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Geochemical characteristics of the main high-temperature geothermal fluids presently known in the Caribbean islands

– Final report –

BRGM/RP-72352-FR

Final version – 16 March 2023

Bernard Sanjuan*, Romain Millot*, Marie-Lise Bernard, Christelle Dixit****

*BRGM, **LARGE laboratory, University of Antilles

Checked by:		**Approved by:**	
Name :	Frédérick Gal	Name :	Ywenn De La Torre
Function :	Geochemist	Function :	Guadeloupe Regional Director
Date :	26/03/2020	Date :	31/03/2023
Signature :		Signature :	

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Keywords: Caribbean area, Guadeloupe, Martinique, Dominica, Montserrat, Saint Lucia, geothermometer, geothermal waters, geochemical data

This report should be cited as follows :

Bernard Sanjuan*, Romain Millot*, Marie-Lise Bernard, Christelle Dixit** (3)** – Geochemical characteristics of the main high-temperature geothermal fluids presently known in the Caribbean islands. BRGM/RP-72352-FR final report, 68 p., 26 Fig., 4 Tab.

Synopsis

This study with a duration of three years (2020-2023) has been carried out within the framework of the Work Package WP4 (Geothermal energy) of the INTERREG V Energy Transition in the Caribbean (ETC) program and has been financially supported by European Union and BRGM.

The Caribbean islands, that are part of the Lesser Antilles volcanic arc such as Guadeloupe, Martinique, Dominique, Montserrat or Saint Lucia, must face the fragility of their energetic system and environment, given their insularity. However, these territories, which are home to young volcanic systems, possess a huge potential for power generation from high-temperature (HT) geothermal energy. These territories are experiencing an increase in energy costs and CO_2 emissions. Geothermal energy is a promising energy source that is essential for them to hope to achieve energy self-sufficiency. Unlike most of other renewable energies, geothermal energy is continuously available for electricity production, is cheaper than fuel-based technologies, can also be used for thermal applications such as cooling, drying uses for agriculture, aquaculture, spa centres and could contribute to create jobs directly and indirectly. However, so far, geothermal energy has remaining difficult to develop in these islands.

Indeed, even though the first exploration works have been carried out in the 1970s in some of these territories, the Bouillante HT (260°C) geothermal power plant in Guadeloupe, exploited since 1986, is currently the unique example of electricity production in the Caribbean area. With two production units (total capacity of 15 MWe) since 2005, its present annual power production is close to 110 GWh and accounts for about 5-6% of the island’s needs. If in the past, some deep wells drilled in the Saint Lucia and Martinique islands had to be abandoned and closed (for their low flow-rates and corrosive fluids in Saint Lucia and their low temperature in Martinique), new exploration works carried out in most of these islands suggest promising geothermal developments.

The main objectives of this report are to present, for the first time:

- the main geochemical characteristics of the deep fluids from the geothermal wells and some thermal springs existing in the Guadeloupe, Martinique, Dominica, Montserrat and Saint Lucia islands;
- the application and test of new auxiliary chemical thermometric relationships such as Na-Li, Na-Rb, Na-Cs, K-Sr, K-Fe, K-Mn, K-F and K-W on these deep fluids, which can be useful for future works of geothermal exploration in these islands.

In order to reach these objectives, this report exploited two types of geochemical data: data obtained from an extensive literature review and data acquired in the Guadeloupe and Martinique islands during this study. For the latter, BRGM and the Antilles University (AU) carried out a field campaign of fluid collection for water chemical and isotope analyses in Martinique between July 5 and 7, 2022. Seven water samples were collected from thermal springs located in the areas of Lamentin plain (4), Anses d’Arlet (2) and Mount Pelée volcano (1). The analyses were carried out in the BRGM and UA laboratories.

As for the Bouillante field, the deep geothermal fluids found in the other islands are neutral pH seawater derived fluids mixed with meteoric fresh waters at different proportions. These mixed fluids interact with reservoir volcanic rocks at temperatures close to 100-110°C and 180°C in Martinique, and 230-260°C in Montserrat and Dominica.

The presence of deep fluids with higher temperatures (≥ 280°C) and different chemical facies in the proximity of the active volcanoes is possible, but can cause problems of exploitation, as observed in the past in the Saint Lucia Island, due to the high salinity and acidity of these fluids and low reservoir permeability.

The geothermometric results obtained in this study show that the different Na-Li thermometric relationships determined in the literature can be an interesting tool for geothermal exploration in the Caribbean areas. The Na-Li thermometric relationships give reliable estimations of reservoir temperatures for most of the waters discharged from geothermal wells and thermal springs. However, for some deep and cold thermal waters (T ≤ 60°C), not equilibrated with the reservoir rocks, no Na-Li thermometric relationship can reasonably be used to obtain reliable estimates of reservoir temperature.

All these results show that it is essential to take into account the type of geological environment to use the different Na-Li thermometric relationships, and combine and compare them with the other geothermometers in order to decrease the uncertainty in the estimation of the reservoir temperature. For all the Na-Li relationships, it is suggested that the presence of micas in the reservoir rocks is the major control of the Li concentrations in the geothermal waters. The use of Li isotope values can be a useful tool to indicate if the waters are rather low- to medium-temperature (≤ 150°C), when most of the chemical geothermometers give discordant temperature estimations. In this case, the δ^7Li values are generally higher than 10‰.

Concerning the use of other auxiliary chemical geothermometers, very few data are available in the literature for geothermal waters from the Caribbean region. Nevertheless, some interesting trends have been obtained for the K-Sr, Na-Rb, and Na-Cs thermometric relationships. They are rather promising, but need to be confirmed. We encourage acquiring more analyses of trace elements such as F, Sr, Rb, Cs, Mn, Fe, and W in future studies in the Caribbean areas, especially in the saline waters where their concentrations are relatively high, in order to develop additional geochemical tools for geothermal exploration in this region.

The perspectives for the Bouillante area, in Guadeloupe, with its existing geothermal power plant and its next increase of production capacity as well as the development of other areas, thanks to promising indices of deep hot fluid escapes brought by thermal submarine springs, are very encouraging. Similarly, the recent deep geothermal wells drilled in the Dominica and Montserrat islands are promising for geothermal development. For the Martinique and Saint Lucia islands, exploration wells are necessary to test and validate the existing geothermal conceptual models.

The ambitious objectives of the energy transition in the world, the recent arrival of some industrials like Ormat, majority owner and operator of the Bouillante power plant since 2015, and new investors, who aim to develop and operate future geothermal fields in the Caribbean islands, encouraged by new types of funds, is an excellent message for the future. The Caribbean Centre of Excellence of Geothermal Energy, currently being created in the Guadeloupe Island within the framework of the INTERREG V ETC program, featuring a network of scientific research, formation and industrial activity, should make it possible to promote and develop this energy in the entire region. In this context, the success of the Bouillante story could become a stepping-stone for the geothermal development in the Caribbean area.

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1. Introduction

The Caribbean islands make up a large subcomponent of the hundreds of islands in the Caribbean Sea, forming a wide arc between Florida in the north and Venezuela in the south, as well as a barrier between the Caribbean Sea and the Atlantic Ocean (Fig. 1).

These islands consist of three main island groups including the Bahamas, the Greater Antilles and the Lesser Antilles. The eastern boundary of the Caribbean plate is a subduction zone, the Lesser Antilles subduction zone, where oceanic crust of the Atlantic plate is being subducted under the Caribbean plate (Fig. 1).

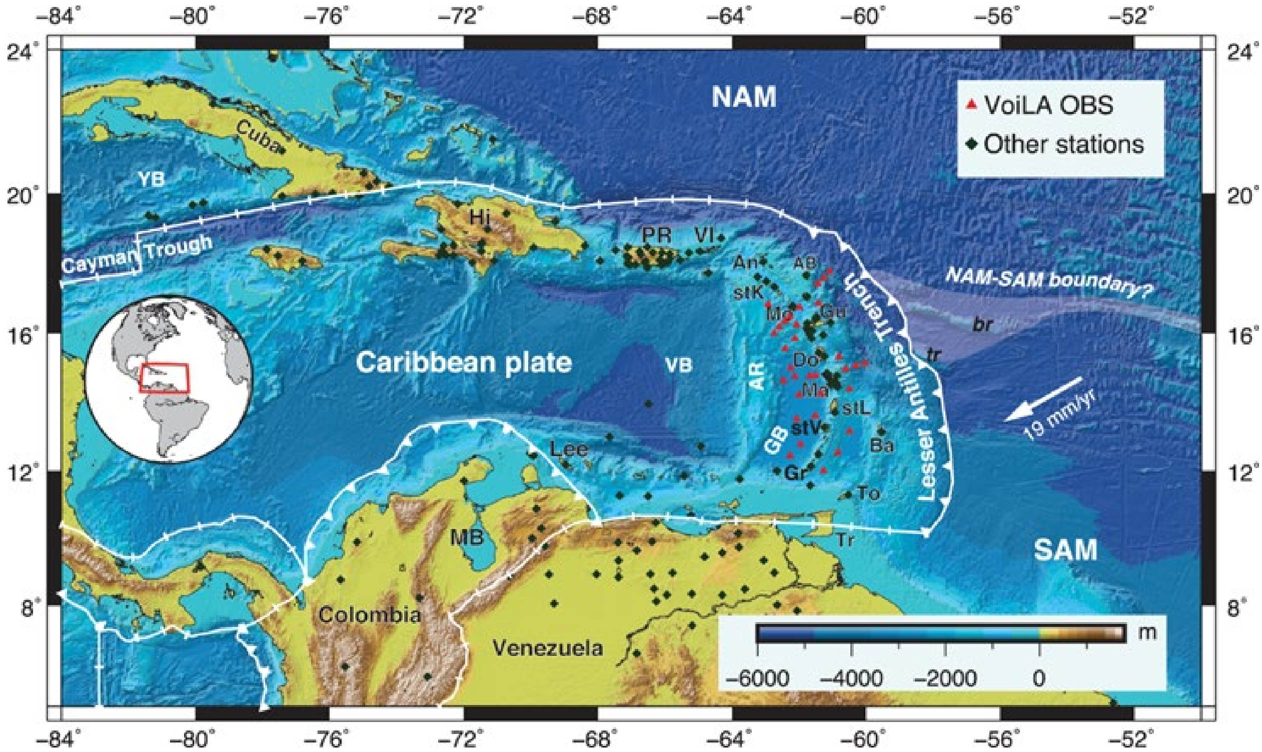

Figure 1 - Plate boundaries from Bird (2003). Uncertainty in the position of the North American (NAM) - South American (SAM) plate boundary is indicated by white shading. Plate motion vector is for Atlantic seafloor relative to the Caribbean plate. An Anguila, AB Antigua and Barbuda (Limestone Caribbees), AR Aves Ridge, Ba Barbados, br Barracuda Ridge, Do Dominica, GB Grenada Basin, Gr Grenada, Gu Guadeloupe, Hi Hispaniola, Lee Leeward Antilles, Ma Martinique, MB Maracaibo Basin, Mo Montserrat, NAM North American plate, PR Puerto Rico, SAM South American plate, stK St Kitts and Nevis, stL St Lucia, stV St. Vincent, To Tobago, Tr Trinidad, tr Tiburon Ridge, VB Venezuela Basin, VI Virgin Islands, YB Yucatán Basin.

Subduction forms the volcanic islands of the Lesser Antilles Volcanic Arc from the Virgin Islands in the north to the islands off the coast of Venezuela in the south. The Caribbean islands such as Guadeloupe, Martinique, Dominique, Montserrat, Saint Lucia, etc., which are part of the Lesser Antilles volcanic arc and home to young volcanic systems (Fig. 2), possess a huge potential for power generation from high-temperature (HT) geothermal energy.

As these islands must face the fragility of their energetic system and environment, given their insularity, and since they are experiencing increasing energy costs and CO_2 emissions, this promising energy source seems to be essential for these islands to hope to achieve energy self-sufficiency. Geothermal energy is continuously available for power production unlike most of other renewable energies, is cheaper than fuel-based technologies, can also be used for thermal applications such as cooling, drying uses for agriculture, aquaculture, spas centres, and could contribute to generate jobs directly and indirectly.

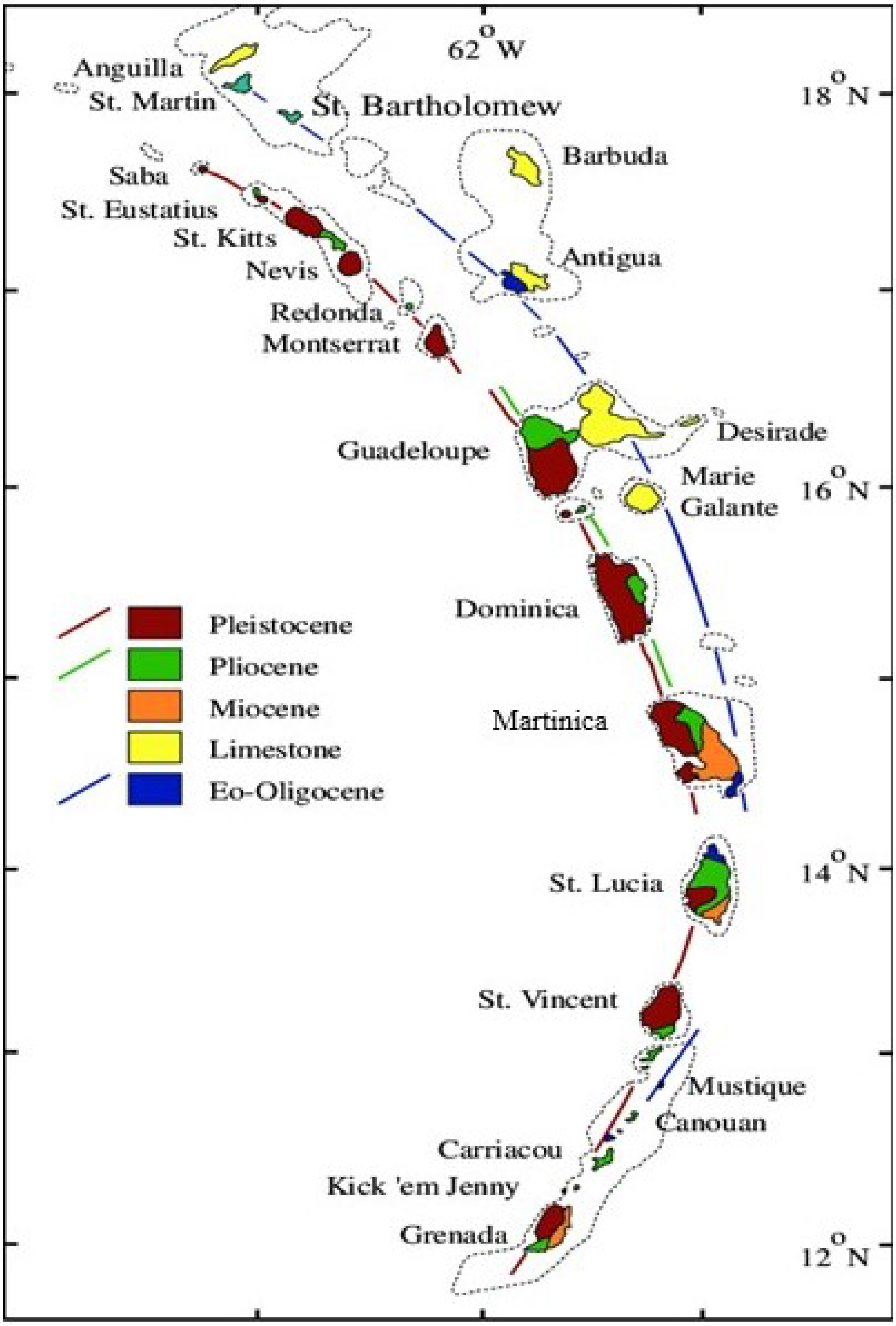

Figure 2 - Map of the Lesser Antilles island arc, showing the ages of the exposed rocks and the positions of the volcanic front during the Eocene-Oligocene (red line), Pliocene (blue line), and Pleistocene (black line) (from Robertson, 2009).

In spite of all these advantages, geothermal energy remains difficult to develop in the Carribean islands. Indeed, even though the first exploration works have been carried out in the 1970s in some of these territories, the Bouillante HT (260°C) geothermal power plant in Guadeloupe, exploited since 1986, remains so far the unique example of electricity production in the Caribbean area. However, if in the past, some deep wells drilled in the Saint Lucia and Martinique islands had to be abandoned and closed (for their low flow-rates and corrosive fluids in Saint Lucia and their low temperature in Martinique), new exploration works carried out in most of these islands, as well as deep wells recently drilled in the Dominica and Montserrat islands, suggest promising geothermal developments.

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In order to reach these objectives, this report has exploited two types of geochemical data: data obtained after an extensive literature review and data acquired in the Guadeloupe and Martinique islands, during this study.

2. Geology setting of Lesser Antilles island Arc and main studied geothermal areas

The 850 km long Lesser Antilles island Arc (Fig. 2) is located at the eastern boundary of the Caribbean plate where Atlantic crust of Upper Cretaceous age is being subducted at a rate of 2 cm/a (Maury *et al.*, 1990; Feuillet *et al.*, 2002). The convergence vector points in East-West direction (Bouysse, 1988). The active arc consists of three segments traced by faults in the overlying plate and kinks in the underlying slab (Wadge and Shepherd, 1984). The major break runs across Martinique, approximately at 2/5 of the arc length and a minor break occurs between Guadeloupe and Montserrat, at 2/3 of the arc length. The Benioff zone, north of Martinique, dips at 50 - 60° with an average depth of 140 km beneath the active arc volcanoes. South of Martinique the dip angle changes gradually from 45 - 50°, beneath St. Lucia, to vertical, south of Grenada, with an average depth of 120 km beneath active volcanoes (Wadge and Shepherd, 1984). The islands of the arc have been largely built by volcanism above a subduction zone, as the Atlantic plate is being subducted under the Caribbean plate.

There are 21 potentially active volcanoes in the Lesser Antilles (Fig. 3).

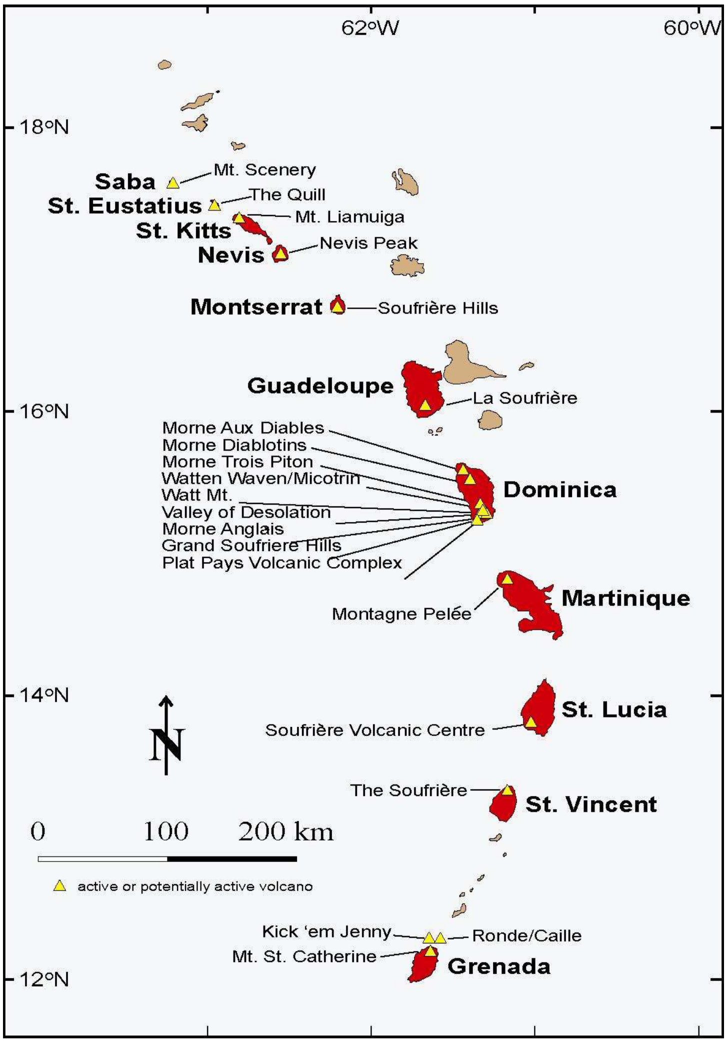


Figure 3 - Map of the main active volcanic centres of the Lesser Antilles (from Joseph, 2008).

Six volcanoes have erupted in the past 400 years, eleven volcanoes have had severe earthquake swarms, have surface hydrothermal activity associated with them, and have deposits dated within the last 10000 years.

Neogene and Quaternary lavas are of four distinct affinities and show a broad systematic progression in time and space (Maury et al., 1990). Mg-rich lavas are found especially in the southern half of the arc (Grenada, Grenadines, Southern St. Vincent). Low-K (0.5% K_2O) island-arc tholeiites occur mainly in the northern islands, and are characteristic of Miocene volcanism in Martinique and St. Lucia. Medium-K (0.9% K_2O) and high-K (0.9% K_2O) alkaline volcanic series are found especially in the southern half of the arc and are characteristic of the Pliocene and Quaternary volcanism. The (broad) along-arc and along-time progression from tholeiitic through calc-alkaline to alkaline lavas is accompanied by a tendency for enrichment of incompatible elements and radiogenic strontium and lead isotopes. This feature has generally been attributed to a contamination of the arc magmas by terrigenous sediments derived from the Guyana shield. There is little agreement, however, on the mechanism by which these lavas are being contaminated.

The main studied geothermal areas in this work are located in the volcanic islands of Guadeloupe, Martinique, Dominica, Montserrat and Saint Lucia (Fig. 1), where deep geothermal wells were drilled and some thermal springs indicate discharges of deep fluids. Detailed documents relative to the water chemical compositions were found during our literature review. Unfortunately, no detailed information was obtained for the deep waters from the Saint Vincent and Grenada islands, even if we know that recent geothermal wells were drilled in the Saint Vincent Island.

2.1. GUADELOUPE ARCHIPELAGO

The Guadeloupe archipelago forms part of the N-S-trending, 850-km-long, Lesser Antilles volcanic arc. The Guadeloupe Island hosts the active Grande Soufriere stratovolcano, on the island of Basse-Terre, which is the highest mountain peak (1467 m) in the Lesser Antilles. The last magmatic eruption was in 1580 ± 50 during which the current lava dome was emplaced. More recent eruptions have been phreatic in type. The figure 4 indicates the main hot springs and geothermal areas of the island. We can distinguish two main areas (in red circles): the Bouillante high-temperature field (250-260°C) and the Grande Soufriere hydrothermal system.

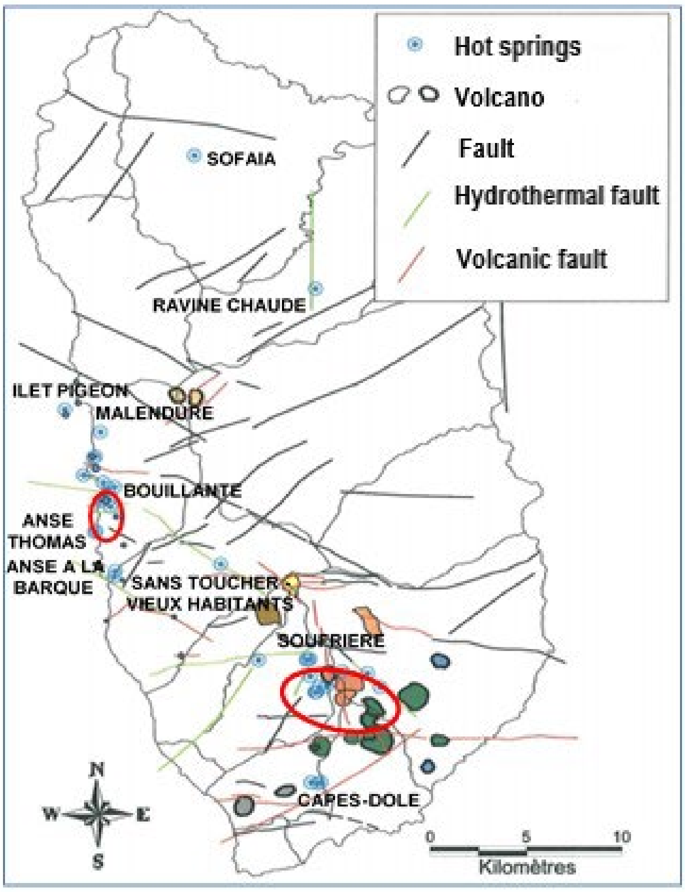


Figure 4 - Map of the main hot springs and geothermal areas in the Guadeloupe Island (from Bourdon et al., 2009).

2.1.1. The Bouillante high-temperature geothermal field (250-260°C)

This field is located on the west coast of the Basse-Terre Island. It lies within the area of both the "axial Chain complex" (1.023 to 0.445 Ma; Samper, 2009) and the "Bouillante Chain complex" (1.1 to 0.2 Ma; Gadalia *et al.*, 1988) whose geographic extension on the western edge of the island is atypical. The north-trending Bouillante volcanic chain complex is probably controlled by the submarine NNW-SSE strike-slip fault, which belongs to the regional normal-sinistral Montserrat-Bouillante-Les Saintes system. The Bouillante field is located at the intersection between this major submarine transfer fault, and the western horsetail fault end of the regional WNW-ESE to NW-SE Bouillante-Capesterre normal fault belonging to the Marie-Galante Graben system (Fig. 5; Calcagno *et al.*, 2012). At the north of Bouillante, this fault is known as the Marsolle-Machette corridor.

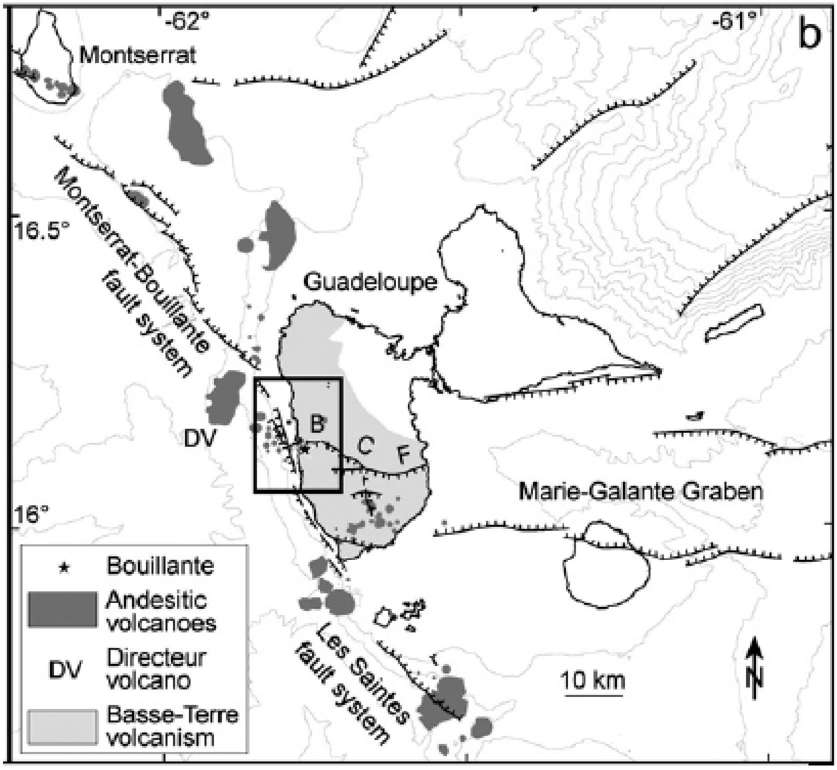


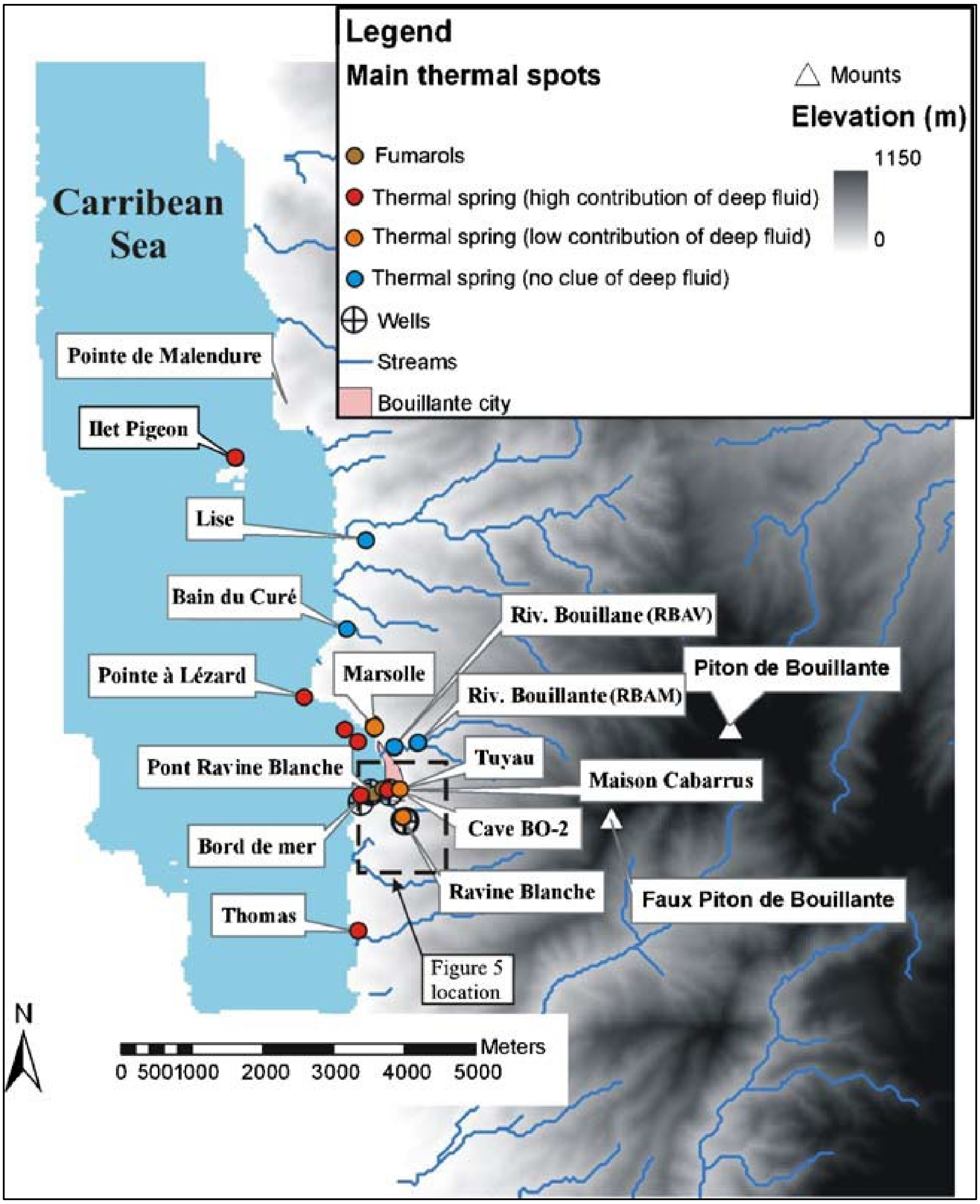
Figure 5 - Regional structural setting of the Guadeloupe from Calcagno et al. (2012). BCF: Bouillante-Capesterre fault system. The trajectory of this hypothetical fault is extracted from the geological, morphological and structural map of southern Basse-Terre realised by Feuillet et al. (2002). It is mainly based on alignments of steps offsetting the topography (this figure is modified from Feuillet et al., 2001 and Thinon et al., 2010).

The Bouillante field is contained within a volcanic substratum largely attributed to sub-product of the axial Pitons de Bouillante chain cropping out along the axis of Basse-Terre Island. The partly detrital and dominantly andesitic volcanic substratum is characterized by a succession of four lithological units. From top to bottom of the volcanic pile, these are: 1) the subaerial volcano-detrital unit 'A' (30 to 130 m thick), 2) the subaerial volcanic unit 'B' (160 to 240 m thick), 3) the shallow submarine to coastal volcano-detrital unit 'C' (225 to 400 m thick) and 4) the submarine volcanic unit 'D' (> 2500 m thick). Recent volcanic centres (1.1 Ma and 0.2 Ma) of the 'Bouillante Chain complex' defined by Gadalia et al. (1988) lie on this substratum. Aligned along a N-S band of some 20 km by 4 km, the 'Bouillante Chain complex' volcanism follows the offshore N160°E-striking fault of the Montserrat-Bouillante system. The volcanic rocks have the characteristics of a weakly potassic tholeiitic series that evolved through fractional crystallization from north to south (basalt, andesite in the north to dacite, rhyolite in the south; Gadalia et al., 1988). The persistence of volcanic activity in the area for almost 1 Ma and the associated magmatic differentiation argue in favour of a common NNW-SSE trending-deep magmatic reservoir below the Bouillante Chain complex.

Immediately north of Bouillante city, volcanic centres developed within the E-W to WNW-trending Marsolle-Machette corridor, suggesting a local tectonic control of this volcanism (Fig. 5). At the scale of the Bouillante field, the lithological pile is cut by a network of high-angle normal faults striking N90°E to N120°E, including the main south-dipping Bouillante-Capesterre-(Marsolle) fault. This network comprises ~10 faults, spaced approximately 500 m to 1 km apart, with decametre to metre throws delimiting a mini graben. This graben is developed on the horsetail fault end of the regional south-dipping normal fault (Fig. 2). These faults developed in a brittle domain during a regional NNE-SSW-trending extension (Feuillet *et al.*, 2001).

Exploited since 1986, the Bouillante geothermal field is the unique example of this type in France and in the Caribbean islands. Presently, the Géothermie Bouillante Company, which exploits this field, is a subsidiary of ORMAT (65%), Caisse des Dépôts et des Consignations (20%), and BRGM (15%). In addition to its electricity-producing role, this field has been also used by BRGM as an outstanding research laboratory for improving the knowledge of a reference high temperature geothermal system in island-arc environment and increase its production capacity. This field has been developed near the coast and around the Bouillante town, where numerous hydrothermal terrestrial and submarine manifestations occur (Fig. 6a and b). The active terrestrial geothermal manifestations such as hot springs, mud pools, steaming grounds and fumaroles are mainly located south of Bouillante Bay (Fig. 6b).

a)



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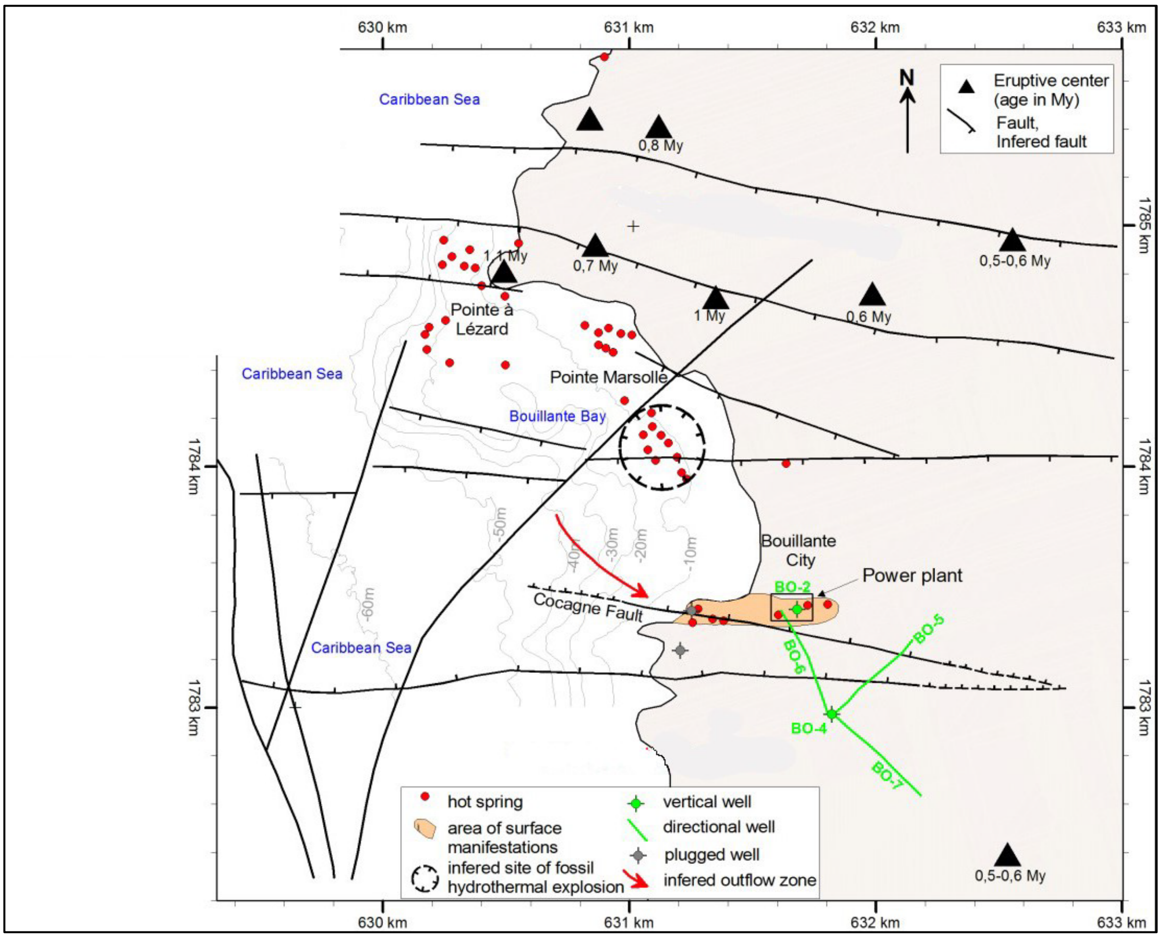


Figure 6 - a) Main hot springs in the Bouillante geothermal area (from Lachassagne et al., 2008). b) Main volcanoes, fault and hot springs in the Bouillante Bay area (from Traineau et al., 2015a).

The first producing well at Bouillante (BO-2, 350 m deep, 150 tons/h of discharged fluid of which 30 tons/h is steam) dates from the beginning of the 1970s and fed the first turbine (4.5 MWe) between 1986 and 2004. The poorly productive BO-4 well was deepened down to 2500 m in 1977, but did not indicate temperature values higher than 260°C. After a thermal stimulation operation in 1998 using cold seawater, the productivity of this well was slightly improved. The last productive wells, BO-5 and BO-6 (about 1000 m deep), were drilled in 2001 (Figs. 6b and 7).

Since 2005, with the second turbine unit, the new geothermal power plant has an installed capacity of 15 MWe gross. These last wells can produce up to 650 tons/h of deep geothermal fluid, and after phase separation, supply about 130 tons/h of steam to the turbines of this power plant, presently representing an annual production close to 110 GWh and about 5-6% of the electricity needs of the island. All the deep geothermal waters are geochemically homogeneous (NaCl waters) and have a TDS value close to 20 g/l. After phase separation at 160°C (20% steam and 80% liquid), the TDS value is close to 25 g/l. Since 2015, the water reinjection is partial (about 100 m^3/h into the surface BO-2 well) and the majority of the produced fluid is discharged in the sea, after mixing and cooling with seawater, and without important environmental impact.

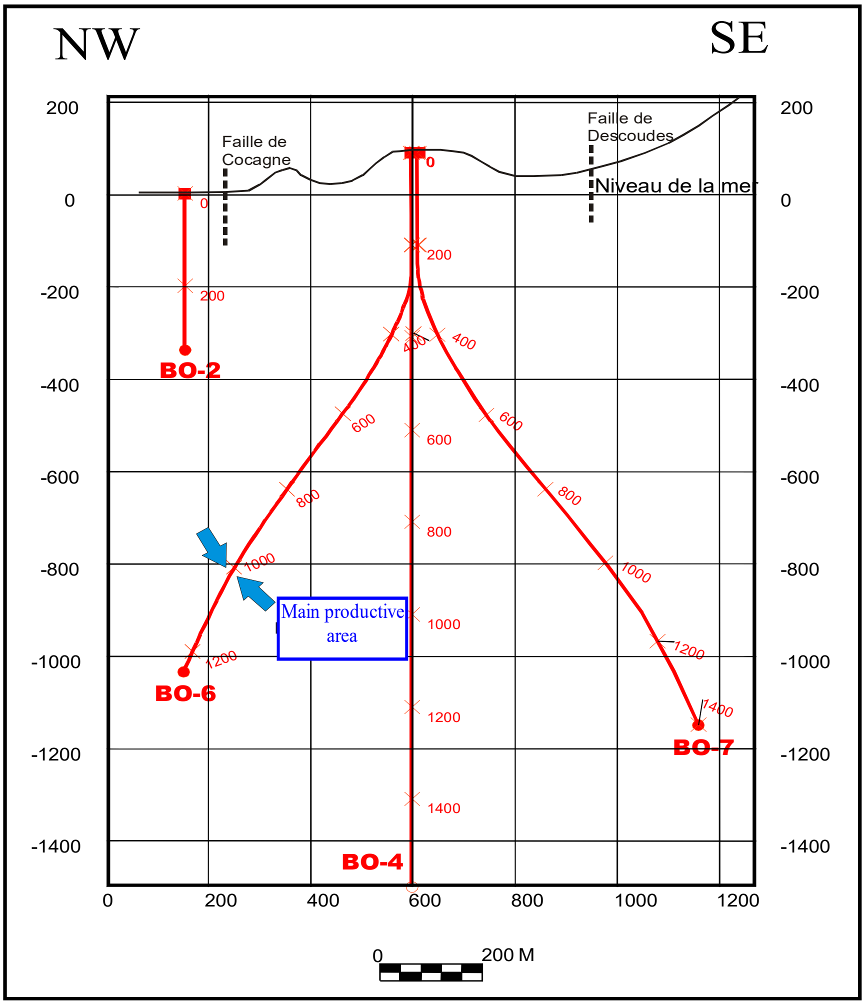


Figure 7 - The Vertical NW-SE cross-section showing the vertical wells BO-2 and BO-4 and the deviated BO-6 and BO-7 wells. BO-5 is in a perpendicular plan (from CFG documentation; Sanjuan et al., 2008).

In 2022, a new deep production well has been drilled near the BO-5 and BO-6 wells to increase the total production capacity of the power plant to 20-25 MWe, but it is not yet producing. Two new injection wells must also be drilled soon.

Since 1995, the research projects, mainly funded by BRGM, ADEME (French Agency for Ecological Transition), Region Guadeloupe and European Union, aiming at stimulating, supporting and developing the exploitation of the geothermal field, have been a key parameter of the Bouillante success and are crucial for its future development. These works (Traineau *et al.*, 1997; Correia *et al.*, 2000; Sanjuan, 2001; Sanjuan *et al.*, 2004; 2005a; 2008; 2013; Truffert *et al.*, 2004; Fabriol *et al.*, 2005) have contributed to increasing from 2 to 5-6% the percentage of Guadeloupe's annual electricity production in 2005.

They have also highlighted new promising areas for geothermal production, such as the north of the Bouillante Bay (Pointe à Lézard), the Anse Thomas area, at the south of Bouillante Bay, and the Ilet Pigeon area (Fig. 6a). In these areas, the discharge of deep geothermal fluid (260°C) mixed with seawater in the hot submarine springs, and with seawater and freshwater in the Anse Thomas onshore thermal spring, was demonstrated using different types of binary diagrams (Sanjuan and Brach, 1997; Traineau *et al.*, 1997: Sanjuan, 2001; Sanjuan *et al.*, 2001a and Millot *et al.*, 2010). As an example, Millot et al. (2010) used a diagram δ^7Li values *versus* Li/Cl ratios, which indicated an outstanding hyperbolic curve representative of mixing.

As shown in Figure 8, the isotope Sr ratio values and Sr concentrations can be also used to highlight these types of mixing and indicate the contribution of deep geothermal fluid at 260°C.

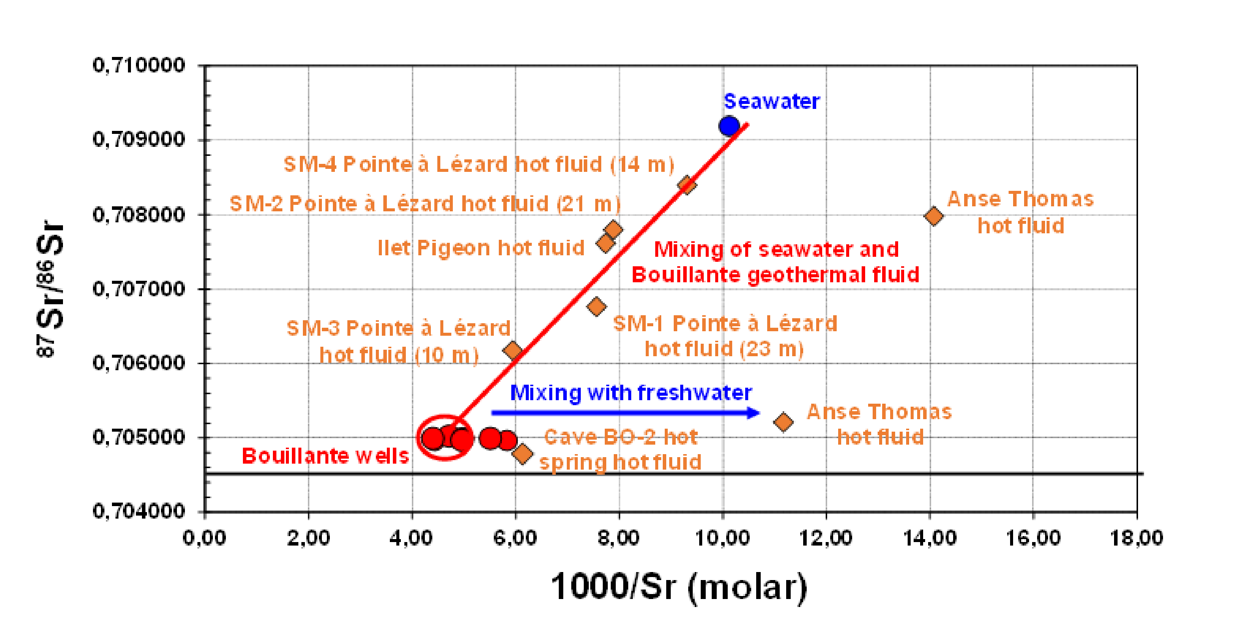


Figure 8 - Diagram $^{87}Sr/^{86}Sr$ ratio versus 1000/Sr concentration for the submarine thermal waters sampled in the Bouillante area (Sanjuan, 2001), indicating a linear relationship between the Bouillante deep geothermal fluid and sea water which results from a mixing between these two end-members. Some terrestrial thermal waters (like Anse Thomas and Cave BO-2) are not aligned because they are also mixed with a third component that is freshwater.

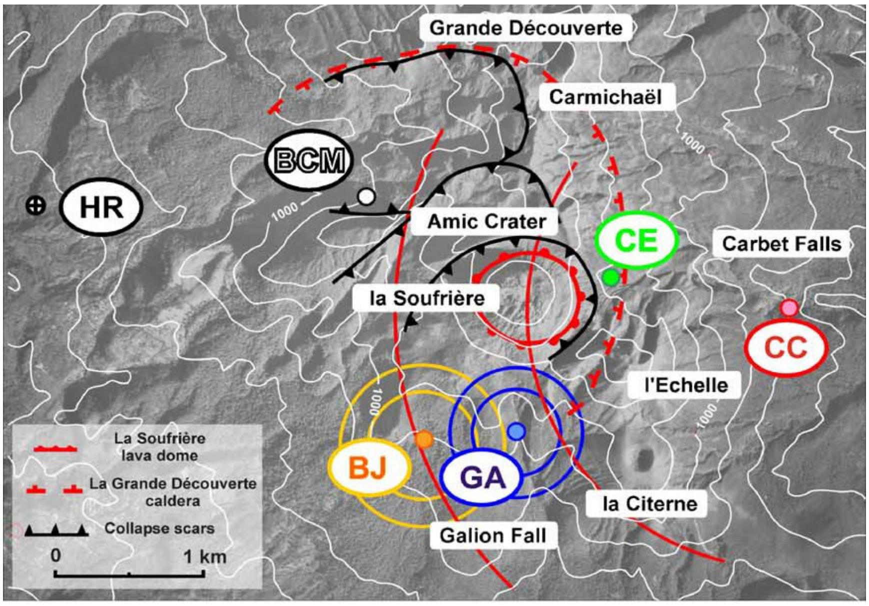
2.1.2. The Grande Soufriere hydrothermal system

The coexistence of an active magma chamber and abundant groundwater fed by a tropical climate regime with abundant rainfall (mean value for 1983-2010: 10 ± 2 m/year) has led to the occurrence of numerous permanent thermal springs (Figs. 9a and b) and permanent to intermittent fumarolic degassing on the summit and at the periphery of the Grande Soufriere dome (Bigot and Hammouya, 1987; Zlotnicki *et al.*, 1992; Villemant *et al.*, 2005; Komorowski *et al.*, 2005; Bernard *et al.*, 2006; Sanjuan *et al.*, 2008; Villemant *et al.*, 2014; Allard *et al.*,2014; Jean-Baptiste *et al.*, 2014). Interaction of the more active summit fumaroles with perched aquifers favours the formation of intermittent acid ponds (Cratère Sud and Tarissan).

Historical observations show that the nature, distribution and intensity of hydrothermal activity have considerably varied over time (Komorowski *et al.*, 2005; Ruzié *et al.*, 2012, 2013; Villemant *et al.*, 2014; Moune *et al.*, 2022). Thermal springs (30-45°C) are concentrated around the base of the dome mainly in the SW, S and NE sectors (Fig. 9a, b).

This distribution is controlled by the structure of the volcanic edifice and the extensive development of clayey hydrothermal alteration along preferential zones (Figs. 9a and b). These thermal waters have a meteoric origin (TDS ≤ 1.3 g/l) and seem to interact with volcanic rocks at 80-100°C.

a)



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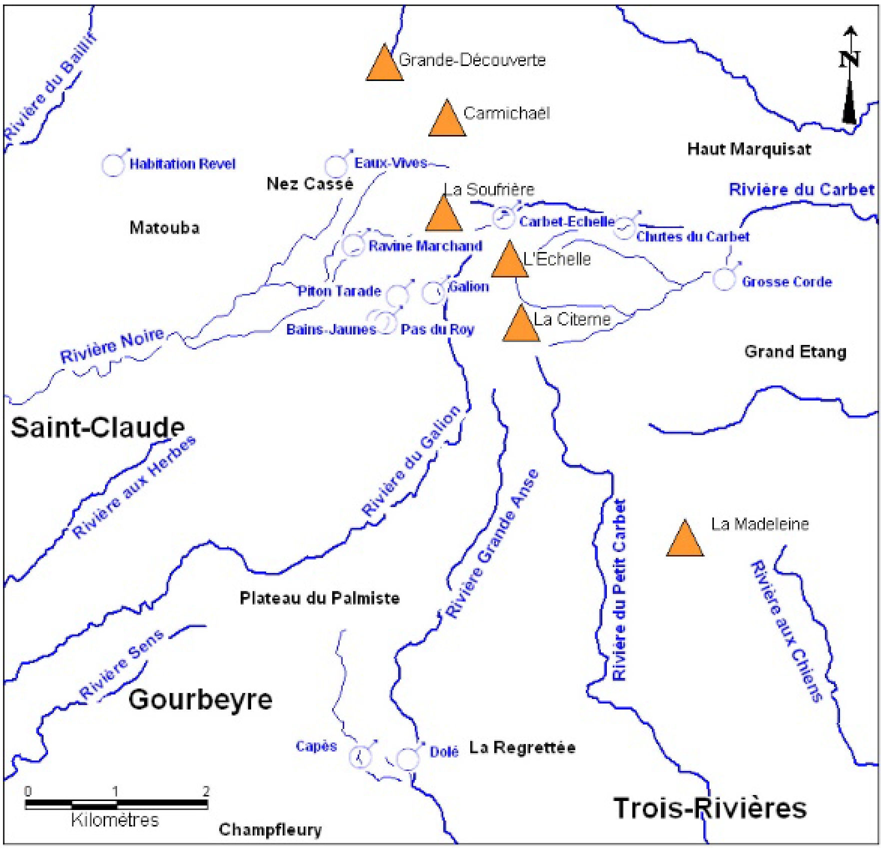


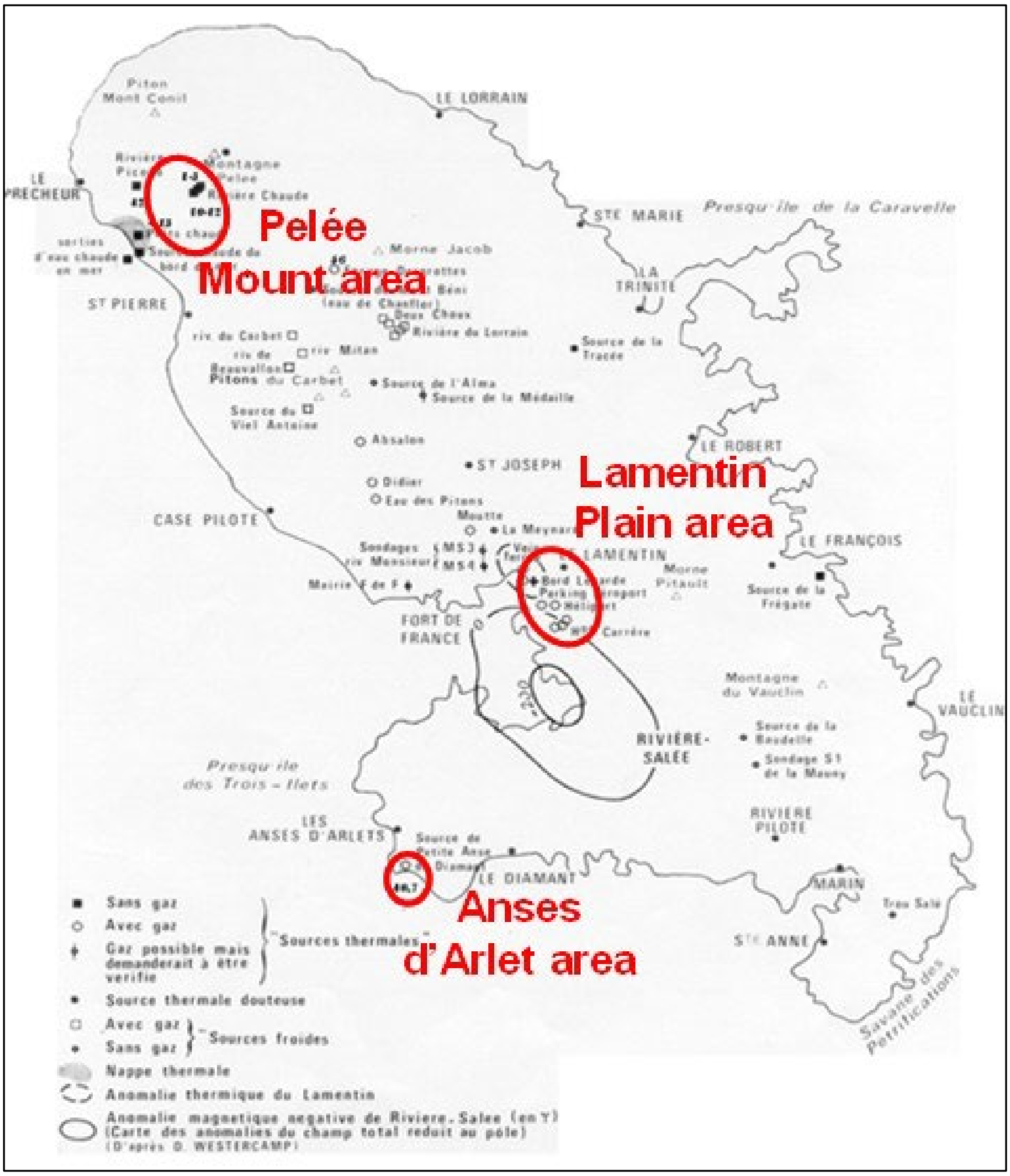
Figure 9 - a) The active hydrothermal system around the lava dome of the La Grande Soufriere of Guadeloupe: main volcano-tectonic structures and distribution of main thermal springs (from Villemant et al., 2005); b) Detailed distribution of thermal springs: Habitation Revel (HR), Eaux Vives (EV), Ravine Marchande (RV), Bains chauds du Matouba (BCM), Bains Jaunes (BJ), Piton Tarade (PT), Pas du Roy (PR), Gallion (GA), Carbet Echelle (CE), Chute du Carbet (CC), Grosse Corde (GC) (from Sanjuan et al., 2008).

2.2. MARTINIQUE ISLAND

Martinique is a volcanic island belonging to the recent Lesser Antilles arc of post-miocene age. The surface geology is known from the 1:50000 geologic map (Westercamp *et al.*, 1989). The thermal springs are scarce in the Martinique Island in relation to the volcanic activity and the rainfalls (Fig. 10 a). Less than 15 thermal springs were found in the studied areas.

Except for the Lamentin plain, the most numerous and hottest springs are situated on the western flank of the Mount Pelée volcano (Fig. 10 b). Most of these manifestations were previously studied by Lopoukhine and Mouret (1977), Barat (1984), Iundt (1984), Traineau *et al.* (1989), Sanjuan *et al.* (2002a, b; 2003; 2005b), Gadalia *et al.* (2014, 2017). The Figure 10a indicates the three areas studied in this work with a focus on the Mount Pelée volcano in Figure 10b, Diamant-Anses d'Arlet in Figure 10c and Lamentin plain in Figure 10 d.

a)



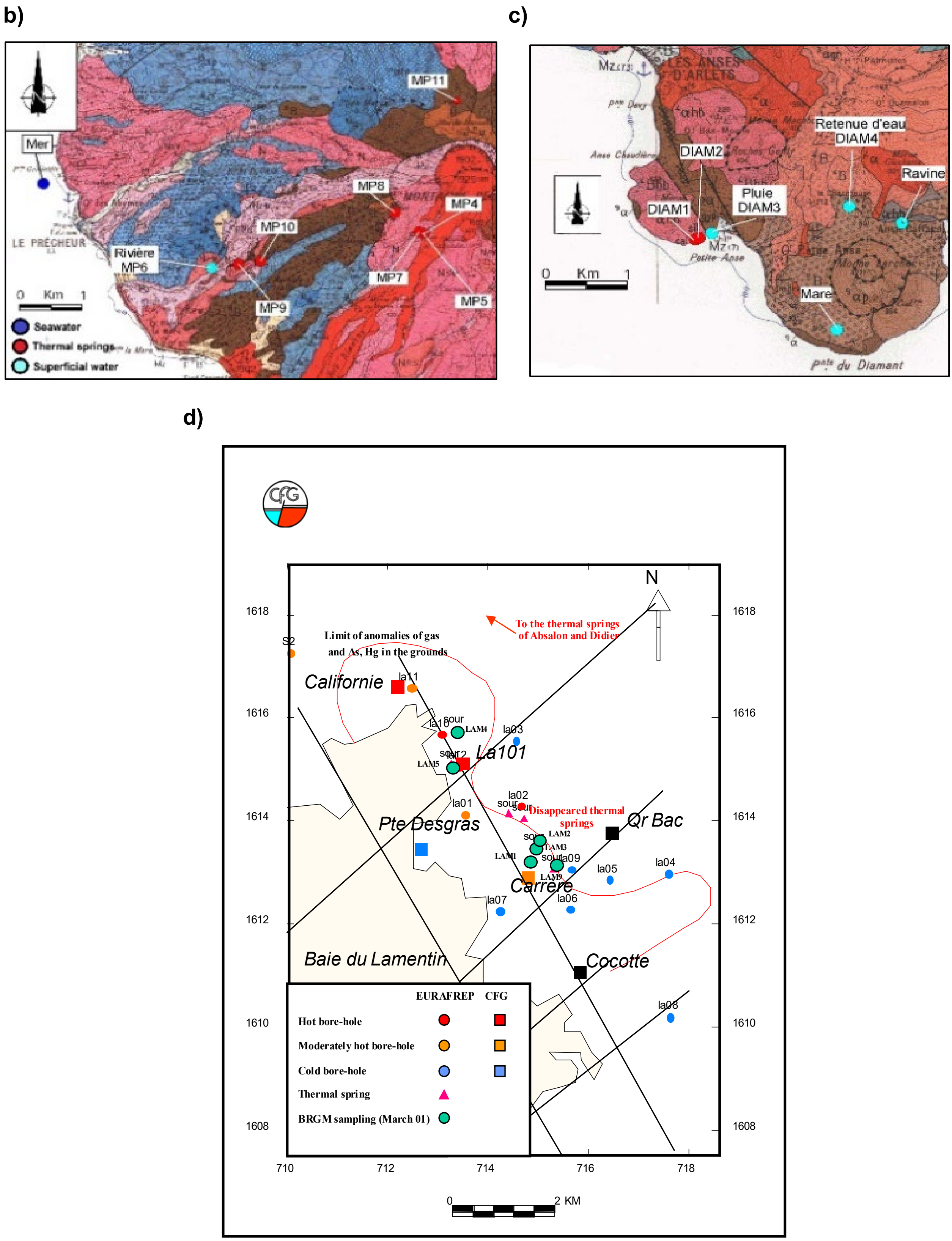


Figure 10 - a) Location map of the main thermal springs in the Martinique Island (from Lopoukhine and Mouret, 1977); b) Location of the thermal waters in the Mount Pelée area (Sanjuan et al., 2003; 2005b); c) Location of the thermal waters in the Anses d'Arlet area (Sanjuan et al., 2003; 2005b); d) Location of the thermal waters in the Lamentin plain area (Sanjuan et al., 2002a, b).

2.2.1. The low-temperature Lamentin plain (90-110°C)

The plain of Lamentin, a mangrove area situated south of Fort de France on the Midwest part of the Martinique Island, constitutes an alluvial zone covering a surface of 100 km^2 approximately (Fig. 10a). The area of Lamentin corresponds to a major graben zone limited by NW-SE faults and intersected by the NE-SW faults (Chovelon, 1984). Based on the geological map of Martinique and previous reconnaissance drilling, several faults are known in the area of Lamentin. The northern part of the Lamentin Graben is limited by the Lamentin fault oriented N60E, which is a normal fault of multi-kilometre size. The eastern border of the graben is limited by a hidden fault oriented N140E (Petit Bourg fault). A fault with the same orientation is suspected in the western part of the Lamentin Graben. Two parallel faults oriented N115E and dipping north are reported close to the Lamentin fault. They cut the Miocene andesitic formation. In the northwestern part, two supposed cartographic faults oriented N140E are also known and cut the Miocene andesitic formations.

The occurrence of many thermal springs located in the Lamentin area has highlighted the presence of a geothermal resource at depth. The thermal springs, whose fluid temperatures vary between 34 and 58°C, are aligned along an axis oriented NNW-SSE to NWSE. Flow rate is generally low and their chemical compositions are characterized by a CO_2 and NaCl rich fluid (Sanjuan *et al.*, 2002b, c). Silica travertine deposits of 300000 years approximately are known at the surface. These current hydrothermal activity indicators had led to a first geothermal exploration phase (EURAFREP, 1969).

During this first geothermal exploration phase, that occurred between 1966 and 1971 in the Lamentin plain, twelve relatively shallow depth wells, La1 to La12, were drilled. The wells located in the northern part of the zone (La1, La2, La10, La11, La12) presented the most interesting thermal anomalies. A deep well LA101 (771 m; Fig. 10d) crossed an artesian reservoir between 155 and 250 m of depth producing a CO_2-rich fluid with a temperature close to 94°C. Its chemical composition is equivalent to that of the thermal surface springs. This reservoir zone corresponds to a network of inclined fractures characterized by silica deposits (EURAFREP, 1970).

Later geochemical studies carried out in 1976, 1984 and 1985 showed no major shallow evidences of the occurrence of a high temperature reservoir in this area. A new exploration phase was carried out in 2001. On the three boreholes drilled by CFG in this area at a depth close to 1000 m, only the borehole located more at north (Californie borehole) and near the old LA-101 borehole (Fig. 10d), indicated the presence of inflows of hot fluid close to 90-95°C, between 400 and 800 m of depth (Sanjuan *et al.*, 2002a, b). A similar geothermal fluid was also found at a depth of about 400 m in the Carrère borehole (Fig. 10d), situated near thermal springs, but with a lower temperature (50°C).

2.2.2. The high-temperature Mount Pelée area (180-210°C)

Mount Pelée volcano is located at the northern end of the Island of Martinique in the Lesser Antilles. It is a composite andesitic stratovolcano that covers an area of about 120 km^2 and rises nearly 1400 m above sea level. Mount Pelée is one of the most active volcanoes of the Lesser Antilles arc, with more than 20 eruptions during the last 5000 years. Despite this abundant potential heat flow, there are few surface manifestations indicative of the existence of a large high-temperature hydrothermal system. A few $Na\text{-}HCO_3\text{-}SO_4$-type hot springs with emergence temperatures not exceeding 65°C occur on the south and west flanks of the volcano (Westercamp and Traineau, 1987; Traineau *et al.*, 1989).

Two small hydrothermal eruptions occurred in 1792 and 1851 on the southwestern flank, on the site of now-extinct sulfur springs. The heat source provided by the Mount Pelée magma chamber should occur, according to petrologic data, at shallow depth (5-8 km) beneath the summit region.

We assume abundant groundwater recharge to take place within the central calderas where faults and magmatic conduits provide vertical channel ways for deep infiltration of cold meteoric water. This would be expected to depress a presumed NaCl hydrothermal system located deep in the core of the volcano. Upwelling of high-temperature fluids and gases is thought to be found at the periphery of the central calderas, along the caldera-related arc faults and/or along regional faults and any permeable stratigraphic levels connected to the central caldera structure. Steam heating of shallow meteoric waters by a degassing NaCl system could produce a Na-HCO_3-SO_4-type system, which would develop preferentially on the periphery of the central caldera structure or even outside it in an adjacent zone of fracture permeability (caldera or regional faults), where cold meteoric flows are less abundant. This Na-HCO_3-SO_4 system is assumed to be located beneath the south flank of the volcano, and the major upflow zone seems to be the southern limit of the intermediate caldera, as evidenced by the location of hot springs and hydrothermal eruptions.

The scarcity of thermal manifestations on Mount Pelée (Fig. 10b) is not surprising in view of its groundwater hydrogeology. The emergence temperature of the thermal waters vary from 36 to 51°C. These thermal waters with TDS values ≤ 1.6 g/l have a meteoric origin (Sanjuan *et al.*, 2003; 2005b). The ascending Na-HCO_3-SO_4 fluids will be masked wherever a highly permeable, sub-horizontal aquifer occurs near the surface, and they commonly mix with cold waters before discharging. No neutral NaCl hot springs are known at Mount Pelée to confirm the existence of a deep NaCl system. The extent of this aquifer is difficult to estimate because the ascending hot waters are cooled and mixed with local cold groundwaters and the natural emergences may be not representative of the deep fluid conditions. However, the probable Na-HCO_3-SO_4 aquifer location within the fractured lava flows and basement rocks beneath the southern flank of the volcano suggest a rather limited size.

2.2.3. The high-temperature Anses d'Arlet - Diamant area (180°C)

In the Anses d'Arlet - Diamant area, the Morne Jacqueline and Morne Larcher volcanoes are the evidences of an eruptive cycle (close to 2.6 My), which spread out from the Anses Marlet (NW) to Diamant (SE) (Gadalia *et al.*, 2014). Afterwards, the volcanic activity resulted in an effusive cycle with andesitic lava flows (2.2 My). The more recent products of the volcanic activity in this area have been dated to 0.9 My (massive andesitic lavas, phreatomagmatic breccias). Only three vertical and normal faults oriented N160-N170E with an horizontal extension of 2 km were identified in this area (Fig. 10c). Presently, they form a 500 m large channel (Gadalia *et al.*, 2014). A main occurrence of thermal spring located near the sea, with a temperature close to 35°C, can be observed with other minor colder neighbouring occurrences (Sanjuan *et al.*, 2003; 2005b).

2.3. DOMINICA ISLAND

Dominica is located in the central Lesser Antilles between the two French islands Guadeloupe and Martinique. It is about 45 km long by 25 km wide and its area is about 800 km^2. Its morphology shows a N-S trending axial ridge formed by several distinct volcanic complexes and covered by dense tropical forests. Dominica is home to nine young volcanic complexes (Fig. 11), of which seven major andesitic-dacitic volcanic centers have been active since the late Pleistocene (Lindsay *et al.*, 2005). Four of these centers have associated active geothermal areas that have been routinely monitored since 2000 by the UWI Seismic Research Centre (SRC) and since 2013 by the Union College. Volcano hydrothermal monitoring provides information on temperature, origin, and temporal changes in chemical composition of volcanic fluids and informs on potential volcanic hazards to which the public may be exposed.

Dominica is made up of predominantly andesitic and dacitic volcanic rocks along with their weathered products (Lindsay *et al.*, 2005; Smith *et al.*, 2013). All of the seven volcanoes active in the last 100 ka are considered likely to erupt again, given the widespread geothermal activity and shallow seismicity (Lindsay *et al.*, 2003; Joseph *et al.*, 2011), as well as recent eruptive history (Frey *et al.*, 2018).

More than 30 geothermal and hydrothermal areas have been identified (Fig. 11) throughout the island and offshore (Smith *et al.*, 2013). Initial characterization of the most prominent hydrothermal fields was done by Joseph *et al.* (2011). Hydrothermal activity at the Cold Soufriere, Morne aux Diables (MAD) in northern Dominica manifests as vigorously bubbling pools and “frying pan” features with temperatures of 23 °C to 28 °C and strongly acidic pH of 1-2. These waters are $Na\text{-}SO_4$ type in composition. The lack of heat is a consequence of its location in a steep terrain, where the meteoric recharge is supplied to the hydrothermal system at a lower elevation than the area overlying the upflow zone (Bogie *et al.*, 1987).

Hydrothermal activity in the Wotten Waven/Micotrin centre manifests in the form of bubbling pools and hot/warm springs of $Na\text{-}SO_4$ type composition with temperatures up to 99 °C and pH values of 1-5 (Joseph *et al.*, 2011). The Plat Pays Volcanic Centre in southern Dominica hosts the hydrothermal areas of Galion, Sulphur Springs (Fig. 11) and underwater diffuse emissions at Champagne Springs. Hot springs of pH value 1-3 with $Na\text{-}SO_4$ type composition and low-temperature fumaroles (90-100 °C) are present in these areas. The fumaroles are particularly abundant at Sulphur Springs, with more than a dozen vents typically active.

About 35 warm and hot springs were identified in the Wotten Waven area and the Boiling Lake - Valley of Desolation area and analysed by BRGM (1985), Lasne and Traineau (2005) and Traineau and Lasne (2008). Hydrothermal fluid discharges in the Valley of Desolation (VOD) and Boiling Lake areas (Fig. 11) are in the form of numerous hot springs, bubbling pools and fumaroles. The Valley of Desolation area has been the site of phreatic explosions in 1863 and 1880. Thermal waters in the VOD generally have temperatures in the range of 74 °C to 98 °C and pH values of 1 to 4, with a predominantly $Na\text{-}SO_4$ composition (Joseph *et al.*, 2011). Acid-sulphate waters are likely derived from the $CO_2\text{-}H_2S$ rich steam up-flow, generated by boiling of meteoric waters, which partially condenses and dissolves in shallow groundwater (Joseph *et al.*, 2011).

Lasne and Traineau (2005) provided a comprehensive map of the surface manifestations classified into eight types: warm spring, hot spring, mineralized-fluid hot spring, fumaroles, cold gas discharge, solfatare and steam vent, fossil alteration area, phreatic crater. The most striking feature of the Roseau Valley geothermal field is the abundance of surface manifestations, which are recorded in two main spots distant of 4 km: the River Blanc valley near the Wotten Waven Village (Sulphur Springs), and the Boiling Lake - Valley of Desolation area on the other side of the axial ridge.

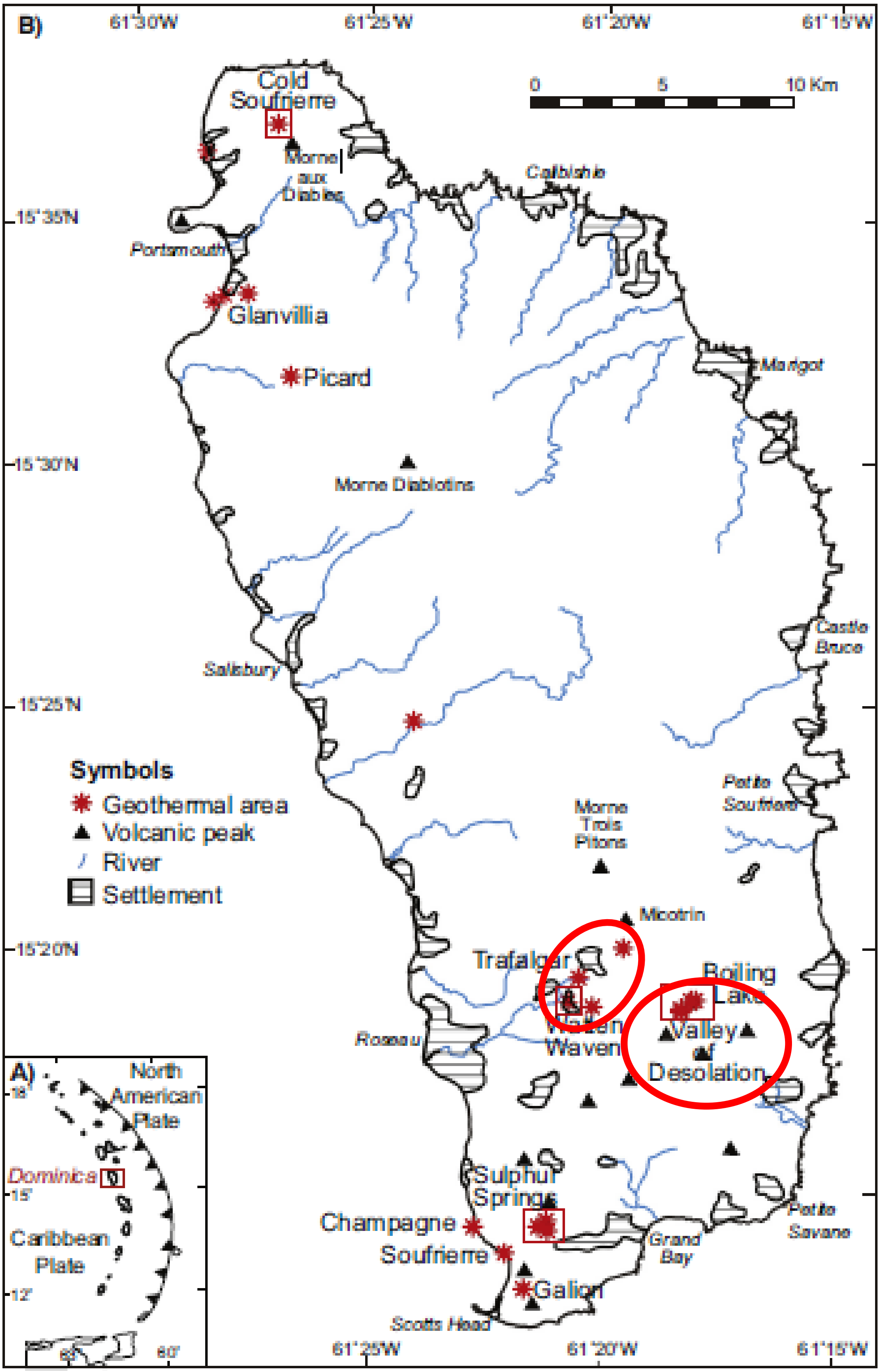


Figure 11 - A map of Dominica (modified from Smith et al., 2013) highlighting geothermal areas (springs, fumaroles, bubbling pools) (from Joseph et al., 2019).

Geothermal potential of Dominica was first reported during an UNDP visit (Barnea *et al.*, 1969). First detailed exploration was done by the French Geological Survey (BRGM) between 1982 and 1984. It included geology, geochemistry and geophysical (gravimetric, resistivity, magnetotelluric) methods (BRGM, 1984 and 1985). Two areas of interest were investigated: Wotten Waven and Soufriere regions (Fig. 11). Wotten Waven is located in the Roseau River valley about 8 km ENE of the Roseau city. Soufriere is located at the southern tip of the island. Later, Geotermica Italiana (1992) carried out an assessment of geothermal resources in the Eastern Caribbean, funded by UN-DTCD and CARICOM.

More recently, a new exploration survey including field geology and fluid geochemistry was done in the region of Wotten Waven as part of the Eastern Caribbean Geothermal Development Programme "Geo-Caraïbes" funded by the OAS (Organization of American States). This survey updated previous data and provided a preliminary conceptual model of the reservoir (Lasne and Traineau, 2005).

In 2008, another programme called "Geothermal Energy in Caribbean islands" or "Géothermie Caraïbes" was initiated by the E.U., the Commonwealth of Dominica and France as part of the European INTERREG III-B Programme "Espaces Caraïbes". It supported a prefeasibility study of the development of the Wotten Waven geothermal field, which is better named “the Roseau Valley geothermal field” because it extends widely outside the area of Wotten Waven village (Fig. 12). It included additional field surveys in geology and fluid geochemistry (Traineau and Lasne, 2008), and a new MT survey done by BRGM (Baltassat *et al.*, 2008). Based on these surveys, the Government of Dominica drilled five deep exploration wells between 2012 and 2014 in order to develop a 7 MWe geothermal power plant.

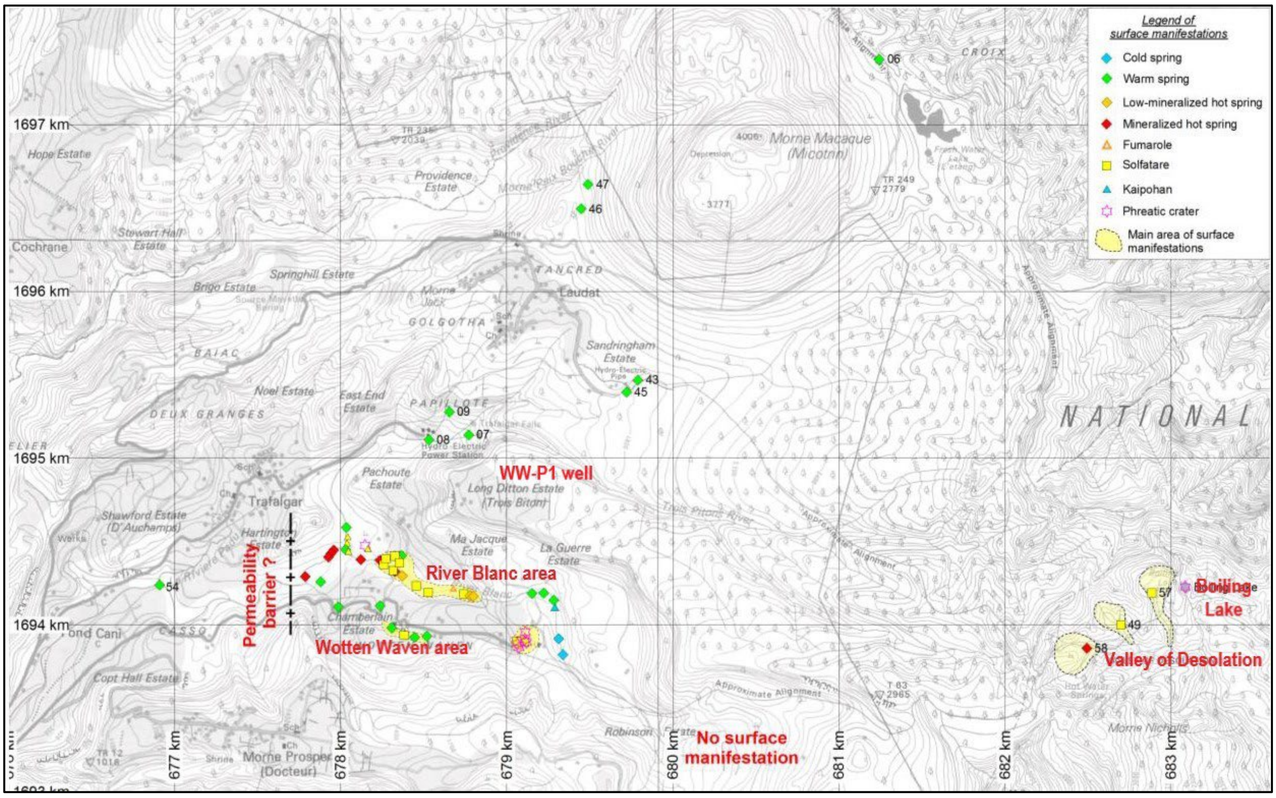


Figure 12 - Type and location of the surface manifestations of the Roseau valley geothermal field compiled by Traineau and Lasne (2008). Coordinates in UTM WGS84. Elevation in feet (from Traineau et al., 2015b).

Among the drilled wells, the chemical composition of the fluids discharged from the WW-P1 geothermal well (about 1500 m deep; Fig. 12) in the Wotten Waven area are presented in the Jacobs report data (2018) and could be used for this study. Six complete samples of vapour and liquid collected during the flow test carried out in June 2014 were analysed. For this study, we selected the chemical composition of the last collected liquid sample (15/06/2014). This NaCl fluid has a TDS value close to 5.2 g/l. In the Jacobs report (2018), the WW-P1 chemical composition was also calculated from that of the six collected vapour and liquid samples, using the chemical speciation programme WATCH and assuming a reservoir temperature of 246°C. This calculated chemical composition was similar to that we selected and the corresponding TDS value was close to 5.0 g/l.

The chemical composition of a sample collected from the RR1 hot spring (Lasne and Traineau, 2005; Fig. 12) in the Roseau River area, characterized by a recent volcanic activity (less than 50000 years BP) with several eruptive centres located in its northern and eastern margins, was also selected for this study. The discharge temperature of this spring is 84.5°C and the salinity of this NaCl fluid is close to 3.1 g/l. Another thermal water from the Blanc River area (BR3 sample; Lasne and Traineau, 2005; Fig. 12) was selected for this study. The discharge temperature of this spring is 92.8°C and the salinity of this NaCl fluid is close to 4.1 g/l.

The Boiling Lake, a vigorously bubbling hot (80-90°C), saline-rich volcanic lake characterized by a strongly degassing plume, is the most prominent volcanic feature of Dominica. A structural control is considered for Boiling Lake with the proximity of a NNW-SSE trending fault. Situated within two kilometres of the Valley of Desolation, the Boiling Lake is a ~ 50 m × 60 m Crater Lake with a depth of 12-15 m (Fig. 12). It is believed to have formed as a result of a phreatic or phreatomagmatic explosion, similar to that which occurred in the nearby Valley of Desolation (Lindsay *et al.*, 2005; Fournier *et al.*, 2009). Ca-rich Na-Cl waters discharge in the Valley of Desolation and the vicinity of the Boiling Lake (Fig. 12). Their higher contents of calcium and chloride could be indicative of a strong degassing before they reach the surface. Na-K geothermometers indicate higher deep equilibrium temperatures (up to 300°C). Three samples of thermal waters from this area were also selected for this study (BRGM, 1985; Lasne and Traineau, 2005; Joseph *et al.*, 2011). The discharge temperatures are 96.6, 96.5 and 84.0°C, respectively. Their TDS values are 10.7, 9.1 and 5.2 g/l.

2.4. MONTSERRAT ISLAND

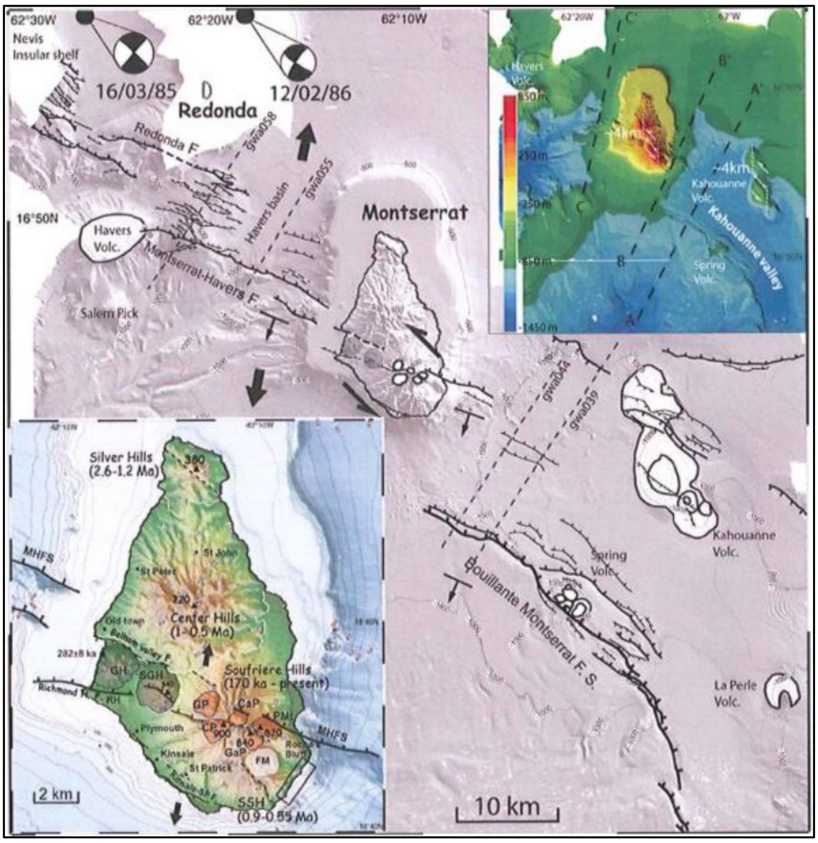
The active volcanic island of Montserrat is part of the northern section of the Lesser Antilles arc, in the eastern Caribbean. This island includes three major volcanic centres that range in age from Pleistocene to present day. Montserrat is built on the south-central part of a submarine bank which is 200 m below sea level, and measures 15 km eastwest by 25 km north-south (Brophy *et al.*, 2014). The island was formed by successive andesitic eruptive centres ranging from the older Silver Hills (2,580 ± 60 ka and 1,160 ± 46 ka), and Centre Hills (954 ± 12 and 550 ± 23 ka) (Harford *et al.*, 2002) in the north to the currently active Soufriere and South Soufriere Hills in the southern half of the island (Fig. 13a).

The summit area of the Soufriere consists primarily of a series of andesitic lava domes emplaced along an ESE-trending zone with block-and-ash flows and surge deposits associated with dome growth predominating on the flanks. Renewed eruptive activity from the Soufriere Hills volcano since 1995 destroyed the main town of Plymouth and left approximately a third of the island uninhabitable. As a result, such an active volcanic heat source suggests a great potential for geothermal electrical power generation.

Two prominent regional fault systems dominate the structural framework of Montserrat (Fig. 13a):

- the NNW-SSE striking Basse-Terre - Montserrat fault (also known as the Montserrat - Marie Galante fault) is an important regional fault system extending from south of Montserrat to the west of Guadeloupe and deforms the southern sector of Montserrat;
- the Redonda fault system, named for a small island located a few miles west of Montserrat, strikes WNW, but is less distinct than the Basse-Terre - Montserrat system and has been mapped in cliff exposures on both east and west coast of Montserrat.

a)



b)

Figure 13 - a) Seism-tectonic map and volcanic Setting of Montserrat (from Feuillet et al., 2010); b) Location map of the geothermal wells MON-1 and MON-2 and of the main thermal springs and fumaroles in the Montserrat Island (from Brophy et al., 2014).

Two major morphological features dominate the prospect area: Garibaldi Hill and St George's Hill (Fig. 13a). A review of aerial photography and satellite imagery suggest that a N-S fault separates the two distinctive blocks. St Georges Hill consists mainly of andesitic block-and-ash flow deposits, pumice-and-ash flow deposits and epiclastic deposits. Garibaldi Hill and Richmond Hill are composed of similar pyroclastic and epiclastic sequences. Consequently, the predominant local lithofacies are more characteristics of modern flank environments or flank-slope deposits derived from a lava dome such as at the currently active Soufriere Hill Volcano, rather than deposits that would form around a small vent.

The most important thermal manifestations of Montserrat are the thermal springs located on the western shore of the island, approximately 1 km NW of Plymouth and the four fumarolic fields located on the slopes of Soufriere Hills Volcano (Fig. 13b). The largest fumarolic field is Galway's Soufriere, on the southern flanks of Soufriere Hills Volcano, where hundreds of fumarolic vents and several mud pools and boiling pools are present in a 400- x 400-m-wide depression. Outlet temperatures of all fumarolic vents (98-99°C) are close to the boiling point of water at the average atmospheric pressure (948-978 mbar) of their altitude of 570-310 m. The Tar River Soufriere comprised approximately 10 fumarolic vents on the northeastern volcano slope. The fumaroles were buried or destroyed by a sequence of explosive ash eruptions that eventually buried the town of Plymouth on the western coast of the island.

Most modern geochemistry methods have been applied on Montserrat data to understanding and monitoring precursors of eruptive events over the past decade (Chiodini *et al.*, 1996; Hammouya *et al.*, 1998; Boudon *et al.*, 1998; Young *et al.*, 1998). The fumaroles that were the basis of early monitoring efforts are destroyed, but the chemistry of their gases provide evidence of continued magmatic input and strong magmatic heat sources for a viable geothermal system on Montserrat.

In 2009, EGS, Inc. (EGS) was contracted by the Government of Montserrat to conduct a scoping survey on geothermal activity on the island, and to develop a conceptual resource model based on existing and new exploration data (Poux and Brophy, 2012). The exploration work completed by EGS included geological, geophysical and geochemical surveys. Fluid geochemistry analyses consisted of both a set of data from previous surveys and a new set of samples. All the data compiled led to a high probability for the occurrence of a geothermal system in the southwestern portion on the island.

Based on the interpretation of these exploration works, high priority areas were defined for exploratory drilling. Preferred sites were identified in a zone protected from potential hazards, mostly pyroclastic flows, within a faulted half-graben between St George's and Garibaldi Hills (Fig. 13a), where MT interpretations suggested an altered clay cap covered a potential hydrothermal system. It was recommended to complete test drilling to demonstrate the presence of such a system. Accessible springs, water supply wells and monitoring wells in central Montserrat were sampled by EGS and ThermoChem in the summer of 2009 and analysed for major and trace elements (Poux and Brophy, 2012).

Two successful wells were drilled in this faulted half-graben in the central-southern part of the island during 2013. MON-1 encountered at least one fractured zone at 2191 m and was drilled to a total depth of 2298 m, where static bottom-hole temperatures of 230°C were measured. MON-2 was drilled approximately 500 m northeast (Fig. 13b) to a total depth of 2870 m. Based on circulation losses, the well crossed several fracture zones and bottom-hole temperatures of 260°C were recorded. The chemical compositions of the fluids discharged from these two wells were presented by Brophy *et al.* (2014) and are used for this study.

The chemical compositions of some thermal waters from St George Hill, South Soufriere volcano and Soufriere Hill areas (Fig. 13b) were also used for this study. In the St George Hill area, the three selected hot springs have discharge temperatures of 47.6, 59°C and 89.8°C, respectively, and their NaCl fluids have TDS values ranging from 25.1 to 30.5 g/l (Chiodini *et al.*, 1996; Poux and Brophy, 2012). In the South Soufriere volcano area, the two selected thermal springs have discharge temperatures of 80.4 and 98.0°C, respectively, and their Na-Ca-SO_4 fluids have relatively low TDS values close to 1.4 - 1.7g/l. In the Soufriere Hill area, the two selected thermal springs have discharge temperatures of 95.4 and 98.0°C, respectively, and their Na-Ca-SO_4 fluids have TDS values of 6.5 and 13.2 g/l.

2.5. SAINT LUCIA ISLAND

The Island of Saint Lucia is located between Martinique and St Vincent, in the southern region of the Lesser Antilles (Fig. 14). It belongs to the Windward Islands and is one of the larger islands of the arc, with an area of approximately 610 km^2 (Joseph *et al.,* 2013). The most pronounced topographic feature is the N-S trending axial range with the highest mountain, Mount Gimie (950 m), located in the south-western part of the range (Fig. 14). Saint Lucia is made up almost exclusively of volcanic rocks, but only one volcano, the Soufriere Volcanic Centre (SVC) in the southwest of the island, is considered to be potentially active (Lindsay *et al.*, 2005). The youngest age dates available for large pyroclastic eruptions at the SVC are 20000 years B.P. (Schmitt *et al.*, 2010). However, several lava domes and explosion craters have formed since then (e.g. Belfond: 13.6 ± 0.4 ka; Terre Blanche: 15.3 ± 0.4 ka; Schmitt *et al.*, 2010). Together with the occurrence of occasional swarms of shallow earthquakes and vigorous hot spring activity in southern Saint Lucia, these features indicate that this area is still potentially active and could generate volcanic eruptions in the future.

The most recent activity occurred within the Qualibou depression whose geology was first described by Tomblin (1964) as a caldera collapse. This hypothesis was further supported by the work of AQUATER (1982) and Wohletz *et al.* (1986). Alternatively, Roobol *et al.* (1983) and Wright *et al.* (1984) have proposed that the Qualibou depression was formed by a gravity slide. The depression edges are no longer circular and are mainly controlled by NE-SW faults.

Intense activity was developed inside this area with the emplacement of various dacitic domes, among which the two spectacular plugs of Gros Piton and Petit Piton are the most characteristic features of the whole island. The age of formation of Qualibou caldera was previously estimated at 0.5 Ma (Aspinall *et al.*, 1976), but new radiocarbon ages proposed by Roobol *et al.* (1983) indicate an age less than 40000 years. This is confirmed by geological works by Wohletz and Heiken (1984), who find that caldera formation postdates that of the Pitons.

The geology of St. Lucia consists of several distinct volcanic sequences interstratified with minor marine sedimentary rocks (AQUATER, 1982). In general, volcanism was initiated in the north around 10 Ma ago and migrated southwards. Rock compositions evolved from basaltic to andesitic to dacitic types through time but andesites volumetrically dominate. The precaldera rocks surrounding Qualibou caldera are composed almost entirely of andesites in the 2.5-Ma range (i.e. Mt. Gimie). Later dome eruptions built the dacite edifices of Petit and Gros Pitons (0.25 Ma) before caldera formation. These extrusive eruptions produced large quantities of breccias and tuffs as well as typical domes and flows.

There are several areas of fumarolic and hot spring activity associated with the Soufriere Volcanic Centre. Several hot springs discharge within Qualibou caldera, but by far the most impressive thermal features occur at the well-known Sulfur Springs Valley (Robson and Willmore, 1955), which is close to the caldera centre and the youngest pyroclastic vents (Fig. 14). The main area of the Sulphur Springs geothermal field is comprised of numerous hot and boiling springs, bubbling mud pools, and fumaroles in an area of strongly clayey altered rock approximately 200 m×100 m in size. According to Williamson (1979), this thermal area is oriented parallel to faults and fractures that strike NW-SE and dip 60 to 70° NE.

Many fumaroles have temperatures of up to 100°C or hotter, with temperatures of up to 172°C being recorded on occasion (Lindsay, 2001). There is an extensive area of hydrothermally altered ground together with stunted vegetation on the flanks of Terre Blanche, indicating that this area was once geothermally active. Thermal springs are also present at Diamond and Cresslands (Fig. 14), which are located about 200-300 m from the northern and eastern base of the Terre Blanche dome, respectively (Wohletz *et al.*, 1986).

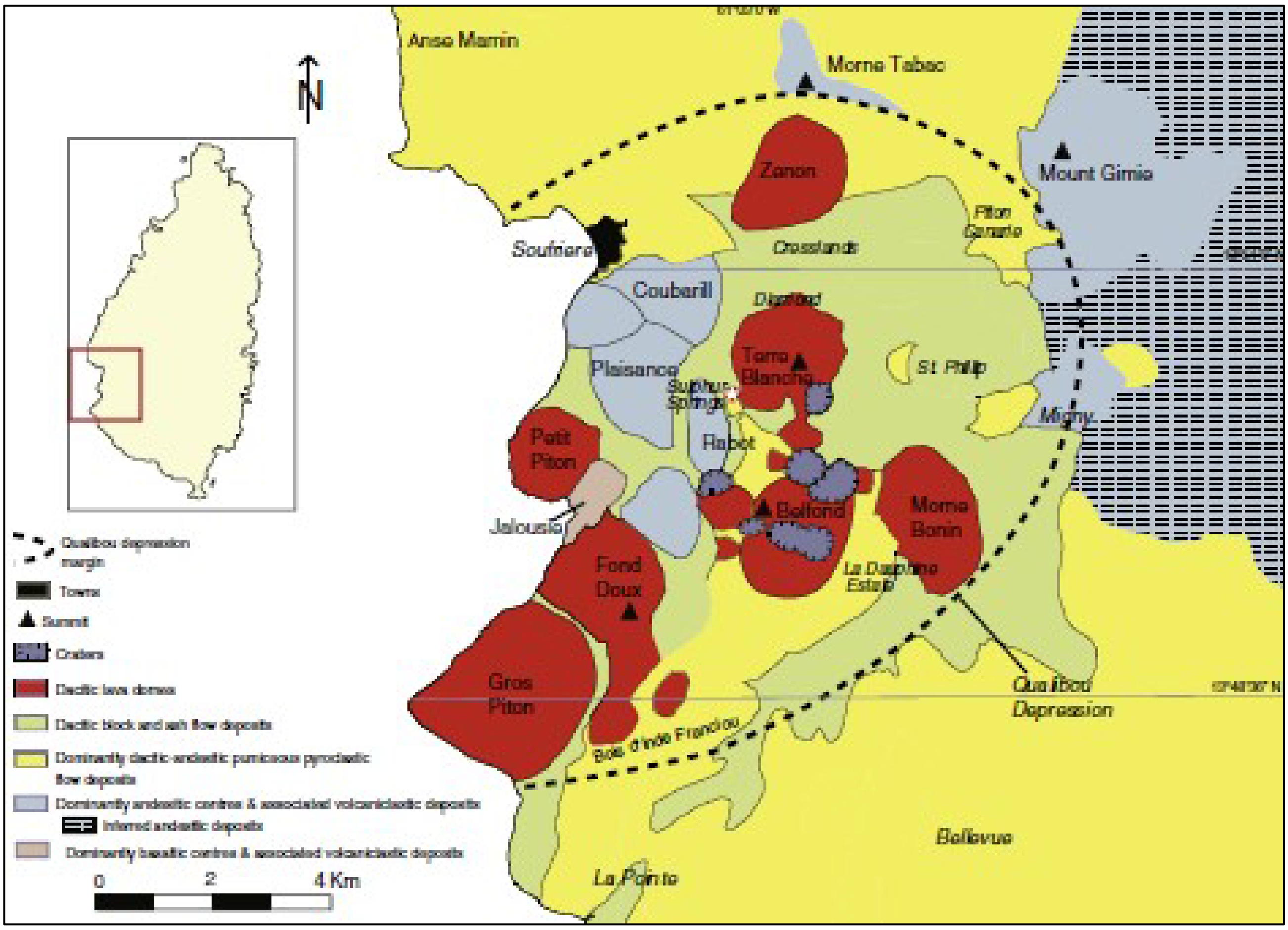


Figure 14 - Map of Saint Lucia showing an outline of the Qualibou Depression and main vents of the Soufriere Volcanic Centre (right) (from Joseph et al., 2013).

Several other sites of geothermal activity can be found in southern Saint Lucia, including the Jalousie warm springs and underwater gas vents offshore between Anse Mamin and Soufriere Bay (Fig. 14) (Lindsay *et al.*, 2005).

Investigations of the geothermal energy potential of the Sulphur Springs area date back to at least 1951 (Bodvarsson, 1951; Robson and Willmore, 1955). In 1974, preliminary geological and geophysical investigations were carried out and a subsequent drilling program followed.

Drilling was carried out in two phases: five wells in 1975 with two additional wells in 1976. The wells ranged in depth from 116 to 725 m and were drilled in and around the Sulphur Springs area (Fig. 14). Three wells were non-productive, while the tests performed on the other four showed that steam viable for commercial electricity production entered boreholes 4, 5 and 7 at depths between 230 and 612 m. Well 3 produced a relatively small amount of dry steam at shallow depth (133 m) (Merz and McLellan, 1976, 1977; Williamson, 1979). The gas content of the steam was generally high, varying from 15 wt% (well 3) to 21 wt% (wells 4 and 7). The gas composition (vol.%) was mainly CO_2 (90%) with lesser amounts of H_2 (6%), H_2S (2%), N_2 (1%) and CH_4 (0.5%) (Williamson, 1979). Maximum measured temperature was 220°C in well 4 at a depth of 300 m, while well 6 showed a temperature gradient of 220°C/km in the section from 320 to 692 m.

In 1982, extensive geological, geophysical and geochemical surveys were performed. The results achieved in the investigations carried out in the period from 1982 to 1984 by AQUATER and Los Alamos National Laboratory encouraged the Government of St Lucia, the United Nations Revolving Fund and the U.S. Agency for International Development to finance a drilling project for deep exploration of the Qualibou area. Under this project, the SL-1 well was drilled from April to July 1987 in the Belfond area and was non-productive.

A high-temperature geothermal resource was located, which was tapped by means of the SL-2 well drilled in 1988 to a total depth of 1413 m, in the Sulphur Springs area. The well encountered mainly dacitic agglomerates and lava flows and a permeable zone below ≈ 1340 m, with a maximum temperature close to 290°C. Well productivity decreased from an initial value close to 62 to about 33 t/h under well-head pressures of 15 bar, after 255 h of production. Initial reservoir static pressure was 75 bar (D'amore *et al.*, 1990). During the first two days of exploitation, the well initially produced a two-phase fluid with high steam fraction, which then developed into superheated steam with a high content of non-condensable gas exceeding 100 l/kg at standard conditions and a computed P_{CO2} of 10 bar. High HCl concentrations of about 300 ppm were present in the condensate steam indicating the presence of a high concentrated boiling brine to the point of halite saturation. All data support the assumption of a hydrothermal hot-water system prior to drilling, which underwent a very rapid drawdown with production (D'Amore *et al.*, 1990).

Unfortunately, only partial chemical compositions of the fluids from some of these deep geothermal wells (well 4 and well SL-2) could be used for this study (Goff and Vuataz, 1984; D'Amore *et al.*, 1990). No trace chemical composition was available.

More detailed chemical compositions of thermal waters from the Qualibou Caldera and Terre Blanche areas were used for this study. In the Qualibou caldera, the four selected thermal springs have discharge temperatures of 35.2, 43.0, 43.1 and 55.7°C, respectively, and Na-HCO_3 fluids with relatively low TDS values (from 0.8 to 2.0 g/l; Ander *et al.*, 1984; Gandino *et al.*, 1985). In the Terre Blanche area, the two selected thermal springs have discharge temperatures of 76 and 90°C, respectively, and Na-SO_4 fluids, with relatively low TDS values (2.2 - 2.6 g/l; Gandino *et al.*, 1985).

3. Analytical data used for this study

The geochemical data used for this study come from two sources:

- an extensive literature review on the waters of deep geothermal wells and thermal springs existing in the Guadeloupe, Martinique, Dominica, Montserrat and Saint Lucia islands;
- data acquisitions in Martinique and Guadeloupe during this study, after collection and/or chemical analyses of fluid samples.

For these last data, a team from BRGM and the LARGE laboratory of Antilles University (AU) carried out a field campaign of water collection in Martinique between July 5 and 7, 2022 (Bernard and Dixit, 2023). Seven water samples were collected from thermal springs located in the areas of Lamentin plain (4), Anses d'Arlet (2) and Mount Pelée volcano (1), and adequately conditioned (0.45 µm filtration for analyses of major anions and F, and 0.45 µm filtration and acidification with Suprapur HNO_3 for analyses of major and trace cations and Li isotopes). The values of temperature, pH, conductivity, Redox and dissolved oxygen were measured on site (Tab. 1).

The Cl and SO_4 major anions, and the Br minor anion, were analyzed in the AU and BRGM laboratories, using ion chromatography. Dissolved silica was analysed in the AU laboratories by spectrophotometry (Bernard and Dixit, 2023). The concentrations of Na, K, Ca and Mg major cations and trace species such as F, Sr, Mn, Fe, Li, Rb, Cs, W were determined in the BRGM laboratories, using ion chromatography for fluoride and Inductively Coupled Plasma Mass Spectrometry (ICP/MS) for the major cations and trace species. Alkalinity was also determined in these laboratories by titration. The relative analytical uncertainty is 5% for the major cations and anions, alkalinity and dissolved silica, and 10% for Br and the trace species. These trace species (or part of them) were also analysed for some fluid samples from Guadeloupe, which had been collected during previous studies and had been adequately stored in the BRGM laboratories. The δ^7Li values were measured in the BRGM laboratories using Thermo Ionization Mass Spectrometry and Neptune Multi Collector ICP-MS. The external reproducibility of the δ^7Li values was estimated at around ± 0.5‰.

All the analytical results used for this study are reported in Table 1 and Table 2.

Area	Sampling point	Date	$T_{surf.}$ °C	Cond. 25°C mS/cm	pH	Eh mV	O_2 %	O_2 mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cl mg/l	Alk. mg/l HCO_3	SO_4 mg/l	TDS g/l
Anses d'Arlet	Petite Anse - Diamant hot spring 1	05/07/2022	32.8	31.70	6.30	-103	100	7.34	5573	335	903	316	9848	1600	677	19.4
	Petite Anse - Diamant hot spring 2	05/07/2022	31.1	31.30	6.33	24.0	23.6	1.80	5608	344	871	252	9723	1550	565	19.1
Lamentin plain	Ferme Perrine hot spring	06/07/2022	38.5	17.10	6.27	-125	1.3	0.08	3678	150	805	137	6982	800	352	13.0
	Habitation Carrère hot spring	06/07/2022	57.3	16.35	6.02	-83.3	5.7	2.00	3589	140	801	130	6688	750	334	12.5
	Maimaine hot spring	06/07/2022	34.0	19.44	6.13	56.1	19.3	1.36	3897	115	789	133	7269	950	176	13.4
	Bord Lézarde hot spring	06/07/2022	59.6	19.00	6.09	-101	40	2.45	3553	155	776	131	6792	780	337	12.6
Mount Pelée volcano	Rivière Chaude - MP4 hot spring	07/07/2022	32.0	1.17	6.04	114	5.2	0.35	220	25.3	60.0	20.6	50.0	610	135	1.2

Sampling point	Date	SiO_2 mg/l	F mg/l	Br mg/l	Fe mg/l	Sr µg/l	Mn µg/l	Li µg/l	Rb µg/l	Cs µg/l	W µg/l	δ^7Li ‰	References
Petite Anse - Diamant hot spring 1	05/07/2022	130	< 0.1	24.5	0.33	14202	1139	9819	879	276	< 0.05	6.96	This study
Petite Anse - Diamant hot spring 2	05/07/2022	134	< 0.1	24.0	6.38	14901	1191	10994	941	269	< 0.05	6.97	This study
Ferme Perrine hot spring	06/07/2022	55	0.40	23.5	0.90	20560	186	1481	566	253	< 0.05	6.61	This study
Habitation Carrère hot spring	06/07/2022	74	0.30	23.0	4.66	20591	274	1456	559	244	< 0.05	7.05	This study
Maimaine hot spring	06/07/2022	60	< 0.1	24.2	0.40	20824	175	1356	494	201	< 0.05	10.05	This study
Bord Lézarde hot spring	06/07/2022	79	0.40	23.1	4.92	20209	281	1329	543	226	< 0.05	8.26	This study
Rivière Chaude - MP4 hot spring	07/07/2022	124	0.30	< 0.1	0.50	297	1818	993	79	10	< 0.05	8.38	This study

Table 1 - On site measurements and chemical and Li isotope analyses of the thermal waters collected during the field campaign carried out by a BRGM-AU team in July 2022 in Martinique.

Island	Area	Sampling point	Date	$T_{surf.}$ °C	$T_{res.}$ °C	1000/T	pH	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cl mg/l	Alk. mg/l HCO_3	SO_4 mg/l	SiO_2 mg/l	TDS g/l
Guadeloupe	Bouillante geothermal field	BO-2 well	05-1996	165.0	250	1.91	7.19	6437	997	2385	1.5	15351	19.8	17.3	603	25.9
		BO-2 well	27/03/1998	165.0	250	1.91	6.92	6195	867	2211	1.4	14890	17.7	16.5	567	24.9
		BO-4 well	23/03/2005	165.0	260	1.88	6.83	5700	840	2020	1.6	13000	24.4	24.5	530	22.2
		BO-4 well	11/12/2007	165.0	260	1.88	6.86	5944	832	2135	1.6	13986	23.0	26.0	571	23.0
		BO-5 well	29/11/2002	165.0	260	1.88	7.06	6650	860	2060	2.2	14501	25.6	20.0	580	24.8
		BO-5 well	11/12/2007	165.0	260	1.88	5.41	6207	900	2118	1.8	13850	18.0	< 0.5	597	23.2
		BO-5 well	26/01/2011	165.0	260	1.88	7.24	6259	968	2096	< 0.5	14545	22.0	19.0	601	24.5
		BO-5 well	07/11/2012	165.0	260	1.88	7.36	5983	950	2178	1.3	14400	23.8	10.7	648	24.2
		BO-6 well	08/07/2003	165.0	260	1.88	6.65	6956	982	2189	2.3	14970	26.8	22.0	602	25.8
		BO-6 well	11/12/2007	165.0	260	1.88	5.10	5880	827	2200	1.8	13891	29.9	19.8	576	22.9
		BO-6 well	07/11/2012	165.0	260	1.88	7.32	6000	926	2158	1.2	14600	23.0	12.0	648	24.4
		BO-6 well	19/01/2021	165.0	260	1.88	5.59	5515	809	2111	1.2	13599	22.0	18.5	561	22.6
	Grande Soufriere volcano	Piton Tarade hot spring	07/12/2006	30.8	60	3.00	7.99	86.4	14.2	184	62.2	144	94.6	612	107	1.3
			2000	44.4	60	3.00	6.07	75.0	14.1	194	58.2	142	104	579	111	1.3
		Pas du Roy hot spring	07/12/2006	33.5	50	3.09	5.65	52.5	8.1	139	37.9	60.8	48.2	474	115	0.9
			2000	40.1	50	3.09	5.59	59.4	8.7	169	49.8	85.9	64.0	580	115	1.1
		Bains Jaunes hot spring	07/12/2006	30.1	50	3.09	5.37	35.8	5.8	95.5	24.4	45.4	13.4	337	107	0.7
			2000	27.7	50	3.09	5.02	40.6	5.0	101	27.3	46.8	18.0	384	102	0.7
			1985	26.4	50	3.09	5.12	52.9	7.0	160	45.7	151	14.6	451	159	1.0
		Eaux vives - Matouba hot spring	07/12/2006	44.6	60	3.00	6.00	33.9	7.7	253	12.4	20.8	12.8	700	25	1.1
			2000	58.8	60	3.00	5.65	33.8	8.2	257	12.0	18.1	23.0	708	37	1.1
			1985	59.0	60	3.00	5.90	32.9	8.2	265	12.4	19.1	20.8	720	34	1.1
		Chute du Carbet hot spring	08/12/2006	43.4	90	2.75	6.58	77.4	19.0	88.2	37.1	141	146	240	96	0.8
			2000	44.9	90	2.75	6.51	116	24.0	188	64.9	368	125	303	110	1.3
			1985	45.2	90	2.75	6.73	82.5	22.7	112	51.0	266	152	185	110	1.0
		Grosse Corde hot spring	09/12/2006	39.2	70	2.91	6.49	85.7	18.7	102	38.8	243	243	189	78	0.9
			2000	48.6	70	2.91	6.37	129	23.6	180	70.9	557	103	180	110	1.4
			1985	35.9	70	2.91	6.46	116	23.5	222	96.0	709	115	96.1	91	1.5
Martinique	Lamentin plain	Californie well (TDP)	15/03/2001	48.0	110	2.61	6.27	2650	168	824	138	4915	1351	274	100	10.4
		Californie well (TDP)	26/03/2002	73.6	110	2.61	6.04	3790	124	725	130	7050	982	316	69	13.2
		Habitation Carrère well (TDP)	21/11/2001	41.0	110	2.61	6.08	3310	125	830	187	6335	1593	333	91	12.8
		Habitation Carrère well (TDP)	05/12/2001	40.1	110	2.61	6.12	3280	122	778	183	6358	1562	127	90	12.5
		Ferme Perrine hot spring	06/07/2022	*38.5*	*110*	*2.61*	*6.27*	*3678*	*150*	*805*	*137*	*6982*	*800*	*352*	*55*	*13.0*
		Habitation Carrère hot spring	06/07/2022	*57.3*	*110*	*2.61*	*6.02*	*3589*	*140*	*801*	*130*	*6688*	*750*	*334*	*74*	*12.5*
		Maimaine hot spring	06/07/2022	*34.0*	*110*	*2.61*	*6.13*	*3897*	*115*	*789*	*133*	*7269*	*950*	*176*	*60*	*13.4*
		Bord Lézarde hot spring	06/07/2022	*59.6*	*110*	*2.61*	*6.09*	*3553*	*155*	*776*	*131*	*6792*	*780*	*337*	*79*	*12.6*
	Anses d'Arlet	Petite Anse - Diamant hot spring 1	06/12/2001	35.3	180	2.21	5.99	5800	295	1100	300	10200	1679	500	131	20.1
		Petite Anse - Diamant hot spring 1	05/07/2022	*32.8*	*180*	*2.21*	*6.30*	*5573*	*335*	*903*	*316*	*9848*	*1600*	*677*	*130*	*19.4*
		Petite Anse - Diamant hot spring 2	05/07/2022	*31.1*	*180*	*2.21*	*6.33*	*5608*	*344*	*871*	*252*	*9723*	*1550*	*565*	*134*	*19.1*
	Mount Pelée volcano	Chaude River - MP4 hot spring	11/12/2001	51.4	200	2.11	6.40	263	25.5	35.9	13.5	68.1	621	153	143	1.3
		Chaude River - MP4 hot spring	07/07/2022	*32.0*	*200*	*2.11*	*6.04*	*220*	*25.3*	*60.0*	*20.6*	*50.0*	*610*	*135*	*124*	*1.2*
		Picodo River - MP10 hot spring	16/03/2003	36.6	150	2.36	6.37	268	33.3	95.4	50.6	451	440	60.5	181	1.6
Dominica	Wotten Waven	WW-P1 well	15/06/2014	201.9	250	1.91	6.23	1680	252	56.4	0.28	2940		20.4	502	5.2
	Roseau River	RR1 hot spring	17/01/2005	84.5	220	2.03	7.30	1060	92.9	91.6	2.0	1787	60.0	25.3	184	3.1
	Blanc River	BR3 hot spring	19/01/2005	92.8	220	2.03	8.31	1331	119	71.5	< 0.5	2450	49.0	45.8	194	4.1
	Valley of Desolation	VD1 hot spring	18/01/2005	96.5	300	1.74	6.90	868	208	1867	117	5892	32.0	93.8	291	9.1
		Boiling Lake hot spring	25/11/2000	84.0	300	1.74	4.20	616	321	1152	42	879		2189		5.2
		Boiling Lake - DM26 hot spring	1985	96.6	300	1.74	6.45	1039	286	2441	178	6308	36.6	96.0	284	10.7
Montserrat	St George Hill	MON-1 well	27/10/2013	153.0	230	1.99		8660	761	3757	10.0	20557		23	383	34.2
		MON-2 well	18/12/2013	153.0	230	1.99		7950	703	3370	8.1	19080		18	355	31.5
		EGS/TCI - MHP-1 hot spring	2012	59.0	230	1.99	5.57	7233	1001	1944	247	16340	161	222	259	27.4
	St George Hill	Hot spring 1	March 1991	89.8	230	1.99	6.60	7880	1030	2510	302	18200	128	161	315	30.5
		Hot spring 2	March 1991	47.6	230	1.99	6.00	6200	758	2070	454	15000	195	174	232	25.1
	South Soufrière volcano	Hot spring 4	March 1991	80.4	200	2.11	6.20	121	8.3	126	59.7	23.2	238	631	180	1.4
		Hot spring 5	March 1991	98.0	200	2.11	6.40	114	12.0	207	42.8	21.2	55.0	1018	216	1.7
	Soufrière Hills	Hot spring 7	March 1991	95.4	230	1.99	1.60	105	4.0	152	93.8			5671	428	6.5
		Hot spring 9	March 1991	98.0	230	1.99	1.80	194	29.3	230	161			12250	380	13.2
Saint Lucia	Sulphur springs	Well 4	02/04/1976	100	180	2.21	5.69	3500	151	5300		18000				
		Well 4	06/04/1976	100	180	2.21	5.85	500	50	1850		6120			88	
		Well 4	22/04/1977	100	180	2.21	4.52	11100	565	22200		70200			103	104
		SL-2 well (25.3 h of production)	February 1988	100	290	1.78	7.10	700	650	1206		3760	49		625	
		SL-2 well (45 h of production)	February 1988	100	290	1.78	5.20			2044		6700				
		SL-2 well (68.5 h of production)	February 1988	100	290	1.78	4.70			4459		15650	0			
	Qualibou Caldera	Diamond - SL12 warm spring	July 1983	43.1	170	2.26	6.45	129	11.0	69.2	42.3	40.0	686	21.8	171	1.2
		Cresslands - SL15 hot spring	July 1983	55.7	150	2.36	6.55	257	16.5	163	56.5	153	1215	0.77	110	2.0
		Malgretoute - SL17 warm spring	July 1983	35.2	150	2.36	8.57	267	15.4	23.1	20.3	74.0	648	105	101	1.3
		Hot spring 103	1985	43.0	170	2.26	7.00	182	14.1	72.1	47.4	33.7	91.5	8.6	198	0.8
	Terre blanche	Hot spring 133	1985	76.0	290	1.78	6.70	62.1	16.4	128	21.9	532	317	624	168	2.6
		Hot spring 134	1985	90.0	290	1.78	6.90	71.3	13.7	102	15.8	245	256	624	168	2.2
Guadeloupe		Seawater	1998	29.0	29.0	3.31	8.23	11000	401	467	1346	20181	169	3000	0.43	36.6
Martinique		Seawater	2001	28.5	28.5	3.32	8.19	11400	309	390	1200	20200	152	2626	0.19	36.3

On site measurements and chemical analyses done within the framework of this study

Table 2 - Chemical and Li isotope analyses of the thermal waters used for this work, selected from the literature review or collected and analyzed during this study (in blue).

Sampling point	F mg/l	Br mg/l	B mg/l	Sr mg/l	Ba mg/l	Mn mg/l	Fe mg/l	Li mg/l	Rb mg/l	Cs mg/l	Ge mg/l	W mg/l	δ^7Li ‰	References
BO-2 well		51.3	14.4	19.8	8.0	4.50		3.89	2.95	0.343			4.4	Sanjuan and Brach (1997)
BO-2 well	1.2	51.3	12.5	20.2	8.3	5.48	0.41	4.10	3.75	0.442		0.01150	4.4	Sanjuan *et al.* (1999)
BO-4 well	1.4	43.7	13.0	15.9	6.1	5.10	0.07	4.08	2.43	0.296	0.0110		4.3	Sanjuan *et al.* (2008)
BO-4 well	< 0.5	45.0		18.7		4.73	0.46	4.80	2.49	0.318		0.00808	4.5	Sanjuan *et al.* (2008)
BO-5 well	1.6	55.0	15.0	18.6	8.0	5.50	< 0.02	4.60	2.70	0.280	0.0110			Sanjuan *et al.* (2004)
BO-5 well	< 0.5	45.0		18.1		6.03	0.63	5.00	2.61	0.339		0.00797		Sanjuan et al. (2008)
BO-5 well	0.5	54.0	14.9	18.8	8.2	5.23	0.12	4.74	2.83	0.357	0.0128	0.00926		Sanjuan et al. (2013)
BO-5 well	1.5	50.0	16.1	20.7	8.3	5.99	0.17	5.33	2.91	0.377	0.0178			Sanjuan *et al.* (2013)
BO-6 well	1.0	56.0	14.8	19.9	8.2	6.05	0.20	6.18	2.97	0.334	0.0126		4.6	Sanjuan *et al.* (2004)
BO-6 well	< 0.5	45.4		18.3		5.79	0.90	5.10	2.59	0.329		0.00837		Sanjuan *et al.* (2008)
BO-6 well	1.5	51.0	15.9	19.7	8.0	5.49	0.17	5.37	2.83	0.375	0.0176	0.00866		Sanjuan *et al.* (2013)
BO-6 well	1.4	63.1	15.3	20.4	7.7	5.37	1.63	4.89	2.49	0.323	0.0105	0.00797		Sanjuan *et al.* (2021)
Piton Tarade hot spring	< 0.5	0.5		0.158		0.189	0.03	0.008	0.0574	0.00133		< 0.00005	20.1	Sanjuan *et al.* (2008)
			0.592	0.122		0.003		0.008						Brombach *et al.* (2000)
Pas du Roy hot spring	< 0.5	< 0.25		0.117		1.375	3.72	0.011	0.0350	< 0.0005		< 0.00005	14.5	Sanjuan *et al.* (2008)
			0.441	0.111		2.060		0.009						Brombach *et al.* (2000)
Bains Jaunes hot spring	< 0.5	< 0.25		0.100		0.564	0.0019	0.010	0.0213	< 0.0005		< 0.00005	9.9	Sanjuan *et al.* (2008)
			0.264	0.094		1.630		0.011						Brombach *et al.* (2000)
	0.40		0.350	0.202			0.019	< 0.02	0.0103	0.00040				Fabriol and Ouzounian (1985)
Eaux vives - Matouba hot spring	1.14	< 0.25		0.610		0.718	0.0242	0.002	0.0083	< 0.0005		< 0.00005		Sanjuan *et al.* (2008)
			0.068	0.515		0.698								Brombach *et al.* (2000)
	1.80		0.070	0.596			0.210	< 0.02	0.0034	< 0.00015				Fabriol and Ouzounian (1985)
Chute du Carbet hot spring	< 0.5	0.5		0.310		0.250	0.0023	0.014	0.0593	0.00151		< 0.00005	16.0	Sanjuan *et al.* (2008)
			0.317	0.477				0.014						Brombach *et al.* (2000)
	0.19		0.249	0.403			0.0017	< 0.02	0.0145	0.00120				Fabriol and Ouzounian (1985)
Grosse Corde hot spring	< 0.5	0.9		0.400		0.270	0.0027	0.007	0.0647	0.00198		< 0.00005	12.5	Sanjuan *et al.* (2008)
				0.661				0.008						Brombach *et al.* (2000)
	0.095		0.400	0.876			0.135	< 0.02	0.0350	0.00306				Fabriol and Ouzounian (1985)
Californie well (TDP)	0.30	18.5	33.3	17.6	0.47	1.720	90.2	1.55	0.510	0.182		0.000096	7.8	Sanjuan *et al.* (2002a, b)
Californie well (TDP)	0.50	22.5	41.5	22.3	0.57	0.816	24.1	1.59	0.528	0.215	0.0120	0.000152		Sanjuan *et al.* (2002a, b)
Habitation Carrère well (TDP)	< 0.2	23.3	35.3	17.9	0.42	3.2	170	1.47	0.569	0.180	0.0120	< 0.00005	6.2	Sanjuan *et al.* (2002a, b)
Habitation Carrère well (TDP)	< 0.2	22.3	35.2	18.1	0.28	2.8	186	1.67	0.567	0.133	0.0100	< 0.00005	6.0	Sanjuan *et al.* (2002a, b)
Ferme Perrine hot spring	0.40	23.5		20.6		0.186	0.90	1.481	0.566	0.253		< 0.00005	6.6	This study
Habitation Carrère hot spring	0.30	23.0		20.6		0.274	4.66	1.456	0.559	0.244		< 0.00005	7.1	This study
Maimaine hot spring	< 0.1	24.2		20.8		0.175	0.40	1.356	0.494	0.201		< 0.00005	10.1	This study
Bord Lézarde hot spring	0.4	23.1		20.2		0.281	4.92	1.329	0.543	0.226		< 0.00005	8.3	This study
Petite Anse - Diamant hot spring 1	< 0.1	25.0	78.2	14.8	0.17	1.7	6.14	10.1	1.01	0.299	0.0639	< 0.00005	6.8	Sanjuan *et al.* (2003; 2005b)
Petite Anse - Diamant hot spring 1	< 0.1	24.5		14.2		1.139	0.33	9.819	0.879	0.276		< 0.00005	7.0	This study
Petite Anse - Diamant hot spring 2	< 0.1	24.0		14.9		1.191	6.38	10.994	0.941	0.269		< 0.00005	7.0	This study
Chaude River - MP4 hot spring	0.30	< 0.2	1.77	0.135	0.06	0.869	0.23	1.50	0.100	0.00959	0.0048	0.000788	8.1	Sanjuan *et al.* (2003; 2005b)
Chaude River - MP4 hot spring	0.30	< 0.1		0.297		1.818	0.50	0.993	0.079	0.00959		< 0.00005	8.4	This study
Picodo River - MP10 hot spring	0.10	1.43	4.74	0.350	0.10	2.5	0.57	0.37	0.085	0.00700	0.0063	0.000145	5.4	Sanjuan *et al.* (2003; 2005b)
WW-P1 well	1.3	12.6	37.2	0.969	0.51	0.176	0.0338	4.10						Jacobs report (2018)
RR1 hot spring	0.60	7.5		0.654	0.049	0.169	< 0.02	2.20	0.544	0.328	0.0270			Lasne and Traineau (2005)
BR3 hot spring	1.0	9.1	28.8	0.646	0.010	0.040	< 0.02	2.55	0.722	0.378	0.0410			Lasne and Traineau (2005)
VD1 hot spring	< 0.1	0.1	53.3	8.64	2.8	33.9	0.38	1.11	0.815	0.159	0.0270			Lasne and Traineau (2005)
Boiling Lake hot spring	0.90	14.0						2.50						Joseph *et al.* (2011)
Boiling Lake - DM26 hot spring			40.7				27							BRGM (1985)
MON-1 well			16.0	47.0										Brophy *et al.* (2014)
MON-2 well			14.0	45.0										Brophy *et al.* (2014)
EGS/TCI - MHP-1 hot spring			22.0											Poux and Brophy (2012)
Hot spring 1	0.22		22.9					8.90						Chiodini *et al.* (1996)
Hot spring 2	0.15		18.6					6.70						Chiodini *et al.* (1996)
Hot spring 4	0.10		0.30					0.050						Chiodini *et al.* (1996)
Hot spring 5	0.15		0.36					0.030						Chiodini *et al.* (1996)
Hot spring 7								0.055						Chiodini *et al.* (1996)
Hot spring 9								0.11						Chiodini *et al.* (1996)
Well 4														Goff and Vuataz (1984)
Well 4														Goff and Vuataz (1984)
Well 4														Goff and Vuataz (1984)
SL-2 well (25.3 h of production)														D'Amore *et al.* (1990)
SL-2 well (45 h of production)														D'Amore *et al.* (1990)
SL-2 well (68.5 h of production)														D'Amore *et al.* (1990)
Diamond - SL12 warm spring	0.15	< 0.1	11.1	0.470	0.09	0.290	0.20	0.22	< 0.01					Ander *et al.* (1984)
Cresslands - SL15 hot spring	2.6	0.5	15.0	1.4	0.40	0.350	1.7	0.67	0.100					Ander *et al.* (1984)
Malgretoute - SL17 warm spring	0.16	0.1	8.91	0.690	0.06	< 0.01	0.030	0.41	< 0.01					Ander *et al.* (1984)
Hot spring 103	0.13		11.9					0.21						Gandino *et al.* (1985)
Hot spring 133	0.11		519					0.041						Gandino *et al.* (1985)
Hot spring 134	0.16		519					0.036						Gandino *et al.* (1985)
Seawater	2.9	67.0	5.24	8.65	0.008	0.021	0.030	0.25	0.089	0.00050			29.3	Sanjuan (2001)
Seawater	1.3	67.0	3.84	7.52	0.008	0.001	0.40	0.226	0.123	0.00054			30.5	Sanjuan *et al.* (2003)

Chemical analyses done within the framework of this study

Table 3 - Continuation.

We can notice that all the waters from the deep geothermal wells have high salinity values ranging from 104 g/l for the Saint Lucia well to 31-34 g/l or the Montserrat wells, 23-26 g/l for the Bouillante wells, 10-13 g/l for the Martinique wells and 5 g/l for the Dominica well. Their pH values vary between 4.5 and 7.3. Numerous thermal springs selected for this study discharge deep high-salinity waters, with TDS values ranging from 6.5 to 31 g/l in Montserrat, from 12 to 20 g/l in Martinique and from 3 to 11 g/l in Dominica. Most of the other thermal springs, especially those located in the volcano flanks in Guadeloupe, Martinique, Montserrat and Saint-Lucia, have fluids with TDS values lower than 3 g/l.

The waters collected from the seven thermal springs located in Martinique and analysed during this study (Tables 1 and 2) indicate chemical compositions similar to those previously reported (Lopoukhine and Mouret, 1977; Barat, 1984; Iundt, 1984; Traineau *et al.*, 1989; Sanjuan *et al.*, 2002a, b, 2003, 2005b; Gadalia *et al.*, 2014, 2017).

Firstly, this allowed confirming the quality of the geochemical data from these previous works.

Secondly, this allowed completing the database with the analyses of the trace elements (Li, Sr, Rb, Cs, F, Fe, Mn and W) that we use to develop the auxiliary chemical geothermometers in this study. We measured the highest value of temperature ever observed (59.6°C) at the discharge of the Bord Lézarde hot spring, in the Lamentin plain. For the Chaude River hot spring, in the Mount Pelée volcano, the temperature measured at its discharge (32°C) was much lower than that recorded in the previous studies (> 50°C), suggesting a decrease of the hydrothermal activity of this volcano at surface.

The Piper diagram (Fig. 15) and the Cl-SO_4-HCO_3 triangular diagram of Giggenbach (1988; Fig. 16) indicate that all the fluids from the deep geothermal wells and thermal springs with high-salinity fluids are Na-Cl types, and can be considered as mature waters.

Some Ca-rich sodium chloride waters are identified in the Boiling Lake area, in the Desolation Valley. For the thermal springs, which have fluids with TDS lower than 3 g/l, their chemical facies can be variable and are distributed between the Na-HCO_3 peripheral waters and the Na-Ca-SO_4 volcanic or steam heated waters, with other different possible combinations between these three endmembers.

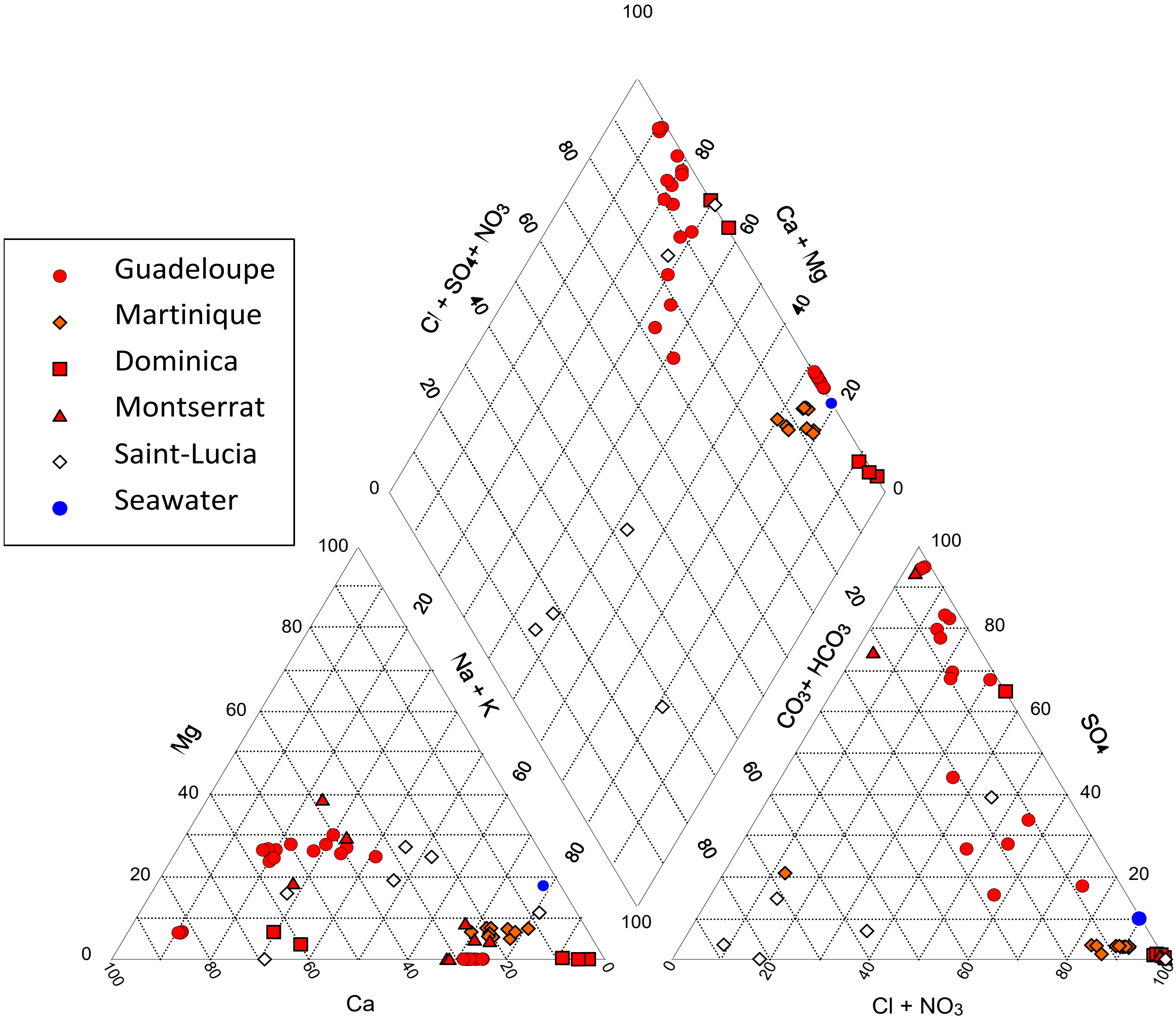


Figure 15 - Piper diagram for the geothermal waters of this study.

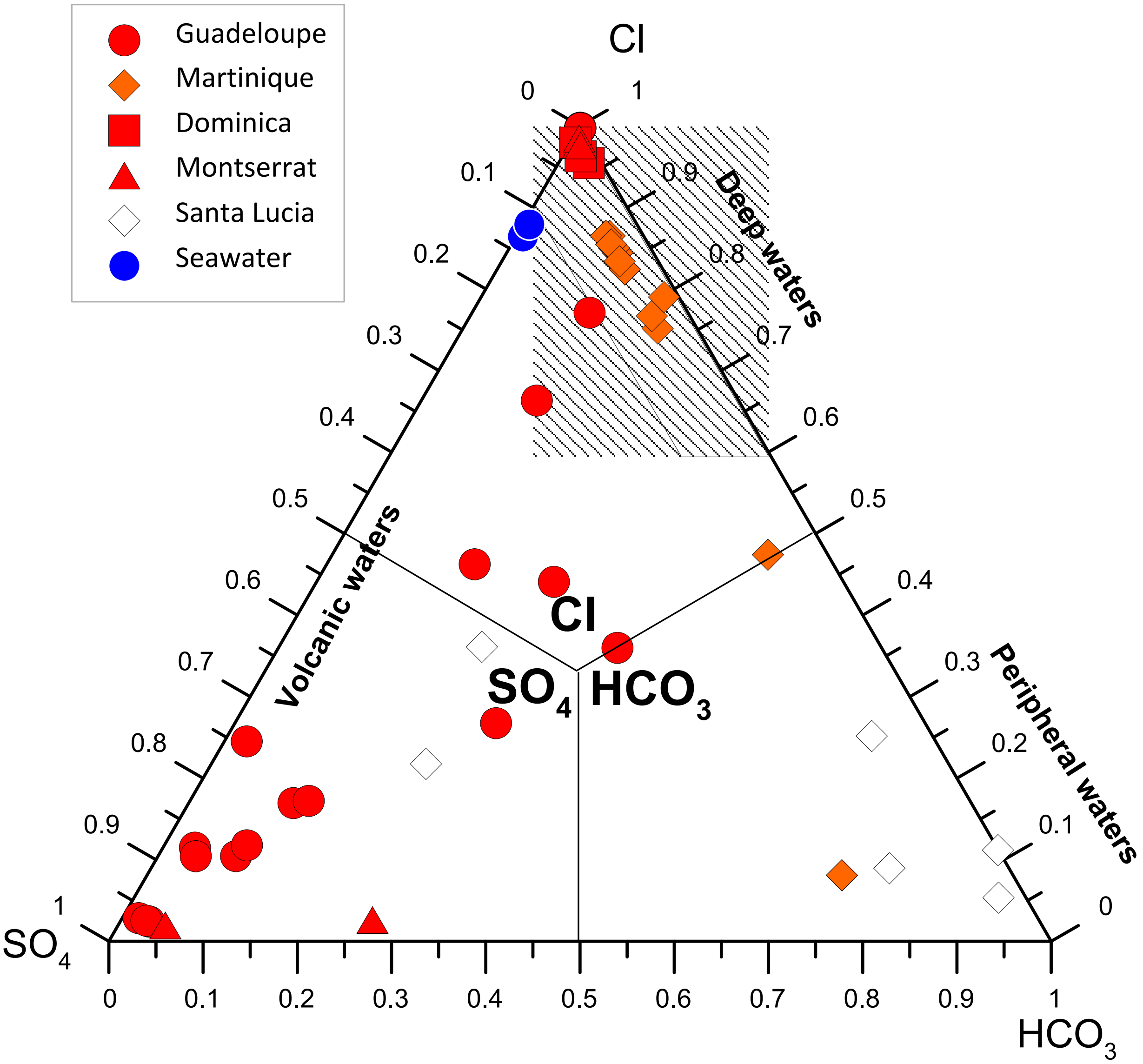


Figure 16 - Cl-SO_4-HCO_3 ternary diagram (Giggenbach, 1988) for the geothermal waters of this study.

4. Discussion

All the deep geothermal fluids from the Guadeloupe, Martinique, Dominica, Montserrat and Saint-Lucia islands are Na-Cl mature waters. Consequently, we have two main objectives to discuss: 1) the water origin and 2) the estimation of the reservoir temperature at which the water-volcanic rock interactions occur in the deep geothermal waters. For this purpose, new auxiliary chemical thermometric relationships such as Na-Li, Na-Rb, Na-Cs, K-Sr, K-Fe, K-Mn, K-F and K-W will be tested and validated on these deep fluids, which can be useful for future works of geothermal exploration in these islands.

4.1. WATER ORIGIN

The Br-Cl binary diagram (Fig. 17), which involves two elements often weakly reactive with the rocks, indicates that most of the deep geothermal waters have an origin resulting from a mixing between seawater and meteoric waters. If the bromide concentrations were not analysed for the waters from the deep wells located in Montserrat and Saint Lucia, the Na-Cl binary diagram (Fig. 18) suggests that the water discharged from the Montserrat wells also results from a mixing between seawater and meteoric waters. In Figure 18, we can also notice that the high-temperature geothermal fluids (from Bouillante, Montserrat, Dominica) are slightly depleted in sodium relative to seawater because a part of sodium has probably been precipitated under the form of albite. By contrast, the colder fluids from the Martinique thermal springs and geothermal wells (110-180°C) have Na/Cl ratios close to that of seawater.

For the Saint Lucia well (well 4), the acid and high-salinity waters (pH = 4.52 and TDS > 104 g/l), enriched in chloride (HCl-rich volatiles), have probably a magmatic origin as well as the waters discharged from the neighbouring SL-2 well and the Boiling Lake hot spring, in Dominica (Fig. 18). The deep waters discharged from the thermal springs located in the Anses d'Arlet, in Martinique, which indicate a slight enrichment in chloride relative to seawater (Fig. 17), could result from seawater with admixture of a low contribution of magmatic fluid (about 20%). This could also explain the low and atypical values of δD (-22 to -17.5‰) observed for these waters in the Caribbean context (Pedroni *et al.*, 1999; Sanjuan *et al.*, 2003; 2005b).

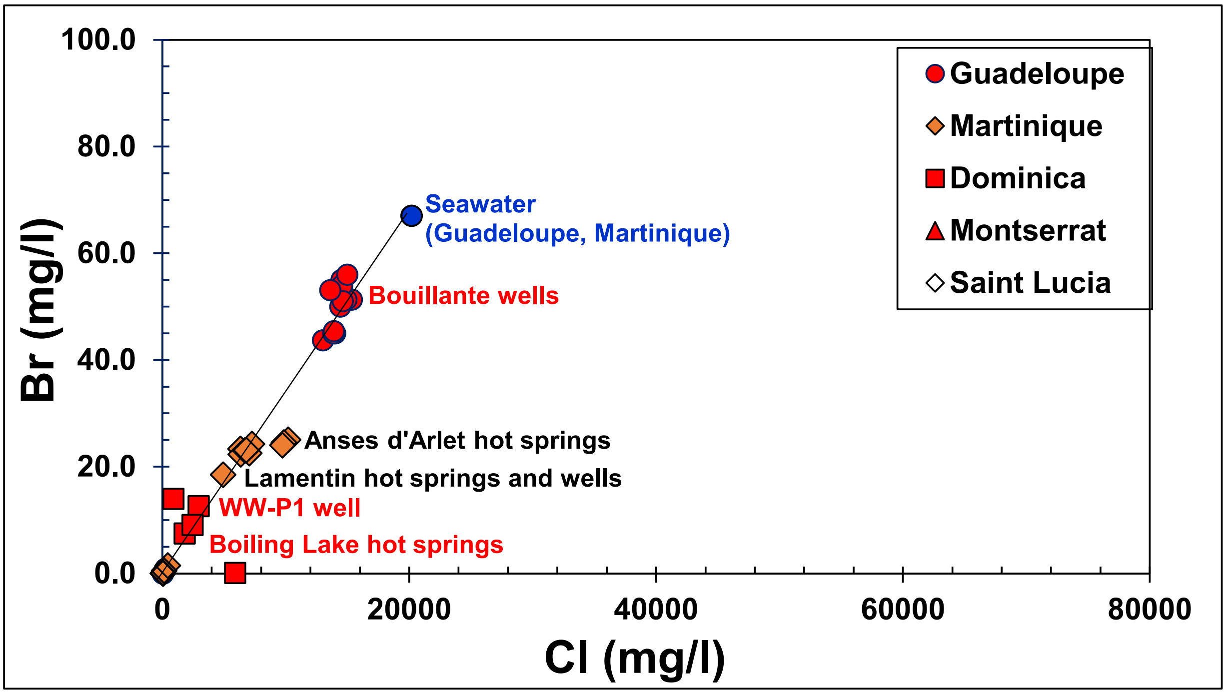


Figure 17 - Br versus Cl concentrations for the geothermal waters of this study.

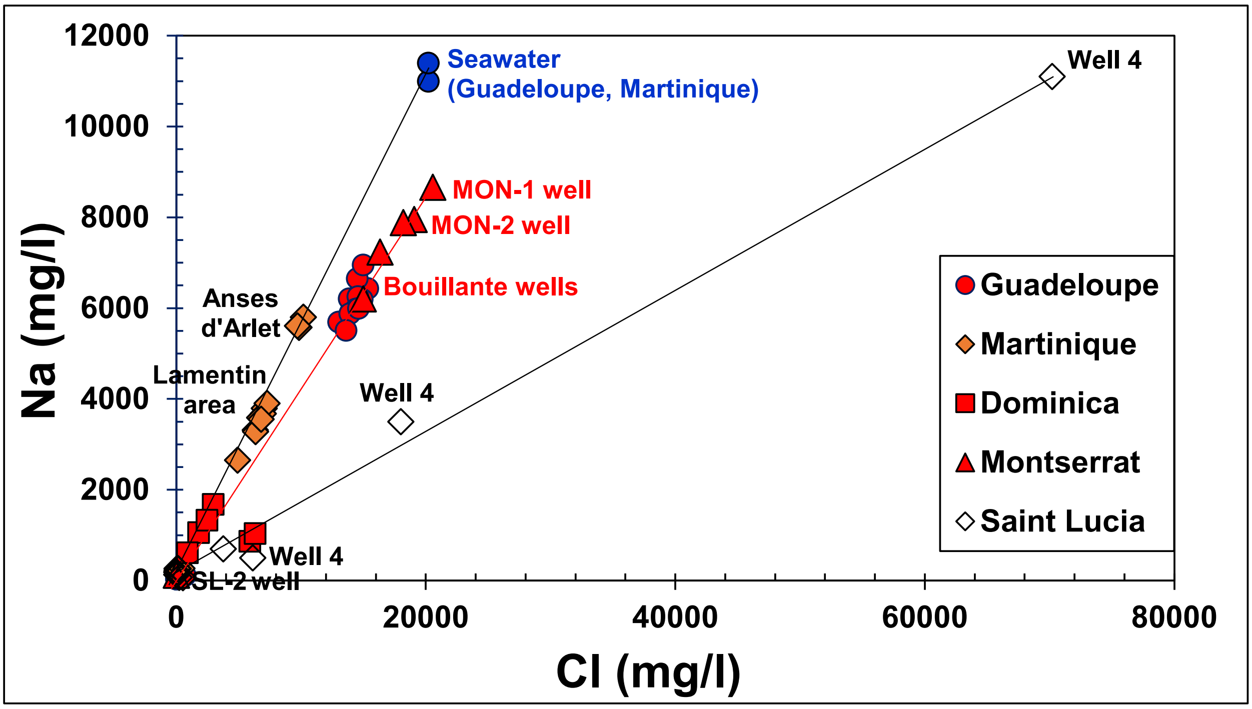


Figure 18 - Na versus Cl concentrations for the geothermal waters of this study.

Using the equation for the Cl concentration of a deep water resulting from a mixing between seawater and meteoric water:

$$[Cl]_{sample} = x\ [Cl]_{seawater} + 1\text{-}x\ [Cl]_{meteoric\ water}$$

and assuming that the Cl concentration of the meteoric water ($[Cl]_{meteoric\ water}$) is close to 0, we can estimate the percentage of seawater (x) in the mixing for each sample using the relation:

$$x = [Cl]_{sample}/[Cl]_{seawater} \times 100 \text{ (in percent)}.$$

Similar calculations can be performed using the bromide concentrations.

As all the water samples from the Bouillante wells were collected after phase separation (Table 2), it is necessary to correct their Cl and Br concentrations, using the percentage of separated liquid (about 80%). Consequently, we obtain a mixing of about 58-60% seawater and 40-42% of meteoric water for the Bouillante geothermal fluids (Sanjuan *et al.*, 2001a). Freshwater probably comes from the neighbouring Pitons of Bouillante, arising from the existence of N100-120° faults (Traineau *et al.*, 1997). Another older network of faults with a general N-S direction is also considered. For the Montserrat wells (Table 2), the geothermal waters seem to be entirely constituted of seawater.

In Martinique (Tables 1 and 2), the geothermal waters from the wells located in the Lamentin plain would be a mixing of about 25-35% of seawater and 65-75% of meteoric water as well as those from the thermal springs analysed before and during this study. The deep water discharged from the main occurrence of the Anses d'Arlet spring would be constituted of about 36-37% of seawater, according to its Br concentration, and about 50% using its Cl concentration. This discrepancy could be due to a possible Cl magmatic contribution, as previously mentioned. In this case, the first calculated percentage of seawater would be the most probable one. The maximum contribution of meteoric water would be 63-64% (but likely less, if the magmatic Cl contribution really exists).

Finally, the percentages of seawater are the poorest in the geothermal water from the WW-P1 well (about 15-19%) and from thermal springs like RR-1 and BR-3 (9-14%), in Dominica.

These results are not surprising because the geothermal wells and these thermal springs in Dominica are the farthest ones from the sea. In Guadeloupe, Martinique and Montserrat, the deep waters discharged from geothermal wells and from thermal springs are relatively near the sea and the existence of major E-W or NE-SW faults favour the mixing between seawater and meteoric water.

All the other thermal springs, with TDS values lower than 3 g/l, are mainly constituted of meteoric waters present in volcanic massifs such as Soufriere in Saint Lucia or Grande Soufriere in Guadeloupe.

Some of them could have very low contributions of seawater (≤ 4%): the Grosse Corde and Chute du Carbet hot springs in Guadeloupe, or MP10 Rivière Picodo in Martinique, for example. Indeed, the Cl/Br mass ratios measured in these three thermal waters (315, 270 and 282, respectively) are fairly close to that of seawater (301; Tab. 2; Sanjuan *et al.*, 2003, 2005b; 2008).

4.2. USE OF CHEMICAL GEOTHERMOMETERS

These geothermometers are commonly used with the chemistry of waters from wells or hot springs to explore for geothermal resources. They rely on the temperature-dependent solubility of particular chemical components to infer the temperature of the reservoir at depth from which springs issue. Many assumptions must be made regarding equilibrium conditions at depth, re-equilibrium situations as the waters rise to cooler surface temperatures, and mixing between aquifers. The geothermometers themselves can be problematic in that many are empirical or depend on solubility relations with chemical phases that may or may not be present. Despite the difficulties, geothermometers are very useful in estimating the probable temperatures of geothermal systems and showing if these systems have reached a full chemical equilibrium at these temperatures.

4.2.1. Reservoir temperatures estimated using classical geothermometers

The use of classical geothermometers such as Silica-Quartz, Silica-Chalcedony (Fournier, 1977), Na-K (Michard, 1979; Arnorsson et al., 1983; Giggenbach, 1988), K-Mg (Giggenbach, 1988), and Na-K-Ca (Fournier and Truesdell, 1973), on the waters from the geothermal wells in the Guadeloupe, Dominica, Montserrat and Martinique islands, indicates that the estimates of their reservoir temperatures (260°C, 250°C, 230°C and 110°C, respectively; see Table 3) are consistent and close to the temperatures measured at bottom-hole.

These estimates can be visualized in the triangular Na-K-Mg diagram (Fig. 19) proposed by Giggenbach (1988). They are also in good agreement with the distribution of the waters in a binary Na-K diagram (Fig. 20). Consequently, with the results from the section 4.1, it can be concluded that these geothermal waters are seawater-derived fluids mixed with different proportions of meteoric waters, which have interacted with volcanic reservoir rocks and reached their full chemical equilibrium at the different estimated temperatures.

As previously shown, the waters of the submarine thermal springs from the Bouillante Bay, in Guadeloupe, result from a mixing between the deep fluid from the geothermal reservoir at 260°C and seawater. Due to this mixing with seawater, no chemical geothermometer can be applied, but the relationships indicating the presence of this mixing in binary diagrams allow highlighting the presence and the contribution of the hot end-member (geothermal water at 260°C).

Island	Area	Sampling point	Date	$T_{surf.}$ °C	T_{Qz} °C	$T_{Chalc.}$ °C	$T_{Na\text{-}K}^{(1)}$ °C	$T_{Na\text{-}K}^{(2)}$ °C	$T_{Na\text{-}K}^{(3)}$ °C	$T_{Na\text{-}K}^{(4)}$ °C	$T_{Na\text{-}K\text{-}Ca\ (\beta=1/3)}$ °C	$T_{K\text{-}Mg}$ °C	$T_{res.}$ °C
Guadeloupe	**Bouillante geothermal field**	**BO-2 well**	05-1996	165	246		270	253	244	249	232	266	250
		BO-4 well	23/03/2005	165	258		265	248	238	242	228	255	260
		BO-5 well	29/11/2002	165	267		254	237	223	226	222	247	260
		BO-6 well	08/07/2003	165	270		261	244	233	237	228	253	260
Martinique	**Lamentin plain**	**Californie well (TDP)**	26/03/2002	74	118	89	156	141	103	103	146	97	110
		Habitation Carrère well (TDP)	05/12/2001	40	132	104	164	148	112	112	150	92	110
		Ferme Perrine hot spring	06/07/2022	39	106	77	169	154	118	118	155	101	110
		Habitation Carrère hot spring	06/07/2022	57	121	93	167	151	115	115	153	85	110
		Maimaine hot spring	06/07/2022	34	111	81	151	135	97	96	141	94	110
		Bord Lézarde hot spring	06/07/2022	60	125	96	174	158	123	123	158	103	110
	Anses d'Arlet	**Petite Anse - Diamant hot spring**	06/12/2001	35	153	128	183	168	135	135	172	109	180
		Petite Anse - Diamant hot spring 1	05/07/2022	33	153	127	195	179	148	149	182	112	180
		Petite Anse - Diamant hot spring 2	05/07/2022	31	154	130	196	180	150	151	183	116	180
	Mount Pelée volcano	**Rivière Chaude - MP4 hot spring**	11/12/2001	51	158	134	230	213	192	194	181	85	200
		Rivière Chaude - MP4 hot spring	07/07/2022	32	150	124	244	227	210	212	183	79	200
Dominica	**Wotten Waven**	**WW-P1 well**	15/06/2014	202	251		269	252	244	248	241	239	250
	Roseau River	**RR-1 hot spring**	17/01/2005	85	175		222	205	182	184	193	152	220
	Blanc River	**BR-3 hot spring**	19/01/2005	93	178		223	207	184	186	201	207	220
	Valley of Desolation	**VD-1 hot spring**	18/01/2005	97	207		313	296	305	312	220	113	300
		Boiling Lake hot spring	25/11/2000	84			410	392	458	475	272	142	300
		DM-26/Boiling Lake hot spring	1985	97	205		328	311	328	336	229	116	300
Montserrat	**St George Hill**	**MON-1 well**	27/10/2013	153	229		222	206	182	184	198	204	230
		MON-2 well	18/12/2013	153	223		223	206	183	184	198	205	230
		EGS/TCI - MHP-1 hot spring	2012	59	198		260	243	231	234	229	151	230
	St George Hill	**Hot spring 1**	March 1991	90	213		254	238	224	227	225	149	230
		Hot spring 2	March 1991	48	190		249	232	216	219	217	132	230
	South Soufrière volcano	**Hot spring 4**	March 1991	80	173		204	188	159	160	141	43	200
		Hot spring 5	March 1991	98	185		236	220	200	203	156	54	200
	Soufrière Hills	**Hot spring 7**	March 1991	95	239		165	150	114	113	113	25	230
		Hot spring 9	March 1991	98	229		267	250	241	245	183	59	230
Saint Lucia	**Sulphur springs**	**Well 4**	22/04/1977	100	184		182	166	133	133	151	125	180
		Well SL-2 (25.3 h of production)	February 1988	100	274		507	489	670	637	325		290
	Qalibou Caldera	**Diamond - SL-12 warm spring**	July 1983	43	170		220	203	179	181	157	52	170
		Cresslands - SL-15 hot spring	July 1983	56	143		199	183	154	155	148	58	150
		Malgretoute - SL-17 warm spring	July 1983	35	138		192	176	145	145	159	68	150
		Hot spring 103	1985	43	179		213	196	170	172	157	57	170
	Terre blanche	**Hot spring 133**	1985	76	169		324	306	321	329	192	61	290
		Hot spring 134	1985	90	169		290	273	273	278	186	68	290

T_{Qz}, $T_{Chalc.}$: Fournier (1977).

$T_{Na\text{-}K}^{(1)}$: Giggenbach (1988) ; $T_{Na\text{-}K}^{(2)}$: Arnorsson *et al.* (1983) for T = 250-350°C; $T_{Na\text{-}K}^{(3)}$: Arnorsson *et al.* (1983) for T = 25-250°C; $T_{Na\text{-}K}^{(4)}$: Michard (1979).

$T_{Na\text{-}K\text{-}Ca}$: Fournier and Truesdell (1973).

$T_{K\text{-}Mg}$: Giggenbach (1988).

Table 4 - Reservoir temperatures estimated using the main chemical geothermometers for the geothermal waters of this study.

The use of the classical geothermometers gives also concordant estimates of temperature (180°C) for the deep geothermal water from the Saint-Lucia well 4 (Table 3 and Fig. 19), which is close to the measured temperature (203°C) at a depth of 600 m in this well (Bath, 1977).

By contrast, only the Silica-Quartz and Na-K-Ca geothermometers give relatively concordant estimates of temperature (270°C and 325°C, respectively; Table 3), which are in the range of the measured temperature at bottom-hole (290°C), while too high and unrealistic estimate is found using the Na-K geothermometer (507°C), probably due to the high-acidity of the fluid.

The deep waters from thermal springs located in Dominica (Roseau Valley and Blanc River), Montserrat (hot springs from St George Hill, South Soufriere volcano and Soufriere Hills) and Martinique (Mount Pelée and Anses d’Arlet hot springs) also indicate relatively concordant temperature estimates between 180 and 230°C (Table 3 and Fig. 19).

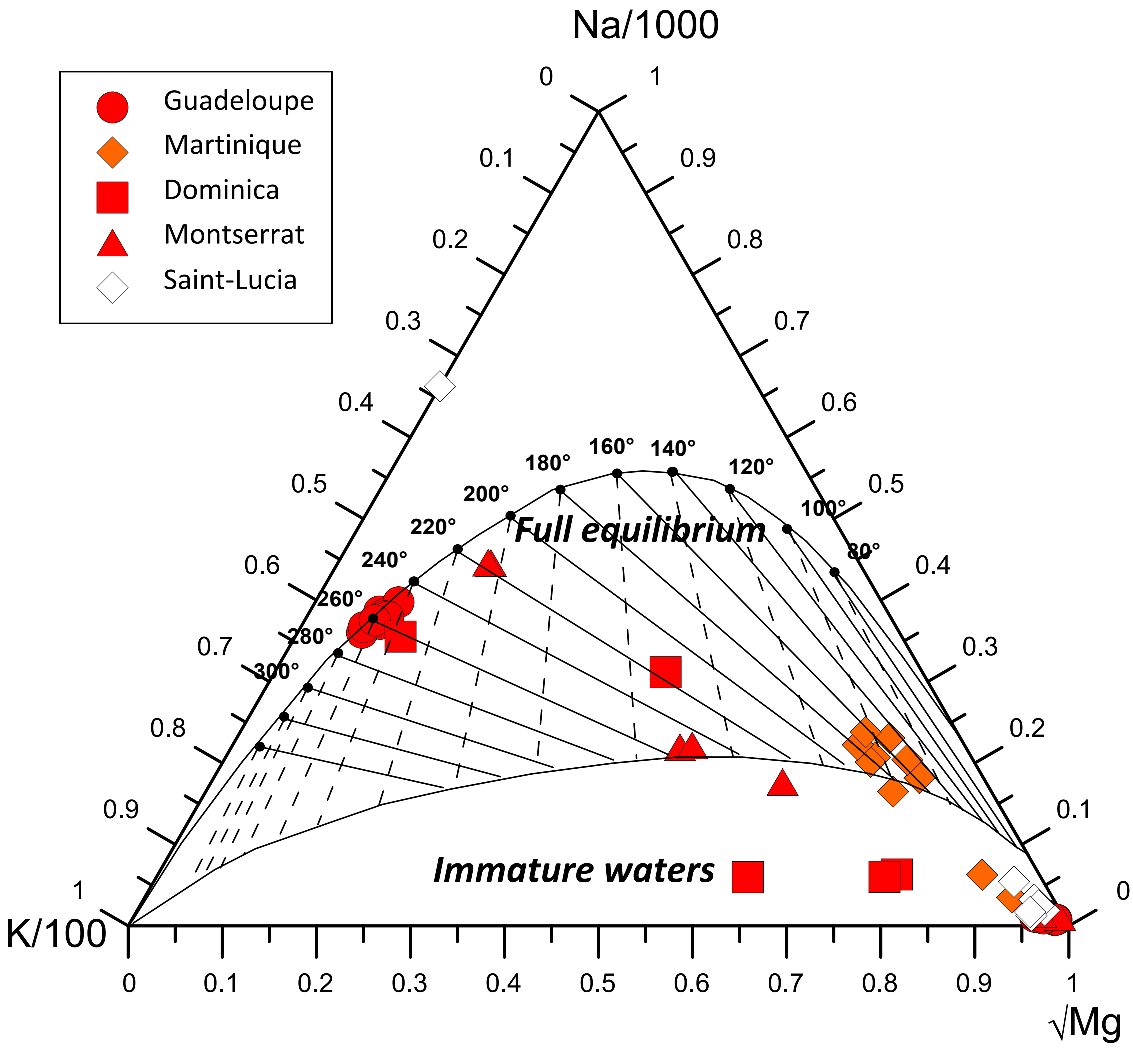


Figure 19 - Na-K-Mg ternary diagram (Giggenbach, 1988) for the geothermal waters of this study.

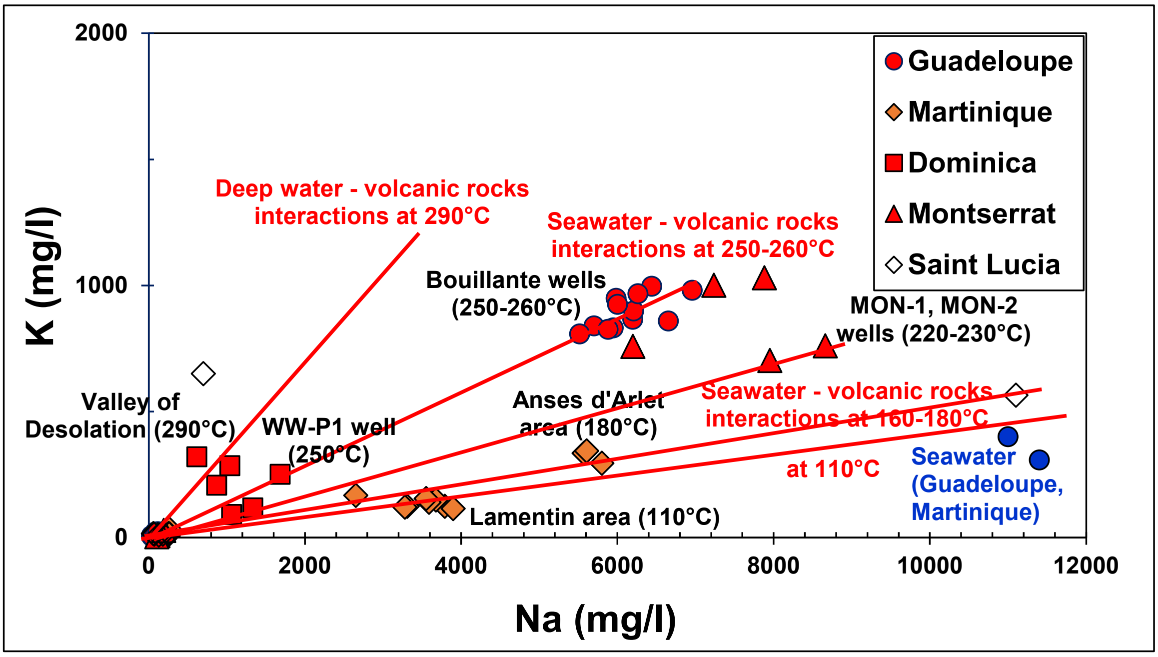


Figure 20 - K versus Na concentrations for the geothermal waters of this study.

For the waters of two hot springs from the Boiling Lake area (VD-1 and DM-28, respectively), in the Valley of Desolation, the classical geothermometers do not give concordant temperature estimates (Table 3). The Na-K geothermometer suggests temperature values close to 300°C while the Silica-Quartz and the Na-K-Ca geothermometers yield lower estimates (Table 3). However, we consider that the estimate given by the Na-K geothermometer is the most representative one because this geothermal water is probably of magmatic origin (see previous section) and mixed with surface waters during its rise towards the surface. This mixing would have modified the concentrations of the dissolved species by dilution of e.g. the dissolved silica and possible enrichment in magnesium, but not the ratios of some elements such as Na/K.

The fluids from the thermal springs located in the Soufriere Volcanic Centre, in Saint Lucia, and in the Grande Soufriere volcanic massif, in Guadeloupe, are surface waters probably heated by mixtures of rising steam (or brine) and gases at high-temperature that condense in the near-surface environment. All these waters, relatively rich in magnesium, are classified as immature waters in the Na-K-Mg ternary diagram (Fig. 19) and have not reached a full chemical equilibrium at the temperature at which they have reacted with the rocks.

The Qualibou Caldera thermal springs, with discharge temperatures from 35 to 56°C, are lowly mineralised Na-HCO_3 waters (TDS values of 1-2 mg/l), relatively poor in sulphate (Figs. 15 and 16), suggesting that the rising gases are mainly constituted of CO_2, with low contents of H_2S. For these waters, the Na-K, Na-K-Ca and Silica-Quartz geothermometers give estimates of deep temperatures between 150 and 170°C (Tab. 3). However, the K-Mg geothermometer gives much lower estimates of temperatures between 50 and 70°C. Although they do not directly tap a deep neutral-chloride system, the HCO_3-rich waters often indicate a zone of condensation above a high-temperature deeper zone of boiling. In the seven shallow wells drilled to depths as great as 700 m, steam was encountered at temperature above 200°C. As mentioned by Ander *et al.* (1984), the most optimistic estimate of temperature at depth is approximately 170°C, if we assume these springs are connected to the deep geothermal system. The most conservative estimate of temperature is 100°C or less, if these springs are not connected to the deep system.

The Terre Blanche thermal springs have discharge temperatures close to 100°C and Na-Ca-Cl-SO_4 waters (Figs. 15 and 16), with TDS values of 2-3 mg/l. A part of SO_4 is probably produced by the oxidation of magmatic H_2S in the near surface oxygenated groundwaters. As for the hot springs from the Valley of Desolation, the different geothermometers give discordant estimates of temperature (Tab. 3). Given the discharge temperature values, the estimate given by the K-Mg geothermometer (61 and 68°C) can be ruled out. The Na-K geothermometers indicate the highest temperature values, which are close to 290-300°C. As a maximum temperature of 290°C was measured in the permeable zone below about 1340 m, intersected by the SL-2 well drilled in 1988 (D'Amore *et al.*, 1990), some connections could be suggested between this permeable zone and the surface waters of the thermal springs. If this assumption is discarded, the most conservative estimate of temperature is 100°C.

The thermal springs located in the flank of the Grande Soufriere volcano, in Guadeloupe, have discharge temperatures from 30 to 60°C. Their waters have relatively low TDS values (< 2 g/l) and two different chemical compositions (Figs. 15 and 16):

- a Ca-SO_4 composition for the Piton Tarade, Pas du Roy, Eaux Vives - Matouba and Bain Jaunes thermal springs located near the Grande Soufriere dome (< 1.2 km from the summit) and at high elevations (950-1170 m a.s.l.). The SO_4 concentrations in these waters decrease with their increasing distance to the volcanic dome because the sulphides react very quickly (Sanjuan *et al.*, 2008);
- a Ca-Na-Cl composition for the Grosse Corde and Chute du Carbet thermal springs, which are farther from the Grande Soufriere dome (about 2.5 and 2 km east of the Grande Soufriere dome at altitudes of 585-605 m a.s.l.).

The Ca-SO_4 waters are neutral to slightly acidic (Tab. 2). Their physical and chemical characteristics suggest that they originate through:

- absorption of H_2S-bearing hydrothermal vapours into shallow oxygen-rich groundwaters, which are heated by these hydrothermal vapours. The groundwaters are fed by an abundant meteoric contribution at these altitudes;
- oxygen-driven oxidation of H_2S to H_2SO_4;
- neutralisation of this acid through water-rock interaction (Brombach *et al.*, 2000).

The Ca-Na-Cl waters have also neutral pH and relatively high SO_4 concentrations, suggesting that SO_4 is produced in the same way as in the Ca-SO_4 waters. Cl can be brought by a seawater contribution, the presence of a deep Na-Cl geothermal brine or have a magmatic origin. As previously mentioned, the Cl/Br ratios measured in the Grosse Corde and Chute du Carbet thermal waters are close to that of seawater. Consequently, a magmatic origin can be ruled out.

Given the position of these waters in the Na-K-Mg ternary diagram (Fig. 19) and their chemical characteristics, the high estimates of temperature given by the Na-K geothermometers (between 230 and 330°C), which are very different from those estimated using the Silica-Quartz, Na-K-Ca and K-Mg geothermometers (between 130 and 210°C), cannot be considered as representative of the deep temperatures.

Contrary to the thermal waters from the Soufriere Volcano Centre, in Saint Lucia (Joseph *et al.*, 2013), the waters from the Grande Soufriere, in Guadeloupe, show no 18-oxygen shift in the diagram δD-$\delta^{18}O$ (Benauges, 1981; Brombach *et al.*, 2000; Sanjuan *et al.*, 2008). Moreover, the concentrations of B and Li are low in these waters (Tab. 2). All these results suggest that these thermal waters would belong to a low-temperature geothermal system and have relatively fast and shallow paths of fluid circulation (Barat, 1986; Villemant *et al.*, 2005; Sanjuan *et al.*, 2008). The use of the Na-K-Ca (β = 4/3 for temperatures ≤ 100°C; Fournier and Truesdell, 1973) and K-Mg geothermometers gives concordant temperature estimations ranging from 50 to 90°C for these waters, which could be the most representative of their reservoir temperatures. These estimations of temperature are reported in Table 2.

4.2.2. Test and validation of auxiliary chemical geothermometers

Most of the classical geothermometers are based on empirical or semi-empirical laws derived from known or unknown chemical equilibrium reactions between water and minerals occurring in the geothermal reservoirs. Unfortunately, these classical tools do not yield always concordant estimates of reservoir temperatures, especially at low and medium temperatures (≤ 150°C) due to different processes: chemical equilibrium not reached, fluid mixing, precipitation/dissolution processes during the fluid ascent to the surface, etc.

Since the early 1980s, numerical multicomponent geochemical models are being developed for direct application to chemical geothermometry for geothermal exploration (Michard and Roeckens, 1983; Reed and Spycher, 1984; Spycher *et al.*, 2014; Peifer *et al.*, 2014; Ystroem *et al.*, 2020). These models allow the equilibration temperature of the geothermal water to be numerically calculated with respect to a series of reservoir minerals, and thus to estimate the reservoir temperature. Multicomponent geothermometry is not intended to replace classical geothermometers, but rather to supplement these geothermometers, and by doing so to increase confidence in temperature estimations.

However, such approach cannot be applied without caution and without a sound conceptual understanding of the area being studied (Al and pH poorly determined, for example). For this approach, reaching a state of full chemical equilibrium is necessary and at low-moderate temperatures, the conditions of this equilibrium state are not always reached.

The Na-Li auxiliary chemical geothermometer, less accurate than the classical geothermometers, but often more reliable (low Li reactivity during the ascent of the hot waters towards the surface), and other auxiliary chemical geothermometers like Na-Rb, Na-Cs, K-Sr, K-Mn, K-Fe, K-F and K-W, can be also very useful for geothermal exploration.

a) Use of the Na-Li auxiliary chemical geothermometer

This auxiliary geothermometer was the first one proposed by Fouillac and Michard (1981). Since this date, different Na-Li thermometric relationships have been developed (Tab. 4) and reported by Sanjuan and Millot (2009) and Sanjuan *et al.* (2014), with the corresponding regression coefficients. The existence of these different relationships suggests that the Na/Li ratio is controlled not only by temperature, but also by other influent factors (composition of the reservoir rock and its minerals, its degree of alteration, the water-rock ratio and fluid salinity…).

Na-Li thermometric relationships	Status	Environment	Reference
T(K) = 1195 / [log (Na/Li) - 0.13] for Cl ≥ 0.3 M	Empirical and statistical thermometric relationship (in molar concentrations)	Fluids from several world geothermal fields mainly located in volcanic ang granitic areas	Fouillac and Michard (1981)
T(K) = 1267 / [log (Na/Li) + 0.07] for Cl ≥ 0.3 M	Empirical and statistical thermometric relationship (in molar concentrations)	Statistical and error propagation treatment of the Fouillac and Michard (1981)'s data	Verma and Santoyo (1997)
T(K) = 1222 / [log (Na/Li) - 0.03] for Cl ≥ 0.3 M	Empirical and statistical thermometric relationship (in molar concentrations)	Integration of more data than in Fouillac and Michard (1981)	Sanjuan *et al.* (2014)
T(K) = 1000 / [log (Na/Li) + 0.38] for Cl < 0.3 M	Empirical and statistical thermometric relationship (in molar concentrations)	Fluids from several world geothermal fields mainly located in volcanic ang granitic areas	Fouillac and Michard (1981)
T(K) = 1040 / [log (Na/Li) + 0.43]	Empirical and statistical thermometric relationship (in molar concentrations)	Dilute waters from 60 thermal springs located in European granitic areas	Michard (1990)
T(K) = 1049 / [log (Na/Li) + 0.44] for Cl < 0.3 M	Empirical and statistical thermometric relationship (in molar concentrations)	Statistical and error propagation treatment of the Fouillac and Michard (1981)'s data	Verma and Santoyo (1997)
T(K) = 1074 / [log (Na/Li) + 0.60] for Cl < 0.3 M	Empirical and statistical thermometric relationship (in molar concentrations)	Integration of more data than in Fouillac and Michard (1981)	Sanjuan *et al.* (2014)
T(K) = 1590 / [log (Na/Li) + 1.299]	Empirical and statistical thermometric relationship (in molar concentrations)	Hot saline fluids from sedimentary basins in world geothermal and US oil fields	Kharaka *et al.* (1982) Kharaka and Mariner (1989)
T(K) = 1588 / [log (Na/Li) + 1.286]	Empirical and statistical thermometric relationship (in molar concentrations)	Integration of more data than in Kharaka *et al.* (1982) and Kharaka and Mariner (1989)	Sanjuan *et al.* (2014)
T(K) = 920 / [log (Na/Li) - 1.105]	Empirical and statistical thermometric relationship (in molar concentrations)	Fluids derived from seawater-basalt interaction processes existing in emerged rifts such as those of Iceland and Djibouti, or in numerous oceanic ridges and rises	Sanjuan *et al.* (2014)
T(K) = 2002 / [log (Na/Li) + 1.322]	Empirical and statistical thermometric relationship (in molar concentrations)	Dilute waters from geothermal wells located in different high-temperature (200-325°C) volcanic areas of Iceland	Sanjuan *et al.* (2014)

Table 5 - Main Na-Li thermometric relationships existing in the literature.

The Li concentrations are determined for most of the geothermal waters of this study. Unfortunately, data are missing for the fluids from the deep geothermal wells in the Saint Lucia and Montserrat islands. However, for Montserrat, we can consider that the hot waters from the St George Hill area, which have similar Na, Cl and SiO_2 concentrations to those of the waters discharged from the MON-1 and MON-2 wells, indicate comparable Li concentrations.

The Figure 21 represents the log (Na/Li) of the geothermal waters of this study (with the Na and Li concentrations expressed in mol/l) as a function of 1000/T, where T (in Kelvin) is the reservoir absolute temperature (see Table 2), compared to the different Na-Li thermometric relationships existing in the literature (Tab. 4).

In this figure, we can note that the high-temperature geothermal waters of this study fit relatively well the Na-Li thermometric relationship defined by Sanjuan *et al.* (2014) for Icelandic dilute waters, except some waters from Dominica. This suggests that the Na/Li ratios are probably controlled by an equilibrium reaction between, at least, K-feldspars, quartz, micas, albite, and illite minerals (Sanjuan *et al.,* 2014).

We can notice that this thermometric relationship, which was defined for dilute geothermal waters in volcanic environment, may be also used for the saline fluids of this study. This has been already observed for saline waters in volcanic areas in Italy, Greece and USA (Sanjuan *et al.*, 2022) and in the East African Rift (Sanjuan, 2022). Consequently, the water salinity seems to have little influence on the use of this Na-Li thermometric relationship. In this temperature range, the temperatures estimated using the Na-Li thermometric relationship defined by Fouillac and Michard (1981) are also relatively close to those given by the relationship proposed by Sanjuan *et al.* (2014).

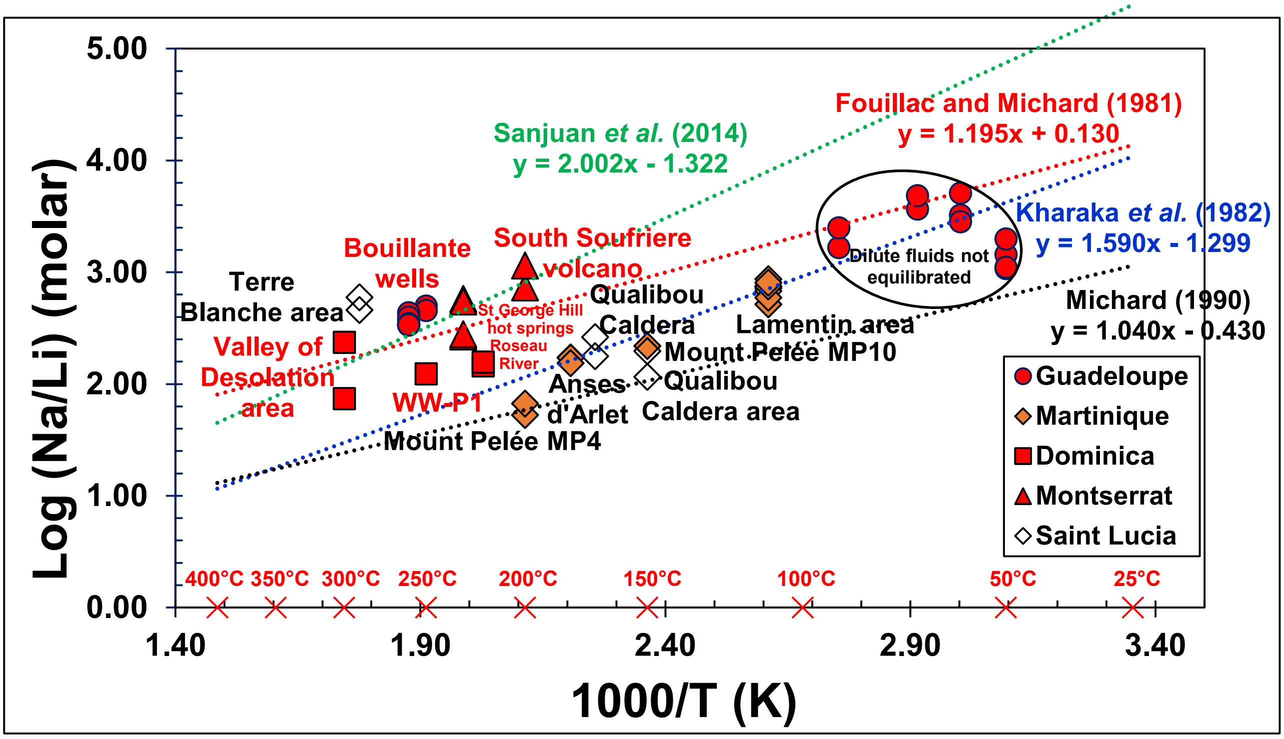


Figure 21 - Logarithm of Na/Li (molar ratio) versus 1000/T (reservoir temperature in K). The data obtained in this study are compared to the different Na-Li thermometric relationships existing in the literature.

The geothermal waters from the Anses d'Arlet and Lamentin plain areas, in Martinique, which have TDS values of 20 and 12-13 g/l respectively, and indicate lower reservoir temperatures (180 and 110°C), rather fit the Na-Li thermometric relationship defined by Kharaka *et al.* (1982) for sedimentary brines (Fig. 18). More surprising, two thermal waters from the Qualibou Caldera, in the Saint Lucia Island, which have relatively low TDS values (< 2 g/l), also fit this relationship. However, the reservoir temperature estimated for these waters could have been overestimated and could be as low as 100°C (see section 4.2.1). In this case, these waters would fit the Na-Li thermometric relationship defined by Michard (1990) for dilute thermal waters in granite environment (Fig. 21). The latter is also followed by the dilute thermal waters from the Mount Pelée, in Martinique, which indicate an estimated reservoir temperature of about 200°C, and two other dilute thermal waters from the Qualibou Caldera, with reservoir temperatures estimated at 150°C (Fig. 21).

Finally, most of the dilute shallow and warm waters from the Grande Soufriere of Guadeloupe, which are not equilibrated with the reservoir rocks, fit more or less the Na-Li thermometric relationship defined by Fouillac and Michard (1981) for saline waters in crystalline and volcanic environment (Fig. 21). The coldest waters (T ≤ 60°C) fit no thermometric Na-Li relationship.

All these results show that it is essential to take into account the type of geological environment to use the different Na-Li thermometric relationships, and combine and compare them with the other geothermometers in order to decrease the uncertainty in the estimation of the reservoir temperature.

For all the Na-Li relationships, it is suggested that Li is probably released by mica dissolution (Sanjuan *et al.*, 2014; 2016a; 2022). The new thermodynamic approach using Li-minerals, such as that carried out by Boschetti (2022a, b; 2023), helps to better define the chemical composition of the main Li-carrier minerals and seems to confirm that the presence of micas in the reservoir rocks is the major control of the Li concentrations in the geothermal waters.

The Li concentrations associated with the Cl concentrations can be also used to highlight the geothermal waters with high contribution of magmatic waters. The result of Kazahaya *et al.* (2014) using 49 thermal waters spread throughout Japan indicated that magmatic water have Li/Cl > 0.001 (in wt. ratio) with 1/Cl < 0.001.

In this study, the Figure 22 shows that the geothermal waters, which seem to have the higher contributions of magmatic waters, come from Dominica (Wotten Waven, Blanc River and Boiling Lake areas) and from Martinique (Anses d'Arlet area). The low δD isotope values observed for this area (Pedroni *et al.*, 1999; Sanjuan *et al.*, 2005b) had already suggested a possible contribution of magmatic water. Smaller contributions of magmatic waters can be attributed to the geothermal waters from the Bouillante area in Guadeloupe, the Lamentin area in Martinique and in Montserrat. The fluids from the deep geothermal wells in Saint Lucia could not be unfortunately interpreted in the absence of available data. For the other thermal springs, the magmatic contributions are much smaller, especially for the Grande Soufriere area in Guadeloupe.

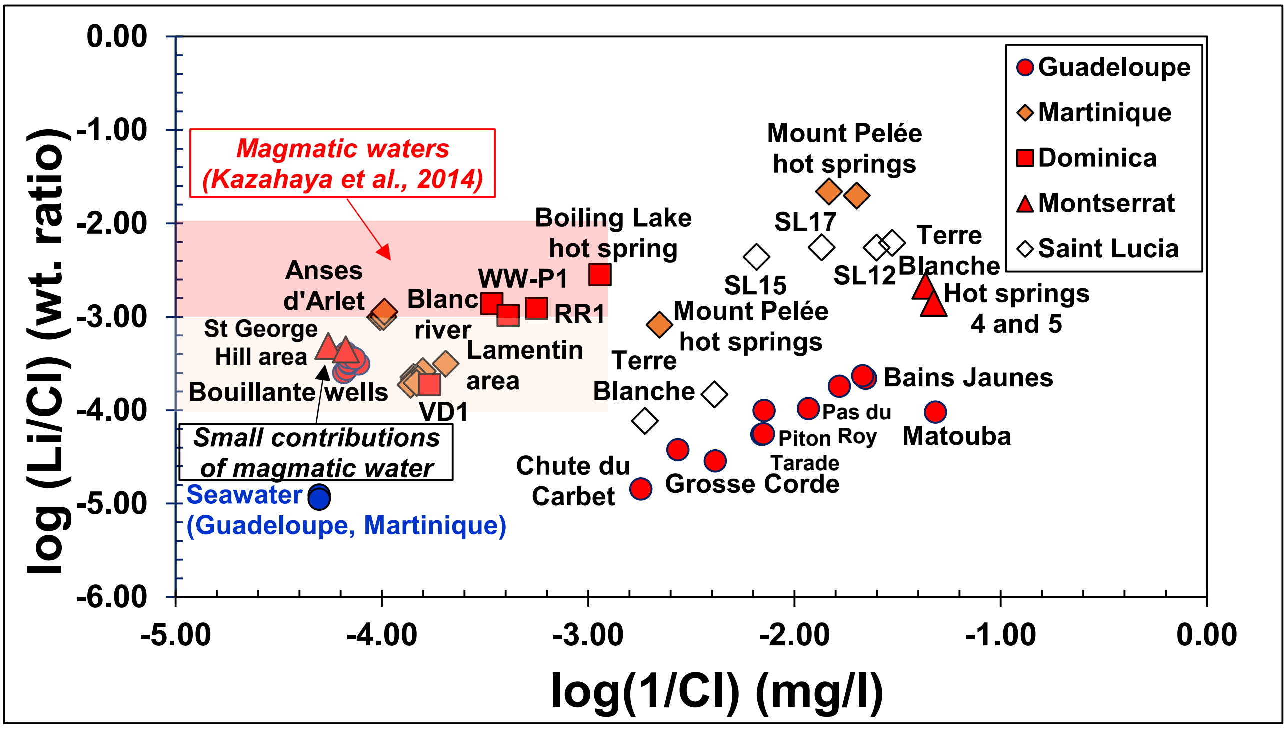


Figure 22 - Logarithm of Li/Cl vs Logarithm of 1/Cl for the geothermal waters of this study.

b) *Use of the Li isotope values as geothermometer?*

Unlike the Na/Li ratios, it is difficult to use the Li isotope values as geothermometer (Sanjuan *et al.*, 2014). Millot *et al.* (2010) used the δ^7Li isotope values in order to estimate the nature of the rocks interacting with the deep fluid in the Bouillante geothermal reservoir at about 260°C, from the δ^7Li values analysed in the deep fluid and the Li isotope fractionation relationship between fluid and rock determined in laboratory experiments of basalt-diluted seawater interaction. Unfortunately, no direct thermometric relationship was found using δ^7Li values.

However, Sanjuan *et al.* (2014) observed that for the Icelandic geothermal fluids with deep temperatures ranging from 200 to 365°C, including seawater-derived waters, the δ^7Li values were lower and less scattered (from 2 to 12‰) than those for the colder geothermal fluids (deep temperatures between 75 and 190°C), which varied from 7 to 31‰. The δ^7Li values higher than 16‰ seem to be always associated with low- to medium-temperature waters. In the Reunion Island, where the maximum temperature was estimated to be close to 160°C from the existing thermal springs, all the δ^7Li values are higher than 10‰ (Sanjuan *et al.*, 2001b; Bénard *et al.*, 2020).

In Figure 23, the hottest geothermal waters from Guadeloupe and Martinique have δ^7Li values lower than 10‰ and relatively high Cl concentrations. The thermal waters from the Grande Soufriere area in Guadeloupe, considered as shallow waters heated by conduction, have relatively high δ^7Li values and low Cl concentrations.

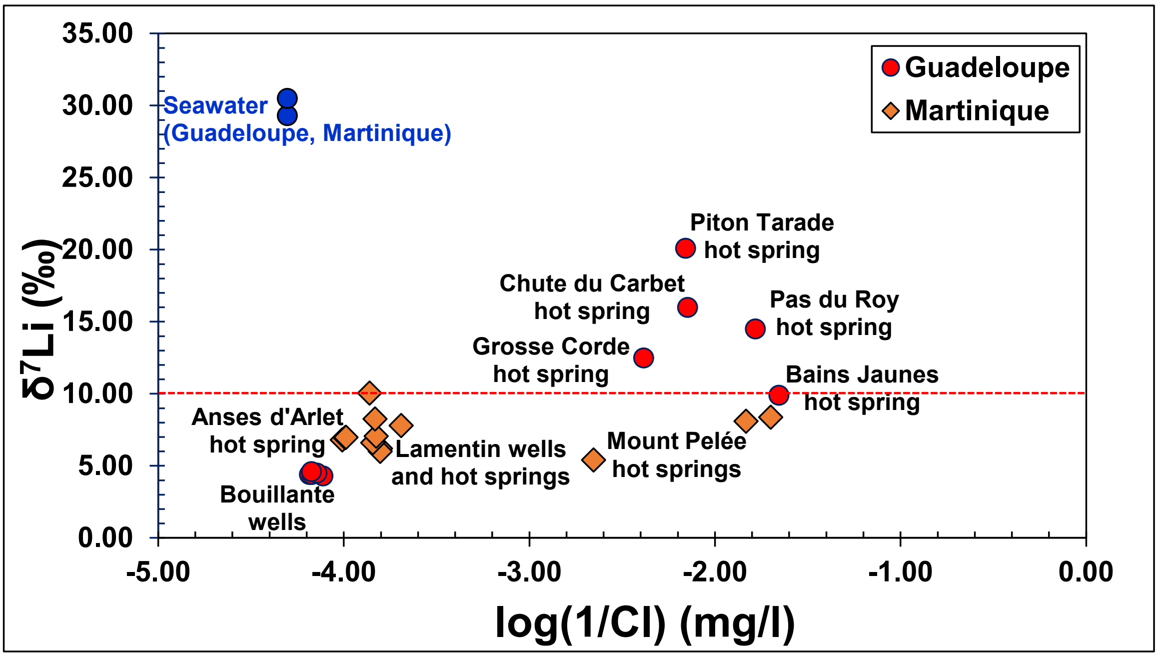


Figure 23 - δ^7Li values vs Logarithm of 1/Cl for the geothermal waters from Guadeloupe and Martinique.

c) Use of other auxiliary chemical geothermometers

Michard (1990) proposed other auxiliary geothermometers, such as Na-Rb, Na-Cs, K-Sr, K-Fe, K-Mn, K-F and K-W, for deep dilute thermal waters discharged from granitic reservoirs between 25 and 150°C in more than 60 European areas (France, Italy, Spain, Bulgaria, Sweden).

Using 20 hot natural brines from granite and sedimentary reservoirs, mainly located in the Rhine Graben, France and Germany (70-230°C; Sanjuan *et al.*, 2016a) - apart two which are at Salton Sea, in the Imperial Valley, in California, USA (300-320°C) - Sanjuan *et al.* (2016b, c) developed additional thermometric relationships, especially for the Na-Rb, Na-Cs and K-Sr geothermometers in a temperature range from 70 to 330°C.

As for the Na-Li geothermometer, the existence of different relationships for a given auxiliary geothermometer suggests that the latter depends not only on temperature, but also on other factors such as the composition of the reservoir rock, its degree of alteration, the water-rock ratio and fluid salinity. Consequently, it is crucial to define the environment in which these geothermometers can be applied before their use, and to carry out additional investigations for each specific environment. For these trace species, chemical data are rare in the literature because they are not often analysed in geochemical studies, and when they are searched for, some of them (W, Cs, Rb…) are not detected due to their very low concentrations, especially in the lowly mineralised waters.

In this study, all these trace species were only determined for the water samples from Guadeloupe and Martinique. However, W and F could not be detected in numerous water samples (Tab. 2). As well, caesium was not detected in three water samples from Grande Soufriere thermal springs.

In the Dominica case, most of these trace elements were analysed in all the geothermal waters, except W, and Rb, Cs in the WW-P1 water (Tab. 2). For the Montserrat waters, only the Sr concentrations were analysed on the water samples from the two geothermal wells and the F concentrations were determined on the water samples from 4 thermal springs located in the St George Hill and South Soufriere volcano areas (Tab. 2). Finally, in Saint Lucia, none of these trace species was analysed in the waters discharged from the geothermal wells. In contrast, the F and Sr concentrations were determined on all the water samples from the thermal springs located in the Qualibou Caldera and Terre Blanche areas. Mn, Fe and Rb were analysed only on the water samples from three Qualibou Caldera thermal springs (Tab. 2). On two of them, the Rb concentrations could not be detected.

In spite of the rare information on trace elements, we could draw up three figures representing the log (K^2/Sr), log (Na/Rb) and log (Na/Cs) of the geothermal waters (with the Na, K, Sr, Rb, and Cs concentrations expressed in mol/l) as a function of 1000/T, where T in Kelvin is the measured or estimated reservoir absolute temperature (Figs. 24, 25 and 26, respectively).

In Figure 24, most of the geothermal and thermal waters are located between the K-Sr thermometric relationship determined by Sanjuan *et al.* (2016b, c) for the brines and that defined by Michard (1990) for dilute waters in granite environment, except for the water samples from three thermal springs located in Saint Lucia and from the VD1 hot spring in Dominica. If we do not take into account these last thermal springs, we obtain a better K-Sr thermometric relationship for the other waters such as:

$$\log\left(\frac{K^2}{Sr}\right) = -\frac{1725}{T} + 3.479$$

with a relatively good regression coefficient R^2 of about 0.88.

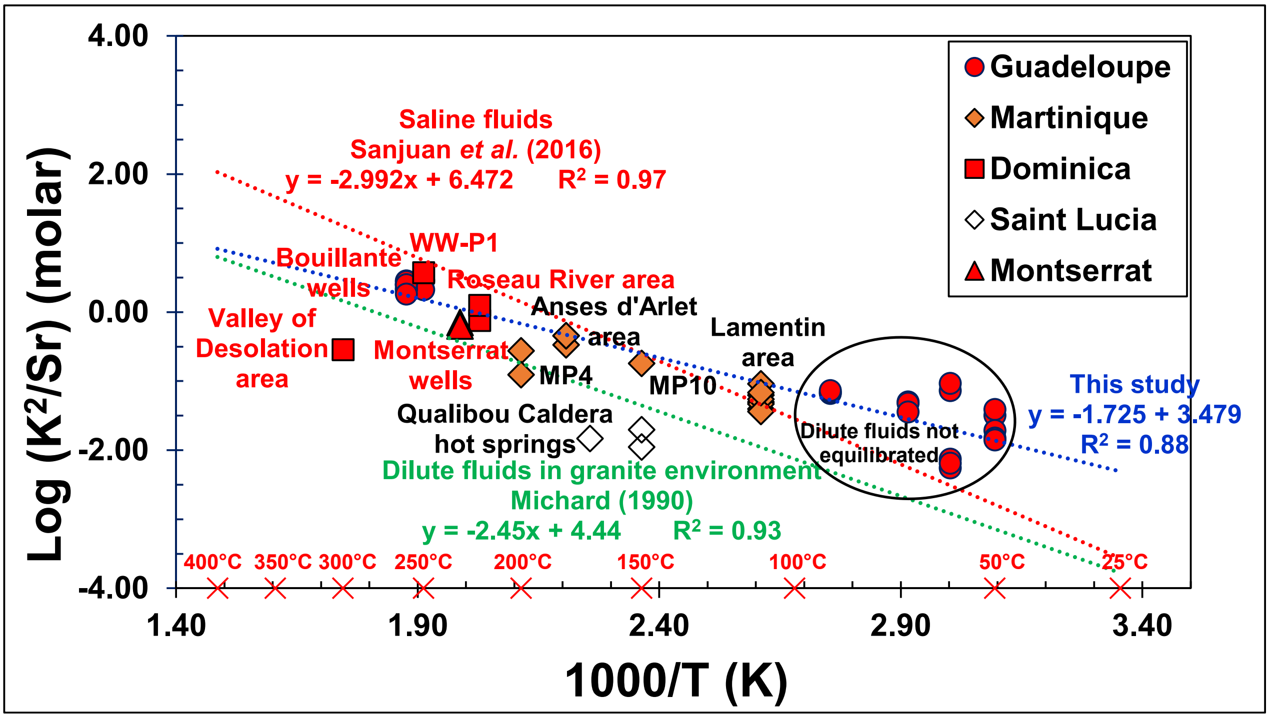


Figure 24 - Logarithm of K²/Sr (molar ratio) versus 1000/T (reservoir temperature in K). The data obtained in this study are compared to the two K-Sr thermometric relationships existing in the literature.

In Figure 25, we can observe that the geothermal waters with reservoir temperature values higher than 150°C fit relatively well the Na-Rb thermometric relationship defined by Sanjuan *et al.* (2016b, c) for hot brines. For lower temperatures, the thermal waters rather fit more or less the Na-Rb thermometric relationship determined by Michard (1990). We can observe similar trends for the Na-Cs thermometric relationships, but the correlations are poorer (Fig. 26).

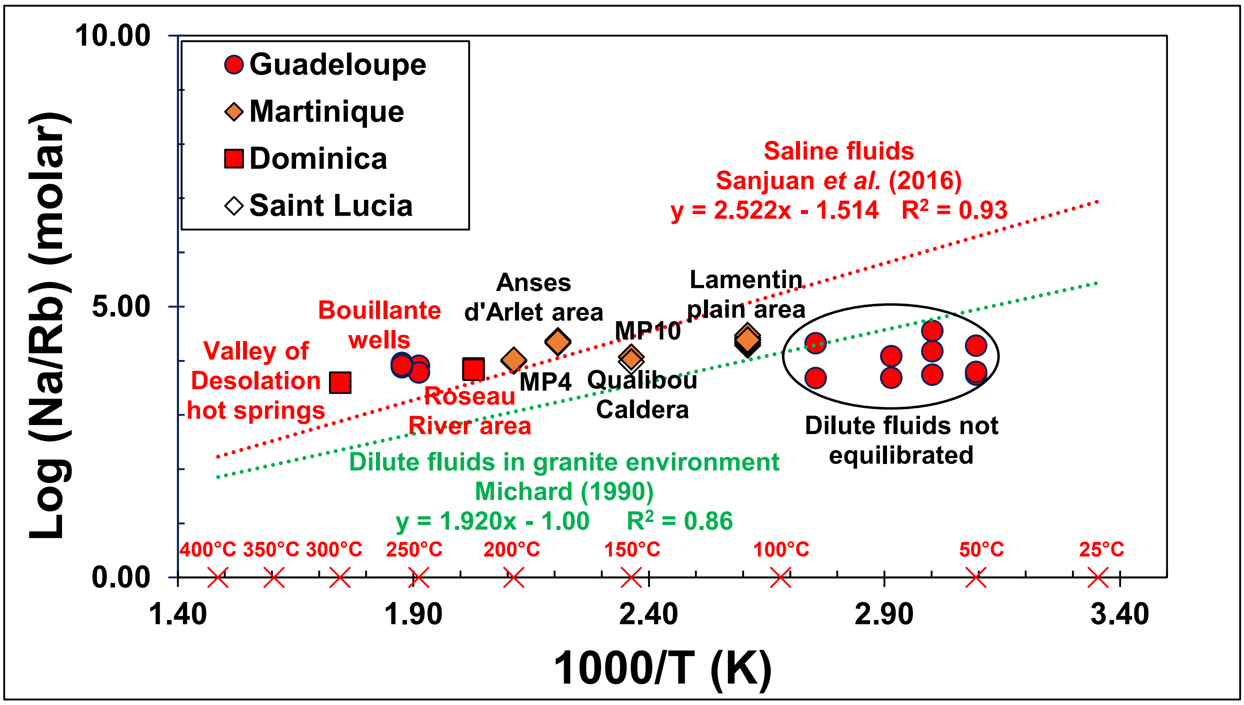


Figure 25 - Logarithm of Na/Rb (molar ratio) versus 1000/T (reservoir temperature in K). The data obtained in this study are compared to the two Na-Rb thermometric relationships existing in the literature.

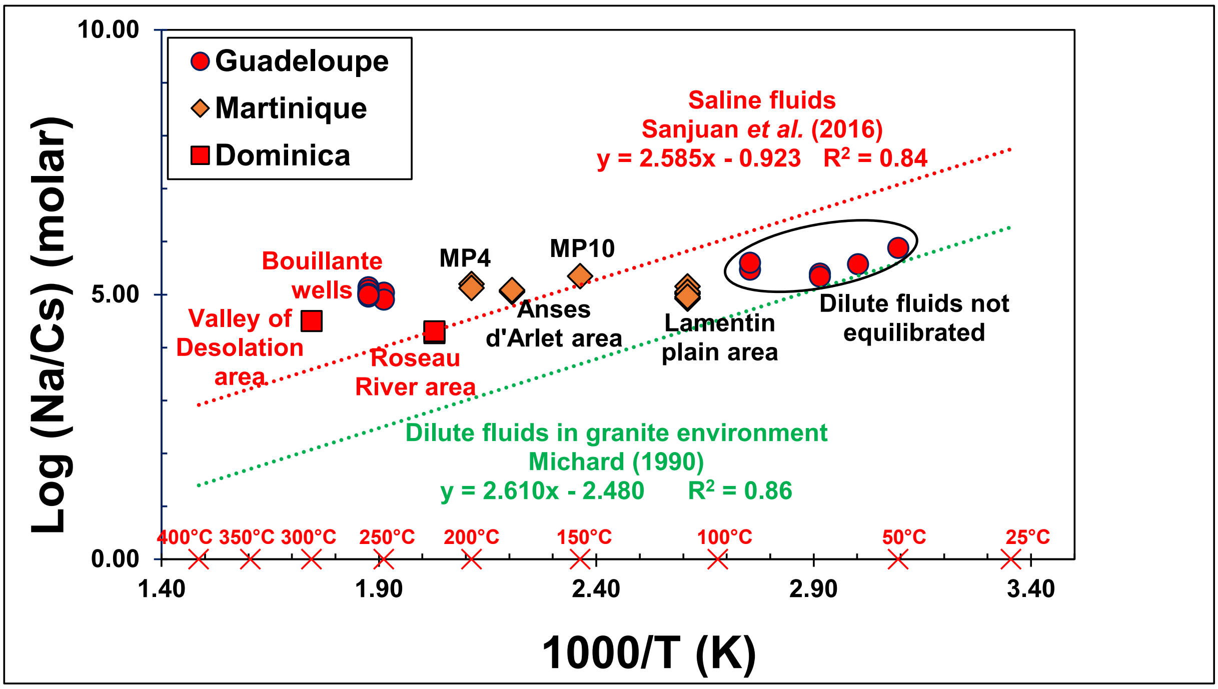


Figure 26 - Logarithm of Na/Cs (molar ratio) versus 1000/T (reservoir temperature in K). The data obtained in this study are compared to the two Na-Cs thermometric relationships existing in the literature.

For the other trace species such as F, Fe and Mn, the geothermal and thermal waters are poorly aligned on the existing thermometric relationships defined in the literature and no new relevant linear regression can be observed. For W, the collected data are not sufficient to use them in a thermometric approach.

To conclude, we can note that more analyses of these trace elements would be necessary in the geothermal waters selected for our study, especially in the saline waters, in order to develop this type of auxiliary chemical geothermometers and understand the processes that control them. However, these first results are rather promising for the development of the K-Sr, Na-Rb and Na-Cs thermometric relationships.

5. Conclusion

This study shows that all the deep waters discharged from the geothermal wells drilled in the islands of Guadeloupe, Dominica, Montserrat and Martinique, as well as from some thermal springs, are neutral Na-Cl fluids derived from seawater, mixed with different proportions of meteoric waters. These mixed fluids interact with volcanic reservoir rocks and reach their full chemical equilibrium at different reservoir temperatures, between 90 and 260°C. In the Saint Lucia Island, the acid high-salinity geothermal fluids discharged from the deep wells have a magmatic contribution and are the hottest fluids (temperature measured up to 290°C), but permeability of these wells was not sufficient for their exploitation. Similar geothermal fluids at 300°C could exist in the Valley of Desolation, in Dominica.

The Li/Cl and 1/Cl ratios of these geothermal waters suggest that the highest contributions of magmatic waters are observed in the Wotten Waven, Blanc River and Boiling Lake areas in the Dominica Island, and in the Anses d'Arlet area, in the Martinique Island. For the geothermal waters from the Bouillante area, in Guadeloupe, for the Lamentin plain area, in Martinique, and for the Montserrat Island, these magmatic contributions seem to be smaller. Unfortunately, these ratios were not available in the literature for the deep geothermal waters from Saint Lucia.

All the other thermal springs, with TDS values below 3 g/l, are mainly meteoric waters present in volcanic massifs such as Soufriere, in Saint Lucia, or Grande Soufriere, in Guadeloupe. Nevertheless, some of them, such as the Grosse Corde and Chute du Carbet thermal springs, in Guadeloupe, or MP10 Rivière Picodo, in Martinique, could have very low contributions of seawater (≤ 4%). Contrary to the majority of the thermal springs from Saint Lucia, Montserrat and Martinique selected in this study, most of the thermal waters from the Grande Soufriere, in Guadeloupe, not equilibrated with the reservoir rocks, would belong to a low-temperature geothermal system (50 - 90°C) and have relatively fast and shallow paths of fluid circulation. This seems to be confirmed by their relatively high δ^7Li isotope values.

The Na-Li thermometric relationship determined by Sanjuan *et al.* (2014) for dilute high-temperature geothermal waters from Iceland, in volcanic environment, can be an interesting tool for geothermal exploration in the Caribbean areas. This thermometric relationship has given reliable estimations of reservoir temperatures for most of the high-temperature geothermal waters from Saint Lucia, Guadeloupe, Dominica, and Montserrat. Most of these waters are relatively saline. Colder (< 200°C) and relatively saline waters, like those from the thermal springs from the Anses d'Arlet and Lamentin plain, in Martinique, and from the Terre Blanche, in Saint Lucia, as well as those from the geothermal wells in Lamentin plain, fit the Na-Li thermometric relationship defined by Kharaka *et al.* (1982) relatively well.

Finally, the dilute thermal waters from the Mount Pelée area, in Martinique, and from the Qualibou Caldera area, in Saint Lucia, are aligned on the Na-Li thermometric relationship determined by Michard (1990) for dilute waters in granite environment. Most of the dilute shallow and warm waters from the Grande Soufriere, in Guadeloupe, not equilibrated with the reservoir rocks, seem to fit more or less the Na-Li thermometric relationship defined by Fouillac and Michard (1981) for saline waters in crystalline and volcanic environment. The coldest waters (T ≤ 60°C) fit no thermometric Na-Li relationship.

All these results show that it is essential to take into account the type of geological environment to use the different Na-Li thermometric relationships, and combine and compare them with the other geothermometers in order to decrease the uncertainty in the estimation of the reservoir temperature.

The use of Li isotope values can be a useful tool to indicate if the waters are rather low- to medium-temperature (≤ 150°C), when most of the chemical geothermometers give discordant temperature estimations. In this case, the δ^7Li values are generally higher than 10‰.

For all the Na-Li thermometric relationships, it is suggested that Li is probably released by mica dissolution (Sanjuan *et al.*, 2014; 2016a; 2022). The new thermodynamic approach using Li-minerals (Boschetti, 2022a, b; 2023) helps to better define the chemical composition of the main Li-carrier minerals and seems to confirm that the presence of micas in the reservoir rocks is the major control of the Li concentrations in the geothermal waters.

Concerning the use of the other auxiliary chemical geothermometers, we have shown that very few data are available in the literature for geothermal waters from the Caribbean region. Moreover, some elements like W, Rb and Cs are difficult to be analysed in lowly mineralised waters because of their very low concentrations. Only some interesting trends have been obtained for the K-Sr, Na-Rb, and Na-Cs thermometric relationships, which need to be confirmed, but are rather promising. We encourage acquiring more analyses of trace elements (F, Sr, Rb, Cs, Mn, Fe, W) in future studies in the Caribbean areas, especially in the saline waters, in order to develop additional geochemical tools for geothermal exploration in this region.

The perspectives for the Bouillante area, in Guadeloupe, with the existing geothermal power plant and the forthcoming increase of its production capacity, as well as the development of other areas, thanks to favourable indices of deep hot fluid escapes brought by the thermal submarine springs, are very encouraging. Similarly, the recent deep geothermal wells drilled in the Dominica and Montserrat islands are promising for geothermal development. For the Martinique and Saint Lucia islands, exploration wells are necessary to test and validate the existing geothermal conceptual models.

The ambitious objectives of the energy transition in the world, the recent arrival of some industrials like Ormat, majority owner and operator of the Bouillante power plant since 2015, and new investors, who aim to develop and operate future geothermal fields in the Caribbean islands, encouraged by new types of funds, is an excellent message for the future. The Caribbean Centre of Excellence of Geothermal Energy, currently being created in the Guadeloupe Island within the framework of the INTERREG V ETC program, featuring a network of scientific research, formation and industrial activity, would have to allow promoting and developing this energy in this entire region. In this context, the success of the Bouillante story could become a stepping-stone for the geothermal development in the Caribbean area.

Acknowledgments:

A major part of this work was carried out within the framework of the Work package 4 (Geothermal Energy) of the INTERREG V ETC program and was co-funded by the European Regional Development Fund (ERDF), the European Development Fund (EDF) and BRGM. We are very grateful to Benoit Vittecoq and Anne-Lise Tailame from the BRGM-Martinique Department for their technical assistance during the field campaign of fluid sampling in Martinique in July 2022 and for their participation to the water collection from the Mount Pelée thermal spring.

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Scientific and Technical Centre
3, avenue Claude-Guillemin
BP 36009
45060 – Orléans Cedex 2 – France
Tél. : 02 38 64 34 34

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