Preliminary Fluid Geochemical Survey in Tete Province and Prospective Development of Geothermics in Mozambique

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Abstract

An evaluation of the feasible development of geothermal energy in Mozambique is proposed based on some thermal springs geochemical characterization in the Tete region. Chemical and isotopic data suggest that the springs have a meteoric origin and do not show connection with any active magmatic system. The proposed circulation model suggests high depths infiltration of meteoric waters along faults and fractures in a system characterised by discrete permeability and reservoir temperature between 90 and 120°C. These results, jointly with low salinity fluids and corrosive components absence suggest that the geothermal system may be conveniently exploited for direct and indirect uses.

1. Introduction

Mozambique is located on the southwestern branch of the East African Rift System (EARS) and borders on Malawi, Zambia, Tanzania, Zimbabwe, South Africa and Swaziland. The total area is about 800,000 km² and divides into 11 provinces. After a long period of colonial rule by Portugal, ended in 1975, Mozambique is, at present, an independent republic. Its economy is mainly based on agriculture (Chambal, 2010), it is rich in a variety of natural resources such as forests, marine resources, minerals and hydro-resources, but it suffers from extremely low access to energy and scarce sustainable utilization. This situation is partly due to the high cost of extending networks and to the high use of conventional fuels (e.g. gasoline) especially in remote and relatively low demand areas. At present, as a matter of fact, only 29% of the population has access to electricity. Therefore, new energy solutions should be thought of, considering and adapting to the reality of the Country and by combining the intensification of electrification by the national electricity grid with the adoption of available and sustainable renewable energy sources. In this view, the development of geothermal energy, in both direct and indirect uses, could represent an important goal to contribute to the economic growth of Mozambique, due to the high geothermal potential of the EARS. Furthermore, in areas where the geothermal gradient it is not so high the utilization of unconventional Geothermal System (i.e. Enhanced Geothermal System, EGS) could be an important solution.

This work proposes an in-depth analysis of the study partly presented in Procesi et al. (2015) through a review of the renewable energy status of Mozambique, with a special focus on geothermal energy and an overview on available data about thermal waters with the presentation of new collected data in the Tete Province (Northwestern Mozambique). The aims of the study are: 1) to estimate the temperature of the potential geothermal reservoir(s) and 2) to define a detailed conceptual circulation model constrained by the chemical–physical conditions of thermal waters and the geological, structural and hydrogeological framework.

2. Status Of Renewable Energy Resources In Mozambique

The power generation potential of Mozambique has been estimated at 187,000 MW (Power Africa, 2018) from coal and renewables such as hydro, gas, wind and solar resources. Hydropower currently accounts about 78% of installed capacity (Mokveld and Von Eije, 2018). More than 80% of the hydropower potential is located in the Zambezi Valley, including the existing Cahora Bassa Dam that represents the primary electricity source in the country, with an installed capacity of 2054 MW. However, most of the power generated by this power station is exported to South Africa. In general, due to lack of power transmission lines and distribution networks, the availability of hydroelectricity is mainly restricted to urban areas and, in general, only 29% of the population has access to electricity. Electricity in rural areas is largely supplied by diesel generators. Other renewable resources have been confined, for about 90% (Chambal, 2010), to traditional biomass uses (i.e. wood for cooking) and rarely to off-grid power supply sources (modern biomass, photovoltaic, wind and geothermics). The potential renewable energy resources in Mozambique are highlighted in Fig. 1, whereas the relative energy potential for each resource is shown in Table 1. There would be several advantages in the renewable energies development in Mozambique, from the mega-hydropower plants to the local small and medium-dimension projects such as small solar power plants with battery and generator, micro-hydro projects, modern biomass fuels and devices, small wind power generation systems and local geothermal power plants. All these choices could represent opportunities for the power grid optimization, life quality improvement, job creation and rural electrification.

2.1 Geothermal energy

The first estimates of the geothermal potential of Mozambique were made by McNitt (1978, 1982), who indicated the northern and the central provinces of the Country as the most promising areas. Other preliminary reports were performed by BRGM (1980), Aquater (1980) and Direcção Nacional de Geologia (1981). The preliminary results were confirmed years later by Martinelli et al. (1995) and, more recently, by Gesto Energia (2014) and Procesi et al. (2015). In particular, the Renewable Energy Atlas of Mozambique (Gesto Energia, 2014), commissioned in 2013 by the Government of Mozambique, reported the preliminary conclusions of the geothermal survey carried out on six provinces of the Country (Manica, Tete, Nampula, Niassa, Zambézia and Sofala). In four sites (Boroma, Namacurra, Morrumbala and Maganja da Costa in Zambézia Province) reservoir temperatures between 150°C and 164°C have been estimated. Moreover, for six selected sites in the provinces of Tete, Zambézia and Niassa, a potential geothermal reservoir depth between 1500 and 2500 m has been estimated by magnetotelluric and gravity surveys and a geothermal potential of 147 MW has been predicted. The existence and the characteristics of these potential reservoirs could only be confirmed through a drilling program but the medium-range estimated reservoir temperatures (~150°C) give back high project costs and potentially high mining risk. Beyond that, the most enigmatic prospect remains probably the Metangula area, where hot springs with outlet temperature > 95°C (the highest of the whole country) were reported to be present on the lake Niassa-Malawi shores before the rise in the lake water level (Martinelli et al. 1995 and references therein) but chemical data are not available. In spite of the favourable geological framework and although the National Government of Mozambique has financed preliminary feasibility studies, at present there is only one exploration project in the whole Country and no active geothermal power plants.

2.2 Other renewable energies

Hydro and small-scale hydro – Apart from the Country's greatest hydropower plant of Cahora Bassa (see above) another mega-scale power station was proposed in the Zambezi River basin (the Mphanda Nkuwa Dam) with an estimated installed capacity of 1500 MW (Hankins, 2009). In addition, several potential sites for micro hydropower projects were identified in the mountainous terrain with perennial streams and rivers of the Manica, Tete and Niassa provinces (Hankins, 2009). Despite this ample potential resource, the overall development focus was limited to mega-scale projects and only a handful of small and micro-hydro projects were completed over the past ten years.

Biomass and biofuels - Biomass is a primary potential source of both electricity and fuel, and is increasingly seen as a modern energy resource for Mozambique (Hankins, 2009). Biomass sources of energy can be divided into two primary categories: 1) traditional fuels and devices (wood, charcoal and agricultural waste) and 2) modern biomass fuels and devices. At present, over 80% of the energy used in the country is from traditional biomass sources.

Solar- Mozambique has a huge and virtually unexploited solar energy potential. Annual incident solar radiation is about 1.49 million GWh, which is thousands of times more than the Country's current annual energy demand. Current government policy is to use solar water heaters in the tourism and building sector and photovoltaic power in remote off-grid applications (Hankins, 2009).

Wind - Wind pumps for supply of water in remote regions were extensively used in Mozambique even though the 2018 Final Energy Report Mozambique (Mokveld and Von Eije, 2018) reports a limited wind resource and circumscribed to the southern part of the Country. Primary wind resources are located along the Country's coastline and in the Niassa highlands. Average wind speeds are as high as 6 m/s, with the windiest periods during June to August. As a part of the program to develop wind power projects in the southern part of the country, 20 meters-high anemometers have been erected to assess the potential for large-scale wind farms, reporting encouraging results (Hankins, 2009).

3. Geological, Structural And Hydrogeochemical Setting Of Tete Province

The territory of Mozambique is part of three major lithospheric plates (East, West and South Gondwana) that collided during the Pan African orogenic cycle (800-550 Ma). West and South Gondwana are divided by an important shear zone: the

Sanangoè Shear zone (SSZ). All of these major plates are present in the Tete Province (Western Mozambique). The most recent tectonic cycle of Mozambique is relative to the Post-Gondwana Cycle. It began 175 Ma ago and consisted of the final break-up of the Gondwana continent, followed by a phase of epeirogenesis and several neo-rifting phases. The rifting processes created lowlands covered by Karoo and post-Karoo Formations, and highlands and mountains constituted by Precambrian crystalline basement rocks (Steinbruch et al., 2008). Despite the paucity of detailed geological, hydrogeological and structural information on the Mozambican territory, the recent mapping, at the scale 1:250.000, of most of the country made by the GTK Consortium (Pekkala et al., 2008) provided an overview on the geological-structural and hydrogeological setting of the Tete Province.

From the structural point of view, the Tete Province is dominated by the Zambezi rift, which trends W-E from the Zambia/Zimbabwe border along Cahora Bassa and swings SE towards Tete and onwards to the coast of Mozambique (Hatton and Fardell, 2012) (Figs. 2a, b). The rift affected the Precambrian basement rocks and developed into a zone of active extensional tectonism with sedimentary deposition. In the study area, two main stratigraphic units are recognized, from top to bottom: the Karoo Supergroup (Carboniferous-Cretaceous) and the Pre-Karoo Formations of the Precambrian Basement (Hatton and Fardell, 2012) (Figs. 2b, c). The Karoo Supergroup overlies the basement rocks with a significant unconformity and comprises detrital sedimentary lithotypes and coal-bearing horizons, intruded at a late stage by doleritic dykes and sills. The rocks of the Karoo Supergroup outcropping in the study area are those of the lower Karoo (Dwyka Stage - Eccu Group; Carboniferous-Early Permian), consisting of tillite, fluvio-glacial deposits and thick sandy-argillaceous deposits with interstratified coal seams (Fig. 2c). The Precambrian basement comprises rocks of the Tete Suite and of the Southern Crystalline Basement. The latter, exposed S of the Sanangoè Shear Zone (SSZ) (Westerhof et al., 2008a) is mainly composed by the Chidué Group and Chacocoma Granite (Westerhof et al., 2008b) (Figs. 2b, c). The Chidué Group is mainly constituted by gneisses, marbles and meta-sandstones. These rocks were modified by contact-parallel tectonic below the Tete Suite. The Chacocoma Granite is highly deformed and the original porphyritic rock is obscured by Augen gneiss texture. Close to the tectonic contact with the Tete Suite, the granitoid was deformed into (blasto)mylonites and phyllonites (Westerhof et al., 2008b). The Tete Suite is a layered intrusive, composed predominantly of gabbro, with subordinate leucogabbro, norite, anorthosite and pyroxenite. Lenses of iron-titanium oxides are also found. Rock fabrics are generally massive un-metamorphosed with medium to very coarse or even pegmatitic grain sizes (Fig. 2c).

The overall hydrogeology of Mozambique was investigated by Ferro and Bouman (1987). Three main hydrogeological units, corresponding to geological units, were identified: 1) aquifers related to the basement complex; 2) aquifers occurring in the Karoo formations and 3) aquifers related to the post-Karoo formations (Tab. 2). The basement complex covers about 60% of the country, occupying the western part of the central region and almost the entire region north of the Zambezi. The permeability of this complex is generally low. The permeability primarily depends on thickness and texture of the unit and presence of fractures and faults. The permeability of the Tete Suite is higher due to the intensive faulting and fracturing, whose effects are more pronounced on rocks formed by brittle and coarse-textured minerals (e.g., anorthosite). Moreover, good permeability may be found along dikes, where aquifers can develop in the fracture zone on the contact between the intrusive body and the adjacent rocks formations (Ferro and Bouman, 1987). The hydrogeological properties of the Karoo formations are known only from a few limited areas. In general, the sequence is characterized by low permeability, although permeability is higher in fractured zones, coarse sandstones, fault-breccias and along intrusions. The post-Karoo formations have extremely variable permeability, from low to high. Higher values correspond to limestone and alluvial deposits, especially in the Zambezi delta (Ferro and Bouman, 1987).

From a geochemical point of view, thermal springs in Mozambique, with water temperature between 40°C and 95°C, are known since the late seventies (McNitt, 1978). These are located in the Niassa Province, where the temperatures reach the highest values (Metangula, 95°C), Zambezia Province (Mossurrie, Gilè, Maganja da Costa, Namacurra, Milange and Morrumbala Districts) where the temperatures of the water range from 45°C to 75°C. In the Tete Province water temperatures close to 80°C were recorded, while the southern Sofala e Maniça Provinces show the highest number of thermal springs presenting, however, lower temperatures ranging from 27°C to 58°C (Martinelli et al., 1995).

In 2013 an extensive geochemical survey for geothermal exploration was carried out and the results have been briefly discussed on the Renewable Energy Atlas of Mozambique (Gesto Energia, 2014). In particular, 22 samples of water were collected from hot springs, mineral springs, water wells, rivers and sea, in six provinces: Manica, Tete, Nampula, Niassa, Zambézia and Sofala. Geothermometric evaluations indicated potential reservoir temperatures usable for electricity production in four sites: Boroma (164°C), Morrumbala (153°C), Maganja da Costa and Namacurra (155°C). Moreover, the analysis of geophysical data allowed to identify areas with low resistivities that may indicate potential geothermal reservoirs at depths ranging between 1500 and 2500 m.

Liquid geothermometer evaluations based on the silica concentrations in thermal waters, reported by Martinelli et al. (1995) and the assumption of equilibrium with chalcedony, highlighted geothermal reservoir temperatures around 100-110°C, somewhat lower than the aquifer temperatures proposed by Gesto (2014).

4. Methods

4.1. Sampling and laboratory analyses

Three thermal springs were sampled at *Nhawóndòc*, *Tenta* and *Mauira* (see Appendix A for photos) close to the *Missao de Boroma* (*Tete Province*). These springs are located in remote areas, so that it was possible to sample them only with the help of local tribes. Water temperature, pH, Eh, electrical conductivity and alkalinity (titration with 0.05 N HCl) were determined in the field. Two aliquots of water were filtered (0.45 mm) and filtered + acidified (with HCl) for major anions (F^- , Cl^- , Br^- , SO_4^{2-} and NO_3^-) and cations (Ca, Mg, Na and K), respectively, and analyzed by ion-chromatography (Thermo Scientific ICS900). The analytical error was < 5%. A third aliquot was filtered and acidified (with HNO_3) for minor and trace elements (Sr, Fe, Mn, Al, B, Li) and analyzed by ICP-MS (Agilent 7500ce). Silica (SiO_2) was determined by molecular spectrophotometry on a filtered-diluted (1:10) sample. The analytical error for minor and trace elements was < 10%.

The $d^{18}O$ and dD ratios (as ‰ vs. VSMOW) were determined by mass spectrometry (Analytical Precision AP 2003 and Finnigan MAT Delta plus, respectively). The analytical uncertainties were $\pm 0.1\text{‰}$ for $d^{18}O$ and $\pm 1\text{‰}$ for dD .

Samples for dissolved gas analyses were collected in glass flasks, and sealed by gas tight rubber/teflon plugs. Gases were extracted according to the method described by Capasso and Inguaggiato (1998) and analysed by gas chromatography (Varian micro GC 4900P). The analytical error was <5%. Dissolved gas composition was calculated from the composition of the exsolved gas phase based on the Henry's law (Whitfield, 1978).

The $d^{13}C$ ratio of total dissolved inorganic carbon (TDIC) (expressed as ‰ vs. VPDB) was analyzed by mass spectrometry (Finnigan Delta Plus) following the procedure described by Favara et al. (2002). The analytical uncertainty was $\pm 0.2\text{‰}$.

The $d^{13}C$ and dD of CH_4 values (expressed as ‰ units vs. VPDB and VSMOW, respectively) were analyzed by mass spectrometry (Varian MAT 250) according to the method described by Schoell (1980). The analytical uncertainty was $\pm 0.15\text{‰}$. The $^3He/^4He$ ratios (expressed as R/R_a , where R is the $^3He/^4He$ measured ratio and R_a is the $^3He/^4He$ ratio in the air: 1.39×10^{-6} ; Mamyrin and Tolstikhin, 1984), as well as the $^4He/^20Ne$ and $^{40}Ar/^36Ar$ ratios, were determined by mass spectrometer (VG 5400-TFT) according to the procedure described by Inguaggiato and Rizzo (2004). The analytical error was $\pm 1\%$.

4.2 Interpretation methods of geochemical data

Speciation-saturation calculations were performed using the PHREEQC code (Parkhurst and Appelo, 2013) and a modified version of the LLNL database as a preliminary step preceding the interpretation of geochemical data. This operation was necessary to separate the distinct components of total alkalinity and, in particular, the carbonate alkalinity, which is the sum of the concentrations (in equivalent units) of HCO_3^- and CO_3^{2-} , including related aqueous complexes, e.g., $CaHCO_3^+$, $MgHCO_3^+$, $CaCO_3^\circ$, and $MgCO_3^\circ$.

Following Cioni and Marini (2020), the chemistry of the thermal springs was investigated by means of triangular plots of major cations (i.e., Na, K, and Ca) and anions (i.e., Cl, SO₄, and carbonate alkalinity). Since these two triangular plots do not provide any information on total ionic salinity (S_{eq}), this parameter was examined by using the binary diagram of Cl vs. SO₄ + Alk_C. In fact, the S_{eq} can be appreciated in the diagram, by comparing the position of each thermal water with the lines of slope -1 which are iso-S_{eq} lines (see Tonani et al., 1998 for further details). All these diagrams were prepared using concentrations in equivalent units, in contrast with the consolidated use of concentrations in weight units. The reason for this choice is that equivalent units are proportional to the amount of electrical charges carried by each ion and, therefore, are more suitable than weight units for the chemical classification of natural waters as recognized long ago (e.g., Zaporozec, 1972 and references therein). Average seawater composition (Nordstrom et al., 1979) is also represented in the relevant plots for comparison.

Chloride diagrams and binary diagrams were inspected to assess the possible effects of different processes such as mixing, precipitation of solid phases, and ionic exchange, on the solutes of interest.

Water geothermometry was performed using: (i) suitably selected, simple traditional solute geothermometric functions, (ii) multicomponent geothermometry and (iii) the theoretical geothermometers of Cioni and Marini (2020).

Generally, solute geothermometers have been used to estimate the temperatures of deep geothermal reservoirs starting from analyses of fluid samples collected at the surface from springs and exploration wells (Fournier, 1977; Fournier, 1989; Truesdell & Fournier, 1977; Arnórsson & Gunnlaugsson, 1985). These geothermometers link the equilibrium temperature of reference reactions to either the concentration of some dissolved components (e.g., SiO₂) or some concentration ratios (e.g., Na/K). Silica geothermometers are based on the temperature-dependent solubility of different silica minerals (i.e., quartz and chalcedony) which are presumably present as authigenic (secondary) solid phases in reservoir rocks and, therefore, in equilibrium with the aqueous solution. The quartz geothermometer is best for reservoir temperatures higher than 180°C whereas, at lower temperatures, chalcedony rather than quartz probably controls the dissolved silica content (Arnórsson et al. 1983; Fournier 1989).

Multicomponent geothermometry was first proposed by Michard (1977), Michard and Roekens (1983), and Reed and Spycher (1984). Multicomponent chemical geothermometry comprises, as first step, the calculation of the saturation indices (SI's) with respect to relevant hydrothermal minerals at the temperature of pH and alkalinity measurement. Then, temperature is increased in a series of steps and the SI's are recomputed at each step. Finally, the computed SI's are plotted against temperature. Since the geothermal liquid is presumably in equilibrium with the considered hydrothermal minerals at the aquifer temperature, ideally all the SI-temperature curves are expected to converge to zero at the aquifer temperature. Again, calculations were performed with the computer program PHREEQC (Parkhurst and Appelo, 2013) operating with the Lawrence Livermore National Laboratory (LLNL) database.

The theoretical Na–K, K–Ca and Na–Ca geoindicators of Cioni and Marini (2020) are based on the temperature dependence of the thermodynamic equilibrium constant of the exchange reactions involving pertinent hydrothermal minerals and take into account the average activities of relevant endmembers in solid solutions as well as Al–Si order-disorder on the tetrahedral sites of adularia.

The isotope data of H and O were interpreted to establish the origin of water and the possible effects of different processes (such as mixing and evaporation), whereas the infiltration elevation of rainwaters possibly involved in the recharge of the thermal circuits of interest cannot be evaluated due to the lack of isotope-elevation relationships specifically calibrated for the Tete area.

The C isotope data of CO₂ and CH₄ and the H isotope data of CH₄ were interpreted to assess the origin of these two C-bearing gases. To this purpose, the d¹³C value of gaseous CO₂ was computed from the measured d¹³C_{TDIC} values by means of the empirical equation of Zhang et al. (1995):

$$\delta^{13}\text{C}_{\text{CO}_2(\text{g})} = \delta^{13}\text{C}_{\text{TDIC}} - \frac{H_2\text{CO}_3}{\text{TDIC}} \varepsilon_{(H_2\text{CO}_3 - \text{CO}_2)} - \frac{\text{HCO}_3^-}{\text{TDIC}} \varepsilon_{(\text{HCO}_3^- - \text{CO}_2)} - \frac{\text{CO}_3^{2-}}{\text{TDIC}} \varepsilon_{(\text{CO}_3^{2-} - \text{CO}_2)} \quad (2)$$

Eq. (2) takes into account the equilibrium molar ratios of aqueous carbon species at sampling temperature and pH, computed with the PHREEQC code (Parkhurst and Appelo, 2013), and the isotope equilibrium fractionation factors (ε) between dissolved carbonate species and gaseous CO_2 (Deuser and Degens, 1967; Mook et al., 1974).

Then, the conceptual model of the geothermal system was elaborated inserting the results of the interpretation of geochemical data into the geological-hydrogeological framework of Tete area.

5. Results Of Chemical And Isotopic Analysis

Results of the chemical and isotopic analyses of sampled waters are listed in Tab. 3. Available data from literature (Martinelli et al., 1995) relative to one thermal spring (*Niaondive*) in the Tete Region were also discussed for comparison. Since pH is not reported by Martinelli et al. (1995), it was computed by the relation of Chiodini et al. (1991) for the P_{CO_2} given by the K-Ca- P_{CO_2} indicator (Giggenbach, 1984) 5×10^{-3} bar, and the chalcedony-temperature, 108°C , obtaining the value of 7.8. The springs of *Nhawóndòc*, *Tenta* and *Niaondive* (indicated by codes 1, 2, and 4, respectively) have TDS values of approximately 1500 mg/L, slightly alkaline pH (7.8 - 8.0) and temperatures from 52 to 80°C . The *Mauira* spring (code 3) shows slightly lower temperature (42°C) and TDS (952 mg/L) and similar pH (7.8). The redox potential is strongly negative for all the sampled waters, varying from -209 to -404 mV.

Speciation-saturation calculations at outlet temperatures indicate that carbonate alkalinity explains 89 to 99 % of total alkalinity, while HCO_3^- and its aqueous complexes explain 93 to 99% of carbonate alkalinity. Therefore, the terms bicarbonate ion and carbonate alkalinity can be used in place of each other. Among the three main cations (Fig. 3a), Na^+ is the dominant one in all four samples, with relative concentrations of 73.7 to 92.4 eq%. The second major cation is Ca^{2+} in samples 1, 2, and 4, with relative concentrations of 16.6 to 22.8 eq%, but in sample 3 the relative concentration of K^+ , 4.3 eq%, is weakly higher than the relative concentration of Ca^{2+} , 3.2 eq%. The comparison of relative chloride, sulphate and bicarbonate concentrations highlights the prevalence of Cl^- and SO_4^{2-} in samples 1, 2, and 4 and that of Cl^- and HCO_3^- in sample 3 (Fig. 3b).

All in all, the three samples 1, 2, and 4 are similar to each other and are clearly separated from sample 3 in both triangular plots, indicating different chemical compositions, Na-Cl(SO_4) and Na-Cl(HCO_3), respectively. The binary diagram of Cl vs. $\text{SO}_4 + \text{Alk}_\text{C}$ (Fig. 4) shows that the three Na-Cl(SO_4) samples are similar to each other also in terms of S_{eq} (42 – 45 meq/kg), whereas the Na-Cl(HCO_3) sample 3 has significantly lower S_{eq} (25 meq/kg). Correlation diagrams highlights a good correlation between K and Cl, HCO_3 and Ca, and SO_4 and Na for the Na-Cl(SO_4) samples.

The two different water types have distinct concentrations of some minor and trace constituents. In fact, the two Na-Cl(SO_4) samples 1 and 2 have lower F, 5.3 – 6.1 mg/L, B, 0.29 mg/L, Fe, 14 – 25 $\mu\text{g/L}$ and Mn, 3.0 – 19 $\mu\text{g/L}$, and higher SiO_2 , 98 – 113 mg/L, Sr, 0.23 – 0.22 mg/L, whereas the Na-Cl(HCO_3) sample 3 has higher F, 22 mg/L, and Fe, 609 $\mu\text{g/L}$, and lower SiO_2 , 75 mg/L, and Sr, 0.09 mg/L.

Saturation indexes calculated at outlet temperatures indicate that all the thermal springs are undersaturated with respect to both anhydrite (SI from -2.78 to -0.78) and amorphous silica (SI from -0.54 to -0.29), whereas samples 1 and 2 are supersaturated with calcite (with SI of +0.85 and +0.52, respectively), sample 4 is close to saturation (with SI of +0.02), and sample 3 is slightly undersaturated (with SI of -0.21).

The d^{18}O and dD values of samples 1, 2, and 3 (Tab. 3) range from -6.79 to -6.75 and from -44.8 to -42.7‰ vs. VSMOW, respectively. The sample of rainwater, collected at Luenha in the Tete Region, has d^{18}O and dD values of +0.21 and +12‰ vs. VSMOW, respectively. In the d^{18}O -dD diagram of Fig. 5, sampled waters plot between the Global Meteoric Water Line (Craig, 1961) and the Regional Meteoric Water Line (Rozanski et al. 1996).

The composition of dissolved gases shows that N₂ is the main species (0.75 to 1.1 mmol/L) followed by O₂ (0.14 to 0.23 mmol/L) (Fig.6). Carbon dioxide concentrations are constantly low (0.024 to 0.03 mmol/L) and somewhat higher than Ar concentrations (0.008 to 0.012 mmol/L), whereas a wide range of variation occur for CH₄ (0.24 to 4.7 mmol/L), He (0.08 to 1.3 mmol/L) and H₂ (0.002 to 0.017 mmol/L). Carbon monoxide is always below the instrumental detection limit. The δ¹³C-CO₂ values, calculated from equation (2), vary from -18.2 to -15.5‰ vs. VPDB (Tab. 3). The helium isotopic ratios, corrected for air contamination by using the He/Ne ratio, range from 0.13 to 0.21 (Tab. 3).

5.1 Results of selected geothermometers

The results of selected traditional geothermometers and theoretical geothermometers of Cioni and Marini (2020) for the four thermal waters of interest are shown in Tab. 4, together with the outlet temperature and the degree of order-disorder of hydrothermal adularia, Z_{Adl} , in hypothetical equilibrium with the thermal waters of interest at the chalcedony temperature.

For the multicomponent geothermometry (Marini and Cioni, 2020), the saturation temperatures are given in Table 5. The considered hydrothermal minerals are quartz, chalcedony, low-albite, two adularias of different order-disorder degree, muscovite, the four typical Ca-Al silicates of the neutral-pH suite (i.e. laumontite, clinozoisite, prehnite, and wairakite), clinocllore-7A, as well as heulandite, calcite, and anhydrite. Fluorite and barite are not considered because their SI are scarcely informative having a weak temperature dependence.

Clinocllore-7A, muscovite, clinozoisite, prehnite, and wairakite were assumed to have average activity based on the related solid solutions from drilled geothermal systems (Cioni and Marini 2020), whereas the other solid phases were assumed to be pure. Aluminum concentration was fixed by saturation with low-albite at the temperature indicated by the chalcedony geothermometer using the EQUILIBRIUM PHASES keyword data block of PhreeqC. Three different models were elaborated for the samples 1 from *Nhawóndòc*, 2 from *Tenta*, and 3 from *Maiura*. In the first model, the sample was simply heated from the outlet temperature to the maximum temperature of 150°C, at fixed steps of 10°C, apart from the first one whose magnitude depends on the outlet temperature. The REACTION TEMPERATURE keyword data block of PhreeqC was utilized to this purpose. Since the aqueous solutions resulted supersaturated with calcite, saturation with calcite at the temperature given by the chalcedony geothermometer was imposed in the second and third models following two distinct approaches. In the second model, calcite equilibrium was attained by precipitation of a suitable amount of calcite, using the EQUILIBRIUM PHASES keyword data block of PhreeqC, whereas in the third model, calcite equilibrium was achieved by addition of an appropriate quantity of gaseous CO₂, at fixed partial pressure, using the GAS PHASE keyword data block of PhreeqC. The SI vs. temperature diagrams for three models elaborated for the samples 1 from *Nhawóndòc*, 2 from *Tenta*, and 3 from *Maiura*, are shown in figures 7, 8, and 9, respectively

6. Discussions

6.1 Processes governing the chemical and isotopic composition of waters

Water-rock interaction at relatively high temperature may be considered as the main process influencing the chemical composition of the collected waters. The Na-Cl(SO₄) composition of thermal springs at *Nhawóndòc*, *Tenta* and *Niaondive* suggests an interaction with low solubility rocks, i.e. gneisses and granitoid rocks of the Crystalline Basement and mafic rocks of the Tete Suite. In fact, the relatively low salinity of waters seems to exclude the interaction with soluble evaporitic rocks and/or mixing with highly saline (connate) waters, which are not reported to be present in the study area. So, the relatively high Cl⁻ concentration may result from the dissolution of minerals in which the Cl⁻ ion occurs as a vicariant of OH⁻, such as micas (mainly biotite, as accessory mineral in the gneisses of the study area), amphiboles, apatite, etc. Consistently, the relatively high SO₄²⁻ concentrations may be produced through pyrite dissolution under O₂-free conditions. Owing to its deleterious environmental impact, the reaction mechanisms and kinetics of O₂-driven pyrite dissolution has received considerable attention (e.g., Moses et al. 1987; Moses and Herman 1991; Williamson and Rimstidt, 1994; Gleisner et al. 2006), whereas pyrite dissolution in O₂-free systems has never been investigated to the best of our knowledge. Since the formal oxidation

state of S in pyrite is -1, it is reasonable to hypothesize, from a purely theoretical point-of-view, the occurrence of the following disproportionation reaction in the absence of O₂:

According to reaction (3), seven of the eight S atoms initially hosted in pyrite are reduced to aqueous sulphide species and only one is oxidized to sulphate, whereas Fe is expected to maintain the formal oxidation state of +2, under strongly reducing conditions. Sulphide and sulphate are considered in reaction (3) because they are the thermodynamically most stable sulfur species (Langmuir, 1997), although several aqueous S species with formal oxidation state intermediate between those of sulphide and sulphate are known (Williamson and Rimstidt, 1992) and could be involved in pyrite disproportionation in the absence of O₂.

It must be underscored that reaction (3) produces aqueous H₂S, which is an acid somewhat weaker than aqueous CO₂ (or carbonic acid) below 115°C. However, H₂S becomes an acid stronger than aqueous CO₂ at higher temperatures. Therefore, pyrite dissolution in O₂-free systems might actually generate the acidity needed for the occurrence of silicate dissolution, thus playing a fundamental role in the overall water-rock interaction process. The good correlation between SO₄ and Na for the three Na-Cl(SO₄) samples could be explained by coupled pyrite-albite dissolution, as schematically indicated by the following reaction:

Reactions (3) and (4) must be considered working hypotheses at this stage. To confirm their occurrence, we suggest to investigate the distribution of pyrite in the rocks of the area of interest and to carry out sulphur isotopic analyses, as done for several thermal sites of Malawi (unpublished reports by LM). The good correlation between HCO₃⁻ and Ca²⁺ for the three Na-Cl(SO₄) samples suggests the occurrence of calcite dissolution/precipitation which, in turn, is probably controlled by acquisition/loss of CO₂. The good correlation between K⁺ and Mg²⁺ is probably explained by acquisition of both constituents upon cooling or occurrence of exchange reactions also involving Na⁺ ion. The possible occurrence of these processes casts some uncertainties on theoretical geothermometric evaluations.

The *Maiura* Na-Cl(HCO₃) spring (#3) is located in an area marked by the presence of rocks belonging to the Karoo and Post-Karoo Formations, largely made of sedimentary rocks with coal-bearing horizons. In this framework, the availability of CO₂ is expected to be higher than in the mafic rocks of the Tete Suite and the underlying crystalline rocks of the Precambrian basement. Therefore, CO₂-driven plagioclase dissolution, at saturation with calcite is expected to be the main reaction leading to the production of Na-Cl(HCO₃) waters (Eq. 5):

These waters are typically characterized by low Ca²⁺ concentrations, owing to saturation with calcite and high HCO₃⁻ concentrations. Consequently, they may acquire high F⁻ concentrations, up to the maximum value constrained by fluorite saturation, through dissolution of minerals in which the F⁻ ion occurs as vicariant of OH⁻ ion, such as apatite, micas, amphiboles, etc. Highly saline waters (over 8000 mg/L) were found in the Karoo and Post-Karoo Formations (Groundwater Consultants Bee Pee (Pty) Ltd and SRK Consulting (Pty) Ltd, 2002) but the low salinity of the *Maiura* spring seems to exclude the hypothesis of mixing with similar brines.

The d¹⁸O and dD values of the collected waters, indicating a meteoric origin, are consistent with the lack of saline (connate) waters from the deeper circuits.

As far as the dissolved gases are concerned, the classical triangular diagram of N₂-Ar-He (Fig. 6; from Giggenbach and Goguel 1989) shows that N₂ and Ar are mostly of atmospheric origin and are driven to depth by infiltrating meteoric waters. The relatively high He contents of samples 1 and 3 point to a prolonged residence time in crustal rocks, leading to accumulation of radiogenic ⁴He produced from α-decay of U- and Th-bearing minerals. The crustal origin of He is confirmed by the low R/R_a ratios (0.13-0.21 R/R_a), based on which it is reasonable to conclude that there is no evidence of primary mantle ³He degassing (Marty and Jambon, 1987). Carbon dioxide shows very low concentrations in the collected waters. The isotopic composition suggests a shallow origin from plant-root respiration and aerobic decay of organic matter contained in soils and/or a deeper one through anaerobic decay of organic matter contained in the sedimentary rocks of the Karoo Supergroup (Cerling et al., 1991), whereas a deep (inorganic) magmatic-metamorphic provenance seems to be ruled out. Shallow alteration of organic matter and/or interaction with coal deposits of the Lower Karoo Formation may be responsible for the relatively high CH₄ content of the *Maiura* spring relative to the other samples. This hypothesis is consistent with the carbon and hydrogen isotopic composition of CH₄, which suggests a probable derivation of methane from biogenic sources.

6.2 Geothermometric estimations

Silica geothermometers are potentially affected by dilution, but the effects of this process are expected to be negligible for the Na-Cl(SO₄) thermal springs at *Nhawóndòc*, *Tenta* and *Niaondive* (samples 1, 2 and 4, respectively) because they have very similar chloride concentrations, suggesting that these springs discharge the same pure thermal endmember. This assumption is fortified by the low concentrations of Mg recognized in the samples and suggesting the negligible presence of shallow fluids. The limited differences in SiO₂ concentrations are probably due to variable re-equilibration upon cooling during their upflow. Chalcedony solubility (Fournier, 1977) indicates aquifer temperatures of 110, 118, and 108°C for samples 1, 2 and 4, respectively, and a somewhat lower aquifer temperature, 93°C, for the *Maiura* spring, (sample 3) (Table 4). Corresponding quartz temperatures (Fournier, 1977) are 26-28°C higher than chalcedony temperatures and, therefore, are probably less likely than latter ones (see section 4.2). The K-Mg geothermometer (Giggenbach, 1988) provides aquifer temperatures of 119, 112, and 113°C for samples 1, 2 and 4, respectively, in good agreement with chalcedony temperatures, whereas the K-Mg temperature of sample 3, 153°C, is significantly higher than the chalcedony temperature and is probably less reliable for the reason given below.

As shown by Cioni and Marini (2020), all the different Na-K geothermometric functions proposed by different authors appear to be plausible and, therefore, there is an infinite number of Na-K geothermometers which are controlled by the exchange reaction between low-albite and variably ordered adularia, from fully ordered maximum-microcline (with order-disorder degree, Z_{Adl} = 1) to completely disordered high-sanidine (with Z_{Adl} = 0). Equilibrium coexistence of low-albite and fully ordered maximum-microcline indicates aquifer temperatures of 210, 132, and 167°C for samples 1, 2 and 4, respectively, whereas equilibrium coexistence of low-albite and completely disordered high-sanidine indicates aquifer temperatures of 92, 27, and 55°C for samples 1, 2 and 4, respectively (Table 4). The limiting Na-K aquifer temperatures of sample 3 compare with those of sample 1, that is, 210 and 93°C. Since there is an infinite number of Na-K geothermometers, there is also an infinite number of other cation geothermometers which are controlled by exchange reactions involving adularia. For this reason, cation geothermometers (e.g., K-Mg, Na-K-Ca, etc.) appear to be less reliable than silica geothermometers.

Following Cioni and Marini (2020) and using the Na-K ratio as indicator of the degree of order-disorder of hydrothermal adularia, in hypothetical equilibrium with the thermal waters of interest at the chalcedony temperature, it turns out that Z_{Adl} is 0.132, 0.848, and 0.422, for samples 1, 2 and 4, respectively, and 0.422 for sample 3. These Z_{Adl} values can then be used to compute K-Ca and Na-Ca temperatures, controlled by clinozoisite (Czo), prehnite (Prh), laumontite (Lmt), and wairakite (Wrk). For the three Na-Cl(SO₄) thermal springs at *Nhawóndòc*, *Tenta* and *Niaondive*, the most plausible K-Ca and Na-Ca temperatures (i.e., closest to the chalcedony temperature) are those controlled by equilibrium with clinozoisite, namely 115, 127, and 124°C and 116, 134, and 137°C, for samples 1, 2 and 4, respectively. For the Na-Cl(HCO₃) *Maiura* spring (sample 3), the most plausible K-Ca and Na-Ca temperatures are those controlled by equilibrium with laumontite, namely 99 and 105°C, respectively. All in all, these K-Ca and Na-Ca temperatures are somewhat higher than chalcedony temperatures. Among the

three Na-Cl(SO₄) thermal springs, sample 1 from *Nhawóndòc* is the one with the K-Ca and Na-Ca temperatures closest to the chalcedony temperature, with differences of 5 and 7°C only. Since this is the sample with the highest Ca concentration, 98.1 mg/kg (vs. 77.1 and 73.7 mg/kg of samples 2 and 4, respectively), the deviations of the K-Ca and Na-Ca temperatures from the chalcedony temperature might be due to variable loss of Ca, probably through precipitation of calcite, as suggested by Ca-HCO₃ relationships (see above).

Regarding multicomponent geothermometry, the obtained SI-T curves (Figures 7-9) are very different from each other, for clinozoisite, prehnite, muscovite, and clinocllore-7A, whereas the SI-T curves of quartz, chalcedony, the two adularias, low-albite, laumontite, wairakite, heulandite, and anhydrite exhibit smaller shifts.

In all three samples, clinozoisite, prehnite, wairakite, and anhydrite do not attain the equilibrium condition within the saturation range of SiO₂ minerals. The deviation from this condition for the Ca-Al silicates could be due to variable loss of Ca and/or the fact that the SI of Ca-Al silicates is strongly influenced by the pH and partial pressure of CO₂, which are poorly defined parameters, at high temperatures, for the thermal springs. The occurrence of hydrothermal anhydrite requires SO₄ concentrations higher than those of the thermal waters of interest. These minerals are therefore poor geothermometric indicators, at least in the considered waters.

Clinocllore-7A and muscovite achieve saturation at different temperatures, either close to the quartz equilibrium temperature in some cases or at even higher temperatures in other cases. The geothermometric indications provided by these two minerals have to be considered with caution due to the variable chemistry of hydrothermal chlorites and illites.

Laumontite attains saturation close to the quartz equilibrium temperature in samples 1 and 2 and near the chalcedony saturation temperature in sample 3. Heulandite achieves saturation near the chalcedony equilibrium temperature in samples 1 and 2 and at somewhat lower temperatures in sample 3.

Low-albite, the two adularias, and heulandite (as well as, obviously, calcite in the second and third models) attain the equilibrium condition within the saturation temperatures of quartz and chalcedony. Since equilibrium with low-albite and calcite (in the second and third models) was forced and the order parameter of the two adularias was suitably chosen, the only independent geothermometric results are given by chalcedony, quartz, and heulandite. Since quartz probably overestimate the aquifer temperature below 180°C (Arnórsson et al., 1983), the results given by multicomponent geothermometry are essentially based on chalcedony and heulandite saturation, with mean values of 109.5 ± 2.0 (1s) °C for sample 1, 117.1 ± 1.5 °C for sample 2, and 87.2 ± 2.2 °C for sample 3. These temperatures are slightly lower than those given by the chalcedony geothermometer of Fournier (1977), 110, 118, and 93°C, respectively, because pH effects (and the heulandite saturation temperature) are considered in multicomponent geothermometry whereas they are neglected by the chalcedony geothermometer.

Anyway, the temperature estimated by multicomponent geothermometry and based on chalcedony and heulandite saturation are fairly consistent with those provided by chalcedony solubility, the K-Mg geothermometer, and the K-Ca and Na-Ca theoretical geothermometers for samples 1, 2 and confirm that these two thermal waters discharge from a thermal aquifer at temperature of 110-120°C, whereas sample 3 comes from an aquifer at 90-100°C.

6.3 Conceptual circulation model

By considering the chemical and isotopic composition of the waters, the geothermometric evaluations and the available geological and hydrogeological information, a conceptual circulation model is proposed for the study area (Fig. 10). Meteoric waters infiltrating through the widespread fracture network of the SSZ circulate for more than 2 km deep in the crust, namely, into the Precambrian Basement. The crustal origin of He (as indicated by the low R/R_a ratios) and the relatively high He contents in the dissolved gas phase provide further evidence for the long circulation underground. The heavier isotopic values of the rainwater sample relative to the thermal springs suggest that the recharge area may be located at higher altitudes than the sampling quote (~100 m asl). The recharge area may correspond to the hills and mountains (up to 1000 m asl) located N

and/or E of the study area (Fig. 10) towards Malawi (Fig. 2a), but this inference is poorly constrained due to the lack of an isotope-altitude relation for the study area. Meteoric waters flowing down into the crust are heated up to maximum temperatures of 110-120°C below sites 1, 2, and 4, and 90-100°C below site 3. Afterward, the heated fluids rise up towards the surface, via fractures and faults. In fact, rock permeability is mostly related to fractures and faults, which drive at the same time the meteoric water downwards and deep waters upwards, according to the position of the fluids in the convective cells.

Water-rock interaction processes at high temperature between the fluids and the metamorphic and mafic rocks control the chemical composition of the deep waters that are finally discharged from the considered thermal springs. The described hydrothermal system does not show connections with any active magmatic system but it seems to be related to a paleo-suture tectonic structure, as observed in intra-cratonic systems (Minissale et al., 2000). This hypothesis agrees with: 1) the low CO₂ concentrations and the negative d¹³C value of CO₂, 2) the isotopic value of CH₄, 3) the relatively high He contents and the low R/R_a ratios, indicating low ³He concentrations, and 4) the N₂/Ar ratio close to the meteoric value.

7. Conclusions

Mozambique is endowed with a variety of natural resources but it suffers for both improper use and extremely low access to energy in a sustainable manner. At present only 13% of the population has access to electricity. In this framework, the development of the geothermal energy, currently unexploited, may represent an important goal to contribute to economic growth of the country. Combining the results of the geochemical survey and the geological-structural and hydrogeological settings, the conceptual circulation model was defined for the Tete geothermal system. The study area, located in the northwestern part of Mozambique, is characterized by the presence of some thermal springs with temperature at the emergence up to 80°C. The main identified geothermal reservoir is hosted in the Precambrian Basement constituted by the Tete Suite and the Crystalline Basement. The fluids have a meteoric origin, as indicated by d¹⁸O and dD values, and are characterized by relatively low salinity and no-aggressive gas components. Their chemical composition is related to water-rock interaction processes with metamorphic and mafic rocks. The large convective circulation is well developed along fractures and faults, connected mainly to the Sanangoè Shear Zone. The maximum estimated temperature of the reservoir fluids ranges from 110 to 120°C below sites 1, 2, and 4, whereas the temperature below site 3 is around 90-100°C. These temperatures are related to a deep aquifer hosted in the Crystalline Basement and the Tete Suite, respectively. The heating of the fluids is connected to a slightly anomalous geothermal gradient, estimated in about 50°C/km. According to these findings and the chemical and isotopic composition of fluids, we can exclude any connection with active magmatic systems.

The above described characteristics of the Tete geothermal system (i.e., discrete permeability and circulation along fractures-faults, slightly anomalous geothermal gradient and absence of a heat source) allows one to consider it as an igneous, basement-type geothermal play *sensu* Moeck (2014) or as an unconventional geothermal system, similar to the Enhanced Geothermal Systems (EGS). The system may be exploited for several geothermal uses, both direct and indirect, such as agriculture, pasteurization, beet sugar extraction, distilled liquor and/or power generation by binary cycle or conventional flash plants (Tab. 6). In particular, the geothermal reservoir hosted into the crystalline basement could be exploited for indirect uses whereas the Tete Suite is more suitable for direct utilization. Moreover, the low salinity of the fluids and the absence of corrosive gas components could be a warranty for a long duration of eventual industrial plants established in such area.

We think that further zones could have similar features as the Zumbo area located westward from Tete city, close to the Zambia border. Additional studies should be carried out to better understand the geothermal systems of Mozambique and to allow strategic energy planning and an improvement of the energy network. The use of geothermal resources in Mozambique could greatly improve and fortify the energy distribution in the country, increasing local distribution especially in the areas in proximity to the potential geothermal fields, such as the city of Tete and its hinterland. These represent expanding areas with many factories and companies that suffer from intermittent energy distribution and that could find in geothermics a precious energy source.

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The authors declare that they have no competing interests.

Authors contributions

MP: sampling, interpretation of the chemical data, conceptualization, manuscript writing and figures' design. LM: interpretation and major contribution in writing and revising the manuscript. DC: major elements analysis, interpretation and major contribution in writing and revising the manuscript. AS: sampling, contribution in writing. PB: conceptualization and writing. TM: conceptualization and writing. FZ: sampling, conceptualization and writing. All authors read and approved the final manuscript.

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References

1. Aquater. Study for high and low enthalpy in Zambezia Province and adjacent areas of Tete, Sofala and Manica Provinces. Preliminary Geothermal Reconnaissance, S.Lorenzo in Campo, 1980, p. 16.
2. Arnórsson S, Gunnlaugsson E, Svavarsson H. The chemistry of geothermalwaters in Iceland. III. Chemical geothermometry in geothermal investigations. *Geochim Cosmochim Acta*. 1983;47:567.
3. Arnórsson S, Gunnlaugsson F. New gas geothermometers for geothermal exploration— calibration and application. *Geochim Cosmochim Acta*. 1985;49:1307–25.
4. BRGM. Project de exploration geothermique an Mozambique. Technical report, Orleans Cedex; 1980. p. 12.
5. Capasso G, Inguaggiato S. A simple method for the determination of dissolved gases in natural waters. An application to thermal waters from Vulcano Island. *Appl Geochem*. 1998;13:631–42.
6. Cerling TE, Solomon DK, Quade J, Bowman JR. On the isotopic composition of carbon in soil carbon dioxide. *Geochim Cosmochim Acta*. 1991;55:3403–5.
7. Chambal H. Energy Security in Mozambique. Series on Trade and Energy Security - Policy Report 3. International Institute for Sustainable Development; 2010. p. 28.
8. Chiodini G, Cioni R, Guidi M, Marini L. Chemical geothermometry and geobarometry in hydrothermal aqueous solutions: a theoretical investigation based on a mineral-solution equilibrium model. *Geochim Cosmochim Ac*. 1991;55:2709–27.
9. Cioni R, Marini L. A thermodynamic Approach to Water Geothermometry. Ed. Springer. 2020. doi.org/10.1007/978-3-030-54318-1.
10. Craig H. Isotopic variations in meteoric waters. *Science*. 1961;133:1702–3.
11. Deuser WG, Degens ET. Carbon isotope fractionation in the system CO₂ (gas)-CO₂ (aqueous)-HCO₃ (aqueous). *Nature*. 1967;215:1033–5.

12. Direcção Nacional de Geologia. Perspectiva sobre os trabalhos de pesquisa preliminar de energia geotermica na RPM, technical report; 1981. p. 6.
13. Favara R, Grassa F, Ingaggiato S, Pecoraino G, Capasso G. A simple method to determine the $\delta^{13}\text{C}$ content of total dissolved inorganic carbon. *Geofis Int.* 2002;41:313–20.
14. Ferro BPA, Bouman D. Explanatory notes to the hydrogeological map of Mozambique scale 1:1,000,000. Project of the hydrogeological map of Mozambique. Ministry of Construction and water. National Directorate for water affairs; 1987.
15. Fournier RO. Chemical geothermometers and mixing models for geothermal systems. *Geothermics.* 1977;5:41–50.
16. Fournier RO. Lecture on Geochemical Interpretation of Hydrothermal Waters; UNU Geothermal Training Programme: Reykjavik, Iceland. 1989;10; p. 66.
17. Gesto Energia. Renewable Energy Atlas of Mozambique, ISBN 978-989-97416-3-8, (1st Edition). 2014.
18. Giggenbach WF. Mass transfer in hydrothermal alterations systems. *Geochim Cosmochimica Acta.* 1984;48:2693–711.
19. Giggenbach WF. Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. *Geochim Cosmochim Acta.* 1988;52:2749–65.
20. Giggenbach WF, Goguel RL., Division C. Collection and analysis of geothermal and volcanic water and gas discharges. Unpublished report. New Zealand: DSIR-Petone; 1989. p. 81.
21. Gleisner M, Herbert JrRB, Kockum PCF. Pyrite oxidation by *Acidithiobacillus ferrooxidans* at various concentrations of dissolved oxygen. *Chem Geol.* 2006;225:16–29.
22. Groundwater Consultants Bee Pee. (Pty) Ltd and SRK Consulting (Pty) Ltd. Compilation of the hydrogeological map atlas: situation analysis Report for the SADC Region. Annex G. 2002.
23. GTK Consortium. Geology of Degree Sheets Inhamambo, Maluwera, chifunde, Zumbo, Fíngoè-Mâgoè, Songo, Cazula and Zóbuè, Mozambique. Direcção Nacional de Geologia (DNG), Maputo. 2006;4; pp.382; sheets 1430-1432 and 1530-1534.
24. Hankins M. A renewable energy Plan for Mozambique. Lori Pottinger, editor, 2009. p.60.
25. Hatton W, Fardell A. New Discoveries of coal in Mozambique - Development of the coal resource estimation methodology for International Resource Reporting standards. *International Journal of Coal Geology.* 2021; 89;2-12.
26. Inguaggiato S, Rizzo A. Dissolved helium isotope ratios in ground waters: a new technique based on gas-water re-equilibration and its application to a volcanic area. *Appl Geochem.* 2004;19:665–73.
27. IRENA. Mozambique. Renewables readiness assessment 2012. pp.73.
28. Langmuir D. Aqueous Environmental Geochemistry. Upper Saddle River: Prentice Hall; 1977. p. 600.
29. Mamyrin BA, Tolstikhin IN. Helium isotopes in nature. Amsterdam: Elsevier; 1984.
30. Martinelli G, Dongarrà G, Jones MQW, Rodriguez A. Geothermal features of Mozambique – country update. *Proc. World Geothermal Congress, Florence, Italy.* 1995;251-261.
31. Marty B, Jambon A. $\text{C}/^3\text{He}$ in volatile fluxes from the solid earth: implications for carbon geodynamics. *Earth Planet Sci Lett.* 1987;83:16–26.
32. Mc Nitt JR. The United Nations approach to geothermal resource assessment. *Geothermics.* 1978;7:231–42.
33. Mc Nitt JR. The Geothermal Potential of East Africa. Nairobi: UNESCO/USAD Geothermal Seminar; 1982. p. 9.
34. Michard G. Modification de la répartition des espèces chimiques lors du refroidissement d'une eau thermale. *CR Acad Sci II.* 1977;284:949–52.
35. Michard G, Roekens E. Modelling of the chemical composition of alkaline hot waters. *Geothermics.* 1983; 12;161–169.
36. Minissale A, Vaselli O, Chandrasekharam D, Magro G, Tassi F, Casiglia A. Origin and evolution of 'intracratonic' thermal fluids from central-western peninsular India. *EPSL.* 2000;181:377–94.
37. Moeck IS. Catalog of geothermal play types based on geologic controls. *Renew Sustain Energy Rev.* 2014;37:867–82.
38. Mokveld K, Von Eije S Final Energy Report Mozambique, Ministry of Foreign Affairs. 2018.

39. Mook WG, Bommerson JC, Staverman WH. Carbon isotope fractionation between dissolved carbonate and gaseous carbon dioxide. *Earth Planet Sci Lett.* 1974;22:169–76.
40. Moses CO, Nordstrom DK, Herman JS, Mills AL. Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. *Geochim Cosmochim Acta.* 1987;51:1561–71.
41. Moses CO, Herman JS. Pyrite oxidation at circumneutral pH. *Geochim Cosmochim Acta.* 1991;55:471–82.
42. Nordstrom DK. Thermochemical redox equilibria of ZoBell's solution. *Geochim Cosmochim Acta.* 1977;41:1835–41.
43. Nordstrom DK, Plummer LN, Wigley TML, Wolery TJ, Ball JW, Jenne EA, Bassett RL, Crerar DA, Florence TM, Fritz B, Hoffman M, Holdren GR, Lafon GM, Mattigod SV, McDuff RE, Morel F, Reddy MM, Sposito G, Thrailkill J. A comparison of computerized chemical models for equilibrium calculations in aqueous systems. In: Jenne EA, editor. *Chemical modeling in aqueous systems*, ACS symposium series. 1979;93:857–892.
44. Parkhurst DL, Appelo AAJ. User's guide to PHREEQC (version 2)-a computer program for speciation, batch-reaction, one dimensional transport and inverse geochemical modeling. U.S.G.S. Water Res. Inv. Rep. 1999;99–4259.
45. Pekkala Y, Lehto T, Mäkitie H. GTK Consortium Geological Surveys in Mozambique 2002–2007. Geological Survey of Finland, Special Paper, 2008. p. 321.
46. Power A. 2018. https://www.usaid.gov/sites/default/files/documents/1860/Mozambique_-_November_2018_Country_Fact_Sheet.pdf last access August 31th 2021.
47. Procesi M, Sciarra A, Cinti D, Quattrocchi F, Zarlenga F. Mozambique and the Feasible Development of the Geothermics – a First Geochemical Survey. Melbourne: WGC; 2015.
48. Reed M, Spycher N. Calculation of pH and mineral equilibria in hydrothermal waters with application to geothermometry and studies of boiling and dilution. *Geochim Cosmochim Acta.* 1984;48:1479–92.
49. Rozanski K, Araguas-Araguas L, Gonfiantini R. Isotope patterns of precipitation in the East African region. In: Johnson T, Odada EO, editors. *Limnology, Climatology and Palaeoclimatology of the East African Lakes*. Amsterdam: Gordon and Breach Publishers; 1996. pp. 79–94.
50. Schoell M. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim Cosmochim Acta.* 1980;44:649–61.
51. Steinbruch F, Merkel BJ. Characterization of a Pleistocene thermal spring in Mozambique. *Hydrogeol J.* 2008;16:1655–68.
52. Tonani FB, Nagao K, Moore J, Natale G, Sperry T. Water and gas geochemistry of the Cove-Fort Sulphurdale geothermal system. In: *Proceedings, twenty-third workshop on geothermal reservoir engineering*. Stanford University, Stanford, California, 1998.
53. Truesdell AH, Fournier RO. Procedure for estimating the temperature of a hot water component in mixed water using a plot of dissolved silica vs. enthalpy. *J Res USA Geol Surv.* 1977;5:49–52.
54. United Nations. African hydrogeology, Mozambique. Department of Technical Co-operation for Development; 1989.
55. Westerhof AB, Lehtonen MI, Mäkitie H, Manninen T, Pekkala Y, Gustafsson B, Tahon A. The Tete-Chiapata Belt: A new multiple terrane element from western Mozambique and southern Zambia. GTK, Consortium Geological Surveys in Mozambique 2002-2007, edited by Geological Survey of Finland. 2008a; 48;145-166.
56. Westerhof AB, Tahon A, Koistinen T, Lehto T, Akerman C. Igneous and Tectonic setting of the allochthonous Tete gabbro-anorthosite suite, Mozambique. GTK, Consortium Geological Surveys in Mozambique 2002-2007, edited by Geological Survey of Finland. 2008b;48;191-210.
57. Whitfield M. Activity coefficients in natural waters. In: ed. Pytkowicz RM. *Activity Coefficients in Electrolyte Solutions*. Boca Raton: CRC Press; 1978. pp. 153–300.
58. Williamson MA, Rimstidt JD. Correlation between structure and thermodynamic properties of aqueous sulfur species. *Geochim Cosmochim Acta.* 1992;56:3867–80.
59. Williamson MA, Rimstidt JD. The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. *Geochim Cosmochim Acta.* 1994;58:5443–54.

60. Zaporozec A. Graphical interpretation of water-quality data. *Ground Water*. 1972;10:32–43.
61. Zhang J, Quay PD, Wilbur DO. Carbon isotope fractionation during gas-water exchange and dissolution of CO₂. *Geochim. Cosmochim. Acta*. 1995;82:161–73.

Tables

Table 1: Typology of renewable resources in Mozambique, location and estimated energy potential (from IRENA, 2012; Mokveld and Von Eije, 2018.).

RESOURCES	SITES	ENERGY POTENTIAL
Hydro	Zambezi Valley & other sites	19 GW (small Hydro >1000 MW)
Biomass	Countrywide	2GW
Solar	Countrywide	2.7 GW (1,785÷2,206 kWh/m ² /year)
Wind	Coast & Niassa Provinces	4.5 GW Speed 7m/s (>7 m/s in some areas)
Geothermal	Tete, Niass, Manica & Zambezia Provinces	Conservative estimate of 25 MW

Table 2: Summary of Mozambique aquifers (modified from Groundwater Consultants Bee Pee (Pty) Ltd and SRK Consulting (Pty) Ltd ,2002).

AQUIFER SYSTEM	OCCURRENCE	LITHOLOGY	PERMEABILITY
Post-Karoo Formation	Most of southern part of the Country.	Sandstones, limestones, conglomerates and alluvial deposits.	Low productivity in sandstone formations. High salinity waters (TDS up to 8500 mg/l). High yields in limestones (50-120 m ³ /h) and alluvial plains (up to 200 m ³ /h).
Karoo Formation	Limpopo, Rovuma and Zambezi valley.	Clastic sedimentary units, basalts and rhyolites.	Low yields (average 1.5 m ³ /h) and very saline waters (TDS up 7000 mg/l).
Basement Complex	North and Centre of the Country	Metamorphosed and intrusive rocks.	1 to 2 m ³ /h occasionally up to 6 m ³ /h. Fractures and faults may increase yields to 40-70 m ³ /h.

Due to technical limitations, table 3 is only available as a download in the Supplemental Files section.

Table 4. Geothermometric results (°C) for the analysed thermal waters of the Tete area.

Sample	Site	Outlet T	T_chc	T_qz	T_K-Mg
1	Nhawóndòc	66	110	136	119
2	Tenta	52	118	144	112
3	Mauira	42	93	121	153
4	Niaondive	80	108	135	113

Sample	Site	T Na-K (Z=1)	T Na-K (Z=0)	Z _{Adl}
1	Nhawóndòc	210	92	0.132
2	Tenta	132	27	0.848
3	Mauira	210	93	0.012
4	Niaondive	167	55	0.422

Sample	Site	T K-Ca,Czo	T K-Ca,Prh	T K-Ca,Lmt	T K-Ca,Wrk
1	Nhawóndòc	115	62	72	153
2	Tenta	127	91	90	154
3	Mauira	138	82	99	173
4	Niaondive	124	79	85	156

Sample	Site	T Na-Ca,Czo	T Na-Ca,Prh	T Na-Ca,Lmt	T Na-Ca,Wrk
1	Nhawóndòc	116	4	18	171
2	Tenta	134	46	30	177
3	Mauira	174	64	105	208
4	Niaondive	137	36	41	183

Table 5: Saturation temperatures indicated by multicomponent geothermometry for the three different models applied to samples 1 from Nhawóndòc, sample 2 from Tenta, and sample 3 from Maiura. Values within brackets are considered poorly reliable.

Sample	Model	Albite-low and adularia	Calcite	Chalcedony	Clinochlore	Heulandite	Laumontite	Muscovite	Quartz
1	1	110	-	105.7	-	110.9	(129.1)	121.9	121.3
1	2	110	110	109.4	120.7	110.1	125.4	(138.9)	125.1
1	3	110	110	109.8	(144.9)	111.3	(129.3)	(149.0)	125.6
2	1	118	-	114.2	-	117.6	-	120.7	130.4
2	2	118	118	117.7	-	117.1	133.3	134.1	133.8
2	3	118	118	118.3	-	117.8	135.5	-	134.5
3	1	93	-	88.5	-	85.6	92.2	-	102.6
3	2	93	93	89.1	-	84.5	88.8	-	103.2
3	3	93	93	89.9	-	85.7	92.0	-	104.1

Table 6: Features summary of the potential geothermal system located in the Tete area.

Main Geothermal Reservoir	Geological Formation	Thickness (m)	Permeability	Estimated temperature (°C)	Type of geothermal system	Chemical features of the fluid	Potential use of the resource
Precambrian Basement	Tete Suite	1500÷2000	Secondary permeability related to fractured-faulted rocks and dikes	90÷100	Igneous, basement-type geothermal play <i>sensu</i> Moeck (2014) or unconventional Geothermal System (e.g. Enhanced Geothermal System-EGS)	- Na-Cl - low TDS - no corrosive gas	Direct Use: livestock farming, agriculture, pasteurization, beet sugar extraction, distilled liquor, lumber, ecc.
	Crystalline basement	>2000		110÷120		phases	Indirect Use: power generation by binary cycle and/or conventional flash plants.

Figures

Figure 1

Distribution of potential renewable resources in Mozambique.

Figure 2

A) Simplified geological map of Mozambique (modified from United Nations, 1989). Temperatures of the thermal springs reported by Martinelli et al. (1995) and the new sampled springs are also shown; B) Zoom of the study area, the detailed geological background is modified from GTK Consortium (2006). * The profile of the conceptual circulation model is shown in fig 10; C) Simplified stratigraphy of the investigated area.

Figure 3

a-b: K-Na-Ca (a) and SO₄-Cl-Alk_C (b) ternary diagrams for the samples Nhawóndòc (#1), Tenta (#2), Mauira (#3) and Niaondive (#4). The concentrations are expressed in equivalent units.

Figure 4

Binary diagram Cl vs. SO₄ + Alk_C for the samples Nhawóndòc (#1), Tenta (#2), Mauira (#3) and Niaondive (#4) (iso-Eq lines from Tonani et al., 1998).

Figure 5

δD - $\delta^{18}O$ scatter plot for the sampled waters. The solid and the dashed lines delineate the isotopic domain for Global Meteoric Waters ($\delta D = 8\delta^{18}O + 10$; Craig, 1961) and that for regional precipitations (Rozanski et al. 1996), respectively.

Figure 6

Ar-N₂-He ternary diagram for the sampled waters. ASW=air saturated water at 20°C.

Figure 7

Saturation Index vs. temperature diagrams for the sample 1 (Nhawóndòc) and considering the models 1-3.

Figure 8

Saturation Index vs. temperature diagrams for the sample 2 (Tenta) and considering the models 1-3.

Figure 9

Saturation Index vs. temperature diagrams for the sample 3 (Mauira) and considering the models 1-3.

Figure 10

Conceptual Circulation Model for the Tete area. The trace of the geological section and the relative geological map are shown in fig.2b.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [AppendixA.docx](#)
- [Table03.docx](#)