

GEOCHEMICAL CHARACTERISTIC OF THE ANALAVORY ITASY GEOTHERMAL PROSPECT: ADDITIONAL REPORT

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Abstract

Springs from Analavory are geothermal waters which have undergone a complete cooling during their way towards the surface. Chemical analysis at emergence show that they are, at depth, anoxic, oversaturated with respect to CO₂ and calcium carbonates. A considerable variation in the chemical composition of the springs is noted. Fluids from volcanic area of Itasy (magmatic-associated system) have higher Na, K and Cl concentrations and have lower Mg and Ca concentrations compared to their extensional counterparts. These differences are observed in spite of the fact pH and conductivity. Outgassing and oxygen input at the surface are the main parameters which allow to explain the observed composition. Applying silica and cation geothermometers lead to an estimation of about 154°C in the deep geothermal reservoir.

Keywords : *Thermal spring, carbonates geochemistry, geothermometers, Madagascar.*

1) INTRODUCTION

In Madagascar, the energy produced by hydroelectric plants does not meet the needs of the entire country. The use of fossil energy based on combustion reactions produces a very large quantity of greenhouse gases. The Ministry of Energy should be responsible for promoting the production of clean energy (wind, biomass, solar, geothermal, etc.). Geothermal energy is one of the cleanest, most accessible and cheapest (in terms of direct use) alternative energies in the world.

A reconnaissance thermal spring exploration work was done from 1927 to 1968 and most of collected samples were analyzed by the Geological Survey of Madagascar (Besairie, 1959a and 1959b). In 2008, research work carried out by "GNS Science" Company, led by Dr. Colin Harvey was undertaken. They focused their work on reconnaissance studies of geothermal features and young volcanoes, as well as the possibilities of using geothermal energy in Madagascar. In 2010, other research work by Andrianaivo & Ramasiarino titled " Geochemical Characteristics of Thermal Springs in Volcanic Areas of Antsirabe-Itasy, Madagascar: Preliminary Results" has been carried out.

Faced with the energy problem in Madagascar, the geothermal prospect of Analavory Itasy is proposed in this study. The aim of this paper is to understand the geochemical characteristic, to study the processes that explain the physico and chemical composition of these waters, such as:

- Reinterpretation of the ancient result analysis and interpretation the recent effect
- Possibility of using the result as tool to aid decision and to help identify productive reservoir (production wells, capacity, nature of the waters, depth and subsurface temperature) to be developed.

2. MATERIAL AND METHOD

2.1 GEOLOGICAL AND GEOTHERMAL CONTEXT OF MADAGASCAR

Geological context: Madagascar lies in the East African Rift region, a geologically active zone that stretches across several East African, which explains the frequent geothermal activity in these regions. With a

highly varied geology, including coastal sedimentary formations and volcanic deposits, the island is indeed marked by sustained geological activity, characterised by phenomena such as tectonic movements, the presence of volcanoes, geological faults and various earthquakes. In addition, the divergent movements of the tectonic plates encourage the formation of faults and fractures in the crust, allowing groundwater to circulate and be heated by the nearest magma. Hence the presence of underground heat reservoirs is possible, creating exploitable sources of geothermal energy

Geothermal context

Several geothermal studies have been carried out in the country since the 1960s [1], focusing mainly on exploration and demonstrating that the Big Island is rich in hot springs and thermal waters, but little major progress has been made on exploitation to date. Generally speaking, the distribution of thermal springs, heat flow and the nature of geothermal reservoirs in Madagascar are controlled by its geological structures, and are therefore divided into three main sections: the volcanic basement, the tectono-metamorphic basement and the sedimentary basins:

- The medium to high enthalpy geothermal zone, mainly linked to fossil magmas;
- The low- to medium-enthalpy geothermal zone, dominated by fossil magmatic fluids and/or along graben boundary faults;
- The low-enthalpy geothermal zone, dominated by sedimentary fluids.

In Madagascar, there are several signs of the presence of geothermal resources, such as volcanoes, geysers, hot springs, travertine mounds, seeps, weathered ground and sinter silica deposits. About 117 springs throughout the island are recognised. The geothermal waters recorded are mostly of the carbonated type, sometimes sulphated but rarely chlorinated, under the influence of volcanic activity and local geochemical conditions. They are rich in carbon dioxide, diluted and saturated with calcite. A partial knowledge of the physico-chemical characteristics of these waters will enable us to estimate the temperatures at depth [Andrianaivo [2].

2.2. METHODS FOR GEOCHEMICAL CHARACTERISTIC OF THE ANALAVORY ITASY GEOTHERMAL PROSPECT

Thermal springs or surface features can serve as a critical tool for evaluating a resource.

2.2.1. Presentation of the site

The geographical coordinates the field geothermal Analavory Itasy area are: 18° 55.562' S: 46° 38.410' E, Altitude: 950 m.

The site is located on the Precambrian basement consisting of gneiss and migmatite granit, locally covered with rocks basaltic and trachytic witnesses of the volcanism that affected the region between the Cenozoic and Quaternary.

2.2.2 Equipment and methods

The strategies of sampling used pH, Conductivity, measurement (Ca, Mg, K, Na, Cl, Fe, Li, B, Si). So with limited measuring equipment, only the following were measured in situ:

- temperature connected to the pH meter.
- conductivity using a conductivity meter. It delivers values in scale 0 to 1999 $\mu\text{S}/\text{cm}$. The measured conductivities being greater than this value, the samples S1 and S2 were precisely diluted five times with demineralized water (conductivity of 1 $\mu\text{S} / \text{cm}$) to obtain measurements in the scale of the device.
- pH was measured at ± 0.02 units using a pH meter and a combined electrode after calibration with two buffer solutions (pH 4.01 and pH 7.00).

The temperature, conductivity and pH were measured immediately after recovery of the sample which was stored in two 50 ml bottle fully filled without gas bubbles. Groundwater was also withdrawn from a well to use for witnessed sampling (fig 1).



Fig 1: Analavory geyser

3. RESULTS LABORATORY MEASUREMENTS

The relative concentrations of Na, K, Ca-Mg, (in mg/l) are reported in table 1. The values from the results of analyze carried out in the laboratory and other element concentration (Li, Fe, B, Si) are used.

Table1: The chemical compositions of waters from Itasy region : (concentration $\mu\text{mol/L}$)

Sample	T °C	pH	Conductivity $\mu\text{S} / \text{cm}$	Na	K	Ca	Mg	Li	Fe	B	Si
S1	28	6.43	6751	26936	1254	26493	450	149	225	83.7	2161
S2	27	6.70	6342	24787	1148	26931	163	134	263	82.4	1941
Reference sample	21	6.64	246	527	416	426	385	0	0	0	276

The chemical composition of water is studied in terms of relative concentrations of Na+K, Ca and Mg. The content is (Na+K) is much higher than that of Ca and Mg. the thermal waters of Analavory-Itasy are sodium.

The precipitations of solids (travertines) from the waters of the cold geysers of Analavory are visible at the evidence on the ground and cover the local rocks in the vicinity of the springs.

The table 2 represent the geochemical analysis, calculated subsurface temperature by geothermometer and characteristics of Madagascar's geothermal zones.

Table 2 : Characteristics of Madagascar's geothermal zones

Region	North		Centre West and South		West	
Location	Ambilobe	Ambanja	Itasy	Antsirabe	Miandrivazo	Morondava
Geological environment	Fault : boundary of a graben	Graben	Volcanic		Fault : boundary of a graben	Sédimentary
Heat source	Shallow Moho	Shallow Moho and magma chamber	Shallow Moho and magma chamber		Shallow Moho	Shallow Moho
Physical state of the mobile fluid phase	Dominated by liquid					
Enthalpy of the	Moderate				Low	

fluid						
Temperature of thermal springs (°C)	47-78	48-72	24-57	38-57	30-55	39-42
Temperature of geothermal reservoirs (°C)	140-180	140-200	170-240	150-240	140-170	120-140
Chemical composition of fluids	Moderate to high CO ₂ content ₂ (200-1000 ppm) and low Cl content (< 300 ppm)		High levels of CO ₂ (1000-4000 ppm) and Cl (400-500 ppm)		Low CO content ₂ (< 200 ppm) and moderate Cl content (500-1200 ppm)	

The presence of volcanoes in several regions, as well as tectonic activity, has highlighted numerous geothermal zones of interest in terms of low and medium enthalpy. Priority areas for further investigation include Antsirabe and Itasy, followed by the North and West.

Initial findings showed high temperatures and promising geothermal resource indices. The results indicate that the geothermal activity in three favourable zones is linked to the volcanic and tectonic contexts of the formations, resulting in a higher heat flux than the surrounding Precambrian crust. Chemical analyses of thermal springs were used to estimate sub-surface temperatures in geothermal systems with the following characteristics.

4. DISCUSSION

The Analavory geothermal field (Itasy, Miarinarivo) is a well-known site in Madagascar. The difference hot geysers, Icelandic or North American, Analavory's carbon springs are "geysers" cold" [1], the water temperature is practically identical to the ambient temperature and the pulsation of the sources is provided by irregular releases of CO₂ that can project water to heights variables from 0.3 to 3 m above the ground.

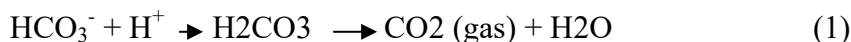
4.1. Geochemical evolution of waters

Examination of the analysis table 2 clearly shows that the S1 and S2 samples differ essentially on the following measured quantities:

- pH
- conductivity
- alkalinity
- concentrations of calcium, magnesium and dissolved iron

4.2. Variations in conductivity

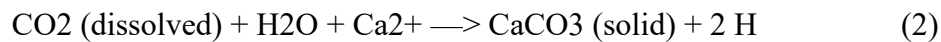
The S1 was taken directly from an emergence (Figure 2) while sample S2 was taken from a natural channel formed from the S1 source and located about ten meters downstream. Despite the shortness of this surface journey water has time to lose CO₂, which may explain both the decline conductivity and pH increase. Indeed, the dissolved CO₂ passes into the gaseous state following the chain of reactions:



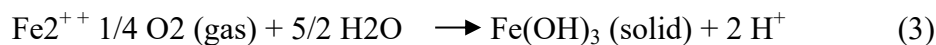
The precipitation of carbonates at the emergence of S1 and during the runoff (S2) that removes ions from water, Ca²⁺, Mg²⁺, Fe²⁺ and CO₃²⁻ is responsible for these variations 'conductivity.

4.3 Variations in alkalinity and precipitation of carbonate phases

The precipitation of ferric carbonates and oxyhydroxides is evident when deposits are observed neofomed minerals (travertines) on rocks in the immediate environment of carbo-gaseous sources. The attack of travertine by a highly concentrated acid (HCl 30%) leaves no visible solid residue. It can therefore be said that it is indeed a mixture of calcium and magnesium carbonates as well as ferric oxy-hydroxides. The precipitation processes of these solids can be described simply by the following reactions:



The calcium carbonate formed may be calcite and / or aragonite, as for magnesium present in water, it does not give its own mineral phase but very partially replaces the Ca^{2+} ion in the rhombohedral network of calcite to give a magnesium calcite. The other process concerns the dissolved iron. The waters, whose undeniably hydrothermal character we will demonstrate below, contain iron dissolved in the state of ferrous ion Fe^{2+} or soluble complexes of this species: ($\text{Fe}(\text{OH})^+$, $\text{Fe}(\text{OH})_2^0$, FeSO_4^0). Indeed, hydrothermal waters, given their deep origin, are anoxic. Under these conditions, leaching from host rocks can release soluble $\text{Fe}(\text{II})$ from ferromagnesian minerals (olivine, pyroxenes, amphiboles, micas etc.). This dissolution is all the faster as the temperature is high. At emergence, in contact with oxygen in the air, oxidation of $\text{Fe}(\text{II})$ insoluble $\text{Fe}(\text{III})$ soluble is immediate:



This oxidation leads to the appearance of orange-colored amorphous phases. Reactions (2) and (3) are responsible, a priori, for significant variations in the chemical composition of the water from its initial state (S1 and S2).

4.4 pH Variation

The observed pH increases correspond to a decrease in the concentration of the H^+ ion by 3.4×10^{-7} and 1.4×10^{-7} mol/L for S1 and S2, respectively. This apparent contradiction with Reactions (2) and (3), which indicate an increase in H^+ concentration and a decrease in pH, is only apparent. This is because Reactions (2) and (3) occur simultaneously with Reaction (1), which partially removes H_2CO_3 from the solution, logically leading to an increase in pH.

5 Geothermal Potentiality of Analavory

5.1. The hydrothermal origin of the springs

The hydrothermal origin of the Analavory springs is a subject of controversy as they are considered cold geysers, i.e., waters of « phreatic » type that have simply come into contact with carbon dioxide gas during their underground journey, a relic of past volcanic activity from the Cenozoic era (66 Ma) to the Quaternary period (8,000 years for the lava flow that formed Lake Itasy by damming the river) [5]. However, an examination of the chemical composition of S1 leaves no doubt about the deep origin of the Analavory springs. A simple comparison with the analysis of phreatic water sampled from a well near the site shows that (Table3): The ionic concentrations of all major elements are consistently higher in the « geysers. » The difference is remarkable for dissolved silica, boron, and lithium; these last two elements, present in S1 and S2, are below the detection limit in the phreatic water.

Table 3: Temperature and composition of different springs

Springs	T °C	Si	Na	Ka
S1	28,2	2161	26936	1254
Ranovisy	37.1	2930	60000	4440
Visy Gasy	27.8	2150	34400	2520
Reference sample	21	276	527	416

The examination of Table 3 clearly shows that the chemical composition of the Analavory springs cannot be explained by a simple dissolution of CO_2 in phreatic water. It is therefore legitimate to attempt to estimate the geothermal potential of the Analavory springs using « geothermometers, » which provide fairly accurate information about the temperature of the deep reservoir.

5.2 Geothermometers result.

A geothermometer is a tool based solely on the measurement of the chemical composition of hydrothermal waters. They were developed in the 1970s following the first oil crisis, which prompted countries to explore alternative energy sources to fossil fuels such as coal, oil, and gas. Geothermometers have been the subject of numerous articles [7][8]. There are two main categories:

- Silica geothermometers

- Cation geothermometers

The purpose of the geothermometer is to estimate the temperature at depth, given by the concentrations of substances dissolved at the surface. This method assumes that concentrations at depth are preserved as waters flow over the surface, and measures the degree to which substances were in equilibrium at depth.

5.2.1. Silica Geothermometers

They are all based on the fact that the solubility of silica (SiO_2) increases rapidly with temperature. The presence of silica in all deep rocks of the Earth's crust, whether magmatic (granite) or volcanic (basalt), gives these geothermometers universal applicability. Furthermore, the existence of the geothermal gradient raises the temperature of rocks and water circulating in fractures, resulting in exponentially increased rates of water-rock interactions. This leads to the hypothesis that at depth, these interactions are in thermodynamic equilibrium.

Silica geothermometers assume as a basic postulate that the reaction:



The equilibrium constant of Reaction (13) can be expressed as a function of temperature using an expression of the form:

$$\text{Log}(\text{H}_4\text{SiO}_4) = a/T + b \quad (5)$$

While quartz is the stable form of silica at high temperatures, there are many allotropes stable at lower temperatures, the most common being chalcedony and amorphous silica. For each variety, the coefficients a and b in equation (5) have the following values (table 4) [8]:

Table 4: coefficient a, b mineral temperature

mineral	a	b
Silica	-1322	0,435
Chalcedony	-1015	-0,11
Amorphous silica	-731	-0,26

The conditions that need to be met for Equation (5) to provide a realistic temperature are as follows:

- The ascent of hot water to the surface through a network of fractures must be rapid. If this is not the case, the equilibrium (4) established at depth is not preserved because the water, on one hand, cools down, and on the other hand, it has time to equilibrate with the rocks it encounters during its ascent to the surface. The temperature of the deep reservoir will be underestimated.
- The thermal water should not undergo significant mixing with subsurface phreatic waters. This would dilute the dissolved silica acquired at depth and underestimate the temperature of the geothermal reservoir.

Table 5 below provides the calculated deep temperatures for S1/S2 using Equation (5):

Sample	Si $\mu\text{mol/L}$	Silica T °C	chalcedony T °C
S1	2161	154	123
S2	1941	146	117

Therefore, we will estimated a temperature range of 121 to 154 °C. These results can be compared to the calculated temperatures for the hottest sources in the Antsirabe geothermal field [6], which fall within the range of 135-170 °C (table 6).

6-2-2. Cation geothermometers

They are based on the existence of water-mineral equilibria at high temperatures in deep geothermal reservoirs. The cations involved in these equilibria are primarily sodium (Na^+) and potassium (K^+). Other, less commonly used geothermometers involve calcium (Ca^{2+}), lithium (Li^+), and magnesium (Mg^{2+}) [7].

The Na-K geothermometer is the most commonly used geothermometer, and its principle is based on the equilibrium between two minerals that are abundant in granitic rocks: potassium feldspar KAlSi_3O_8 and sodium plagioclase (albite) $\text{NaAlSi}_3\text{O}_8$. The equilibrium involves an ion exchange between the two solids:



The equilibrium constant can be written as:

$$K(T) = (\text{Na}^+)/(\text{K}^+) \quad (7)$$

For all springs, the Na-K-Ca geothermometer calculations show globally elevated temperature (more than 200°C) and indicate a higher temperature than the silica geothermometers (Table 6). This method assumes that the water contains dissolved elements in equilibrium with aluminosilicate minerals such as feldspars that contain Na, K and Ca [7]. Thermal waters have relatively higher amounts of Na and K, two elements which would be produced from dissolution of volcanic glasses which are common in the studied areas. However, there are other sources of these elements; in particular, clay in the sedimentary basin fill material in the Antsirabe area. Then, since the samples were collected in close proximity to a salt flat, the concentrations of Na, K, and Ca are likely to be unrelially high. Thus, the Na, K and Ca content of water springs in the studied area have elevated sulfate content compared to other geothermal systems worldwide [6].

Table 6: Estimated temperature of geothermal reservoir for the Antsirabe-Itasy thermal waters (Temperature in °C, nd: not determined). [3]

No.	$T_{\text{Na-K-Ca}}$	T_{quartz}	$T_{\text{amorphous silica}}$	$T_{\text{chalcedony}}$	$T \Delta^{18}\text{O}$ (SO ₄ -H ₂ O)
1*	252	158	36	134	nd
2*	244	165	42	142	nd
3	221	154	32	129	nd
4*	249	151	29	125	nd
5	215	154	32	129	nd
6*	248	156	34	132	nd
7	222	157	35	132	137
8*	255	154	32	129	nd
9*	253	165	42	142	nd
10	220	161	38	137	nd
11*	265	140	19	114	nd
12*	195	154	32	130	nd
13	240	132	12	105	nd
14	135	117	-1	88	nd
15	185	104	-12	75	nd
16	227	171	48	149	140
17	176	151	30	126	129
18	166	154	32	129	nd
19	169	149	28	124	149
20	174	121	2	92	152
21	151	141	20	115	nd
22	138	136	16	109	nd
23	144	126	7	98	nd

Compared with quartz geothermometer, the chalcedony geothermometer display relatively lower reservoir temperatures between 75 and 149°C. Since chalcedony, rather than quartz, controls silica saturation at temperatures less than 180°C (Fournier, 1991), it appears that the chalcedony geothermometers better reflect the reservoir temperatures for the Antsirabe -Itasy field, but this is further checked with cation geothermometers. If the chalcedony temperature values are not in the accepted 140-180°C temperature range for this geothermometer, they are also unlikely to be accurate. But the values from Ranomafana II site N^o.2 (142°C), Ranovisy site N^o.9 (142°C) and Sahasarotra site N^o.16 (149°C) (table 6) have relatively low geothermal potential. It is also of interest to note that cold springs (e.g. Amparakly site No.20) can provide anomalous geothermometer

temperatures indicating a geothermal resource, and that sampling of cold springs can be used as an exploration tool in areas with no surface expression of geothermal systems.

The negative temperatures given by the amorphous silica geothermometer are clearly incorrect. Since the 140°C temperature range corresponds to the amorphous silica geothermometer, the amorphous silica geothermometer equation was considered. Because most of surface temperatures of thermal springs (in the range 26 to $58^{\circ}\text{C}</math>) are lower than those of calculated by the amorphous silica geothermometer considered as in equilibrium at depth, this method may not be applicable.$

CONCLUSION

This geochemical study provides a better understanding of the physicochemical mechanisms that account for the evolution of the « cold geysers » in Analavory when they come into contact with the atmosphere. We have also clearly demonstrated the hydrothermal nature of these waters. They originate from a deep geothermal reservoir and are not simply surface waters that have dissolved « relic » CO_2 from ancient volcanic activity. At most of the sites, it seems that the waters are not fully equilibrated, and hence, quartz, amorphous silica and Na-K/Ca geothermometer used in this research are approximately unreliable; however the $\Delta_{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$ temperatures and chalcedony temperature values seem more reasonable. In summary, the geothermal waters of the Analavory Itasy areas, have temperature in the range 120 to $154^{\circ}\text{C}</math>. This conclusion is not especially helpful in determining whether or not the studied areas contain exploitable resource. This additional evaluation of geothermometer temperatures indicates that these areas have relatively low to medium geothermal potential; however, possible mixing and re-equilibration at lower, near surface temperatures needs to be evaluated at some of the sites. For the future works, further investigation based mainly on thermal gradient drilling, geophysical and geological explorations, is necessary to determine the geothermal resource potential of selected sites (resource assessment) and to help identify if they have commercial reservoirs. These steps are of fundamental importance to the successful implementation of geothermal energy as a viable source of energy in Madagascar.$

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