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The geothermal resources of the Republic of Djibouti — II: Geochemical study of the Lake Abhe geothermal field



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ABSTRACT

The Lake Abhe Geothermal Field is located in the South-Western region of the Republic of Djibouti, on the border with Ethiopia. The Lake Abhe geothermal system occurs within a rift basin filled with Pliocene-Quaternary volcanic (mainly basalt) and lacustrine sediments. The thermal water in Lake Abhe geothermal field discharges as hot springs at the bottom of hydrothermal carbonate chimneys distributed along the main faults.

Hot springs of Lake Abhe geothermal field as well as ground- and surface waters were sampled and major elements, trace elements, and isotopic (^{18}O / ^{16}O , ^{2}H / ^{1}H , ^{34}S / ^{32}S , ^{87}Sr / ^{86}Sr) compositions were analyzed. Hydrochemical features of the hot springs are dissimilar from those of warm waters: the former are mainly Na–Cl dominated whereas the latter were mostly Na–HCO₃–Cl–SO₄ and Na–HCO₃–Cl. The isotopic composition of sulfur and oxygen in dissolved sulfates suggests equilibrium with anhydrite as the major source of sulfates in the thermal waters.

Chemical (mainly Na/K and SiO₂), isotope (bisulfate- and anhydrite- water), and multiple mineral equilibrium approaches were applied to estimate the reservoir temperature of the hot springs in the Lake Abhe geothermal field. These different geothermometric approaches estimated a temperature range of the deep geothermal reservoir of 120–160 °C. In spite of the relatively wide range, the three different approaches led to a same mean of about 135 °C. The hot spring and warm borehole waters from the southwestern part of the Republic of Djibouti showed a possible mixing with hydrothermal waters from the local rift. The negligible tritium content and the low deuterium values ($\delta^2 H < -10\%$) suggest a deeper circulation and an old age for geothermal water, in comparison with surface waters and the local aquifers recharged by modern precipitations ($\delta^2 H > -10\%$).

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1. Introduction

The Republic of Djibouti is one of several African countries located on the East African Rift System, where the geology is influenced by tectonic lineaments associated with the Red Sea and the Gulf of Aden (Fig. 1). The activity of the East African Rift System involves significant seismic, tectonic and volcanic processes that are well-expressed in both east and west rift branches (Barberi et al., 1975; Mlynarski and Zlotnicki, 2001).

In Djibouti, most of the widespread geothermal activity, manifested in the form of numerous hot springs, fumaroles and hydrothermal alteration, is located mainly in the western part of the country and along the Gulf of Tadjourah ridge (Fig. 1A).

The most geologically active area in Djibouti is the Lake Asal area, and the Asal rift is one of two emergent oceanic ridges in the world, the other being Iceland (Mlynarski and Zlotnicki, 2001). Accordingly, numerous geological and geophysical studies were completed in Lake Asal in

* Corresponding author. *E-mail address:* awaleh@gmail.com (M.O. Awaleh). order to understand the phenomena related to sea floor spreading (Mlynarski and Zlotnicki, 2001; Pinzuti et al., 2010; Daher and Axelsson, 2010; Dvorak and Dzurisin, 1997; Stein et al., 1991). Moreover, the geochemistry of the Lake Asal geothermal field has been studied previously, either for identifying and establishing igneous activity or for estimating the geothermal potential (Fontes et al., 1989; SanJuan et al., 1990; D'Amore et al., 1998). However, due to remote and poorly accessible sites, which are far from economic centers, few investigations address the geothermal activity of the Lake Abhe geothermal field (LAGF from here forward; Fontes and Pouchan, 1975; Aquater, 1980; Dekov et al., 2014)..

Houssein et al. (2013) reported the geochemical characteristic of four hot springs in the Lake Abhe area, as well as some boreholes waters. The authors inferred a reservoir temperature higher than 200°, supposed by a hypothetical connection between the Abhe springs with the Tendaho geothermal waters (Ali, 2005; Houssein et al., 2013). However, it should be noted that the results from chemical geothermometers and the previous isotope data of the hot springs (Fontes et al., 1980; Schoell and Faber, 1976) were not considered (Houssein et al., 2013).





Fig. 1. A: Schematical geological map of the Republic of Djibouti (SE Afar Rift) after Vellutini and Piguet (1994) and hydrothermal activity of the Republic of Djibouti. B: SHCi: small hydrothermal chimney geothermal spring waters; GHCi: great hydrothermal chimney geothermal spring waters. Black thick lines: local faults. In the inset: schematic map of the Afar Depression with the location of Djibouti (black rectangle).

In this paper, we report an exhaustive survey of hot springs in the Lake Abhe area (sixteen hot springs were sampled and analyzed) as well as surface waters and well and borehole warm waters. Furthermore, to have an unequivocal estimate of the LAGF reservoir temperature, classical and updated chemical and isotopic geothermometers were compared, then combined with the result of a mineral equilibrium approach.



Fig. 2. A: Localization of water samples in the study area. B: Digital elevation model (DEM) of the Asal Rift, Gaggade, Hanle and Gob Aad tectonic basins located in Djibouti. The vertical color scale represent the altitude in meters. Lake Abhe is in the western end of the Gob Aad Basin. The red lines correspond to the extensional faulting network between Lake Asal and Lake Abhe. C: Example of carbonate chimney with hot spring (~100 °C) at its base. Thermal water samples have been collected from this type of area.



Fig. 2 (continued).

2. Geological setting

Djibouti is located in the southeastern part of the Afar Rift (Fig. 1; Fig. 2) and has a complex tectonic and volcanic history. All stages of formation of oceanic crust are observed in this area, from initial lithospheric thinning, rupture of continental crust, to the formation of oceanic ridges (Manighetti et al., 2004). The first evidence of synrift magmatism in the Republic of Djibouti is the 28-19 Ma Ali Sabieh mafic complex, and the more widespread Mablas rhyolites, which erupted at 15-11 Ma (Gadalia, 1980). The subsequent volcanic events were essentially basaltic with locally minor acidic differentiates. They include the Dalha series (9–4 Ma), the trap or Stratoid series (3-1 Ma), the Gulf series (3-1 Ma) (Varet and Gasse, 1978) and the Ribta rhyolites (3–1 Ma) (Robineau, 1979). The Stratoid series is commonly regarded as incipient oceanic crust and covering the two-thirds of the Afar Depression, comprise a number of felsic centers. Three major acidic complexes, namely the Eaysilo, the Babba Alou (<2 Ma) and the Egerealeyta massifs (<1 Ma), are aligned along a NE-SW transverse volcanic lineament from the Gob Aad graben to the western margin of modern Asal rift, to the NE (Gaulier and Huchon, 1991).

The LAGF is located in the South-Western region of the Republic of Djibouti, on the border with Ethiopia. The lake occupies the western part of the closed Gob Aad tectonic basin which was produced by complex extensional tectonics (Gasse and Street, 1978; Beyene and Abdelsalam, 2005; Fig. 2B). It is situated at the eastern, downstream end of the Awash river valley, which emerges from the high Ethiopian plateau. The Gob Aad basin is characterized by Quaternary lacustrine sediments, which are slightly deformed and post-dated a N100°E-trending horst-and-graben network (Demange and Stieltjes, 1975). The horst bordering the Gob Aad basin is composed of lavas of the Stratoid Series (Deniel et al., 1994) and felsic domes. The lake sediment floor is underlain by a thick sequence of Stratoid basalts dated between 4 and 1 m.y (Gasse and Street, 1978).

During the Plio-Pleistocene, these Stratoid basalts were dislocated by extensional faulting, with fault-scarps exceeding 1000 m in height in some areas, allowing the development of deep lakes in the Central Afar and favoring groundwater movement between the different basins (Abhe, Dobi-Hanle and Asal) (Gasse and Street, 1978). Lake Abhe is particularly rich with surface hydrothermal features, including fumaroles, hot springs and hydrothermal chimneys structures (Fig. 2C, Dekov et al., 2014; Houssein et al., 2013). These are aligned WNW–ESE, parallel to the regional extensional fault network (Gasse and Street, 1978; Dekov et al., 2014). The surface hydrothermal manifestations are spread over an area of about 100 km². Some of the chimneys, including AsBahalto chimney with an approximate height of 60 m, discharge hot steam at their apex.

The Lake Abhe has substantially fluctuated in volume and surface elevation during the Quaternary (Gasse, 1977). Based on ¹⁴C geochronology, the water level curve revealed three major transgressions in response to climatic changes (Fontes and Pouchan, 1975; Gasse and Street, 1978). The Lake Abhe core studied by Gasse and Street (1978) showed that the oldest sediments correspond to the Lower Pleistocene deposits. These sediments are composed of lacustrine shales interstratified with Stratoid basaltic lava flows and calcareous diatomites, gypsum and ash flows, and silts containing basaltic pebbles (Gasse and Street, 1978). The clay fractions, located at 50 to 30.5 m consist of montmorillonite to illite-montmorillonite, with a high content of calcite. In addition, Valette (1975) reported chlorite, montmorillonite, kaolinite, illite and sepiolite minerals in samples from the bottom of the lake.

3. Sampling and analytical methods

A total of sixteen hot springs, three warm springs, the surface waters of the Lake Abhe and seven warm wells and boreholes waters from areas near the lake were sampled in January 2012. Unstable hydrochemical parameters, including temperature (± 0.1 °C), pH (± 0.01 unit) and electrical conductivity ($\pm 1 \mu$ S/cm), were measured on site using the following portable instruments: 1) temperature – CheckTemp (Hanna); 2) pH – pH 610 (Eutech Instruments); and 3) conductivity – COND 610 (Eutech Instruments). Each was calibrated in the field prior to sampling.

Water samples were collected in polyethylene containers after filtration through 0.45 μ m membrane filters. All samples used for determination of cations were acidified after collection through addition of Suprapure® HNO₃ (Merck) to bring the pH below 2.

Analyses of anions and major cations were carried out by ionic chromatography with a Dionex ICS 3000 Ion Chromatograph using analytical and quality assurance procedures for geothermal water chemistry, following Pang and Armannsson (2006). A AS4A-SC-4 mm analytical column (250 mm \times 4 mm ID) coupled with AG4A-SC 4 mm guard and CS12A analytical column (250 mm \times 4 mm ID) coupled with CG12A guard was used respectively for anions and cations analyses. The ion chromatograph was calibrated through repeated analysis of five working anion and cation standards, with concentrations within the range of analyses. The analytical precision was determined to be \pm 5%. Peaks were identified using Chromeleon software (Dionex, Sunnyvale, California) and were verified visually. Analyses of minor/trace elements were conducted using an Ultima 2 (Horiba Jobin Yvon) Inductively Couple Plasma Atomic Emission Spectrometer (ICP-AES). National Institute of Standards and Technology traceable commercial standards were used for quality control. These standards were analyzed to within $\pm 3\%$ of the known values for all minor cations. For the analysis of aqueous SiO₂, the water samples were diluted tenfold using deionized water to prevent SiO₂ precipitation. SiO₂ contents were determined by colorimetry and analyzed using a Jenway 6300 spectrophotometer, while HCO₃ was analyzed by titration with 0.1 M HCl. The global analytical error for these techniques was less than 5% (as ionic balance).

Additional samples of untreated waters were collected in 50 mL glass bottles (Quorpak) for analyses of stable isotopes of the water molecule, $\delta^2 H(H_2O)$ and $\delta^{18}O(H_2O)$, and 1000 mL plastic bottles for tritium (³H) analysis. The isotope ratios of hydrogen and oxygen were analyzed using a Finnigan MAT 252 mass spectrometer and converted in per mil delta values(δ_{∞}) versus the Vienna Standard Mean Ocean Water(V-SMOW) standard following δ (∞) = [($R_{sample} / R_{standard}) - 1$] × 10³, where R is the isotopic ratio of interest (²H/¹H or ¹⁸O/¹⁶O). The average precision, based on multiple analyses of various samples and laboratory standards was $\pm 0.1\%$ for $\delta^{18}O(H_2O)$ and $\pm 0.8\%$ for $\delta^{2}H(H_2O)$. Tritium activity measurements were done by direct liquid scintillation counting. The detection limit was 0.6 TU (Tritium Unit with 1 TU equal to 1 tritium atom in 10¹⁸ hydrogen atoms).

Samples for sulfur and oxygen isotope analyses were collected at the outlet of columns using 250 mL pre-acid-washed plastic perplex bottles. Cd-acetate was already added in the bottles (5% v/v) prior to sample collection (to fix sulfur as CdS) and then the aliquot was filtered through a 0.2 µm nitrocellulose filter before chemical determination of residual sulfate. Dissolved sulfate was precipitated as BaSO₄ at pH < 4 (in order to remove HCO₃⁻ and CO₃²⁻ species) by adding a BaCl₂ solution. The isotopic analyses on BaSO₄ were carried out using a Delta + XP mass spectrometer coupled in continuous-flow mode to a Thermo Elemental Analyzer. Sulfate-isotope compositions are reported in the usual δ -scale in % with reference to V-CDT (Vienna Canyon Diablo Troilite) and V-SMOW (Vienna Standard Mean Ocean Water). Sulfate-isotope compositions (δ^{34} S(SO₄) and δ^{18} O(SO₄)) were measured with a precision of \pm 0.3‰ vs. V-CDT for δ^{34} S(SO₄) and \pm 0.5‰ vs. V-SMOW for δ^{18} O(SO₄).

 $^{87}{\rm Sr}/^{86}{\rm Sr}$ ratios of groundwater were measured using a Finnigan MAT 262 multiple collector mass spectrometer. The $^{87}{\rm Sr}/^{86}{\rm Sr}$ ratios were normalized to an $^{86}{\rm Sr}/^{88}{\rm Sr}$ ratio of 0.1194. The reproducibility of the $^{87}{\rm Sr}/^{86}{\rm Sr}$ ratio measurements was tested through duplicate analyses of the NBS 987 standard and the mean value was 0.710243 \pm 12.10⁻⁵ (2, N = 18).

4. Results and discussion

4.1. Hydrochemistry

Hydrothermal activity in LAGF is characterized by boiling springs with low water fluxes (1.5 I s^{-1}) (Fontes and Pouchan, 1975). Temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), sampling locations, and hydrochemical types of all water samples are listed in Table 1. The major, minor and trace elements of the geothermal and warm waters from LAGF are reported in Table 2.

The temperatures of the geothermal water samples at LAGF ranged from 71 to 99.7 °C (Table 1). Geothermal waters are moderately alkaline (pH = 7.61–8.80) with TDS values of 1918–3795 mg/L. As the geothermal waters also the warm waters show moderately alkaline pH values of 7.2 to 8.9 units. On the other hand, the TDS of the warm spring waters and warm borehole waters from LAGF ranged respectively 3669–5914 mg/L and 663–1312 mg/L (Table 2).

In the LAGF, the hydrochemistry of geothermal and warm waters is quite different. The geothermal waters contain Cl^- and Na^+ as the predominant anion and cation, whereas the warm waters have HCO_3^- and Na^+ as the major ions (Table 2). Classification of the waters samples in Table 1 was made according to principles of IAH (IAH (International Association of Hydrogeologists), 1979) and Kresic (2006) for chemistry and temperature (warm: T < 45 °C; hot: T > 45 °C), respectively. Total equivalents of cations and anions were separately accepted as 100% and ions with more than 20% (meq/L) were taken into consideration in this classification. Moreover, chemical compositions of the waters are plotted in the diagram of Piper (1944), as shown in Fig. 3. The chemical composition of the waters is described in terms of relative concentrations of the main anion and cation, which allows discrimination of the following four groups of waters (Table 1, Fig. 3):

- (1) Geothermal hot spring waters are of the Na–Cl type.
- (2) Warm well and borehole waters (Haloyta, Sabalou, Galamo, Abuyoussouf, Kantali, Gourabous, and Koutaboua) are mostly of the Na–HCO₃–Cl–SO₄ type. The high alkalinity of these waters is typical of the Rift groundwaters where high rate of carbon dioxide out gassing from mantle and which enhances rock water interaction at shallow depth (e.g. Kebede, 2013):

 $CO_2+H_2O + Na, K-silicates ->HCO_3 + Na, K + H-silicates.$

- (3) Warm spring waters (Lali Dara, Asbahtou and Abakara) are mostly of the Na-HCO₃-Cl type.
- (4) Lake Abhe waters are of the Na–Cl–HCO₃–SO₄ type.

Ternary diagram based on the relative concentrations of the three major anions Cl^{-} , SO_{4}^{2-} , and HCO_{3}^{-} (Giggenbach, 1991; Fig. 4) is used for the classification of the hot springs from LAGF sampled in this study and literature over the past several decades (Table 2; Aquater, 1980; Geotermica Italiana srl, 1983). Those waters plot in Cl corner along the SO₄-Cl axis, and accordingly can be considered as almost "mature waters". Neither significant variations in fluid geochemistry of the Lake Abhe geothermal system were observed between 1980 and 2012 (Table 2, Fig. 4), nor noticeable seasonal variation in the water chemistry of those hot spring waters (Centre d'Etudes et de Recherche de Djibouti, CERD, 2012). Such consistent chemical characteristics of LAGF geothermal spring waters may point to the presence of a thermal reservoir, large enough such that it does not modify the main chemistry when fed by the limited meteoric recharge associated with the local arid climate. The Republic of Djibouti experiences a dry climate with a mean annual rainfall of about 150 mm. Average daytime temperatures vary between 17 °C and 42 °C and relative humidity is fairly high, between 40% and 90%..

There are two types of geothermal springs in LAGF: 1) those jetting around the base of the Great Travertine Chimneys (GHCi samples) and 2) those occurring at the bottom of Small Travertine Chimneys (SHCi samples) (Fig. 1B). The geothermal water samples from the SHCi and GHCi have almost the same temperature, pH and chemical composition, with the exception of chloride, sodium, calcium and potassium (Table 2). The chloride, sodium, calcium and potassium contents of SHCi waters are almost double as those of GHCi waters. However, those two groups of water samples have similar Na/Ca (SHCi: 4.7–5.0; GHCi: 3.3–4.7), Na/K (SHCi: 31.8–39.8; GHCi: 28.9–39.1), and Cl/Na

Sampling locations, T, pH, EC, TDS and hydrochemical types of the sampled waters.

N°	Samples		<u>Latitude</u> 00°00/00″	Longitude 00°00/00″	<u>,</u> C	рН	$\frac{EC}{(\mu S/cm)}$	$\tfrac{TDS}{(mg/l)}$	hydrochemical types
1	SHC1		11°08′53.2″	041°52′51.9″	94.5	8.22	5495	3488	Na – Cl
2	SHC2		11°08′41.4″	041°52′54.1″	98.1	8.34	5576	3482	Na – Cl
3	SHC3		11°08′50.9″	041°52′52.8″	98.5	8.49	5610	3503	Na – Cl
4	SHC4		11°08′53.0″	041°52′50.2″	82.2	7.61	5866	3747	Na – Cl
5	SHC5		11°08′54.7″	041°52′44.9″	98.8	8.33	5332	3466	Na – Cl
6	SHC6		11°08′54.7″	041°52′44.7″	98.1	7.97	5409	3795	Na – Cl
7	SHC7		11°08′54.6″	041°52′44.4″	97.1	8.06	5411	3511	Na – Cl
8	GHC1		11°06′49.6″	041°52′30.1″	92.1	8.6	3224	2129	Na – Cl
9	GHC2	Geothermal spring waters	11°06′49.8″	041°52′13.2″	71	8.62	3191	1958	Na – Cl
10	GHC3		11°06′46.5″	041°52′12.7″	86	8.52	3192	2236	Na – Cl
11	GHC4		11°06′46.7″	041°52′11.9″	99.7	8.69	3124	2072	Na – Cl
12	GHC5		11°06′47.1″	041°52′10.6″	84.2	8.72	3138	2023	Na – Cl
13	GHC6		11°06′48.6″	041°52′09.5″	92.5	8.62	3105	2016	Na – Cl
14	GHC7		11°06′48.6″	041°52′09.6″	82.4	8.79	3124	1918	Na – Cl
15	GHC8		11°06′49.6″	041°52′10.0″	93	8.69	3095	2037	Na – Cl
16	GHC9		11°06′50.6″	041°52′39.0″	76.6	8.11	3314	2089	Na – Cl
17	Lali dara		11°06′20.8″	041°53′24.5″	36.8	8.93	7028	5914	Na – HCO3 – Cl
18	Asbahtou	Warm spring waters	11°06′08.7″	041°53′41.9″	37.2	8.90	4476	3669	Na – HCO ₃ – Cl
19	Abakara		11°07′39.8″	041°53′39.0″	37	8.79	5276	3845	Na – HCO3 – Cl
20	Haloyta		11°07′04.9″	042°10′05.0″	40	7.59	919.9	750	Na – HCO ₃ – Cl – SO ₄
21	Sabalou	Warm boreholes waters	11°06′49.6″	041°52′10.0″	33	8.01	850	731	$Na - HCO_3 - SO_4$
22	Galamo		11°12′33.9″	042°15′33.9″	45	8.03	828.8	707	Na – HCO ₃ – Cl – SO ₄
23	Abuyoussouf		11°05′33.6″	042°14′46.2″	34	7.21	725	663	$Na - Ca - HCO_3 - SO_4$
24	Kantali		11°08′14.7″	041°16′21.1″	35.5	8.01	1717	1312	Na – HCO ₃ – Cl – SO ₄
25	Gourabous	Warm wells waters	11°16′59.9″	042°13′23.8″	39	7.2	1099	933	Na – HCO ₃ – Cl – SO ₄
26	Koutaboua		11°01′01.7″	041°57′48.0″	35.6	7.91	1330	1117	$Na - HCO_3 - SO_4$
27	Lake Abhe	Lake water	11°09′52.2″	041°53′24.2″	29	9.86	96084	92622	Na – Cl – HCO ₃ – SO ₄

ratios (SHCi: 1.6–1.8; GHCi: 1.4–1.7). These findings suggest that SHCi and GHCi hot springs may be genetically related.

The geothermal waters from LAGF have a considerable quantity of sulfate that is typical of geothermal waters in the rift settings of the region (Aquater, 1980; D'Amore et al., 1997, 1998; BFGUR, 1999). This relatively high quantity of sulfate may be generated by the circulation of relatively deep waters within a thick sedimentary surface sequence (D'Amore et al., 1997). Indeed the drilling of a 50 m core at a site within LAGF provides a continuous record of lacustrine sedimentation (Gasse and Street, 1978). A thin bed of anhydrite was recorded, which overlies calcareous sediment (Gasse and Street, 1978). Moreover, a recent geophysical study reported that the sediment fill likely totals as much as 300 m in LAGF (CERD, 2012).

Mineral saturation indices for LAGF thermal waters were calculated on the basis of the sampling temperatures using SOLVEQ (Reed, 1982) computer program (Table 3). All of the geothermal waters are oversaturated with respect to carbonate minerals (calcite, aragonite and dolomite) and undersaturated with respect to anhydrite, gypsum, fluorite and halite (Table 3). Therefore, during their ascent, geothermal waters could be enriched in sulfate and calcium from the dissolution of anhydrite and gypsum (Fontes and Pouchan, 1975). Furthermore and in a similar way to Ethiopian Rift waters, the fluorite could also be a supplementary source of fluoride to the geothermal waters (Gizaw, 1996).

In the hyper-saline waters of Lake Abhe (TDS = 92,622 mg/L), the high sulfate content (13,365 mg/L) and the extremely low Ca/HCO₃ (1/500) and Mg/HCO₃ (1/1417) ratios indicate nearly complete removal of Mg and Ca by carbonate precipitation.

4.2. Statistical analysis

The computer program R2.15.1 (2012) was used to conduct several multivariate statistical techniques, including cluster analysis and principal components analysis. The use of these multivariate statistical methods is common in hydrogeochemical studies (Meng and Maynard, 2001; Swanson et al., 2001).

4.2.1. Hierarchical cluster analysis results

Hierarchical cluster analysis (HCA) is a commonly used method to classify observations or variables, in order to define more or less homogeneous groups and emphasize their genetic relations (Davis, 1986). A classification scheme using Euclidean distance for similarity measurement, together with Ward's method for linkage (Ward, 1963), produces the most distinctive groups where each member within the group is more similar to its fellow members than to any member outside the group (Güler et al., 2002). The hierarchical classification is often used in hydrogeochemical data classification (Güler et al., 2002).

In this study, HCA was applied to the raw data. Thirteen variables (pH, EC, Na, K, Mg, Ca, Cl, HCO₃, SO₄, NO₃, F, Br, and Li) were considered to classify all the water samples from this study. In HCA the variables are log transformed and normalized so that each variable has equal weight. The HCA results were presented in a dendrogram (Fig. 5).

The hierarchical analysis allowed us to distinguish four clusters of water: Cluster 1 (small chimney geothermal spring waters); Cluster 2 (warm spring waters); Cluster 3 (warm well and borehole waters) and Cluster 4 (Lake Abhe waters). Based on the clusters, the geothermal spring waters from the small chimneys (sample SHCi) and those from the great chimneys (samples GHCi) formed one group of waters (Cluster 1).

4.2.2. Principal component analysis results

Principal components analysis (PCA) allows one to define eigenvectors of a variance–covariance or a correlation matrix from a data set corresponding to a raw matrix of n rows of observations by p columns of variables (Davis, 1986).

PCA was performed on a data set of thirteen chemical variables (pH, EC, Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻, Br⁻, F-, Na⁺, K⁺, Mg²⁺, Ca²⁺, and Li⁺) and twenty seven water samples.

Principal components analysis of water chemical variables produced two components (Table 4), accounting for 86.14% of the total variance of the dataset. Table 4 presents the principal component loadings, as well as their respective explained variance. Loadings, that represent the importance of the variables for the components are in bold for values greater than 0.7 (Table 4).

Table 2
Chemical analyses of thermal and cold waters from LAGF.

	<u>Ca</u> ppm	Mg ppm	<u>Na</u> ppm	<u>K</u> ppm	CO ₃	HCO ₃ ppm	<u>Cl</u> ppm	SO ₄ ppm	NO ₃ ppm	IB %	F ppm	Br ppm	SiO ₂ ppm	B ppm	Li ppm	<u>Cd</u> ppb	<u>Mn</u> ppb	Zn ppb	Al ppb	<u>Cr</u> ppb	<u>Ni</u> ppb	<u>Co</u> ppb	<u>Cu</u> ppb	V ppb	<u>Sr</u> ppb	<u>Fe</u> ppb
SHC1	229.17	3.23	1083.2	30.5		19.27	1712	346	1.46	3	1.24	9.83	120.29	2.64	0.48	4.3	8.3	1.8	41.8	7.0	8.2	2.3	6.1	231	225	6.9
SHC2	225	0.93	1074	27	0.15	15.26	1737	349	0.62	2	0.93	9.89	129.01	5.11	0.29	4.7	9.0	2.6	42.6	7.5	8.6	6.6	6.5	248	236	7.1
SHC3	232	0.94	1096	31.5	0.22	15.67	1721	348	0.77	4	0.73	9.88	115.06	2.4	0.34	4.4	5.2	2.2	42.5	7.8	9.3	6.3	5.9	260	246	6.4
SHC4	241	1.64	1156	30.74		20.26	1846	361	2.31	2	0.88	9.13	126.40	2.35	0.3	4.5	6.0	2.6	52.6	9.7	12.5	6.0	6.0	287	233	8.2
SHC5	224	0.91	1086	31.47	0.19	18.95	1713	349	0.32	3	0.52	9.77	122.91	2.5	0.3	4.8	6.3	2.0	39.0	7.8	10.6	6.8	6.7	246	241	8.5
SHC6	221	0.88	1089	33		22.14	1994	349	37	4	3.35	11.94	132.50	2.52	0.31	4.9	8.1	2.6	41.6	6.4	11.8	6.2	6.4	257	235	6.8
SHC7	224	0.9	1111	34.96		23.53	1721	348	0.34	4	0.88	10.77	144.26	4.48	0.34	3.5	5.0	2.7	37.6	5.5	11.8	6.7	6.1	254	238	7
GHC1	165	0.45	624	19.29	0.35	19.33	906	343	0.61	4	2.21	5.97	97.63	3.53	0.13	3.9	5.0	2.0	59.2	4.8	6.2	5.7	8.6	233	238	8.1
GHC2	157	0.27	587	15	0.37	19.25	845	333	0.99	4	0.79	5.85	99.37	3.14	0.13	3.4	5.1	3.0	44.3	4.3	5.8	5.4	8.3	269	214	7.6
GHC3	166	0.59	607	21	0.30	19.98	1020	362	3.83	-3	4.73	9.7	101.99	3.33	0.12	2.4	6.2	5.0	70.8	5.5	9.0	5.1	8.0	273	245	8.3
GHC4	176	2.96	582	16.9	0.45	19.86	938	313	3.36	2	2.15	6.73	100.24	3.02	0.94	2.9	2.1	4.1	60.9	6.2	7.8	5.6	8.4	235	217	7.9
GHC5	155	2.95	575	15.44	0.49	20.21	886	366	0.95	1	2.32	6.8	99.37	2.99	0.23	2.8	0.5	2.1	61.2	4.8	8.2	5.9	8.6	288	231	8.3
GHC6	156	0.7	574	15.79	0.40	20.95	884	362	1.57	1	0.92	5.44	96.76	3.33	0.14	3.2	2.5	5.2	55.1	5.7	78	5.3	8.0	295	211	7.4
GHC/	152	0.7	562	16.98	0.57	20.18	825	338	1.65	3	0.92	5.79	96.32	1.99	0.14	3.5	1.5	3.1	61.0	5.8	6.5	5.2	9.3	269	218	8.7
GHC8	153	0.52	568	15.5	0.33	14.53	908	371	5.99	-1	0.79	5.19	102.86	1.68	0.12	2.7	2.1	2.0	63.2	5.5	8.2	5.6	12.3	220	224	8.2
GHC9	136.57	2.96	640	16.7		22.93	958	307	4.60	2	1.17	4.32	84.43	1.82	0.25	4.6	2.6	2.3	62.1	4.1	5.3	6.4	8	247	238	7.2
GHC(1980) ^a	159	0.24	551.7	16.8		39.1	923	321.8		-4					0.30											
GHC(1980) ^a	162	0.23	551./	15.6		43.3	923	317		-1					0.58											
SHC(1980) ^b	228	0.24	1005.5	30.5		28.1	1704	341		-2					0.59											
SHC(1980) ⁵	231	0.24	1011.5	32.1		55.5	17017	355.4	0.02		2 00			1 20	0.58											
SHC(1983)	240.5	0.18	988.5	29.3		20.2	1772.0	341.1	1.02		3.80			1.20												
SAC(1965)	240.5	0.21 < I D	2010	25.1		19.5	1/72.0	545.9	1.05	2	11.02	11 75	6 4E	1.75	0.20											
Idii udid	4.02	< LD	1240	20.2 10.5		060	046	747 500	0.9	2	11.75 < ID	/ DI	0.45	2.71	0.20											
Aspantou	2.37	< LD 9 10	1240	19.5		900 671.9	940 1107	562.6	1.2 < DI	2	< LD 5.02	< DL 5.02	5.70	2.10	0.005											
Halovta	20	10	200	24.0		327	72	102.0	< DL Q	4	1.53	1.53	0.61	J.40	0.23											
Sabalou	15.24	6.68	184	44		307	60.1	145	83	-2	1.55	1.55	0.01	n 2	0.04											
Calamo	14.09	17.61	176	2.4		309.5	81.9	83.3	21.5	-2	1.75	1.75	0.34	n 2	0.05											
Abuvoussouf	56.25	13 39	127	2.0		261.5	56.7	138.1	73	2	2.02	2.02	0.40	n 2	0.01											
Kantali	15.60	14.28	400	13		350.8	127.7	390	12	5	1 37	1 37	0.51	n 2	0.01											
Gourabous	74.05	24 19	181	5.8		327.2	150.1	151 5	193	2	1.03	1.03	0.96	na	0.01											
Koutaboua	17.95	7 44	320	1.8		220	80.6	443.9	26	0	< LD	< DL	0.29	na	0.03											
Lake Abhe	27.26	9.6	33659	408.5	4534	13603	26778	13365	2.16	2	100	127	0.20	n.a	0.76											

SHC = Small Hydrothermal Chimneys springs; GHC = Great Hydrothermal Chimneys springs; IB = Ionic Balance; n.a. = no analyzed; DL = Detection Limit. ^a Great chimney hot spring water analyzed in 1980. Aquater. ^b Small chimney hot spring water analyzed in 1980. Aquater. ^c Small chimney hot spring water analyzed in 1983. Geotermica Italiana srl



Fig. 3. Piper diagram of geothermal spring waters waters (SHCi, GHCi), warm borehole and wells waters, and Lake Abhe water.

Most of the variance is contained in the PC1 (59.51%) which is associated with the variables EC, Na, K, HCO₃, Cl, SO₄ and F, with squared regression coefficients of 0.99, 0.99, 0.99, 0.99, 0.99, 0.99 and 0.99 respectively. PC2 (26.63%) is mainly related to Ca, Mg, NO₃, and Br, with squared regression coefficients of 0.85, -0.83, -0.84, and 0.89, respectively.

The water sample observations of the two principal component axes are plotted in Fig. 6. In score plot PC1 vs. PC2 (Fig. 6) the water samples are divided into four distinct clusters mainly according to their geotectonic units: Cluster 1 (geothermal spring waters); Cluster 2 (warm springs waters); Cluster 3 (warm well and borehole waters) and Cluster 4 (Lake Abhe waters).



Fig. 4. Cl–SO₄–HCO₃ classification diagram of Giggenbach (1991) for the thermal and warm waters from LAGF.

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Mineral saturation indices of LAGF hot springs waters calculated at the sampling conditions.

Saturation indices	Aragonite	Calcite	Dolomite	Anhydrite	Fluorite	Gypsum	Halite
SHC1	0.77	0.91	0.91	-0.47	-1.43	-0.27	- 4.45
SHC2	0.79	0.93	0.42	-0.42	-1.69	-0.32	-4.46
SHC3	0.92	1.07	0.68	-0.41	-1.89	-0.37	-4.44
SHC4	0.12	0.26	0.36	-0.60	-1.72	-0.48	-4.40
SHC5	0.88	1.03	0.61	-0.41	-2.19	-0.38	-4.45
SHC6	0.64	0.79	0.12	-0.42	-0.58	-0.35	-4.44
SHC7	0.74	0.88	0.31	-0.44	-1.74	-0.37	-4.43
GHC1	0.98	1.13	0.59	-0.50	-0.98	-0.49	-4.93
GHC2	0.79	0.93	0.41	-0.79	-1.88	-0.68	-4.99
GHC3	0.89	1.03	0.48	-0.55	-0.32	-0.50	-4.96
GHC4	0.90	1.29	1.17	-0.41	0.97	-0.33	-4.96
GHC5	1.00	1.14	1.42	-0.59	-0.96	-0.52	-5.02
GHC6	1.02	1.17	0.87	-0.48	-1.76	-0.44	-5.01
GHC7	1.03	1.17	0.86	-0.65	-1.77	-0.60	-5.03
GHC8	0.91	1.05	0.52	-0.47	-1.90	-0.43	-5.03
GHC9	0.44	0.58	0.35	-0.81	-1.60	-0.78	-4.91

The principal component analyses of the water samples show the same groupings that were apparent in the hierarchical clusters analyses.

4.3. Isotope composition

4.3.1. Water isotope composition: $\delta^{18}O(H_2O)$ and $\delta^2H(H_2O)$

It appears from the PCA and HCA results (Figs. 5, 6) that the geothermal waters from the small chimneys (SHCi) and those from the great chimneys (GHCi) formed the same group of water (Cluster 1). On the other hand, it was reported that waters which fall in a statistical group may have similar residence time, similar recharge history, and identical flow paths or reservoir (Swanson et al., 2001; Güler and Thyne, 2004). These results suggest that the small chimney geothermal spring waters and the great chimney geothermal spring waters may have a common origin.

in studying the natural water circulation and groundwater movement (Aboubaker et al., 2013). The stable isotope compositions of LAGF waters are shown in Fig. 7 and in Table 5, along with the Global Meteoric Water Line (GMWL)

tracers for determining the origin of groundwater and are widely used

The oxygen $\delta^{18}O(H_2O)$ and hydrogen $\delta^2H(H_2O)$ values are excellent

 $\delta^2 H(H_2O) = 8 \times \delta^{18}O(H_2O) + 10$ defined by Craig (1961), and the Local Meteoric Water Line (LMWL) as defined by Fontes et al. (1980). This latter meteoric line has the same slope of the GWML but with



Fig. 5. Four clusters in the dendrogram for the water sample in the Lake Abhe area. The black line is "phenon line".

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Table 4

Results from the principal component analysis. Vectors, eigenvalues and cumulative variance (principal vectors are in bold).

Parameters	PC1	PC2
рН	0.627	0.408
EC	0.996	-0.012
Ca	-0.184	0.846
Mg	0.062	-0.834
Na	0.995	-0.048
K	0.992	0.0263
HCO ₃	0.987	-0.142
Cl	0.993	0.018
SO ₄	0.994	-0.064
NO ₃	-0.180	-0.842
F	0.990	-0.0498
Br	-0.177	0.893
Li	0.553	0.558
Variance explained	7.69	2.87
% Total variance	59.51	26.63
Cumulative (%)	59.2	86.14

null deuterium excess (d = 0); therefore it intercepts SMOW and local seawaters (Fig. 7; Awaleh et al., 2015).

The warm boreholes and groundwaters in the study area are plotted along the GMWL, suggesting that they are of meteoric origin (Fig. 7). However, all the warm waters in the study area are more enriched in δ^2 H(H₂O) than the geothermal spring waters by about 25‰ (Table 5), an indication that the former cannot be a source of recharge of the latter. Moreover, the water isotope values of the warm waters are quite similar to the wadi aquifers (mainly Wadi Ambouli, a coastal aquifer recharged by the creek that flows between the cities of Balbala and Djibouti; Fontes et al., 1980; Schoell and Faber, 1976) and to the Awash River water (Ayenew et al., 2008; Yitbarek et al., 2012) which feed the Lake Abhe, suggesting that recharge occurred from heavy non-evaporated monsoon rains which generated heavy floods (Fig. 7).

In comparison with warm boreholes and groundwater samples, the stable isotope composition of the hot spring waters from this study and literature (Fontes et al., 1980; Schoell and Faber, 1976) have lower $\delta^2 H(H_2O)$ values and are clustered near the LMWL, thus showing a



Fig. 6. Principal Components analysis results. PC1 versus PC2 plot for samples (a) and for variables (b).



Fig. 7. δ^{18} O(H₂O) vs. δ^{2} H(H₂O) diagram of the waters from LAGF and surroundings area of Republic of Djibouti. Colored symbols: Table 5 data. Data are compared with Global Meteoric Water Line (GMWL; Craig, 1961) and Local Meteoric Water Line (LMWL; Fontes et al., 1980). Open, shaded, black and gray symbols are also from literature. In particular: Gulf of Aden seawater and Obock's coastal geothermal spring waters are from Awaleh et al. (2015). Lake Asal from Fontes et al. (1979). Asal Rift waters—1972 field from Fontes et al. (1980). Tendaho geothermal wells from Ali (2005). Filwuha Fault thermal waters from Demlie et al. (2008). TLNO: Terminal Lake with No Outflow (Kebede et al., 2009).

different meteoric recharge of probable deep origin (Fig. 7; Fontes et al., 1980).

The ¹⁸O-enriched composition (*O-shift* in Fig. 7) that characterizes the rift/geothermal waters of the surrounding areas (Asal Rift waters, Fontes et al., 1980; Tendaho geothermal wells, Ali, 2005) are showed in Fig. 7 as comparison. Kebede et al. (2008) reported a similar δ^{18} O shift in the geothermal waters of the Afar region (Ethiopia), which also encompasses the Lake Abhe area, as a result of the exchange between the geothermal waters and silicates. However, evaporation is the main process that enriches the isotope composition of the lakes in arid environments (Boschetti et al., 2007; Gonfiantini et al., 1973). This effect also produces $\delta^2 H(H_2O)$ -enriched values, which coupled with $\delta^{18}O(H_2O)$ generates a characteristic evaporation path starting from GMWL with slope near 5 (Boschetti et al., 2007). Therefore, the $\delta^{18}O(H_2O) = +6.5\%$ and $\delta^2 H(H_2O) = +43.9\%$ values of the Lake Abhe water sampled in this study should be the result of isotope fractionation that takes place during evaporation (Table 5; Fig. 7), as similarly occurs for Lake Asal. Indeed, these values are quite similar to the values of Ethiopian terminal lakes with no outflow (Kebede, 2013; TLNO in Fig. 7).

According to Nuti (1991) the minimum temperature needed for a geothermal oxygen shift is about 200 °C. As evident from tritium values (Table 5), hot spring waters may have long residence time within the hard rock aquifers that could have promoted an oxygen exchange between thermal waters and host rocks at high temperature, but this latter hypothesis clash with the relatively low temperature inferred by geothermometers. However, a mixing between (old) meteoric waters and the local shifted waters (Asal Rift or Tendaho shifted waters) cannot be excluded (Fig. 7). In particular, it should be noted that the data obtained in 1970s from these basins (Fontes et al., 1980) are more shifted towards the Asal Rift Field (Fig. 7). In other terms, the supposed connection between thermal waters from northeastern and southwestern part of the Republic of Djibouti may now be confirmed (Gasse and Street, 1978). Nevertheless, further studies are needed to better understand

Table 5

Isotope data of thermal and cold waters from LAGF.

	δ^{18} O(H ₂ O) (‰ vs V-SMOW)	δ^{2} H(H ₂ O) (‰ vs V-SMOW)	Tritium (T.U.)	δ^{34} S(SO ₄) (‰ vs V-CDT)	δ18O(SO ₄) (‰ vs SMOW)	87Sr/87Sr
SHC1	-3.4	-26.3	<0.6	14.2 ± 0.5	11.5 ± 0.5	0.703809
SHC2	-3.3	-26.0	<0.6	14.3 ± 0.5	11.2 ± 0.5	0.703811
SHC3	-3.4	-24.7	<0.6	14.3 ± 0.5	11.8 ± 0.5	0.703865
GHC1	-3.4	-24.4	<0.6	13.2 ± 0.5	10.3 ± 0.5	0.703912
GHC2	-3.2	-27.0	<0.6	13.2 ± 0.5	9.8 ± 0.5	0.704018
GHC3	-3.1	-24.0	<0.6	13.3 ± 0.5	8.8 ± 0.5	0.703958
GHC5	-3.4	-27.6	<0.6			0.703976
Koutaboua	-0.7	3.7	3.1 ± 0.7			
Kantali	-1.1	2.0	3.3 ± 0.7			
Haloyta	-1.3	-2.9				
Gourabous	-1.2	-3.6	2.9 ± 0.7			
Galamo	-1.2	-3.7				
Abuyoussouf	-1.1	2.6				
Abakara	-0.3	2.8	<0.6	12.1 ± 0.5	12.6 ± 0.5	
Lake Abhe	6.5	43.9	3.9 ± 0.7	20.6 ± 0.5	23.8 ± 0.5	0.706565
R1bis ^a	-2.92	-20.4	<0.6			
R2 ^a	-2.86	-21.7	< 0.6			
R3 ^a	-2.23	- 17.7	<0.6			
R4 ^a	-2.66	- 18.8	<0.6			
H2 ^b	-3.52	-21.9	<0.6			
Teweo ^a	-2.75	-18.4	<0.6			

^a Cold groundwater from borehole (deep range 180–220 m) in Hanle-Gaggade region (BFGUR, Bundesanstalt fur Geowissenschaften und Rohstoffe, 1999).

^b Hanle 2 geothermal well (2038 m deep) in Hanle-Gaggade region (Aquater, 1987).

the water basin mixings and relations with the surroundings rift waters. The Hanle 2 geothermal well and the more cold borehole waters (samples R1bis - R4 and Teweo; BFGUR, 1999) located in the same area, display an evaporative path with a minor slope (s = 3.5; Fig. 7) compared to the arid lakes, probably because evaporation occurred at depth. Furthermore, their low temperature and silica concentrations should exclude a relation with Tendaho waters, which fall within the values of geothermal ¹⁸O-enriched waters from the Ethiopian Rift: about $-10\% > \delta^2 H(H_2O) > -20\%$; -2% > $\delta^{18}O(H_2O) > +1\%$ (IAEA, 2007). It has been reported that those borehole waters were mainly recharged from the regional aquifer (Aquater, 1987; BFGUR, Bundesanstalt fur Geowissenschaften und Rohstoffe, 1999), as shall do LAGF. However, underground evaporation and mixing path point towards a common source meteoric endmember between the GMWL and the Filwuha Fault thermal waters (Fig. 7). It should be noted that these latter thermal waters were issued along an east-west trending fault in the Addis Ababa area, which is about 500 km far from the Lake Abhe area. However, their chemistry and the very low tritium content have been interpreted as due to a water-rock interaction under high temperature conditions and long groundwater residence time probably recharged in a cold climate than today, respectively (Demlie et al., 2008; Kebede, 2013)..

4.3.2. Sulfate isotopes: $\delta^{34}S(SO_4)$ and $\delta^{18}O(SO_4)$

Gasse and Fontes (1989) reported isotope values from gypsum crust forming in Djibouti sediment basins: $\delta^{18}O(SO_4)$ from +11.7% to + 14.6‰ vs. V-SMOW and δ^{34} S(SO₄) from + 15.30‰ to + 21.8‰ vs. V-CDT. These values are plotted and compared with the isotopic values measured in the dissolved sulfates of LAGF's geothermal spring waters (Table 5; Fig. 8). The GHCi and SHCi springs sampled in this study and other water samples from the Lake Asal area (Fontes et al., 1979) are grouped below a hypothetical aqueous-solid sulfate divide line (Fig. 8). This isotope divide may be due to the fractionation that occurs during precipitation of sulfate minerals from solutions (Thode and Monster, 1965; Lloyd, 1967). Curiously, GHCi and SHCi springs fall on a line that has the same slope of fractionation during sulfate precipitation (S \approx 2.1). Considering the general undersaturation in sulfate minerals of the water samples, this is probably only a coincidence. However, it should be noted that the SHC₁ water sample is near to equilibrium with gypsum (SI_{gypsum} = -0.27), assuming a precision of ± 0.2 in the calculation of saturation indexes. Therefore, it seems that the near proximity of the SHCi samples to the divide line testify that the dissolution of anhydrite and/or gypsum as one of the main sources contributing sulfate to the ascending thermal waters. In contrast, the increased undersaturation in sulfate minerals from SHCi to GHCi springs is in accord with mixing.

The δ^{34} S compositions measured in lake water are about + 20.6‰. V-CDT. Those values are similar to that of seawater (δ^{34} S = +21.1‰ V-CDT; Coplen et al., 2001) although Lake Abhe is three times more saline (TDS = 92,622 mg/L) than seawater, with a high sulfate concentration (13,365 mg/L). Moreover, the $\delta^{18}O(SO_4)$ compositions measured in lake water, +23.8‰ V-SMOW, are much higher than that of seawater $\delta^{18}O(SO_4) = +8.6‰$ V-SMOW (Boschetti and lacumin, 2005) and Lake Asal water $\delta^{18}O(SO_4) = +7.5‰$ V-SMOW (Fontes et al., 1979). This could be explained by the combined effect of the high evaporation of the lake water, due to the arid climate conditions prevailing in the Republic of Djibouti, and to the bacterial effect on the lake sediments.

4.3.3. Strontium isotopes: ⁸⁷Sr/⁸⁶Sr

The ⁸⁷Sr/⁸⁶Sr isotopic ratios of LAGF geothermal waters range from 0.703809 to 0.704018 (Table 5) and agree well with the ranges of volcanic rock ⁸⁷Sr/⁸⁶Sr (0.703–0.707) from Djibouti (Vidal et al., 1991; Barrat et al., 1993). The relatively low ⁸⁷Sr/⁸⁶Sr (0.703809–0.704018) observed in geothermal waters from LAGF indicates that Sr is predominantly leached from the underlying volcanic rocks, most likely from the Stratoid Series that dominate the bedrock in the Southwestern region of the Republic of Djibouti. On the other hand, the elevated ⁸⁷Sr/⁸⁶Sr in the Lake Abhe water, 0.7066, reflects the contribution from Awash river, with ⁸⁷Sr/⁸⁶Sr ratios ranging from 0.7068 to 0.7072 (Bretzler et al., 2011).

4.3.4. Tritium

Tritium (³H) concentrations in geothermal water and groundwater of the study area range from values below the detection limit (0.6 TU) to the highest value of 3.9 TU (Table 5). Coastal/low latitude tritium table of Clark and Fritz (1997) has been used to distinguish modern and sub-modern (pre-bomb) waters.

There are no recent tritium data for Djiboutian precipitation. However, the lake water tritium content, 3.9, is in the range of the Awash River (3.7–5.2 TU) which recharge somehow the lake, and both are close to the current tritium concentrations measured in Ethiopian precipitation



Fig. 8. $\delta^{34}S(SO_4)$ vs. $\delta^{18}O(SO_4)$ diagram. Dashed line divides solid (X: sulfate minerals from Lake Asal area; Fontes et al., 1979) and aqueous sulfate from LAGF (this study with error bars) and Lake Asal area (open squares: springs; Fontes et al., 1979). Arrow represents the aqueous-solid isotope fractionation after precipitation of the sulfate minerals (S = slope; Thode and Monster, 1965, Lloyd, 1967). Open circles: seawater from the NBS127 standard: $\delta^{18}O(SO_4) = +8.6\%$ (Boschetti and Lacumin, 2005) and $\delta^{34}S(SO_4) = +21.1\%$ (Coplen et al., 2001).

(2.80–5.9 TU) (IAEA, 2007; IAEA/WMO, 2006). Moreover, groundwater in the study area contain tritium (Table 5, Fig. 2A), suggesting that these waters are modern and locally recharged.

The hot springs in LAGF have consistently very low tritium concentrations (i.e., less than 0.6 TU; Table 5) and may therefore recharged prior to the 1960s (Clark and Fritz, 1997). This is in accord with the ¹⁴C dating of Fontes et al. (1980), which estimated an age of about 1200 years for Abhe hot springs. The almost constant water chemistry maintained for years (Fig. 4) coupled with very low tritium concentrations (<0.6 TU) indicates that the limited meteoric recharge, associated with the local arid climate, does not modify meaningfully the main chemistry of the Lake Abhe thermal waters. Therefore, Lake Abhe geothermal waters can be considered as representative of the reservoir chemistry at depth.

A previous geothermal pre-feasibility study, in Hanle-Gaggada zone (Southwestern part of the Republic of Djibouti), reported tritium concentration less than 0.6 TU for one geothermal well (sample H2 in Table 5) as deep as 2038 m (Aquater, 1987). In addition, cold groundwater originating from deep boreholes (180-220 m deep; samples R1bis-R4 and Teweo in Table 5) in the same area presents tritium concentration less than 0.6 TU (BFGUR, 1999). These studies concluded that the volcanic regional aquifer can be tapped at about 200 m in the southwestern part of the Republic of Djibouti. Therefore, LAGF geothermal spring waters could be recharged mainly from a deep circulating regional aquifer. Furthermore, the very low tritium content coupled with the depleted δ^2 H suggests that the deep aquifer is a "paleowater" (in accord with the ¹⁴C dating of Fontes et al., 1980, which estimated an age of about 1200 years for Abhe hot springs), feed during a relatively colder climate in a similar way to the Filwuha Thermal Springs (Fig. 7; Kebede, 2013).

4.4. Geothermometry

4.4.1. Classical chemical geothermometers

The Na/1000–K/100–Mg^{0.5} ternary plot of Giggenbach (1988) can be used to discriminate mature waters, which have attained equilibrium with a primary silicatic mineral paragenesis, from immature waters and waters affected by mixing and/or re-equilibration along their circulation path (Fig. 9A). This provides an indication of the suitability of the waters for the application of cation geothermometers. Since all geothermal spring waters from LAGF are partially equilibrated (Fig. 9A), the K–Mg geothermometer cannot be used to estimate geothermal reservoir temperature (Arnórsson et al., 1983; Giggenbach, 1988). Among several existing silica geothermometers, those proposed by Fournier (1977) for quartz, and that of Arnórsson et al. (1983) for chalcedony, have been successfully used both in alkaline thermal waters and for waters with T < 180 °C (Michard and Beaucaire, 1993; Marques et al., 2003; Asta et al., 2012; Fournier, 1991). Therefore, only silica (chalcedony, quartz) and Na–K geothermometers have been applied to LAGF (Table 6).

In the present study, the quartz geothermometers estimate the temperature of the LAGF geothermal reservoir in the range of 117-154 °C (Table 6). On the other hand, silica geothermometers which are valid for steam loss by adiabatic boiling to 100 °C have been used to estimate silica temperatures for boiling geothermal spring waters in LAGF (Fournier and Potter, 1982). Those "adiabatic" silica geothermometers estimate the geothermal reservoir temperature in the range of 126–152 °C (Table 6). These values are of the same order of magnitude as those obtained with non-adiabatic quartz geothermometers (Table 6). On the other hand, reservoir temperature values estimated by the chalcedony geothermometers are about 100–131 °C (Table 6). It should be noted that plotting the samples on a silica vs. enthalpy of



Fig. 9. A) Relative Na/1000, K/100 and Mg^{1/2} contents (on ppm basis) of hot spring and warm well waters from Lake Abhe geothermal area (Na–K–Mg triangular plot after Giggenbach, 1988). B) Dissolved silica-enthalpy diagram. Considering the probable lost of steam from the sample GCH4, it has been plotted on the quartz steam loss curve, Vertical line is drawn from the enthalpy value corresponding to the mean estimated temperature of LAGF reservoir (135 °C). Quart steam and no-steam loss are from Arnórsson (2000). Amorphous silica-water equilibrium (Gunnarsson and Arnórsson, 2000) is also represented for comparison.

liquid water diagram (Fig. 9B), GHCi springs follow a mixing path that starts from SHCi springs, which probably were affected by conductive cooling, and continues towards local warm waters. Considering that diluted waters may be re-equilibrated with chalcedony at a lower temperature than the reservoir, only Na–K and quartz geothermometers should applied to GHCi, whereas quartz and chalcedony applied to SHCi will give the mean reservoir temperature.

Several Na–K geothermometers have been proposed and applied to calculate reservoir temperature in the past three decades. Concerning

the hot spring waters of the present study, the Na–K equations of Truesdell (1976) and Tonani (1980) estimated a temperature range of the geothermal reservoir, respectively, of about 75–96 °C and 76–98 °C. On the other hand, the Na–K geothermometer of Arnórsson et al. (1983) estimated a temperature range of the geothermal reservoir of about 86–107 °C, with an average temperature of 94.8 °C. The temperatures measured at the outflow of the LAGF geothermal spring waters are about 71–99.7 °C, with an average temperature of 90.6 °C. Since the subsurface temperatures are expected to be higher than those of

Table 6

Geothermometric estimations of the LAGF deep temperature calculated from the hot spring water samples. All displayed values are in °C.In the chemical geothermometer equations, aqueous silica (SiO₂), Na and K concentration in ppm were used, whereas $\delta^{18}O(SO_4)$ and $\delta^{18}O(H_2O)$ values were used in the isotope geothermometer equations. Only the results in bold were used for calculations of the mean temperature (\pm standard deviation). Other results are showed for comparison. See text for details.

	Fournier (1977) ^a	Fournier and Potter (1982) ^b	Arnórsson et al. (1998) ^c	Fournier and Potter (1982) ^{d,e}	Verma (2001) ^f	Arnórsson et al. (1983) ^g	Fournier (1979) ^h	Giggenbach (1988) ⁱ	Verma and Santoyo (1997) ^j	Zheng (1999) ^k	Seal et al. (2000) ¹
	Quartz	Quartz	Quartz	Quartz	Quartz	Chalcedony	Na – K	Na – K	Na-K	CaSO ₄ -H ₂ O	$HSO_4^H_2O$
	Chemical	geothermom	eters							Isotope geothermon	neters
SHC1	148	148	137	143	147	120	134	148	134	-	-
SHC2	152	152	141	147	151	124	127	142	128	143	124
SHC3	145	145	134	141	144	117	135	149	135	147	128
SHC4	151	151	140	146	150	123	131	145	131	-	-
SHC5	149	149	138	144	148	121	136	150	136	139	121
SHC6	154	154	143	148	153	126	139	152	138	-	-
SHC7	159	159	148	152	159	131	141	154	140	-	-
$\text{Mean} \pm \text{SD}$	151 ± 5	151 ± 5	140 ± 5	145 ± 4	150 ± 5	123 ± 5	135 ± 5	149 ± 4	135 ± 4	143 ± 4	125 ± 3
GHC1	136	136	124	133	134	108	140	153	139	-	_
GHC2	137	137	125	134	135	109	128	143	129	nd	nd
GHC3	138	138	126	135	136	110	147	160	146	nd	nd
GHC4	138	138	125	134	135	109	136	150	136	nd	nd
GHC5	137	137	125	134	135	109	131	145	131	-	-
GHC6	136	136	123	132	133	107	133	147	133	-	-
GHC7	135	135	123	132	133	107	138	152	138	-	-
GHC8	139	139	127	135	137	111	132	146	132	-	-
GHC9	128	128	117	126	125	100	130	144	130	-	-
$\text{Mean} \pm \text{SD}$	136 ± 3	136 ± 3	124 ± 3	133 ± 3	134 ± 4	108 ± 3	135 ± 6	149 ± 5	136 ± 3	nd	nd

S = silica concentration in the geothermal waters(ppm).

^a Fournier (1977): $T = 1309 / (5.19 - \log (S)) - 273.15$.

^b Fournier and Potter (1982): $T = -42.2 + 0.28831 \times S - 3.6686 \times 10^{-4} \times S^2 + 3.1665 \times 10^{-7} \times S^3 + 77.034 \times \log (S)$.

^c Arnórsson et al. (1998): $T = -55.3 + 0.3659 \times S - 5.3954 \times 10^4 \times S^2 + 5.5132 \times 10^{-7}xS^3 + 87.841 \times \log(S)$.

^d Fournier and Potter (1982): $T = -53.5 + 0.11236 \times S - 0.5559 \times 10^{-4} \times S^2 + 0.1772 \times 10^{-7} \times S^3 + 87.84 \times \log(S)$.

^e Silica concentration in water initially in equilibrium with quartz after adiabatic boiling to 100 °C Verma (2001).

^f (-(1175.7 / (log(S) - 4.88))) - 273.15. Na, K = sodium and potassium concentration in geothermal waters (ppm), respectively.

^h Fournier (1979): $T = 1217 / (1.438 + \log (Na / K)) - 273.15$.

ⁱ Giggenbach (1988): T = 1390 / (1.75 + log(Na / K)) - 273.15; Verma and Santoyo (1997).

^j T = (1289 / (1.615 + log(Na / K)) - 273.15); Zheng (1999).

^k $1000 \ln \alpha = 4.19 \times (10^6 / T^2) - 4.59 \times (10^3 / T) + 1.71$; Seal et al. (2000).

 1 1000ln $\alpha = 3.26 \times (10^6$ / $T^2) - 5.81.$ For isotopic equations, T is in Kelvin.

emergences, the Na-K geothermometers of Truesdell (1976); Tonani (1980) and Arnórsson et al. (1983) cannot be considered reliable for the Lake Abhe geothermal system. Whereas, the Na-K geothermometer of Giggenbach (1988) gives an equilibrium temperature of deep parent fluids of about 142-160 °C, the Na-K geothermometer of Fournier (1979) estimated the temperature of the geothermal reservoir at about 128–147 °C. The wide discrepancies between the results obtained applying the various Na-K geothermometric equations are due to the different data applied to the albite-K-feldspar equilibrium reaction, which in turn are due to: i) obsolete thermodynamic data available in the past decades (Cortecci et al., 2005); ii) existence of various mineral polymorphs (low-T and high-T albites; microcline, sanidine, orthoclase for K-feldspar); and iii) the difference between theoretical and experimental approaches. In other geothermal system (Cortecci et al., 2005), better concordance between temperatures estimated by guartz and Na-K geothermometers were obtained by using the equation of Verma (2001) and Verma and Santoyo (1997), respectively. For this reason, these latter Na-K and quartz equations were applied to the GHCi spring waters and a mean temperature of 134 ± 4 °C is obtained (Table 6). This is consistent with that of 136 \pm 4 °C obtained for SHCi waters averaging the temperatures calculated by the chalcedony (Arnórsson et al., 1983), quartz (Verma, 2001) and Na-K (Verma and Santoyo, 1997) equations (Table 6).

4.4.2. Evaluation of the equilibrium between $\delta^{18} O(SO_4)$ and $\delta^{18} O(H_2O)$ values

The application of the bisulphate–water or sulfate–water isotopic geothermometers, which are based on the equilibrium exchange of

the oxygen isotopes of aqueous HSO_4^- or SO_4^{2-} and H_2O_2 , respectively, depends by various factors, mainly: i) the dominant dissolved sulfur species in solution; ii) the kinetic of equilibration; and iii) the presence of conductive and/or mixing cooling (Boschetti, 2013). Considering the conductive cooling of SHCi geothermal spring waters, the mixing between GHCi and the local warm waters (Fig. 9b) and to check if the mother thermal water equilibrated with HSO_4^- or SO_4^{2-} , the $\delta^{18}O(SO_4)$ and $\delta^{18}O(H_2O)$ values obtained in this study were plotted on a $10^{3} \ln \alpha (SO_{4}-H_{2}O)$ versus $10^{6}/T^{2}$ diagram and compared with the equilibrium fractionation factors available in literature (Fig. 10; Boschetti, 2013). In that diagram, it is noteworthy how SHCi and GHCi plot between $HSO_4^--H_2O$ and $SO_4^2^--H_2O$ equilibrium lines, similarly to the rift hydrothermal waters from Obock (Awaleh et al., 2015) and Atlantis II (Zierenberg and Shanks, 1986). However, whereas these latter waters originated from or mixed with seawater, LAGF's waters have a meteoric origin. Furthermore, it's interesting to note that the LAGF reservoir temperature value of 135 °C obtained by silica and cation geothermometers corresponds to a 10^{3} ln α (SO₄-H₂O) value that falls between HSO₄⁻-H₂O and CaSO₄-H₂O equilibrium lines (Table 6; Fig. 10). This could indicate an equilibrium-oversaturation with anhydrite at depth, as often occur in other hydrothermal systems (Boschetti, 2013). To check this hypothesis, the mineral saturation indexes of the SHCi hot spring waters have been recalculated (Table 7) by using their mean composition at T =135 °C and P = 3 bar (equilibrium vapor pressure) and PHREEQCi software, version 3, coupled with the *lln.dat* thermodynamic database (Parkhurst and Appelo, 2013). The results testify that anhydrite is in equilibrium with water at depth, whereas the recalculated slight



Fig. 10. Sulfate–water oxygen isotope fractionation vs. temperature (after Boschetti, 2013) for LAGF waters (colored symbols; this study). $CaSO_4-H_2O$ and HSO_4-H_2O lines represent the fractionation equations of Zheng (1999) and Seal et al. (2000), respectively (Table 6). SO_4-H_2O is the best fit between the theoretical and the experimental study of Zeebe (2010) and Halas and Pluta (2000), respectively. Horizontal and oblique arrows represent conductive cooling and mixing, respectively. Water samples from Obock (Awaleh et al., 2015), Atlantis II (Zierenberg and Shanks, 1986) and Lake Asal (Fontes et al., 1979) are also shown for comparison: gray symbols are the hot water outflows, whereas black symbols are the estimated temperature of the reservoirs. Mean ocean seawater has been calculated using $T = 5 \degree C$, $\delta^{18}O(SO_4) = +8.6\%$ and $\delta^{18}O(H_2O) = 0\%$. Gulf of Aden and Red Sea seawaters are from Awaleh et al. (2015) and Craig (1969), respectively.

alkaline pH indicates that the mother acid water has been buffered by reaction with the rocks of the aquifer. In those circumstances, the best geothermometric estimation should be obtained inserting the mean data of Table 6 for SHCi geothermal spring waters in the $HSO_4^--H_2O$ (Seal et al., 2000) and $CaSO_4-H_2O$ (Zheng, 1999) fractionation factor equations (Boschetti, 2013). In this manner, conditions for simultaneous equilibrium are assumed and the results compare reasonably well with those of the solute geothermometers (Table 6). The approach is not suitable to GHCi waters due to mixing with warm waters; however, Fig. 10 suggests that oxygen isotope equilibrium between water and dissolved sulfate molecules approaches the temperature of the spring outflows, probably due to the combined effect of bacteria and the high residence time of the waters (Boschetti, 2013; Halas and Pluta, 2000; Zeebe, 2010).

4.4.3. Geothermometrical modeling

The state of equilibrium between water and mineral is a function of temperature; therefore saturation indices (SI) can be used as geothermometers (Reed and Spycher, 1984; Pang and Reed, 1998). In other

able 7
nhydrite and gypsum saturation index of LAGF reservoir recalculated at deep conditions.

	pН	Anhydrite	Gypsum
LAGF (T = 135 °C, P = 3 bar)	7.86	0.11	-0.62

words, estimation of reservoir temperature can be achieved by simultaneous consideration of the equilibrium state between specific water and many hydrothermal minerals as a function of temperature.

Geothermometric modeling calculations have been performed for the LAGF geothermal spring waters using the SOLVEQ computer program (Reed, 1982).

Fig. 11 depicts the mineral saturation indices versus increasing temperature for Lake Abhe geothermal spring waters. For those geothermal spring waters, saturation indices with respect to albite, microcline, muscovite, forsterite, quartz, chalcedony and anhydrite minerals tend to get closer to zero around the temperature of 130–170 °C at which temperature of these minerals are assumed to be in equilibrium with water giving rise to the estimated reservoir temperature (Fig. 11). These mineral phases were identified as the main hydrothermal minerals in the Southwestern geothermal fields of the Republic of Djibouti (Zan et al., 1990; D'Amore et al., 1998).

It is also noteworthy that for the Lake Abhe geothermal spring waters the temperature estimated from the multiple mineral equilibrium approach (about 130–170 °C) agrees well with the temperatures calculated from the chemical and isotopic geothermometers.

The prediction of the scaling tendencies from geothermal waters is important in evaluating the production characteristics of geothermal aquifers and for taking necessary precautions to prevent or control scale formation (Tarcan, 2005). The saturation indices of some minerals can help to estimate which one of these minerals may precipitate during the extraction and use of the geothermal fluids (Gemici and Tarcan, 2002).



Fig. 11. Diagrams showing the change in calculated saturation indices (log Q/K) of various minerals as a function of temperature. The temperature range with the convergence of saturation indices to zero is assumed to indicate the temperature of deep thermal reservoir for Lake Abbe geothermal spring waters: (A) (geothermal spring GHC9), (B) (geothermal spring SHC2). It should be noted that the 130 to 170 °C range of values at SI \approx 0 observed for GHC9 and SHC2 is closely obtained also for the other geothermal spring waters.

In other words, assessment of scaling tendencies involves calculation of the saturation state of the scale-forming minerals. The SOLVEQ computer code (Reed, 1982; Reed and Spycher, 1984) was used to calculate the saturation index of minerals that have been identified as the main hydrothermal minerals in the Southwestern geothermal fields of the Republic of Djibouti (Zan et al., 1990; D'Amore et al., 1998). The saturation indices (log Q/K) of those minerals were computed as a function of temperature.

The carbonate minerals calcite, aragonite, and dolomite were found to be oversaturated at 80–260 °C in almost all geothermal waters in the Lake Abhe geothermal area. Therefore, carbonate minerals will be most likely to precipitate as scales from the geothermal waters of LAGF during future geothermal production. The precipitation of carbonate minerals from geothermal spring waters in LAGF is best illustrated by the widespread occurrences of travertine deposits at the discharge sites (Dekov et al., 2014).

4.5. Conceptual hydrogeological model of LAGF

The schematic geological profile (Fig. 12) illustrates the flow patterns of LAGF, indicating that the recharge origin of geothermal water is mainly regional aquifer inflow, and concentration of heat depends on groundwater transport processes in the fault and fracture zones in bedrock, where the main heat source is located. A previous geophysical study estimated the depth of the major heat reservoir at about 1000 m in LAGF (Centre d'Etudes et de Recherche de Djibouti, CERD, 2012). In addition to regional aquifer inflow, rainfall in the area penetrates through deep fault and fracture zones, flowing downward to join with deep circulating regional water and absorbing heat from the surrounding rocks. The thermal water is then transported upwards along fault and fracture zones and discharges as geothermal spring waters at the surface.

5. Conclusions

The hot springs in Lake Abhe geothermal field occur at the bottom of travertine chimneys aligned generally WNW–ESE. Multivariate statistical analysis supports the notion that the geothermal spring waters from the small chimneys (SHCi) and those from the great chimneys (GHCi) have a common origin.

Because of their constant chemistry over annual-decadal time scales, the thermal hot spring waters can be considered as representative of the reservoir chemistry at depth.

Alkaline thermal hot spring waters in Lake Abhe geothermal field are of the Na–Cl type, while warm non-thermal groundwaters are mostly Na–HCO₃–Cl–SO₄ and Na–HCO₃–Cl and the lake waters are of the Na–Cl–HCO₃–SO₄ type with very high TDS.

Saturation index and isotopic composition $\delta^{34}S(SO_4)$ and $\delta^{18}O(SO_4)$ suggest the dissolution of evaporites as the main sources contributing sulfate to the ascending thermal waters.

The reservoir temperatures in LAGF were assessed using various geothermometric techniques. Chemical (Na/K, SiO₂) and isotope (bisulfate– and anhydrite-water) geothermometers as well as multiple mineral equilibrium approaches estimate a temperature range of the deep geothermal reservoir of 120–160 °C, with a mean temperature of about 135 °C.

The geothermal reservoir in Lake Abhe area is fed by meteoric water mainly from the regional aquifer. Rainfall in the area penetrates through fractured systems in Stratoid Series volcanic bedrock, flowing downwards to combine with deep circulating regional water and absorbing heat from the surrounding rocks. The maximum depth reached by the descending waters, i.e. the depth of the thermal aquifer, is on the order of 1 km, according to a recent geophysical study (Centre d'Etudes et de Recherche de Djibouti, CERD, 2012). The thermal water is then transported upwards along fault and fracture zones and discharges as hot springs at the bottom of travertine chimneys distributed along the main fault.

The thermal spring waters and warm borehole waters from the southwestern part of the Republic of Djibouti indicate a possible mixing with hydrothermal waters from the local rift. The negligible tritium content and the low deuterium values ($\delta^2 H < 10$ %) suggest a deeper circulation in comparison with the local, more recent wadi aquifers and surface waters ($\delta^2 H > 10$ %).

Finally, geochemical studies and field observations suggest that the most likely scales to be precipitated during the extraction of thermal waters in the study area are carbonate minerals.

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Fig. 12. Simplified sketch of the conceptual model of the Lake Abhe geothermal system.

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