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## Boron isotope variations in geothermal systems on Java, Indonesia



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#### ABSTRACT

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

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#### 1. Introduction

Geothermal waters are known to have a large range of  $\delta^{11}$ 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  $\delta^{11}$ 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  $\delta^{11}$ B values in the geothermal fluids on the Argentine Puna Plateau (Kasemann et al., 2004). The heavy  $\delta^{11}$ 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  $\delta^{11}B$  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  $^{10}{\rm B}$  isotope in the solid phases and thus increase the  $\delta^{11}{\rm B}$  of thermal waters. Thermal waters that condensed from the vapor phase of a geothermal system are potentially enriched in  $^{11}{\rm B}$  because of  $^{11}{\rm B}$  fractionation into the vapor phase. The  $\delta^{11}{\rm B}$  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  $\delta^{11}B$  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  $\delta^{11}B$  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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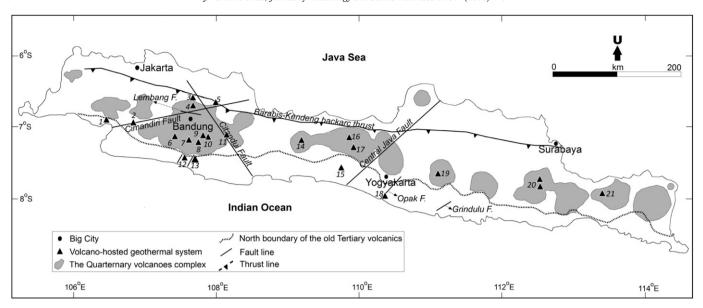


Fig. 1. The sampling location of geothermal fields on Java, i.e., (1) Cisolok, (2) Cikundul, (3) Batu Kapur, (4) Tangkuban Parahu, (5) Tampomas, (6) Patuha, (7) Pangalengan, (8) Darajat, (9) Kamojang, (10) Cipanas, (11) Ciawi, (12) Cilayu, (13) Pakenjeng, (14) Slamet, (15) Krakal, (16) Dieng, (17) Kalianget, (18) Parangtritis, (19) Lawu, (20) Arjuna-Welirang 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 Prahu volcano, Cileungsing 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<sub>3</sub>. 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 multicollector 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<sub>3</sub> in the samples was substituted with H<sub>2</sub>O to minimize the memory effects, in addition washing using 0.05 NH₄OH 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  $\pm$  0.1 °C in a thermostatic hot plate rack. The <sup>11</sup>B data were reported in  $\delta$  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 ( $\delta^{18}$ O,  $\delta^{2}$ H and  $\delta^{11}$ 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  $\delta^{11}$ B, i.e., -2.4 to +28.7% and +0.6 to 34.9%, respectively. In contrast to the B content, acid sulfate

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