Incipient rifting accompanied by the release of subcontinental lithospheric mantle volatiles in the Magadi and Natron basin, East Africa

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Abstract

Geochemical investigations of volatiles in hydrothermal systems are used to understand heat sources and subsurface processes occurring at volcanic-tectonic settings. This study reports new results of gas chemistry and isotopes (O, H, N, C, and He) of thermal spring samples (T = 36.8–83.5 °C; pH = 8.5–10.3) from the Magadi and Natron basin (MNB) in the East African Rift (EAR). Although a number of thermal springs are shown to ascend along normal faults and feed into major lakes (Magadi, Little Magadi, and Natron), volatile sources and fluxes of these fluids are poorly constrained. CO2 is the most abundant phase (up to 996.325 mmol/mol), and the N2/He-Ar abundances show a mixture of dissolved gases from deep (mantle-derived) and shallow (air/air saturated water) sources. The H2-He-Ar-Ch4-CO2 geothermometers indicate that equilibrium temperatures range from ~100 to ~150 °C. δ18O (−4.4 to −0.2‰) and δ13C (−28.9 to −3.9‰) values of the MNB thermal waters still lie slightly to the right of the local meteoric water lines, reflecting minor evaporation. Each mixing relationship of N2, CO2, C (δ13C = −5.7 to 1.6‰; CO2/He = 7.24 × 105–1.81 × 107) suggests that the predominant mantle component of the MNB volatiles is Subcontinental Lithospheric Mantle (SCLM). However, N2 is mostly atmospheric, and minor CO2 is contributed by the limestone end-member. 3He/4He ratios (0.64–4.00 Ra) also indicate a contribution of SCLM (Ra/Ra = 6.1 ± 0.9), with radiogenic 3He derived from a crustal source (R/Ra = 0.02). The MNB 4He flux rates (3.64 × 1011 to 3.34 × 1014 atoms/m2 s) are significantly greater than the reported mean of global continental flux values (4.18 × 1010 atoms/m2 s), implying that magma intrusions could supply mantle 3He, and related heating and fracturing release crustal 4He from the Tanzanian craton and Mozambique belt. Total flux values (mol/yr) of He, N2, and CO2 are 8.18, 4.07 × 107, and 5.31 × 109, which are 1.28%, 2.04%, and 0.24% of global 4He fluxes, respectively. Our results suggest that the primary source of magmatic volatiles in the MNB is SCLM, with additional crustal contributions, which is different from the KRV volatiles that have more asthenospheric mantle components. Volatiles from SCLM in magmas stall in the crust to heat and fracture country rock, with accompanying crustal volatile release. These volatile signatures reveal that MORB-type mantle replaces a relatively small volume of SCLM during incipient rifting (<10 Ma) in the EAR.

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1. Introduction

Maggmatic volatile percolation plays a key role in assisting continental rifting processes. Recent studies illustrate the potential for massive volatile fluxes at magma-rich settings like the East African Rift (EAR), highlighting continental rifts as significant contributors to Earth’s carbon cycle (Lee et al., 2016). Additionally, volatile release is inferred to initiate swarms of earthquake activity in the lower crust (Reyners et al., 2007; Lindenfeld et al., 2012; Albaric et al., 2014), and localize upper crustal strain as continental rifts evolve to sea-floor spreading ridges (Muirhead et al., 2016). Constraining the sources, transport mechanism, and volumetric fluxes of magmatic volatiles at continental rift settings therefore provides important insights into how continental rifting initiates and evolves.

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Geochemistry and isotopes of volatiles (N2, CO2, and He) from volcanic and hydrothermal systems allow tracing of their sources in the Earth system (Sano and Fischer, 2013; Fischer and Chiodini, 2015). Active volcanism is the primary source of volatile emissions to the atmosphere, via volcanic eruption and diffuse degassing (Burton et al., 2013). Mantle-derived volatiles are also transported by fluids along extensional and compressional faults which are known as permeable pathways through the ductile-brittle transition zone (Kennedy et al., 1997; Kennedy and van Soest, 2007; Lee et al., 2016). In the East African rift (EAR), a number of currently active volcanoes (e.g., Erta Ale, Nyiragongo, Nyamuragira, and Oldoinyo Lengai) are emitting volatiles (Sawyer et al., 2008a, 2008b; Fischer et al., 2009; de Moor et al., 2013). The EAR hydrothermal areas also release mantle-derived volatiles, which have been reported at the Lake Kivu, Kenya rift valley (KRV), and Rungwe regions (Darling et al., 1995; Tedesco et al., 2010; Barry et al., 2013; de Moor et al., 2013). Helium isotope ratios indicate mantle plume components in the Afar, Ethiopian, and Rungwe areas (3He/4He = 9–20 Ra; Marty et al., 1996; Hilton et al., 2011; Darrah et al., 2013), yet no mantle plume signature is observed in other parts of the EAR such as the Kivu and KRV regions (e.g., Darling et al., 1995; Tedesco et al., 2010; Fischer et al., 2009). Despite these findings the sources and fluxes of volatiles from hydrothermal systems along much of the >3000 km-long EAR are yet to be investigated.

The present study focuses on the sources and fluxes of volatiles from hydrothermal systems in the Magadi-Natron basin (MNB) at the border of Kenya and Tanzania (Fig. 1). Although volatile geochemistry has been reported previously for the area (Crane, 1981; Crane and O’Connell, 1983; Barry et al., 2013; Lee et al., 2016; Muirhead et al., 2016), little is currently known about possible volatile sources for the MNB hydrothermal system, because geochemistry and isotopes of dissolved gases (N2, CO2, and He) in the MNB thermal springs have not been investigated nor have fluxes of volatiles transported by hydrothermal systems been studied in detail. Here, we report results of gas chemistry, isotope compositions, and fluxes of volatiles from thermal spring samples in order to constrain volatile sources and fluxes through the MNB. In addition, this study first reports nitrogen isotope values of the KRV samples as well as contents of H2S, HF, and HCl, which provide insights into better understanding of volatile sources and processes in the KRV.

Fig. 1. Map of the Magadi and Natron basin (MNB), made by GeoMapApp (Ryan et al., 2009). The inset displays the western and eastern rifts as well as the Kenya rift valley (KRV) and the study area (MNB). Locations of the 15 sampled thermal springs show different colour based on 3He/4He isotope ratios. Also, seismic swarms reported in Ibs-von Seht et al. (2001) and Calais et al. (2008) are highlighted.
2. Regional setting

The EAR is the largest and most active continental rift in the world, extending from Afar to Mozambique (~3000 km), and bifurcating into western and eastern rifts (Ebinger and Scholz, 2012). Although related volcanism in the eastern rift is oldest at its northern extent in Afar (~30–45 Ma; Baker, 1987; Ebinger et al., 1989; George et al., 1998; Nyblade and Brazier, 2002), rifting is thought to have initiated at ~25 Ma in both the Afar and Lake Turkana regions (Ebinger et al., 2000). The youngest basins in the eastern rift occur in the south, where it reaches the Archean Tanzanian craton in northern Tanzania (Foster et al., 1997; Le Gall et al., 2008; Machevelli et al., 2008). By comparison, the western rift, composed of the Toro-Ankolean, Virunga, Kivu, Mwenga-Kamituga, and Rungwe provinces, initiated after the eastern rift, with basins dated between 24 and 1 Ma (Ebinger, 1989; Pastels et al., 1989; Kampunzu et al., 1998; Roberts et al., 2012).

Current models for rift development in the eastern rift suggest that, during the earliest stage of continental rifting (<10 Ma), a relatively small volume of the stretched and heated subcontinental lithospheric mantle (SCLM) is replaced by the asthenosphere, accompanied by decompression melting and release of mafic fluids, making the overlying lithospheric thinner and hotter (Ebinger, 2005; Corti, 2009). As rifting process continued, the asthenosphere rose upward and decompression melting occurred, leading to volumetric increase in volcanism. Magmatism accommodated a larger proportion of the plate boundary strain, finally resulting in the formation of sea-floor spreading ridges (e.g., Buck, 2004; Ebinger, 2005).

The Kenya Rift Valley (KRV) extends from the Turkana region to Northern Tanzania (Fig. 1), and exhibits a series of lakes within the subsiding basins (Turkana, Baringo, Bogoria Elementeita, Nakuru, Naivasha, Magadi and Natron) (Darling et al., 1995). In addition, a number of volcanic centers (Barrier, Namaramunu, Emuruangorak, Silali, Paka, Korosi, Menengai, Eburr, Longonot, Olkajem, Suswa, and Oldoinyo Lengai) and related geothermal areas are utilized for geothermal exploration (Hochstein et al., 2000). Darling et al. (1995) noted that the KRV releases mantle-derived gases via fumaroles, boreholes and seeps associated with volcanic centers. Recently magmatic volatile release has been quantified at Longonot volcano (Robertson et al., 2016).

The Magadi and Natron basin (MNB) is located in the southern section of the eastern rift (KRV), at the border of southern Kenya and Tanzania and are partly filled by lakes Magadi, Little Magadi, and Natron. The MNB hereafter will be distinguished from northern areas of the KRV as the Magadi and Natron basins are in an earlier stage of continental rifting (Muirhead et al., 2016), with rifting initiating at ca. 7 and 3 Ma, respectively (Crossey, 1979; Baker, 1987; Foster et al., 1997). The rift developed in Archean and Late Proterozoic crust, and the ~N-S suture between the two crustal provinces lies ~50 km west of the EAR. Crystalline basement is overlain by widespread Miocene trachytes and recent sediments (e.g., Baker, 1987; Ebinger et al., 1997). Several volcanoes lie within the MNB: Lunderer, Shompole, Geltai, Oldoinyo Lengai, and Karisimbi volcanoes, with historic eruptions at Oldoinyo Lengai volcano, and a dike intrusion along the southern flank of Geltai volcano in a broad monogenetic cone complex (Muirhead et al., 2015). Several other Quaternary volcanoes lie on the uplifted western footwall (Muirhead et al., 2016). In addition, the area is tectonically active, with seismic swarm events in 1997–1998 and 2007 at northern Magadi and eastern Natron (near Geltai volcano) areas (Ibs-von Seht et al., 2001; Calais et al., 2008) (Fig. 1). Lakes Magadi, Little Magadi, and Natron are fed by hot springs (T ~ 86 °C) which discharge saline alkaline fluids (Eugster, 1970; Hochstein et al., 2000). Lake Magadi has a thick trona (Na2CO3·NaHCO3·2H2O) deposit that resulted from evaporation of saline alkaline waters (Jones et al., 1977). The hydrology of lake Magadi is subdivided into dilute streamflow, dilute groundwater, saline groundwater, saturated brine, and remain brines on the basis of water chemistry (Jones et al., 1977). It has been reported that the saline spring waters of both the Magadi and Natron regions are Na-HCO3 waters (Jones et al., 1977; Hochstein et al., 2000). Several geothermal exploration studies have been previously conducted in the MNB (Crane, 1981; Crane and O’Connell, 1983). Additionally, Barry et al. (2013) reported on two spring samples at the western side of Lake Natron, giving radiogenic 4He-rich isotope values (He/4He = 0.61–0.67 Ra), as well as flux of total CO2 and 4He, of 5.0 × 1018 mol/yr and 0.46 mol/yr, respectively. Muirhead et al. (2016) also reported data from 5 thermal springs in the MNB which show a two-component mixing relationship between the mantle and air. Lee et al. (2016) made the first measurements of diffuse CO2 emission in the MNB and analyzed carbon isotopes, proposing that 4.05 Mt/yr of the mantle-derived CO2 degasses

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along faults that penetrate to lower crustal levels. A recent study of Muirhead et al. (2016) also suggests that these areas of magmatic volatile release in the MNB coincide with zones of high fault strain. However, sources as well as the flux of volatiles from hydrothermal systems in the MNB is poorly known, despite having important implications for the role of volatile release in early-stage rifting processes.

3. Samples and analytical methods

The thermal spring samples in the MNB (T = 36.8–83.5 °C) and the KRV (T = 40.0–79.6 °C) were collected in pre-evacuated Giggenbach bottles. Gas samples from fumaroles and bubbling thermal springs from Siliali to Suswa in the KRV were collected in pre-evacuated Giggenbach bottles filled with 4 N–NaOH solution. Locations and types of samples are summarized in Table 1. Dissolved gas compositions in the thermal waters and solutions were determined in the Volatiles Laboratory at the University of New Mexico (UNM) generally following the procedures of Giggenbach and Goguel (1989). Concentrations of CO₂, CH₄, H₂, Ar + O₂, N₂, and CO were measured on a Gow-Mac series G-M 816 Gas Chromatograph (GC) using a helium carrier gas, with experimental errors of ~2%. Gas species were separated on the GC using a Hayes Sep pre-column and 5 A molecular sieve columns. A discharge ionization detector was used for CO₂, CH₄, H₂, Ar + O₂, N₂, and CO, respectively. He, Ar, O₂, and N₂ were also measured in dynamic mode on a Pfeiffer Quadrupole Mass Spectrometer (QMS) with a mass range from 0 to 120 amu and a secondary electron multiplier detector. Analytical errors on the QMS are ~2%. Concentrations of all gas components were acquired after merging the data from GC and QMS. Concentrations of CO₂ and total sulfur (SO₂) in the NaOH solution were determined by CO₂ titration and BaSO₄ precipitation/alkaline iodine titration methods, respectively (Giggenbach and Goguel, 1989). Argon isotope ratios (40Ar/36Ar) were determined in static mode on QMS. Hydrogen (3H) and oxygen (18O) isotopes in water samples were simultaneously analyzed by a Los Gatos Research (LGR) liquid water isotopic analyzer in the Center for Stable Isotopes (CSI), at UNM. Total dissolved inorganic carbon (TDIC) contents including HCO₃⁻ and CO₃²⁻ were obtained by titration using 0.1 N or 0.01 N-H₂SO₄ solution. Because we assumed that extensive dissolution of CO₂ occurs in the alkaline spring waters, the total CO₂ contents in Table 2 were calculated by taking TDIC and gaseous CO₂ contents. Nitrogen isotope and carbon isotope compositions were analyzed on an Isotope Ratio Mass Spectrometer (Thermo Delta V Plus) with a gas bench in CSI at UNM, following methods described in Fischer et al. (2002), Zimmer et al. (2004), Elkins et al. (2006), Newell et al. (2008), and de Moor et al. (2013). Experimental errors for both 13N and 15N are 0.1‰ (1σ). For helium isotopes, copper tubes were used to collect fumarole and thermal spring samples. ³He/⁴He ratios were analyzed on noble gas mass spectrometers (Helix-SFT and VG-5400) at the Atmosphere and Ocean Research institute of the University of Tokyo (AORI). He and Ne were purified using hot titanium getters (at 400 °C) and charcoal traps (at liquid nitrogen temperature). The ²⁸Ne/¹²Ne ratios were acquired by an on-line QMS. Neon was removed using a cryogenic trap (at 40 K). Experimental errors for and ³He/⁴He and ²⁸Ne/²⁰Ne ratios are about 1% and 5% (1σ, SFT-Helix) and about 3.5% and 5% (1σ, VG5400), respectively (Sano et al., 2008). The correction of ³He/⁴He ratios for atmospheric helium used measured ³He/²⁸Ne ratios (Craig et al., 1975) because ²⁸Ne is assumed as almost atmospheric. According to Craig et al. (1975):

\[
\frac{R_c}{R_a} = \left( \frac{\text{He}}{\text{Ne}} \right)_{\text{measured}} \left( 1 - \frac{(\text{He}/\text{Ne})_{ASW}}{(\text{He}/\text{Ne})_{\text{measured}}} \right)
\]

where \(R_c/R_a\) denotes the air-corrected ³He/⁴He ratio, and (³He/²⁸Ne)ASW is the ³He/²⁸Ne ratio of ASW (air-saturated water ratio).

Table 2

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<th>Sample ID</th>
<th>CO₂</th>
<th>N₂</th>
<th>Ar</th>
<th>He</th>
<th>O₂</th>
<th>H₂</th>
<th>CH₄</th>
<th>CO</th>
<th>N₂/He</th>
<th>N₂/Ar</th>
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<td>10.012</td>
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<td>0.052</td>
<td>0.002</td>
<td>0.003</td>
<td>0.005</td>
<td>0.0005</td>
<td>0.0008</td>
<td>194</td>
<td>41.5</td>
</tr>
<tr>
<td>KN14-S02</td>
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<td>12.771</td>
<td>0.168</td>
<td>0.004</td>
<td>0.004</td>
<td>0.002</td>
<td>0.008</td>
<td>0.0001</td>
<td>0.0007</td>
<td>197</td>
<td>51.1</td>
</tr>
<tr>
<td>KN14-S03</td>
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<td>12.748</td>
<td>0.191</td>
<td>0.017</td>
<td>0.009</td>
<td>0.003</td>
<td>0.016</td>
<td>0.0003</td>
<td>0.001</td>
<td>363</td>
<td>52.6</td>
</tr>
</tbody>
</table>

* Data reported in Muirhead et al. (2016).
Chemistry of dissolved gases is summarized in Table 2. CO₂ is the major volatile component (966–996 mmol/mol) of the MNB thermal springs like the KRV samples (up to 981 mmol/mol), followed by N₂. Most of the samples show minor O₂ concentration (≤16 mmol/mol) except for KN13-F13, KN13-F14, and KN13-F15 which reflect significant air contribution (≥114 mmol/mol). The KRV fumarole samples contain H₂S (up to 108 mmol/mol) without SO₂ and minor amount of HF and HCl, but the bubbling springs have lower concentrations of H₂S (<1 mmol/mol). CH₄ and H₂ are minor in the MNB in comparison with the KRV samples, which have CH₄ up to 47 mmol/mol and H₂ up to 28 mmol/mol. Ar is also minor (<1 mmol/mol), but the samples with severe air contribution display higher Ar contents (e.g., KN13-F13, KN13-F14, and KN13-F15), indicating such Ar is mostly derived from air. Helium and CO are minor too, but most of He/Ar ratios are >0.01 distinguished from air (Table 2).

δ¹³C and δD values of the MNB and KRV waters average −4.4 to −0.2‰ and −28.9 to −3.9‰, respectively (Table 3). KRV springs have δ¹³C and δD values of (−3.4 to −0.2‰) and δD (−19.0 to −4.2‰), respectively (Table 3). δ¹³N-N₂ values of all samples (MNB and KRV) show a narrow range (−1.6 to +2.6‰) except for KN14-S11 (+5.9‰) that likely reflects a locally biogenic N₂-rich sampling site (Table 4). δ¹³C-TDIC values of the MNB thermal springs range from −0.4 to +3.7‰ (Table 4). ⁴⁰Ar/³⁶Ar ratios of the MNB springs range from 303.5 to 451.9 (Table 4) which are two orders of magnitude lower than the MORB value (³⁶Ar/³⁶Ar = 44,000, Moreira et al., 1998). The highest value comes from samples from Olidonyo Lengai fumaroles (947, Fischer et al., 2009), indicating that they are significantly affected by air (³⁶Ar/³⁶Ar = 295.5). The range of ⁴⁰Ar/³⁶Ar ratios in the KRV are 273.2 to 322.0, and show less Ar that the MNB samples. They are consistent with measurements of Darling et al. (1995) who proposed Ar is mainly atmospheric.

δ¹³C-CO₂ values of the MNB thermal springs are calculated based on two equilibrium reactions (HCO₃⁻ + CO₂ + CO₂⁻ + H₂O) in alkaline aquifer systems, following the approaches of Allard et al. (1997) and Gilli et al. (2009):

δ¹³C-CO₂ = δ¹³C-TDIC - δ¹³C-CO₃ - δ¹³C-CO₃ (2)

4. Results

Chemistry of dissolved gases is summarized in Table 2. CO₂ is the major volatile component (966–996 mmol/mol) of the MNB thermal springs like the KRV samples (up to 981 mmol/mol), followed by N₂. Most of the samples show minor O₂ concentration (≤16 mmol/mol) except for KN13-F13, KN13-F14, and KN13-F15 which reflect significant air contribution (≥114 mmol/mol). The KRV fumarole samples contain H₂S (up to 108 mmol/mol) without SO₂ and minor amount of HF and HCl, but the bubbling springs have lower concentrations of H₂S (<1 mmol/mol). CH₄ and H₂ are minor in the MNB in comparison with the KRV samples, which have CH₄ up to 47 mmol/mol and H₂ up to 28 mmol/mol. Ar is also minor (<1 mmol/mol), but the samples with severe air contribution display higher Ar contents (e.g., KN13-F13, KN13-F14, and KN13-F15), indicating such Ar is mostly derived from air. Helium and CO are minor too, but most of He/Ar ratios are >0.01 distinguished from air (Table 2).

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where $\delta^{13}$C-CO$_2$ and $\delta^{18}$O-H$_2$O are the fractionation factors (as $\%$) during gas-water transfer and dissolution of CO$_2$ (Zhang et al., 1995), respectively, and $\delta^{18}$O-TDIC is the molar fraction of HCO$_3$ relative to TDIC.

Values are from Bräuer et al. (2004) and Crossey et al. (2009), respectively. For two samples at Little Magadi ($-0.9$ and $+1.6\%$) (Table 4). $^{4}$He/$^{20}$Ne ratios of the MNB and KRV samples range from $0.7 \times 10^8$ to $1.84 \times 10^{11}$ (Table 4). The MNB thermal springs have higher $^{3}$He/$^{4}$He ratios ($0.64$ and $4.00$ Ra) than the crustal end-member ($0.02$ Ra; Ozima and Podosek, 1983) (Table 4). $^{4}$He/$^{40}$Ar ratios of the MNB thermal springs range from $2.13$ to $7.49$ Ra, which are similar as Darling et al. (1995) have reported. In Table 4, the corrected $^{4}$He/$^{40}$Ar ratios ($R_c/R_a$) are similar to $R/R_a$ values because $^{4}$He/$^{20}$Ne ratios of the Rungwe volcanic province, and Dallol data points are previously reported in the EAR (Fischer et al., 2009; de Moor et al., 2013; Darrah et al., 2013). Eger rift and Colorado Plateau springs have higher $^{3}$He/$^{4}$He ratios ($0.64$ and $4.00$ Ra) than the crustal end-member ($0.02$ Ra; Ozima and Podosek, 1983) (Table 4). $^{4}$He/$^{40}$Ar ratios of the MNB thermal springs range from $2.13$ to $7.49$ Ra, which are similar as Darling et al. (1995) have reported. In Table 4, the corrected $^{4}$He/$^{40}$Ar ratios ($R_c/R_a$) are similar to $R/R_a$ values because $^{4}$He/$^{20}$Ne ratios of the MNB thermal springs (mean = $218.7$) and the KRV samples (mean = $127.3$) are much greater than those of ASW (0.273) or air (0.318), indicating minor air contribution to the samples. Some samples, such as KN14-S1, TZ14-S6, KN13-F13, and KN13-F14, show somewhat higher air contributions based on $^{4}$He/$^{20}$Ne ratios (Table 4). As shown in Fig. 1 and Table 4, higher $^{4}$He/$^{40}$Ar ratios are observed at the Little Magadi (up to $3.51$ Ra) and eastern Natron (up to $4.00$ Ra) areas. The lowest $^{4}$He/$^{40}$Ar ratios are $0.64$ and $0.70$ Ra (this study) at western Natron where lower $^{3}$He/$^{4}$He ratios ($0.61$ – $0.67$ Ra) have also been reported by Barry et al. (2013). Amounts of $^{4}$He in all waters range from $1.59 \times 10^{-4}$ to $3.55 \times 10^{-16}$ ccSTP/g (Table 4).

### 5. Discussion

#### 5.1. Gas geochemistry

The $N_2$-$He$-$Ar$ relative abundances of the MNB samples (Fig. 2) show a two-component mixing relationship between deep (mantle-derived) and shallow (air/ASW) sources (Fig. 2). This is consistent with other areas in the EAR, for example, the KRV (Darling et al., 1995; Muirhead et al., 2016; this study), Oldoinyo Lengai fumaroles (Fischer et al., 2009), the Rungwe volcanic province (RVP, de Moor et al., 2013), and the Dallol region (Darrah et al., 2013) as well as other continental areas, such as the Eger rift (Bräuer et al., 2004) and the Colorado Plateau (Crossey et al., 2009). Some of the MNB samples have lower $N_2/He$ ratios (40–84, Table 2) than the MORB value (150; Marty and Zimmermann, 1999). High He concentrations (up to 10.2 vol%) were observed in central Tanzania (Macheyeki et al., 2008), and this is ascribed to release of radiogenic He from the Archean Tanzanian Craton and Proterozoic Mozambique belt composed of plutonic and metamorphic rocks by heating and fracturing (Danabalan et al., 2016). Similarly, lower $N_2/He$ ratios than MORB are observed in the Eger rift samples, ranging from 20 to 6500 (Weinlich et al., 1999; Bräuer et al., 2004). The MNB and Eger rift areas are both continental rifts, associated with old plutonic and metamorphic rocks (Tanzanian craton and Variscan massif, respectively) which likely contain abundant U and Th rich rocks to produce and release radiogenic $^{4}$He. Detailed crustal He degassing is discussed in Section 5.5.

$CO_2$, $CH_4$, $H_2S$, He, and Ar data indicate that the gases are affected by both magmatic and thermogenic processes, and suggest that $CH_4$ is mainly produced by thermogenesis. $CH_4$ and $H_2S$ are observed in the KRV samples (Table 2) as observed in the RVP (de Moor et al., 2013) and Dallol (Darrah et al., 2013) gases. The $CO_2$-$H_2S$-$CH_4$ relationships (Fig. 3a) show that the KRV fumaroles are in the field of volcanic-hosted geothermal systems like the majority of Dallol gases, with $CO_2/H_2S$ ratios ranging from 6.4 to 55.7. The KRV bubbling springs are all associated with soda springs, coinciding with the RVP and several Dallol gases, which are related to travertine depositing springs (Crossey et al., 2009; de Moor et al., 2013). In comparison with other MNB springs, $CH_4$ is relatively more abundant in the Little Magadi springs (Table 2), with $CH_4/He$ ratios higher than 50 as well as the KRV samples with the $CH_4/He$ ratios ranging from 91 to 4482 (Fig. 3b). These $CH_4/He$ ratios likely reflect $CH_4$ addition because they are significantly higher than the...
ratios of Oldoinyo Lengai fumaroles (0.1–8.5, Fischer and Lee, unpublished), which could represent more mantle-like compositions. Darling et al. (1995) proposed that CH$_4$ in the KRV is derived from thermogenic decomposition of organic matter. In the Dallol bubbling springs, several samples have abundant CH$_4$ that is associated with thermogenic production (Darrah et al., 2013). In Fig. 3b, two Little Magadi springs and the majority of KRV and Dallol samples reflect the contribution by organic sediments to increase CH$_4$/He ratios. Other MNB springs, RVP, and a few of KRV and Dallol samples show two component mixing relationship between mantle/crust and air/ASW.

5.2. Gas geothermometry

Gas geothermometers are well constrained by the H$_2$O-CO$_2$-H$_2$-CO-CH$_4$ abundances in hydrothermal fluids, which are utilized in gas geothermometry (Chiodini and Marini, 1998). Using molar fractions of H$_2$, Ar, CO$_2$, and CH$_4$ (Table 2), the CO$_2$-H$_2$-CH$_4$ equilibria of the MNB and KRV samples as well as the RVP samples (reported in de Moor et al., 2013) are defined using the approaches of Tassi et al. (2010) and Benavente et al. (2016) as follows:

\[
\log\left(\frac{H_2}{Ar}\right)_{\text{vapor}} = R_H + 6.52
\]

(3)

\[
\log\left(\frac{H_2}{Ar}\right)_{\text{liquid}} = R_H - \log(B_{H2}) + 6.52
\]

(4)

\[
Ar^* = Ar - O_2/22
\]

(5)

\[
\log(\frac{CH_4}{CO_2})_{\text{vapor}} = 4R_H + 5.181/T(K)
\]

(6)

\[
\log(\frac{CH_4}{CO_2})_{\text{liquid}} = 4R_H + 5.181/T(K) + \log(B_{CO2}) - \log(B_{CH4})
\]

(7)

where $R_H$ is $\log(H_2/H_2O)$, and $B_{H2}$, $B_{CO2}$, and $B_{CH4}$ are distribution coefficients depending on temperature between vapor and liquid phases (Giggenbach, 1980, 1987). Assuming hydrothermal fluids are O$_2$-free, $Ar^*$ is a value taking into account air contamination at the surface (Tassi et al., 2010; Benavente et al., 2016). The $R_H$ of the Fe(II)-Fe(III) redox buffer is $-2.8$, which represents typical hydrothermal fluids (Giggenbach, 1987).

Using this approach, gas geothermometry of the MNB thermal springs indicates low temperatures, suggesting that magmatic volatiles were cooled down and oxidized in the shallow subsurface. The KRV fumarolic gases are clearly distinguished from other samples, implying that the fumaroles are a mixture of vapor and liquid phases in the hydrothermal systems (Fig. 4). $R_H$ values of the KRV fumaroles ($-2.4$ to $-2.8$) show that the equilibrium conditions are more reduced than the Fe(II)-Fe(III) buffer, with equilibrium temperatures ranging from $-280$ to $-340$ °C. This could indicate magmatic volatiles discharging at the fumaroles are reduced, coinciding with H$_2$S dominated sulfur species (Table 2). The Oldoinyo Lengai fumaroles show hotter ($T = -300$ to $-400$ °C) and more oxidized ($R_H = -3.2$ to $-3.4$) equilibrium conditions than the buffer and KRV fumaroles (Fig. 4). SO$_2$ flux at Oldoinyo Lengai measured by Fischer et al. (2006) supports the release of oxidized magmatic fluids. The MNB spring gases are oxidized ($R_H = -3.6$ to $-4.4$), similar to the KRV springs ($R_H = -3.2$ to $-3.4$).
−3.8) and RVP samples that include samples from both gas vents and springs \( (R_{\text{m}} = −3.6 \text{ to } −4.0) \). Hence, equilibrated temperatures of the MNB springs range from −100 to −150 °C. However, the temperature range is colder than the RVP gas vents and springs \( (\text{up to } −230 \, \text{°C}) \) and KRV springs \( (\text{up to } −180 \, \text{°C}) \) \( (\text{Fig. 4}) \) as well as the calculated maximum temperature \( (255 \, \text{°C}) \) at the RVP using the \( \text{CO}_2-\text{CH}_4 \) geothermometer \( (\text{de Moor et al., 2013}) \). Thus, the dissolved gases are likely magmatic, but masked by shallow re-equilibration processes associated with crustal material and groundwater \( (\text{Fig. 4}) \).

5.3. Stable isotopes

5.3.1. O and H isotopes

\( \delta^{18} \text{O} \) and \( \delta^D \) values of the MNB spring waters all plot slightly to the right of both the Kenyan Meteoric Water Line \( (\text{KMWL}, \delta^{18} \text{O} = 5.56 \times \delta^{18} \text{O} + 2.04) \) and Kenyan Rift Ground Water \( (\text{KRGW}, \delta^{18} \text{O} = 5.49 \times \delta^{18} \text{O} + 0.08) \) which already reflected evaporative trends compared to the Global meteoric water line \( (\text{Allen et al., 1989}) \) \( (\text{Fig. 5}) \). \( \delta^{18} \text{O} \) and \( \delta^D \) values are consistent with those reported by Allen et al. \( (1989) \), which show a slightly positive \( O \)-isotope shift. The isotopic shift could be attributed to mixing between meteoric and magmatic waters, water-rock interactions, or evaporation. It is unlikely that meteoric water is mixed with basaltic waters because the \( \delta^{18} \text{O} \) values are still lighter than the proposed basaltic magmatic waters \( (\delta^{18} \text{O} = 6 \text{ to } 10 \, \%_, \text{ Allard, 1983}) \) or even Oldoinyo Lengai rocks \( (\delta^{18} \text{O} = 7.4 \text{ to } 24.1 \, \%_\text{c}, \text{ Mangler et al., 2014}) \). Also, the reservoir temperatures \( (T = −100 \text{ to } −150 \, \text{°C}) \) based on the geothermometers are insufficient to reach at O-isotope exchange according to Truesdell and Hulston \( (1980) \) and Capaccioni et al. \( (2014) \). Lastly, Allen et al. \( (1989) \) noted that the KMWL and KRGW already reflect evaporative trends in this area. Moreover, they suggested that the \( O-H \) isotopes of the Magadi hot springs represent unaltered meteoric water \( (\text{local rivers}) \). Hence, it is unlikely that isotope exchange could occur with host rocks.

5.3.2. \( \text{N}_2 \) sources

\( \text{N}_2 \) is one of the major dissolved gases in both the MNB and KRV regions and susceptible to air contamination due to abundance in air (78%). As nitrogen isotopes are contributed by air, mantle, and sediment, many studies have used \( \delta^{15} \text{N} \) versus \( ^{40} \text{Ar}/^{36} \text{Ar} \) \( (\text{Marty and Humbert, 1997}) \), \( N_2/^{36} \text{Ar} \) \( (\text{Sano et al., 1998, 2001}) \), \( N_2/\text{He} \) \( (\text{Fischer et al., 2002; Clor et al., 2005; Elkins et al., 2006; de Moor et al., 2013}) \), and \( N_2/^{36} \text{He} \) \( (\text{Sano et al., 1998, 2001; Bräuer et al., 2004, 2016}) \) values to constrain \( N_2 \) sources. In \( \text{Fig. 6} \), the relationships between \( \delta^{15} \text{N} \) and \( ^{40} \text{Ar}/^{36} \text{Ar} \) values show that most of the MNB and KRV samples plot near \( \delta^{15} \text{N} = 0 \%_c, \delta^{15} \text{N} = 7.4 \text{ to } 24.1 \, \%_c \). \( \delta^{15} \text{N} \) values decrease as \( ^{40} \text{Ar}/^{36} \text{Ar} \) values increase, implying both \( N \) and \( \text{Ar} \) are derived in part from the mantle and sediment compositions.

To constrain mixing relationships between mantle, ASW/air, and sediment-derived-\( N_2 \), we apply the approach of Sano et al. \( (2001) \), using \( \delta^{15} \text{N} \) and \( N_2/^{36} \text{He} \) values after consideration of the lower \( N_2/^{36} \text{He} \) ratios of the samples \( (\text{Section 5.1}) \) and lack of reported \( ^{40} \text{Ar}/^{36} \text{Ar} \) values in the RVP and Eger rift regions for comparison:

\[
\delta^{15} \text{N}_{\text{measured}} = \delta^{15} \text{N}_{\text{air}} \times f_{\text{air}} + \delta^{15} \text{N}_{\text{mantle}} \times f_{\text{mantle}} + \delta^{15} \text{N}_{\text{sediment}} \times f_{\text{sediment}}
\]

\[
\frac{1}{(N_2/^{36} \text{He})_{\text{measured}}} = \frac{1}{(N_2/^{36} \text{He})_{\text{air}}} \times f_{\text{air}} + \frac{1}{(N_2/^{36} \text{He})_{\text{mantle}}} \times f_{\text{mantle}} + \frac{1}{(N_2/^{36} \text{He})_{\text{sediment}}} \times f_{\text{sediment}}
\]

where \( f \) is a fraction of each component. \( \delta^{15} \text{N}_{\text{air}}, \delta^{15} \text{N}_{\text{mantle}}, \text{and } \delta^{15} \text{N}_{\text{sediment}} \) are \( 0 \%_c, −5 \%_c \text{ to } 7 \%_c \), and \( 7 \%_c \text{ to } 8 \%_c \), respectively. \( \delta^{15} \text{N}_{\text{air}}, (N_2/^{36} \text{He})_{\text{air}}, (N_2/^{36} \text{He})_{\text{mantle}} \) and \( (N_2/^{36} \text{He})_{\text{sediment}} \) are \( 1.1 \times 10^{11}, 8.9 \times 10^5, \text{ and } 1.4 \times 10^{12} \), respectively \( (\text{Sano and Wakita, 1983; Marty, 1995; Marty and Humbert, 1997; Sano et al., 2001}) \). In \( \text{Fig. 7a} \), the majority of the MNB \( \delta^{15} \text{N} \) values are on the mixing line between mantle and air, and are similar to the KRV samples.

However, most of the data plot left of the mantle-air mixing line on the \( \delta^{15} \text{N} \) and \( N_2/\text{He} \) diagram as was seen in previously reported data from Central America, Indonesia, and RVP \( (\text{Zimmer et al., 2004; Clor et al., 2005; Elkins et al., 2006; de Moor et al., 2013}) \). We identify three possible scenarios to account for this observation. First, the \( \delta^{15} \text{N} \) values could be negatively shifted due to fractionation between gases and water depending on water temperature. In order to resolve this issue,
Lee et al. (2015) proposed that $\delta^{15}$N values of dissolved gases in water are negatively fractionated as water temperature increases compared to ambient air (25 °C) based on a modeling experiment at temperatures between 5 °C and 60 °C. Temperatures of the MNB thermal springs range from 36.8 to 83.5 °C, which is likely to cause the negative N isotope shift from the mixing line by up to about 1‰. However, most of the corrected $\delta^{15}$N values still plot to the left of the mixing line (Fig. 7a), and thus do not fully resolve this issue. Second, the $\delta^{15}$N value of MORB ($-5 \pm 2$‰, Marty and Humbert, 1997) could be inappropriate as an end-member for the mixing lines. Clor et al. (2005) and Elkins et al. (2006) have alternatively taken the extreme $\delta^{15}$N values of $-15$‰ (Mohapatra and Murty, 2004) to resolve this mantle end-member issue. In Fig. 7b, some of the $\delta^{15}$N and $N_2/3He$ values still plot near the mixing lines with the $-15$‰ mantle value, suggesting that an extreme mantle end-member is not present beneath the MNB and KRV areas. Finally, the $N_2/3He$ ratio of the mantle beneath the MNB may be different from MORB. Bräuer et al. (2004) observed that all of their data ($\delta^{15}$N $=$ $-4.4$ to $-1.1$‰, $N_2/3He$ $=$ $8.21 \times 10^6$–$3.92 \times 10^6$) from the Cheb basin in the Eger rift plot left of the mantle-air mixing line on a $\delta^{15}$N and $N_2/3He$ diagram. To resolve this issue, they applied an alternative $N_2/3He$ ($5 \times 10^6$) for the mantle source, European Subcontinental Mantle (ESCM, assumed $R/Ra$ $=$ 6.5), which is similar to the upper limit of $N_2/3He$ ($3.76 \times 10^6$) for MORB reported by Marty and Zimmermann (1999). Using the $N_2/3He$ of $5 \times 10^6$ as the SCLM end-member instead of MORB, the values still show a negative shift of $\delta^{15}$N values (Fig. 7c). In Fischer et al. (2009), $N_2/3He$ values of Oldoinyo Lengai fumaroles range from $1.88 \times 10^6$ to $4.02 \times 10^7$, which is higher than that of ESCM, although $CO_2/3He$ ratios ($3.6 \times 10^9$ to $4.1 \times 10^9$) fall in the MORB range (Fischer et al., 2009). Taking the Oldoinyo Lengai values into consideration, we suggest alternative values ($\delta^{15}$N $=$ $-5$‰, $N_2/3He$ $=$ $1.5 \times 10^7$) of the SCLM component beneath the MNB region. Using this end-member, most of the EAR and Cheb basin values are included in the mixing lines (Fig. 7c), which indicates the SCLM beneath the MNB may have a higher $N_2/3He$ ratio than ESCM. Also, Mana et al. (2015) proposed that magmatism occurs in lithosphere beneath the northern Tanzania. Overall, these observations are consistent with Lee et al. (2016) who proposed that the volatiles in the MNB are derived from the lower crust and upper mantle, which implies the SCLM could be the source for the mantle-derived volatiles. According to the theoretical mixing equations with the SCLM end-member ($\delta^{15}$N $=$ $-5$‰, $N_2/3He$ $=$ $1.5 \times 10^7$), atmospheric $N_2$ is significant for both the MNB (up to 90.7% of $f_{atm}$) and KRV (up to 99.9% of $f_{atm}$) (Table 5), as originally noted by Darling et al. (1995) for the KRV. Atmospheric $N_2$ is dissolved in ASW and dilutes deeper $N_2$ sources at shallow levels (Giggenbach and Poreda, 1993). However, in Table 5, a component of SCLM-derived $N_2$ is still significant for some samples in both the MNB (up to 64.9% of $f_{mantle}$) and KRV (up to 69.0% of $f_{mantle}$). This indicates that SCLM is the likely predominant mantle end-member in this region.

### 5.3.3. $CO_2$ sources

$\delta^{13}CO_2$ values of the MNB thermal springs ($-5.7$ to $-3.1$‰), except for two Little Magadi thermal springs ($1.6$ and $-0.9$‰), overlap with the KRV samples ($-7.1$ to $-3.3$‰ (Table 4) and RVP values ($-6.45$ to $-3.1$‰) (Table 4).
In Fig. 8a, CO2/3He ratios and dissolved 4He concentrations of First, He is significant enough to separate a vapor phase (Table 1). Second, additional CO2 were observed in two springs, and temperatures of fumaroles are high in the case of the KRV samples, it is plausible to lose He because bubbles produced because water temperatures are lower than 100 °C (Podosek, 1983; Bräuer et al., 2013). However, there is no bubbling gas (Sano and Marty, 1995). For individual samples from both the MNB and KRV areas, CO2 sources are primarily either mantle (up to 2.0 × 109, 1 × 1013, and 1 × 1013, respectively (Marty and Jambon, 2002) reported a wide range of CO2/3He ratios (~109 to ~1013) from worldwide-sampled SCLM xenoliths implying additional CO2 could be derived from SCLM. Bräuer et al. (2016), based on their selected samples, proposed higher δ13C and CO2/3He ratios of the MNB thermal springs. The gray area is the range of the CO2/3He ratios of MORB (1 × 106 to 6 × 106, Marty and Zimmermann, 1999).

Table 5 Results of calculated end-member contributions for N2 and CO2.

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Table 5 Results of calculated end-member contributions for N2 and CO2.

a A fraction of SCLM instead of MORB.
b CO2/3He ratios of TZ14-S03 and TZ14-S05 are assumed as 2 × 109.

to −2.7‰ (Barry et al., 2013). Darling et al. (1995) suggested that CO2 from the KRV is derived from the mantle, with δ13CCO2 values ranging from −7.1 to −1.7‰. According to recovered CO2/3He ratios and δ13CCO2 values, CO2 sources are quantified by these mixing equations:

δ13C_mantle = δ13C_limestone × fmantle + δ13C_sediment × flimestone

(11)

1/(CO2/3He)_measured = fmantle/(CO2/3He)mantle + flimestone/(CO2/3He)limestone + fsediment/(CO2/3He)sediment

(12)

defmantle + deflimestone + defsediment = 1

(13)

where δ13C_mantle, δ13C_limestone, and δ13C_sediment are −6.5 ± 2.5, 0, and −30‰, and (CO2/3He)mantle, (CO2/3He)limestone, and (CO2/3He)sediment are 2.0 × 109, 1 × 1013, and 1 × 1013, respectively (Marty and Jambon, 1987; Sano and Marty, 1995). For individual samples from both the MNB and KRV areas, CO2 sources are primarily either mantle (up to 97%) or crustal limestone (up to 90.0%) without significant sediment input which is <20% for all samples (Table 5). Heavier δ13CCO2 Values are observed in two Little Magadi springs likely due to dissolution of CO2 from carbonate rocks surrounding aquifer systems, which has been suggested for similar lithologies in the US (Crossey et al., 2009; Sherwood-Lollar and Ballentine, 2009; Zhou et al., 2012).

Most of the MNB and KRV samples have elevated CO2/3He ratios relative to MORB values (1 × 106 to 6 × 109, Marty and Zimmermann, 1999). In Fig. 8a, CO2/3He ratios and dissolved 4He concentrations of the MNB thermal springs (Table 6) show a negative correlation, and a majority of values plot above the MORB range, except for two samples (CO2/3He < 1 × 1010). This may be attributed to He loss or CO2 addition. First, He is significantly less soluble in CO2 water than in water (Ozima and Podosek, 1983; Bräuer et al., 2013). However, there is no bubbling gas in the MNB thermal springs. Moreover, a vapor phase is unlikely to be produced because water temperatures are lower than 100 °C (Table 1), making preferential partitioning of He into vapor unlikely. In the case of the KRV samples, it is plausible to lose He because bubbles were observed in two springs, and temperatures of fumaroles are high enough to separate a vapor phase (Table 1). Second, additional CO2 has affected the elevated CO2/3He ratios. This additional CO2 could be derived from crust that is a mixture of both limestone and organic sediments, but these rocks are minor in surface outcrops (Table 5). A more likely scenario is that the CO2 is SCLM-dominated in the MNB area consistent with Lee et al. (2016) who suggested that the deep source of CO2 appears to be the lower crust and upper mantle. Dunai and Porcelli (2002) reported a wide range of CO2/3He ratios (~109 to ~1013) from worldwide-sampled SCLM xenoliths implying additional CO2 could be derived from SCLM. Bräuer et al. (2016), based on their selected samples, proposed higher δ13C and CO2/3He values (δ13C = −3.5‰, CO2/3He = 7 × 109) than MORB for the ESCM. To determine SCLM
compositions in the MNB, we selected samples with values of $\delta^{13}$C $< -2\%$ and $2 \times 10^9 < \text{CO}_2 / \text{He} < 1 \times 10^{11}$ as well as taking Oldoinyo Lengai samples (Fischer et al., 2009), because the $\delta^{13}$C values of SCLM xenoliths range from $-2$ to $-8\%$ (Cartigny, 2005), and crustal CO$_2$/He ratios are $> 1 \times 10^{11}$ (Barry et al., 2013). Based on these constraints, we suggest that the MNB area has SCLM compositions ($\delta^{13}$C $= -3.5\%$ and CO$_2$/He $= 7.31 \times 10^6$) similar to ESCM. Two samples with lower CO$_2$/He ratios (Fig. 8b) probably gained more radiogenic He compared to the amount of CO$_2$ loss (Table 4).

### 5.4. Helium sources

All $\text{R}/\text{Ra}$ ratios of the MNB thermal springs are $> 0.1$ (Table 4), which implies that the mantle-derived fluids have relatively short residence time in the crust during transport to the shallow subsurface (Ballentine et al., 2002). However, the highest $\text{He}/\text{Ra}$ ratio observed (4.0 Ra) is still lower than both the ratios for SCLM (6.1 ± 0.9 Ra, Gautheron and Moreira, 2002) and for MORB (8.0 ± 1.0 Ra, Graham, 2002), showing a plume signature (9–20 Ra, Marty et al., 1996) is unlikely detected in the MNB. Although a MORB $\text{He}/\text{Ra}$ ratio is observed at the Silali volcano fumaroles (7.49 and 8.00 Ra) in the KRV (Darling et al., 1995; this study), the highest reported $\text{He}/\text{Ra}$ ratio of 6.86 Ra at Oldoinyo Lengai is lower than the MORB value (Fischer et al., 2009). Additionally, Hopp et al. (2007) showed that at Chyulu Hills in south Kenya, an active off-axis volcanic field ~100 km east of the study region, $\text{He}/\text{Ra}$ ratios of mantle xenoliths ($5.62$ to $7.59$ Ra) are within the range of SCLM. Moreover, SCLM-related He-Ne systematics are found in mantle xenoliths and basaltic rocks in the southern Kenya rift (Halldórsson et al., 2014).

Lithospheric thickness decreases with increasing extension and heating. Along-strike variations in lithospheric thickness associated with southward younging (Magadi < 7 Ma and Natron < 3 Ma, Crossley, 1979; Foster et al., 1997), may be factor in the variations we see. It is likely that SCLM-derived volatiles instead of MORB-type volatiles are contributing to the MNB hydrothermal system, which is consistent the model suggested by Mana et al. (2015). Taking the SCLM value as the mantle end member we can quantify He sources of the MNB thermal springs. Mantle contributions to each thermal spring source are calculated by the following equation:

$$ f_{\text{mantle}} = \frac{\left[(\text{R}/\text{Ra})_{\text{measured}} - (\text{R}/\text{Ra})_{\text{crust}}\right]}{\left[(\text{R}/\text{Ra})_{\text{SCLM}} - (\text{R}/\text{Ra})_{\text{crust}}\right]} $$ (14)

$$ f_{\text{crust}} = 1 - f_{\text{mantle}} $$ (15)

where $f_{\text{mantle}}$ is a fraction of mantle-derived He, and (R/Ra)$_{\text{SCLM}}$ and (R/Ra)$_{\text{crust}}$ are $\text{He}/\text{Ra}$ ratios of SCLM (6.1 ± 0.9 Ra, Gautheron and Moreira, 2002) and crust (0.02 Ra, Ozima and Podosek, 1983).
respectively. The $f_{\text{crust}}$ values range from 34 to 90%, showing that significant amounts of continental crustal fluids have been incorporated into the MNB hydrothermal systems (Fig. 9). In volcano-hydrothermal systems, it has been shown that $^{4}\text{He}/^{3}\text{He}$ ratios decrease with distance from the volcanic center due to the increasing contribution of $^{4}\text{He}$-rich groundwaters from crustal sources (Sano and Fischer, 2013). Underneath the MNB, Precambrian metamorphic basement rocks (Archean Tanzanian craton and late Proterozoic Mozambique belt) are covered by Pliocene-Pleistocene trachyte (Baker, 1986; Ebinger et al., 1997), likely containing abundant U and Th to produce radiogenic $^{4}\text{He}$. Therefore, we suggest it is likely that the MNB thermal springs, with lower $^{4}\text{He}/^{3}\text{He}$ ratios, have been affected by interactions with $^{4}\text{He}$-rich groundwater. The highest $^{4}\text{He}/^{3}\text{He}$ ratios are observed at the Little Magadi (up to 3.5 Ra) and eastern Natron (up to 4.0 Ra) areas (Fig. 1), implying less interaction with $^{4}\text{He}$-rich groundwater, and possibly lower residence times in the crust; consequently, we suggest these springs are in close proximity to the primary conduits for deeply sourced volatiles. This is supported by the occurrence of recent seismic swarm in the Little Magadi region in 1997–1998, which may have represented the migration of magmatic fluids within a developing fracture network (Ibs-von Seht et al., 2001). Similarly, in the eastern Natron area the highest $^{4}\text{He}/^{3}\text{He}$ ratio (4.0 Ra) is adjacent to the Gelai magmatic- tectonic event in 2007 (Fig. 1). Since this event, the region has been subject to ongoing earthquake activity, with frequently occurring NE-trending swarms of relatively low magnitude earthquakes ($M_w$ < 4.5) occurring between Oldoinyo Lengai and the northern flanks of Gelai (Lee et al., 2016). Consistent with interpretations of seismic swarms elsewhere in the EAR (e.g., Albertine and Manyara basins; Lindenfeld et al., 2012; Albaric et al., 2014), this seismicity may represent hydraulic fracturing in response to high fluid pressures resulting from volatile release from underlying magma bodies (Lee et al., 2016).

### 5.5. Continental $^{4}\text{He}$ flux

In the MNB, a number of thermal springs discharge along fault zones, releasing volatiles ($N_2$, $CO_2$, and $He$). As stated above, the MNB thermal springs show higher He contents, which are likely affected by release of radiogenic He through alpha decay of U and Th from the Archean Tanzanian craton and Mozambique Proterozoic metamorphic belt (Danabalan et al., 2016). The radiogenic $^{4}\text{He}$ flux values of the MNB thermal springs are calculated as:

$$\phi^{4}\text{He} = 6.022 \times 10^{21}/22.400 \times \phi_{\text{spring}} \times [^{4}\text{He}]$$

where $\phi^{4}\text{He}$ is a flux rate of $^{4}\text{He}$ (as atoms m$^{-2}$ s$^{-1}$), $\phi_{\text{spring}}$ is each flow rate of spring in the MNB reported by Crane (1981) and Crane and O’Connell (1983) (Table 6), and $[^{4}\text{He}]$ is the concentration of $^{4}\text{He}$ dissolved in each sample spring (Table 6). The calculated spring $^{4}\text{He}$ range from $3.74 \times 10^{11}$ to $3.34 \times 10^{14}$ atoms m$^{-2}$ s$^{-1}$, which is four orders of magnitude higher than the global continental $^{4}\text{He}$ flux compiled from calculated results of helium excesses in lakes and aquifers as well as gradients in gas wells ($2.8 \times 10^{10}$ atoms m$^{-2}$ s$^{-1}$, O’Nions and Oxburgh, 1988). In order to account for higher spring $^{4}\text{He}$ flux than the expected production rate through alpha decay of U and Th, the host rocks must release their accumulated radiogenic He (Lowenstern et al., 2014). Caracausi and Paternoster (2015) suggested that high crustal $^{4}\text{He}$ flux may be a temporal effect after moderate to large magnitude earthquakes to cause intense rock fracturing.

The mean of continental $^{4}\text{He}$ fluxes of the MNB springs ($5.86 \times 10^{14}$ atoms m$^{-2}$ s$^{-1}$) is greater than that of the global $^{4}\text{He}$ flux ($4.18 \times 10^{10}$ atoms m$^{-2}$ s$^{-1}$, Torgersen, 2010) calculated from reported measurements in various geological environments (e.g., lakes, groundwater basins, and volcanic areas) by a factor of ~1000. According to the approach of Torgersen (2010), the $^{4}\text{He}$ flux of the MNB can be subdivided into mantle and crustal flux values (Table 6). Using this approach, the MNB spring $^{4}\text{He}$ fluxes ($2.8 \times 10^{10}$–$2.5 \times 10^{14}$ atoms m$^{-2}$ s$^{-1}$) (Table 6) are higher than the previously reported tectonic strain values ($2.0 \times 10^{9}$–$1.8 \times 10^{11}$ atoms m$^{-2}$ s$^{-1}$, Torgersen, 2010), which suggests that fracturing released crustal $^{4}\text{He}$. A swarm of teleseismic earthquakes of magnitude $\geq$ 5 occurred in 2007 in the southern Natron basin, but no earthquakes of magnitude $> 4.5$ have occurred in the Magadi basin in historic time (Ebinger, unpublished results). Observed spatial variations, therefore, are not well explained by the intense fracturing model.

Torgersen (2010) separated worldwide-reported $^{4}\text{He}$ fluxes into regions of volcanic and tectonic-strain, considering that the continental $^{4}\text{He}$ flux increases due to releasing $^{4}\text{He}$ from fracturing of rocks by tectonic strain or additional mantle helium via magmatism. Higher continental $^{4}\text{He}$ flux values are found in volcanic areas, such as Lake Nyos (3.0–$10^{14}$ atoms m$^{-2}$ s$^{-1}$, Kipfer et al., 2002), Laacher See (1.0–$10^{13}$ atoms m$^{-2}$ s$^{-1}$, Kipfer et al., 2002) and Yellowstone (3.16–$10^{12}$ atoms m$^{-2}$ s$^{-1}$, Lowenstern et al., 2014). Also, the mantle $^{4}\text{He}$ fluxes of the MNB ($4.2 \times 10^{11}$–$7.5 \times 10^{12}$ atoms m$^{-2}$ s$^{-1}$) are higher than the range of tectonic strain region values ($1.0 \times 10^{5}$–$3.5 \times 10^{10}$ atoms m$^{-2}$ s$^{-1}$, Torgersen, 2010), indicating that the addition of mantle $^{4}\text{He}$ has occurred. Similarly, other volcanic areas show higher mantle $^{4}\text{He}$ fluxes that range between $3.23 \times 10^{5}$ atoms m$^{-2}$ s$^{-1}$ and $1.96 \times 10^{14}$ atoms m$^{-2}$ s$^{-1}$ (e.g., Taiwan, Yellowstone, and Lake Nyos). When plotted on an empirical $^{4}\text{He}$ flux diagram, the MNB $^{4}\text{He}$ flux data appears more representative of volcanic areas rather than tectonic strain (Fig. 10).

Magma intrusions transfer heat to the crust, and repeated dike intrusions lead to a reduction in strength locally (e.g., Buck, 2004; Daniels et al., 2014; Muirhead et al., 2016). New and existing seismic data from the Magadi and Natron basins indicate regular magma intrusions (e.g., dikes and sills) into the crust within the central basins, and evidence for one or more lower crustal magma chambers (Calais et al., 2008; Biggs et al., 2009). Thus we suggest magma intrusions likely play a key role in supplying and transporting mantle $^{4}\text{He}$, and related heating and fracturing release crustal $^{4}\text{He}$ from Archean Tanzanian craton and/or the late Proterozoic Mozambique belt into the fluids in the MNB.
5.6. Mantle-derived volatile fluxes in the MNB hydrothermal system

Finally, it is likely that a number of thermal springs release mantle-derived volatiles (\(3\text{He}, N_2, \text{and CO}_2\)). Fluxes of these mantle-derived volatiles transferred by fluids have not yet been calculated, although a massive amount of CO\(_2\) (4.05 Mt/yr) from diffuse degassing along the faults in the MNB has been reported (Lee et al., 2016). Using our results from the MNB thermal springs and \(\phi\)\(^{3}\text{He}\) values calculated, the fluxes of fluid-derived \(3\text{He}, N_2, \text{and CO}_2\) can be acquired using these equations:

\[
\phi_{3\text{He}} = \phi^{4}\text{He} \times (3\text{He} / 4\text{He})
\]

\[
\phi_{N_2} = \phi^{3}\text{He} \times N_2 / \phi_{3\text{He}}
\]

\[
\phi_{\text{CO}_2} = \phi^{3}\text{He} \times \text{CO}_2 / \phi_{3\text{He}}
\]

where \(\phi^{3}\text{He}, \phi_{N_2}, \text{and } \phi_{\text{CO}_2}\) are flux rates (atoms m\(^{-2}\) s\(^{-1}\)) of \(3\text{He}, N_2, \text{and CO}_2\), respectively. \(\phi_{\text{spring}}\) is the flow rate of each spring (Crane, 1981; Crane and O’Connell, 1983), and \(f_{N_2-\text{mantle}}\) and \(f_{\text{CO}_2-\text{mantle}}\) are the contribution of mantle end-member to \(N_2\) and \(\text{CO}_2\), respectively (Table 6). Total flux values of \(\phi^{3}\text{He}, \phi_{N_2}, \text{and } \phi_{\text{CO}_2}\) were calculated in the MNB thermal area, (1193.2 km\(^2\), Crane, 1981; Crane and O’Connell, 1983), which exclude areas without samples in this study. The values of \(3\text{He}, N_2, \text{and CO}_2\) are 8.18 mol/yr, 4.07 \(\times\) 10\(^7\) mol/yr and 5.31 \(\times\) 10\(^8\) mol/yr, respectively (Table 6). The total \(\phi_{\text{CO}_2}\) and \(\phi^{3}\text{He}\) values are better constrained than previously reported values (total \(\phi_{\text{co}_2}=5.68 \text{ Mt/yr, respectively (Table 6). In the MNB, the total}\)

\[\begin{array}{c}
\text{5.7. Geochemical implications for continental rifting}
\end{array}\]

The MNB area is a young section of the EAR (Section 2), and the hydrothermal system shows a variety of geochemical features of incipient magmatic rifting. Our isotope modeling of \(N_2\) (Fig. 7c) and \(\text{CO}_2\) (Fig. 8a) shows that MORB is inappropriate as a mantle end-member. Instead, the SCLM is more likely the primary magma source beneath the MNB (Fig. 11), which is also consistent with observations in a magmatic Eger rift in the European continent (Bräuer et al., 2004; Bräuer et al., 2013). Additionally, \(3\text{He}/4\text{He}\) ratios of the MNB thermal springs (0.64–4.00 Ra) (Table 4) and Oldoinyo Lengai (6.68–6.86 Ra, Fischer et al., 2009) support the contribution of SCLM (6.1 \(\pm\) 0.9 Ra, Gautheron and Moreira, 2002) beneath the MNB. As discussed in Section 5.5, SCLM-derived(300,334),(652,638) volatiles are supplied and transported by magma intrusions that also heat and fracture host rocks to release crustal volatiles (Fig. 11). The mixture of SCLM and crustal volatiles is contaminated by atmospheric components in ASW or air-infiltration in the shallow subsurface (Fig. 11). The SCLM-derived volatiles in the MNB support the rift development model of Ebinger (2005), which suggests that the asthenosphere (MORB-type mantle) replaces a relatively small volume of...
SCLM during the early stage of continental rifting. Further south in Tanzania, near the southern end of the eastern rift, 3He/4He ratios are all <0.1 (0.039–0.053 Ra) and dominantly crustal (Danabalans, 2016). This implies that a smaller fraction of lithosphere is replaced by the asthenosphere underneath the youngest sectors of the eastern rift.

6. Conclusions

Our results show new data of gas chemistry and isotopes (O, H, N, C, and He) of the MNB thermal springs. Dissolved gases are a mixture of deep (mantle-derived) and shallow (air/ASW) sources according to the N2-He Ar systematics. Equilibrated temperatures of the hydrothermal systems range from 100 to 150 °C using the log(H2/Ar) and log (CH4/CO2) geothermometry. N2 is mostly atmospheric with minor mantle-derived contribution. CO2 which is the most abundant gas component in the MNB thermal springs is contributed by both mantle and limestone, similar to the KRV samples. Helium is derived from both mantle and crust. However, SCLM can be the dominant mantle source for N2, CO2, and He in the MNB, with the contribution of continental crust. The higher continental 4He flux values in the MNB relative to the mean global continental flux suggest that magma intrusion, and related heating and fracturing, releases additional mantle and crustal helium into the hydrothermal system. Fluxes of mantle-derived volatiles (4He, N2, and CO2) represent 1.28%, 2.04%, and 0.24% of global fluxes. Our results suggest the MNB thermal springs discharge magmatic volatiles from SCLM, which significantly interacted with continental crust and demonstrate that a small volume of SCLM is replaced by the asthenosphere during the incipient stages of continental rifting (<10 Ma) in the EAR.

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