Geochemical characteristics of the main high-temperature geothermal fluids presently highlighted in Caribbean Islands

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ABSTRACT

The Caribbean Islands being part of the Lesser Antilles volcanic arc such as Guadeloupe, Martinique, Dominique, Montserrat, Saint Lucia, etc., 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. Although they are experiencing mounting energy costs and CO_2 emissions, this promising energy source which is indispensable for them to be able to hope to achieve energy self-sufficiency, is available continuously for electricity 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, fishing farmers, balneology, etc., and could contribute to generate jobs directly and indirectly, remains difficult to develop in these islands. Unfortunately, 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 alone example of electricity production in the Caribbean area. With two production units (total capacity of 15 MWe) since 2005, its present annual electricity production is close to 110 GWh (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, 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. As for the Bouillante field, the deep geothermal fluids highlighted in the other Islands are neutral pH seawater derived fluids mixed with meteoric fresh waters at different proportions, which 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 the low reservoir permeability. 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 Caribbean Energetic Transition 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.

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). 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 they are experiencing mounting energy costs and CO_2 emissions, this promising energy source seems to be indispensable for them to be able to hope to achieve energy self-sufficiency. Geothermal energy is available continuously for electricity 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, fishing farmers, balneology, etc., and could contribute to generate jobs directly and indirectly. In spite of all these advantages, this energy remains difficult to develop in these islands. Unfortunately, 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 alone 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, 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.

The main objectives of this paper 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, and test 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 paper has exploited two types of geochemical data: data obtained after an important literature review and data acquired in the Guadeloupe and Martinique Islands, during this study.

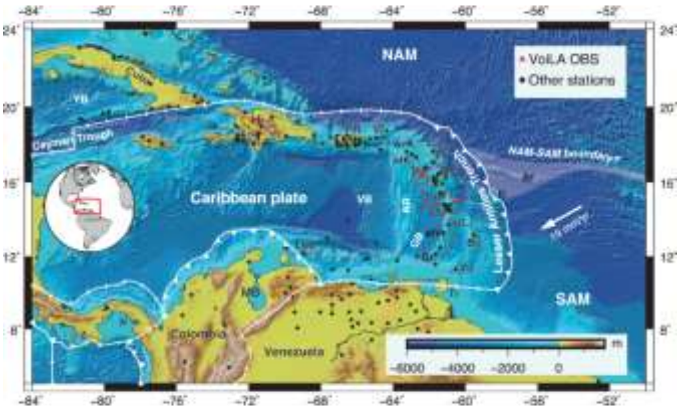

Figure 1: Plate boundaries from Bird (2003). Uncertainty in the position of the North American (NAM) - South American (SAM) plate boundary is indicated by white shading. Plate motion vector is for Atlantic seafloor relative to the Caribbean plate. An Anguila, AB Antigua and Barbuda (Limestone Caribbees), 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.

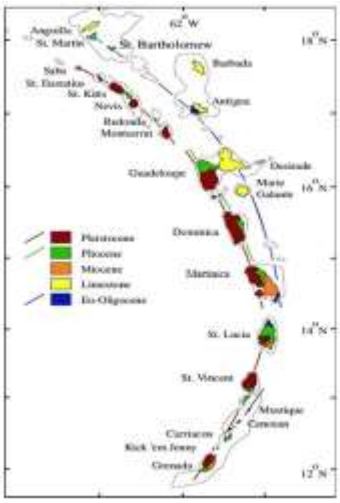

Figure 2: Map of the Lesser Antilles island arc, showing the ages of the exposed rocks and the positions of the volcanic front during the Eocene-Oligocene (red line), Pliocene (blue line), and Pleistocene (black line) (from Robertson, 2009).

2. GEOLOGY SETTING OF LESSER ANTILLES ISLAND ARC AND MAIN STUDIED GEOTHERMAL AREAS

2.1 Geology setting of Lesser Antilles

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). 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 past 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 element 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.

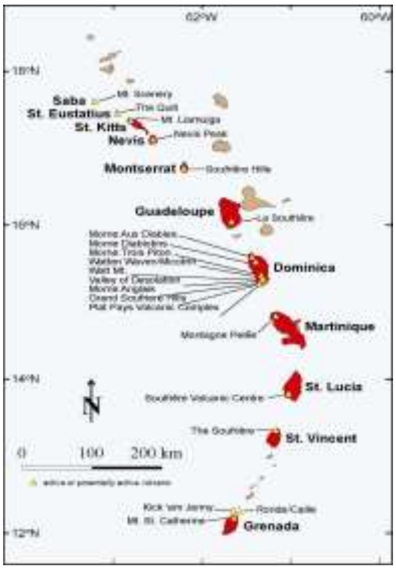

Figure 3: Map of the main active volcanic centers of the Lesser Antilles (from Joseph, 2008).

2.2 Main studied geothermal areas

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, some thermal springs indicate discharges of deep fluids and 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.

2.2.1 The 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.

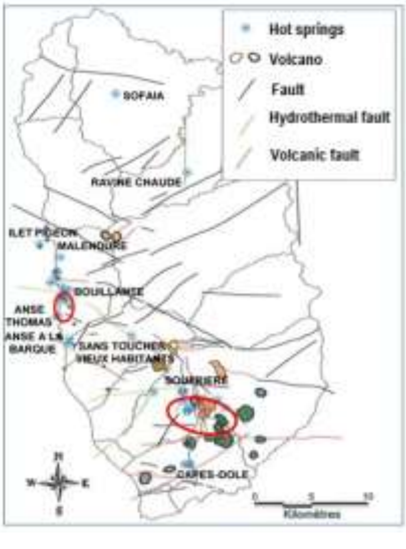

Figure 4: Map of the main hot springs and geothermal areas in the Guadeloupe Island (from Bourdon *et al.*, 2009).

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

Exploited since 1986, the Bouillante geothermal field, which is located on the west coast of the Basse-Terre Island, 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 (Thinon *et al.*, 2010; Calcagno *et al.*, 2012), is the alone 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. 5a 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. 5b).

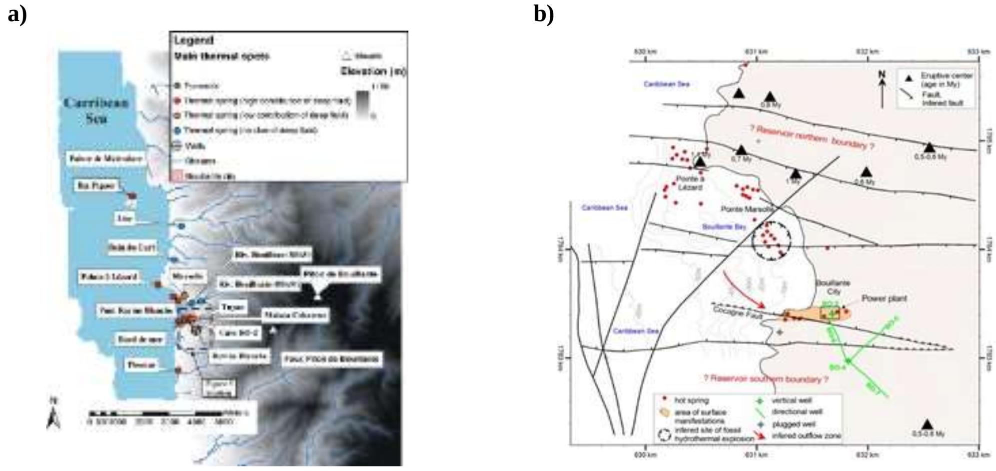

Figure 5: a) Main hot springs in the Bouillante geothermal area (from Lachassagne *et al.*, 2008). b) Main volcanoes, fault and hot springs in the Bouillante Bay area (from Traineau *et al.*, 2015a)

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 (Fig. 5b). 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. For the moment and since 2015, the water reinjection is partial (about 100 m^3/h into the surface BO-2 well) and the majority of produced fluid is discharged in the sea, after mixing and cooling with seawater, and without important environmental impact. In 2022, a new deep production well has been recently drilled near the BO-5 and BO-6 wells to increase the total production capacity of the power plant to 20-25 MWe, but is not still 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. 6). 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 terrestrial thermal spring, was demonstrated using different types of binary diagrams (Sanjuan and Brach, 1997; Traineau *et al.*, 1997; Sanjuan, 2001; Sanjuan *et al.*, 2001a; 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 6, 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.

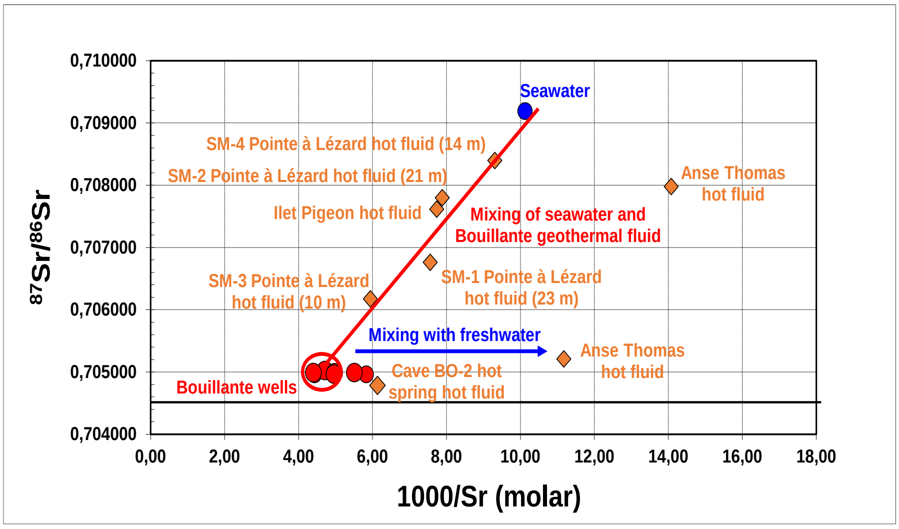

Figure 6: Diagram $^{87}Sr/^{86}Sr$ ratio *versus* 1000/Sr concentration for the submarine thermal waters sampled in the Bouillante area (Sanjuan, 2001), indicating a linear relationship between the Bouillante deep geothermal fluid and sea water which results from a mixing between these two end-members. Some terrestrial thermal waters (like Anse Thomas and Cave BO2) are not aligned because they are also mixed with a third component that is freshwater.

b) 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 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; Moune *et al.*, 2022). 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; Villemant *et al.*, 2014). Thermal springs (30-45°C) are concentrated around the base of the dome mainly in the SW, S and NE sectors (Fig. 8). This distribution is controlled by the structure of the volcanic edifice and the extensive development of argilic hydrothermal alteration along preferential zones. These thermal waters have a meteoric origin (TDS ≤ 1.3 g/l) and seem to interact with volcanic rocks at 80-100°C.

2.2.2 Martinique Island

Martinique is a volcanic island belonging to the recent Lesser Antilles arc of post-miocene age, with a well-known surface geology (Westercamp *et al.*, 1989). The thermal springs are scarce in the Martinique Island in relation to the volcanic activity and the rainfalls (Fig. 7 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. 7 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 7a indicates the three areas studied in this work, with a focus on Mount Pelée volcano in Figure 7b, Diamant-Anses d'Arlet in Figure 7c and Lamentin plain in Figure 7d.

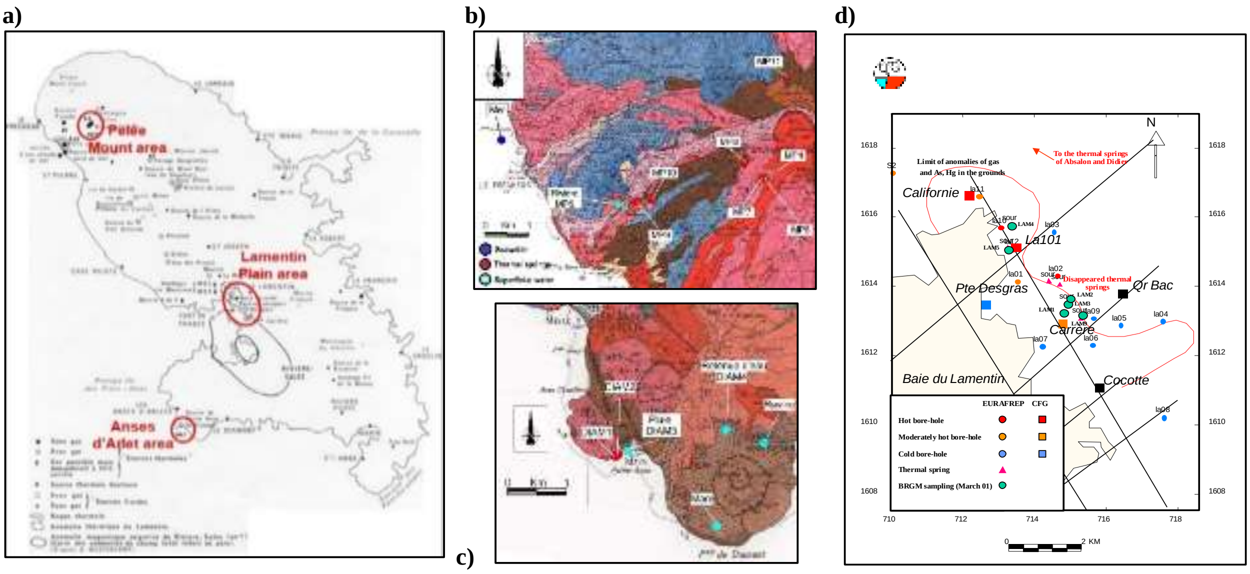

Figure 7: a) Location map of the main thermal springs in the Martinique Island (from Lopoukhine and Mouret, 1977). b) Location of the thermal waters in the Mount Pelée area (Sanjuan *et al.*, 2003; 2005b). c) Location of the thermal waters in the Anses d'Arlet area (Sanjuan *et al.*, 2003; 2005b). d) Location of the thermal waters in the Lamentin plain area (Sanjuan *et al.*, 2002a, b).

a) 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. 7a). The area of Lamentin corresponds to a major Graben zone limited by NW-SE faults and intersected by the NESW faults (Chovelon, 1984). The occurrence of many thermal springs localized in the area of Lamentin 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. During the first geothermal exploration phase, that occurred between 1966 and 1971 in the Lamentin plain (EURAFREP, 1969; 1970), a deep well LA101 (771 m; Fig. 7d) 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 springs of surface. 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 bore-holes drilled by CFG in this area at a depth close to 1000 m, only the bore-hole located more at north (Californie bore-hole) 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 bore-hole (Fig. 7d), situated near thermal springs, but with a lower temperature (50°C).

b) 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 (Traineau *et al*., 1989). Despite this abundant potential heat flow, there are few surface manifestations indicative of the existence of a large high-temperature hydrothermal system (Westercamp and Traineau, 1987; Traineau *et al.*, 1989). The emergence temperature of the thermal waters vary from 36 to 51°C (Fig. 7b). These thermal waters with TDS values ≤ 1.6 g/l have a meteoric origin (Sanjuan *et al.*, 2003; 2005b).

c) 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. 7c). 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 neighboring occurrences (Sanjuan *et al.*, 2003; 2005b).

2.2.3 Dominica Island

Dominica is located in the central Lesser Antilles between the two French Guadeloupe and Martinique Islands. 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. 8), of which seven major andesitic-dacitic volcanic centers have been active since the late Pleistocene (Lindsay *et al.*, 2005).

More than 30 geothermal and hydrothermal areas have been identified (Fig. 8) throughout the island and off-shore (Smith *et al.*, 2013) and initial characterization of the most prominent hydrothermal fields was done by Joseph *et al.* (2011). 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 (Fig. 9). About 35 warm and hot springs have been recorded in the Wotten Waven area and the Boiling Lake - Valley of Desolation area and analyzed by the BRGM French Geological Survey (1985), Lasne and Traineau (2005) and Traineau and Lasne (2008). Lasne and Traineau (2005) provided a comprehensive map of the surface manifestations classified into eight types (Fig. 9): warm spring, hot spring, mineralized-fluid hot spring, fumaroles, cold gas discharge, solfatare and steam vent, fossil alteration area, phreatic crater.

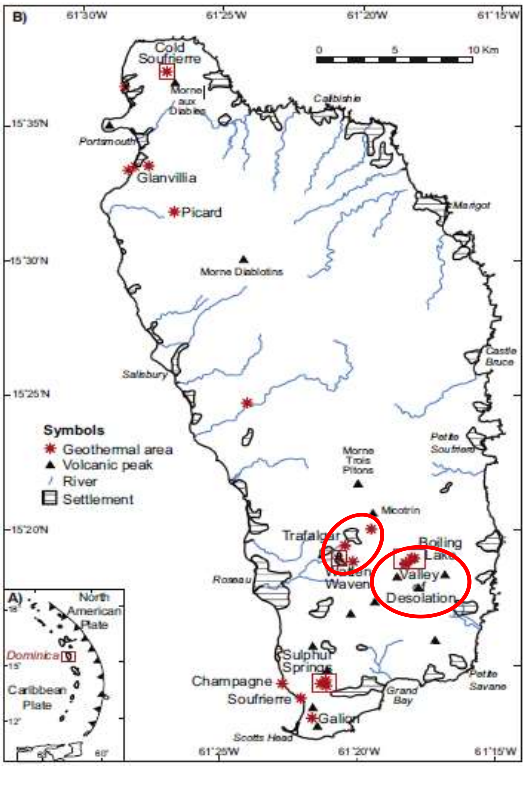

Figure 8: A map of Dominica (modified from Smith *et al.*, 2013) highlighting geothermal areas (springs, fumaroles, bubbling pools) (from Joseph *et al.*, 2019).

Geothermal potential of Dominica has been first reported during an UNDP visit (Barnea *et al.*, 1969). First detailed exploration has been done by BRGM between 1982 and 1984. It included geology, geochemistry and geophysical (gravimetric, resistivity, magnetotelluric) methods (BRGM, 1984 and 1985). Two areas of interest had been investigated: Wotten Waven and Soufriere regions (Fig. 8). Other exploration works were still carried out. 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.

Among the drilled wells, the chemical composition of the fluid discharged from the WW-P1 geothermal well (about 1500 m deep; Fig. 9) 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 have selected and the corresponding TDS value was close to 5.0 g/l.

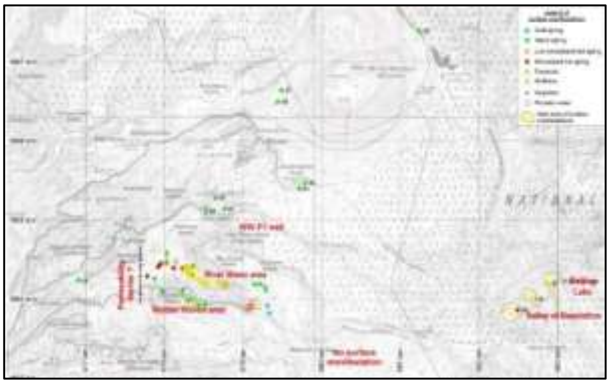

Figure 9: Type and location of the surface manifestations of the Roseau valley geothermal field compiled by Traineau and Lasne (2008). Coordinates in UTM WGS84. Elevation in feet (from Traineau *et al.*, 2015b).

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 centers 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 chosen 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 kilometers 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 occurs in the nearby Valley of Desolation (Lindsay *et al.*, 2005; Fournier *et al.*, 2009). Ca-rich Na-Cl waters are discharged 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.

2.2.4 Montserrat Island

The active volcanic island of Montserrat is in the northern section of the Lesser Antilles arc, in the eastern Caribbean. This island includes three major volcanic centers 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 centers 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). 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. 10a):

- 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)**

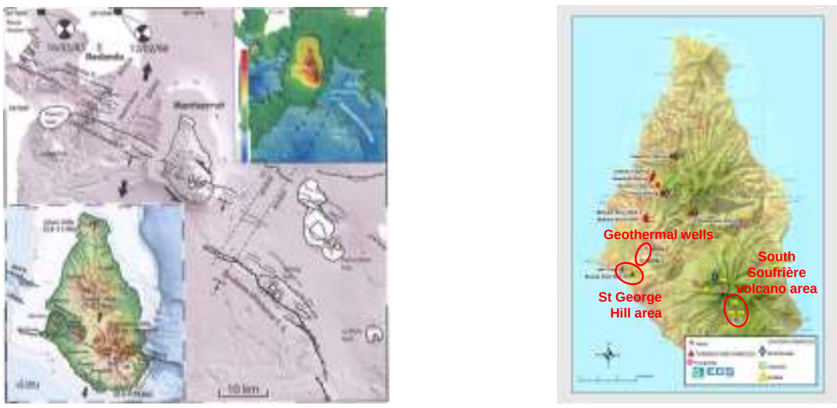

Figure 10: a) Seism-tectonic map and volcanic Setting of Montserrat (from Feuillet *et al.*, 2010); b) Location map of the geothermal wells MON-1 and MON-2 and of the main thermal springs and fumaroles in the Montserrat Island (from Brophy *et al.*, 2014).

Two major morphological features dominate the prospect area: Garibaldi Hill and St George's Hill (Fig. 10a). 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. 10b). 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 continuing 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). After these exploration works, two successful wells were drilled in the faulted half-Graben between St George's and Garibaldi Hills, in the central-southern part of the island (Fig. 10a), 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 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.

2.2.5 Saint Lucia Island

The Island of Saint Lucia is located between Martinique and St Vincent, in the southern region of the Lesser Antilles (Fig. 11). 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. 11). 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) which, together with the occurrence of occasional swarms of shallow earthquakes and vigorous hot spring activity in southern Saint Lucia, indicates that this area is still potentially active and could generate volcanic eruptions in the future.

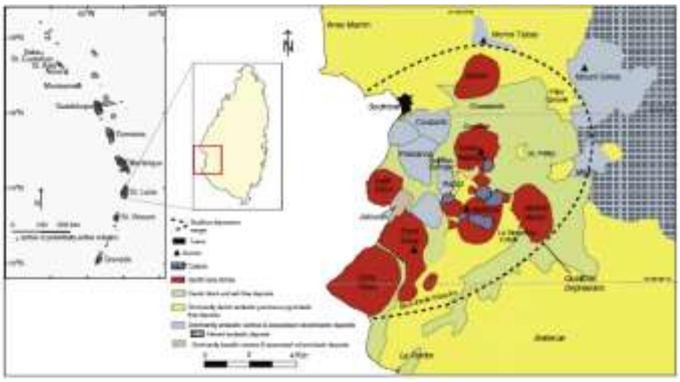

Figure 11: Map of Lesser Antilles showing the location of Saint Lucia (left), and map of Saint Lucia showing an outline of the Qualibou Depression and main vents of the Soufriere Volcanic Centre (right) (from Joseph *et al.*, 2013).

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 exact age of formation of Qualibou caldera was previously estimated at 0.5 Ma (Aspinall *et al.*, 1976), but new radiocarbon ages by Roobol *et al.* (1983) indicate an age less than 40000 years. This is confirmed by geologic works by Wohletz and Heiken (1984) who find that caldera formation postdates the Pitons.

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 Sulfur springs (Robson and Willmore, 1955), which is close to the caldera center and the youngest pyroclastic vents. The main site of geothermal activity occurs at the well-known Sulphur Springs area (Fig. 11). Thermal manifestations at Sulphur Springs include features such as boiling springs and pools, fumaroles with strong gas flux, hot ground, and extensive rock alteration (Fig. 11). Thermal springs are present at Diamond and Cresslands (Fig. 11), which are located about 200-300 m from the northern and eastern base, respectively of the Terre Blanche dome (Wohletz *et al.*, 1986). Several other sites of geothermal activity can be found in southern Saint Lucia, amongst them are the warm springs at Jalousie, and underwater gas vents offshore between Anse Mamin and Soufriere Bay (Fig. 11) (Lindsay *et al.*, 2005). According to Williamson (1979), the main thermal area, Sulphur Springs valley, is oriented parallel to faults and fractures that strike NW-SE and dip 60 to 70° NE. The main area of the Sulphur Springs geothermal field is comprised of numerous hot springs, bubbling mud pools, boiling springs, and fumaroles in an area of strongly argillic altered rock approximately 200 m×100 min size. 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.

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 holes in 1976. The wells ranged in depth from 116 to 725 m and were drilled in and around the Sulphur Springs area (Fig. 11). 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 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 HCI 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 important literature review about the waters of deep geothermal wells and thermal springs existing in the Guadeloupe, Martinique, Dominica, Montserrat and Saint Lucia Islands;
- data acquisition in Martinique and Guadeloupe during this study, after collection and/or chemical analyses of fluid samples.

For these last data, BRGM and the Antilles University (AU) carried out a field campaign of fluid collection 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), 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 (Table 1). The Cl and SO_4 major anions, and Br, were analyzed using ion chromatography in the AU laboratories. Dissolved silica was also analyzed in these laboratories by spectrophotometry. The concentrations of the 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 the other 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 other trace species. These trace species (or part of them) were also analyzed 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 performed 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 these results are reported in Table 1.

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.

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	SiO_2 mg/l	TDS g/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
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	130	19.4	< 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	31.1	31.30	6.33	24.0	23.6	1.80	5608	344	871	252	9723	1550	565	134	19.1	< 0.1	24.0	6.38	14901	1191	10994	941	269	< 0.05	6.97	This study
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	55	13.0	0.40	23.5	0.90	20560	186	1481	566	253	< 0.05	6.61	This study
	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	74	12.5	0.30	23.0	4.66	20591	274	1456	559	244	< 0.05	7.05	This study
	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	60	13.4	< 0.1	24.2	0.40	20824	175	1356	494	201	< 0.05	10.05	This study
	Bord Lézarde hot spring	06/07/2022	59.6	19.00	6.09	-101	40	2.45	3553	155	776	131	6792	780	337	79	12.6	0.40	23.1	4.92	20209	281	1329	543	226	< 0.05	8.26	This study
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	124	1.2	0.30	< 0.1	0.50	297	1818	993	79	10	< 0.05	8.38	This study

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

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

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	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
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		51.3	14.4	19.8	8.0	4.50		3.89	2.95	0.343			4.4	Sanjuan and Brach (1998)
		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	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	23/03/2005	165.0	260	1.88	6.83	5700	840	2020	1.6	13000	24.4	24.5	530	22.2	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	11/12/2007	165.0	260	1.88	6.86	5944	832	2135	1.6	13986	23.0	26.0	571	23.0	< 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	29/11/2002	165.0	260	1.88	7.06	6650	860	2060	2.2	14501	25.6	20.0	580	24.8	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	11/12/2007	165.0	260	1.88	5.41	6207	900	2118	1.8	13850	18.0	< 0.5	597	23.2	< 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	26/01/2011	165.0	260	1.88	7.24	6259	968	2096	< 0.5	14545	22.0	19.0	601	24.5	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	07/11/2012	165.0	260	1.88	7.36	5983	950	2178	1.3	14400	23.8	10.7	648	24.2	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	08/07/2003	165.0	260	1.88	6.65	6956	982	2189	2.3	14970	26.8	22.0	602	25.8	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	11/12/2007	165.0	260	1.88	5.10	5880	827	2200	1.8	13891	29.9	19.8	576	22.9	< 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	07/11/2012	165.0	260	1.88	7.32	6000	926	2158	1.2	14600	23.0	12.0	648	24.4	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	19/01/2021	165.0	260	1.88	5.59	5515	809	2111	1.2	13599	22.0	18.5	561	22.6	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)
	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	< 0.5	0.5		0.158		0.189	0.03	0.008	0.0574	0.00133		< 0.00005	20.1	Sanjuan *et al.* (2008)
			2000	44.4	60	3.00	6.07	75.0	14.1	194	58.2	142	104	579	111	1.3			0.592	0.122		0.003		0.008						Brombach *et al.* (2000)
		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	< 0.5	< 0.25		0.117		1.375	3.72	0.011	0.0350	< 0.0005		< 0.00005	14.5	Sanjuan *et al.* (2008)
			2000	40.1	50	3.09	5.59	59.4	8.7	169	49.8	85.9	64.0	580	115	1.1			0.441	0.111		2.060		0.009						Brombach *et al.* (2000)
		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	< 0.5	< 0.25		0.100		0.564	0.0019	0.010	0.0213	< 0.0005		< 0.00005	9.9	Sanjuan *et al.* (2008)
			2000	27.7	50	3.09	5.02	40.6	5.0	101	27.3	46.8	18.0	384	102	0.7			0.264	0.094		1.630		0.011						Brombach *et al.* (2000)
			1985	26.4	50	3.09	5.12	52.9	7.0	160	45.7	151	14.6	451	159	1.0	0.40		0.350	0.202			0.019	< 0.02	0.0103	0.00040				Fabriol and Ouzounian (1985)
		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	1.14	< 0.25		0.610		0.718	0.0242	0.002	0.0083	< 0.0005		< 0.00005		Sanjuan *et al.* (2008)
			2000	58.8	60	3.00	5.65	33.8	8.2	257	12.0	18.1	23.0	708	37	1.1			0.068	0.515		0.698								Brombach *et al.* (2000)
			1985	59.0	60	3.00	5.90	32.9	8.2	265	12.4	19.1	20.8	720	34	1.1	1.80		0.070	0.596			0.210	< 0.02	0.0034	< 0.00015				Fabriol and Ouzounian (1985)
		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	< 0.5	0.5		0.310		0.250	0.0023	0.014	0.0593	0.00151		< 0.00005	16.0	Sanjuan *et al.* (2008)
			2000	44.9	90	2.75	6.51	116	24.0	188	64.9	368	125	303	110	1.3			0.317	0.477				0.014						Brombach *et al.* (2000)
			1985	45.2	90	2.75	6.73	82.5	22.7	112	51.0	266	152	185	110	1.0	0.19		0.249	0.403			0.0017	< 0.02	0.0145	0.00120				Fabriol and Ouzounian (1985)
		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	< 0.5	0.9		0.400		0.270	0.0027	0.007	0.0647	0.00198		< 0.00005	12.5	Sanjuan *et al.* (2008)
			2000	48.6	70	2.91	6.37	129	23.6	180	70.9	557	103	180	110	1.4				0.661				0.008						Brombach *et al.* (2000)
			1985	35.9	70	2.91	6.46	116	23.5	222	96.0	709	115	96.1	91	1.5	0.095		0.400	0.876			0.135	< 0.02	0.0350	0.00306				Fabriol and Ouzounian (1985)
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	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.* (2002)
		Californie well (TDP)	26/03/2002	73.6	110	2.61	6.04	3790	124	725	130	7050	982	316	69	13.2	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.* (2002)
		Habitation Carrère well (TDP)	21/11/2001	41.0	110	2.61	6.08	3310	125	830	187	6335	1593	333	91	12.8	< 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.* (2002)
		Habitation Carrère well (TDP)	05/12/2001	40.1	110	2.61	6.12	3280	122	778	183	6358	1562	127	90	12.5	< 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.* (2002)
		Ferme Perrine hot spring	06/07/2022	38.5	110	2.61	6.27	3678	150	805	137	6982	800	352	55	13.0	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	06/07/2022	57.3	110	2.61	6.02	3589	140	801	130	6688	750	334	74	12.5	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	06/07/2022	34.0	110	2.61	6.13	3897	115	789	133	7269	950	176	60	13.4	< 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	06/07/2022	59.6	110	2.61	6.09	3553	155	776	131	6792	780	337	79	12.6	0.4	23.1		20.2		0.281	4.92	1.329	0.543	0.226		< 0.00005	8.3	This study
	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	< 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)
		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	< 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	05/07/2022	31.1	180	2.21	6.33	5608	344	871	252	9723	1550	565	134	19.1	< 0.1	24.0		14.9		1.191	6.38	10.994	0.941	0.269		< 0.00005	7.0	This study
	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	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)
		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	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	16/03/2003	36.6	150	2.36	6.37	268	33.3	95.4	50.6	451	440	60.5	181	1.6	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)
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	1.3	12.6	37.2	0.969	0.51	0.176	0.0338	4.10						Jacobs report (2018)
	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	0.60	7.5		0.654	0.049	0.169	< 0.02	2.20	0.544	0.328	0.0270			Lasne and Traineau (2005)
	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	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)
	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	< 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	25/11/2000	84.0	300	1.74	4.20	616	321	1152	42	879		2189		5.2	0.90	14.0						2.50						Joseph *et al.* (2011)
		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			40.7				27							BRGM (1985)
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			16.0	47.0										Brophy *et al.* (2014)
		MON-2 well	18/12/2013	153.0	230	1.99		7950	703	3370	8.1	19080		18	355	31.5			14.0	45.0										Brophy *et al.* (2014)
		EGS/TCI - MHP-1 hot spring	2012	59.0	230	1.99	5.57	7233	1001	1944	247	16340	161	222	259	27.4			22.0											Poux and Brophy (2012)
	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	0.22		22.9					8.90						Chiodini *et al.* (1996)
		Hot spring 2	March 1991	47.6	230	1.99	6.00	6200	758	2070	454	15000	195	174	232	25.1	0.15		18.6					6.70						Chiodini *et al.* (1996)
	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	0.10		0.30					0.050						Chiodini *et al.* (1996)
		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	0.15		0.36					0.030						Chiodini *et al.* (1996)
	Soufrière Hills	Hot spring 7	March 1991	95.4	230	1.99	1.60	105	4.0	152	93.8			5671	428	6.5								0.055						Chiodini *et al.* (1996)
		Hot spring 9	March 1991	98.0	230	1.99	1.80	194	29.3	230	161			12250	380	13.2								0.11						Chiodini *et al.* (1996)
Saint Lucia	Sulphur springs	Well 4	02/04/1976	100	180	2.21	5.69	3500	151	5300		18000																		Goff and Vuataz (1984)
		Well 4	06/04/1976	100	180	2.21	5.85	500	50	1850		6120			88															Goff and Vuataz (1984)
		Well 4	22/04/1977	100	180	2.21	4.52	11100	565	22200		70200			103	104														Goff and Vuataz (1984)
		SL-2 well (25.3 h of production)	February 1988	100	290	1.78	7.10	700	650	1206		3760	49		625															D'Amore *et al.* (1990)
		SL-2 well (45 h of production)	February 1988	100	290	1.78	5.20			2044		6700																		D'Amore *et al.* (1990)
		SL-2 well (68.5 h of production)	February 1988	100	290	1.78	4.70			4459		15650	0																	D'Amore *et al.* (1990)
	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	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	July 1983	55.7	150	2.36	6.55	257	16.5	163	56.5	153	1215	0.77	110	2.0	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	July 1983	35.2	150	2.36	8.57	267	15.4	23.1	20.3	74.0	648	105	101	1.3	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	1985	43.0	170	2.26	7.00	182	14.1	72.1	47.4	33.7	91.5	8.6	198	0.8	0.13		11.9					0.21						Gandino *et al.* (1985)
	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	0.11		519					0.041						Gandino *et al.* (1985)
		Hot spring 134	1985	90.0	290	1.78	6.90	71.3	13.7	102	15.8	245	256	624	168	2.2	0.16		519					0.036						Gandino *et al.* (1985)
Guadeloupe		Seawater	1998	29.0	29.0	3.31	8.23	11000	401	467	1346	20181	169	3000	0.43	36.6	2.9	67.0	5.24	8.65	0.008	0.021	0.030	0.25	0.089	0.00050			29.3	Sanjuan (2001)
Martinique		Seawater	2001	28.5	28.5	3.32	8.19	11400	309	390	1200	20200	152	2626	0.19	36.3	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

We can note 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 for 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 31 to 6.5 g/l in Montserrat, from 20 to 12 g/l in Martinique and from 11 to 3 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 analyzed during this study (Tables 1 and 2) indicate similar chemical compositions to those previously studied (Lopoukhine and Mouret, 1977; Barat, 1984; Iundt, 1984; Traineau *et al.*, 1989; Sanjuan *et al.*, 2002a, b, 2003, 2005b; Gadalia *et al.*, 2014, 2017). They have allowed confirming the existing geochemical data from these previous works and complete them 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 even 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, the temperature measured at its discharge (32°C) was much lower than that recorded in the previous studies (> 50°C).

The Piper diagram (Fig. 12) and the Cl-SO_4-HCO_3 triangular diagram of Giggenbach (1988; Fig. 13) indicate that all the fluids from the deep geothermal wells and thermal springs, which have 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.

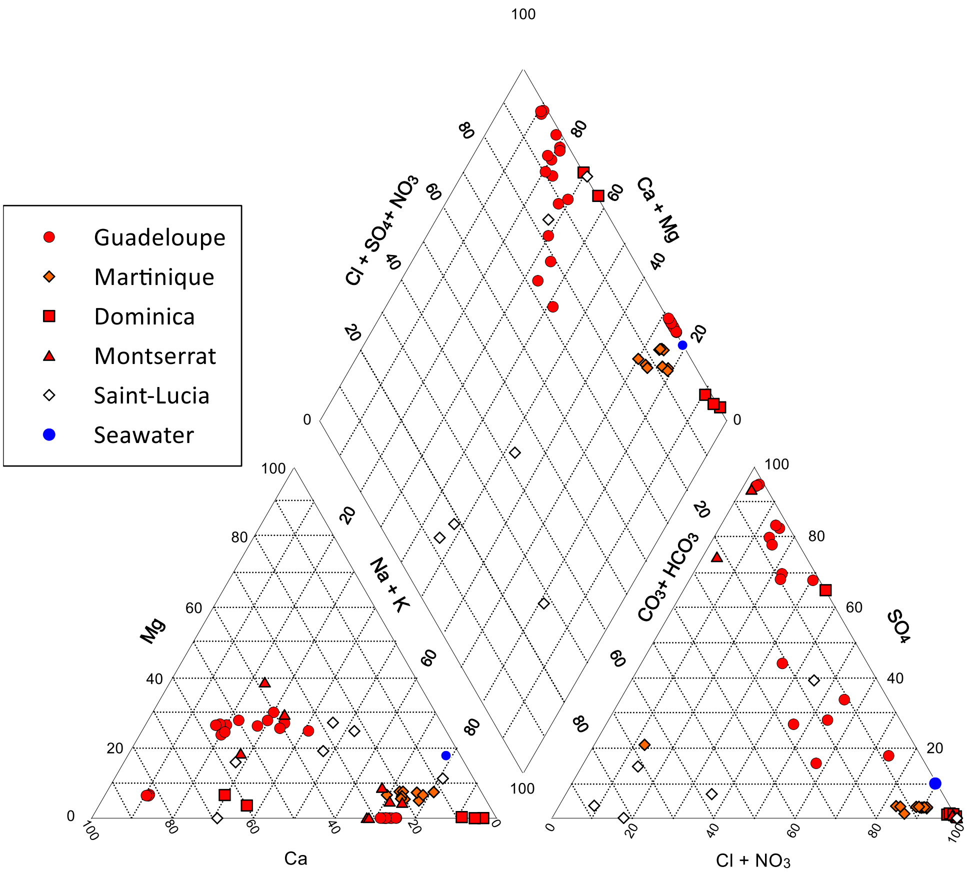

Figure 12: Piper diagram for the geothermal waters of this study.

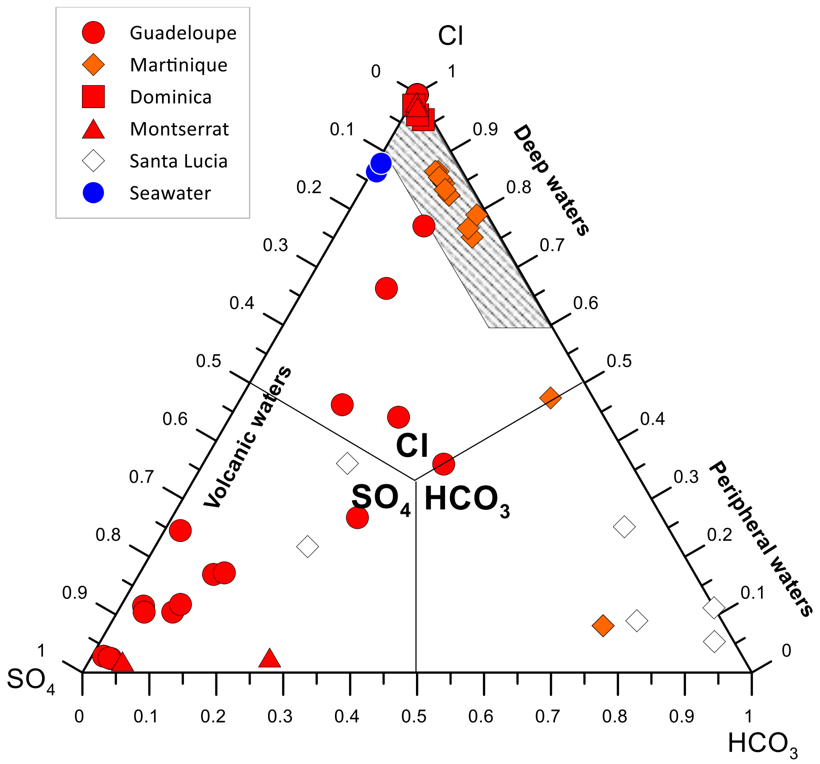

Figure 13: Cl-SO$_4$-HCO$_3$ ternary diagram (Giggenbach, 1988) for the geothermal waters of this study.

4. DISCUSSION

As we have seen that all the deep geothermal fluids from the Guadeloupe, Martinique, Dominica, Montserrat and Saint-Lucia Islands are Na-Cl mature waters, two main objectives will be subject to our discussion: the water origin and 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. 14), which involves two elements often lowly 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 analyzed for the waters from the deep wells located in Montserrat and Saint Lucia, the Na-Cl binary diagram (Fig. 15) suggests that the water discharged from the Montserrat wells also results from a mixing between seawater and meteoric waters. In this last figure, we can also see 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 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 high-salinity waters (pH = 4.52 and TDS > 104 g/l), enriched in chloride (HCl-rich volatiles), has probably a magmatic origin as well as the waters discharged from the neighboring SL-2 well and the Boiling Lake hot spring, in Dominica (Fig. 15). 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. 14), could result from seawater with admixture of meteoric waters and a low contribution of magmatic fluid. This could also explain the low and atypical values of δD (-22.0 to -17.5 ‰) observed for these waters in the Caribbean context (Pedroni *et al.*, 1999; Sanjuan *et al.*, 2003; 2005b).

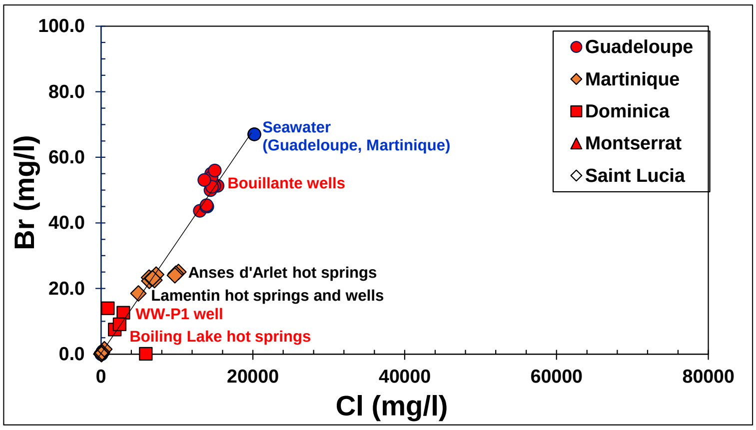

Figure 14: Br versus Cl concentrations for the geothermal waters of this study.

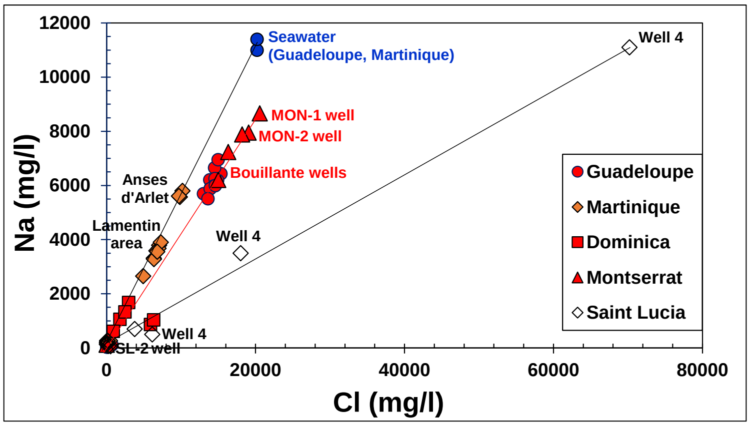

Figure 15: Na versus Cl concentrations for the geothermal waters of this study.

Using the mixing equation for the deep waters resulting from a seawater contribution: $[Cl]_{sample} = x\ [Cl]_{seawater} + 1\text{-}x\ [Cl]_{meteoric\ water}$ and assuming that the Cl concentration of meteoric water $[Cl]_{meteoric\ water}$ is close to 0, we can estimate the percentage of seawater (x) in the mixing for each sample, with:

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

Similar calculations can be performed using the Br 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 neighboring 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 deep geothermal waters seem to be entirely constituted of seawater. In Martinique, the deep 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 reported in the literature or sampled and analyzed during this study (Tables 1 and 2). The deep water discharged from the main occurrence of the Anses d'Arlet thermal spring (Tables 1 and 2) 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 deep geothermal waters from the WW-P1 well (about 15-19%) and from thermal springs, like RR-1 and BR-3 (9-14%), in Dominica (Table 2). 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 thermal springs are relatively near the sea and the existence of major E-W or NE-SW faults favor the mixing between seawater and meteoric water.

All the other thermal springs, which have 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, even if some of them could have very low contributions of seawater ($\leq$ 4%): 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; Table 2; Sanjuan *et al.*, 2003, 2005b; 2008).

4.2 Use of chemical geothermometers

Chemical 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, the geothermometers are very useful in approximating 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-Qz, 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 Guadeloupe, Dominica, Montserrat and Martinique, indicates that the estimations of their reservoir temperatures (260°C, 250°C, 230°C and 110°C, respectively; see Table 3) are concordant and close to the measured temperatures at bottom-hole.

Table 3: Reservoir temperatures estimated using the main chemical geothermometers for the geothermal waters of this study.

Island	Area	Sampling point	Date	$T_{surf.}$ °C	T_{Qz} °C	$T_{Chalc.}$ °C	$T_{Na-K}^{(1)}$ °C	$T_{Na-K}^{(2)}$ °C	$T_{Na-K}^{(3)}$ °C	$T_{Na-K}^{(4)}$ °C	$T_{Na-K-Ca\ (\beta=1/3)}$ °C	T_{K-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).

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

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

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

These estimations can be visualized in the triangular Na-K-Mg diagram (Fig. 16) proposed by Giggenbach (1988). They are also in good agreement with the distribution of the waters in a binary Na-K diagram (Fig. 17). 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 showed, 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).

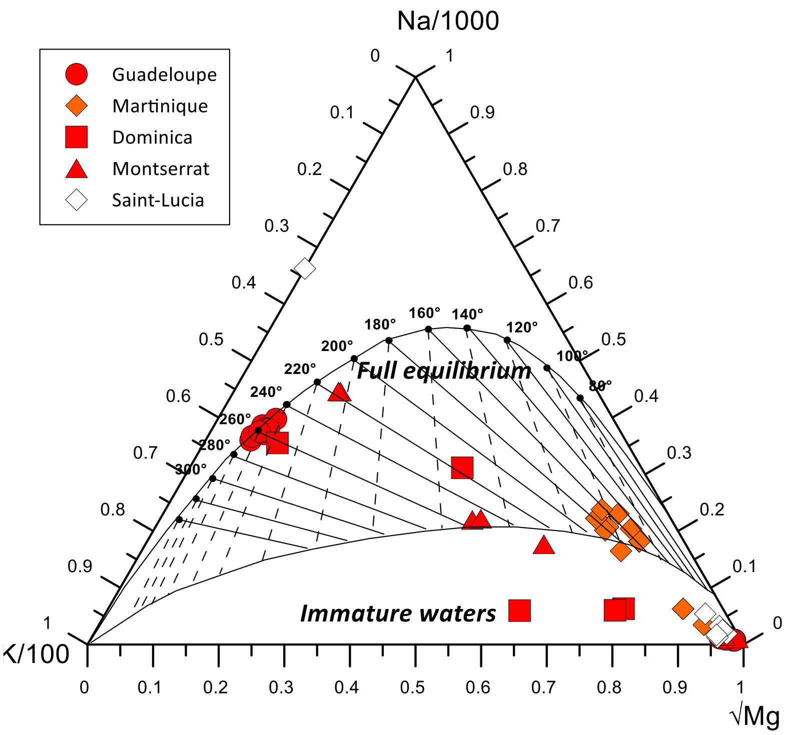

Figure 16: Na-K-Mg ternary diagram (Giggenbach, 1988) for the geothermal waters of this study.

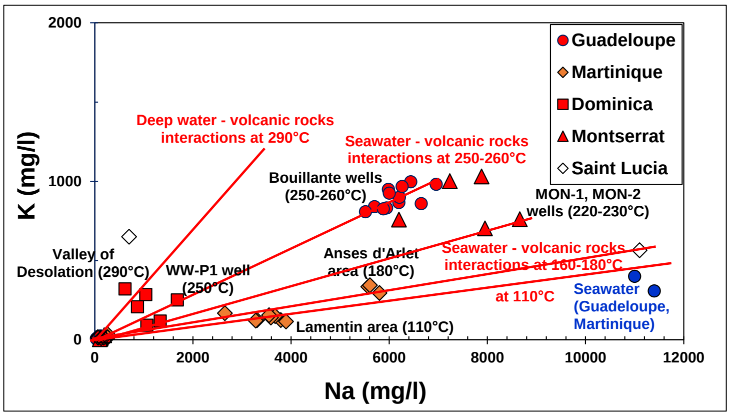

Figure 17: K versus Na concentrations for the geothermal waters of this study.

The use of the classical geothermometers gives also concordant estimations of temperature (180°C) for the deep geothermal water from the Saint-Lucia well 4 (Table 3 and Fig. 16), which is close to the measured temperature (203°C) at a depth of 600 m into this well (Bath, 1977). By contrast, only the Silica-Quartz and Na-K-Ca geothermometers give relatively concordant estimations of temperature (270°C and 325°C, respectively; Table 3), which are in the range of the measured temperature at bottom-hole (290°C), whereas a too much high and unrealistic estimation 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 estimations between 180 and 230°C (Table 3 and Fig. 16).

For the hot springs from the Boiling Lake area, in the Valley of Desolation, the classical geothermometers do not give concordant temperature estimations (Table 3). The Na-K geothermometer suggests temperature values close to 300°C whereas the Silica-Quartz and the Na-K-Ca geothermometers indicate lower estimations (Table 3). As this geothermal water is probably of magmatic origin (see previous section) and could have been mixed with surface waters during its rise towards the surface (which would have modified the concentrations of the dissolved species by dilution of dissolved silica and possible enrichment in magnesium, for example, but not the ratios of some elements like the Na/K ratio, for example), we consider that the estimation given by the Na-K geothermometer is the most representative one.

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. 16) 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 temperatures of discharge from 35 to 56°C, have Na-HCO_3 waters, lowly mineralized (TDS values of 1-2 mg/l) and relatively poor in sulfate (Figs. 12 and 13), 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 indicate estimations of deep temperature between 150 and 170°C (Table 3). However, the K-Mg geothermometer gives much lower estimations 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 the outlying 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. 12 and 13), 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 Valley of Desolation hot springs, the different geothermometers give discordant estimations of temperature (Table 3). Given the discharge temperature values, the estimation given by the K-Mg geothermometers (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), it could be suggested some connections between this permeable zone and the surface waters of the thermal springs. If this assumption is eliminated, the most conservative estimation of temperature is 100°C.

The thermal springs located in the flank of the Grande Soufriere volcano, in Guadeloupe, have temperature discharge from 30 to 60°C. Their waters have relatively low TDS values (< 2 g/l) and two different chemical compositions (Figs. 12 and 13):

- 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 sulfides 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 (Table 2). Their physical and chemical characteristics suggest that they originate through:

- absorption of H_2S-bearing hydrothermal vapors into shallow oxygen-rich groundwaters, which are heated by these hydrothermal vapors. The groundwaters are fed by an abundant meteoric contribution at these altitudes;
- oxygen-driven oxidation of H_2S to H_2SO_4;
- neutralization 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, the magmatic origin can be ruled out.

Given the position of these waters in the Na-K-Mg ternary diagram (Fig. 16) and their chemical characteristics, the high estimations 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 (Table 2). All these results are in agreement with the fact 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 ($\beta = 4/3$ 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 estimations of reservoir temperatures, especially at low and medium temperature (≤ 150°C) due to different processes: chemical equilibrium not reached, fluid mixing, precipitation/dissolution processes during the fluid ascent to the surface....

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 numerical calculations of equilibration temperature of the geothermal water with respect to a suite of reservoir minerals, and thus the estimation of 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 carelessly and without a sound conceptual understanding of the area being studied (Al and pH poorly determined, for example). For this approach, 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 to be proposed by Fouillac and Michard (1981). Since this date, different existing Na-Li thermometric relationships have been developed (Table 4) and have been reported in 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 not only controlled 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…).

Table 4: Main Na-Li thermometric relationships existing in the literature.

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)

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 as those of the waters discharged from the MON-1 and MON-2 wells, indicate comparable Li concentrations.

The Figure 18 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 (Table 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).

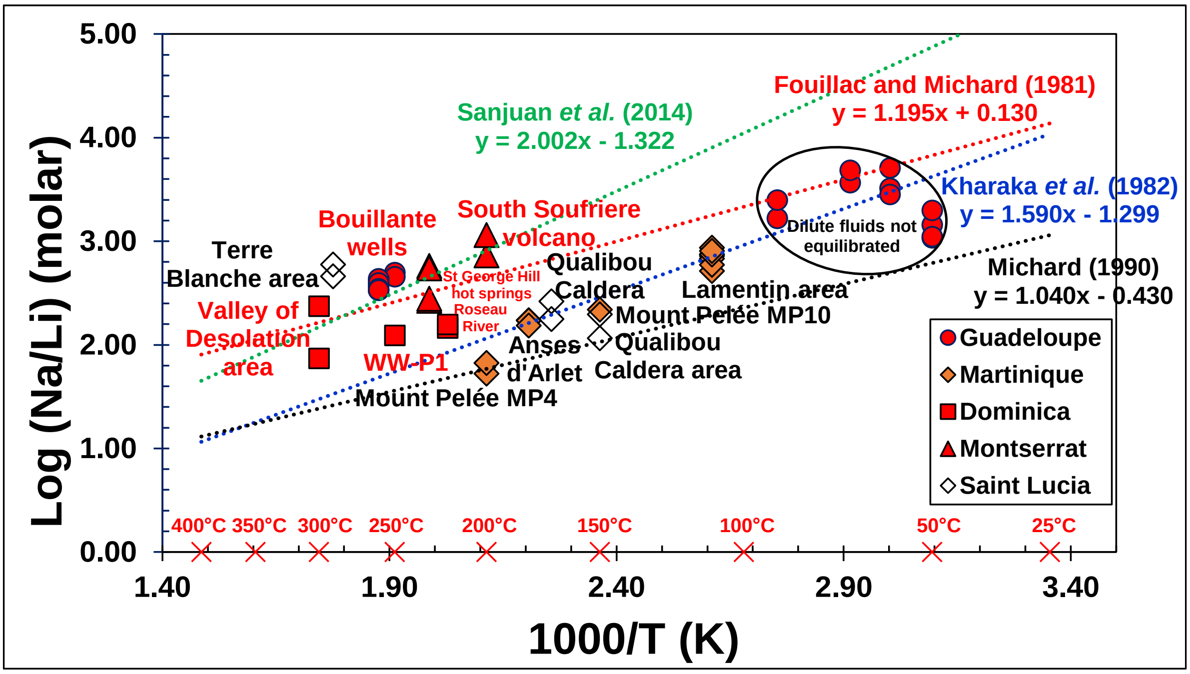

Figure 18: Logarithm of Na/Li (molar ratio) *versus* 1000/T (reservoir temperature in K). The data obtained in this study are compared to the different Na-Li thermometric relationships existing in the literature.

We can notice that this thermometric relationship, which had been defined for dilute geothermal waters in volcanic environment, may be also used for saline fluids of this study. This had been already observed for saline waters from 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 in the use of the Na-Li thermometric relationship. Moreover, in this temperature range, the temperatures estimated using the Na-Li thermometric relationship defined by Fouillac and Michard (1981) are relatively close to those given by the relationship proposed by Sanjuan *et al.* (2014).

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 relationship defined by Michard (1990) for dilute thermal waters in granite environment (Fig. 18). This last thermometric relationship is also followed by the dilute thermal waters from the Mount Pelée, in Martinique, which indicate an estimation of reservoir temperature of about 200°C, and two other dilute thermal waters from the Qualibou Caldera, with reservoir temperatures estimated at 150°C (Fig. 18).

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. 18). The coldest waters fit no thermometric Na-Li relationship.

For all these Na-Li relationships, it is suggested that Li could be released by mica dissolution. The new thermodynamic approach using Li-minerals as that carried out by Boschetti (2022) could help to better determine the main Li-carrier minerals. Unlike the Na/Li ratios, it is difficult to use the isotope Li values as geothermometer (Sanjuan *et al.*, 2014). However, these authors observed that for the Icelandic geothermal fluids, which indicated deep temperatures ranging from 200 to 365°C including the 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‰ were always associated with low-to medium temperature 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 showed that magmatic water have Li/Cl > 0.001 (in wt. ratio) with 1/Cl < 0.001. In this study, the Figure 19 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 the Martinique Island (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.

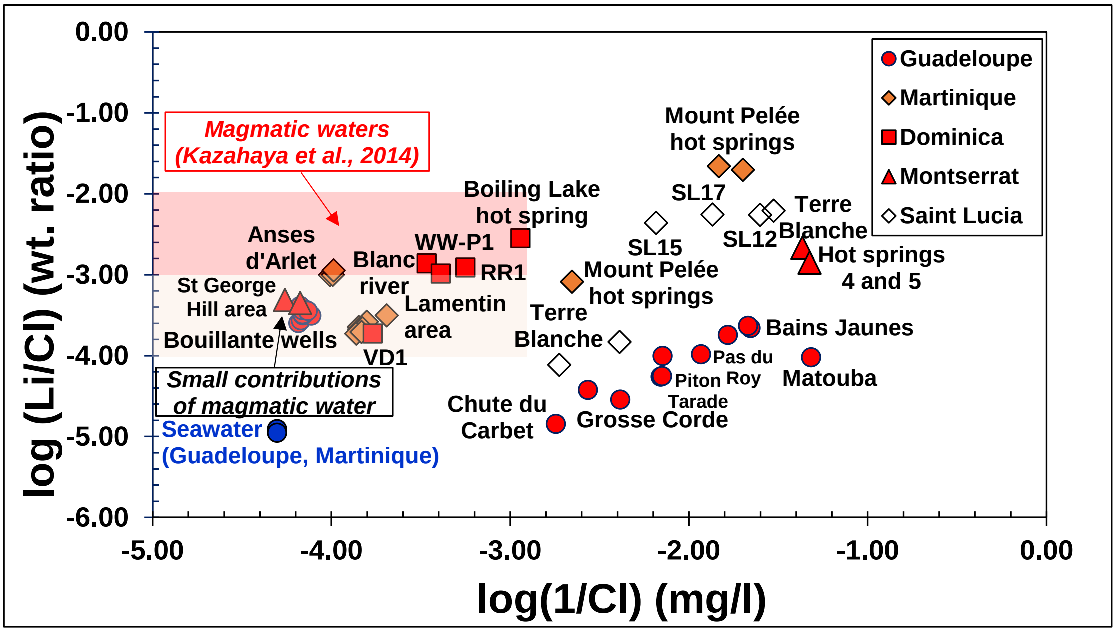

Figure 19: Logarithm of Li/Cl (wt. ratio) *versus* Logarithm of 1/Cl (mg/l) for the geothermal waters of this study.

The δ^7Li isotope values were used by Millot *et al.* (2010) to estimate the nature of the rocks interacting with the deep fluid in the Bouillante geothermal reservoir at about 260°C, using the δ^7Li values determined 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 high-temperature (200-365°C) geothermal waters including those which had a marine origin, the δ^7Li values were lower and less scattered (from 2 to 12‰) than those of colder waters (from 75 to 190°C), which ranged 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 the Figure 20, we can see 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.

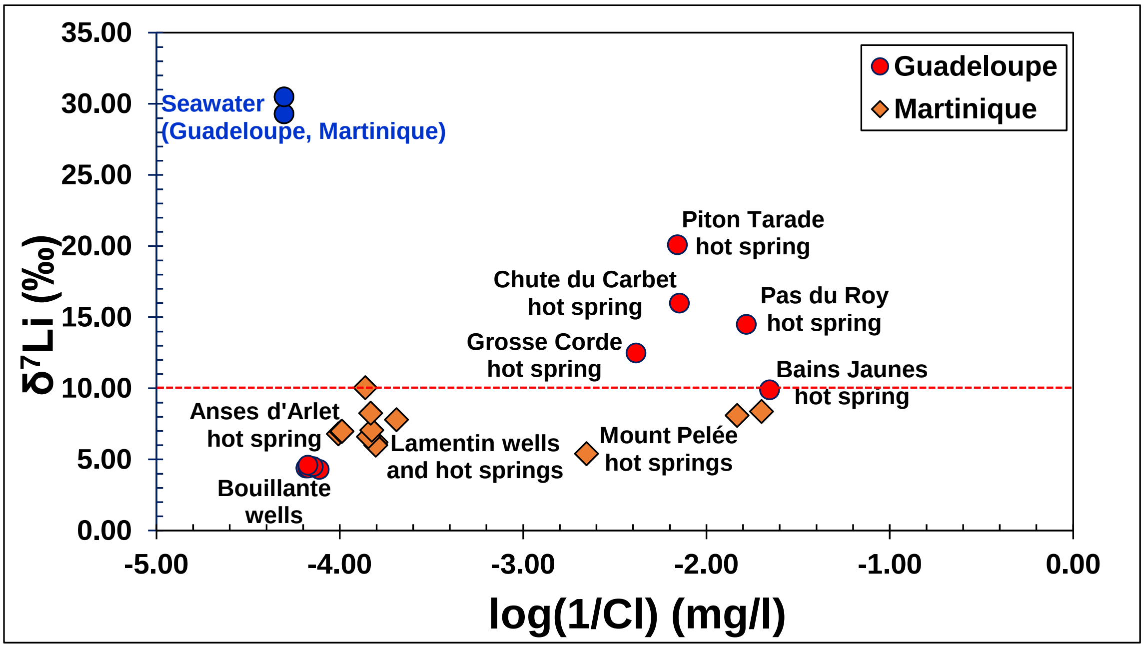

Figure 20: δ^7Li values *versus* Logarithm of 1/Cl (mg/l) for the geothermal waters from the Guadeloupe and Martinique.

b) 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, within the framework of the European FP7-IMAGE project (2013-2017).

As for the Na-Li geothermometer, the existence of different relationships for a given auxiliary geothermometer suggests that the latter not only depends 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 essential to well define the environment in which these geothermometers will be applied before their use, which implies additional investigations for each specific environment.

For these trace species, data are rare in the literature because they are little analyzed in geochemical studies and when they are analyzed, they are often not detected due to their very low concentration. In this study, all these trace species were determined only for the water samples from Guadeloupe and Martinique. However, tungsten and fluoride could not be detected in numerous water samples (Table 2). As well, cesium was not detected in three water samples from Grande Soufriere thermal springs. In the Dominica case, most of these trace elements were analyzed in all the geothermal waters, except W, and Rb, Cs in the WW-P1 water (Table 2). For the Montserrat waters, only the Sr concentrations were analyzed on the samples from the two geothermal wells and the F concentrations were determined on the samples from 4 thermal springs located in the St George Hill and South Soufriere volcano areas (Table 2). Finally, in the Saint Lucia case, none of these trace species was analyzed 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 analyzed only on the water samples from three Qualibou Caldera thermal springs (Table 2). On two of them, the Rb concentrations could not be detected.

In spite of the rare data relative to the 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. 21, 22 and 23, respectively).

In Figure 21, 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.

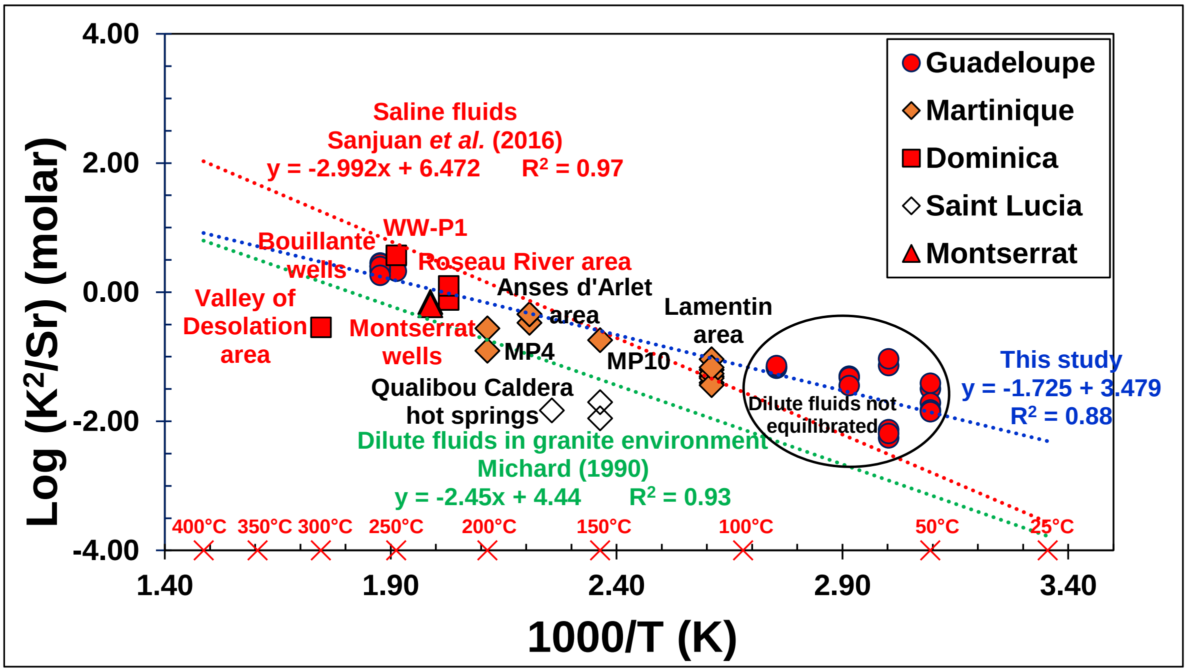

Figure 21: Logarithm of K^2/Sr (molar ratio) *versus* 1000/T (reservoir temperature in K). The data obtained in this study are compared to the two K-Sr thermometric relationships existing in the literature.

In Figure 22, 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 (Fig. 25), the thermal waters rather fit more or less the Na-Rb thermometric relationship determined by Michard (1990).

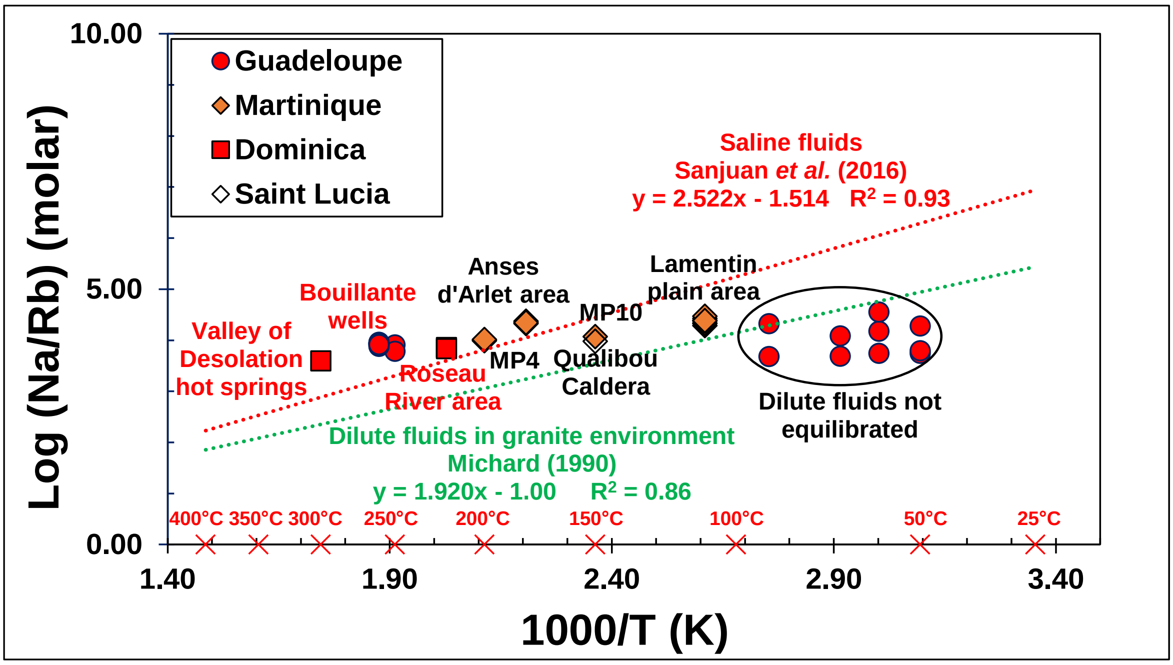

Figure 22: Logarithm of Na/Rb (molar ratio) *versus* 1000/T (reservoir temperature in K). The data obtained in this study are compared to the two Na-Rb thermometric relationships existing in the literature.

We can observe similar trends for the Na-Cs thermometric relationships, but the correlation is poorer (Fig. 23).

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 is 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 to develop this type of auxiliary chemical geothermometers and understand the processes that control them, but these first results are rather promising for the development of the K-Sr, Na-Rb and Na-Cs thermometric relationships.

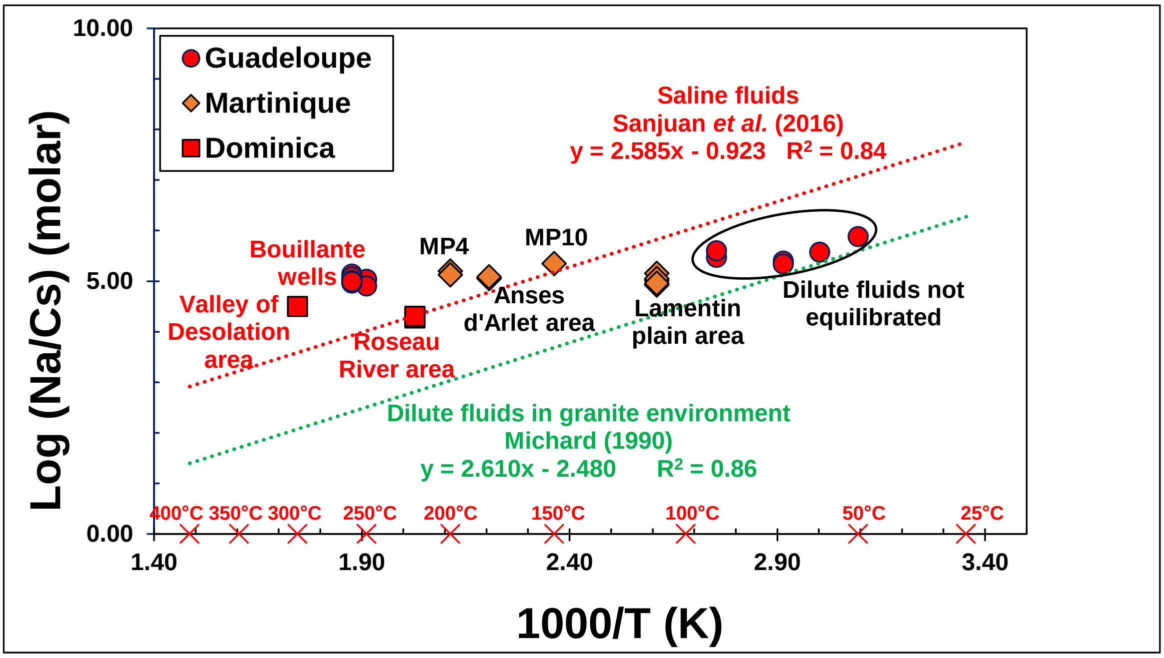

Figure 23: Logarithm of Na/Cs (molar ratio) *versus* 1000/T (reservoir temperature in K). The data obtained in this study are compared to the two Na-Cs thermometric relationships existing in the literature.

5. CONCLUSION

This study has shown that all the deep waters from the geothermal wells drilled in the Guadeloupe, Dominica, Montserrat and Martinique Islands and from some thermal springs are neutral Na-Cl seawater-derived fluids mixed with different proportions of meteoric waters, which have interacted with volcanic reservoir rocks and reached 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, from the Lamentin plain area, in Martinique, and from 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, which have 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, even if some of them (Grosse Corde and Chute du Carbet thermal springs in Guadeloupe or MP10 Rivière Picodo in Martinique, for example) 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 fit no thermometric Na-Li relationship. For all these Na-Li thermometric relationships, it is suggested that Li could be released by mica dissolution. The new thermodynamic approach using Li-minerals as that carried out by Boschetti (2022) could help to better determine the main Li-carrier minerals.

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. 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 such as F, Sr, Rb, Cs, Mn, Fe, and W in future studies in the Caribbean areas, 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 station and its extension as well as the development of other areas, thanks to favorable 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 Caribbean Energetic Transition 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.

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