Geochemical signatures of geothermal systems at Kibiro and Ngozi geothermal prospects

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Ngozi geothermal prospect and nearby areas

Data from:
Barry, 2012; Barry et al., 2013; Basy and Mayila, 1986; Branchu et al., 2005; Delalande, 2009; Delalande et al., 2008a; Delalande et al., 2008b; Delalande et al., 2011; Delalande-Le Mouëllic et al., 2015; de Moor, 2013; de Moor et al., 2013; Fontijn et al., 2010; Fontijn et al., 2013; Furman, 1995; Hochstein et al., 2000; Kraml et al., 2008; Kraml et al., 2010; Kraml et al., 2012; Kraml et al., 2014; Makundi and Kifua, 1985; Maqway, 2011; Mnjokava, 2007; Nzaro, 1970; Ochmann and Garofalo, 2013; Pisarskii et al., 1998; Teale and Oates, 1934.
Several thermal springs (red symbols) and gas emissions (yellow symbols) are present in the Ngozi geothermal prospect and nearby areas. Most of them are evidently controlled by faults.

From the GEOTHERM Project report 2013
The **Songwe hot springs** are the most important thermal manifestations. The hot springs of Kaguri and Madibira were sampled for the first time during this project.
The summit caldera of Ngozi volcano hosts a crater lake. The lake is 2.5 km long and 1.6 km wide, has a surface of about 3.1 km$^2$ and a volume of $72.7 \cdot 10^{-3}$ km$^3$.

High temperature sites at lake bottom:
yellow = temperature $>$ 20.6°C
orange = temperature $>$ 24.6°C
red = temperature of 65°C to 89°C
Figure 2.6. Gas fluxes measurement undertaken at Lake Ngozi (2038 m a.s.l.) by means of the floating accumulation chamber method (e.g. Chiodini et al. 1998; WestSystems 2007) in July-August 2010. Two profiles were (total of 46 measurements) acquired. Areas of visible degassing (bubbling) activity at surface (yellow circles) and concurrent efflux of CO$_2$, CH$_4$ and H$_2$S are indicated by green dots. Sites of highest CO$_2$ efflux are indicated by pink dots. CO$_2$ efflux varied between 2±350 g·m$^{-2}$·d$^{-1}$ with a mean value of ca. 130 g·m$^{-2}$·d$^{-1}$. CH$_4$ and H$_2$S were most of the time below the detection limit.
“The geothermal reservoir, whose recharge is from high elevated areas, is located between the Ngozi crater and Mbeya town and the thermal waters are flowing through active faults, related to the major Rift trend, towards the discharge areas, (outflow zones) mainly in the Songwe valley, following the natural hydraulic gradient” (From the GEOTHERM Project report, 2013).
Lake waters have constant pH of 6.4 to 6.7 below 10-20 m and relatively high alkalinity. Hence $P_{CO_2}$ values exceed at all depths and during all the surveys the average $P_{CO_2}$ atmospheric value by 100–200 times.

Na and Cl are the major solutes, with average contents of 960 mg/kg and 1460 mg/kg, respectively.

Delalande et al (2015) computed the water, oxygen-18, deuterium, and chloride budgets for Lake Ngozi, considering three possible scenarios for each year.

The computed chloride concentration interval of the water entering the lake, 62 to 265 mM/L, corresponds to 2200 to 9400 mg/L.
The scenarios presented by Delalande et al. (2015) are not the only possible ones. A virtually infinite number of scenarios is possible. To find a single solution we adapted the iso-chemical geothermometric mixing model (details in the next presentation).

Results obtained for the water entering Lake Ngozi, extending the calculations to other solutes and stable H$_2$O isotopes, are summarized in the following two tables.

<table>
<thead>
<tr>
<th>Date</th>
<th>T (°C)</th>
<th>Na (mg/kg)</th>
<th>K (mg/kg)</th>
<th>Ca (mg/kg)</th>
<th>Mg (mg/kg)</th>
<th>B (mg/kg)</th>
<th>SiO$_2$ (mg/kg)</th>
<th>Li (mg/kg)</th>
<th>Cl (mg/kg)</th>
<th>F (mg/kg)</th>
<th>Br (mg/kg)</th>
<th>SO$_4$ (mg/kg)</th>
<th>δ$^2$H (% vs. VSMOW)</th>
<th>δ$^{18}$O (% vs. VSMOW)</th>
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<tr>
<td>Mar-05</td>
<td>230</td>
<td>4918</td>
<td>572</td>
<td>21.1</td>
<td>4.77</td>
<td>7.93</td>
<td>389</td>
<td>3.63</td>
<td>8050</td>
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<td>5257</td>
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<td>5.10</td>
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<td>27.7</td>
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<td>232</td>
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<tr>
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<td>227</td>
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<td>3.96</td>
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<td>21.7</td>
<td>945</td>
<td>-46.21</td>
<td>-1.71</td>
</tr>
</tbody>
</table>

High SO$_4$ and F are probably of magmatic derivation.
High DIC, HCO₃, and P_{CO₂} due to the high supply of deep CO₂. Water is close to equilibrium with anhydrite, illite and muscovite. It is oversaturated with 14Å-clinochlore due to overestimation of Mg.

Mg* is the Mg concentration computed inserting the Na-K/SiO₂ equilibrium temperatures and the K contents reported in the table of the previous slide into the K-Mg geothermometer.

The water results undersaturated with 14Å-clinochlore if the recomputed Mg* contents are considered instead of Mg in speciation-saturation calculations.
The computed $\delta^2$H vs. $\delta^{18}$O values of the water entering Lake Ngozi (Ngozi hydrothermal-magmatic water, HMW) are positioned along the local rainwater - primary magmatic water mixing line, indicating percentage of primary magmatic water of 49-52 % in March 2005, 39-41 % in September 2006, and 28-33 % in October 2007. Apart from Lake Ngozi (which is affected by evaporation), all the other waters (hot-, warm-, cold- springs and rivers) are along the MWLs.
Lake Ngozi and the related HMW are the only Cl water. Hot springs, warm springs, cold springs and rivers (apart from Igogwe), are all HCO$_3^-$ waters. Hot springs have SO$_4^2-/HCO_3^-$ and Cl/HCO$_3^-$ ratio higher than warm springs, cold springs and rivers.

Hot springs have similar SO$_4^2-/HCO_3^-$ ratio apart from that of Ibayi which has slightly higher SO$_4^2-/HCO_3^-$ ratio.
The chloride diagrams involving the conservative or nearly-conservative components B, Li, and As (see next slide) have similar spread of points, with the Na-HCO$_3$ hot springs situated far away from the Ngozi hydrothermal-magmatic waters and well above its dilution line.
These differences between the Na-HCO₃ hot springs and the Ngozi HMW are possibly due to occurrence of water-rock interaction under different conditions (i.e., provenance from different geothermal systems).

However, this evidence was not considered conclusive by previous authors. In fact:

- either loss of B, Li, and As might occur in lake waters, thus leading to underestimate their concentrations in the Ngozi HMW
- or B, Li, and As acquisition might take place upon dilution of HMW and water-rock interaction governed by conversion of CO₂ to HCO₃.
Also the isotope-chloride plots are not conclusive for the provenance of the hot springs from different geothermal systems.

However, assuming that chloride is entirely supplied to the hot springs through dilution of the Ngozi hydrothermal-magmatic waters, the percentage of these waters in the average Songwe hot spring waters would be $2.7 \pm 0.4\%$, which represents a close to negligible amount. Therefore, it seems more likely that the hot springs come from different geothermal systems.
Lake Ngozi is in the field of the partially equilibrated waters owing to a moderate disequilibrium between Na-K (239 ± 9°C or 224 ± 9°C) and K-Mg (171 ± 3°C). The Ngozi HMW are close to full equilibrium (see above).

The Songwe hot springs (N=13) are in the field of the immature waters due to a high disequilibrium between Na-K (245 ± 9°C or 231 ± 10°C) and K-Mg (124 ± 3°C).
The other hot spring waters form a separate trend and are in the field of the partially equilibrated waters and in the field of the immature waters, with variable disequilibrium between Na-K and K-Mg. For instance, Kilambo hot springs (N = 8) have Na-K temperatures of 179 ± 9°C, and 160 ± 9°C, and K-Mg temperatures of 103 ± 9°C. These are ambiguous situations of difficult interpretation. Conservatively, it is advisable to adopt the K-Mg temperature as representative of the geothermal aquifer of provenance.
The Songwe hot springs are situated close to Lake Ngozi. Both show a considerable Na-K/silica disequilibrium. Lake Ngozi has T-silica of $101 \pm 3^\circ$C and T-quartz of $122 \pm 3^\circ$C. The Songwe hot springs have T-silica of $94 \pm 10^\circ$C and T-quartz of $116 \pm 8^\circ$C. The other hot spring waters are closer to the full equilibrium curves and have lower Na-K/silica disequilibrium. For instance: Kilambo hot springs have T-silica of $141 \pm 8^\circ$C and T-quartz of $155 \pm 7^\circ$C; Kasimulo hot springs have T-silica of $128 \pm 13^\circ$C and T-quartz of $145 \pm 7^\circ$C.
The hot springs have a moderate K-Mg/silica disequilibrium:
- Ibayi (N=1) has T-KMg of 122 °C, T-silica of 106°C, T-quartz of 127°C;
- Songwe (N=13) have T-KMg of 124 ± 3°C, T-silica of 94 ± 10°C, T-quartz of 116 ± 8°C;
- Ilwalilo (N=2) have T-KMg of 110 ± 4°C, T-silica of 106 ± 5°C, T-quartz of 127 ± 4°C.
- Kajala (N=1) has T-KMg of 94 °C, T-silica of 120 °C, T-quartz 138 °C.
- Kilambo (N=8) have T-KMg of 103 ± 9°C, T-silica of 141 ± 8°C, T-quartz of 155 ± 7°C;
- Mapulo-Kandete (N=4) have T-KMg of 108 ± 2°C, T-silica of 131 ± 6°C T-quartz of 147 ± 5°C.
- Kasimulo (N=6) have T-KMg of 109 ± 2°C, T-silica of 128 ± 13°C, T-quartz of 145 ± 10°C.
- Udindilwa (N=1) has T-KMg of 104 °C, T-silica of 99°C, T-quartz of 120°C.

These temperatures are probably representative of the portions of the geothermal aquifer systems attainable through drilling.
Gas samples are found along a trend between an He-rich endmember and ASW, apart from three samples affected by entrainment of atmospheric air.

(i) Gases of cold vents have typical mantle $^{3}$He/$^{4}$He ratios of 6 to 7 $R_A$,
(ii) Gas of Kafwira Njuni cold spring has $^{3}$He/$^{4}$He ratio of 5.5 $R_A$,
(iii) Gases of hot springs have $^{3}$He/$^{4}$He values of 1 to 4 $R_A$, due to mixing between mantle-derived He and $^{4}$He generated by radioactive decay of U and Th in the crust (Barry et al., 2013).
From Fontijn et al. (2010), modified.
Summing up:

**Ngozi**
- A geothermal reservoir at $232 \pm 13^\circ C$ hosting a Na-Cl liquid with Cl concentration of $7600 \pm 1100$ mg/kg is present below Ngozi volcano.
- The geothermal system is sustained by a degassing magma chamber determining high $\text{SO}_4$, F, $\text{HCO}_3$ contents and high $\text{P}_{\text{CO}_2}$, 15 $\pm$ 4 bar.
- The system could have a subterranean outflow towards NW as indicated by the warm springs of Inyala, Iyela, Swaya, Shongo, and Shimilaa.
**Songwe**

- Similar to all the other hot springs of the region, the Songwe hot springs are probably the discharge of a local fault-controlled thermal circuit.

- Songwe thermal waters have Na-HCO$_3$ composition, but their relatively low Na/K ratios reflect in unusually high Na-K temperatures of \( 231 \pm 10^\circ \text{C} \) (Fournier) and \( 245 \pm 9^\circ \text{C} \) (Giggenbach). These high Na-K temperatures contrast with the K-Mg temperature of \( 124 \pm 3^\circ \text{C} \), silica temperature of \( 94 \pm 10^\circ \text{C} \), and quartz temperature of \( 116 \pm 8^\circ \text{C} \).

- The H$_2$-Ar and H$_2$-N$_2$ geothermometers, recalibrated for an \( R_H \) value of -3.79, gives equilibrium temperatures of 132-146°C (details in the next presentation). These temperatures are somewhat higher than the K-Mg and silica/quartz temperatures but much lower than the Na-K temperatures suggesting that the latter might be present at depths possibly unreachable by drilling or unexistent.
Kibiro geothermal prospect


Old water analyses by Arad and Morton, 1969, Bazaale-Dolo, 1986, Dixon and Morton, 1970 were disregarded.
Location map of the sampled water points in the Kibiro geothermal prospect and nearby areas, including the Kibiro hot springs as well as several boreholes, streams and rivers, dug wells, one cold spring, and Lake Albert.
The Kibiro hot springs lies on a narrow plain of about 750 m in width, between the lake shore and the foot of the Toro-Bunyoro fault escarpment.

The main hot spring area, **Mukabiga**, is located in a ravine at the base of the fault escarpment (T = 87 - 81°C).

A second group of hot or warm springs in found downstream, in an area of salt gardens called **Mwibanda** (T up to 72°C).

**Muntere**, directly north of Mukabiga, is the largest salt garden (T = 40 - 45°C).
In the triangular diagram of major anions the Kibiro hot springs are close to the Cl vertex. They are, therefore, Cl waters.

All the boreholes, dug wells, one cold spring, streams, rivers and Lake Albert (apart from the Ndalagi1 borehole), are in the HCO₃ field and are, therefore, HCO₃ waters.

Most HCO₃ waters are close to the HCO₃ vertex, but some waters are somewhat enriched in SO₄, whereas relative Cl concentrations are generally low apart from a few samples.
As pointed out by Armannsson (1994), the hot springs of Kibiro are mixtures of a geothermal endmember and shallow brackish water. The mixing process was modelled using the iso-chemical geothermometric mixing model (details on the next presentation).

The geothermal endmember has $T_{KMg} = T_{silica} = 153^\circ C$ at $Cl = 2870$ mg/L.

The brackish water (BW) has minimum $Cl$ of $\sim 1700$ mg/L ($Ca$ is negative below this $Cl$ content). It shows $K$-$Mg/silica$ disequilibrium.
The geothermal endmember exhibits a considerable K-Mg/Na-K disequilibrium (see plot), with K-Mg temperature of 153°C, Na-K Fournier’s temperature of 236°C and Na-K Giggenbach’s temperature of 250°C.
The geothermal endmember exhibits also a considerable silica/Na-K disequilibrium with silica temperature of 153°C, Na-K Fournier’s temperature of 236°C and Na-K Giggenbach’s temperature of 250°C.
Relevant chloride plots are shown in this slide and next ones.

BW might have been produced through dilution of the geothermal endmember (GE) with conservation of Na and loss of K.
BW might have been produced through dilution of GE accompanied by loss of both Ca and Mg and gain of HCO$_3$. 
BW might have been produced through dilution of GE accompanied by conservation of Br, loss of B and gain of Li.
BW might have been produced through dilution of GE accompanied by loss of both F and SiO$_2$. 
The mixing line was assumed to be constrained by the samples of lowest SO\textsubscript{4} content. The 1993 samples of Mukabiga and Muntere are above the mixing line due to addition of SO\textsubscript{4}.

This excess SO\textsubscript{4} comes from oxidation of sulfide (H\textsubscript{2}S):

\[ \text{H}_2\text{S} + 2\text{O}_2 = \text{H}^+ + \text{SO}_4^{2-} \]

as suggested by the reverse trend in this plot, i.e., H\textsubscript{2}S Mwibanda > H\textsubscript{2}S Mukabiga > H\textsubscript{2}S Muntere.
SO$_4$ and H$_2$S molalities are compared in this plot.

The 1993 samples have total S (H$_2$S + SO$_4$) of 0.66 mmol/kg on average.

Not measured H$_2$S or SO$_4$ contents of the other samples are recalculated assuming total S of 0.66 mol/kg.

These calculations are done because the $\delta^{34}$S values are known for the two samples collected on 10-May-01 (sulfide not measured) and one sample taken on 5-Dec-05 (sulfate not measured).
The production of $SO_4$ through sulfide oxidation increases $SO_4$ concentration and decreases considerably its $\delta^{34}S$ value (see plot). The initial $SO_4$ is expected to have a low concentration and to be isotopically very heavy (see plot).

Isotopically heavy $SO_4$ is typically generated through bacterial sulfate reduction:

$$2CH_2O + SO_4^{2-} = H_2S + 2HCO_3^-.$$  

$CH_2O$ represents the average composition of the organic matter which sustains the process. This reaction cannot occur without the supply of organic matter, which is abundant at Kibiro.

Based on these considerations, sulfate is unlikely to be of magmatic origin, as suggested in previous studies.
Tritium is plotted against electric conductivity (EC) as the chemical analysis is known for one of the two samples from the Kibiro hot springs.

Assuming a linear relation between EC and $^3$H (which is certainly wrong) and that the pure geothermal endmember is $^3$H-free (which is plausible), Kibiro hot springs discharge mixed waters.

The process cannot be quantified due to lack of data.
Let us now consider the stable isotopes of water.

The highly evaporated water of Lake Albert is not shown in this plot of δ²H vs. δ¹⁸O values.

The Kibiro hot spring have a small oxygen shift of ~1 ‰ unit compared to the regional MWL (dynamic system?). The Kibiro hot spring have δ²H lower than all sampled waters (higher recharge elevation or palaeo-waters?).
Kibiro gas chemistry

<table>
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<tr>
<th></th>
<th>CO2</th>
<th>H2S</th>
<th>H2</th>
<th>O2</th>
<th>CH4</th>
<th>N2</th>
<th>Ar</th>
<th>C2H6</th>
<th>Sum</th>
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<tbody>
<tr>
<td>%</td>
<td>4.76</td>
<td>0.04</td>
<td>0.23</td>
<td>7.06</td>
<td>67.29</td>
<td>19.26</td>
<td>0.05</td>
<td>1.3</td>
<td>99.99</td>
</tr>
</tbody>
</table>

Kibiro gases are dominated by CH$_4$, followed by N$_2$, O$_2$, and CO$_2$.

Redox potential is unlikely to be controlled by the Fayalite-Hematite-Quartz (FHQ) buffer, $R_H$ is different from -2.82 and H$_2$-based geothermometers have to be calibrated if possible (work in progress).

Other gas geothermometers are affected by considerable uncertainties.
The $\delta^{13}C$ values of CH$_4$ and CO$_2$ of Kibiro gases are consistent with their production from an organic source.

The isotopic CH$_4$-CO$_2$ geothermometer indicates an equilibrium temperature of 209°C. However, the half-time of isotope exchange is in the order of 135,000 years (Giggenbach, 1997). Approach to isotope equilibrium requires too much time.
The theoretical grid is based on the recommendation of Sakai (1977), who suggested to use the $\text{BaSO}_4(\text{s})-\text{H}_2\text{O}$ equation (Kusakabe and Robinson, 1977):

$$1000 \ln \alpha_{\text{BaSO}_4-\text{H}_2\text{O}} = \frac{3.01 \cdot 10^6}{T^2} - 7.30$$

in near-neutral or basic, high-enthalpy geothermal systems to mimic the isotopic effects on dissolved $\text{SO}_4^{2-}$.

The results provided by the $\Delta^{18}\text{O}(\text{SO}_4-\text{H}_2\text{O})$ geothermometer (75-120°C) may be affected by mixing and production of sulfate by oxidation of sulfide.
Summing up:

- The Kibiro hot springs discharge Na-Cl water of meteoric origin with Cl concentration of 2440-2580 mg/kg (samples collected in 1993). They represent the outflow of a local, fault-controlled thermal circuit hosted in the basement rocks below the lacustine sediments.

- As already recognized by Armannson (1994) mixing with Na-Cl brackish water takes place.

- An iso-chemical geothermometric mixing model indicates an equilibrium temperature of $153^\circ$C (K-Mg and silica geothermometers) for the geothermal endmember, whose Cl concentration is 2870 mg/kg.

- Na-K temperatures (Fournier 236°C; Giggenbach 250°C), are higher and might be present at greater depths, possibly unreachable by drilling, or might be inexistent.
The $\Delta^{18}$O(SO$_4$-H$_2$O) geothermometer indicates equilibrium temperatures of $75\text{-}120^\circ$C, which are uncertain due to (i) mixing and (ii) production of sulfate by near-surface oxidation of sulfide.

The $\delta^{34}$S values of dissolved sulfate are affected by (i) production of sulfate by near-surface oxidation of sulfide and (ii) bacterial sulfate reduction sustained by oxidation of organic matter. The magmatic origin of sulfur (indicated by previous studies) appears unlikely.

Kibiro gases are dominated by CH$_4$, followed by N$_2$, O$_2$, and CO$_2$. Redox potential is unlikely to be controlled by the FHQ buffer. H$_2$-based geothermometers have to be calibrated (work in progress). Other gas geothermometers are uncertain.

The $\delta^{13}$C values of CH$_4$ and CO$_2$ of Kibiro gases are consistent with their production from an organic source. The isotopic CH$_4$-CO$_2$ geothermometer indicates an equilibrium temperature of $209^\circ$C. However, the half-time of isotope exchange is too high for the approach of isotope equilibrium.
Thank you