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Geothermal exploration in the Mount Pelée volcano-Morne Rouge and Diamant areas (Martinique, West French Indies): Geochemical data

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ABSTRACT

The increasing demand for energy in the Caribbean islands and the aim to enlarge energy autonomy have resulted in starting again geothermal research on the Martinique island, in the Lesser Antilles. The first works, which were the drilling of three deep wells (1000 m) in the Lamentin plain in 2001, did not show the existence of high temperature geothermal resources. Consequently, new studies of geothermal exploration were carried out between 2001 and 2003 in two other areas which had already been noticed for their geothermal interest: Mount Pelée volcano-Morne Rouge and Diamant. These areas belong to the recent arc of post-miocene age. All the data obtained in water geochemistry during these studies have led to a better comprehension of the geothermal systems associated to the thermal springs known in these areas (less than 15). Sixteen soil gas profiles (CO_2, CH_4, O_2, He) could be carried out in July 2002 in the studied areas, which represents approximately 260 analyzed gas samples. Among these samples, 11 were selected in order to perform additional chemical and isotopic (^{13}C, $^{3}He/^{4}He$) analyses. The geochemical results obtained during these studies made it possible to select three areas of high temperature geothermal interest: 1) the area of the thermal spring of Petite Anse du Diamant, whose the relatively saline water (TDS ≈ 20 g/l) and the CO_2 gas emanations indicated high temperature conditions (around 180 °C) at depth, despite a low flow rate and temperature (35°C) at the emergence. 2) the area of the upper Chaude river, where the chemical and isotopic compositions of the waters collected from the thermal springs (TDS from 1.0 to 1.5 g/l, the hottest temperatures at the emergence in the island: from 38 to 65°C) suggested the existence of a deep geothermal reservoir at about 200 °C and the presence of primarily magmatic CO_2 gas. The deep hot water is after diluted and cooled by superficial fresh waters, during its rise. 3) the area of the Desgrottes drill-hole, where the gas emanations testified of a magmatic origin but where no index of deep hot water was observed at the surface. For these three areas, results obtained from geological and geophysical studies supported the geochemical data. However, only the drilling of several deep exploration wells will be able to confirm the existence of workable high temperature geothermal resources in these areas.

1. INTRODUCTION

Geothermal research on the Martinique island, in the Lesser Antilles (French West Indies), has been started again in order to answer to the increasing demand for energy and to enlarge energy autonomy. After the drilling of three deep exploratory wells (1000 m) in the Lamentin plain in 2001, which only showed the existence of low temperature geothermal resources (90-120°C; Genter et al., 2002; Sanjuan et al., 2002), a new geothermal exploration program was conducted by BRGM between 2001 and 2003 in two other areas already known for their geothermal interest: Mount Pelée volcano-Morne Rouge and Diamant (Lopoukhine et Mouret, 1977; Iundt, 1984; Barat, 1984; Traineau et al., 1989; Zlotnicki et al., 1998; Sanjuan et al, 2003a).

These works, including geological, geochemical and geophysical studies, were carried out in order to detect high temperature geothermal resources. The objective of this paper is to present and to discuss the main geochemical results obtained in these studies.

2. GEOLOGICAL BACKGROUND

Martinique is a volcanic island belonging to the Lesser Antilles arc, which draws an 850 km length curve. The two studied areas (Mount Pelée volcano-Morne Rouge and Diamant) are located in the northern and southern parts of the island, respectively (Fig.1). They belong to the recent arc of post-miocene age.

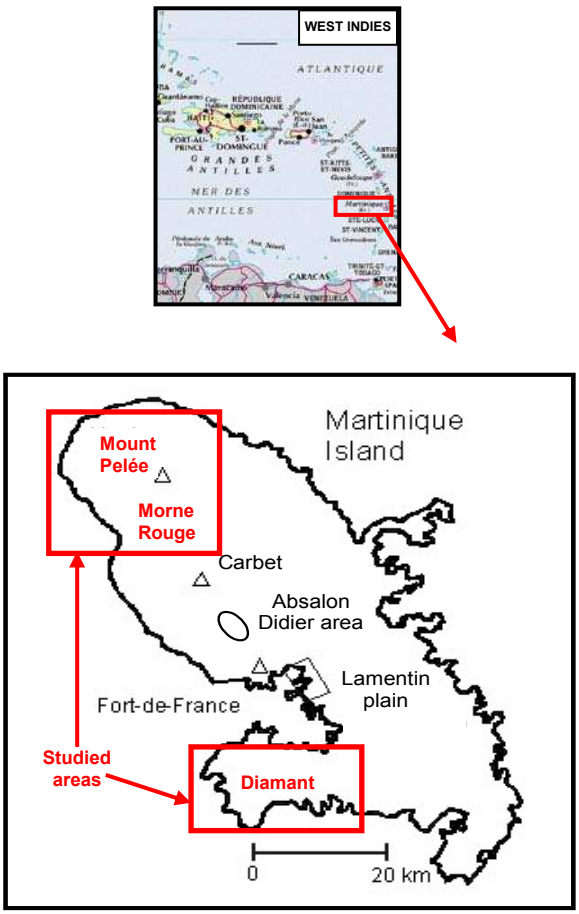

Figure 1: Location map of the Martinique island.

The surface geology is known from the 1:50,000 geologic map (Westercamp et al., 1989).

The Mount Pelée volcano has been edified in three stages, which have their own characteristics and emission point (Traineau et al., 1989). During the first stage dated to about 0.3-0.4 My, the primitive volcano was built (Vincent et al., 1989). It is mainly composed of indurate volcanic breccias, interpreted as brecciated lava flows and of scarce thick lava flows. Then took place a period of quiescence and erosion of at least 0.1 My.

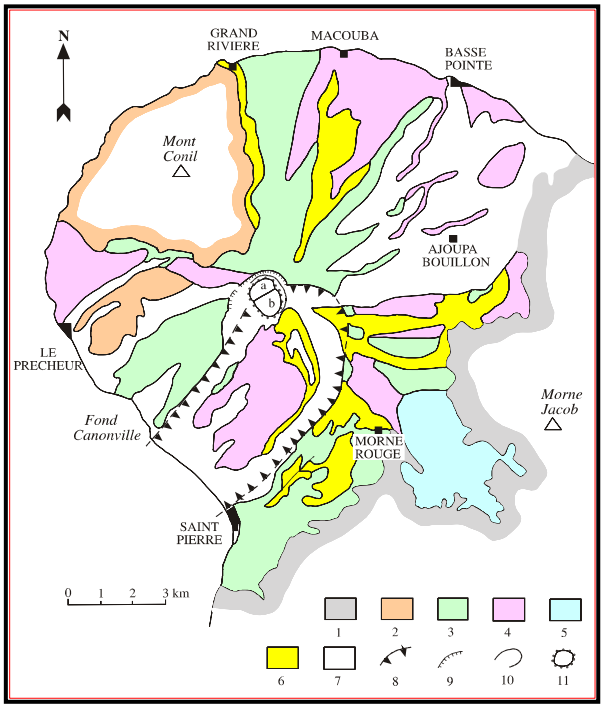

Figure 2: Geological scheme of the Mount Pelée volcano (*In Sanjuan et al., 2003a*). 1: Substratum of the Pitons du Carbet and Morne Jacob; 2: Mont Conil formations; 3: Mount Pelée - initial stage; 4: Pelée - intermediate stage; 5: lacustrine deposits; 6: Pelée - recent stage (from 13,500 to 5,000 years B.P.); 7: Pelée - recent stage (less than 5,000 years B.P.); 8: rim of the collapsed caldera defined by Vincent et al. (1989); 9: rim of the Macouba caldera; 10: rim of the Etang Sec caldera; 11: historical dome of lava (1902-1905; 1929-1932).

The second stage (> 40,000-20,000 years B.P.) corresponds to the emplacement of numerous scoria flows issued from column collapses. The deposits filled the deep valleys formed by erosion. Morne Macouba caldera was probably formed during this period. A major flank collapse event took place during this stage (25,000 years B.P. or before). It produced a horseshoe-shaped structure, 3.5 km wide and 6 km long, on the southwestern flank of the volcano opened toward the Carribean Sea (Fig. 2). A major sea floor drop followed by the accumulation of volcanic products on the SW volcano slopes presumably caused this (Vincent et al., 1989). The morphological rim oriented NE-SW from Saint Pierre to Morne Rouge is, presently, interpreted as the southern limit of the horseshoe-shaped structure. During recent works of structural geology, no evidence of tectonic fracturation was observed in this area (Gros, 2002). The intermediate edifice is the result of the formation of a new volcano in the middle of the horseshoe-shaped caldera, dominated by explosive events (Fig. 2).

The third stage started after a period of quiescence (20,000-14,000 years B.P.). It built the upper part of the new cone of Mount Pelée inside the horseshoe-shaped structure. Two types of eruptions occurred: pumiceous plinian eruptions (plinian fallouts and ash and pumice flows) and dome-forming eruptions with associated block- and ash-flows, and "pelean nuées ardentes". During the last 14,000 years, 25 magmatic eruptions at least were evidenced by Traineau et al. (1983). Several lava domes, including Aileron, were built in the upper part of the horseshoe-shaped structure (Fig. 2). The two younger domes (1902 and 1929) filled the summit Etang Sec caldera, probably formed during the last pumiceous event (650 years B.P.). The geological formations of the old edifice are estimated rather as impermeable whereas those of the intermediate and recent edifice are considered as being permeable.

During the formation of the early Mount Pelée volcano, volcanic sandstones and clays were deposed in the neighboring Champflore basin (Fig. 2). According to Sanjuan et al. (2003a), this area is a depressive basin or graben with faults orientated NW-SE and N-S, and whose the formation would be dated to about 1 My. It is very difficult to do structural measurements in this zone because of the bad conditions of outcrop. No recent volcanic activity is associated to the formation of this basin. Few evidences of hydrothermal activity were found in this area.

In the Diamant area, the Morne Jacqueline and Morne Larcher volcanoes are the evidences of an eruptive cycle (2.6 My), which spread out from the Anses Marlet (NW) to Diamant (SE). After, 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, phreato-magmatic breccias). Only three vertical and normal faults oriented N160-N170E with an horizontal extension of 2 km were identified in this area (Fig. 3). Presently, they form a 500 m large channel.

3. THERMAL SPRINGS

The thermal springs are scarce in the Martinique island in relation to the volcanic activity and the rainfalls. Less than 15 thermal springs were found in the studied areas. Except the Lamentin plain, where the thermal manifestations were previously studied (Sanjuan et al., 2003a), the most numerous and hottest springs are situated on the western flank of the Mount Pelée volcano. Most of these manifestations were previously studied by Lopoukhine and Mouret (1977), Barat (1984), Iundt (1984) and Traineau et al. (1989).

In order to select areas of high temperature geothermal interest, it was necessary to validate the previous data and to obtain additional results concerning some specific isotopes (^{3}H, ^{13}C, ^{34}S and ^{18}O of the dissolved sulfate, $^{87}Sr/^{86}Sr$, ^{11}B, ^{7}Li) and trace elements. Fieldwork to discover new thermal springs was done in the studied areas.

3.1 Fluid sampling

Fluids from 12 thermal springs located in the areas of Mount Pelée volcano and Petite Anse du Diamant (Figs. 3 and 4; Table 1a) were collected. Among the thermal springs previously studied, 3 springs of Chaude river (MP4, MP5 and MP7), 1 spring of Mitan river (MP9), 1 spring of Picodo river (MP10) and 2 emergences of the spring of Petite Anse du Diamant (DIAM1 and DIAM2) were sampled. 4 thermal springs were sampled for the first time.

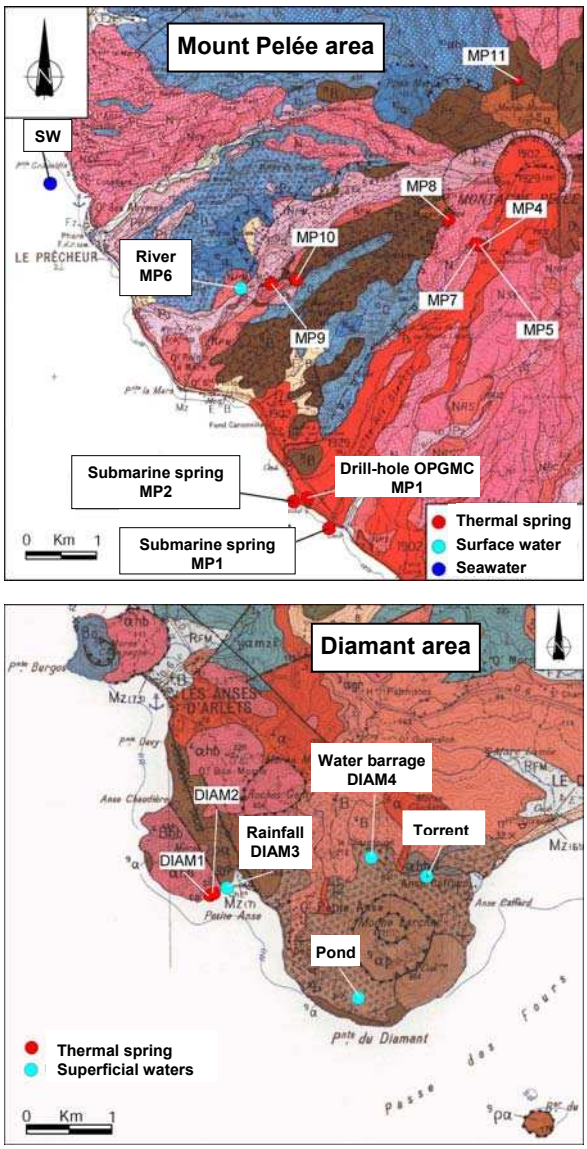

Figure 3: Location maps of the thermal springs and superficial waters sampled during this study.

The results of physico-chemical parameters measured on site such as temperature, conductivity at 25°C, pH, Redox potential (Eh) and alkalinity are reported in Table 1a. Absolute uncertainty on the measurements of temperature and pH is 0.1°C and 0.05 unit pH, respectively. For the other parameters, relative uncertainty is about 5%. The samples were conditioned on site according to the required specifications for analyses (Sanjuan et al., 2003b).

The thermal springs of Chaude river are situated in a gorge of the upper Chaude river, at an elevation of 600-620 m and less than 1 km from the summit domes, with temperatures ranging between 28 and 65°C. Barat (1984) estimated their total discharge in the river to be about 20 l s^{-1}. From a structural point of view, these springs emerge above the concealed southern limit of the intermediate caldera, which is thought to act as a conduit for upflows of thermal fluids. These hot springs appeared after the 1902-1905 magmatic eruption. Since 1960, they are monitored by the Observatoire de Physique du Globe du Morne des Cadets (OPGMC), which has observed that the temperature at their emergence tends to decrease after 1970. As their dissolved chloride concentrations also decrease, it can be suggested that the proportions of cold superficial fresh water in the deep hot fluid are became more significant. The highest temperature measured at the emergence of the springs of Chaude river was 51,4°C in this study (table 1a; instead of 65°C in the past).

The thermal springs of Mitan and Picodo river were reached with difficulty because of their location. Several thermal springs occur along these rivers, issuing from pyroclastic deposits that lie on impermeable rocks of the early volcano. Temperatures range from 25 to 30°C for the springs of Mitan river and up to 38°C for the springs of Picodo river. The rate of discharge is unknown but probably low. Among the many emergences, only the hottest and most saline fluids of the springs of Mitan and Picodo river were collected (MP9 and MP10, respectively). The fluid sampled from the spring of Picodo river was more saline than in the previous studies (Sanjuan et al., 2003a).

The thermal springs, first reported in 1968, situated near the coast, near and in the Claire river are related to a shallow heated aquifer which discharges mainly into the Claire river after rain. The maximum recorded temperature comes from a 6 m deep well near the mouth of the Claire river (47°C) and from a hot spring emerging on a beach (36°C). These waters exhibit evidence of contamination by sea water, with an increase in Cl and Na concentrations. In this study, the 6 m deep well was replaced by a neighboring 10 m deep drill-hole (MP1 fluid), belonging to the OPGMC and used for fluid and temperature monitoring. The fluid temperature measured in this drill-hole was 36.4°C (table 1a) and is lower than that determined for the 6 m deep well.

The thermal spring of Petite Anse du Diamant, located near sea, at the foot of Morne Jacqueline and at the west of the beach of Petite Anse du Diamant, has several emergences. These emergences are situated at the foot of a relief constituted of volcanic formations belonging to a final stage of a plio-quaternary eruptive cycle (Westercamp et al., 1989). These formations are andesitic dome and flows, ashes and scoria dated to 2-2.2 My. They are above an older substratum represented by dacite with quartz and hornblende (4 to 5.5 My). The more recent andesitic formations in this area, present in the Morne Jacqueline and Larcher, are dated to 0.9 My. Hydrothermal deposits constituted of calcite, iron hydroxides, amorphous silica and sulfates (gypsum, jarosite) are formed during the cooling, degassing and oxidation of the fluids at the emergences of this spring. The total flow rate of this spring is about 0.5 l/s and the highest temperature at the emergence is 35°C. A similar temperature was measured at the main emergence in this study (DIAM1; table 1a). The DIAM2 fluid collected in another emergence was less hot and saline than DIAM1.

The thermal springs sampled for the first time were: two submarine springs (MP2 and MP3), a spring of Claire river in its upper part (MP8) and a spring of Grande river (MP11).

The two submarine thermal springs were sampled with the help of scuba divers of the TROPICASUB association. A motorboat equipped with a peristaltic pump, a plastic tube and a funnel was used to collect the fluid samples. After that the funnel was installed above the emergence of the submarine spring by a diver, the thermal fluid was pumped up to the boat using the peristaltic pump. The continuous measurement of temperature, conductivity and pH allowed to start the fluid sampling (after stabilization of conductivity and pH values lower than those of sea water).

The thermal springs of upper Claire and Grande river were reached with much difficulty because of their dangerous

location. Grande river is the only spring discovered on the north flank of the Mount Pelée volcano. The low temperature and conductivity of the fluids collected from these two springs suggest the presence of significant proportions of cold superficial waters.

Local superficial waters were also sampled (Fig. 3): river water (MP6), rain water (DIAM3), barrage water (DIAM4) and sea water (SW).

3.2 Fluid analyses

With the exception of the isotopic ^{14}C and ^{13}C analyses, which were performed in the Beta Analytic laboratory (Florida, USA), all the chemical and isotopic analyses were carried out in the BRGM laboratories, at Orleans. These were performed using standard water analytical techniques such as titration, potentiometry, colorimetry, ion electrode, atomic absorption spectrophotometry, ion chromatography, inductively coupled plasma-mass spectrometry (ICP-MS), ICP-MS-MultiCollector and mass spectrometry. The precision of major and trace species is better than ± 5 and 15%, respectively. The precision on δD, $\delta^{18}O$ values and ^{3}H activity is ± 0.8‰, ± 0.1‰ and ± 1 UT, respectively. That determined on the $^{87}Sr/^{86}Sr$ isotopic ratio, $\delta^{34}S$ and $\delta^{18}O$ of the dissolved sulfate, $\delta^{13}C$, $\delta^{11}B$ and $\delta^{7}Li$ is ± 0.00001, ± 0.3‰, ±0.3‰, ±0.1‰, ±0.2‰ and ±0.5‰, respectively. Relative uncertainty on the analysis of ^{14}C activity is around 1 to 2%. Ion balance values lower than 5% suggested a good quality of the analyses of the dissolved major species. Results are reported in Tables 1a, 1b and 1c.

3.3 Fluid chemical characteristics

Despite some little differences, the chemical compositions of the fluids collected from the thermal springs of Petite Anse du Diamant and Chaude river are similar to those previously determined (Sanjuan et al., 2003a). The fluid sampled from the thermal spring of Mitan river during this study indicates concentrations of dissolved sodium, potassium, chloride and bicarbonate about two times higher than those previously determined whereas the concentrations of dissolved calcium, magnesium and sulfate are lower (Sanjuan et al., 2003a). This fluid sample seems to have a deeper signature. The chemical composition of the fluid collected from the thermal spring of Picodo river is different from the previous data (Sanjuan et al., 2003a).

In the ternary diagram of the figure 4, five chemical types of thermal fluids can be distinguished.

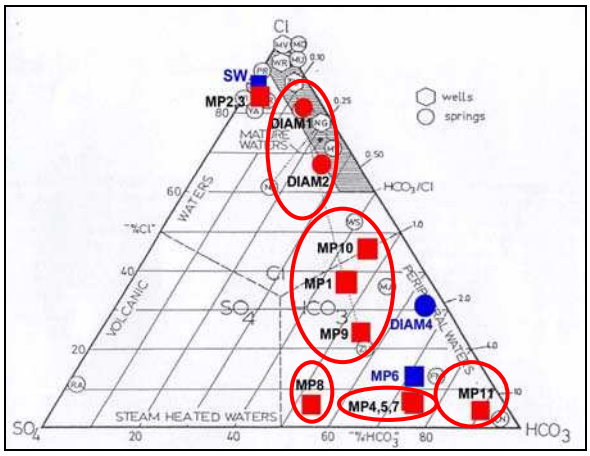

Figure 4: Position of the thermal fluids in a ternary Cl-HCO_3-SO_4 diagram (Giggenbach, 1991).

The group of Petite Anse du Diamant is constituted of NaCl type and CO_2 rich thermal fluids (DIAM1 and DIAM2), which have a high salinity (12-20 g/l) and pH values from 6.0 to 7.1. They can be considered as mature fluids having interacted with volcanic rocks (Fig. 4).

The group gathering the OPGMC drill-hole and thermal springs of Mitan and Picodo river (MP1, MP9 and MP10 fluids, respectively) represents Na-HCO_3-Cl fluids, which have a salinity ranging from 0.6 to 1.6 g/l and are near neutral in pH (6-7). Their chemical composition suggests a low contribution of sea water (< 2.5 %) before interaction with volcanic rocks. The differences in temperature and salinity of the numerous springs of Mitan and Picodo river can be explained by mixing between a deeper thermal fluid and cold superficial waters. The fluid collected from the thermal spring of Picodo river seems to be less affected by this mixing process.

The group of Chaude river is constituted of Na-HCO_3 and CO_2 rich thermal fluids (MP4, MP5 and MP7), which have a salinity ranging from 1 to 1.4 g/l and are near neutral in pH (6-7). Their chemical characteristics reflect mixing between a hot deep fluid and cold superficial fresh waters. The most saline fluid (MP4) also indicates the hottest temperature and the lowest pH. This fluid is less affected by mixing processes with cold superficial waters than the MP5 and MP7 fluids.

The group of upper Claire river is represented by an only fluid sample (MP8), which is a Na-HCO_3-SO_4 water and has a low salinity of 0.4 g/l. These characteristics rather belong to a superficial water. However, the relatively high concentration of dissolved sulfate could be originated by the presence of H_2S rich steam or H_2S gas emanations.

The fifth group (Grande river) is also constituted of an only fluid sample (MP11), which is a Na-HCO_3 water and has a low salinity of 0.4 g/l. As for the previous fluid sample, these data are rather characteristic of a slightly warm superficial water.

The fluids sampled from the two submarine thermal springs (MP2 and MP3) are close to sea water because they are constituted of significant proportions of sea water and the other fluid of the mixing is lowly saline.

3.4 Fluid origin and age

Chloride, bromide and sodium are conservative ions which can be often used as tracers of fluid origin or mixing as well as deuterium and sometimes, 18-oxygen isotopes.

The location of the submarine thermal springs, their temperatures at the emergence and figures 5 and 6 suggest that the MP2 and MP3 fluids are a mixing between sea water and the MP1 fluid. According to the concentrations of dissolved Cl, Br and Na, the proportions of sea water are about 72% for MP2 and 30% for MP3.

It can be also observed in these figures that the DIAM2 fluid results from a mixing between the DIAM1 fluid and a superficial fresh water. The location of the thermal spring of Petite Anse du Diamant, the relative high salinity of the DIAM1 fluid and the Na-Cl diagram (Fig. 5) suggest a marine origin for this fluid. However, the Br-Cl diagram (Fig. 5) is not in agreement with this origin except if bromide has been trapped (by organic matter?). Additional isotopic analyses of ^{36}Cl and ^{37}Cl would allow to accurately define the Cl origin. The δD value of the DIAM1 fluid, also analyzed by Iundt (1984) and Pedroni et al. (1999), is

exceedingly low in relation to the other values observed in the fluids of Martinique and the Lesser Antilles. Pedroni et al. (1999) noted that this value was hardly a feature inherited from recharge meteoric (or sea) water because the highest elevations in the surroundings are only 470 m above the sea level. Consequently, this low value could be explained by admixture of magmatic fluid (δD ≈ -80‰) or another component of up to now still unknown origin.

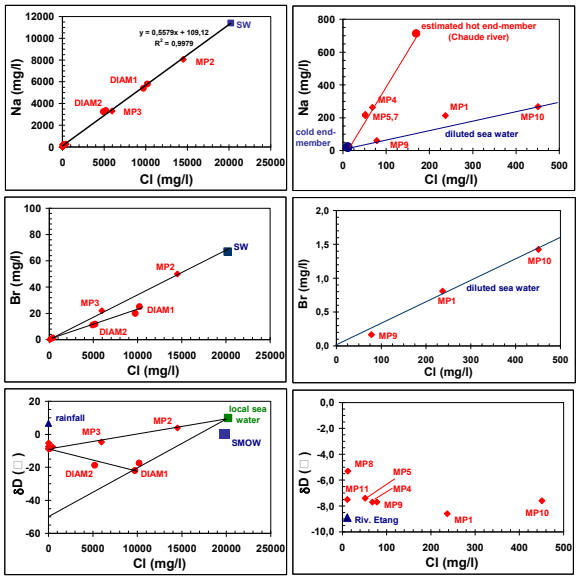

Figure 5: Na-Cl, Br-Cl and δD-Cl diagrams for the thermal fluids collected during this study.

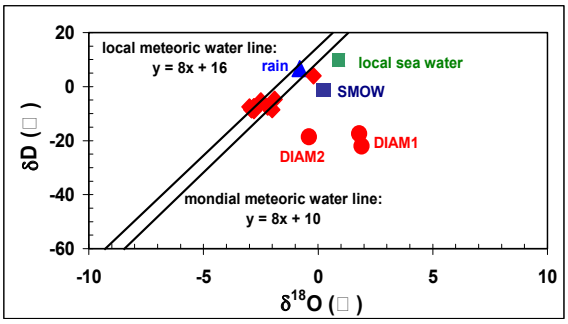

Figure 6: δD-δ^{18}O diagram for the thermal fluids collected during this study.

The figures 5 and 6 reveal that most of the other thermal fluids are constituted of local meteoric waters with similar isotopic signatures.

For the thermal springs of Chaude river, the figure 5 confirms that the MP5 and MP7 fluids are more affected by mixing with cold superficial waters than MP4.

The figure 5 suggests low contributions of sea water in the MP1, MP9 and MP10 fluids (close to 1, 0.4 and 2%, respectively, using the concentrations of dissolved Cl and Na). According to Barat (1984) and Traineau et al. (1989), the general volcanic structure of the Mount Pelée would favor superficial lateral outflow of the thermal fluid discharged in the upper area of Chaude river beneath the south and west flanks of the volcano, which would explain the location of the thermal springs encountered near the sea and the mouth of Claire river (6 m deep well, OPGMC drill-hole, coastal thermal spring) as well as the chemical composition of their fluids. The presence of this lateral outflow is a possible explanation of the gravity and resistivity anomalies detected on the lower flank of the volcano by Benderitter (1987). Its existence was demonstrated by the distribution of a positive Self-Potential (SP) anomaly (Zlotnicki et al., 1998). The weakness of its amplitude expresses that either the water table belonging to the hydrothermal system is of small volume, or that the thermal exchanges with the surface are difficult due to the strong argillization of the deposits along the interface of the horseshoe-shaped structure and/or along the floors of the different calderas.

Traineau et al. (1989) also suggested that the fluids of the thermal springs of Mitan and Picodo river could be partly fed by this lateral outflow coming from the upper area of Chaude river. However, no geochemical data allows to maintain this assumption.

The samples of superficial waters (DIAM4 and MP6) have an ^{3}H activity equal to 2 TU whereas the ^{3}H activity measured on the sample of rain water (DIAM3) is < 1 TU (Table 1c). In these conditions, it is difficult to interpret the values found for the DIAM1, DIAM2, MP9 and MP10 fluid samples, which also are < 1 (age older than 50 years or very recent?). However, it is probable that the age of these thermal waters is older than 50 years. The age of the MP1, MP4 and MP11 fluids (^{3}H = 2-3 TU) is rather recent and in any case, younger than 50 years.

The ^{14}C activities and the δ^{13}C values analyzed in the samples of surface fresh waters (DIAM4 and MP6) confirm that these waters are present (Table 1c). Processes of carbon isotope exchange most likely play a decisive role in hydrothermal systems. The application of ^{14}C exchange dating for local conditions cannot elucidate the ages because isotope exchange processes happen very quickly at high temperatures in the water-rock-gas system. For the DIAM1, MP1, MP4 and MP5 fluids, the ages estimated using ^{14}C activities cannot be considered as representative because these activities are strongly influenced by the dissolution of carbonate minerals or magmatic CO_2 (null ^{14}C activity), as indicated by the δ^{13}C values (Table 1c, see next chapter). The δ^{13}C values also suggest that the proportions of superficial water increase from MP4 to MP5 and from MP5 to MP1.

3.5 Water-rock-gas interaction processses

3.5.1 Thermal spring of Petite Anse du Diamant

Compared to a sea water diluted by fresh water, the fluids of the thermal spring of Petite Anse du Diamant (DIAM1 and DIAM2) are enriched in Ca, HCO_3, SiO_2, Sr, Ba, B, As, Fe, Mn, Li, Rb, Cs and Ge. They are depleted in Mg and SO_4 (Fig. 7). These results are characteristic of interaction processes between sea water and volcanic rocks (basalts, andesites…), which have been observed in laboratory and in natural environment (Sanjuan et al., 1990).

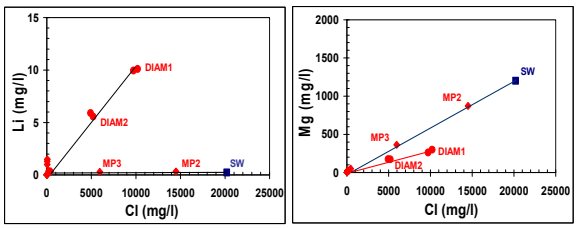

Figure 7: Li-Cl and Mg-Cl diagrams for the thermal fluids collected during this study.

The existence of a significant ^{18}O enrichment from the rocks (Fig. 6), already observed by Iundt (1984) and Pedroni et al. (1999), confirms that the DIAM1 fluid has a strong interaction with the rocks at relatively high temperature. This shift is attributed to hydrothermal water-rock isotope exchange. However, it could also traduce the existence a low water-rock ratio or fluid circulation rate. This ^{18}O enrichment is in good agreement with the high concentrations of dissolved silica, lithium, boron and arsenic and as we shall see it, with the estimated deep temperature.

The Cl/B ratio values measured on these samples vary from 119 to 130. They are much lower than for sea water (≈ 5260) and close to the values generally determined for most of the geothermal waters (from 10 to 100). The B concentrations of these samples and their isotopic B signature (Table 1c) suggest a gaseous B origin (between 2 and 8‰ for fumarole vapors; Mossadik, 1997). The Cl/Li ratio values (from 861 to 1010) are also much lower than for sea water (≈ 87826) and suggest a strong interaction with the volcanic rocks at relatively high temperature.

The $^{87}Sr/^{86}Sr$ values of these fluids (Table 1c) are close to those measured on volcanic rocks (andesite, basalt…) and consequently, testify of a strong interaction with these rocks. However, these values slightly higher than those analyzed on the fluid samples collected from the thermal springs of Chaude river, which are merely meteoric waters, could be an evidence of the sea water contribution ($^{87}Sr/^{86}Sr$ = 0.709188) that feeds the thermal spring of Petite Anse du Diamant. The $\delta^{34}S$ value of these fluids (Table 1c) is very different from that analyzed for primary sulfur minerals (0‰). It is close to that measured for the arc andesites (from 0 to 12‰; Taylor, 1986).

The $\delta^{13}C$ values of these fluids (Table 1c) are not in equilibrium with the $\delta^{13}C$ value measured in the gas emanations ($\delta^{13}C$ = - 4.4‰ in this study) associated to this thermal spring, that testifies of a mainly magmatic origin (-8.6‰ < $\delta^{13}C$ < -2.4‰; Faure, 1986). Higher $\delta^{13}C$ values (-3.08 to -2.70‰) were measured in the thermal fluids by Pedroni et al. (1999). These values are more in agreement with those determined in the gas emanations. The high alkalinity values and $\delta^{13}C$ found in this study suggest that marine carbonate minerals can have been dissolved during the rise and cooling of these fluids. As shown by the deposits observed at the emergences of this thermal spring, this dissolution process is after replaced by calcite precipitation after degassing. Calculations performed using the geochemical EQ3NR code (Wolery, 1992) indicate that partial CO_2 pressure (P_{CO2}) is close to 1.25 bar at the main emergence and show that the thermal fluid is saturated with respect to calcite, disordered dolomite and strontianite. It is over-saturated with respect to chalcedony, main clays and zeolites. This is in agreement with the mineralogical observations. The P_{CO2} value is probably higher because degassing occurs at the emergence. A simulation run performed from 35 to 200°C using the geochemical EQ6 code (Wolery and Daveler, 1992) and assuming equilibrium between thermal fluid and calcite at any temperature shows that the P_{CO2} value is close to 4-5 bar (pH of about 5.35) at the deep conditions.

3.5.2 Thermal springs of Chaude river

The fluids of these springs show a relatively high water-volcanic rock interaction degree. Indeed, they have the lowest values of Cl/B, Cl/Li, Cl/Cs, Cl/Rb, Cl/As and Cl/Ge ratio among the studied thermal springs. For example, the Cl/B and Cl/Li values are about 30-40 and 40-50, respectively. Their isotopic $\delta^{11}B$, $\delta^{34}S$ and Sr values (Table 1c) are in agreement with this process of strong interaction.

Calculations performed using the geochemical EQ3NR code indicate that the minimal P_{CO2} value is 0.34 bar at the emergence of these springs and show that the thermal fluids are under-saturated with respect to the main carbonate minerals. This under-saturation can be explained by the fact that all these fluids are issued from a mixing between a deep hot mineralized fluid saturated with respect to calcite and cold superficial fresh waters.

The $\delta^{13}C$ values reported in Table 1c can be used to estimate the $\delta^{13}C$ value of the CO_2 emanations associated to the emergences of these thermal springs. The reconstructed value ($\delta^{13}C$ = -2.8‰) testifies of a magmatic origin but compared to the value directly analyzed in the CO_2 gas emanations associated to the thermal spring of Petite Anse du Diamant, it also suggests the presence of marine carbonate probably brought during the rise and cooling of the thermal fluids. An higher $\delta^{13}C$ value (-4.2‰) was determined on the fluid of one of these thermal springs by Van Soest et al. (1998) in good agreement with the $^{3}He/^{4}He$ measurement (7.78 times the atmospheric ratio Ra). The $^{3}He/^{4}He$ value was one of the highest measurements found by Van Soest et al. (1998) in the Lesser Antilles and is close to that of the helium from the upper mantle (8 times Ra).

Assuming that the deep hot fluid, which partly constitutes these thermal fluids, is in equilibrium with respect to quartz at 200°C (deep temperature determined using chemical geothermometers), its concentration of dissolved silica can be determined and the corresponding Cl concentration can also be estimated from the data reported in the SiO_2-Cl diagram (Fig. 8). Applying the mixing equation for the chloride concentrations on the MP4, MP5 and MP7 fluid samples, the dilution factor due to the mixing can be evaluated. For the MP4 sample, it can be estimated that the deep fluid is diluted by 60% of superficial fresh water; by about 70% for the MP5 and MP7 samples. The chemical composition of the deep hot fluid (Table 2) can be reconstituted for numerous species from linear regressions such as those shown in figures 5 and 8 and the Cl concentration determined for the deep fluid.

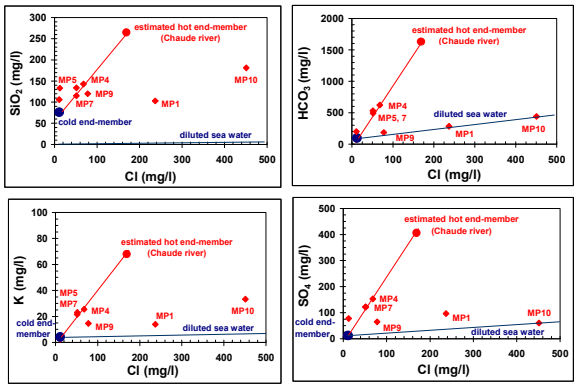

Figure 8: SiO_2-Cl, HCO_3-Cl, K-Cl and SO_4-Cl diagrams for the low salinity thermal fluids collected during this study.

This deep Na-HCO_3 fluid has a probable salinity of 3-4 g/l. A simulation run performed from 51 to 200°C using the geochemical EQ6 code and assuming equilibrium between

this thermal fluid and calcite at any temperature shows that the P_{CO2} value is close to 2.5 bar (pH of about 7.0) at the deep conditions.

3.5.3 OPGMC drill-hole and thermal springs of Mitan and Picodo river

All these thermal waters, originally constituted of a predominant contribution of meteoric water and a small proportion of sea water, are enriched in most of the chemical species relative to a diluted sea water (Fig. 8), except in Na and Br (Fig. 5). The enrichment in Mg and SO_4 species (Fig. 8) suggests that these fluids have significant proportions of cold superficial waters.

Calculations performed using the geochemical EQ3NR code indicate that the minimal P_{CO2} values are 0.09 and 0.12 bar respectively, in the OPGMG drill-hole and at the emergences of the MP9 and MP10 thermal springs. These values are inferior to those estimated for the thermal springs of Chaude river and suggest a lower degree of water-rock-gas interaction. Calculations also show that the thermal fluids are under-saturated with respect to the main carbonate minerals. As for the thermal springs of Chaude river, these under-saturations can be explained by the fact that all these fluids are issued from a mixing between a deep fluid saturated with respect to calcite and cold superficial waters.

The $^{87}Sr/^{86}Sr$ value determined for the MP1 fluid sample (Table 1c) is not close to those determined in volcanic rocks but is the result of a mixing between a fluid in equilibrium with these rocks and sea water. The contribution of sea water estimated from the mixing equation (1%), similar to that previously determined, confirms this assumption. This indicates that this mixture is not performed at high temperature. In opposite of the MP1 fluid sample, the $^{87}Sr/^{86}Sr$ values determined for MP9 and MP10 (Table 1c) are similar and close to those determined in the volcanic rocks. They are slightly higher than those determined in the fluids of the thermal springs of Chaude river. This suggests that the MP9 and MP10 fluids come from a geothermal reservoir different from that feeding the thermal springs of Chaude river.

As for most of the studied fluid samples, the $\delta^{34}S$ values determined on the MP1 and MP10 samples (Table 1c) are characteristic of arc andesites. The $\delta^{13}C$ value estimated for the CO_2 gas emanations associated to the MP1 drill-hole was -5.6‰. This value obtained from the $\delta^{13}C$ analyzed in the MP1 fluid testifies of a magmatic origin but when compared with the value directly analyzed in the CO_2 gas emanations associated to the thermal spring of Petite Anse du Diamant, it also suggests the presence of carbonate brought by superficial fresh waters ($\delta^{13}C_{atmosphere}$ = -7.5‰, $\delta^{13}C$ = - 14.8‰ for L'Etang river).

3.5.4 Thermal springs of upper Claire and Grande river

Even if these two thermal waters (MP8 and MP11, respectively) belong to two different chemical groups, their characteristics testify of slightly warm superficial fluids and low degree of water-rock-gas interaction.

3.6 Chemical geothermometers

The triangular diagram of the figure 9 indicates that all the thermal fluids are located in the area classified like that of the immature fluids, out of a full equilibrium with the rocks. However, the DIAM1 fluid, collected from the thermal spring of Petite Anse du Diamant, is very close to the area of partial equilibrium. By applying the main chemical and isotopic geothermometers, a deep temperature of about 180°C is found for this fluid and DIAM2 (Table 3). Most of the geothermometers also give a deep temperature of 190-200°C for the fluids collected from the thermal springs of Chaude river and the OPGMC drill-hole. Similar deep temperature values were estimated in previous studies (Iundt, 1984; Traineau et al., 1989; Sanjuan et al., 2003a).

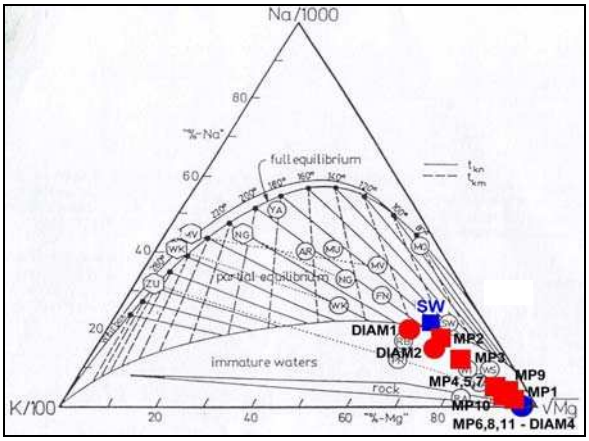

Figure 9: Position of the thermal fluids in a ternary Na-K-Mg diagram (Giggenbach, 1988).

For the fluids collected from the thermal springs of Picodo and Mitan river, a deep temperature close to 150°C is estimated (Table 3). The fluids sampled from the thermal springs of Claire river and Grande river are too much closer to the Mg end-member (Fig. 9), which characterizes the cold superficial waters, to determine a deep temperature.

According to Michard (1990), in volcanic environment, the dissolved silica is rather controlled by quartz at temperatures higher than 160°C and by chalcedony at lower temperatures. Given that most of the thermal fluids are diluted by cold superficial waters during their rise, the temperature values using the silica geothermometer are under-estimated.

For the MP8, MP9, MP10 and MP11 fluid samples, the deep temperatures estimated using the Na/K and Na/K/Ca geothermometers are not representative because the Na/K ratio is not controlled by the equilibrium reaction between the sodium and potassium feldspars, which is at the basis of the use of these geothermometers. For the MP2 and MP3 fluid samples, which contain a significant proportion of sea water, it is known that these geothermometers give bad temperatures (Giggenbach, 1988).

For the thermal CO_2-rich fluids, that are partly constituted of sea water, the Na/Li geothermometer of Kharakha et al. (1982) seems to be better adapted (Table 3) than that described by Fouillac and Michard (1981), which gives best temperature estimations for the thermal fresh waters.

A linear regression is observed between 150 and 200°C in figure 10 where the δ^7Li values of the thermal fluids have been plotted as a function of the deep temperatures estimated using the geothermometers. The more temperature increases, the more δ^7Li value is high. Figure 10 suggests that the thermal fluids of the springs of Picodo and Mitan river (MP10 and MP9, respectively), which have similar $^{87}Sr/^{86}Sr$ and δ^7Li values, belong to a same geothermal reservoir where the deep temperature is close to 150°C. MP9 is more diluted by cold superficial fresh waters during its rise than MP10. Contrary to the

assumption supported by Traineau et al. (1989), the reservoir of these fluids would be different from that feeding the thermal springs of Chaude river (MP4 and MP5 fluids), whose the deep temperature is 190-200°C, the δ^7Li value is higher and the $^{87}Sr/^{86}Sr$ ratio is lower.

On the other hand, the MP1 thermal fluid would come from this last reservoir (Fig. 10). It would be, after, diluted by cold superficial fresh waters during its rise and its lateral outflow up to the coastal emergences, and mixed with a small contribution of sea water. The δ^7Li signature of the reservoir fluid is conserved given the low concentrations of dissolved Li in the superficial waters and sea water relative to the reservoir fluid. The P_{CO2} value estimated for MP1, lower than for MP4, is in agreement with a longer superficial fluid circulation (higher degassing).

The δ^7Li value of the fluid collected from the thermal spring of Claire river (MP8) is similar to that measured for the superficial waters (MP6; Table 1c; Fig. 10) and seems to confirm the low temperature at which this fluid interacts with the volcanic rocks.

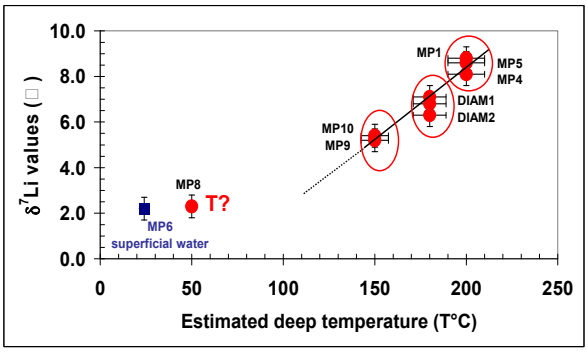

Figure 10: δ^7Li-T diagram for some studied thermal fluids.

We can conclude that the chemical geothermometers and δ^7Li values have allowed to clearly identify different geothermal reservoirs despite the complexity of the characteristics of some thermal fluids. Without these useful tools, it would have been very difficult to identify these reservoirs.

4. SOIL GAS PROSPECTING

Soil gas prospecting has received much attention in recent years as a useful tool for geothermal exploration. Studies carried out over active faults or fractures have shown that these geological structures act as preferential pathways for the discharge of gases such as CO_2, CH_4, He, Rn, etc. Among these gases, He is probably the best indicator of deep discharge.

4.1 Selected areas

During the July 2002 survey, sixteen soil gas profiles were performed on selected areas of geothermal interest (Fig. 11). 260 soil gas samples were analyzed for CO_2, CH_4 and O_2. He was only determined on selected samples.

4.2 Sampling and analytical methods

The soil gases were sampled at a depth of 0.5 m with a steel probe, equipped with a Teflon pipe and sunk in the ground with a sliding hammer. A gas sample was also directly collected from the Deux Choux drill-hole.

The measurements of CO_2, CH_4 and O_2 were performed on site using an infra-red apparatus LFG20 TELEGAN, that simultaneously gave the percentages of volume of these three gases. Analytical accuracy is 0.5% for CO_2 and CH_4 and 0.4% for O_2. The internal pump of this apparatus also was used to sample the gases in Teflon bags TEDLAR for He analyses. He was determined using a specific mass spectrometer ALCATEL ASM 100. Analytical precision is 0.02 ppm.

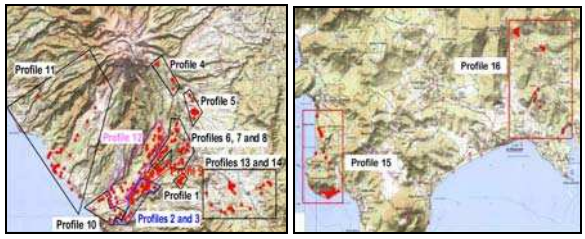

Figure 11: Soil gas profiles carried out during this study.

Among the 260 analyzed gas samples, 11 were selected in order to perform additional chemical and isotopic analyses. The gas samples were collected in 250 ml glass flasks. The additional gas chemical analyses and δ^{13}C measurements on CO_2 gas were performed in the BRGM laboratories using gas chromatography and mass spectrometry, respectively. For chromatography, analytical relative uncertainty was 3%. For spectrometry, analytical absolute accuracy was 0.1‰. The $^3He/^4He$ values were determined using mass spectrometry in the MAGIE laboratory (Magmatologie et Géochimie Inorganique et Expérimentale) of the Paris 6 University. Analytical relative uncertainty varied from 4 to 12% (Table 4).

4.3 Results and interpretation

All the data are reported in Sanjuan et al. (2003b). The results of the additional chemical and isotopic analyses are presented in Table 4. In this table, we can also notice that the analytical results obtained on site were confirmed in laboratory.

From all these data, two areas of geothermal interest can be determined.

The area of the Desgrottes drill-hole (depth of 32 m), where this drill-hole has crossed gas emanations under a cover of pumices and peat (Lopoukhine and Mouret, 1977), indicates the presence of magmatic gas emanations mixed to atmospheric and organic gases (high contents of CO_2, mixed ^{13}C and $^3He/^4He$ signatures, O_2 presence, N_2/Ar ratio close to the atmospheric ratio of 84). A similar chemical gas composition (51% CO_2, 31% CH_4 and 17% N_2) had been given by Lopoukhine and Mouret (1977). A comparable $^3He/^4He$ value (4.43 times Ra) had been measured by Pedroni et al. (1999) and is found in the emanations collected from the neighboring Deux Choux drill-hole (Table 4; Pedroni et al., 1999). In this last drill-hole, the δ^{13}C value of CO_2 is similar to that determined by Pedroni et al. (1999; δ^{13}C = -6.37‰) but slightly higher than that measured for the Desgrottes drill-hole. The Desgrottes drill-hole also discharges a Na-Ca-HCO_3 fluid, which has a temperature of 28.6°C, a pH value of 6.7 and a salinity < 0.7 g/l (Lopoukhine and Mouret, 1977). The δD and δ^{18}O values (-6.60 and -2.61‰, respectively), measured by Pedroni et al. (1999), indicate a meteoric origin for this fluid and are similar to those of the neighboring cold waters of the Champflore basin (-5.90 and -2.11‰, respectively). The chemical characteristics of this fluid and its low salinity suggest a predominant superficial origin and don't show a significant high temperature geothermal interest.

In the area of the thermal spring of Petite Anse du Diamant, the presence of significant magmatic gas emanations is also observed in and near this thermal spring, in hydrotermally altered soils (Table 4; high contents of CO_2 and He, ^{13}C and $^{3}He/^{4}He$ signatures). For the thermal spring, Pedroni et al. (1999) had found $^{3}He/^{4}He$ values (from 7.75-7.93 times Ra) and $\delta^{13}C$ slightly higher than those analyzed in this study. This confirms the significance of the magmatic signature in these superficial manifestations.

The ^{13}C and $^{3}He/^{4}He$ analyzes performed in gas samples collected from other areas, which indicate CO_2 or He anomalies (Roxelane river, Morne Calebasse, Camp Chazeau, Petite Savane, Ecrevisses river, Propriété De Paz, Table 4), suggest an organic origin for CO_2 ($\delta^{13}C$ values from -26.1 to -16.1‰) or an atmospheric origin for He ($^{3}He/^{4}He$ values close to Ra).

5. AREAS SELECTED FOR THEIR HIGH TEMPERATURE GEOTHERMAL INTEREST

Before and during the works of geothermal exploration performed in the Mount Pelée-Morne Rouge and Diamant areas, several geophysical anomalies were found (Figs. 12 and 13; Sanjuan et al., 2003a; Baltassat et al., 2003).

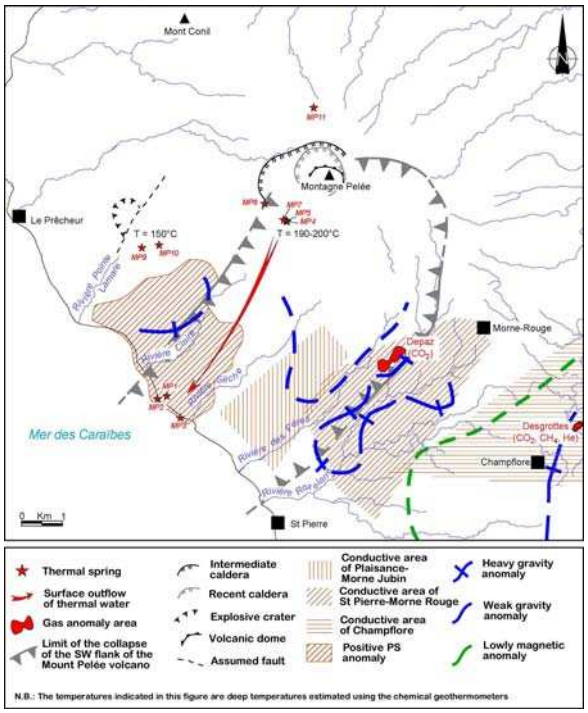

Figure 12: Map showing the main geophysical anomalies obtained in the Mount Pelée volcano-Morne Rouge area.

In particular, Magneto-Telluric (MT) soundings allowed to discover several conductive areas from the surface up to depths of 1000-1500 m on the southwestern flank of the Mount Pelée, in the Champflore tectonic basin (Fig. 12), between Les Anses d'Arlets and Petite Anse du Diamant or near Les Trois Ilets (Fig. 13). These conductive areas can be indicative of the existence of fluids but also clay minerals of hydrothermal alteration. For three of these areas (Champflore basin, Anses d'Arlets and Petite Anse du Diamant), lowly magnetic anomalies were also found (Figs. 12 and 13). Heavy gravity anomalies, which could result of the presence of a source of heat, were identified under four of these MT conductive areas (Roxelane river-Morne Rouge, Champflore basin, Anses d'Arlets and Petite Anse du Diamant; Figs. 12 and 13). The convergence of these different geophysical anomalies could traduce the presence of a geothermal reservoir in these four areas.

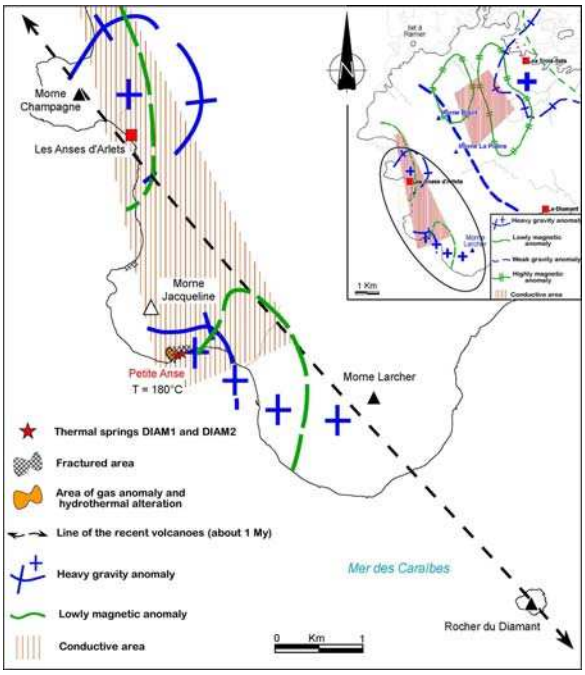

Figure 13: Map showing the main geophysical anomalies obtained in the Diamant area.

However, among the areas of high temperature geothermal interest, only those where hydrothermal manifestations (discharges of deep waters or gases, hydrothermal deposits) were observed and confirmed by geochemical interpretation, were selected as priority to drill future exploration wells. These areas are:

- the coastal area of the thermal spring of Petite Anse du Diamant (Fig. 13) where numerous discharges of deep waters and gases and hydrothermal deposits are associated to the convergence of three geophysical anomalies (heavy gravity anomaly from a depth of 1000-1500 m, superficial conductive area up to a depth of 1000 m, lowly magnetic anomaly), which could traduce the presence of a geothermal reservoir at 180°C;
- the area of the upper Chaude river (Fig. 12), where several hot springs, located in the rims of the intermediate caldera of the Mount Pelée and near the sites of the main phreatic eruptions of 1792 and 1851, occur and suggest the existence of a geothermal reservoir at 190-200°C;
- the area of the Desgrottes drill-hole, in the Champflore basin (Fig. 12), where discharges of deep gases are observed and associated to the presence of three geophysical anomalies. Given that the formation of this basin and the corresponding faults oriented NW-SE and N-S are dated to 1 My and no discharge of hot water is observed, these areas seem to be of a lesser geothermal interest.

The area of the thermal springs located on the Caribbean seashore and near the mouth of Claire river, on the southwestern flank of the Mount Pelée (Fig. 12), was not selected as priority area. Indeed, the SP surveys of Zlotnicki et al. (1998) and the geochemical works of this study confirmed that these springs were partly fed by warm

superficial outflows along the northwestern rim of the horseshoe-shaped structure, coming from the thermal area of the upper Chaude river (Fig. 12).

6. CONCLUSION

In this study, several surveys of water geochemistry and soil gas were performed in the Mount Pelée volcano-Morne Rouge and Diamant areas. All the geochemical results were compared to the previous data as well as the new geological and geophysical results and interpreted in order to select zones of high temperature geothermal interest. After these studies, these zones will have to be validated by drilling deep exploration wells.

The geochemical characteristics of the thermal fluids and especially, the use of helpful tools such as the chemical geothermometers and isotopic $^{87}Sr/^{86}Sr$ and $\delta^{7}Li$ values have allowed to identify and to distinguish several geothermal reservoirs in the studied areas. A geothermal reservoir at about 180°C was identified under the thermal spring of Petite Anse du Diamant. Another geothermal reservoir at 190-200°C is probably present under the thermal springs of the upper Chaude river, located in the rims of the intermediate caldera of the Mount Pelée. It also seems to feed the thermal springs situated on the Caribbean seashore and near the mouth of Claire river by lateral superficial outflows. This geothermal reservoir would be different from that feeding the thermal springs of Mitan and Picodo river, which would be only at a temperature of about 150°C and not interesting for our objective. The existence of the two high temperature geothermal reservoirs (temperatures higher than 180°C) is supported by geological and geophysical data. Among the thermal springs discovered during this study, the two terrestrial springs sampled for the first time (upper Claire river and Grande river) indicate slightly warm superficial fluids and then have not high temperature geothermal interest.

The soil gas and geophysical results suggest another area where a high temperature geothermal reservoir could exist (Desgrottes drill-hole, in the Champflore basin). However, this area is lesser geothermal interest than the two previous zones because of the old age of the formation of this basin and the absence of hot waters at surface.

In a first approach, the other areas where geophysical anomalies were discovered, were not selected because no superficial discharge of deep waters and gases was observed.

Acknowledgments

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Fluid sample	n°	Sampling date	$T_{emerg.}$ °C	Cond. 25°C mS/cm	pH	Eh mV	$O_{2diss.}$ mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cl mg/l	Alkalinity mg/l HCO_3	SO_4 mg/l	NO_3 mg/l	SiO_2 mg/l	TDS g/l	B.I. %	Cl/Br
Thermal spring of Petite Anse du Diamant	DIAM1	06/12/01	35.3	28.4	5.99	-23	0.22	5800	295	1100	300	10200	1679	500	< 1	131	20.1	4.14	408
Thermal spring of Petite Anse du Diamant	DIAM1	25/03/01	34.0	23.8	6.15	-35	*n.a.*	5396	237	991	263	9730	1500	493	< 1	154	18.9	0.83	489
Thermal spring of Petite Anse du Diamant	DIAM2	06/12/01	31.3	17.6	6.53	-53	1.70	3340	178	565	174	5200	1709	817	< 1	137	12.1	0.34	441
Thermal spring of Petite Anse du Diamant	DIAM2	25/03/01	30.4	14.7	7.10	-55	*n.a.*	3253	161	594	175	5070	1700	760	< 1	151	11.9	1.57	457
Water barrage La Charmeuse	DIAM4	07/12/01	26.6	0.158	6.76	230	3.38	19.8	4.2	5.5	4.0	23.6	50	3.1	< 0.1	26.3	0.14	1.43	> 118
Drill-hole OPGMC Bord de Mer	MP1	07/12/01	36.4	1.38	6.55	-125	0.11	213	13.9	34.3	25.9	237	282	96.6	< 0.1	103	1.01	1.08	293
1st submarine thermal spring	MP2	09/12/01	33.0	42.1	7.00	57	3.40	8060	240	299	872	14500	180	2311	< 1	26.6	26.5	-3.69	290
2nd submarine thermal spring	MP3	09/12/01	36.0	17.7	6.65	-105	1.92	3320	103	141	362	5960	219	888	< 1	75.5	11.1	-3.38	271
Sea water	SW	09/12/01	28.5	53.5	8.19	-32	2.23	11400	309	390	1200	20200	143	2626	< 1	0.19	36.3	-0.77	301
Thermal spring of Chaude river	MP4	11/12/01	51.4	1.49	6.40	-43	0.50	263	25.5	35.9	13.5	68.1	621	153	< 0.1	143	1.33	-1.93	> 340
Thermal spring of Chaude river	MP5	11/12/01	39.6	1.06	6.47	-63	1.92	220	21.6	31.6	12.1	51.5	531	121	< 0.1	134	1.13	0.14	> 258
L'Etang river (near a bridge)	MP6	11/12/01	24.4	0.176	7.15	140	7.70	16.3	2.4	13.1	4.0	12.7	69	14.6	< 0.1	76.3	0.21	-2.26	> 64
Thermal spring of Chaude river	MP7	16/07/02	38.0	1.09	6.58	*n.a.*	*n.a.*	212	23.0	29.0	13.4	51.6	491	123	< 1	115	1.06	2.41	> 258
Thermal spring of Claire river	MP8	11/03/03	22.9	0.356	6.23	-19	*n.a.*	24.0	3.9	35.7	8.5	12.3	97	78.0	< 0.4	133	0.39	1.04	> 123
Thermal spring of Mitan river	MP9	14/03/03	28.3	0.637	6.29	222	*n.a.*	60.8	14.6	51.6	18.5	78.1	185	65.0	< 0.4	120	0.63	-2.48	473
Thermal spring of Picodo river	MP10	16/03/03	36.6	2.15	6.37	-103	*n.a.*	268	33.3	95.4	50.6	451	440	60.5	< 0.4	181	1.59	1.04	316
Thermal spring of Grande river	MP11	12/05/03	27.1	0.353	6.29	-68	*n.a.*	21.1	4.2	24.5	17.0	9.2	200	12.7	< 0.1	106	0.40	-2.39	> 920

n.a.: not analyzed

Table 1a: Chemical results (major species) of the fluid samples collected from the thermal springs and superficial waters (river, rainfall, sea, etc.) located in the Mount Pelée volcano-Morne Rouge and Diamant areas, during this study.

n° sample	NH_4 mg/l	PO_4 mg/l	NO_2 mg/l	Br mg/l	F mg/l	B mg/l	As mg/l	Al mg/l	Fe mg/l	Li mg/l	Sr mg/l	Ba mg/l	Mn mg/l	Cs mg/l	Rb mg/l	Ge µg/l	Ag µg/l	Cd µg/l	Co µg/l	Cr µg/l	Cu µg/l	Ni µg/l	Pb µg/l	Zn µg/l	U µg/l
DIAM1	0.9	3.3	*n.a.*	25.0	< 0.1	78.2	2.500	0.058	6.14	10.1	14.84	0.168	1.689	0.299	1.011	64	1.0	2	2.6	2.0	7.0	13	1.4	32	< 0.1
DIAM1	0.9	< 5	< 0.01	19.9	< 0.1	79.5	2.530	0.490	0.31	9.95	9.62	0.054	1.641	0.327	0.920	*n.a.*	< 50	< 20	< 20	2.3	< 20	< 50	< 20	111	*n.a.*
DIAM2	0.7	1.8	*n.a.*	11.8	0.3	*n.a.*	*n.a.*	*n.a.*	*n.a.*	5.52	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
DIAM2	0.3	< 5	< 0.01	11.1	< 0.1	42.5	0.808	< 0.3	0.02	5.89	5.41	< 0.05	1.635	0.172	0.586	*n.a.*	< 50	< 20	< 20	1.2	< 20	< 50	< 20	90	*n.a.*
DIAM4	0.1	< 0.1	*n.a.*	< 0.2	0.1	0.043	0.016	0.507	1.92	< 0.005	0.034	0.0077	0.0428	0.00008	0.00329	0.12	0.03	0.51	0.43	2.0	10	4.1	0.45	20	0.02
MP1	< 0.1	< 0.1	*n.a.*	0.81	0.4	1.03	0.005	0.0079	1.02	0.39	0.185	0.0052	0.679	0.0017	0.0418	0.42	0.09	0.14	0.16	< 1	1.5	< 0.8	0.43	15	< 0.01
MP2	0.2	8.8	*n.a.*	50.0	1.0	2.98	0.056	0.132	0.30	0.34	5.63	0.0125	0.217	0.0012	0.105	0.8	0.9	1	0.98	13	10	4.3	0.70	14	3.1
MP3	0.2	< 0.1	*n.a.*	22.0	0.6	2.15	0.037	< 0.024	0.09	0.30	2.49	0.0063	0.0013	0.0022	0.0639	1.2	0.9	1	< 0.2	< 9	4.0	< 0.8	0.40	15	1.0
SW	< 0.1	< 0.1	*n.a.*	67.0	1.3	3.84	0.093	0.056	0.40	0.23	7.52	0.0076	0.0010	0.00054	0.123	1.5	1.1	1	1.04	13	10	6.4	0.60	22	3.5
MP4	< 0.1	< 0.1	*n.a.*	< 0.2	0.3	1.77	0.015	0.010	0.23	1.50	0.135	0.060	0.869	0.00959	0.100	4.8	0.09	0.15	0.37	< 1	0.4	< 0.8	0.28	16	0.2
MP5	< 0.1	< 0.1	*n.a.*	< 0.2	0.4	1.42	0.008	0.0098	0.24	1.30	0.114	0.040	0.636	0.00704	0.0801	4.1	0.09	0.09	0.24	< 1	0.7	< 0.8	0.17	5.5	0.05
MP6	< 0.1	< 0.1	*n.a.*	< 0.2	0.3	0.059	0.003	0.010	0.02	0.008	0.04	0.00097	0.0010	0.00007	0.0090	0.033	0.03	0.04	0.029	0.2	0.58	0.3	0.06	2.2	0.011
MP7	< 0.1	< 0.1	*n.a.*	< 0.2	0.2	1.60	0.003	0.0177	0.16	0.99	0.120	0.0246	0.134	0.00412	0.0701	3.0	0.02	0.06	0.11	< 2	1.95	0.88	0.23	4.7	*n.a.*
MP8	< 0.1	0.7	< 0.01	< 0.1	0.2	0.119	< 0.001	0.006	1.06	0.059	0.140	0.014	0.907	0.0011	0.011	< 0.5	< 0.5	0.4	< 0.5	< 0.5	0.5	0.9	< 1	3.0	*n.a.*
MP9	0.5	< 0.1	32.4	0.165	0.2	0.785	< 0.001	0.006	< 0.02	0.055	0.170	0.011	0.659	0.0006	0.029	< 0.5	< 0.5	0.4	< 0.5	< 0.5	1.8	0.7	< 1	4.0	*n.a.*
MP10	< 0.1	0.2	< 0.01	1.43	0.1	4.74	0.005	0.020	0.57	0.37	0.350	0.098	2.480	0.007	0.085	6.3	< 0.5	0.4	1.1	< 0.5	0.9	2.8	3.0	2.0	*n.a.*
MP11	< 0.1	0.1	< 0.01	< 0.01	0.1	0.073	< 0.001	0.001	1.67	0.034	0.080	0.009	0.173	0.0006	0.014	0.9	< 0.5	0.2	< 0.5	< 0.5	< 0.5	0.7	< 1	2.0	*n.a.*

n.a.: not analyzed

Table 1b: Chemical results (trace species) of the fluid samples collected from the thermal springs and superficial waters (river, rainfall, sea, etc.) located in the Mount Pelée volcano-Morne Rouge and Diamant areas, during this study.

Fluid sample	n°	δD_{SMOW} □	$\delta^{18}O_{SMOW}$ □	^3H UT	$\delta^{34}S_{CD}$ (SO_4) □	$\delta^{18}O_{SMOW}$ (SO_4) □	$\delta^{13}C_{PDB}$ □	^{14}C □	Age ^{14}C years	$^{87}Sr/^{86}Sr$	$\delta^{11}B$ □	δ^7Li □
Thermal spring of Petite Anse du Diamant	**DIAM1**	-17.5	1.8	< 1	*n.a.*	*n.a.*	4.6	< 0.3	> 46970	0.704822	9.05	6.8
Thermal spring of Petite Anse du Diamant	**DIAM1**	-22.0	1.9	< 1	11.6	10.0	2.4	< 0.3	> 46970	0.704812	*n.a.*	7.1
Thermal spring of Petite Anse du Diamant	**DIAM2**	-18.7	-0.4	< 1	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	6.3
Rain water sampled on 6/12/01	**DIAM3**	6.7	-0.8	< 1	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*
Water barrage La Charmeuse	**DIAM4**	-8.6	-2.0	2	17.0	7.2	-13.4	187.4	modern	*n.a.*	*n.a.*	*n.a.*
Drill-hole OPGMC Bord de Mer	**MP1**	-8.6	-2.9	3	11.4	8.7	-1.3	19.2	13260	0.706276	*n.a.*	8.8
1st submarine thermal spring	**MP2**	3.9	-0.2	*n.a.*	19.7	9.5	*n.a.*	*n.a.*	*n.a.*	0.709141	*n.a.*	18.7
2nd submarine thermal spring	**MP3**	-4.7	-1.9	*n.a.*	20.0	9.5	*n.a.*	*n.a.*	*n.a.*	0.709017	*n.a.*	10.1
Sea water	**SW**	9.8	0.9	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	0.709188	*n.a.*	30.1
Thermal spring of Chaude river	**MP4**	-7.7	-2.8	3	11.7	9.1	0.1	15.2	15130	0.704233	6.25	8.1
Thermal spring of Chaude river	**MP5**	-7.4	-2.8	*n.a.*	10.7	9.0	-0.3	12.0	17050	0.704247	*n.a.*	8.6
L'Etang river (near a bridge)	**MP6**	-8.9	-2.8	2	5.8	7.4	-14.8	161.6	modern	0.704484	*n.a.*	2.2
Thermal spring of Claire river	**MP8**	-5.3	-2.5	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	0.704250	*n.a.*	2.3
Thermal spring of Mitan river	**MP9**	-7.7	-2.7	< 1	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	0.704383	*n.a.*	5.2
Thermal spring of Picodo river	**MP10**	-7.6	-2.2	< 1	10.4	8.6	*n.a.*	*n.a.*	*n.a.*	0.704317	*n.a.*	5.4
Thermal spring of Grande river	**MP11**	-7.5	-3.0	2	11.4	12.9	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*	*n.a.*

n.a.: not analyzed

Table 1c: Isotopic results of the fluid samples collected from the thermal springs and superficial waters (river, rainfall, sea, etc.) located in the Mount Pelée volcano-Morne Rouge and Diamant areas, during this study.

Na mg/l	K mg/l	Ca mg/l	Mg mg/l	HCO_3 mg/l	Cl mg/l	SO_4 mg/l	SiO_2 mg/l	TDS mg/l	B mg/l	Li mg/l	Rb mg/l	Cs mg/l	Sr mg/l	Fe mg/l	Ge µg/l	Co µg/l	Cu µg/l
714	68	78	31	1630	169	406	265	3.4	5	4	0.26	0.025	0.33	0.65	12	1	4

Table 2: Reconstructed chemical composition of the hot end-member, which partly feeds the thermal springs of Chaude river.

Fluid sample	n°	$T_{emerg.}$ °C	T_{Qz} °C	$T_{Calcéd.}$ °C	$T_{SiO2am.}$ °C	$T_{Na/K\ (1)}$ °C	$T_{Na/K\ (2)}$ °C	$T_{Na/K/Ca}$ (β=4/3) °C	$T_{Na/K/Ca}$ (β=1/3) °C	$T_{Ca/K\ (1)}$ °C	$T_{K/Mg}$ °C	$T_{Na/Li\ (1)}$ °C	$T_{Na/Li\ (2)}$ °C	$T_{Mg/Li}$ °C	$T_{K/Sr}$ °C	$T_{Na/Rb}$ °C	$T_{Na/Cs}$ °C	$T_{\delta\ O(H2O-SO4)}^{18}$	$T_{estimated}$ °C
Thermal spring of Petite Anse du Diamant	**DIAM1**	35.3	153	91	31	135	165	195	172	239	109	176	109	113	226	87	73	211	**180±20**
Thermal spring of Petite Anse du Diamant	**DIAM2**	30.4	162	99	39	133	163	173	166	217	100	133	61	81	217	88	74		**180±20**
Drill-hole OPGMC Bord de Mer	**MP1**	36.4	139	78	19	156	182	108	158	153	63	178	111	60	159	91	40	155	**190±20**
Thermal spring of Chaude river	**MP4**	51.4	158	96	36	194	214	134	181	187	85	253	202	102	217	112	67	151	**190±20**
Thermal spring of Claire river	**MP8**	22.9	154	92	32	255	262	44	167	93	47	196	132	34	96	118	99		**?**
Thermal spring of Mitan river	**MP9**	28.3	148	86	27	312	305	85	202	145	68	143	71	26	166	119	43		**150±15**
Thermal spring of Picodo river	**MP10**	36.6	173	110	50	236	247	134	197	193	84	155	85	54	223	100	57	166	**150±15**
Thermal spring of Grande river	**MP11**	27.1	141	79	20	283	283	51	178	104	42	170	104	18	113	131	62	106	**?**

T_{Qz}, $T_{SiO2am.}$: Fournier and Rowe (1966) ; $T_{Calced.}$: Truesdell (1975).
$T_{Na/K\ (1)}$: Michard (1979) ; $T_{Na/K\ (2)}$: Fournier (1979).
$T_{Na/K/Ca}$: Fournier and Truesdell (1973).
$T_{K/Mg}$: Giggenbach (1988).
$T_{Ca/K}$, $T_{K/Sr}$, $T_{Na/Rb}$, $T_{Na/Cs}$: Michard (1990).
$T_{Na/Li\ (1)}$: Kharaka et al. (1982) ; $T_{Na/Li\ (2)}$: Fouillac and Michard (1981).
$T_{Mg/Li}$: Kharaka and Mariner (1989).
$T_{\delta 18O(H2O-SO4)}$: Mizutani and Rafter (1969).

Table 3: Deep temperatures estimated using the chemical and isotopic geothermometers.

Gas sample	n°	Sampling date	CO_2 % vol.	CH_4 % vol.	O_2 % vol.	He ppm	Laboratory chemical analyses % volume	$\delta^{13}C_{PDB}$ □	$^3He/^4He$	Accuracy %	R_s/R_a
Deux Choux drill-hole	**MPG1**	10/07/2002	86.9	0.2	0.0	2.18	90,2% CO_2 . 1,21% O_2 . 6,51% N_2 . 0,08% CH_4 . 0,06% Ar	-6.1	6.64E-06	4.5	4.74
Roxelane river	**MPG2**	11/07/2002	8.2	0.0	11.4	5.24		-24.5			
Morne Calebasse	**MPG3**	12/07/2002	8.1	0.0	11.7	5.29		-16.1			
Camp Chazeau - Petite Savane	**MPG4**	12/07/2002	20.4	1.0	0.0	5.28	19,7% CO_2 . 0,78% O_2 . 80,6% N_2 . 0,57% CH_4 . 1,00% Ar	-17.2	1.36E-06	10	0.97
Riv. des Ecrevisses - Chazeau	**MPG5**	13/07/2002	10.0	0.0	1.8	5.43	10,7% CO_2 . 3,61% O_2 . 84,4% N_2 . < 0,0002% CH_4 . 1,09% Ar	-26.1	1.48E-06	10	1.05
Propriété De Paz - Chemin principal	**MPG6**	15/07/2002	9.8	0.0	8.7	5.24		-21.8			
Propriété De Paz - Chemin principal	**MPG7**	15/07/2002	15.2	0.0	0.2	5.45	14,9% CO_2 . 1,39% O_2 . 82,0% N_2 . < 0,0002% CH_4 . 1,03% Ar		1.28E-06	12	0.91
Desgrottes drill-hole	**MPG8**	17/07/2002	61.2	30.6	0.5	5.21	44,5% CO_2 . 1,85% O_2 . 23,5% N_2 . 30,0% CH_4 . 0,32% Ar	-8.3	6.16E-06	4	4.40
Thermal spring of Petite Anse du Diamant	**DIAMG1**	19/07/2002	98.1	0.0	2.4	5.83	97,2% CO_2 . < 0,001% O_2 . 0,17% N_2 . < 0,0002% CH_4 . < 0,001% Ar	-4.4	6.20E-06	10	4.43
Altered area - thermal spring Diamant 1	**DIAMG2**	19/07/2002	42.5	0.0	10.3	6.11	34,7% CO_2 . 12,5% O_2 . 50,3% N_2 . < 0,0002% CH_4 . 0,64% Ar	-1.7	3.93E-06	4.5	2.81
Altered area - thermal spring Diamant 2	**DIAMG3**	20/07/2002	99.2	0.0	0.0	7.56	81,1% CO_2 . 3,14% O_2 . 14,8% N_2 . 0,002% CH_4 . 0,16% Ar	-2.5	7.49E-06	9	5.35

R_s/R_a : $(^3He/^4He)_{sample}/(^3He/^4He)_{atmosphere}$

Table 4: On site and laboratory chemical analyses and isotopic measurements for 11 gas samples selected during this study.