CHEMICAL AND ISOTOPIC ANALYSIS OF HOT SPRINGS IN ZAMBIA; NO EVIDENCE FOR NEAR SURFACE RIFT- RELATED MAGMATIC BODY

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Abstract: Zambia exhibits extensive geothermal activity in an amagmatic rift zone. Current models for rift initiation suggest magma plays an important role in softening the lithosphere, allowing extension. In Zambia, lack of surface magmatism calls these models into question. Recent studies suggest continental scale links between the mantle and groundwater suggesting surface waters can be used as a proxy of mantle tectonism. This study investigated the geochemistry of hot/cold springs and streams within the Luangwa rift and the surrounding Proterozoic basement. The objectives were: 1) to determine if the chemistry of hot springs have a mantle derived component and 2) determine the temperature and depth of reservoirs sourcing the hot springs. Water samples collected from hot/cold springs and streams were analyzed for physical parameters, anions, cations, silica, dissolved inorganic carbon (DIC) and stable hydrogen (δD), oxygen ($\delta^{18}O$) and carbon isotopes ($\delta^{13}C_{DIC}$), and reservoir temperatures were calculated. The δD and $\delta^{18}O$ for the cold springs and hot springs lie along a similar trend to the local meteoric water line. The DIC concentrations of hot springs are 5 to 20 mgC/L, similar to streams, lower than cold springs, 45 to 125 mgC/L. Except for one group of hot springs (the Lochinvar Group) with $\delta^{13}C_{DIC}$ of -6 to -4‰ most of the hot springs' range of $\delta^{13}C_{DIC}$ 20 to -4‰. The more positive $\delta^{13}C_{DIC}$ of the Lochnivar Group could be from addition of magmatic body sourced CO_2 or CO_2 from deep sedimentary carbonates. The temperature of the hot springs ranged from 31 to 85ºC. Geothermometry estimated reservoir temperatures of 150ºC of the springs confirm the local geothermal gradient of 23ºC/km is sufficient to generate the surface temperatures that were measured. In conclusion, (1) source of water for the hot springs is meteoric, (2) hot springs have not experienced extensive water-rock interaction, (3) $CO_{2(g)}$ from the soil zone is the source of DIC for most hot springs and (4) the apparent absence of magmatic influence on the $\delta^{18}O$ and the $\delta^{13}C_{DIC}$ of the spring samples, means they are heated by locally high geothermal gradient at a depth of 5 km based on the reservoir temperatures.

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CHAPTER I

INTRODUCTION

The current accepted model for rift initiation suggests that magma/mantle fluids play an important role in softening the lithosphere, which allows for extension to take place (Buck, 2006). This model holds true for most rifts studied to date that seem to have large amounts of magmatism associated with them and are at more advanced stages of rifting (e.g., the eastern branch of the East African Rift System (EARS)). However, in other parts of the EARS, magma is absent at the surface thus questioning the role of magma in rift initiation. This lack of understanding of what drives rifting in an amagmatic rift results largely from the lack of geological and geophysical data from these rift systems. The National Science Foundation's Project PRIDE: Project for Rift Initiation Development and Evolution was funded to address this knowledge gap by targeting amagmatic rift systems of the southwestern branch of the EAR, specifically the Okavango Rift Zone, Luangwa Rift and Malawi Rift (Fig. 1). PRIDE is a multi-disciplinary (includes geophysics (seismic, potential fields, magnetotelluric), structural geology and remote sensing and geochemistry) and multi-institutional research program.

The lack of surface magmatism does not rule out magmatism at depth. Magma may play a role in rifting but has yet to breach the surface. Studies by Newell et al. (2005) and Crossey et al. (2006) have clearly established continental scale links between mantle tectonism and water quality for the western United States. Newell et al. (2005) used helium data from hot springs, gas fields, and travertine depositing cold springs and compared this data with mantle velocity structure determined from seismic tomographic studies. Newell et al. (2005) showed that regions of the highest helium isotopes ($^3He/^4He$) in groundwater corresponded to regions of lowest mantle velocity, which the authors suggested reflected tectonically active and partially molten mantle.. Continental scale faults could serve as conduits not only for magma but also water, gases and volatiles from mantle derived sources to be brought to the surface. Hence, if a mantle body was present below the surface in the Zambia section of the EARS, the hot springs in the rift zone may contain geochemical characteristics of mantle signatures similar to those measured in the western US and Tibet by Newell et al. (2005; 2008) and in other hot springs in Ethiopia (Kebede et al., 2008; 2010).

The geochemical and stable isotopic composition of hot springs is related to the extent of heating, the source of water, the nature of volatiles entrained and water-rock interactions during water decent into the subsurface and accent to the surface (Frape et al., 1984). In continental rift systems, hot springs can entrain mass from a shallow degassing lithosphere and from igneous processes related to rifting (Kebede et al., 2008; 2010; Gautason and Muehlenbachs, 1998). Multiple studies in the Main Ethiopian Rift (MER), the most advance rifted segment of the EARS, have use trace elements and stable isotopes of hydrogen (δD), oxygen ($\delta^{18}O$), carbon ($\delta^{13}C$) in water and strontium ($^{87}Sr/^{86}Sr$) isotopes and helium ($^4He/^3He$) in gases to demonstrate the connection between deep crustal (magmatic) and shallow crustal (e.g., ground water evolution) processes (Demlie et al., 2008; Kebede et al., 2008; Kebede et al., 2010; Bretzler et al., 2011). The geothermal heat in the MER is attributed to shallow magma bodies associated with rhyolitic volcanoes, mantle upwelling and igneous intrusions resulting from thinner than average crust (Omenda, 2009). The shallow magmatic bodies contribute $CO_{2(g)}$ to thermal waters as determined by their enriched $\delta^{13}C$ values of dissolved inorganic carbon (DIC) (Kebede et al., 2008; Kebede et al., 2010; Bretzler, 2011; D'Alessandro et al., 1997; Villermant et al., 2005). In addition, the $\delta^{18}O$ for the thermal springs show evidence of enrichment relative to the δD, which is interpreted as isotopic exchange of O between water and silicate minerals (Kebede et al., 2008). The chemical and isotopic characteristics imparted to hot springs can also be from deep sedimentary sources (Kebede et al., 2010). For example, heat can breakdown carbonates to produce $CO_{2(g)}$ which can alter the isotopic composition, stable oxygen ($\delta^{18}O$), of hot springs (Goff et al., 1985).

The widespread occurrence of hot springs, over 80 documented, (Musonda and Sikazwe, 2005) in Zambia provides a geologic setting in which an investigation into possible subsurface processes interacting with surface processes to be assessed. These hot springs are distributed across the region with some occurring along the rift axis and others remote from the Luangwa Rift axis. The Luangwa Rift is a western arm of the East African Rift system (Chorowicz, 2005). The Luangwa Rift is a Karroo rift and shows no evidence of surface igneous activity related to rifting (Chorowicz, 2005 and Legg, 1974). Thus, unlike the MER, the source of the heat cannot be attributed to igneous activity although a shallow mantle resulting from rifting may provide heat. Therefore a comparison of the chemical and isotopic characteristics between hot springs within the Luangwa Rift and beyond the rift, and with cold springs and streams, which are recharged by shallow groundwater with a meteoric source, provides a basis for evaluating deep crustal–shallow crustal interaction along the Luangwa Rift.

Hot springs in Zambia have been studied for geothermal power generation potential (Legg, 1974; Dominco and Liguri, 1986; Sakungo, 1988). These studies have provided valuable information about the major ion and metal chemistry. However, δD, $\delta^{18}O$, and $\delta^{13}C$ isotope data that is vital for determining the origin and chemical and isotopic evolution of water in the hot springs, the extent of water-rock interaction and if the hot spring have entrained solutes, volatiles and gases from deep seated sedimentary rocks, igneous intrusions or the shallow mantle have not been collected.

It is hypothesized that an elevated asthenosphere and shallow magmatic intrusions, if present, will contribute mass (water, solutes, volatiles and gas) to the near subsurface. It is further hypothesized that mass contributed from deep crustal processes will be identifiable in the chemical and isotopic composition of hot springs. The objectives of this study are to (1) conduct a comparative assessment of the chemical and isotopic composition of hot springs, cold springs, and streams throughout Zambia for evidence of additions of mantle mass, specifically water and carbon, (2) determine the processes that control the chemical and isotopic evolution of hot springs and (3) Determine if the chemistry of hot spings/surface waters have a mantle derived component determine the temperature and depth of reservoirs sourcing the hot springs. The anticipated results from this study will be integrated with the geophysical data to be acquired as part of project PRIDE to understand the controls of rifting in amagamtic rifts..

CHAPTER II

STUDY SITE

Section 1. Geology

The Luangwa Valley is a series of well preserve rift units of Mesozoic age that form a rift zone that is very similar to the Tanganyika and Malawi rift zones (Rosendahl, 1987). The Valley is basically a Karroo Lake Malawi without the water (Rosendahl, 1987). The Luangwa Valley is underlain by two Karoo half-graben separated by a central accommodation or transfer zone (Banks et al., 1995). Rifting appears to have been initiated in the early Permian with subsequent rifting events has been related to strike-slip movements along the Mwembeshi Shear Zone (Banks et al., 1995).

Previous studies have documented the presence of 80+ hot springs in Zambia (Musonda and Sikazwe, 2005). The hot springs sampled are grouped into 8 groups based on geographic locations proposed by Legg (1974) and supported by geology of Key et al. (2001) and van Straaten (2002) (Fig. 1). The groups are the Northern, Eastern, Mansa-Copperbelt, Western, Southeastern, Lochinvar, Choma and Kasane Group (Fig. 3). Most hot springs in Zambia are associated with major faults along the contacts of Karroo basement rocks (Legg, 1974). The Northern Group is found along the Mweru rift and is largely underlain by the Bangweulu Block. The Bangweulu Block, is composed of granites, gneisses, schists, migmatites, amphibolites, granulites, charnockites, khondalites, phyllites, limestones and metaquartzites (Schluter, 2008). The Bangweulu Block was deformed during the Paleoproterozic (van Straaten, 2002). The Irumide Belt and the Katanga Supergroup outcrop in northern and north-western Zambia. The Irumide Belt is dated at 1.1 Ga and trends NE-SW (Schluter, 2008). The orogeny that formed the Irumide Belt affected pre-Katanga rocks (Schluter, 2008). The Eastern Group of hot springs includes hot springs in the Luangwa Valley as well as springs outside the valley. Kapishya Hot Spring 1 and 2, located in the Eastern Group but out of the Luangwa Valley, issue along major fractures in pre-Katanga age quartzites (Legg, 1974). The hot springs in the Luangwa Valley, which include the Luangwa River Bluff Springs, Chifunda Mineral Spring and Nsefu Hot Spring issue out of Karroo sandstones (Legg, 1974). The Karoo Supergroup is composed of clastic sediments, coal and tillites, Carboniferous to lower Cretaceous in age. Karoo sediments fill the rift troughs of the Kafu, Luangwa, Luano-Lukusahi and Mid-Zambezi Valleys (Ministry of Mines and Mineral Development, accessed September 2013). The Luangwa, Zambezi and Luano-Lukasashi Valleys are all formed as a result of Karoo rifting (Schluter, 2008). Carbonatites are related spatially to the rift valley structures, the Nkombwa carbonaite specifically is associated with the Luangwa Rift Valley (van Straaten, 2002). The Mansa-Copperbelt Group issues from granites and the contact between the Lower Roan of the Katanga Supergroup marine sediments, conglomerates, dolomites, limestones, sedimentary schists and sandstones (Legg, 1974; van Straaten, 2002). The Western Group is located at the intersection of 2 or 3 faults (depending on location) within Upper Katanga age (Legg, 1974). Bilili Hot Spring, which is a part of the Western Group, occurs along a major fault that separates Katanga age rocks from Lower Karroo rocks (Legg, 1974). The Chinyunyu Hot Spring is part of the Southeastern Group and issues out of basement rocks (Legg, 1973). Southeastern Zambia is also the location of the intersected

Neoproterozoic Zambezi Belt with the Mozambique Belt, the Lufilian Arc and the Damara Belt (van Staaten, 2002). The Lochinvar Group discharge along a major fault that separates Karroo sediments and pre-Katanga rocks. The Lochinvar Group also discharges from an area with gypsum in the upper layers of the alluvium (Legg, 1974). The Choma Group is underlain by the Kalomo Batholith (Legg, 1974). The Kasane Group discharges out of a salt plain on the banks of the Chobe River in Botswana.

Section 2. Climate and hydrology

Zambia is subtropical and experiences dry winters and hot summer (Bäumle et al., 2007). The rainy season, November to April, is warm and wet. The cold season is from April to August and is mild to cool and dry, where the hot season which extends from September to November and is hot and dry (Bäumle et al., 2007). The average rainy season lasts 97 days with an average precipitation of 1000 mm (Groundwater Consultants Bee Pee (Pty) Ltd, SRK Consulting (Pty) Ltd, 2002). The annual temperatures range from 19.3 to 22.1ºC (Bäumle et al, 2007). The main catchment systems are the Zambezi, Kafue, Luangwa, Chambeshi, Luapula Rivers and Lake Tanganyika (Groundwater Consultants Bee Pee (Pty) Ltd, SRK Consulting (Pty) Ltd, 2002). The main rivers are the Zambezi, Kafue, Luangwa and Luapula (Groundwater Consultants Bee Pee (Pty) Ltd, SRK Consulting (Pty) Ltd, 2002). The four natural lakes are Bangweulu, Mweru, Tanganyika and Mweru-wantipa (Groundwater Consultants Bee Pee (Pty) Ltd, SRK Consulting (Pty) Ltd, 2002). Groundwater recharge is estimated to be 57.5 billion cubic meters per year (Groundwater Consultants Bee Pee (Pty) Ltd, SRK Consulting (Pty) Ltd, 2002).

CHAPTER III

METHODOLOGY

Section 1. Sample Collection

Water samples were collected from hot springs, cold springs and streams (Fig. 2) along the Luangwa Rift and other locations in Zambia in June - July 2009 and May - July 2013. Some hot springs were sampled during both field collection seasons (summer 2009 and summer 2013). Water samples from hot springs and cold springs were collected at the source. Water samples from streams were collected in easily accessed areas (e.g., under bridges).

Water samples were collected using the grab technique, sampling at a single point near the water surface. Water samples were filtered in the field using a 0.45 μM nylon filter and stored in 30 mL high density polyethylene (HDPE) bottles for anions and in pre-acidified (high purity HNO_3) 60 mL HDPE bottles for cations. Water samples collected for determination of DIC and $\delta^{13}C_{DIC}$ were collected in 15 mL vacutainer tubes pre-loaded with 1 mL of 85% H_3PO_4 and a magnetic stir bar (Atekwana and Krishnamurthy, 1998). Water sampled for δD and $\delta^{18}O$ isotopes were collected in 20 mL glass scintillation vials with inverted cone closure. All the samples were kept cool in a 12 V portable refrigerated cooler for up to 8 weeks before transportation to Oklahoma State University, where they were stored in a 4°C refrigerator until analysis.

Section 2. Measurements and Sample Analysis

At each sampling location, the temperature, specific conductance (SPC), total dissolved solids (TDS), dissolved oxygen (DO), pH and oxygen-reduction potential (ORP) were measured in situ with a Yellow Spring Instrument (YSI-556® MPS) probe calibrated in accordance with manufacture's recommendations. The temperature and TDS of hot springs with temperatures above 45°C were measured with a Hanna Instruments HI 9124 Waterproof Portable pH Meter with an HI 1006-3007 Industrial Flat Tip pH Electrode and an HI 9835 Portable EC/TDS/NaCl/°C Meter, calibrated in accordance with Hanna Instrument's recommendations. Water from hot springs with water temperatures above 45°C was collected in 1L HDPE bottle, allowed to cool and then the SPC, TDS, ORP and pH were measured with the YSI meter. Physical parameters measured by the YSI are not temperature dependent but had to be collected within the temperature threshold range of the instrument specified by the manufacturer, less than -5 to +45°C with a threshold of ± 0.15°C.

In field, alkalinity was determined by H_2SO_4 titration to an acid equivalent point of 4.2 using a digital titrator (Hatch Company, 1992). Dissolved silica was measured in the field using Heteropoly Blue Chemistry® to determine the "molybdate reactive" silica and measured with a CHEMetrics® V-2000 Photometer at 815 nm (CHEMetrics, 2012). In the laboratory, anions (SO_4^-, Cl^-, PO_4^{3-}, NO_3^-) were determined by ion chromatography (Dionex Ion Chromatography System ICS-3000). Major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) were determined by inductively coupled plasma-optical emission spectrometer (PerkinElmer Optima™ 2000 DV). Dissolved Inorganic Carbon (DIC) concentrations were calculated empirically from $CO_{2(g)}$ extracted from vacutainer tubes under vacuum. The $CO_{2(g)}$ was sealed in Pyrex tubes and later analyzed for $\delta^{13}C$ on a Thermo Finnigan Delta Plus XL isotope ratio mass spectrometer (IRMS). The δD and $\delta^{18}O$ of the water samples were measured by a high temperature elemental conversion analyzer coupled to a

Thermo Finnigan Delta Plus XL IRMS per the Gehre et al. (2004) method. Stable isotopes are reported in delta (δ) notation in per mil (‰):

$$\delta(‰) = [(R_{sample}/R_{standard}) - 1)] \times 1000$$

Where R is D/H, $^{18}O/^{16}O$ or $^{13}C/^{12}C$. The δ values are measured against Vienna Standard Mean Ocean Water (VSMOW) for hydrogen and oxygen isotopes and against Vienna Peedee Belemnite (VPDB) for carbon isotopes. Routine measurements of in-house standards and samples have a precision of better than 2.0‰ for δD, 0.1‰ for $\delta^{18}O$ and 0.1‰ for $\delta^{13}C$.

The $\delta^{18}O$ and δD for precipitation in Ndola (13º00'00" S, 28º39'00" E) Zambia was obtained from the International Atomic Energy Agency/World Meteorological Organization's (IAEA/WMO, 2006) Isotope Hydrology Information System (ISOHIS) database. The Ndola station has average monthly data from 1968 to 2009 (http://isohis.iaea.org; accessed on 16 January 2014).

Section 3. Geochemical Modeling

Saturation indices (SI) with respect to minerals calcite, gypsum, chalcedony, quartz, chrysotile and kaolinite) were calculated using PHREEQC version 2.8 (Parkhurst and Appelo, 1999).

Section 4. Chemical Geothermometry

Subsurface reservoir temperatures for the hot springs were estimated from SiO_2 and cation (Na-K, K^2-Mg and Na-K-Ca) geothermometers using equations from Fournier (1977), Giggenbach (1988) and Fournier and Truesdell (1973).

The hot spring reservoir temperature estimated from silica geothermometers was obtain from:

$$T = \frac{1309}{5.19 - logS} - 273.15, \text{ S= } SiO_{2(aq)} \text{ in mg/L, T in ºC} \qquad (SiO_2) \qquad (1)$$

The hot spring reservoir temperature estimated from cation geothermometers were calculated using:

$$\text{T} = \frac{1390}{1.750 + log\frac{Na}{K}} - 273.15, \text{ Na \& K in mg/L, T in ºC} \qquad (\text{Na-K}) \qquad (2)$$

$$\text{T} = \frac{4410}{14.00 - log\frac{K^2}{Mg}} - 273.15, \text{ K \& Mg in mg/L, T in ºC} \qquad (K^2\text{-Mg}) \qquad (3)$$

$$\text{T} = \frac{1647}{log\frac{Na}{K} + \beta\left(\log\left(\frac{\sqrt{Ca}}{Na}\right) + 2.60\right) + 2.47} - 273.15, \text{ Na, K \& Ca in mg/L, T in ºC (Na-K-Ca)} \qquad (4)$$

(1) if $\left(\log\left(\frac{\sqrt{Ca}}{Na}\right) + 2.60\right)$ >0, use β= 4/3

(2) if T >100°C in (1) recalculate using (3)

(3) if $\left(\log\left(\frac{\sqrt{Ca}}{Na}\right) + 2.60\right)$ <0, use β= 1/3

CHAPTER IV

RESULTS

Section 1. Temperature, pH, TDS and Silica

Temperatures of hot springs are an important parameter of geochemistry because of the impact heat has on the chemical and isotopic alterations that are occurring throughout the migration of the water. Surface temperatures of the hot springs range from 31.1ºC to 83.4ºC. The Northern Group and the hot springs of the Eastern Group outside of the Luangwa Rift in the Game Management Areas (GMA) adjacent to South Luangwa National Park and North Luangwa National Park have the lowest surface temperatures; 35.6ºC to 46.6ºC for the Northern Group and 31.1ºC to 49.9ºC in the Eastern Group. The hot springs of the Eastern Group inside the Luangwa Rift, Luangwa River Bluff East 1, 3 and 4, display some of the highest surface temperatures recorded in this study, 79.3ºC to 84.7ºC. Temperatures this high were only encountered at 3 other locations outside of the Luangwa Rift. Surface temperature of 75.6ºC was measured at Kafue National Park in the Western Group. Surface temperature of 72.9ºC was measured at Bwanda Hot Spring and 71.6ºC at Main Gwisho Hot Spring, both in the Lochinvar Group.

The pH for hot springs ranges from 4.7 to 9.2, from 6.2 to 7.6 for cold springs and from 4.2 to 7.0

for streams. Hot springs in the Eastern Group/Luangwa Valley have pH values in the 7.0 to 9.2 range. The pH values for the Kapishya Hot Springs are in the 4.7 to 5.3 range. Hot springs in the Northern, Mansa- Copperbelt and Western Groups have pH values in the 6.4 to 7.4 range. The pH for the Lochinvar Group ranges from 6.9 to 7.3, 7.5 to 8.5 for the Choma Group and 7.7 for the Kasane Group.

The total dissolved solids of the hot springs range from 0.01 to 9.48 g/L, from 0.03 to 0.80 g/L for cold springs and 0.01 to 0.32 g/L for streams. The Northern Group of hot springs have high TDS concentrations in the 5.6 to 9.4 g/L range. Hot springs in the Luangwa Valley in the Eastern Group have TDS values that range from 0.27 to 1.41 g/L. The Kapishya Hot Springs have very low total dissolved solids, which range from 0.01 to 0.03 g/L. The hot springs of the Mansa-Copperbelt and Western Group have TDS values similar to the Eastern Group of hot springs which range from 0.36 to 1.8 g/L. The TDS values fro the Southeastern Group range from 0.45 to 0.49 g/L. The Lochinvar Group has TDS values in the 1.37 to 1.61 g/L range and the Choma Group ranges from 0.29 to 0.37 g/L. The Kasane Hot Spring in northern Botswana has the highest TDS of all the hot springs with a value of 9.5 g/L. The temperature of the hot springs relative to the TDS is shown in Figure 4a.

Silica concentration ranged from 18 to 120 mg/L in the hot springs, from 5 to 76 mg/L for cold springs and from 3 to 13 mg/L in the streams (Fig. 4b). The Northern Group and Mansa-Copperbelt Group were not analyzed for silica concentration (Table 2). The Kapishya Hot Springs of the Eastern Group have low silica concentrations of 18 to 26 mg/L. The Western Group has a large range of silica concentration values from 42 to 116 mg/L, where the Southeastern Group has a small range in concentrations, 72 to 75 mg/L. The Lochinvar Group (in the south near Lochinvar National Park) have high silica concentrations of 91 to 107 mg/L. The Choma Group also has high silica concentrations of 75 to 120 mg/L. The Kasane Group has lower silica concentrations of 42 mg/L. The Kapishya Hot Springs of the Eastern Group and the Lochinvar Group are the only groups that exhibit distinct spatial patterns based on silica concentrations. The temperature of the hot springs relative to the silica concentrations are shown in Figure 4b. The silica concentrations of all hot springs are higher compared to cold springs and stream samples.

Section 2. Major Ions

The cations K^+, Na^+, Mg^{2+} and Ca^{2+} and the anions HCO_3^-, Cl^- and SO_4^{2-} concentrations in hot springs, cold springs and streams are presented in Table 2 and shown in the Piper Plot (Fig. 5). There are three distinct groups of hot springs based on the concentration of cations: (1) Na +K rich, less than 60% Ca (2) Ca rich, more than 60% Ca and (3) Mg rich, more than 79% Mg (Fig. 5). The hot springs have a Na-K cation facies with mostly Cl-SO_4 anion facies, while the cold springs and streams have a predominantly Ca-Mg cation facies with mostly HCO_3 anion facies. Three distinct groups of hot springs can be distinguished from the anion abundance: HCO_3^--rich, Cl^--rich and SO_4^{2-}-rich. These anion abundance groups can be tied to the geology the springs flow through and issues from. The SO_4^{2-} rich group includes hot springs in the Eastern Group in the Luangwa Valley, Southeastern Group, Lochinvar Group and the hot spring in Kasane in northern Botswana. These groups Eastern Group, issues out of fractures in the Karroo basement contact (Legg, 1974). The Lochinvar Group issues out of the Choma-Kaloma Block and the Kasane Group issues out of a salt pan. The HCO_3^- -rich group is composed of the Kapishya Hot Springs, the springs outside of the Luangwa Rift of the Eastern Group to the northwest. These springs flow from major fractures of pre-Katanga age (Legg, 1974). The Cl^--rich springs are the springs in the Northern, Mansa-Copperbelt, Western and Choma Groups. Water from hot springs of the Cl^--rich Northern Group derive their chemical signature from fractures through the Plateau Series, a group of ancient platform sedimentary rocks including shales with possible Cl^--rich clays (Legg, 1974). This area is also known for its salt production due to the high Cl^- (Legg, 1974). Cl^--rich springs are also in the Mansa-Copper Belt and Western Group which issue out of the Katanga Supergroup that includes sedimentary rocks.

Section 3. Stable Oxygen and Hydrogen Isotopes

The results of the δD and $\delta^{18}O$ for the hot springs, cold springs and streams are given in Table 2. The $\delta^{18}O$ ratios for hot springs range from -8.5 to -6.4‰, -7.8 to -6.4‰ for cold springs and -7.4 to -2.6‰ for streams. The δD ratios for hot springs range from -54 to -39 ‰, -46 to -38‰ for cold springs and -44 to -19‰ for streams. The Kapishya Hot Springs have $\delta^{18}O$ values that range from -6.9 to -6.5‰, while the rest of the Eastern Group within the Luangwa Valley have $\delta^{18}O$ from -8.0 to -7.0‰. This difference may be due to the oxygen isotope shift, oxygen isotopes change at high temperature between the water and the rock (Ármannsson, 2012), the temperatures of hot springs inside the rift are hotter than those outside the rift. The $\delta^{18}O$ values for the Choma and Western Group range from -8.5 to -7.6‰. The Kasane hot spring in Botswana has a $\delta^{18}O$ ratio of -6.6‰ which is more positive than the other hot springs nearby in the Choma (-8.4 to -7.6‰) and Western (-8.2 to -7.5‰) Groups. These higher $\delta^{18}O$ ratios may be due to elevation, higher relief results in lighter, more negative $\delta^{18}O$ ratios (Ármannsson, 2012). The δD-$\delta^{18}O$ behavior for hot springs, cold springs and stream is shown in Figure 6. Both the hot springs and colds spring lie along the Local Meteoric Water Line (LMWL) and the Global Meteoric Water Line (GMWL; Craig, 1961). Some of the δD- $\delta^{18}O$ for stream water samples do not lie along the LMWL and GMWL, but rather fall along an evaporation line with a slope of 5.1. Overall the hot spring samples show more negative values compared to cold springs and streams.

Section 4. Alkalinity, DIC and $\delta^{13}C_{DIC}$

Total alkalinity concentrations range from 7 to 279 mg/L for hot springs, 23 to 440 mg/L for cold springs, and 3 to 271 mg/L for streams (Table 2). The Northern Group has mid range alkalinity of 90 to 114 mg/L. The Kapishya Hot Springs have low alkalinity concentrations of 7 to 18 mg/L, while Chilonga Lusa and Chilonga Lusa 2 Hot Springs also in the Eastern Group outside the Luangwa Valley have higher alkalinity concentrations of 147 and 136 mg/L. The rest of the hot springs in the Eastern Group in the Luangwa Valley have alkalinity concentration ranging from 35 to 51 mg/L. The Mansa-Copperbelt Group has alkalinity concentrations in 71 to 87 mg/L range. The Western Group has the largest range in alkalinity from 29 to 279 mg/L. The Southeastern Group has relatively low alkalinity, 36 to 63 mg/L, as does the Lochinvar Group which ranges from 52 to 57 mg/L. The Choma Group has relatively high alkalinity with concentrations in the 82 to 109 mg/L range and the Kasane Group has an alkalinity of 79 mg/L. DIC concentrations and the $\delta^{13}C_{DIC}$ for hot springs, cold springs, and streams are given in Table 2. DIC concentrations of the hot springs range from 5 to 94 mg C/L, the cold springs range from 5 to 124 mg C/L. The DIC concentrations of both hot springs and cold springs are much higher than those of streams, which range from 0.1 to 40 mg C/L. The $\delta^{13}C_{DIC}$ for the hot springs have a wide range from -20.0 to -4.1‰, the cold springs have a range from -13.0 to -4.3‰ and streams have a range from -14.1 to 5.0‰ (Fig. 7a). The streams samples may have additional carbon added to the system via the atmosphere which would make the $\delta^{13}C_{DIC}$ more positive. The Northern Group has $\delta^{13}C$ of DIC of -16.5 to -9.2‰, Eastern Group -20.1 to -8.6‰, Mansa-Copperfield Group -19.7 to -16.8‰, Western Group -14.4 to -6.2‰ and Southeastern Group -14.4 to -13.4‰. The higher $\delta^{13}C$ of DIC of the Eastern Group are the hot springs outside the rift and have a range of -20.1 to -18.3‰. The Lochinvar Group has the most positive $\delta^{13}C$ of DIC of -5.6 to -4.1‰. The Choma Group has $\delta^{13}C$ of DIC of -14.7 to -12.0‰ and Kasane -9.7‰. These differences can be explained by the geology the hot springs migrate through, the initial carbon input based on the surface vegetation and soil carbon as well as any additional carbon that is added to the hot spring system. The $\delta^{13}C_{DIC}$ range of the cold springs is not similar to any of the hot spring groups, it does not fall within any of the ranges for the hot spring groups. The streams also have a wide range of $\delta^{13}C_{DIC}$ values, including some values that are positive.

Section 5. Hydrogeochemical Thermometry

There are different ways to estimate temperatures below the surface based on calculations using different cations. Hot springs with different concentrations of cation resulted in markedly different subsurface reservoir temperatures for the different geothermometers (Table 4) (Fig. 8a-d). Temperatures from silica geothermometry (Fournier, 1977) ranged from 59.9°C to 147°C. Temperatures from Na-K geothermometry (Giggenbach, 1988) yielded subsurface reservoir temperatures between 123° to 443°C, while K^2-Mg geothermometry (Giggenbach, 1988) yielded temperatures from 13.1°C to 149°C. Fouriner and Tuesdell (1973) Na-K-Ca geothermometry gave reservoir temperatures from 122°C to 209°C.

CHAPTER V

DISCUSSION

In hot spring systems, meteoric water flows to the subsurface through faults and fractures where it is heated and then returned to the surface. During circulation, water- rock interactions modify the water's chemical and isotopic characteristics. The circulating water can entrain volatiles and gases from the surface and from deep sources including the shallow mantle, magmatic bodies and sedimentary carbonates (Kebede et al., 2010). In addition, during ascent, near surface groundwater may further modify the chemical and isotopic characteristics by mixing (Frape et. al., 1984). Thus, examining the temperature, and the chemical and isotopic properties of hot springs relative to cold spring and streams sourced from shallow groundwaters can help provide insights into the extent to which the chemical and isotopic properties of the hot springs are altered during and after heating in the subsurface.

Section 1. Geothermometry

Measuring the surface temperature as well as the cations and anions present in the hot spring water allows the subsurface reservoir temperatures to be estimated empirically. It is to be noted that differences in surface temperatures can be the result of differences in the reservoir temperatures at depth, and the rate of cooling (either due to the rock type or ascension rate) over distance during accent. Some limitations exist when using certain geothermometers. Na-K thermometer should not be used when hot springs are precipitating calcite or when the calculated temperatures <200°C (Fournier and Truesdell, 1973). The Na-K-Ca thermometer should be used in hot springs that migrate through carbonate bedrock due to the relationship between Na, K, and Ca being controlled primarily by equilibration with silicate minerals (Fournier and Truesdell, 1973). The K- Mg thermometer is sensitive to shallow groundwater mixing and will resulting in too low temperature estimates (Giggenbach, 1988). Silica thermometry is also sensitive to mixing and dilution, giving too low temperature estimates. All 4 of the geothermometers used are sensitive to the extent of water- rock interaction, mixing along the flow path with groundwater, and precipitation of minerals.

Reservoir temperatures calculated using chemical geothermometry resulted in a wide range of temperatures, 59.9ºC to 146ºC for SiO_2, 125ºC to 443ºC for Na-K, 16.9ºC to 148ºC for K^2-Mg and 101ºC to 209ºC for Na-K-Ca. To determine which geothermometry is reasonable, plots were constructed showing the temperature measured for each hot spring at the surface verse the estimated reservoir temperature (Fig. 8a-d). Based on the statistical relation depicted in Figure 8a-d, inferences can be made regarding which geothermometer to use to estimate reservoir temperature. The R^2 for K^2- Mg (Fig. 8c) reservoir temperatures is the highest followed by SiO_2 (Fig. 8a), Na-K (Fig. 8b) and finally Na-K-Ca (Fig. 8d). However there are some discrepancies when individual estimated reservoir temperature values are examined. This is most likely due to the fact that some of the thermometry techniques may not be suitable for all the hot springs because of the type of rock the water migrates through (Fournier and Truesdell, 1973; Giggenbach, 1988). Subsurface reservoir temperatures for Na-K geothermometry were higher than K^2-Mg and Na-K-Ca geothermometers. Subsurface reservoir temperatures for K^2-Mg geothermometry appear to be too low especially for Kapishya Hot Spring due to the very low concentration of K of 0.3 and 0.2 mg/L (Table 2). The estimated geothermal temperature using K^2-Mg are 16.9°C and 13.1°C while the surface temperature for this spring is 38.9°C and 38.4°C. There is no K^+ in the quartzite rocks that the Kapishya Hot Springs issues from (Legg, 1973). Using the Na-K geothermometers, Kapishya Hot Spring 2 has the highest reservoir temperature of about 443°C. Na-K-C geothermometry temperatures result in Kapishya Hot Spring 2 as having the highest subsurface temperature of about 209°C. Luangwa River Bluff East 1, which had the highest surface temperature, has the highest K^2-Mg reservoir temperature of 149 °C.

Silica geothermometry yielded subsurface temperatures with the most likely reservoir temperatures when geothermal gradient and fracture depth (from Legg, 1973) constraints are examined. Reservoir temperatures estimated using silica geothermometry verse surface temperature of hot springs have a R^2 value of 0.60. Analysis of the silica saturation and temperature data for the hot springs (Fig. 9) shows that all the samples fall between the quartz and amorphous silica geothermometer equations, indicating silica geothermometry as a reasonable choice of geothermometers to use in these Zambian hot spring. K^2-Mg geothermometry also is a reasonable thermometry to use for most springs in this area because of the igneous rocks at depth that contribute K^+ and Mg^{+2} to the hot spring water (van Straaten, 2002). The K^2-Mg geothermometry relationship can also be used to suggest that the hot springs are not mixing with cold shallow groundwater. If this were occurring, lower surface temperatures would be observed as the result from the cooler water mixing with the much hotter ascending hot spring water. Expected increases in concentration of chemical species, Ca and HCO_3, contributed from cooler groundwater, are not present in hot spring samples, therefore mixing is negligible.

Given the reservoir temperature (through empirical calculation) and a geothermal gradient, depths of the hot spring reservoirs can be estimated. This is important to know because if a geochemical signature, i.e. carbon with an isotopic value in the -10 to -1‰, indicating mantle source material is observed, the depth to the mantle source can be estimated. The geothermal gradient for basement rocks in Zambia is around 23 °C/km (Legg, 1974). Given this gradient springs with reservoir temperatures of 100 °C would be heated at 4.3 km depth. Hot springs throughout Zambia lie along deep, major faults that are roughly 5 km deep at the contacts of Karroo sediments with older rocks (Legg, 1974). A geothermal gradient of 23 °C is sufficient with 5 km of migration to result in reservoir temperatures of ~115 °C. Reservoir water temperatures of roughly this range, 65 to 141°C, are calculated using silica geothermometry (Table 4). However, the Karroo sediments in the Western and Central Providence (Chapman and Pollack, 1976) where the Lochinvar Group are located, have a very low thermal conductivity which leads to an elevated geothermal gradient, possibility over 50 °C/km (Legg, 1974). Here reservoir temperatures from silica geothermometry (Fournier, 1977) ranged from 59.9°C to 146°C (Table 4). Hot springs in the Lochinvar group exhibit subsurface reservoir temperatures that average 135.8°C for SiO^2 geothermometry, 190.5°C for Na-K geothermometry, 117.8°C for K^2-Mg geothermometry and 158°C for Na-K-Ca geothermometry (Table 4). The water from the Lochinvar Group issues out of faults that separate lower thermally conductive Karroo sediments from the older Katanga and pre-Katanga age rocks that exhibit the average local normal geothermal gradient of 23°C per kilometer (Legg, 1974). Springs in the Lochinvar Group with a surface temperature of 20°C and a geothermal gradient of 58°C would have to have water only descend 1.5 km to get to temperatures above 100°C. Thus, with the exception of the Lochinvar Group, hot springs in Zambia gain heat by a normal geothermal gradient of 23°C while percolating downward. The Lochinvar Group exhibits higher surface temperatures due to higher subsurface reservoir temperatures that stem from the groundwater migration path that percolates to the Karroo sediments and its low thermal conductivity.

Section 2. Origin of Water

The source of water in hot springs and the extent to which the water is altered by the addition of non meteoric water or by rock-water interaction can be traced by the δD and $\delta^{18}O$ ratios (Kebede et al., 2010). The relationship between δD and $\delta^{18}O$ for hot springs, cold springs and streams show the $\delta^{18}O$ values of hot springs and cold springs lie along the LMWL and GMWL (Fig. 6). The $\delta^{18}O$ in most stream samples are more enriched compared to hot springs and cold springs due to the fractionation effect from evaporation (Clark and Fritz, 1997). The ^{18}O-enriched stream samples define an evaporation line.

The δD and $\delta^{18}O$ for the hot springs are typically more negative (-54 to -39 ‰; -8.5 to -6.4‰) than cold springs and streams samples (-46 to -38‰; -7.8 to -6.4‰ and -44 to -19‰; -7.4 to -2.6‰,). The more positive $\delta^{18}O$ water in cold springs and streams could be due to the mixing with groundwater/ surface water and the evaporation effect or different recharge periods (Clark and Fritz, 1997). There is negligible enrichment in the ^{18}O relative to D from the LMWL (Fig. 6). The lack of enrichment of the ^{18}O relative to D for the hot springs indicates that the hot springs did not undergo extensive rock water interactions that would preferentially alter the ^{18}O (Kebede et al., 2008). For limited rock-water interactions to be observed, there must be rapid circulation occurring within the fault systems if they are very deep or that the geothermal gradient is high and the water is heated at shallow depths (Frape et. al., 1984). The δD and $\delta^{18}O$ results show that the δD and $\delta^{18}O$ values for the hot springs lie along the LMWL and thus indicate negligible contribution of water from magmatic or connate sources (Taylor, 1968). This also means that the hot springs do not interact with a significant source of $CO_{2(g)}$ in the subsurface which could exchange oxygen and affect the $\delta^{18}O$ of the hot springs (Diamond and Harris, 2000; Villermant et. al., 2005).

Section 3. Water-Rock Interaction

The chemical and isotopic properties of hot springs measured at the surface are a function of water-rock interactions controlled by rock type, intensity of weathering and mixing with non thermal water subjected to different water-rock interaction (Yock, 2009). An increase in the amount of weathering is expected in hot water. If weathering in the hot springs was solely the result of interaction between hot water and rock, a positive correlation between both TDS and temperature and silica and temperature would be seen (Fig 4). The poor statistical relationship for TDS and temperature suggest other processes are occurring. One way to elucidate these processes is to access the behavior of the anions and cations.

The cations and anions for the hot springs can be distributed into three distinct groups. The cations for the hot springs can be grouped into $Na^+ + K^+$ –poor, Mg^{2+} –poor and Ca^{2+} –poor. The anions however can be used best to characterize the different hot springs. The HCO_3^- -rich, Cl^--rich, and SO_4^{2-}-rich groups for anions give indications of geologic units the hot springs water flows through. Water from hot springs of the Cl^--rich Northern Group derive their chemical signature from fractures through the Plateau Series, a group of ancient platform sedimentary rocks including shales with possible Cl^--rich clays (Legg, 1974). This area is also known for its salt production due to the high Cl^- (Legg, 1974). Cl^- -rich springs are also in the Mansa-Copper Belt and Western Group, which issue out of the Katanga Supergroup that includes sedimentary rocks (van van Straaten, 2002). Hot springs of the SO_4^{2-} group in the Eastern Group, issue out of fractures in the Karroo basement contact (Legg, 1974). The Lochinvar Group and the Kasane Group is also part of the SO_4^{2-} group. The Lochinvar Group issues out of the Choma-Kalomo Block, an area rich in sulfide ore (Burnard et al., 1993), and the Kasane Group issues out a salt pan. Many of the hot springs in the SO_4^{2-} group have younger sedimentary evaporites such as gypsum deposit close to the surface (Legg, 1974). These sedimentary units are dissolved by spring water as it migrates and forms evaporite deposits in and around the springs when the spring water evaporates (Legg, 1974). Evaporite deposits were seen extensively at Nchindi Hot Spring of the Eastern Group in the Luangwa Valley,which results in the hot spring water being SO_4^{2-} rich. The HCO_3^--rich group of hot springs is the Eastern Group outside the Luangwa Valley.

Section 4. Carbon in Hot Springs

The range of the $\delta^{13}C$ values for hot springs in Zambia is -20 to -4‰ suggesting multiple sources of carbon and fractional evolution of carbon in the hot springs. Carbon can be added to the hot springs from surface processes, from carbonates in fractures, CO_2 degassed from deep seated carbonate rocks or from CO_2 derived from the mantle (Ármannsson, 2012; D'Alessandro et al., 1997). Different carbon sources are characterized by unique isotopic compositions that can be used to evaluate contribution to the DIC pool in hot springs. The isotopic compositions of $CO_{2(g)}$ incorporated into the thermal waters at the surface is dictated by surface vegetation. The semiarid climate of Zambia (Houston, 1982) is dominated by C3 vegetation with typical $\delta^{13}C$ values of -27 to -25‰ (Bird et. al, 2004). The initial $\delta^{13}C$ value of DIC in water from $CO_{2(g)}$ dissolution depends on (1) isotopic composition of the organic matter, (2) isotopic fractionation from diffusion of CO_2 in the soil zone and (3) isotopic fractionation during dissolution (temperature dependent) and (4) carbonate weathering. The most negative $\delta^{13}C$ of DIC for hot springs is -20‰, which is consistent with a soil $CO_{2(g)}$ produced from microbial degradation of C-3 vegetation (Bird et. al., 2004). The isotopic composition of DIC will be different in hot springs that have multiple additional sources of carbon during the chemical and isotopic evolution of the spring water compared to hot springs that only have soil carbon as their only source of carbon. Determining when carbon is being added to the hot springs is not clear as carbon could be added as the water flows into the subsurface or up to the surface or both, or from mixing with groundwater. To assess if carbon is being added to the hot springs during its chemical and isotopic evolution, a plot of DIC* $\delta^{13}C$ vs DIC (Fig. 7b) can be used (Hu and Burdige, 2007; Hu et al., 2010). This plot, with the hot springs regression plotted, shows the mixing of two end members (DIC and $\delta^{13}C$) and can be used to infer the isotopic composition of carbon that is added to the hot springs DIC pool. This plot suggests that the isotopic composition of the carbon added to the hot springs is -10‰.

The only way to end with $\delta^{13}C$ of DIC in the hot springs of -20 to -4‰ range when C with an isotopic composition of -10‰ is added to an initial composition of -21 to -15‰, is to add additional carbon with an isotopic value more positive than -5. Assuming the water is meteoric in nature and starts with an isotopic value <-20‰ from organic carbon, the carbon added to the hot springs is sufficiently heavy, enriches the carbon in the water enough to suggest a magmatic source, -10 to -1‰, or CO_2 from deep sedimentary source such marine limestone, -2 to +2‰ (Ármannsson, 2012). The limited number of hot springs with enriched $\delta^{13}C$ indicates that there is not a shallow magmatic body underlying the entire country of Zambia contributing heavy $CO_{2(g)}$ to all of the hot springs. Waters of the Lochinvar Group have $\delta^{13}C$ values of -6 to -4‰. The enrichment of $\delta^{13}C$ at this group of springs could indicate a shallow mantle source that is contributing mantle carbon to these springs, but could also come from sedimentary carbonate weathering or from adding sedimentary or metamorphic CO_2. It is unlikely that an isolated mantle source is contributing carbon to only the Lochinvar Group due to the proximal location to the Choma Group. It is more likely that the geology plays a role in the more positive $\delta^{13}C$ values in this group. The Lochinvar Group discharges along major faults that separates Karroo sediments and pre-Katanga rocks, and so there could be some carbon enrichment coming from the sedimentary rocks, which are carbonates from the Roan Group (van Straaten, 2002).

CHAPTER VI

CONCLUSIONS

In this study, the physical parameters as well as chemical and stable isotope compositions of water from hot springs, cold springs and streams throughout Zambia were measured. These results show that the source of the water for the hot springs is meteoric with little isotopic alteration and negligible contribution of water from a magmatic source or connate water. Alteration of $\delta^{18}O$ of the water of hot springs was limited, which also suggest limited water-rock interaction and/or carbon exchange with $CO_{2(g)}$ from deep sedimentary or magmatic sources. The $\delta^{13}C$ of DIC of the hot springs suggest soil zone (C-3 vegetation) $CO_{2(g)}$ as original carbon source. Using different geothermometry reservoir temperatures of springs were estimated and confirm that the local geothermal gradient of 23ºC/km is sufficient to generate the surface temperatures that were recorded. These results are consistent with ongoing geophysical work that shows no evidence of a thermal anomaly beneath the Luangwa Rift (Matende, 2014).

CHAPTER VII

FUTURE WORK

The conclusions drawn from this study are the results of three spatial surveys, conducted in the winter season in Zambia. Continued sampling of hot springs, cold springs and streams, annually and seasonally, will result in a robust data set that can be applied to cement these findings. Continuous sampling and analysis would allow observation of seasonal changes, if they occur in response to seasonal rains as well as if seasonality plays a role in the geochemistry of spring systems. Scouting additional springs to increase the density and sampling for δD, $\delta^{18}O$ and $\delta^{13}C$ can be used to create a more robust data set. Additional analysis of water samples for rare earth isotope, helium ($^{4}He/^{3}He$) and strontium ($^{87}Sr/^{86}Sr$), would be beneficial in determining the types of rocks that are weathered and the extent of weathering that is occurring in the hot springs systems. Determining the age of the water using ^{14}C, would allow models to be created that assess time scale of water evolution and circulation. Ground water samples from boreholes would increase the sample size and also aid in the determination of extent of weathering by comparing cation and anion concentrations to hot spring water samples.

The results from this study will be integrated into other parts of the multidisciplinary Project PRIDE including geophysics (passive/active seismic, gravity, magnetics, magnetotelluric), structural geology, remote sensing, geochemistry and numerical modeling. The data collected will provide important constraints for the numerical modeling. Integration with other geophysical data e.g. heatflow determination from Luangwa and magnetotelluric results from Luangwa. Geochemical data will be compared with the seismic velocities to understand the role of magma in rifting. The integration of data will reduce knowledge gaps in areas fundamental to the understanding of the development of amagmatic rifts.

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Table 1
Background information on sampling sites

Spring No.	Site	Geographic Coordinates		Altitude	Description	Spring Group
		S°	E°	(m)		
1	Mukupa Hot Spring	8.6397	29.1613	-	Hot spring	Northern
2	Ingansa Hot Spring	8.6770	29.1759	-	Hot spring	Northern
3	Kalembwe Hot Springs	8.7750	29.1228	-	Hot spring	Northern
4	Kalembwe Hot Springs 2	8.7772	29.1220	-	Hot spring	Northern
5	Kapishya Hot Spring 2	11.1301	31.6421	1449	Hot spring	Eastern
6	Kapishya Hot Spring	11.1706	31.6004	1444	Hot spring	Eastern
7	Chilonga Lusa	11.4490	32.2104	919	Hot spring	Eastern
8	Chilonga Lusa 2	11.4517	32.2111	917	Hot spring	Eastern
9	Luangwa River Bluff East 3	12.1167	32.2850	-	Hot spring	Eastern
10	Luangwa River Bluff East 1	12.1171	32.2847	-	Hot spring	Eastern
11	Luangwa River Bluff East 4	12.1178	32.2845	584	Hot spring	Eastern
12	Nsefu Hot Spring	12.9414	32.0342	-	Hot spring	Eastern
13	Nchindeni Hot Spring	13.3605	31.6687	-	Hot spring	Eastern
14	Namwandwe Hot Spring	11.1970	28.9161	-	Hot spring	Mansa-Copperbelt
15	Kapisha Hot	12.5512	27.8632	-	Hot spring	Mansa-Copperbelt
16	Kapisha Hot	12.5512	27.8632	-	Hot spring	Mansa-Copperbelt
16	Kapisha Hot Spring 2	12.5512	27.8632	-	Hot spring	Mansa-Copperbelt
17	Kafue National Park	14.5573	26.4497	-	Hot spring	Western
18	Kafue National Park Hippo Lodge	14.6774	26.3835	-	Hot spring	Western
19	Mumbwa Hot Spring	14.9746	27.0803	-	Hot spring	Western
20	Bilili Hot Spring	16.6573	26.1394	-	Hot spring	Western
21	Chinyunyu Hot Spring	15.2586	29.0242	-	Hot spring	Southeastern
22	East Gwisho Hot Spring	15.9853	27.2471	-	Hot spring	Lochinvar
23	Main Gwisho Hot Spring	15.9870	27.2429	-	Hot spring	Lochinvar
24	Bwanda Hot Spring	16.0124	27.2194	-	Hot spring	Lochinvar
25	Namululu Hot	16.0259	27.2064	-	Hot spring	Lochinvar

	Spring					
26	West Lake Farm Hot Spring	16.6028	26.9958	-	Hot spring	Choma
27	Miller Hot Spring	16.6451	26.9979	-	Hot spring	Choma
28	Bruce Miller Farm 1	16.6479	26.9977	-	Hot spring	Choma
29	Bruce Miller Farm 2	16.6482	26.9969	-	Hot spring	Choma
30	Kasane Hot Spring	17.7911	25.1981	928	Hot spring	Kasane
	State Lodge	15.4613	28.4294	1280	Cold spring	
	Good Hope Farms/Monkey Ponds	15.4669	28.4507	1272	Cold spring	
	Palabana Dairy Spring	15.4557	28.5372	1236	Cold spring	
	Laughing Waters Spring	15.3714	28.1757	1206	Cold spring	
	Loma [Ba-koma]	15.3806	28.1863	1233	Cold spring	
	St Charles Spring	15.3852	28.2023	1264	Cold spring	
	Zingalume Spring	15.3720	28.2278	1254	Cold spring	
	Linda	15.5436	28.2278	1204	Cold spring	
	Mupwasha	15.0513	29.8473	969	Cold spring	
	Chifunda Mineral Spring	12.0711	32.3550	588	Cold spring	
	Kafue River	15.8338	28.2378	-	River	
	Luapula River	10.1667	28.6289	-	Stream	
	Kulungwishi River	9.0435	29.0454	-	Stream	
	Kundabwika Falls	0.0000	0.0000	-	Stream	
	Chambeshi River	10.9264	31.0771	-	Stream	
	Lunsemfya River	13.7509	29.0745	-	Stream	
	Mulungushi River	14.2963	28.5487	-	Stream	
	Chongwe River	15.3230	28.7026	1051	Stream	
	Lukusashi River	15.0055	30.2158	372	Stream	
	Mama Rula River	13.5938	32.6066	1048	Stream	
	Kanakanapa River	15.2962	28.6373	1070	Stream	
	Luangwa River	13.0973	31.7860	524	Stream	
	Mulungushi River	14.2963	28.5487	1110	Stream	
	Chikwana Stream	11.5011	31.6448	-	Stream	
	Mansha River	11.1706	31.6014	1429	Stream	
	Louviloa River	11.4509	32.2112	919	Stream	
	Mwaloeshi River	11.6070	32.0168	1160	Stream	
	Chobe River	17.7911	25.1981	924	Stream	

Dash (-) no data

Table 2
Physical, chemical and isotope results for hot springs, cold springs, and streams

	Location	Spring	Spring Group	Date	T	pH

		No.				
					°C	
Hot Springs	Mukupa Hot Spring	1	Northern	6/30/09	35.6	6.8
	Ingansa Hot Spring	2	Northern	6/30/09	46.1	7.2
	Kalembwe Hot Springs	3	Northern	7/1/09	46.1	7.4
	Kalembwe Hot Springs 2	4	Northern	7/1/09	46.6	6.9
	Kapishya Hot Spring 2	5	Eastern	4/18/13	31.1	5.7
	Kapishya Hot Spring 2	5	Eastern	7/14/13	32.0	4.7
	Kapishya Hot Spring	6	Eastern	4/18/13	38.9	5.3
	Kapishya Hot Spring	6	Eastern	7/14/13	38.4	5.0
	Chilonga Lusa	7	Eastern	7/15/13	49.9	9.2
	Chilonga Lusa 2	8	Eastern	7/15/13	42.4	7.4
	Luangwa River Bluff East 3	9	Eastern	7/6/13	79.4	8.6
	Luangwa River Bluff East 1	10	Eastern	7/6/13	83.4	8.3
	Luangwa River Bluff East 4	11	Eastern	7/6/13	79.3	8.6
	Nsefu Hot Spring	12	Eastern	7/2/13	57.9	7.7
	Nchindeni Hot Spring	13	Eastern	7/2/13	74.0	8.2
	Namwandwe Hot Spring	14	Mansa-Copperbelt	6/26/09	35.4	6.6
	Kapisha Hot Spring	15	Mansa-Copperbelt	6/24/09	50.0	6.7
	Kapisha Hot Spring 2	16	Mansa-Copperbelt	6/24/09	48.3	6.4
	Kafue National Park	17	Western	4/22/13	75.6	6.9
	Kafue National Park Hippo Lodge	18	Western	4/22/13	35.1	6.8
	Mumbwa Hot Spring	19	Western	4/23/13	41.5	6.9
	Bilili Hot Spring	20	Western	4/25/13	66.2	7.3
	Chinyunyu Hot Spring	21	Southeastern	6/22/09	64.4	8.9
	Chinyunyu Hot Spring	21	Southeastern	4/16/13	61.4	8.6
	Chinyunyu Hot Spring	21	Southeastern	4/16/13	61.0	8.6
	Chinyunyu Hot Spring	21	Southeastern	6/28/13	52.1	9.2
	East Gwisho Hot Spring	22	Lochinvar	4/24/13	65.2	7.2
	Main Gwisho Hot Spring	23	Lochinvar	4/24/13	71.6	7.1
	Bwanda Hot Spring	24	Lochinvar	4/24/13	72.9	7.3
	Namululu Hot Spring	25	Lochinvar	4/24/13	45.8	6.9
	West Lake Farm Hot Spring	26	Choma	4/26/13	56.5	7.5
	Miller Hot Spring	27	Choma	6/21/09	69.9	7.9
	Bruce Miller Farm 1	28	Choma	4/26/13	69.0	8.0
	Bruce Miller Farm 2	29	Choma	4/26/13	43.5	8.5
	Kasane Hot Spring	30	Kasane	7/29/13	43.2	7.7
Cold Springs	State Lodge			6/22/13	21.7	7.6
	Good Hope Farms/Monkey Ponds			6/22/13	22.1	7.0
	Palabana Dairy Spring			6/23/13	22.5	6.7

	Laughing Waters Spring			6/24/13	20.7	7.2
	Loma [Ba-koma]			6/24/13	23.7	7.2
	St Charles Spring			6/24/13	25.6	7.0
	Zingalume Spring			6/24/13	22.9	6.9
	Linda			6/24/13	20.2	6.8
	Mupwasha			6/28/13	15.7	6.2
	Chifunda Mineral Spring			7/5/13	17.7	6.9
Streams	Kafue River			6/19/09	20.5	7.0
	Kafue River			6/24/09	19.0	6.8
	Magoya River			6/19/09	19.1	6.3
	Zambezi River			6/20/09	20.2	6.3
	Zambezi River			6/20/09	20.6	4.8
	Kolomo River			6/21/09	16.9	7.3
	Chambeshi River			6/25/09	22.0	5.0
	Luongo River			6/27/09	21.8	7.2
	Luapula River			6/27/09	23.3	6.6
	Kulungwishi River			6/29/09	21.1	7.3
	Kundabwika Falls			7/5/09	19.8	7.2
	Chambeshi River			7/12/09	19.4	3.1
	Lunsemfya River			7/13/09	14.4	5.4
	Mulungushi River			7/13/09	14.3	6.1
	Chongwe River			6/27/13	15.4	7.4
	Lukusashi River			6/27/13	22.7	7.3
	Mama Rula River			7/1/13	16.9	7.9
	Kanakanapa River			6/28/13	13.4	7.3
	Luangwa River			7/1/13	25.6	7.1
	Mulungushi River			7/13/13	12.9	5.6
	Chikwana Stream			7/14/13	20.8	4.4
	Mansha River			7/14/13	16.8	4.2
	Louviloa River			7/15/13	15.4	4.9
	Mwaloeshi River			7/15/13	14.5	4.7
	Chobe River			7/29/13	20.9	6.8

Dash (-) no data

TDS	**EC**	**Alkalinity**	**SO_4^{2-}**	**Cl^-**	**PO_4^{2-}**	**NO_3^-**
g/L	**µS/cm**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
5.63	8660	109	6.2	182.7	-	1.2
9.38	14433	114	1.6	194.5	-	1.1
8.36	12864	90	27.8	147.4	-	1.4

8.34	12825	96	30.2	159.7	-	1.2
0.03	39	16	1.4	0.8	0.1	-
0.02	48	17	1.2	0.8	0.1	-
0.01	17	18	0.5	0.6	0.1	-
0.03	24	7	0.5	0.6	0.1	-
0.32	502	147	28.8	15.3	0.1	-
0.27	421	136	27.1	14.8	0.1	-
1.04	1536	35	522.8	99.0	0.1	-
1.10	1703	35	528.6	100.0	0.5	-
1.08	1659	39	531.5	100.7	0.1	-
1.41	2166	51	839.5	69.0	0.3	-
1.37	2140	-	754.0	99.5	0.1	-
0.84	1300	71	24.0	105.7	-	1.7
0.36	554	87	29.9	71.4	-	2.3
0.36	548	84	33.7	66.9	-	2.9
1.75	2640	29	987.5	791.7	0.1	4.9
0.54	807	181	126.1	113.6	0.1	1.5
0.75	1120	279	279.0	73.3	0.1	-
0.90	1352	49	566.3	19.3	0.1	-
0.49	753	63	52.6	23.7	-	0.4
0.45	676	36	167.0	49.0	0.1	-
0.45	674	37	167.3	49.0	0.1	-
0.49	656	52	166.2	48.9	0.1	-
1.61	2420	53	909.0	430.3	0.1	8.1
1.59	2390	52	907.1	427.1	0.1	6.0
1.39	2090	52	800.9	266.2	0.1	4.4
1.37	2060	57	791.5	261.5	0.1	-
0.29	436	90	78.7	14.0	0.2	1.7
0.37	562	109	66.9	18.6	-	1.3
0.35	526	82	99.0	17.7	0.1	-
0.36	540	83	102.8	18.1	0.1	-
9.48	14588	79	2756.1	3011.0	0.1	46.5
0.38	588	314	0.4	0.9	0.1	-
0.48	744	398	0.8	1.6	0.1	-
0.35	545	378	6.2	1.9	0.8	-
0.40	619	283	10.5	15.9	1.0	-
0.39	592	255	9.7	16.0	2.6	-
0.50	775	316	12.9	20.3	7.6	-
0.80	1228	336	48.8	94.4	21.5	0.8
0.67	1029	440	27.4	27.7	11.1	-
0.03	53	23	0.4	1.1	0.1	-
0.31	476	165	52.3	4.3	0.1	-
0.12	183	71	0.7	0.1	-	0.1
0.20	314	59	5.0	0.2	-	0.2
0.32	498	271	0.1	0.1	-	0.1
0.03	55	26	0.2	0.3	-	0.4
0.04	55	29	0.2	0.3	-	0.4
0.06	97	35	0.0	0.4	-	0.4
0.06	92	13	0.0	0.1	-	0.2
0.01	21	12	0.0	0.2	-	0.2

0.03	52	23	0.4	0.4	-	0.0
0.01	18	9.6	0.1	0.1	-	0.1
0.01	18	9.6	0.1	0.1	-	0.1
0.03	37	16	0.0	0.2	-	0.2
0.04	63	42	0.4	0.3	-	0.1
0.04	64	44	0.2	0.3	-	0.1
0.26	404	155	4.5	21.9	0.1	-
0.05	70	41	1.9	1.1	0.1	-
0.25	389	179	2.9	13.0	0.1	-
0.17	250	109	4.2	10.6	0.1	-
0.06	91	51	2.3	1.2	0.1	-
0.15	92	45	0.7	1.1	0.1	-
0.24	382	3	0.5	0.7	0.1	-
0.03	30	3	0.3	0.4	0.1	-
0.03	24	5	0.6	0.5	0.1	-
0.01	15	5	0.3	0.4	0.1	-
0.05	73	40	3.3	2.5	0.1	-

Dash (-) no data

F^-	**SiO_2**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
mg/L	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
-	-	119.1	2.1	12.2	1.0
-	-	113.2	4.9	12.5	0.4

-	-	105.8	3.9	28.2	1.8
-	-	90.8	3.3	22.9	1.5
0.1	26	1.3	0.8	4.1	1.1
0.1	21	1.4	0.7	4.7	1.2
0.0	23	0.5	0.3	0.6	1.4
0.1	18	0.4	0.2	0.7	1.4
10.4	48	114.9	2.1	1.4	0.0
9.6	47	107.3	2.5	1.2	0.1
12.6	71	287.2	8.9	24.5	0.0
12.6	70	311.2	10.9	22.1	0.0
12.0	71	352.6	11.7	29.1	0.0
6.6	108	351.0	12.7	83.6	2.3
7.0	54	378.8	17.7	43.7	1.0
-	-	62.5	3.3	28.3	0.3
4.2	-	90.5	7.4	16.2	0.3
-	-	87.1	7.2	18.1	0.3
3.6	76	585.5	23.4	607.3	2.6
2.6	58	106.3	5.8	144.8	7.1
1.0	42	231.8	16.7	92.4	28.8
8.1	116	291.7	17.4	61.5	0.4
7.4	-	71.7	3.2	3.3	0.0
15.1	73	146.4	4.8	6.1	0.0
15.1	75	150.6	4.9	6.6	0.0
15.2	72	140.7	4.7	6.1	0.0
6.9	97	605.4	32.3	219.1	2.4
6.8	94	705.2	34.7	117.1	2.3
8.9	107	569.8	36.1	86.0	0.9
8.1	91	578.3	35.6	89.8	6.2
7.4	75	104.7	5.7	8.3	0.4
9.0	-	121.5	7.2	4.4	0.1
9.0	111	131.9	6.9	4.2	0.0
9.4	120	136.5	6.8	3.9	0.1
3.0	42	213.7	29.4	339.4	18.1
0.1	9	2.4	0.4	88.7	24.3
0.2	-	1.9	0.6	123.0	25.3
0.3	11	3.1	0.4	132.6	18.9
0.2	9	-	-	-	0.0
0.1	8	-	-	-	0.0
0.2	8	14.3	1.6	110.3	25.0
0.2	10	43.9	1.9	141.5	41.3
0.5	28	20.0	1.6	101.6	50.9
0.1	5	1.3	0.3	3.5	2.7
0.7	76	104.8	2.9	1.3	0.4
-	-	1.4	0.5	5.4	3.1
-	-	1.2	0.6	7.6	4.6
-	-	4.3	1.0	9.1	6.8
-	-	2.3	0.6	6.7	3.3
-	-	2.3	0.6	6.6	3.1
-	-	4.5	1.4	3.9	2.3
-	-	2.3	0.9	1.2	0.9

-	-	1.4	0.5	1.5	1.2
-	-	3.6	0.9	4.5	3.2
-	-	0.6	0.5	2.1	1.5
-	-	0.7	0.5	2.1	1.5
-	-	3.1	1.0	2.3	1.3
-	-	2.0	0.4	8.6	7.7
-	-	1.9	0.4	5.2	5.0
0.2	9	23.9	3.4	37.9	13.6
0.1	13	4.9	1.8	8.4	2.8
0.3	3	13.8	2.1	30.2	20.1
0.1	9	14.8	2.6	21.7	8.0
0.2	14	6.2	2.6	9.8	2.7
0.1	13	5.1	1.3	8.1	4.1
0.0	10	0.4	0.1	0.3	0.7
0.0	7	1.4	0.1	4.7	1.2
0.1	11	1.2	0.6	0.7	0.5
0.1	7	1.2	0.6	0.7	0.5
0.1	13	8.3	0.9	9.6	2.9

Dash (-) no data

Li^+	**DIC**	**$\delta^{18}O$**	**δD**	**$\delta^{13}C$**
mg/L	**mg C/L**	**‰**	**‰**	**‰**
0.0	16	-	-	-16.5

0.0	21	-	-	-16.0
0.0	13	-	-	-9.2
0.0	22	-	-	-9.6
-	14	-6.6	-39	-18.7
-	16	-6.5	-40	-20.1
-	11	-6.9	-40	-
-	13	-6.9	-41	-18.3
-	25	-7.4	-46	-14.4
-	23	-7.1	-46	-13.5
0.2	6	-7.0	-46	-8.9
0.2	5	-6.4	-40	-8.8
0.3	5	-6.1	-43	-8.6
0.2	10	-7.1	-42	-12.3
0.2	10	-7.8	-45	-
0.1	17	-	-	-16.8
0.2	29	-	-	-19.7
0.2	29	-	-	-19.4
0.7	6	-8.5	-51	-10.0
0.0	65	-7.7	-47	-14.4
0.1	94	-7.5	-46	-6.2
0.5	14	-8.2	-54	-12.9
0.1	6	-	-	-14.4
0.1	6	-8.1	-50	-13.7
0.1	6	-8.2	-	-13.5
0.1	7	-6.6	-39	-13.4
0.5	13	-7.9	-53	-4.1
0.7	15	-8.2	-54	-4.4
0.6	11	-	-	-4.1
0.5	15	-7.8	-52	-5.6
0.0	24	-7.6	-47	-12.2
0.1	21	-	-	-14.7
0.0	23	-8.4	-52	-19.6
0.0	22	-7.6	-50	-12.0
0.6	14	-6.6	-44	-9.7
-	77	-6.6	-39	-4.4
-	109	-7.8	-45	-11
-	112	-7.1	-42	-13
-	71	-6.4	-40	-10
-	69	-6.5	-38	-8.4
-	89	-6.6	-41	-10
-	96	-6.5	-39	-8.9
-	124	-6.8	-43	-12
-	5	-7.4	-46	-12
-	44	-6.2	-39	-12
-	17	-	-	-9.1
-	11	-	-	-9.3
-	47	-	-	-7.7
-	4	-	-	-
-	3	-	-	-5.6
-	8	-	-	-8.2

-	3	-	-	-11
-	2	-	-	-7.5
-	5	-	-	-5.5
-	3	-	-	-14
-	2	-	-	-8.8
-	2	-	-	-7.2
-	5	-	-	-9.4
-	10	-	-	-9.8
-	37	-3.6	-25	-8.8
-	9	-4.5	-28	-5.9
-	40	-5.4	-31	-8.9
-	26	-2.6	-21	-9.4
-	10	-4.5	-27	-5.0
-	10	-5.5	-33	-9.8
-	0	-7.4	-44	-16
-	0	-4.9	-32	-11
-	0	-6.1	-38	-9.9
-	1	-6.1	-36	-7.0
-	6	-2.9	-19	-5.1

Dash (-) no data

Table 3
Saturation indices of hot springs, cold springs and streams

				Saturation Index

Site	Spring No	Spring Group	Date	Calcite	Dolomite
Mukupa Hot Spring	1	Northern	6/30/09	-1.28	-3.19
Ingansa Hot Spring	2	Northern	6/30/09	-0.73	-2.50
Kalembwe Hot Springs	3	Northern	7/1/09	-0.32	-1.34
Kalembwe Hot Springs 2	4	Northern	7/1/09	-0.88	-2.43
Kapishya Hot Spring 2	5	Eastern	4/18/13	-3.57	-7.30
Kapishya Hot Spring 2	5	Eastern	7/14/13	-4.52	-9.21
Kapishya Hot Spring	6	Eastern	4/18/13	-4.65	-8.44
Kapishya Hot Spring	6	Eastern	7/14/13	-5.26	-9.75
Chilonga Lusa	7	Eastern	7/15/13	0.13	-1.02
Chilonga Lusa 2	8	Eastern	7/15/13	-1.53	-3.84
Luangwa River Bluff East 3	9	Eastern	7/6/13	0.16	-2.32
Luangwa River Bluff East 1	10	Eastern	7/6/13	0.06	-2.50
Luangwa River Bluff East 4	11	Eastern	7/6/13	0.30	-2.01
Nsefu Hot Spring	12	Eastern	7/2/13	0.05	-1.06
Nchindeni Hot Spring	13	Eastern	7/2/13	-	-
Namwandwe Hot Spring	14	Mansa-Copperbelt	6/26/09	-1.27	-4.02
Kapisha Hot Spring	15	Mansa-Copperbelt	6/24/09	-1.19	-3.66
Kapisha Hot Spring 2	16	Mansa-Copperbelt	6/24/09	-1.48	-4.20
Kafue National Park	17	Western	4/22/13	-0.03	-2.11
Kafue National Park Hippo Lodge	18	Western	4/22/13	-0.09	-1.06
Mumbwa Hot Spring	19	Western	4/23/13	-0.03	-0.10
Bilili Hot Spring	20	Western	4/25/13	-0.38	-2.58
Chinyunyu Hot Spring	21	Southeastern	6/22/09	0.19	-1.66
Chinyunyu Hot Spring	21	Southeastern	4/16/13	-0.27	-2.89
Chinyunyu Hot Spring	21	Southeastern	4/16/13	-0.22	-2.71
Chinyunyu Hot Spring	21	Southeastern	6/28/13	0.13	-1.74
East Gwisho Hot Spring	22	Lochinvar	4/24/13	0.08	-1.42
Main Gwisho Hot Spring	23	Lochinvar	4/24/13	-0.27	-1.92
Bwanda Hot Spring	24	Lochinvar	4/24/13	-0.17	-2.03
Namululu Hot Spring	25	Lochinvar	4/24/13	-0.80	-2.31
West Lake Farm Hot Spring	26	Choma	4/26/13	-0.57	-1.96
Miller Hot Spring	27	Choma	6/21/09	-0.26	-1.66
Bruce Miller Farm 1	28	Choma	4/26/13	-0.37	-2.50
Bruce Miller Farm 2	29	Choma	4/26/13	-0.25	-1.91
Kasane Hot Spring	30	Kasane	7/29/13	0.43	-0.01
State Lodge			6/22/13	0.57	0.88
Good Hope Farms/Monkey Ponds			6/22/13	0.20	0.04
Palabana Dairy Spring			6/23/13	-0.02	-0.56
Laughing Waters Spring			6/24/13	-	-
Loma [Ba-koma]			6/24/13	-	-
St Charles Spring			6/24/13	0.12	-0.04
Zingalume Spring			6/24/13	0.07	-0.06
Linda			6/24/13	-0.04	-0.09

Mupwasha			6/28/13	-3.27	-6.44
Chifunda Mineral Spring			7/5/13	-2.19	-4.63
Kafue River			6/19/09	-1.75	-3.45
Kafue River			6/24/09	-1.94	-3.84
Magoya River			6/19/09	-1.76	-3.37
Zambezi River			6/20/09	-2.73	-5.50
Zambezi River			6/20/09	-4.18	-8.41
Kolomo River			6/21/09	-1.95	-3.89
Chambeshi River			6/25/09	-5.08	-9.98
Luongo River			6/27/09	-2.81	-5.41
Luapula River			6/27/09	-2.61	-5.04
Kulungwishi River			6/29/09	-2.71	-5.29
Kundabwika Falls			7/5/09	-2.84	-5.54
Chambeshi River			7/12/09	-6.13	-12.2
Lunsemfya River			7/13/09	-3.49	-6.84
Mulungushi River			7/13/09	-2.96	-5.75
Chongwe River			6/27/13	-0.34	-0.91
Lukusashi River			6/27/13	-1.40	-2.96
Mama Rula River			7/1/13	0.20	0.46
Kanakanapa River			6/28/13	-0.79	-1.83
Luangwa River			7/1/13	-1.42	-3.06
Mulungushi River			7/13/13	-3.27	-6.67
Chikwana Stream			7/14/13	-6.64	-12.7
Mansha River			7/14/13	-5.64	-11.6
Louviloa River			7/15/13	-5.87	-11.7
Mwaloeshi River			7/15/13	-6.05	-12.1
Chobe River			7/29/13	-1.89	-4.01

Dash (-) no data

Saturation Index				
Gypsum	**Chalcedony**	**Quartz**	**Chrysotile**	**Kaolinite**
-3.46	-	-	-	-
-4.03	-	-	-	-
-2.46	-	-	-	-

-2.50	-	-	-	-
-4.35	0.11	0.53	-16.98	-
-4.36	0.02	0.43	-23.38	-
-5.62	-0.02	0.36	-18.24	-
-5.55	-0.12	0.27	-20.32	-
-3.83	0.02	0.38	-0.01	-
-3.76	0.25	0.63	-9.37	5.22
-1.46	-0.01	0.27	-0.29	-
-1.49	0.00	0.27	-1.69	-
-1.40	-0.01	0.27	-0.01	-
-0.91	0.45	0.79	-1.55	-
-1.16	-0.02	0.28	0.89	-
-2.49	-	-	-	-
-2.61	-	-	-	-
-2.52	-	-	-	-
-0.20	0.16	0.45	-5.15	-
-1.32	0.43	0.82	-7.47	-
-1.24	0.22	0.60	-5.10	-
-1.09	0.42	0.73	-5.61	-
-3.05	-	-	-	-
-2.37	0.19	0.52	-2.91	-
-2.34	0.20	0.53	-2.46	-
-2.41	0.16	0.51	0.52	-
-0.56	0.35	0.67	-3.76	-
-0.79	0.28	0.59	-4.20	-
-0.92	0.32	0.62	-4.01	-
-0.95	0.51	0.88	-6.35	-
-2.49	0.31	0.66	-4.31	-
-2.80	-	-	-	-
-2.68	0.35	0.66	-3.77	-
-2.76	0.61	0.99	-2.49	1.31
-0.20	0.20	0.58	-1.75	-
-3.88	-0.26	0.18	-4.45	-
-3.51	-0.11	0.33	-7.65	-
-2.61	-0.17	0.27	-9.52	-
-	-0.20	0.24	-15.95	-
-	-0.33	0.10	-15.81	-
-2.37	-0.33	0.10	-7.50	-
-1.76	-0.20	0.23	-7.71	-
-2.12	0.28	0.72	-7.21	-
-4.97	-0.38	0.08	-16.4	-
-3.46	0.74	1.19	-12.2	-
-4.59	-	-	-	-
-3.60	-	-	-	-
-5.36	-	-	-	-
-5.08	-	-	-	-
-5.10	-	-	-	-
-5.96	-	-	-	-
-6.86	-	-	-	-
-6.37	-	-	-	-

-4.93	-	-	-	-
-5.74	-	-	-	-
-5.64	-	-	-	-
-6.84	-	-	-	-
-4.70	-	-	-	-
-5.24	-	-	-	-
-3.11	-0.17	0.29	-7.07	-
-3.96	-0.09	0.35	-7.81	-
-3.40	-0.70	-0.24	-4.03	-
-3.30	-0.15	0.31	-8.31	-
-3.82	-0.09	0.34	-8.79	-
-4.38	0.04	0.51	-19.1	-
-5.87	-0.17	0.28	-27.5	-
-4.94	-0.30	0.16	-28.7	-
-5.44	-0.09	0.37	-26.0	-
-5.71	-0.26	0.20	-27.7	-
-3.68	-0.07	0.38	-11.1	-

Dash (-) no data

Table 4
Temperature results from silica, sodium-potassium, potassium-magnesium and sodium-potassium-calcium for hot springs

Spring	Spring Group	Date	Temperature (°C)				
			Surface	SiO_2[a]	Na-K[b]	K^2-Mg[c]	Na-K-Ca[d]

Mukupa Hot Spring	Northern	6/30/09	35.6	-	123	56.6	101
Ingansa Hot Spring	Northern	6/30/09	46.1	-	173	89.2	137
Kalembwe Hot Springs	Northern	7/1/09	46.1	-	164	64.6	123
Kalembwe Hot Springs 2	Northern	7/1/09	46.6	-	163	62.4	122
Kapishya Hot Spring 2	Eastern	4/18/13	31.1	73.2	443	36.8	209
Kapishya Hot Spring 2	Eastern	7/14/13	32.0	65.5	404	33.9	195
Kapishya Hot Spring	Eastern	4/18/13	38.9	68.4	417	16.9	201
Kapishya Hot Spring	Eastern	7/14/13	38.4	59.9	433	13.1	199
Chilonga Lusa	Eastern	7/15/13	49.9	100	125	106	116
Chilonga Lusa 2	Eastern	7/15/13	42.4	98.5	138	94.1	126
Luangwa River Bluff East 3	Eastern	7/6/13	79.4	119	154	142	131
Luangwa River Bluff East 1	Eastern	7/6/13	83.4	118	161	149	138
Luangwa River Bluff East 4	Eastern	7/6/13	79.3	119	157	148	135
Nsefu Hot Spring	Eastern	7/2/13	57.9	141	162	89.9	132
Nchindeni Hot Spring	Eastern	7/2/13	74.0	105	178	111	149
Namwandwe Hot Spring	Mansa-Copperbelt	6/26/09	35.4	-	186	79.7	131
Kapisha Hot Spring	Mansa-Copperbelt	6/24/09	50.0	-	217	104	161
Kapisha Hot Spring 2	Mansa-Copperbelt	6/24/09	48.3	-	217	101	160
Kafue National Park	Western	4/22/13	75.6	122	168	105	129
Kafue National Park	Western	4/22/13	35.1	109	189	57.9	128

Hippo Lodge							
Mumbwa Hot Spring	Western	4/23/13	41.5	93.9	207	65.6	156
Bilili Hot Spring	Western	4/25/13	66.2	146	194	124	154
Chinyunyu Hot Spring	Southeastern	6/22/09	64.4	-	175	129	141
Chinyunyu Hot Spring	Southeastern	4/16/13	61.4	120	157	143	134
Chinyunyu Hot Spring	Southeastern	4/16/13	61.0	121	157	139	133
Chinyunyu Hot Spring	Southeastern	6/28/13	52.1	119	157	129	133
East Gwisho Hot Spring	Lochinvar	4/24/13	65.2	136	187	115	150
Main Gwisho Hot Spring	Lochinvar	4/24/13	71.6	134	181	118	154
Bwanda Hot Spring	Lochinvar	4/24/13	72.9	141	198	134	165
Namululu Hot Spring	Lochinvar	4/24/13	45.8	132	196	104	163
West Lake Farm Hot Spring	Choma	4/26/13	56.5	122	188	91.4	149
Miller Hot Spring	Choma	6/21/09	69.9	-	194	116	161
Bruce Miller Farm 1	Choma	4/26/13	69.0	143	185	137	156
Bruce Miller Farm 2	Choma	4/26/13	43.5	147	182	126	155
Kasane Hot Spring	Kasane	7/29/13	43.2	93.6	259	84.8	176

Dash (-) no data

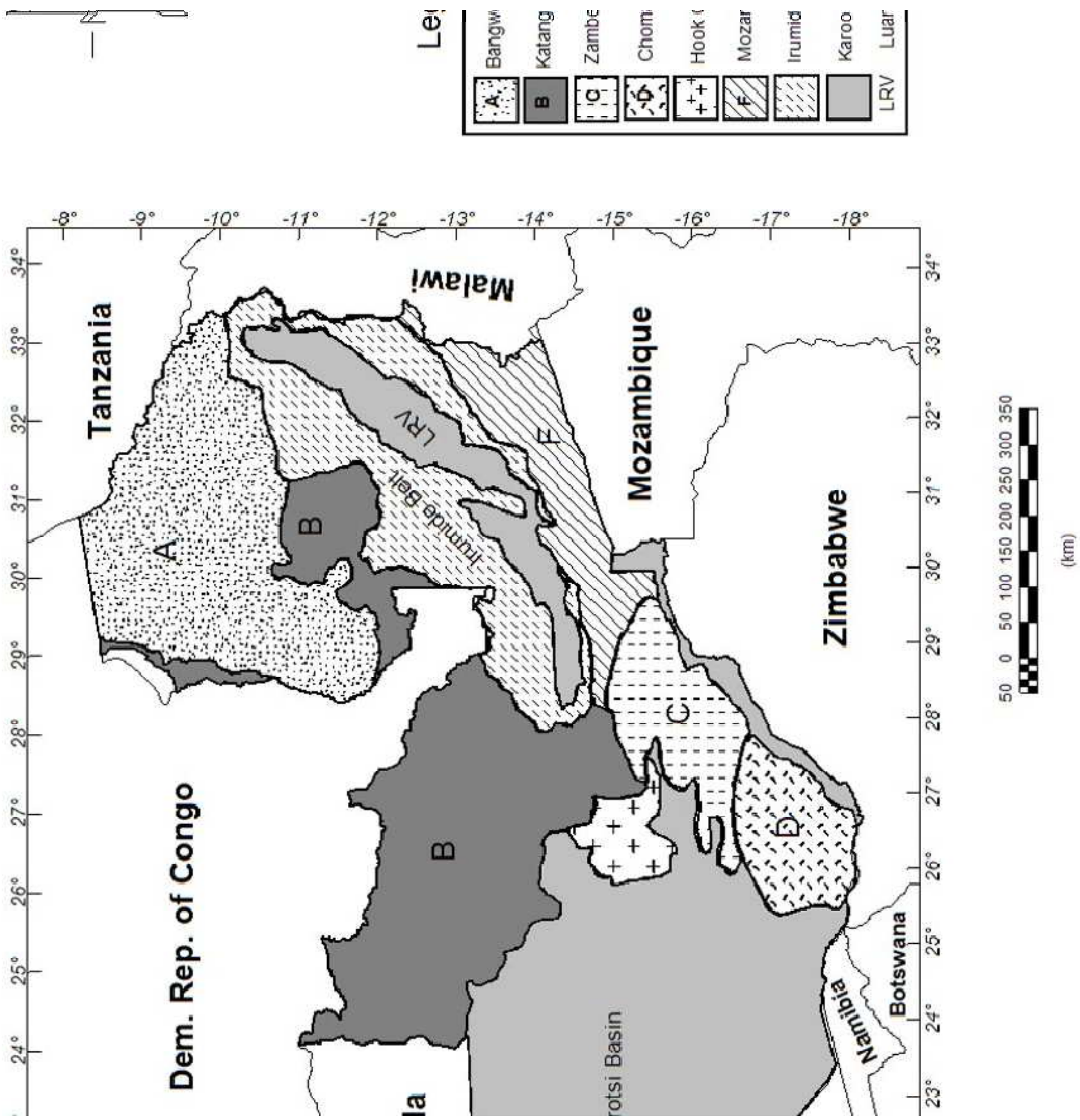


Figure 1. (a) Map of the general geology of Zambia (from Matende, 2014).

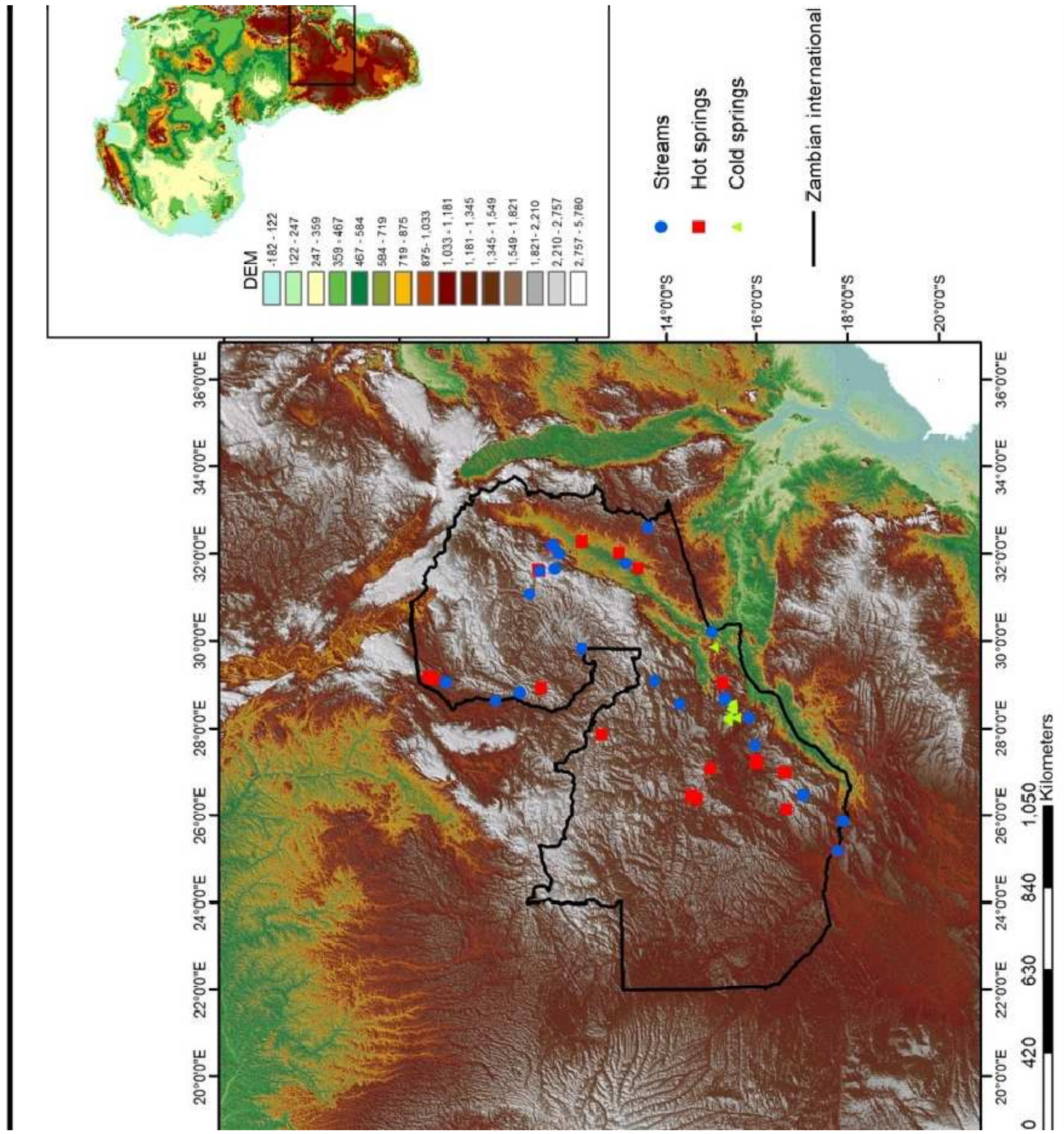


Figure 2. Shuttle Radar Topography Mission (SRTM) map overlain with sample sites (from Matende et al., 2014).

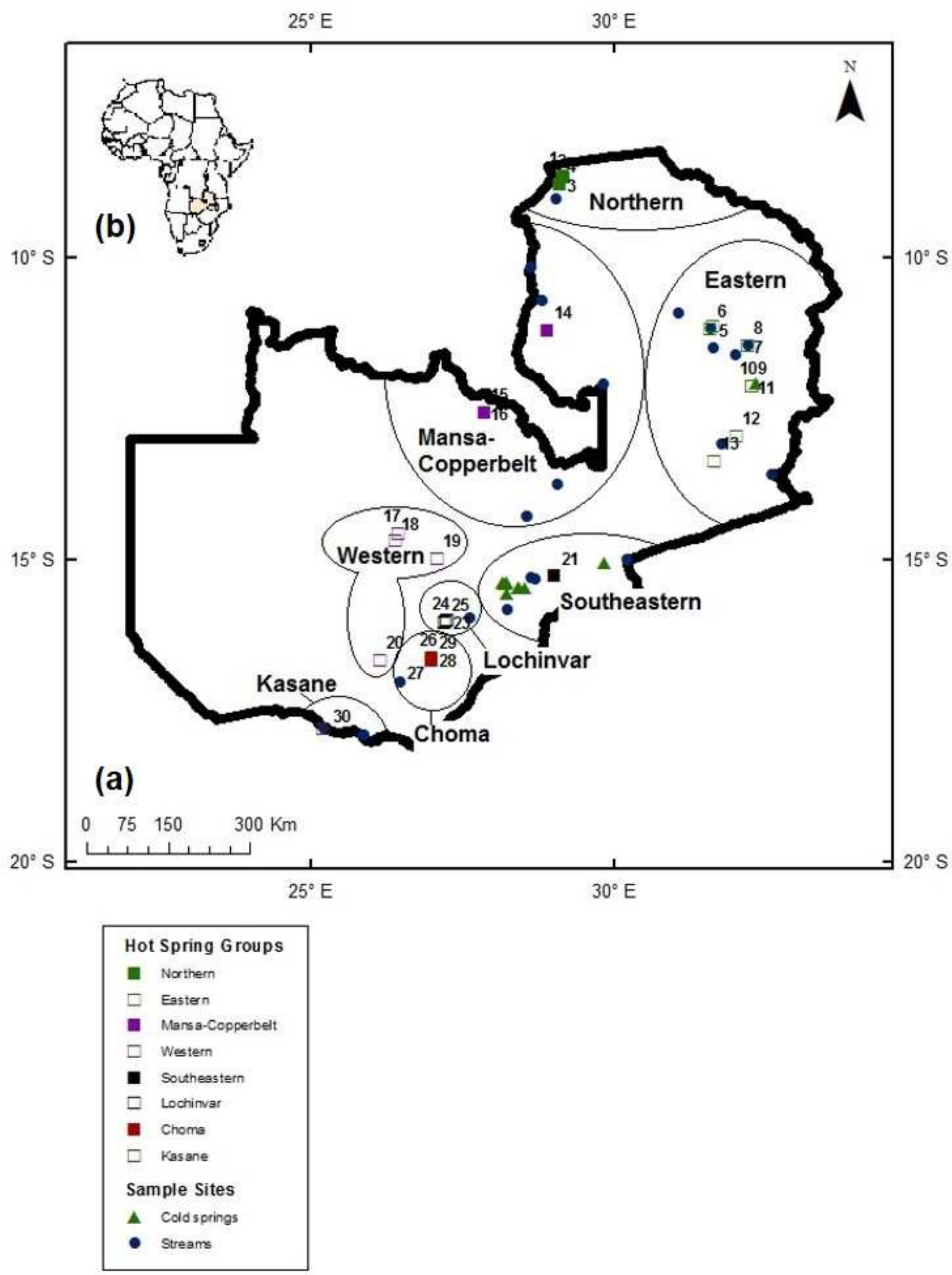


Figure 3. (a) Distribution of sampling locations in Zambia, labeled and groupings of hot springs adapted from Legg, 1974. (b) Shows the location of Zambia in southern Africa.

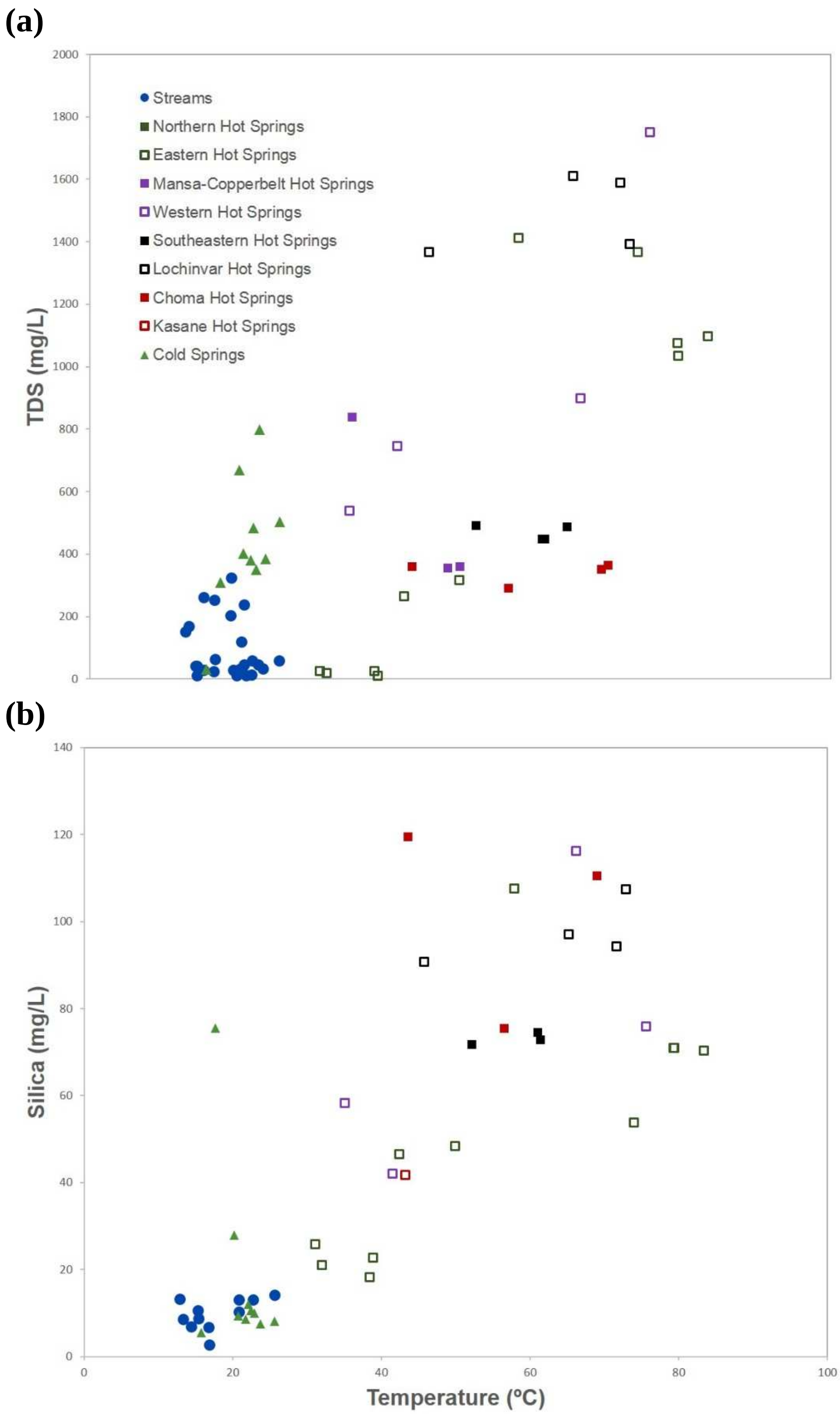


Figure 4. Cross plots of temperature vs. total dissolved solids (TDS) (a) and temperature vs. silica (b) for hot spring, cold spring and stream water samples from Zambia.

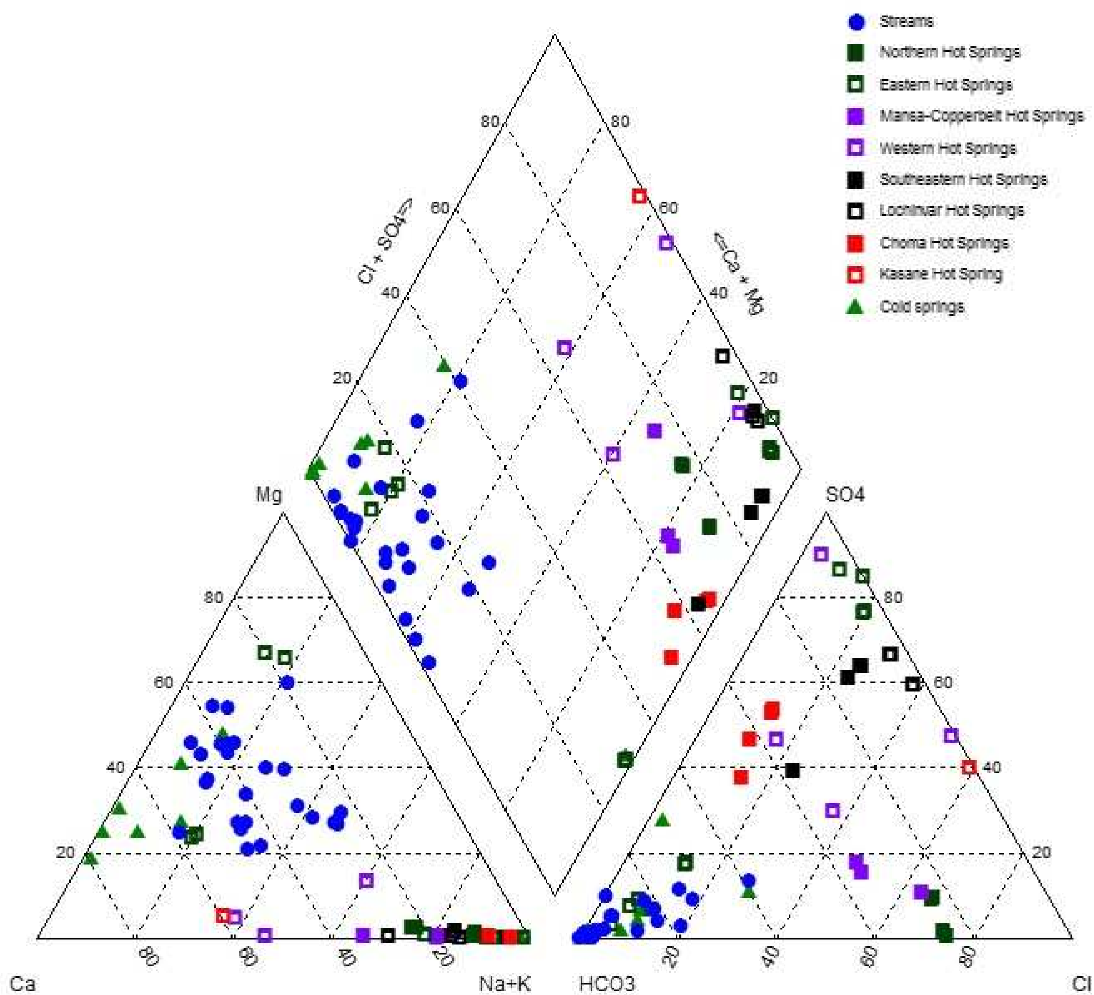


Figure 5. Piper plot of hot springs, cold springs and streams samples from Zambia.

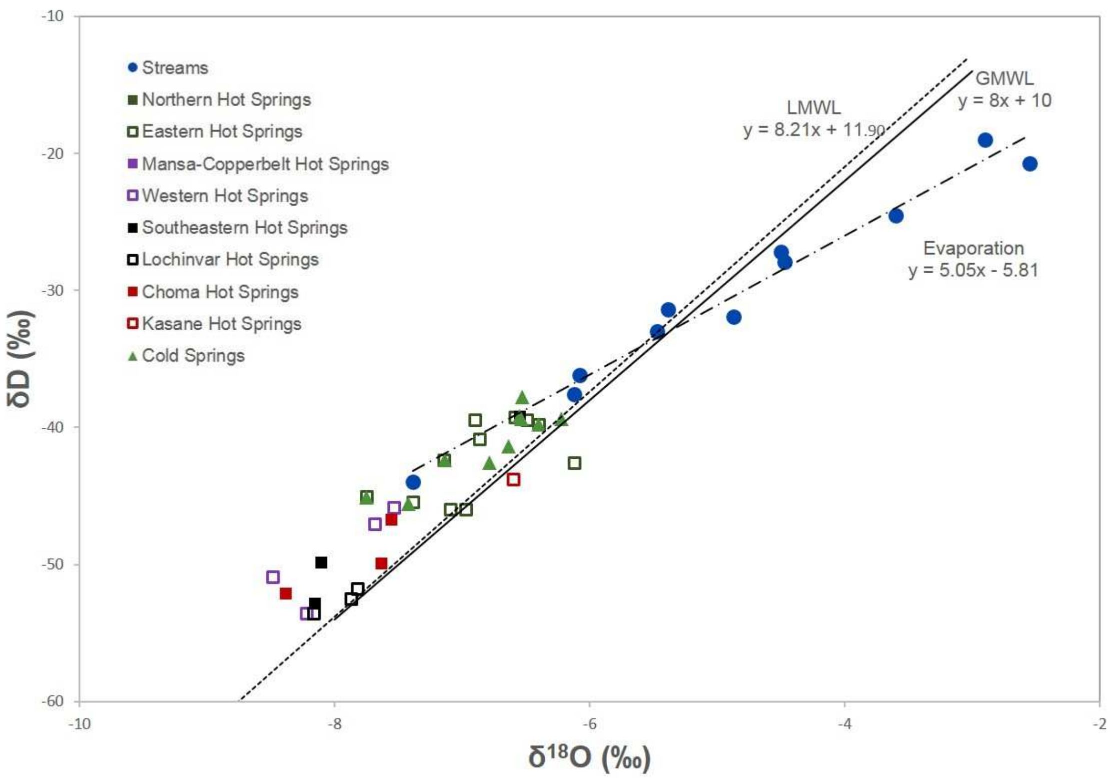
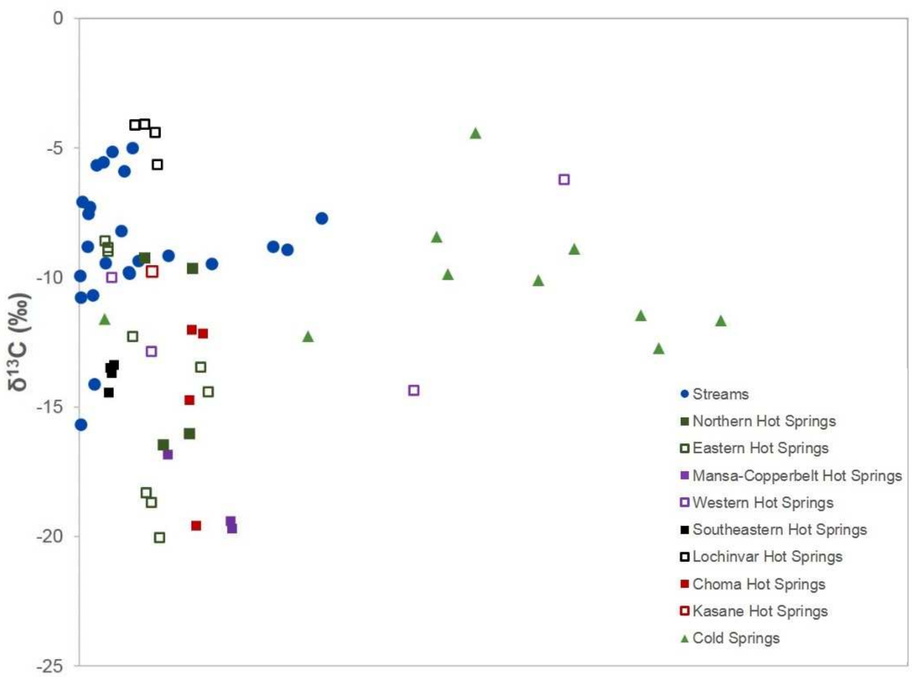


Figure 6. Cross plot of the isotopic composition of oxygen ($\delta^{18}O$) vs. hydrogen (δD) for hot springs, cold springs and stream samples. Also plotted is the Global Meteroric Water Line (GMWL, dashed) (Craig, 1961) and local rainfall average (LMWL, solid) (IAES/WMO, 2006).

(a)



(b)

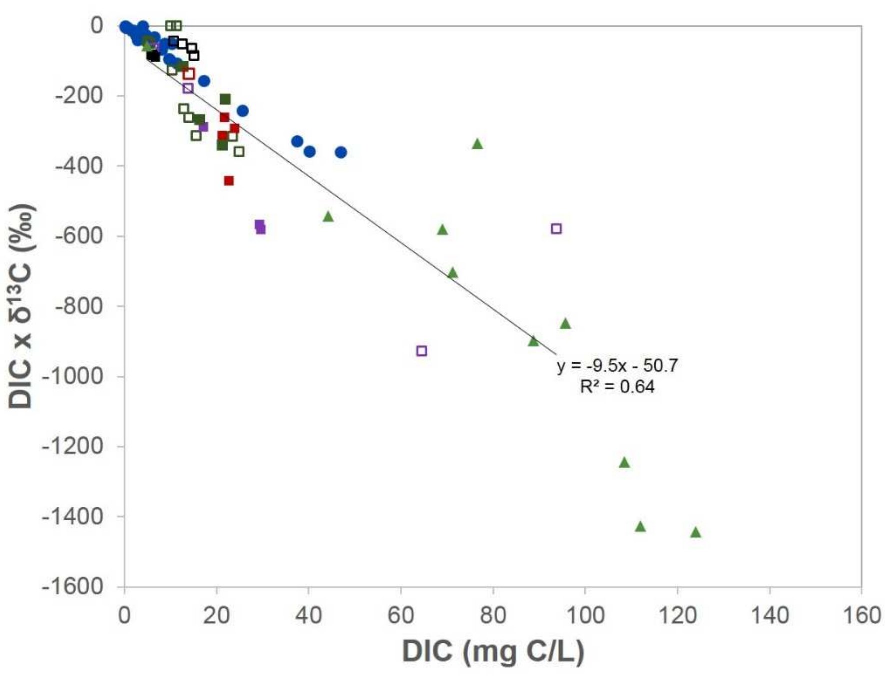


Figure 7. (a) Cross plot of dissolved inorganic carbon (DIC)vs. isotopic composition of carbon ($\delta^{13}C$) of DIC and (b) DIC vs. DIC* $\delta^{13}C$.

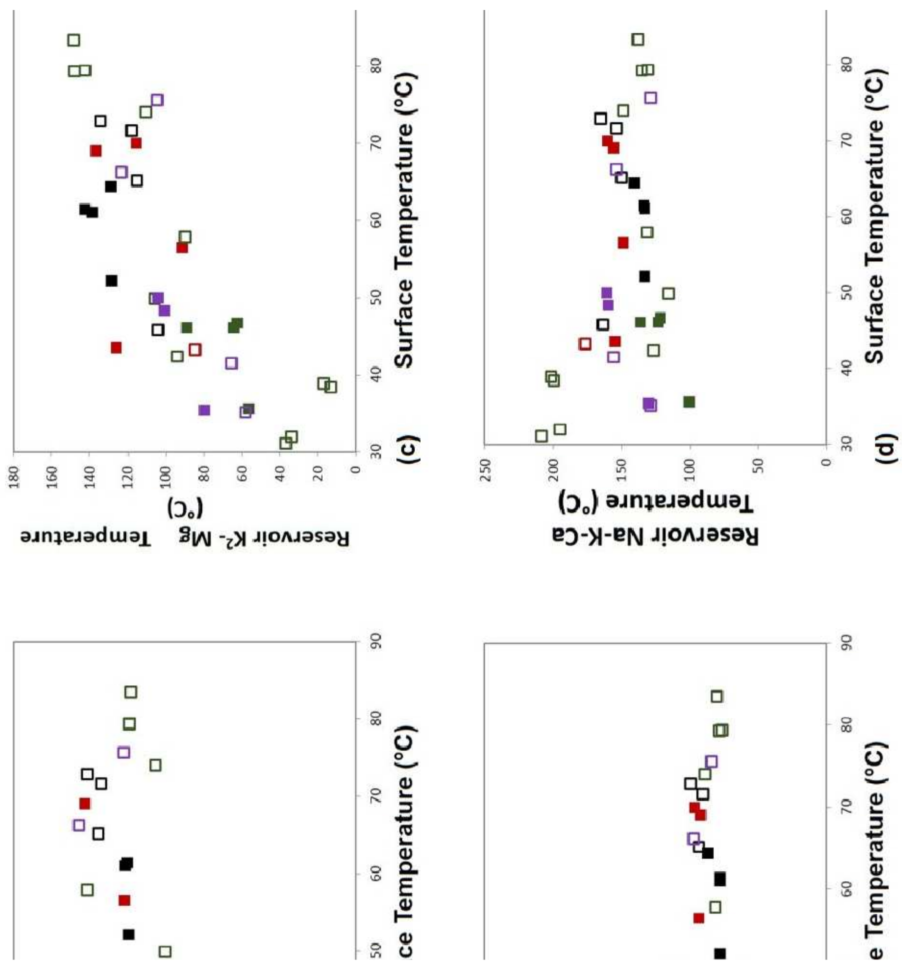


Figure 8. Cross plots of spring temperature at the surface vs. estimated reservoir temperature using (a) SiO_2 (b) Na-K (c) K^2-Mg and (d) Na-K-Ca geothermometer equations.

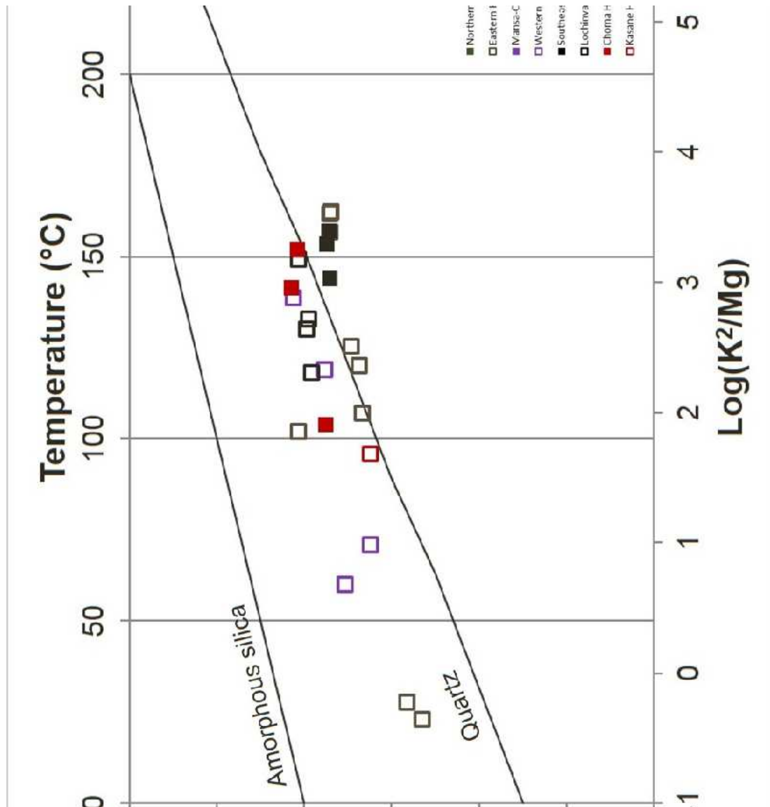


Figure 9. A plot of log SiO_2 against the logarithm of the K^2/Mg ratio for hot spring samples from Zambia on amorphus silica and quartz geothermometer equations.

APPENDICES

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Appendix A. Field Notes

STATE LODGE

- Type of sample: Cold spring
- Physical parameters: pH= 7.53 Temp= 21.74°C
- Location: 15.46128° S 28.42941° E
- Date: 6/22/2013
- About 20 km east of Lusaka on State Lodge Road off of Leopards Hills Road. We are not sure if this is the correct spring that was mentioned in the German report.
- This spring issues in the middle of a pond (depression) in a large field. The spring appears to issues as a diffuse source.
- We collected samples and made measurements in the middle of the ponded water. There were no bubbles present and no smell of sulfur.
- Photo 1 and Photo 2.

GOOD HOPE FARMS/ MONKEY PONDS

- Type of sample: Cold spring
- Physical parameters: pH= 7.09 Temp= 22.10°C
- Location: 15.46688° S 28.45067° E
- Date: 6/22/2013
- About 20 km east of Lusaka on Leopards Hill Road/ D152. There are a series of several springs that discharge into this valley.
- We walked upstream and collected a sample and took measurements below a concrete pad that used to be used to house a pump. There were no bubbles present and no smell of sulfur.
- The owner "Chaos" was very interesting and wanted to make sure that we wouldn't bring too much publicity to her secret spot just outside of Lusaka. She also told us about all of the Chinese driven activity in the area and is concerned that the continuous blasting with dynamite may disrupt her springs.
- Photo 3 and Photo 4.

PALABANA DAIRY SPRING

- Type of sample: Cold spring
- Physical parameters: pH= 6.74 Temp= 22.49°C
- Location: 15.45568° S 28.53719° E
- Date: 6/23/2013
- About 30 km east of Lusaka on Leopards Hill Road then 5 km north.
- This spring issues out of the grass then flows into a concrete dam then across the road into a holding area for the dairy to use.
- The spring was bubbling and there was no sulfur smell.
- Finding this spring was quite difficult, it is located at the USAID funded Palabana Dairy quite a ways out of Lusaka on Leopard Hills Road.
- Photo 5 and Photo 6.

LAUGHING WATERS SPRING

- Type of sample: Cold spring
- Physical parameters: pH= 7.23 Temp= 20.74°C
- Location: 15.37141° S 28.17566° E
- Date: 6/24/2013
- About 13 km west of Lusaka in Central Lusaka along Mungwi Road at Laughing Waters Resort.
- The spring issues inside the gated game management area that is home to deer and non-dangerous African animals.
- Issues out of the base of a hill and then flows into a stream, down elevation to a small water fall. There was some bubbling and no sulfur smell.
- A stream gauge is installed but our guide couldn't tell us by whom or if it is in working order.
- Photo 7 and Photo 8.

LOMA (BA-KOMA)

- Type of sample: Cold spring
- Physical parameters: pH= 7.20 Temp= 23.73°C
- Location: 15.38058° S 28.18626° E
- Date: 6/24/2013
- About 11 km west of Lusaka in Central Lusaka along Mungwi Road.
- This spring issues out of fractures in the gneiss. The pool was green in color due to algae growth.
- Three were a few issuing site. We gathered water at the issuing site where the water was the cleanest.
- The pools closest to the small village were impacted by human activities like washing and trash dumping
- We were not the only people here taking measurements, we saw vehicles from the Dutch Embassy and the Zambian government and one or more groups.
- Photo 9 and Photo 10.

ST. CHARLES SPRING

- Type of sample: Cold spring
- Physical parameters: pH= 6.99 Temp= 25.64°C
- Location: 15.38520° S 28.18626° E
- Date: 6/24/2013
- About 10 km west of Lusaka in Central Lusaka along Mungwi Road south of the St. Charles Boys School. According to the German study belongs to the school but we learned that it is privately owned (after getting permission to sample from 3 people that didn't have the authority to grant permission).
- There is a pipe that takes water from the source down the stream bed to the school.
- The owner told us that during the rainy season they have been told that their water has e-coli but he was adamant that his water is safe. This spring smells like sewage.
- Photo 11 and Photo 12.

ZINGALUME SPRING

- Type of sample: Cold spring
- Physical parameters: pH= 6.89 Temp= 22.89°C
- Location: 15.37203° S 28.22775° E
- Date: 6/24/2013
- About 8 km northwest of Lusaka City centre north of Mungwi Road in the Lilanda area.
- The spring issues out of a outcrop of rocks in the middle of the village.
- A concrete/ rock barrier pools water that then flows into a stream that is also a washing area and playground for children.
- Photo 13 and Photo 14.

LINDA

- Type of sample: Cold spring
- Physical parameters: pH= 6.83 Temp= 20.22°C
- Location: 15.54357° S 28.22776° E
- Date: 6/24/2013
- About 16 km southwest of Lusaka City centre off the west fork of the Kafue Road south of the village of Linda.
- Dense vegetation and palm trees indicated a spring… the spring issued in the middle of vegetated green fields.
- The spring issued out of an outcrop of rocks and then flowed to an area where it pooled and women were washing clothes.
- Photo 15, Photo 16 and Photo 17.

CHONGWE RIVER

- Type of sample: Stream
- Physical parameters: pH= 7.37 Temp= 15.41°C
- Location: 15.32297°S 28.7026° E
- Date: 6/27/2013
- About 40 km northeast of Lusaka and 3 km east of Chongwe on the Great East Road.
- We collected samples and made measurements on the north side of the bridge.
- The river had a greenish tint.
- Photo 18 and Photo 19.

LUKASHI RIVER

- Type of sample: Stream
- Physical parameters: pH= 7.34 Temp= 22.74°C
- Location: 15.00553°S 28.21578° E
- Date: 6/27/2013
- About 200 km east of Lusaka on the Great East Road across from Bridge Camp. The Lukashi River that divides Zambia, Malawi and Mozambique.
- We were worried about the crocodiles that we had been warned lurk in the river.
- Our Hanna meters were having issues so only YSI physical parameters we recorded.
- Photo 20 and Photo 21.

MUPWASHA

- Type of sample: Stream
- Physical parameters: pH= 5.78 and 6.18 Temp= 15.74°C
- Location: 15.05129°S 29.84725° E
- Date: 6/28/2013
- About 45 km west of Bridge Camp and 170 km east of Lusaka on the Great East Road (GER).

- We were looking for the source of the stream and water fall but do not think we actually made it to the source.
- Mpwasha Falls is a tourist attraction, there is an area off of the GER to park and walk down the valley to the falls and possibility the source?
- Photo 22 and Photo 23.

CHINYUNYU HOT SPRING

- Type of sample: Hot spring
- Physical parameters: pH= 8.52 and 9.17 Temp= 52.1°C
- Location: 15.26133° S 29.02403° E
- Date: 6/28/2013
- The spring is right off the Great East Road about 90 km from Lusaka about 200 m to the north side of the road.
- The spring discharges through a metal casing to the surface. Rocks have been arranged around the spring discharge to presumably help pool the water. There are several issues of hot water to the surface besides the metal casing. There is another discharge of this spring south of the road at about 200 m.
- We collected samples and made measurements at the main spring on the north side of the road. (Hanna measurements were taken in situ and YSI were taken once the water had cooled).
- People come to collect the water for spiritual reasons. There is a strong sulfur smell.
- Photo 24 and Photo 25.

CHINYUNYU HOT SPRING (CHIN1 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 8.57 Temp= 61.4 °C
- Location: 15.26133° S 29.02403° E
- Date: 4/16/2013
- Located East of Lusaka by about an hour drive.
- There was one main vent site that had a manmade pipe situated on top of it.
- Numerous smaller vents sites were observed.
- The site smelled slightly of sulfur.
- Water samples were taken for OSU colleagues. Duplicates were taken for the serum vials at both springs (1a and 1b; 2a and 2b). Samples were collected directly from the hot spring.
- Photo 26, Photo 27 and Photo 28.

KANAKANAPA RIVER

- Type of sample: Stream
- Physical parameters: pH= 7.31 Temp= 13.35°C
- Location: 15.29615° S 29.63726° E
- Date: 6/28/2013
- The river is 5.5 km north of Chongwe along the Great East Road about 45 km from Lusaka.
- This river was sampled after not being able to find a spring.

- The river was sampled on the east side under the bridge. There has been quite a bit of construction done to try to control the river but it is now in disrepair.
- Photo 29 and Photo 30.

MAMA RULA

- Type of sample: Stream
- Physical parameters: pH= 7.93 Temp= 16.86°C
- Location: 13.59376° S 32.60656° E
- Date: 7/01/2013
- The river is 0.5 km east off the main Mfuwe Road on the way to Mama Rula's Rest House about 5 km north of the Great East Road in Chipata. The river cannot be identified by its proper name so shall be called Mama Rula for this research.
- There is a very nicely concrete bridge and drainage system in place. We took our measurements on the north side of the road on the upstream side.
- Photo 31 and Photo 32.

LUANGWA RIVER

- Type of sample: Stream
- Physical parameters: pH= 7.12 Temp= 25.6°C
- Location: 13.09725° S 31.78603° E
- Date: 7/01/2013
- The river was sampled on the north side of the river under the South Luangwa National Park Mfuwe Bridge about 115 km from Chipata.
- Permission and a ranger who accompanied us to the location were gained from the South Luangwa Zambian Wildlife Authority (ZAWA) office south of the Mfuwe Bridge off of Old Petauke Road (signs are posted in Mfuwe) before entering the park.
- The river was full of hippos and crocs!
- We used the pole to collect water from the edge of the river below the Mfuwe Bridge.
- Photo 33.

NCHINDENI HOT SPRING

- Type of sample: Hot Spring
- Physical parameters: pH= 7.43 and 8.19 Temp= 74.0°C
- Location: 13.36048° S 31.66869° E
- Date: 7/02/2013
- The spring is 30 km southwest north of the South Luangwa National Park Mfuwe Bridge.
- We were accompanied/ taken to this site by a ZAWA ranger from the South Luangwa National Park main ZAWA station in Mfuwe.
- The spring is very hot, with steam coming off the issuing sites and then for quite a ways before the springs formed a stream.
- There is white precipitates that covers all rocks at the spring site and we smelled a strong sulfur odor.
- The vegetation around the spring is very lush compared to the surrounding vegetation.
- Photo 34, Photo 35 and Photo 36.

NSEFU HOT SPRING

- Type of sample: Hot Spring
- Physical parameters: pH= 7.18 and 7.74 Temp= 57.1°C
- Location: 12.94135° S 32.03416° E
- Date: 7/02/2013
- The spring is 32 km northwest of the South Luangwa National Park Mfuwe Bridge.
- We were accompanied/ taken to this site by a ZAWA ranger from the South Luangwa National Park main ZAWA station in Mfuwe.
- The spring is inside the South Luangwa National Park and has been engineered with a metal casing to control the flow.
- The spring issues in the middle of a grassy field and then flowed into a marshy area.
- The area immediately adjacent to the spring is lush green grass that turns into brown dead grass.
- There is no sulfur smell associated with this spring.
- Photo 37 and Photo 38.

CHIFUNDA MINERAL SPRING

- Type of sample: Cold Spring
- Physical parameters: pH= 6.92 Temp= 17.79°C
- Location: 12.07107° S 32.35503° E
- Date: 7/05/2013
- The spring is 1 km northwest of the Kanunshya Scout Camp of the North Luangwa National Park.
- We were taken to this site by a ZAWA ranger that we picked up in Chifunda at the ZAWA headquarters for North Luangwa National Park. We traveled from Lundazi to Magodi to Chizizi to Chifunda.
- The "spring" is probably more like a seepage area. The ground is very spongy and full of hippo holes and dung.
- The spring may issue in the reeds but we were not willing to face elephants on foot to collect water form the source.
- The water was very dark (full of tannin) and we went through many filters and the water still had a yellowish brown ting when collected.
- Our samples were also not able to get into the cooler until days later due to being stuck at the Kanunshya Scout Camp for 3 days.
- Photo 39, Photo 40, Photo 41 and Photo 42.

LUANGWA RIVER BLUFF EAST 1

- Type of sample: Hot Spring
- Physical parameters: pH= 6.66 and 8.30 Temp= 83.1°C
- Location: 12.11714° S 32.28472° E
- Date: 7/06/2013
- The spring is 10 km southwest of Kanunshya South Camp of the North Luangwa National Park.

- We were taken to this site by a ZAWA ranger we picked up in Chifunda at the ZAWA headquarters for North Luangwa National Park.
- The spring issued out of the side of the bluff and flowed into the Luangwa River. This was the first issuing point measured but we counted 20 issuing spots along the bluff.
- The springs along the bluff appear to be controlled by faulting. The metamorphic rock were about 5 m high from the river valley.
- There was a dead turtle and lizard that had been cooked in the hot water.
- We had to dig down a bit to get a hole big enough to get our probes in to measure. There was a sulfur smell with lot of bubbles issuing out of the source.
- The spring issued out of metamorphosed gneiss. Mica flakes bubbled out of the source.
- The spring flowed into a small stream with other issuing sites and then made its way into the Luangwa River.
- Photo 43 and Photo 44.

LUANGWA RIVER BLUFF EAST 2

- Type of sample: Hot Spring
- Physical parameters: pH= 7.06 Temp= 84.7°C
- Location: 12.11714° S 32.28472° E
- Date: 7/06/2013
- The spring is 10 km southwest of Kanunshya South Camp of the North Luangwa National Park and 2 meters away from Luangwa River Bluff East 1.
- We were taken to this site by a ZAWA ranger we picked up in Chifunda at the ZAWA headquarters for North Luangwa National Park.
- There were no water samples taken but precipitate and in situ parameters were collected.
- Photo 45.

LUANGWA RIVER BLUFF EAST 3

- Type of sample: Hot Spring
- Physical parameters: pH= 7.84 and 8.61 Temp= 79.4°C
- Location: 12.11671° S 32.28504° E
- Date: 7/06/2013
- The spring is 10 km southwest of Kanunshya South Camp of the North Luangwa National Park and further up (north) the bluff from Luangwa River Bluff East 1.
- We were taken to this site by a ZAWA ranger we picked up in Chifunda at the ZAWA headquarters for North Luangwa National Park.
- It issues at a higher elevation out of the gneiss. This was very difficult to sample because the rocks made collecting water no easy task and the temperature of water was HOT!
- Photo 46.

LUANGWA RIVER BLUFF EAST 4

- Type of sample: Hot Spring
- Physical parameters: pH= 7.70 and 8.61 Temp= 79.3°C
- Location: 12.11784° S 32.28448° E

- Date: 7/06/2013
- The spring is 10 km southwest of Kanunshya South Camp of the North Luangwa National Park to the south of Luangwa River Bluff East 1 and sampled on our way back to the car.
- We were taken to this site by a ZAWA ranger we picked up in Chifunda at the ZAWA headquarters for North Luangwa National Park.
- Dr. E. got stuck and had to be pulled out of the hot water.
- Photo 47 and Photo 48.

MULUNGUSHI RIVER

- Type of sample: Stream
- Physical parameters: pH= 6.11 Temp= 12.88°C
- Location: 14.29632° S 28.54873° E
- Date: 7/13/2013
- The river is 20 km north of Kabwe on the Great North Road.
- The river was difficult to get to due to the reeds that were along both sides of the river.
- We collected the samples on the south west side of the river just before Mulungushi University.
- Photo 49 and Photo 50.

CHIKWANA STREAM

- Type of sample: Stream
- Physical parameters: pH= 7.85 Temp= 20.80°C
- Location: 11.501097° S 31.64480° E
- Date: 7/14/2013
- The stream is 12 km south of Chitembo on the Great North Road.
- This is another spring fed steam that we sampled because we could not get to the spring source. The stream is sampled along the trail that we took looking for the source.
- We lost our Hanna meter here and had to have the locals that were interested in what we were doing help us located it.
- The area is very waterlogged and quite squishy.
- Photo 51.

KAPISHA HOT SPRING

- Type of sample: Hot Spring
- Physical parameters: pH= 4.4 Temp= 37.73°C
- Location: 11.17063° S 31.60040° E
- Date: 7/14/2013
- The spring is located on the Shiwa Ng'andu estate about 87 km northeast of Mpika.
- The spring was measured in the middle of the large pool that has been dammed into a swimming pool.
- There were many places where bubbling occurred, we sampled where bubbling was most constant.
- The base of the pool is composed of sand and no sulfur smell is associated with this spring

- The Kapishya Hot Springs Lodge is own by Mark Harvey a wealth of knowledge!
- Photo 52 and Photo 53.

KAPISHYA HOT SPRING (KAP1 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 5.33 Temp= 38.9°C
- Location: 11.17063° S 31.60039° E
- Date: 4/18//2013
- The spring is located on the Shiwa Ng'andu estate about 87 km northeast of Mpika.
- Main Site: This vent site is situated in a large pool at the head of a stream. The floor is made of sand and organic matter. There were numerous places within the pool that were bubbling. The bubbles are fairly constant but not vigorous. They churn up the sand where they are bubbling. It is does not smell of sulfur.
- Temperature and pH measurements were taken at three of the main bubbling sites. We sampled the hottest area with the most vigorous bubbling (#1 on the hand sketch). Samples were collected from two locations within this area. Samples called KAP 1a and KAP 1b.
- Water samples were taken for OSU at the same location as gas samples taken. Called KAP 1 (a and b on test tube vials).
- Photo 54 and Photo 55.

MANSHYA RIVER

- Type of sample: Stream
- Physical parameters: pH= 4.24 Temp= 16.78°C
- Location: 11.17055° S 31.60141° E
- Date: 7/14/2013
- The river is located on the Shiwa Ng'andu estate about 87 km northeast of Mpika
- The river was measured near the pool at the Kapishya Hot Springs Lodge.
- The water was quite a bit colder than the spring that we had just measured.
- We sampled at the edge of the river due to the strong current.
- Photo 56.

SHIWA NGANDU/ KAPISHYA HOT SPRING 2

- Type of sample: Hot Spring
- Physical parameters: pH= 4.66 Temp= 31.23°C
- Location: 11.13005° S 31.64205° E
- Date: 7/14/2013
- The spring is located on the Shiwa Ng'andu estate about 87 km northeast of Mpika in a sugar cane field some 6 km from the Kapishya Lodge.
- The source was diffused so we sampled where the water was flowing.
- Photo 57 and Photo 58.

KAPISHYA HOT SPRING 2 (KAP2 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 5.73 Temp= 31.1°C
- Location: 11.13014° S 31.64219° E
- Date: 4/18/2013
- The spring is located on the Shiwa Ng'andu estate about 87 km northeast of Mpika in a sugar cane field some 6 km from the Kapishya Lodge.
- Located 6 km south of the Kapishyia Hot Spring and lodge. Walked down a river valley then up about 100 meters towards granite (?) hills. Very small stream comes out of the ground in a field of sugar cane. Pools are very muddy and required digging to find warm water and gas bubbles. Dug in several places and finally found a place with diffuse bubbling. Gas samples taken here. Samples were called SKAP 2a and SKAP 2b.There was no sulfur smell and water was not very warm.
- Gas samples taken from bubbling vent but water samples taken from approximately 0.5 meters away due to excessive mud in the water at the vent site. Samples labeled KAP 2 (2a and 2b for tubes).
- Photo 59.

CHILONGA LUSA

- Type of sample: Hot Spring
- Physical parameters: pH= 9.16 Temp= 49.33°C
- Location: 11.44902° S 32.21044° E
- Date: 7/15/2013
- The spring is 5 km east of Chibesa in a Game Management Area (GMA).
- We were taken to this site by a ZAWA ranger we picked up at Mano Gate for North Luangwa National Park. They knew we would be visiting after talking to our ranger from Chifunda
- There is a yellowish algal mat with minor amounts of green.
- There is intermittent bubbling every 3-5 seconds with big burps every 10 seconds.
- The spring issues in the middle of a field in the GMA.
- There is no smell associated with the spring.
- Photo 60 and Photo 61.

CHILONGA LUSA 2

- Type of sample: Hot Spring
- Physical parameters: pH= 7.37 Temp= 39.91°C
- Location: 11.45168° S 32.21109° E
- Date: 7/15/2013
- The spring is 0.3 km south of Chilonga Lusa 1 in the Game Management Area (GMA).
- We were taken to this site by a ZAWA ranger we picked up in Mano Gate for North Luangwa National Park.
- This spring issued in to a muddle pool that has been deepened by hippos.
- There is bubbling in multiple locations with possible gas interactions with mud because when the bubbles come to the surface they bring mud and organic matter with them.
- The source is diffused over ~10 square meter area.
- Photo 62 and Photo 63.

LOUVILOA RIVER

- Type of sample: Stream
- Physical parameters: pH= 4.87 Temp= 15.36°C
- Location: 11.45093° S 32.21115° E
- Date: 7/15/2013
- The stream is 800 m north of the Chilonga Lusa 2.
- We were taken to this site by a ZAWA ranger we picked up in Mano Gate for North Luangwa National Park.
- The water is very cold and clear.
- Photo 64.

MWALOESHI RIVER

- Type of sample: Stream
- Physical parameters: pH= 4.66 Temp= 14.45°C
- Location: 11.60695° S 32.01675° E
- Date: 7/15/2013
- The river is adjacent to the Natwangwe Community Camp.
- We were taken to this site by a ZAWA ranger we picked up in Mano Gate for North Luangwa National Park.
- This river was sampled on our way out of the GMA off the side of the bridge
- No photos were taken of this sample location.

KASANE HOT SPRING

- Type of sample: Hot Spring
- Physical parameters: pH= 7.71 Temp= 43.23°C
- Location: 17.79110° S 25.19807° E
- Date: 7/29/2013
- About 5 km east of Kasane just off the highway to the north.
- There is intermittent bubbling.
- Lots of white precipitant is all over the salt flat. The spring is quite silty.
- The spring is located next to Chobe River. Many animals come to the spring, hippos, elephants and lions.
- Kyle fell into an elephant hole.
- Photo 65 and Photo 66.
-

CHOBE RIVER

- Type of sample: Stream
- Physical parameters: pH= 6.56 Temp= 19.81°C
- Location: 17.789542° S 25.198387° E
- Date: 7/29/2013
- About 5 km east of Kasane just off the highway to north meters from Kasane Hot Spring.

- The river is large and moving very rapidly.
- We did not use the sampling pole.
- Photo 67 and Photo 68.

KAFU NATIONAL PARK (KPM1 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 8.57 Temp= 61.4 °C
- Location: 14.67739° S 26.38345° E
- Date: 4/22/2013
- Located 220 km northwest of Lusaka, 6 km southwest of Belama and 13 km northwest of Kalubilo.
- The KPM site is located on the property of the Hippo Lodge. It is a large pool surrounded by reeds and lily pads. The bottom is composed of organic rich mud. There are numerous different gas bubble streams visible within the small pond. Gas streams were fairly constant but not vigorous. They are all about the same temperature. The water is about 1.5 meters deep. Waders were necessary. There was no smell of sulfur.
- Three gas samples were collected here. They are all from the pool but were collected from different bubble streams. They are called KPM 1a, 1b, 1c. Water samples were collected from near one of the bubbling vents.
- Photo 69.

KAFU NATIONAL PARK (LUB1 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 6.87 Temp= 75.6°C
- Location: 14.55725° S 26.44967° E
- Date: 4/22/2013
- Located 220 northwest of Lusaka and 0.6 km northwest of Lubungu.
- The LUB site is located just outside the park boundary, just after the pontoon. The hot spring is radioactive, according to numerous sources. It forms a mound of precipitates several meters high and has numerous active bubbling vents on the top. Bubbling is vigorous. There is a strong smell of sulfur. There are numerous dead animals in the water (frog, bird, and lizard).
- Two samples were collected from the same stream of venting site. They are called LUB 1a and 1b.
- Photo 70, Photo 71 and Photo 72.

MUMBWA SITE (MUM1 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 6.88 Temp= 41.5°C
- Location: 14.97456° S 27.08026° E
- Date: 4/23/2013
- Located 85 km northwest of Lusaka and 2.30 km northeast of Mumbwa.

- We heard about another hot spring near the town of Mumbwa and had a local man guide us there to the spring. It is a small hot spring with very diffuse bubbling but stream is fairly constant. There is only one noticeable stream of gas bubbles so both gas samples were taken there. The spring is a small pool with muddy bottom. No smell of sulfur. We saw a green mamba next to the spring.
- We call it the Mumbwa hot spring and samples are labeled MUM 1a and 1b. Water samples taken near the bubbling stream.
- Photo 73.

EAST GWISHO SITE (EGWI from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 7.24 Temp= 65.2°C
- Location: 15.98534° S 27.24706° E
- Date: 4/24/2013
- Located 80 km southwest of Lusaka and 0.7 km from Lochinvar Ranch.
- This hot spring is one of three sampled in the Locinvar National Park. All three sampes were taken from the southern end of Locinvar. We thought that there might be one to the north near the Lagoon but were told that there was no spring. We did not attempt to find it. This is not the main Gwisho hot spring.
- The E. Gwisho hot spring forms the mouth of a small stream. It is surrounded by a grassy marsh/field. There were several dead frogs near the vents. The gas bubbles were very sporadic and diffuse. It took approximately 30 minutes for each gas sample to be collected. The gas may be contaminated with atmospheric gases, as a stick was poked in the mud to help release more gas. No smell of sulfur in the region.
- Two samples were taken from the same venting site. They are called EGWI 1a and 1b.
- Water samples were collected from the same site.
- Photo 74 and Photo 75.

MAIN GWISHO SITE (GWI1 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 7.1 Temp= 71.6°C
- Location: 15.98697° S 27.24285° E
- Date: 4/24/2013
- Located 80 km southwest of Lusaka and 1 km from Lochinvar Ranch.
- The main Gwisho spring emanates from a rock edifice with some precipitants observed around the edges. Several small streams of gas are observed but very diffuse and intermittent bubbling. Hottest region comes from under a ledge of rock, so difficult to sample. But we were able to trap a significant amount of gas.
- Two gas samples were taken. Called GWI 1a and 1b. Water samples taken from the same spot as gas samples.
- Photo 76 and Photo 77.

NAMULULU SITE (NOMA1 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring

- Physical parameters: pH= 6.9 Temp= 45.8°C
- Location: 16.02588° S 27.20636° E
- Date: 4/24/2013
- Located 85 km southwest of Lusaka and 1 km from Bwanda.
- I labeled these Noma but it should have been Namu.
- This is a small hot spring located just outside of Locinvar National Park. It is very close to Bwanda Hot Spring. The spring occurs in the middle of a small stream (not at the head). The water around the site is cold. The gas bubbles are large but fairly diffuse.
- Two gas samples were taken from the same location. These were called NOMA 1a and 1b. Water samples were taken from the same location.
- Photo 78.

BILILI SITE (BILI1 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 7.25 Temp= 66.2°C
- Location: 16.65726° S 26.13943° E
- Date: 4/25/2013
- Located 35 km northwest of Kalomo and about 5 km from Kaingu.
- Bilili Hot Springs are located west of the town Koloma (?). The hot spring formed the head of a small stream that emanates from the base of a tree. There were lots of bees around the spring. There were intermittent gas bubbles from near the tree but a slightly more vigorous bubbling downstream by ~3 meters. Samples were taken from this region. The site smells of slightly of sulfur.
- Two gas samples were taken from the same location. Samples were called BILI 1a and 1b. Water samples were taken from the same location.
- Photo 79, Photo 80 and Photo 81.

BRUCE MILLER FARM (BM1 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 7.98 Temp= 69.0°C
- Location: 16.64787° S 26.9977° E
- Date: 4/26/2013
- Located about 20 km north of Choma.
- Samples were taken from the Bruce Miller farm and two nearby farms. Many of these hot springs have man made structures surrounding them. Samples came from the Bruce Miller Farm (2), the Ross Farm (1), and the West Acres Farm (2). The samples are thought to lie above the same fault system.
- The Bruce Miller Farm has 4 hot springs. Due to limitations in sample containers we only sampled the two hottest springs.
- The Bruce Miller 1 site is located very close to the farmhouse. There is a cement structure constructed on top of the hot spring. Gas bubbles are intermittent but large and numerous with each burst. Small stream emanates from the hot spring, which is surrounded by grass field/marsh. No smell of sulfur.
- Two gas samples collected from this hot spring. They are called BM 1a and 1b. Water samples taken from same location.

- Photo 82.

BRUCE MILLER 2 (BM2 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 8.46 Temp= 43.5°C
- Location: 16.64821° S 26.99692° E
- Date: 4/26/2013
- Located about 20 km north of Choma.
- Samples were taken from the Bruce Miller farm and two nearby farms. Many of these hot springs have man made structures surrounding them. Samples came from the Bruce Miller Farm (2), the Ross Farm (1), and the West Acres Farm (2). The samples are thought to lie above the same fault system.
- Bruce Miller site two is in a grassy marsh. It is a medium sized pool with a muddy bottom. There is diffuse bubbling in several locations in the pool. Samples were collected from the same stream of gas bubbles. There is no smell of sulfur.
- We took two gas samples here along with water samples. Samples are called BM2a and BM2b.
- Photo 83.

WEST LAKE DAM (WLD1 from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 7.53 Temp= 56.3 °C
- Location: 16.60284° S 26.99584° E
- Date: 4/26/2013
- Located about 25 km north of Choma.
- Samples were taken from the Bruce Miller farm and two nearby farms. Many of these hot springs have man made structures surrounding them. Samples came from the Bruce Miller Farm (2), the Ross Farm (1), and the West Acres Farm (2). The samples are thought to lie above the same fault system.
- This site is on the West Acres Farm, near Bruce Miller Farm. This is in a small stream with a small dam constructed downstream from the hot spring. The streambed is composed primarily of sand. There is very constant but small gas bubbling in several locations. No sulfur smell. Not a very high water flux but it is warm.
- Two gas samples were taken from this location. The samples are called WLD 1a and 1b. Water samples are taken here but there was no 30 mL Nalgene.
- Photo 84 and Photo 85.

- **WEST ACRES FARM (WA1 from Wanless and Elsenbeck, 2013)**
- Type of sample: Hot spring
- Physical parameters: pH= 6.94 Temp= 43.2 °C
- Location: 16.53123° S 27.02647° E
- Date: 4/26/2013
- Located about 30 km north of Choma.
- Samples were taken from the Bruce Miller farm and two nearby farms. Many of these hot springs have man made structures surrounding them. Samples came from the Bruce Miller

Farm (2), the Ross Farm (1), and the West Acres Farm (2). The samples are thought to lie above the same fault system.

- This spring is enclosed in a circular brick structure that is about 2 m high but water flows out of the base. We collect the gas samples from inside the brick structure. The temperature may not be accurate because it was taken just outside the brick structure. The spring is located at the head of a small stream. There is a relatively high water flux at this spring. There is no sulfur smell.
- Two gas samples were taken from this location. They are called WA1a and 1b. Only test tube samples were collected for water (because there are no more containers).
- Photo 86 and Photo 87.

MUSALE (MSU from Wanless and Elsenbeck, 2013)

- Type of sample: Hot spring
- Physical parameters: pH= 8.24 Temp= 47.9 °C
- Location: 16.47916° S 27.02647° E
- Date: 4/26/2013
- Located about 40 km north of Choma.
- Musale hot spring is a small pool near a grassy marsh/field. There is no stream associated with this hot spring. The floor of the pool is mud and organic matter. It has a very low water flux and intermittent gas bubbles. There is a very slight smell of sulfur.
- Two gas samples were collected from the same stream of gas bubbles. They are called MSU1a and MSU1b. Test tube water samples were also collected.
- Photo 88 and Photo 89.

Appendix B. Field Photos

Photo 1. State Lodge spring looking towards the island in the center of the pond made by the spring.

Photo 2. Looking to the right from the edge of the pond formed by State Lodge spring.

Photo 3. Looking down from the concrete pad at the valley edge of Good Hope Farms/ Money Ponds.

Photo 4. Looking downstream from Good Hope Farms/ Monkey Ponds at the stream formed from several spring discharges.

Photo 5. Palabana Dairy Spring issuing out of the grass.

Photo 6. Looking upstream from Palabana Dairy Spring along the path the spring flows into the concrete dam.


Photo 7. Laughing Waters Spring issuing site.


Photo 8. The clarity of the water from Laughing Waters Spring.

Photo 9. Loma issues out of fractures in gneiss.

Photo 10. The pool formed from Loma spring is green from algae buildup.

Photo 11. The drainage area of the stream formed by St. Charles Spring but it has been diverted into a pipe.

Photo 12. The concrete collection area just prior to diversion to the pipe

Photo 13. Children playing and the garbage in the pool formed from Zingalume Spring.

Photo 14. Zingalume Spring source of issue and measuring in situ physical parameters.

Photo 15. Issuing site of Linda Spring.

Photo 16. Densely vegetated area where Linda Spring issues.

Photo 17. In situ measurements of physical parameters at Linda Spring.

Photo 18. Chongwe River looking west on the north side of the bridge.

Photo 19. Chongwe River looking downstream towards the south. Note the lodge on the left side of the river.

Photo 20. Lukashi River looking north.

Photo 21. Dr. Eliot Atekwana making in situ physical parameter measurements.

Photo 22. Location where Mupwasha stream physical parameters were measured.

Photo 23. Pool created by Mupwasha stream.

Photo 24. Main Chinyunyu Hot spring, north of the Great East Road.


Photo 25. Close up of Chinyunyu Hot Spring discharge.


Photo 26. Close up of Chinyunyu Hot Spring discharge.

Photo 27. Sample collection from Chinyunyu Hot Spring.

Photo 28. Chinyunyu Hot Spring source looking east.

Photo 29. Sample collection from the Kanakanapa River.


Photo 30. Bridge over the Kanakanapa River near sampling location.

Photo 31. Mama Rula River looking west.

Photo 32. Mama Rula River, sampling off the bridge over the river.

Photo 33. Sample collection under the Mfuwe Bridge with a Zambia Wildlife Authority (ZAWA) ranger with hippos in the Luangwa River.

Photo 34. White precipitate covering rocks at Nchindeni Hot Spring.

Photo 35. Stream formed from the discharge from Nchindeni Hot Spring.

Photo 36. Nchindeni Hot Spring issues then forms a stream.

Photo 37. Nsefu Hot Spring issues out of metal casing.

Photo 38. Field that Nsefu Hot Spring water flows into.

Photo 39. Chifunda Mineral Spring area.

Photo 40. Collecting samples from Chifunda Mineral Spring.

Photo 41. Graduate student Mary Niles securing samples after falling into the marshy spring area of Chifunda Mineral Spring.

Photo 42. Chifunda Mineral Spring area covered with holes created by hippos.


Photo 43. Up close of the issuing site of Luangwa River Bluff East 1.


Photo 44. Luangwa River Bluff East 1 and 2 converge into one and flow into the Luangwa River.

Photo 45. Luangwa River Bluff East 2 directly next to Luangwa River Bluff East 1.

Photo 46. Collecting water samples from Luangwa River Bluff East 3 before the spring water flows into the Luangwa River.

Photo 47. Elevation change of the bluff and the Luangwa River results in the spring water flowing from the bluff into the river (looking south).

Photo 48. Luangwa River looking north, haziness of photo is due to steam from the springs.

Photo 49. Mulungushi River looking west.

Photo 50. Sampling Mulungushi River at the river's bank.

Photo 51. Sampling location of Chikwana Stream. We crossed the stream here and headed further northwest looking for the source before turning around and sampling where we crossed.

Photo 52. Concrete barrier that dams Kapisha Hot Spring is on the right.

Photo 53. OSU students sampling in the middle of the pool at the issuing site.

Photo 54. Pool that is created by damming Kapisha Hot Spring from further back.

Photo 55. WHOI student and Zambian assistant collecting gas from Kapisha Hot Spring.

Photo 56. Manshya River looking south.


Photo 57. OSU student and guide determining where to sample.


Photo 58. Pool that the Kapisha Hot Spring 2 feeds and the extensive sugar cane crop very close to the spring.

Photo 59. WHOI student and Zambian assistant collecting gas from Kapisha Hot Spring 2.

Photo 60. Algae mat covering Chilonga Lusa prior to taking samples.

Photo 61. Collecting water samples from Chilonga Lusa at the site of issue.

Photo 62. Sampling location of Chilonga Lusa 2 from across the pond formed by the spring.

Photo 63. Pond formed by Chilonga Lusa 2 and hippos.

Photo 64. Sampling the Louviloa River looking north.

Photo 65. Sample location of Kasane Hot Spring in the middle of the salt flat.

Photo 66. Close up of the white precipitant (evaporite) that covered the salt flat.

Photo 67. Sampling the Chobe River looking north towards Namibia.

Photo 68. The Chobe River looking est with Botswana on the left bank and Namibia on the right bank.

Photo 69. Pool that has been created by the Kafu National Park Spring at Hippo Lodge .

Photo 70. Pool that has been created by Kafu National Park Lubungu Spring.

Photo 71. Two vents at the by Kafu National Park Lubungu Spring.

Photo 72. Collecting water samples at by Kafu National Park Lubungu Spring.

Photo 73. Pool created by Mumbwa Spring.

Photo 74. East Gwisho Spring issuing site in the grass.

Photo 75. Collection of gas by WHOI at the East Gwisho Spring.

Photo 76. Pool created by the Main Gwisho Spring.

Photo 77. In situ measurements at the Main Gwisho Spring.

Photo 78. Collection of water samples and physical parameters at the Namululu Spring.

Photo 79. Issuing site at Bilili Hot Spring.

Photo 80. Close up of the issuing site at Bilili Hot Spring.

Photo 81. Bilili Hot Spring from a distance.

Photo 82. Cement structure built up around the spring at Bruce Miller Farm.

Photo 83. Collection of gas by WHOI at Bruce Miller 2 site.

Photo 84. Dam that has been built to pool water at the West Lake Dam site.


Photo 85. Up close of the water in the dam at the West Lake Dam site.


Photo 86. Circular brick structure build around the spring at West Acres Farm.

Photo 87. Creative way to collect sample from the circular brick structure at West Acres Farm.

Photo 88. Grassy/ marshy field at the Musale site.

Photo 89. WHOI collecting gas at the Musale site

VITA

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