969; Palmer et al., 1987; Spivack and

Edmond, 1987; Vengosh et al., 1991b; Williams et al., 2001; Lemarchand et al., 2007), calcite (Vengosh et al., 1991a; Hemming and Hanson, 1992) and evaporite minerals (McMullen et al., 1961; Agyei and McMullen, 1968; Swihart et al., 1986; Oi et al., 1989; Vengosh et al., 1992). These processes enrich the ^{10}B isotope in the solid phases and thus increase the $\delta^{11}\text{B}$ of thermal waters. Thermal waters that condensed from the vapor phase of a geothermal system are potentially enriched in ^{11}B because of ^{11}B fractionation into the vapor phase. The $\delta^{11}\text{B}$ enrichment during this process was generally considered insignificant (Kanzaki et al., 1979; Nomura et al., 1982; Spivack et al., 1990; Leeman et al., 1992; Yuan et al., 2014), but potentially should not be neglected in vapor-dominated geothermal systems.

In this paper we investigate the processes that produced a wide range $\delta^{11}\text{B}$ values in the thermal waters on Java, which in some locations might be also affected by seawater input, as indicated by Purnomo and Pichler (2014). In addition, the $\delta^{11}\text{B}$ composition of two contrasting acid crater lakes, Cl-rich and Cl-poor, was examined.

2. Geological setting

Java is located approximately in the middle part of the Sumatera–Nusa Tenggara island arc (Fig. 1). The island arc was formed due to subduction of the Indo-Australian and Eurasian plate (Hamilton, 1979; Simandjuntak and Barber, 1996). The subduction produced three volcanic belts on Java, the Paleogene, the Neogene and the active Quaternary volcanic belts (Van Bemellen, 1949; Hall, 2002). The volcanism produced andesitic rocks, where the Quaternary volcanics are more alkaline than the Tertiary volcanics (Soeria-Atmadja et al., 1994). In

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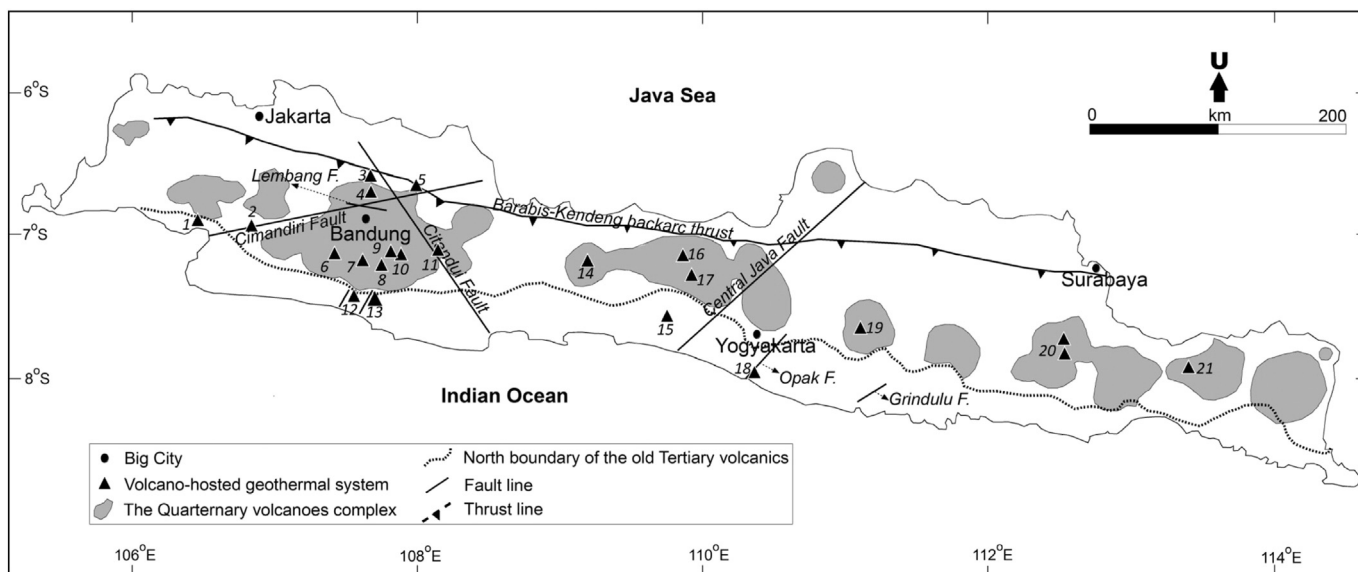


Fig. 1. The sampling location of geothermal fields on Java, i.e., (1) Cisolok, (2) Cikundul, (3) Batu Kapur, (4) Tangkuban Parahu, (5) Tampomas, (6) Patuha, (7) Pangalengan, (8) Darajat, (9) Kamojang, (10) Cipanas, (11) Ciawi, (12) Cilayu, (13) Pakenjeng, (14) Slamet, (15) Krakal, (16) Dieng, (17) Kalianget, (18) Parangtritis, (19) Lawu, (20) Arjuna-Weilrang and (21) Segaran. Geological structures and volcanic belts were based on Hamilton (1979); Simandjuntak and Barber (1996), Hoffmann-Rothe et al. (2001) and Soeria-Atmadja et al. (1994). Modified from Purnomo and Pichler (2014).

addition to the volcanic belts, subduction generated faults, e.g., the Cimandiri fault, the Citandui fault, the Central Java fault, the Lembang fault and the Opak fault.

Purnomo and Pichler (2014) divided the geothermal systems on Java into two groups, volcano-hosted and fault-hosted, where the former is the dominant group. Due to the presence of magmatic-fluid input, volcano-hosted systems produced a large variation of surface features, i.e., hot springs, fumaroles, acid crater lakes, steam vents and altered ground, in contrast, the fault-hosted systems have mainly neutral hot springs, as a result of the absence of magmatic fluid input (Purnomo and Pichler, 2014). The volcano-hosted geothermal systems are distributed in the Quaternary volcanic complex, stretched E–W direction in the middle part of the island. The Kamojang, Darajat and Wayang-Windu are located in the Kendang volcanic complex (Rejeki et al., 2005). The Patuha geothermal system is located in the flat volcanic highland of the Patuha volcano (Layman and Soemarinda, 2003). The Sari Ater geothermal system is hosted by the Tangkuban Prahua volcano, Cileungsi by the Tampomas volcano and Segaran by the Lamongan volcano. The Gucci and Baturaden geothermal systems are hosted by the Slamet volcano. Another single volcano, the Lawu volcano is hosting the Lawu geothermal system. The Songgoriti and Padusan geothermal systems are located in the Arjuna–Weilrang volcano complex and the Dieng geothermal system is located in the Dieng caldera. Meanwhile the fault-hosted systems are located in the Tertiary volcanic belt, in the southern part of the island. Two identified fault-hosted geothermal systems, Cikundul and the Parangtritis, are hosted in the major fault zones of Cimandiri and Opak, respectively (Effendi et al., 1998; Rahardjo et al., 1995), while other fault-hosted systems, i.e., Cisolok, Batu Kapur, Cilayu, Pakenjeng and Krakal, are hosted in minor fault zones (Alzwar et al., 1992; Asikin et al., 1992; Silitonga, 1973; Sujatmiko and Santosa, 1992).

3. Sampling and analysis

Water samples from hot springs, hot crater lakes, cold springs and geothermal brines were collected from July to September 2012 and from August to October 2013. Temperature, pH, conductivity and oxidation reduction potential (ORP) were measured by probe, while alkalinity was titrated. The samples were filtered through a 0.45 μm nylon membrane and stored in polyethylene bottles. The bottles were rinsed

three times using the filtered samples. The samples were split and the B isotope splits were preserved by acidification to 1% concentrated HNO_3 . A complete description of field methods and analytical procedures other than for B isotopes can be found elsewhere (Purnomo and Pichler, 2014). The B isotope composition was analyzed using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS, Neptune, Thermo Fisher Scientific) at the Isotope Geochemistry Laboratory, National Cheng Kung University by following the procedure of Wang et al. (2010). A volume of 0.5 or 1 mL sample containing a minimum of 50 ng B was used in the measurement to ensure duplicated analysis. Prior to measurement, the HNO_3 in the samples was substituted with H_2O to minimize the memory effects, in addition washing using 0.05 NH_4OH solution was done for every 5 analyses. The memory effect was also suppressed by keeping the low concentration of B (20 ppb) for each analysis. Any residue blank was corrected using standard-sample bracketing (SSB) approach of Aggarwal et al. (2003). To ensure the data quality, independent replicate measurements of the standard, SRM NBS 951, is continuously in progress. B was purified from the samples by micro-sublimation technique at 98 ± 0.1 °C in a thermostatic hot plate rack. The ^{11}B data were reported in δ per mil (‰) relative to the standard of SRM NBS 951 with an analytical uncertainty of <0.2%.

4. Results

The physicochemical data and isotopes values ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^{11}\text{B}$) values are reported in Table 1, including the data of samples from the Kawah Kreta steam vent (J73), the Krakal hot spring (J74), the Kawah Domas crater lake (J72) and two geothermal brines of well AFT-28 (J70) and PAD-7C (J71) from the Dieng geothermal field.

The B concentrations of hot springs and acid crater lakes had a similar large range, from 2.1 to 93.2 mg/L and from 1.4 to 94.4 mg/L, respectively. The two geothermal brines from the Dieng geothermal field had B contents of 262.5 and 593.6 mg/L. The Kawah Kreta steam vent (J73) had a B content of 3.5 mg/L, higher than its Cl^- concentration, which was below detection limit. The B concentration in the acid sulfate crater lakes ranged from 1.4 to 73.3 mg/L, while the Kawah Putih (J51) acid chloride crater lake had a slightly higher value of 94.4 mg/L.

In accordance with the B concentration, the hot springs and hot crater lakes had relatively similar ranges of $\delta^{11}\text{B}$, i.e., -2.4 to $+28.7\%$ and $+0.6$ to 34.9% , respectively. In contrast to the B content, acid sulfate

Table 1Physicochemical data and isotopes values ($\delta^{11}\text{B}$, $\delta^{18}\text{O}$ and $\delta^2\text{H}$) values of hot springs, acid crater lakes, geothermal brines and a steam vent from Java.

ID	Location	T (°C)	pH	Cl (mg/L)	HCO ₃	B	Fe	$\delta^{11}\text{B}$ (‰)	$\delta^{18}\text{O}$	$\delta^2\text{H}$
<i>Hot springs</i>										
J2	Baturaden (Slamet volc.) ^a	52.1	6.9	777.3	722.2	4.33	2.98	5.90	−9.1	−60.6
J4	Ciawi ^a	53.4	6.7	165.3	976.0	6.84	0.63	−0.70	−6.2	−38.9
J7	Cipanas ^a	48.3	6.3	119.0	383.1	2.43	0.01	4.58	−7.5	−49.8
J10	Kawah Hujan (Kamojang) ^a	95.4	4.9	7.2	22.0	4.63	0.06	2.30	−1.3	−21.4
J13	Padusan (Arjuna-Welirang) ^a	48.3	6.5	246.2	1104.1	4.97	1.72	11.98	−9.3	−62.4
J18	Songgoriti (Arjuna-Welirang) ^a	46.4	6.3	1303.5	1378.6	50.56	6.24	7.12	−5.9	−46.2
J21	Segaran (Lamongan) ^a	44.9	6.5	550.5	1625.0	21.37	0.03	6.67	−5.0	−29.9
J24	Banyuasin (Lawu) ^a	38.4	6.1	5948.7	835.7	93.23	9.38	8.07	−4.0	−42.4
J28	Kondo (Lawu) ^a	36.4	6.3	4382.4	1634.8	55.60	1.85	4.53	−5.4	−39.6
J30	Ngunut (Lawu) ^a	33.2	6.4	904.9	878.4	17.37	0.02	1.33	−6.3	−37.0
J34	Gucci (Slamet) ^a	53.3	7.5	52.6	556.3	7.15	0.16	7.77	−8.3	−63.8
J74	Krakal, Kebumen	38.9	8.2	8671.8	31.2	14.51	<dl	28.70	−3.4	−41.1
J36	Sari Ater (T. Parahu) ^a	46.6	2.0	822.5	<dl	2.07	21.56	2.4	−6.9	−44.6
J38	Batu Kapur ^a	40.9	6.4	312.7	1085.8	3.12	1.26	−2.36	−6.4	−39.3
J39	Cibolang (Pangalengan) ^a	68.9	7.1	24.0	219.6	6.48	0.01	0.40	−6.5	−47.3
J42	Pakenjeng ^a	59.9	7.4	126.0	40.3	7.21	0.06	0.04	−6.5	−35.6
J44	Cilayu ^a	70.3	8.1	1387.2	372.1	58.22	0.11	0.2	−5.3	−40.8
J47	Kalianget ^a	40.0	6.5	424.8	732.0	3.73	1.11	8.90	−9.0	−59.5
J48	Cikundul ^a	50.5	7.8	180.2	61.0	10.72	0.01	9.31	−5.7	−39.4
J49	Cisolok ^a	102.0	8.1	305.6	129.3	3.58	0.01	−0.70	−5.9	−33.0
J54	Cileungsing (Tampomas) ^a	48.5	7.1	757.2	732.0	5.28	1.81	−0.95	−6.6	−41.2
J55	Darajat ^a	60.0	2.8	13.3	<dl	6.97	8.64	12.81	−7.9	−50.6
J58	Parangtritis ^a	39.2	7.6	6184.5	43.9	9.51	0.18	24.84	−4.3	−24.2
J60	Kawah Sileri (Dieng) ^a	57	6.3	77.7	266.0	6.67	0.02	0.27	−4.3	−47.4
J61	Pulosari (Dieng) ^a	54	6.2	330.6	183.0	6.41	0.06	4.62	−8.0	−57.2
J64	Bitingan (Dieng) ^a	60	7.3	21.5	329.4	2.08	0.01	3.2	−8.0	−57.1
<i>Hot crater lakes</i>										
J9	Kawah Kamojang (Kamojang) ^a	40.0	2.9	12.8	<dl	1.39	4.87	9.27	7.7	−4.1
J72	Kawah Domas (T. Parahu)	85	1.8	<dl	<dl	2.68	17.44	5.54	−1.3	−16.8
J51	Kawah Putih (Patuha) ^a	32.9	1.0	8084.2	<dl	94.40	35.33	0.59	7.9	−4.0
J59	Kawah Sikidang (Dieng) ^a	87	2.5	14.4	<dl	73.29	7.60	34.86	7.5	−7.6
<i>Geothermal brines</i>										
J70	GW AFT-28 (Dieng)	150	6.3	22,242.5	39.0	593.60	1.25	0.26	−42.1	−1.8
J71	GW PAD-7C (Dieng)	150	5.8	13,384.0	14.6	262.54	2.29	−0.02	−46.7	−1.7
<i>Steam vent</i>										
J73	Kawah Kreta (Kamojang)		nd	<dl	nd	3.49	<dl	3.84	nd	nd

nd = not defined, <dl = below detection limit.

^a Except for the $\delta^{11}\text{B}$ values, data are taken from Purnomo and Pichler (2014).

crater lakes had relatively heavy $\delta^{11}\text{B}$ values from +5.6 to 34.9‰ compared to the acid chloride crater lake, which had a value of +0.6‰. The J74 and J58 hot springs as well as J59 acid sulfate crater lake had a $\delta^{11}\text{B}$ value close to that of seawater, i.e., +39.6‰ (Foster et al., 2010). The $\delta^{11}\text{B}$ of the thermal waters were poorly correlated with their temperature, pH, Cl[−], B, HCO₃[−] and Fe concentrations (Fig. 2). Thermal waters with temperatures above 65 °C generally had relatively light $\delta^{11}\text{B}$ values, close to 0‰, while below this temperatures most of the thermal waters were ¹¹B enriched (Fig. 2a). This indicates more significant of ¹¹B enrichment at low temperatures, as suggested by others, e.g., Palmer et al. (1987) and Aggarwal and Palmer (1995).

5. Discussion

5.1. Boron in thermal waters and seawater input

Boron has been known to be scavenged into steam phase during liquid–vapor separation in high temperatures of above 300 °C (Truesdell et al., 1989). This characteristic was applied to identify phase separation in geothermal systems (Arnorsson and Andresdottir, 1995; Valentino and Stanzione, 2003). The B/Cl ratios of thermal waters on Java were used to identify steam separation for J9, J10, J34, J39, J55, J59 and J64; andesitic host-rock leaching for most of the thermal waters; seawater input for J58; and B adsorption for J2, J36, J38, J47, J49 and J54

(Purnomo and Pichler, 2014). The Krakal (J74) hot spring plotted close to the seawater line, similar to J58, indicating seawater input, while the Kawah Domas acid sulfate crater lake (J72) plotted in the vapor phase separation and the geothermal brines from Dieng, J70 and J71, plotted close to the andesitic rock leaching line (Fig. 3).

The boron isotope composition can be a powerful tool to detect seawater input into geothermal systems, as demonstrated for two geothermal fields on Iceland (the Reykjanes and Svartsengi), three areas in Japan (the Izu–Bonin arc, Kusatsu–Shirane area, and Kagoshima) and in Italy (Vulcano Island) (Nomura et al., 1982; Kakihana et al., 1987; Musashi et al., 1988; Oi et al., 1993; Aggarwal and Palmer, 1995; Aggarwal et al., 2000; Leeman et al., 2005; Millot et al., 2009). A similar approach was used to investigate seawater input in the thermal waters at Krakal (J74) and Parangtritis (J58). These two thermal waters plotted close to the mixing line between seawater and thermal waters (Fig. 4 and 5), which proves the presence of seawater. The acid sulfate crater lake of Kawah Sikidang (J59) also had a heavy $\delta^{11}\text{B}$ of +34.9‰, close to seawater, hence plotted close to the mixing line of seawater and thermal waters in the $\delta^{11}\text{B}$ vs. $\delta^{18}\text{O}$ (Fig. 5a) and $\delta^{11}\text{B}$ vs. $\delta^2\text{H}$ (Fig. 5b). However, this acid sulfate crater lake had a Cl/B ratio of five magnitudes lower than seawater (Fig. 4), thus seawater input could be excluded. The fluid source of Kawah Sikidang, which is the deep reservoir of the Dieng geothermal field, J70 and J71, also showed the absence of seawater input. The geothermal brines had a light $\delta^{11}\text{B}$ of approximately 0‰

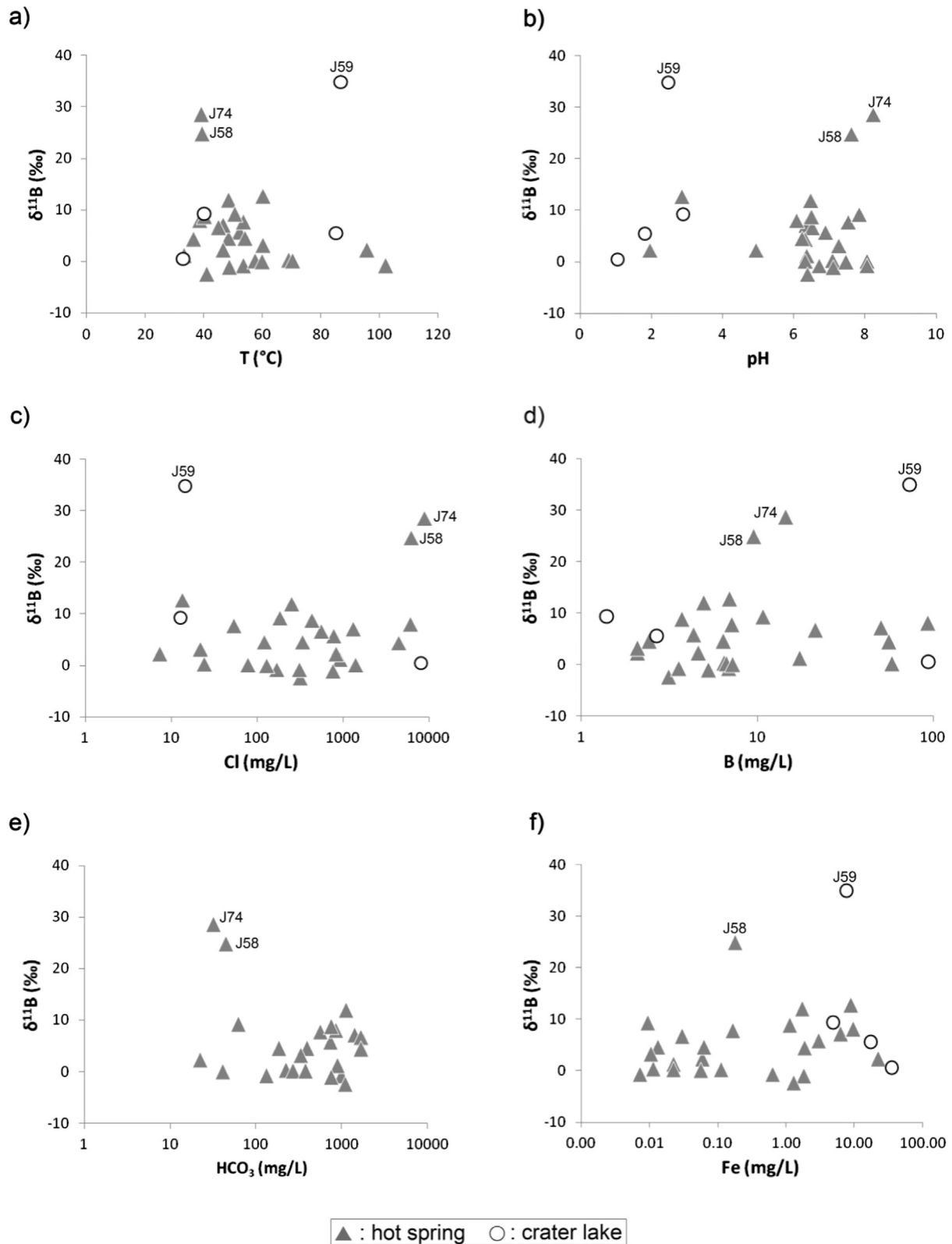


Fig. 2. a) $\delta^{11}\text{B}$ vs. T, b) $\delta^{11}\text{B}$ vs. pH, c) $\delta^{11}\text{B}$ vs. Cl, d) $\delta^{11}\text{B}$ vs. B, e) $\delta^{11}\text{B}$ vs. HCO_3^- and f) $\delta^{11}\text{B}$ vs. Fe diagrams of thermal waters on Java show poor correlations of $\delta^{11}\text{B}$ with T, pH, Cl^- , B, HCO_3^- and Fe. The $\delta^{11}\text{B}$ vs. T indicates generally lower $\delta^{11}\text{B}$ enrichment at temperatures above 65 °C.

and Cl/B ratios of two magnitudes lower than seawater (Fig. 4). If there was seawater input during the vapor phase ascent, the resulting thermal water should have a higher Cl^- content corresponding to the vapor/seawater mixing ratio.

5.2. The $\delta^{11}\text{B}$ of acid crater lakes

The four acid crater lakes from Java, Kawah Kamojang (J9), Kawah Domas (J72), Kawah Putih (J51) and Kawah Sikidang (J59) had low

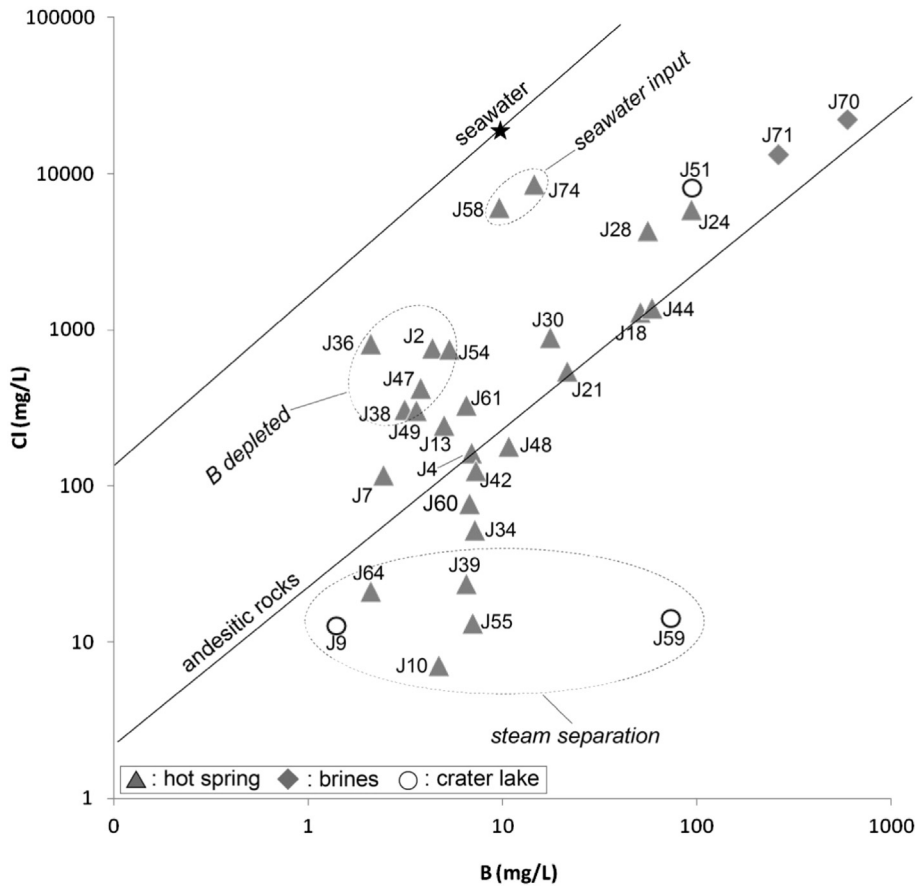


Fig. 3. Cl vs. B diagram of thermal waters (modified from Purnomo and Pichler, 2014). Thermal waters underwent seawater input, B depletion, steam phase separation and andesitic rock leaching. Seawater input is indicated for J58 and J74 hot springs, while most thermal waters were resulted by andesitic rock leaching. The Cl/B ratio of andesitic rocks is taken from Trompetter et al. (1999).

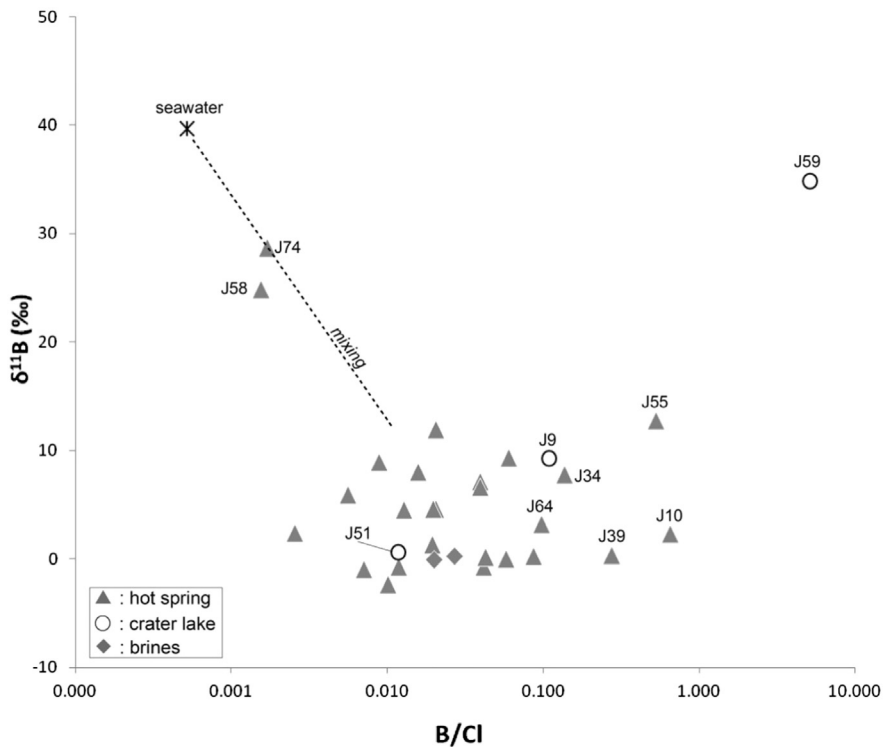


Fig. 4. $\delta^{11}\text{B}$ vs. B/Cl diagram of hot springs, acid crater lakes and geothermal brines. Seawater input is confirmed for two J58 and J74 hot springs, but not for the Kawah Sikidang (J59) acid sulfate crater lake. The $\delta^{11}\text{B}$ value of +39.6‰ for seawater (Foster et al., 2010) and B/Cl ratio of the Indian Ocean (Purnomo and Pichler, 2014) are used in this diagram.

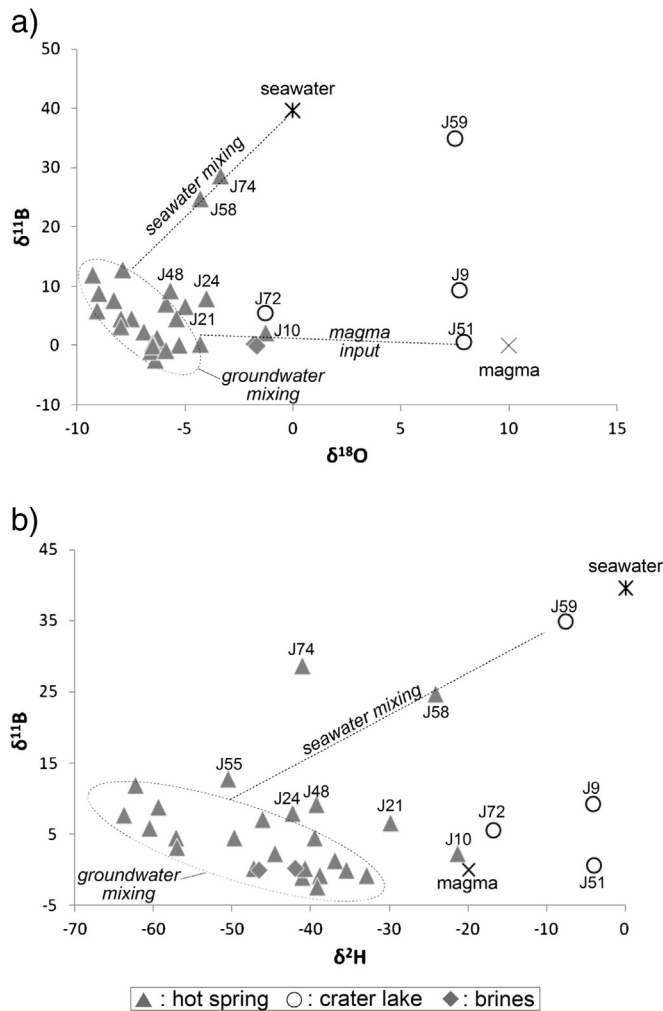


Fig. 5. a) $\delta^{11}\text{B}$ vs. $\delta^{18}\text{O}$ and b) $\delta^{11}\text{B}$ vs. $\delta^2\text{H}$ show three main processes that produced a wide range of $\delta^{11}\text{B}$ values of the thermal waters, i.e., seawater mixing for J58 and J74; magma input for three crater lakes (J9, J51 and J72) and J72 hot spring; and groundwater mixing for most of the hot springs. The B isotope of magma is based on Palmer (1991), while ^2H and ^{18}O isotopes based on Giggenbach (1992).

pH values ranging from 1 to 2.9. The B/Cl ratios indicate that, except for Kawah Putih, the three other crater lakes were formed due to condensation of the geothermal vapor phase (Fig. 3). The significance input of magmatic component in the crater lakes fluid on Java has been proven by the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope (Purnomo and Pichler, 2014), which is also supported by the correlation of $\delta^{11}\text{B}$ with $\delta^{18}\text{O}$ (Fig. 5a). The isotopes indicate magmatic fluids input in the crater lakes, except for Kawah Sikidang that plot above magmatic input line, due to the heavy $\delta^{11}\text{B}$ composition (Fig. 5a).

The $\delta^{11}\text{B}$ value of vapor phase of geothermal systems is generally enriched by up to 4‰ relative to the remaining liquid phase (Kanzaki et al., 1979; Nomura et al., 1982; Spivack et al., 1990; Leeman et al., 1992; Yuan et al., 2014). The difference in $\delta^{11}\text{B}$ between the Dieng geothermal brines and the Kawah Kreta vapor phase was approximately 3.8‰ confirming condensation as the main process of fractionation. Assuming steam condensation from a similar vapor phase as Kawah Kreta, the Kawah Domas, Kawah Kamojang and Kawah Sikidang crater lakes were enriched in $\delta^{11}\text{B}$ by 1.7‰, 5.5‰ and 31.1‰, respectively. The Kawah Kreta steam vent had a B concentration of 3.5 mg/L, which was slightly higher than Kawah Kamojang with 1.4 mg/L and Kawah Domas with 2.7 mg/L. Smith et al. (1987) reported for the Geyser geothermal field (USA) that the water of the vapor trap was approximately 50 times enriched in B concentration compared to the steam phase.

Accordingly, an acid crater lake originated from vapor phase condensation is expected to have a higher B concentration than the vapor phase. Therefore, the low B concentration of the Kawah Kamojang and Kawah Domas crater lakes in comparison to the vapor phase should indicate additional processes that lowered the B concentration. This could have been caused either by precipitation of a B-rich mineral phase and/or adsorption by clay minerals. Both processes reduce the B concentration of the remaining water and thus enrich ^{11}B due to adsorption of ^{10}B by the solid phases (McMullen et al., 1961; Agyei and McMullen, 1968; Schwarcz et al., 1969; Swihart et al., 1986; Palmer et al., 1987; Spivack and Edmond, 1987; Oi et al., 1989; Vengosh et al., 1991b; Vengosh et al., 1992). Palmer and Sturchio (1990) reported more significant B isotope fractionation at low temperature and thus the high temperature of Kawah Domas (85 °C) should allow only little B isotope fractionation, causing the lighter $\delta^{11}\text{B}$ values compared to Kawah Kamojang, where the temperature was 40 °C. Meanwhile, the heavy $\delta^{11}\text{B}$ value in Kawah Sikidang, which was by 31‰ heavier than the vapor phase, cannot be explained exclusively by steam phase separation. Other mechanisms must have produced such a B-rich and heavy $\delta^{11}\text{B}$ signature in this acid sulfate crater lake.

Apart from its heavy $\delta^{11}\text{B}$, the Kawah Sikidang crater lake had a noticeable B enrichment of 73.3 mg/L. This value is higher than that of the other acid sulfate crater lakes and only comparable to the acid chloride crater lake Kawah Putih, which had a B concentration of 94.4 mg/L. However, Kawah Putih was Cl-rich (8084 mg/L) and its $\delta^{11}\text{B}$ was +0.6‰, whereas Kawah Sikidang in contrast was Cl-poor (14.4 mg/L) with a $\delta^{11}\text{B}$ of +34.9‰. The B-rich and light $\delta^{11}\text{B}$ of the Kawah Putih is likely produced by leaching of andesitic rocks that fall from the crater wall, as has been indicated for the Kawah Ijen (Delmelle and Bernard, 1994; van Hinsberg et al., 2010), while the Cl-rich is sourced from the magmatic gas. Delmelle and Bernard (1994) explained that the chemical composition of an acid chloride crater lake is the result of condensation and oxidation of magmatic gases, such as, SO_2 , H_2S and HCl , upon contact with oxygenated groundwater, followed by water-rock interaction.

The main mechanism that produced the heavy $\delta^{11}\text{B}$ (+34.9‰) of Kawah Sikidang probably was evaporation. Vengosh et al. (1992) reported that during the latest stage of evaporation the $\delta^{11}\text{B}$ of seawater could be enriched up to 30‰ due to incorporation of ^{10}B into evaporate minerals, e.g., halite. Kawah Sikidang had a temperature of 87 °C without outflow to the nearby river, hence excessive evaporation could be expected. The condition is contrary to the Kawah Domas acid sulfate crater lake which had a temperature of 85 °C but the water was drained out to the adjacent river and thus the effect of evaporation was less significant than at Kawah Sikidang. Evaporation should have lowered the B concentration of Kawah Sikidang due to incorporation of B into evaporate deposits. Therefore, the elevated B content of 73.3 mg/L of the crater lake has to be sustained by constant addition of subsurface B. The reservoir vapor phase probably had an initial B content comparable to the Kawah Kreta steam vent of 3.5 mg/L, however, in the shallow depth the vapor was B enriched due to interaction with B-rich minerals. This assumption was supported by the elevated B concentration of altered ground surrounding Kawah Sikidang which was up to 25.5 mg/kg, compared to the less than 0.02 mg/kg of unaltered ground in Dieng. However, the excessive evaporation and B enrichment in the shallow depth are still hypothetical, hence further research is needed to prove the presence of evaporate deposits and B rich minerals in the shallow depth.

5.3. Processes affecting the $\delta^{11}\text{B}$ value of thermal springs

During thermal water ascent to the ground surface, the $\delta^{11}\text{B}$ value could be modified by groundwater mixing and B isotope fractionation (Schwarcz et al., 1969; Palmer et al., 1987; Spivack and Edmond, 1987; Palmer and Sturchio, 1990; Vengosh et al., 1991b; Williams et al., 2001; Lemarchand et al., 2007; Yuan et al., 2014). Groundwater

Table 2

Saturation indices with respect to carbonate, clay and goethite minerals were calculated using PHREEQC (Parkhurst and Appelo, 1999).

Sample ID	Location	Saturation Index					
		Calcite	Dolomite	Strontianite	Illite	Smectite	Goethite
J10	Kawah Hujan (Kamojang)	−4.27	−7.78	−5.49	2.12	−2.54	1.40
J21	Segaran (Lamongan volc.)	0.15	2.13	−0.33	-	-	−1.31
J24	Banyuasin (Lawu volc.)	−0.28	0.38	−0.08	-	-	1.16
J48	Cikundul	−0.14	−0.36	-	3.69	2.02	−0.01

has a wide range of $\delta^{11}\text{B}$ values, from -15.9 to $+44\%$ (Barth, 1993; Pennisi et al., 2011), hence it could either lower or enrich the $\delta^{11}\text{B}$ of thermal waters that originally had $\delta^{11}\text{B}$ value of $\pm 0\%$. A factor that produced the wide range of $\delta^{11}\text{B}$ values is the precipitation water that also has a wide range of $\delta^{11}\text{B}$ values, from -13 to $+48\%$, which tend to decrease toward land (Rose et al., 2000b; Chetelat et al., 2005; Louvat et al., 2011).

Following the procedure of Leeman et al. (2005), the $\delta^{11}\text{B}$ values of thermal waters plot again the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Fig. 5a,b). The figures indicate that the $\delta^{11}\text{B}$ composition of the most of thermal waters on Java was dominantly affected by groundwater mixing. This is indicated by the well correlation of $\delta^{11}\text{B}$ with their $\delta^{18}\text{O}$ and $\delta^2\text{H}$, with R^2 of 0.7 and 0.6, respectively. These 'imperfect' correlations are caused by fractionation of B isotope during the flow in the aquifer, while in contrast O and H isotope behave conservatively. In Fig. 5, J10 (Kawah Hujan), J21 (Segaran), J24 (Banyuasin) and J48 (Cikundul) plotted outside the groundwater mixing zone, point to additional processes. The B isotope of J24 and J10 is likely also dominated by groundwater mixing; however these thermal waters are shifted away from the groundwater mixing zone due to the enrichment of ^{18}O and ^2H isotope by magmatic fluid input for J24 and evaporation for J10 (Purnomo and Pichler, 2014). Meanwhile, for the J21 and J48, the ^{11}B isotope was likely enriched by adsorption of B into minerals, i.e., clay and carbonate minerals, respectively, as indicated by the saturation index calculation (Table 2).

6. Conclusions

The $\delta^{11}\text{B}$ compositions of the most of thermal waters on Java were dominantly affected by groundwater mixing. Nevertheless hot springs and hot crater lakes had a range of $\delta^{11}\text{B}$ from -2.4 to $+34.9\%$, which is similar to other geothermal systems (Barth, 1993). Seawater input was detected for two thermal waters, Parangtritis and Krakal, and is considered as a source of their heavy $\delta^{11}\text{B}$. The Kawah Sikidang acid sulfate crater lake had a $\delta^{11}\text{B}$ indicating seawater addition; however, it was disproved by the low Cl/B ratio.

Two types of hot acid crater lakes, Cl-poor ($\text{Cl}^- < 15$ mg/L) and Cl-rich ($\text{Cl}^- = 8084$ mg/L), showed a contrasting $\delta^{11}\text{B}$ composition. The Cl-poor crater lakes had relatively heavy $\delta^{11}\text{B}$ values ranging from $+5.5$ to $+34.9\%$, while the Cl-rich lake had a lighter $\delta^{11}\text{B}$ of $+0.6\%$, similar to the Dieng geothermal brines. The heavier $\delta^{11}\text{B}$ values of the acid sulfate crater lakes are a combination of vapor phase separation, evaporation after discharge and preferential adsorption of ^{10}B by clay minerals. The heavy $\delta^{11}\text{B}$ ($+34.9\%$) of the Kawah Sikidang acid sulfate crater lake was presumed to be produced by excessive evaporation, while its B content of 73.3 mg/L was due to input from B-rich minerals in the shallow subsurface. Meanwhile, the light $\delta^{11}\text{B}$ and B-rich of the Kawah Putih acid chloride crater lake were due to rocks leaching by acid water.

The B isotope of hot springs on Java represented their groundwater mixing origin, except for J21 (Segaran) and J48 (Cikundul) that underwent enrichment by B adsorption into minerals.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jvolgeores.2015.12.014>. These data include the Google map of the most important areas described in this article.

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