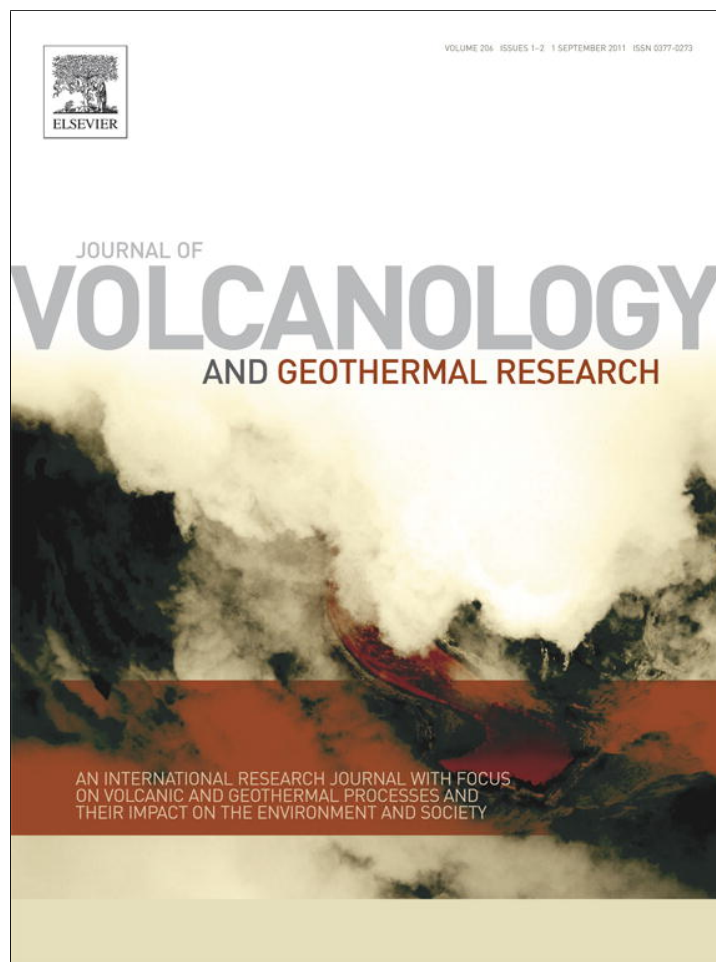


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Gas and water geochemistry of geothermal systems in Dominica, Lesser Antilles island arc

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ABSTRACT

Four of the nine potentially active volcanoes on the island of Dominica in the Lesser Antilles volcanic island arc have associated active volcanic-hydrothermal systems. Between 2000 and 2006 the gas and thermal waters from these systems were investigated to geochemically characterise the fluids, gain insight into the temperature and equilibrium state of the underlying reservoirs, and evaluate the feasibility of monitoring geothermal features as a volcano surveillance tool in Dominica. The geothermal gases are typical of those found in arc-type settings, with N₂ excess and low amounts of He and Ar. The dry gas is dominated by CO₂ (ranging from 492 to 993 mmol/mol), and has a hydrothermal signature with hydrogen sulphide as the main sulphurous gas. The waters are predominantly acid-sulphate (SO₄ = 100–4200 mg/L, pH ≤ 4), and likely formed as a result of dilution of acidic gases in near surface oxygenated groundwater. Enrichment in both δ¹⁸O and δD with respect to the global meteoric water line (GMWL) confirms that the waters are of primarily meteoric origin, but have been affected by evaporation processes. Quartz geothermometers gave equilibrium temperatures of 83 °C–203 °C. These temperatures contrast with the higher equilibrium temperature ranges (170 °C–350 °C) obtained for the gases using the H₂/Ar*–CH₄/CO₂ gas ratios plot, suggesting that the quartz geothermometers are affected by non-attainment of equilibrium. This may be a result of precipitation of the dissolved silica and/or dilution by relatively cold shallow aquifers of the thermal fluids. Generally, no significant variations in fluid gas chemistry of the hydrothermal systems were observed during the study period, and we propose that there were no changes in the state of volcanic activity in this period. One exception to this occurred in a feature known as the Boiling Lake, which underwent a month-long period of significant compositional, temperature and water level fluctuations ascribed to a drastic decrease of hydrothermal input related to a perturbation in the lake (probably seismically induced). This geochemical study is part of an ongoing monitoring programme of Dominica geothermal systems, aimed at establishing long-term geochemical observations for the purpose of volcano monitoring.

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1. Introduction

The high mobility of magmatic volatiles, much greater than that of magma itself, makes them valuable indicators of change in the state of activity of volcanic systems (Menyailov et al., 1985; Cioni et al., 1989; Giggenbach et al., 1990; Giggenbach, 1997; Brombach et al., 2000; Fischer, 2002). The recording of changes in the chemistry of hot springs and fumaroles associated with volcanic-hydrothermal systems, and its use as a tool for monitoring volcanic activity has been outlined by many authors (Aguilera et al., 2005; Caracausi et al., 2005; Tassi et al., 2005; Lopez et al., 2006; Principe and Marini, 2008; Taran et al., 2008). This technique has been thus far under-utilised in the

volcanic islands of the Lesser Antilles, and as a result there is a lack of long-term geochemical surveillance data for the region.

The Lesser Antilles arc includes 21 potentially active volcanoes spread across 11 volcanically active islands (Fig. 1), and volcanic eruptions are one of the main hazards that threaten the eastern Caribbean region. Most of the islands of the Lesser Antilles (e.g. Saba, St. Vincent, Nevis, Montserrat, Guadeloupe, and Saint Vincent) have a single main vent. The other islands are more complicated, and none more so than Dominica, which has nine young volcanic centres resulting in an exceptionally high level of volcanic risk (Lindsay et al., 2005). Many of these islands have active geothermal systems associated with the young volcanic activity, and in the French islands (Guadeloupe and Martinique) geothermal monitoring is part of routine volcano surveillance (Bigot and Hammouya, 1987; Bigot et al., 1994; Komorowski et al., 2002).

Robson and Willmore (1955) performed the first investigations of geothermal systems in the Lesser Antilles. Their studies involved the measurement of thermal outputs of several geothermal areas in the

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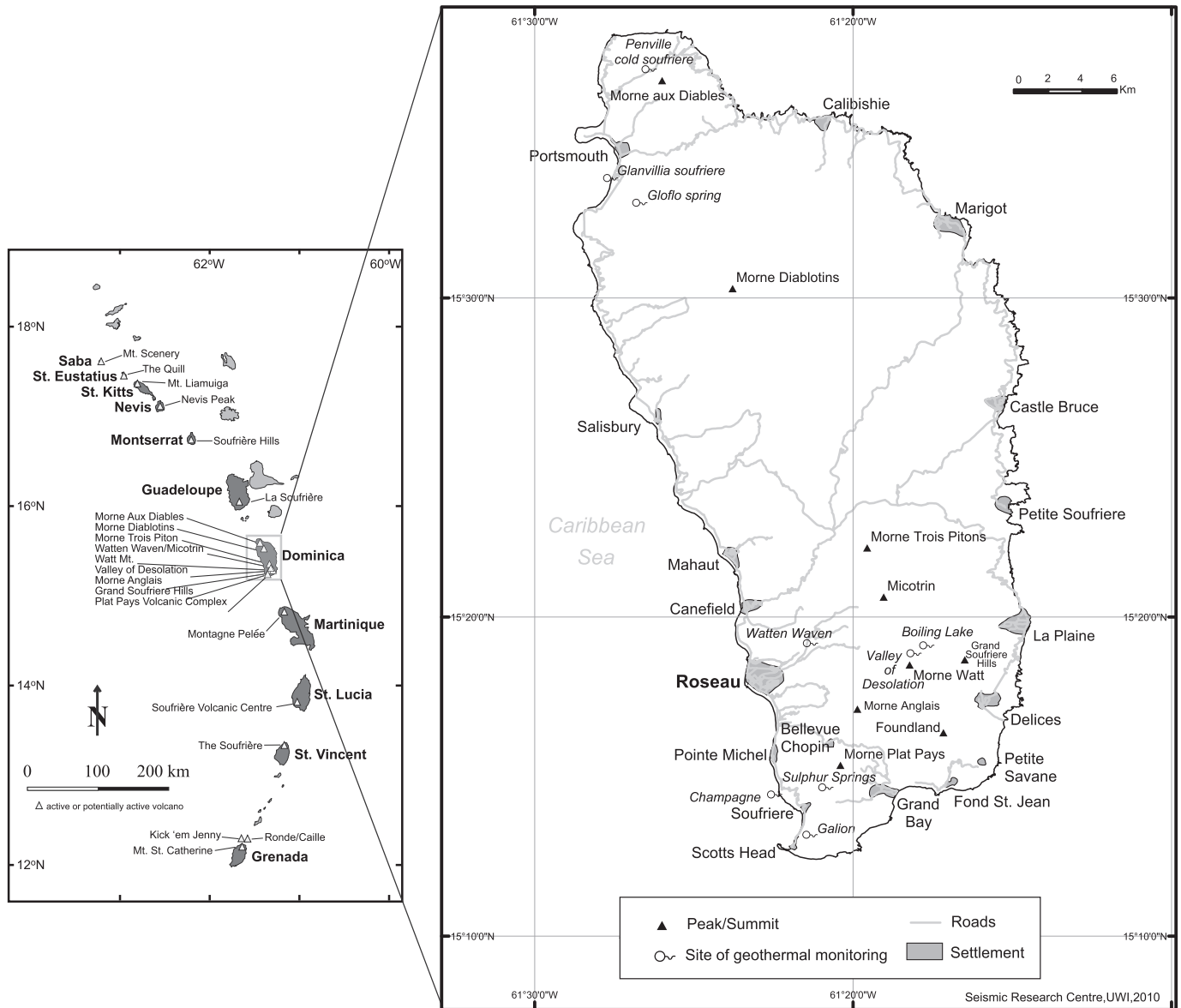


Fig. 1. Map of the Lesser Antilles showing the location of Dominica (left) and a map of Dominica showing sites of geothermal activity and monitoring (right).

Lesser Antilles, including Dominica, and their contribution to the overall heat balance of the Earth. Research into He, Ne, Sr, Ar and C isotopes of hydrothermal fluids in the Lesser Antilles was later carried out by Pedroni et al. (1999) and Van Soest et al., (1998). These studies focused on the use of these isotopes to trace the recycling of subducted terrigenous sediments in arc magmas, through volatile provenance at summit fumaroles. Oxygen and hydrogen isotopic composition of hydrothermal brines from Dominica reported by Pedroni et al. (1999) showed an essentially meteoric-hydrothermal origin, while isotope compositions, element ratios, and concentrations of Ne and Ar suggested that these noble gases were almost wholly derived from the atmosphere.

More recently, Herlihy et al. (2005) conducted studies relating the geology of Dominica with the geochemistry of associated hot springs. They categorised most of the hot springs studied as Ca–Mg–SO₄ type in chemistry, and stable isotopic analyses of δ¹⁸O and δD suggested that water–rock interaction and alteration had occurred. A more specific study of the geothermal springs in northern Dominica was conducted by Harrell et al. (2008). They analysed δ¹⁸O and δD isotopes of these springs compared to Vienna Standard Mean Ocean Water (VSMOW) and found that they lie on a trend between the

meteoric water line (MWL) and a magmatic source, in contrast to other studies which showed a meteoric origin affected by water–rock interaction. Furthermore, the chemical composition of the springs was interpreted to represent mixing of variable amounts of freshwater or seawater with a magmatic source that appeared to be constant for the northern springs. Four of the nine young volcanic centres in Dominica have associated geothermal activity in the form of hot and cold springs, fumaroles, mud pools, and steaming ground. A complete data set of chemical and isotopic compositions of the geothermal gas and waters from these features may improve our understanding of the dynamics of the island's volcanic systems, complement the existing routine seismic monitoring programme; as well as contribute to a more long-term geochemical surveillance of these volcanic systems.

In this paper we describe and report on the chemical composition of fumarolic and hydrothermal spring discharges of Dominica based on gas and water samples collected during the period 2000 to 2006. We discuss the origin of the discharged fluids, and we propose an evaluation of the hydrothermal reservoir temperatures on the basis of fluid geochemistry. This information is then used to make recommendations on the usefulness of long-term geochemical observation as part of the overall volcano monitoring efforts on the island.

2. Geology and hydrology

2.1. Geology

Dominica has an area of 750 km² and, with the exception of a minor discontinuous formation of uplifted Pleistocene to Holocene conglomerates and corals along the west coast, is made up almost entirely of volcanic rocks (Lindsay et al., 2005). Based on 43 K-Ar and 50 radiocarbon ages the stratigraphy of the island can be divided into four units: Miocene, Pliocene, 'Older Pleistocene', and 'Younger Pleistocene' – Recent (Lindsay et al., 2005). The four units are separated by three unconformities, which are not all island-wide, as volcanism continued at some centres while weathering and erosion took place at others that had become extinct. A major shift in the focus of volcanism was evident about 1.6 Ma ago with activity switching from the northern to southern half of the island. Despite this general shift to the south, volcanism still continued in the north at Morne Diablotin and Morne aux Diables, with low levels of hydrothermal activity and significant seismic activity suggesting that these centres are still potentially active. Seven major andesitic–dacitic volcanic centres have been active in southern Dominica since the late Pleistocene: Morne Trois Piton, Watten Waven/Micotrin, Valley of Desolation, Watt Mountain, Grand Soufrière Hills, Morne Anglais/John, and the Plat Pays volcanic complex (Lindsay et al., 2003, 2005). Available ages for these centres range from ~50,000 to 450 years BP, and most have had eruptions within the last 10 ka (Lindsay et al., 2003). These centres are associated with geothermal and shallow seismic activity and are considered likely to erupt again.

2.2. Hydrology

Dominica has a humid tropical climate, with microclimates that can range from highly seasonal on the leeward coast and weakly seasonal on the windward coast to perennial wet in the mountainous interior (Walsh, 1980). The prevailing trade winds are from the east, and are responsible for the orographic precipitation effect with rainfalls varying from 2000 mm/year on the east coast to 1000 mm/year on the west coast (Reading, 1991). The interior mountain rain forest experiences annual values found to exceed 10,000 mm/year (Reading, 1991). The long-term monthly average rainfall data for the Melville Hall Airport (20 year record), as recorded by National Oceanic and Atmospheric Administration (NOAA), confirmed a wet season from June to December and a dry season from January to May. Mean maximum monthly temperature ranges from 28.0 °C in January to 30.5 °C in August (<http://worldweather.wmo.int/134/c00287.htm>).

3. Geothermal areas in Dominica

Dominica has several areas of geothermal activity located throughout the island and related to the volcanic regions outlined above (Fig. 1). The main area characterised by hydrothermal activity is known as the Valley of Desolation (VoD) (Fig. 2a), and is the location of the 'Boiling Lake' of Dominica (Fig. 2a). In past studies this area has also been referred to as the "Grand Soufrière" (e.g. Sapper, 1903; Robson and Willmore, 1955). The Watten Waven geothermal area (Fig. 2b), associated with the Watten Waven/Micotrin volcanic centre, is located in the Roseau Valley. The Sulphur Springs, Galion, and Champagne geothermal areas are all associated with the Plat Pays Volcanic Centre (Fig. 2c). An area of cold fumarolic activity, known as the Penville 'cold soufrière', is associated with the Morne Aux Diables volcanic centre (Fig. 1). In addition to these main geothermal areas, there are a number of thermal fluid discharges associated with Morne Diablotin and Micotrin. Detailed descriptions of these geothermal features are given below, and additional information (particularly regarding early descriptions by previous workers) can be found in Lindsay et al. (2005).

3.1. Valley of Desolation

3.1.1. Valley of Desolation

The Valley of Desolation is characterised by numerous hot springs, bubbling pools and fumaroles over an area of ~0.5 km² (Fig. 2a) at an altitude of 800 m. It also includes areas identified by Robson and Willmore (1955) as the Eastern and Western Hot Springs. Two historical phreatic eruptions have occurred in the Valley of Desolation, in 1880 and 1997 (see Lindsay et al., 2005 and references therein). Geothermal studies of the area conducted by several researchers over the last 100 years have reported stable temperature ranges of fumaroles to be between 91 °C and 99 °C, and those of springs and bubbling mud pools between 40 °C and 96 °C (Sapper, 1903; Robson and Willmore, 1955; Brown, 2002).

3.1.2. Boiling Lake

The Boiling Lake is a high-temperature volcanic crater lake located on a hill above the Valley of Desolation area. It is approximately 50 m × 60 m in size and ca. 12 to 15 m deep, with an estimated volume of ~1.22 × 10⁴ m³ when filled (Fournier et al., 2009), and gives the impression of boiling through vigorous upwelling of gas. It is believed to have formed as a result of a phreatic or phreatomagmatic explosion similar to that of 1880 event in the Valley of Desolation. There is a fresh water inflow on the northern side via a stream, and an outflow on the southern rim onto the Rivière Blanche river bed. The inflow and outflow of the lake generally remain constant except for periods of heavy rainfall, when both are temporarily increased. Over the last 150 years, temperatures taken at the edge of the lake have generally ranged between 80 °C and 90 °C, and the pH from 4 to 6 (Sapper, 1903; Robson and Willmore, 1955; Komorowski and Hammouya 1997; Brown, 2002) during periods of 'steady-state' activity (i.e. long term depth stability, near boiling temperature, acidic pH, vigorous water convection, with steam and gas emitted at the apex of the convection cell). The lake water levels and temperature have been known to undergo rapid fluctuations in the past, such as in 1876, 1900, 1901, 1971, 1972 and in 1988 (Ober, 1880; James, 1988). This abnormal activity results in the rapid emptying and subsequent gradual refilling of the lake, probably in response to either a landslide or seismic activity, and has been described by Fournier et al. (2009).

The most recent emptying of the lake occurred in December 2004, when the lake water level dropped by ~8–10 m, and the temperature at the water's edge fell to <30 °C (James, 2004; James, 2005), this was followed by a period during which the hydrothermal activity and water levels fluctuated significantly until late-April 2005. Water acidity went from the usual acidic pH of 4–6 to neutral, while Cl concentration dropped from the typical 2000–6000 mg/L to 29–50 mg/L, and SO₄ concentration dropped from 1500–4000 mg/L to 100–270 mg/L (Table 1), indicating a drastic decrease of hydrothermal fluid input into the lake. The lake then returned to its steady-state of activity.

3.2. Watten Waven/Micotrin

3.2.1. Watten Waven

The hydrothermal activity associated with the Watten Waven/Micotrin centre (Fig. 2b) is concentrated in and adjacent to the River Blanc, a tributary of the Roseau River, near the Watten Waven caldera margin. The area is characterised by the presence of numerous bubbling pools and fumaroles with temperatures of up to 99 °C. Descriptions of the geothermal activity at Watten Waven were first reported by Drumm (1849), who noted the manifestation of hot, bubbling streams emitting sulphurous gases and active fumaroles on the stream bank with a larger vent at the mouth of a nearby cave (Joseph and Lindsay, 2002). Presently, the cave is ~2 m wide and approximately 6 m above the riverbed on the northern side of the river. A few smaller vigorously bubbling pools can also be found about 40 m north of the cave, above the River Blanc.

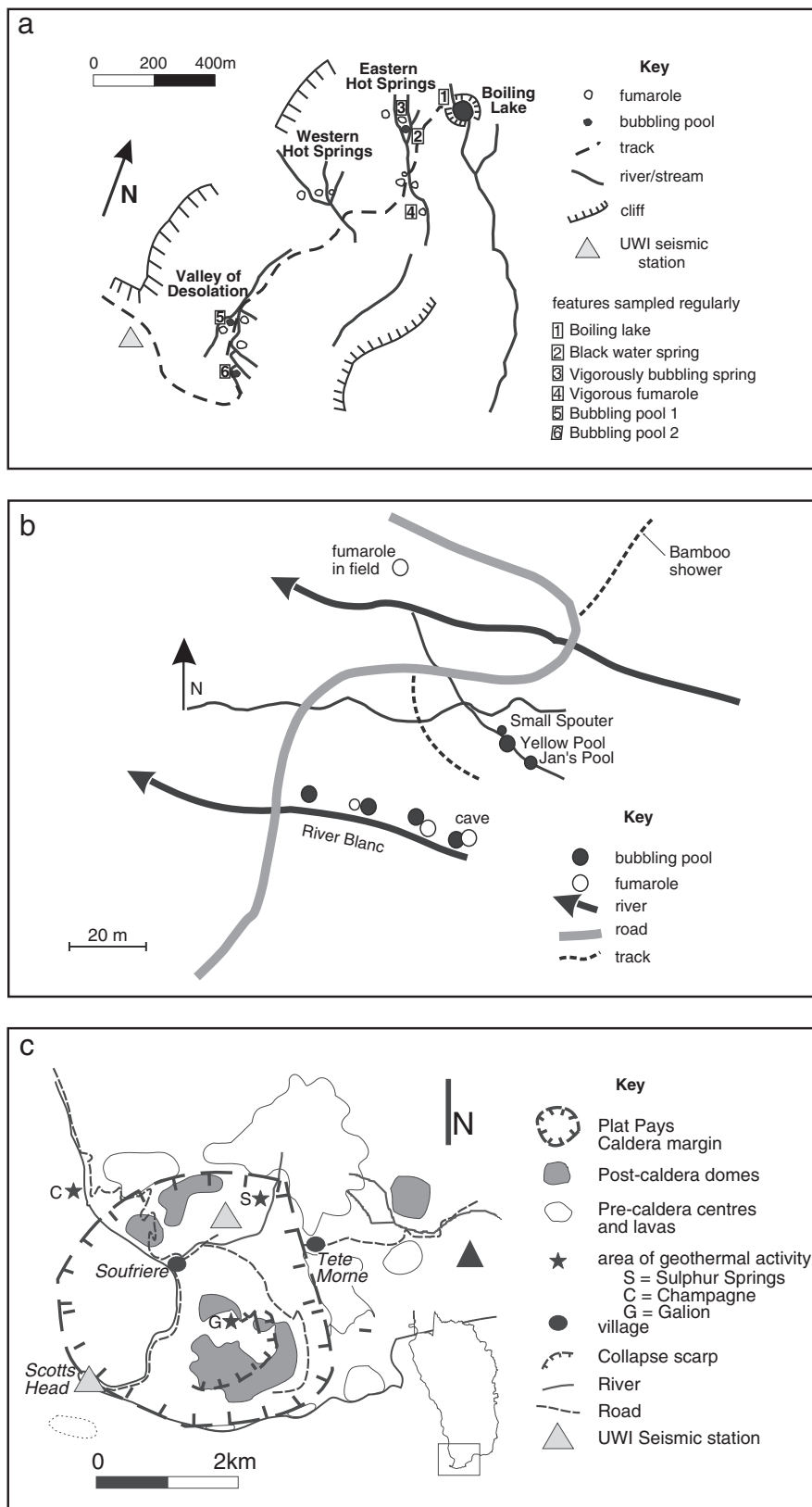


Fig. 2. Sketch maps of (a) the Valley of Desolation/Boiling Lake geothermal area; (b) the Watten Waven geothermal field; (c) the Plat Pays Volcanic complex, showing sampling sites and/or features (after Lindsay et al., 2005a).

3.2.2. Minor activity associated with Micotrin

Some of the streams directly adjacent to the Micotrin dome have patches of orange stained rocks on their banks. This is an indication

that there may be some unidentified warm springs higher up on the dome. In 1974 hydrothermal activity was reported in the area west and east of the dome in the 'moat' surrounding the dome near the

3.3. Plat Pays Volcanic Centre

There are three main areas of hydrothermal activity associated with the Plat Pays Volcanic Centre, which lies in the Soufrière depression: Sulphur Springs, Galion and Champagne springs (Fig. 2c). Some minor fumaroles in the crater of Morne Patates were described by Wills (1974), however, recent visits to the area show that they are no longer present (Lindsay et al., 2003).

3.3.1. Sulphur Springs

The largest area, Sulphur Springs, is located on the margin of the Soufrière depression in the Sulphur Springs National Park region at an altitude of 275 m above sea level, and was previously called the Terre Elm fumaroles by Wadge (1985). The fumaroles at Sulphur Springs were previously mapped by Martin-Kaye (1959), and very little change in the area has since been observed. Measurements taken in the last 100 years indicate that fumarole temperatures are between 90 °C and 100 °C (Sapper, 1903; Van-Soest et al., 1998; Brown, 2002).

3.3.2. Galion

Another smaller area of hydrothermal activity is situated in a cliff on the northern side of the Crabier dome close to the Galion village (Fig. 2c). There is also an area of hot ground behind Galion village, with ground temperatures of up to 98 °C. Both areas are characterised by steam emissions, altered ground with numerous sulphur-coated fumaroles and minor hot springs.

3.3.3. Champagne

The third area of fumarolic emissions is found at Champagne (Fig. 2c), in a zone of gas emission 200 m north of Point Guignard on the beach and extending to at least 20 m offshore. Bubble trains rising towards the water surface manifest the underwater fumaroles found here. They appear to be aligned along roughly east–west trending fractures in lava, which can be correlated with similarly-trending fractures in adjacent lava onshore (Lindsay et al., 2003). Minor thermal activity is present at the foreshore near Soufrière village, where diffuse gas discharge occurs in shallow water.

3.4. Morne aux Diables

3.4.1. Penville 'cold soufrière'

The Penville 'cold soufrière' is located on Morne aux Diables, at the northern end of Dominica (Fig. 1) at an elevation of 475 m a.s.l., and may be referred to as a kaipohan feature. The term kaipohan, proposed by Bogie et al. (1987), is used to define areas of diffuse cold fluid emissions, usually actively forming argillic (and occasionally advanced argillic) alteration. The soil at this site is an allophonic clay since the development of kaolin has not yet occurred in this region (Osler, 2003). This cold soufrière occupies an area of ~25 m² and is situated to the north of the main summit area. The activity manifests as milky-to-clear vigorously bubbling pools and cold "frying pan" features with temperatures of 23 °C–28 °C and a strongly acidic pH (1–2) (Lindsay et al., 2003). While no fumarolic activity exists in the area, there is a strong odour of hydrogen sulphide (H₂S) and the vegetation immediately surrounding the feature is dead. There are also several bubbling springs in a nearby stream with large patches of filamentous white algae growing in it.

3.4.2. Glanvillia Hot Springs

Numerous hot springs and patches of hot ground are present in the vicinity of Glanvillia south of Portsmouth (Fig. 1). They form an area of thermal activity 2.5 km × 1.5 km in size, roughly half of which is immersed in the shallow waters of Prince Rupert Bay at depths of 6 m to 21 m. Onshore temperatures of up to 102 °C were recorded in February 2004 from an area of hot ground near the mouth of the Picard River in Glanvillia. The submarine springs occur as both large isolated

springs and as areas of more diffuse degassing via many smaller springs. The largest and deepest solitary spring is located in 21 m of water to the south of the thermal area. Vigorous venting of hot discoloured water from this feature has led to the formation of a depression in the seabed 33 m in diameter. Bubbles from this spring reach the water surface despite the 21 m water depth (compared to a maximum depth of origin of only 4.5 m at Champagne Pool in the south). Divers visiting the area in February 2004 reported the seabed too hot to push their hands into the sand, and the boat anchor, when raised, was still warm to the touch.

3.5. Other minor activity in northern Dominica

Minor fumarolic activity has also been reported on the north western slopes of Morne Diablotins (Robson and Tomblin, 1966), to the west of Morne aux Diables on the coast at Toucari village (in a roadside excavation now filled in) and on Morne Turner (A. James pers. comm. 2003).

4. Sampling and analytical methodology

Sampling of gas and thermal waters from the fluid discharges described above took place during the period 2000–2006, with a frequency of once or twice per year. A total of 62 water samples were collected for this study: 11 from the Boiling Lake, 15 from the Valley of Desolation, 14 from Watten Waven, 9 from Sulphur Springs, and 13 from the Penville cold soufrière. Each water sample comprised of three aliquots (for cation, anion and isotope analyses). A total of 23 gas samples were analysed: 8 from the Valley of Desolation, 4 from Watten Waven, 4 from Sulphur Springs, 3 from Galion, 2 from Champagne, and 2 from the Penville cold soufrière.

4.1. Water sampling and analysis

Samples were filtered on site through a 0.45 µm membrane prior to collection in sterile polyethylene bottles. Samples for the determination of cation and silica (SiO₂) were preserved with concentrated HNO₃ in separate bottles. Filtered un-acidified samples were collected and stored in polyethylene bottles for analyses of anions. Raw water samples were stored in glass Quorpak bottles for stable isotope analyses. Outlet temperature (±0.1 °C) and pH (±0.1 units) were measured in the field, using an Omega (HH509) thermocouple meter and Hach (Sension 1) meter, respectively.

All water analyses were conducted at the University of the West Indies in Trinidad, using standard procedures outlined in the Standard Methods for the Examination of Water and Wastewater, 21st edition (Eaton et al., 2005). Analyses of Mg, Ca, Fe, Al, Na, and K were carried out by atomic absorption spectrophotometry (AAS) using a Varian AA800 Atomic Absorption Spectrophotometer, and/or flame photometry (FP) using a Jenway (FPF 7) Flame Photometer. Analysis of F, Cl, Br, PO₄ and SO₄ was conducted by ion chromatography (IC) using a Dionex DX-100 Ion Chromatograph and an AS14 column. SiO₂ was measured in selected water samples by visible spectrophotometry (VS) using a Bran and Luebbe Autoanalyzer (Multitest MT19), according to procedures outlined for the colorimetric determination of silica in freshwater (ASTM, 1991; APHA, 2005). HCO₃ was analysed volumetrically by titration with 0.1 N HCl. The analytical error for AAS, FP, IC, and VS was ≤ 10%. The ionic balances were calculated from the analyses and only those with ≤ 10% maximum residuals are presented in Table 1.

A suite of water samples collected in 2002 was selected for stable isotopic analysis. δ¹⁸O and δD determinations were conducted at the NERC Isotope Geosciences Laboratory (NIGL) in Keyworth, Nottingham, UK. δ¹⁸O analysis was performed using an Isoprep 18 CO₂/H₂O equilibration system coupled to a SIRA 10 split-flight mass spectrometer following standard principles outlined in Gonfiantini (1981). δD analysis was performed using a continuous flow EuroPyrOH–3110 system coupled to a Micromass Isoprime Mass Spectrometer. Internal

reference standards for $\delta^{18}\text{O}$ and δD analyses were used. These internal standards were calibrated against international reference materials VSMOW, SLAP, and GISP with an analytical precision of $\pm 0.05\%$ for $\delta^{18}\text{O}$, and $\pm 1.0\%$ for δD .

4.2. Gas sampling and analysis

Gas samples were collected from bubbling springs and fumaroles in Giggenbach flasks using the standard methods described by Giggenbach and Goguel (1989). The glass flasks were equipped with a Teflon stopcock and contained approximately 50 ml of 5 N NaOH solution. The underwater vents at Champagne were sampled using a slightly different method. Polyethylene bottles were initially filled with seawater and submerged underwater. A plastic funnel with teflon tubing attached to the spout was then inverted over the vent and the tubing purged with the fumarolic gases. This tubing was then inserted into the mouth of the polyethylene bottle and the seawater was displaced by the gases. When the seawater was fully displaced the bottled was capped with a cover, which was fitted with a short length of tubing passing through its centre. This piece of tubing was clamped to prevent atmospheric contamination of the gas sample when the bottle was returned to the surface. The tubing from the bottle was then connected directly to a prepared Giggenbach flask and the geothermal gas sample was transferred to the flask.

The gas samples were analysed at the Volcanic and Hydrothermal Fluid Analysis Laboratory at the University of New Mexico, USA using gas chromatography techniques detailed in Zimmer et al. (2004). The headspace gases (N_2 , O_2 , CO , H_2 , He , Ar , Ne , CH_4) were analysed by gas chromatography using a Gow Mac (600) Gas Chromatograph fitted with both TCD and FID detectors, using Chrom Perfect software. He , H_2 , and O_2 were analysed with Ar carrier gas; and Ar , N_2 , CH_4 and CO were analysed with H_2 carrier gas. Water vapour and the acidic gas species dissolved in the alkaline solution. The main acidic species (CO_2 , H_2S , and HCl) were analysed by wet chemistry techniques involving the use of acidimetric titration with 0.1 N HCl (for CO_2 as CO_3^{2-}), titration with 0.01 N thiosulphate (for H_2S), and titration with 1 N AgNO_3 (for HCl).

5. Water chemistry

5.1. Water classification

The temperature, pH, and composition of major chemical species of the waters are presented in Table 1. Oxygen and hydrogen stable isotope data are shown in Table 2. The pH of the waters ranges from 1 to 7 (acidic to neutral). Surface temperatures range from ambient to near boiling (18 °C–98 °C). Total dissolved solids were mainly moderate to high (TDS = 500–14,230 ppm), with the exception of a few samples where it was relatively low (135–500 ppm). Most waters had moderate to high concentrations of Na (40–3600 ppm), K (40–2300 ppm), and Ca (100–1400 ppm). The waters were generally rich in SO_4 (500–4200 ppm) and Cl (40–6000 ppm).

Chemical compositions of the waters are plotted in the ternary diagrams based on the relative amounts of $\text{Cl-SO}_4\text{-HCO}_3$ and $\text{Na-SO}_4\text{-Mg}$ (Fig. 3). The waters of the Boiling Lake show compositions that varied between Na-SO_4 with temperatures of 70 °C to 90 °C, and pH = 4 to 6.4, and Na-Cl with temperatures of 18 °C to 89 °C, and pH = 3 to 7.3 (Fig. 3a). The hydrothermal waters from the Valley of Desolation (Fig. 3a), Watten Waven, Sulphur Springs and Penville (Fig. 3b) all have a Na-SO_4 composition. The water samples from the Valley of Desolation ranged in temperature from 74 °C to 98 °C and pH = 1 to 4, with the exception of samples taken during heavy thundershowers in August 2003, which had a lower temperature and higher pH. Sample temperatures at Sulphur Springs ranged from 41 °C to 97 °C and pH = 1.3 to 3.3, while water samples from Watten Waven had temperatures in the range 39 °C to 95 °C, and pH values of 1.8 to 5.3.

Table 2
 $\delta^{18}\text{O}$ vs. δD composition of hydrothermal waters from Dominica.

Feature	Site	Date	d18O VSMOW	dD VSMOW
Boiling Lake	Valley of Desolation	11/17/2002	+6.05	6.5
Boiling Lake	Valley of Desolation	11/17/2002	+6.00	7.4
Bubbling Pool 1	Valley of Desolation	11/17/2002	+10.67	14.5
Bubbling Pool 1	Valley of Desolation	11/17/2002	+10.57	14.5
Bubbling Pool 2	Valley of Desolation	11/17/2002	-0.86	-3.4
Bubbling Pool 2	Valley of Desolation	11/17/2002	-0.83	-3.5
EHS stream fumarole	Valley of Desolation	11/17/2002	-1.30	-4.5
EHS stream fumarole	Valley of Desolation	11/17/2002	-1.29	-4.9
Sulphur hole 1	Sulphur Springs	11/19/2002	+4.62	7.2
Sulphur hole 1	Sulphur Springs	11/19/2002	+4.60	7.0
Nancy's Pool	Penville	11/18/2002	-4.37	1.3
Nancy's Pool	Penville	11/18/2002	-4.43	1.0
Eric's pool	Penville	11/18/2002	-2.57	-6.1
Eric's pool	Penville	11/18/2002	-2.55	-5.8
Jan's pool	Watten Waven	11/20/2002	-1.62	-4.2
Jan's pool	Watten Waven	11/20/2002	-1.75	-4.8
Yellow Pool	Watten Waven	11/20/2002	-1.47	-4.7
Yellow Pool	Watten Waven	11/20/2002	-1.46	-4.7

Waters from the Penville cold soufrière had temperatures of 18.5 °C to 32 °C, and pH = 1 to 4.

5.2. Isotope geochemistry

The stable isotope contents for the hydrothermal waters of Dominica show variations in $\delta^{18}\text{O}$ ranging from -1.75 to 10.67‰, and δD from -6.1 to 14.5‰ (Table 2). Hydrothermal waters in general exhibit a positive 'oxygen shift' from the global meteoric water line (GMWL), which is attributed to high temperature (≤ 300 °C) exchange of ^{18}O between fluids and reservoir rocks; typically no effect on δD composition is observed (Craig, 1963; Clark and Fritz, 1997). Interestingly, the hydrothermal waters of the VoD, Boiling Lake, and Sulphur Springs show an enrichment in both ^{18}O and D when compared with meteoric waters (Fig. 4). This is not an unusual occurrence for acidic hydrothermal waters, such as those present in Dominica. Acidic thermal waters such as El Tatio in northern Chile, and the Geysers and Lassen Park in California (Craig, 1963; Giggenbach, 1978) frequently exhibit a positive correlation between D and ^{18}O contents. The parallel enrichment in the two isotopes has been attributed to evaporation taking place at shallow depth and/or at the surface, at temperatures ranging from 70 °C–90 °C. The ultimate origin of these waters is meteoric, since the lines extend from the local meteoric water isotopic composition.

Samples from Watten Waven show relatively little deviation from the GMWL, indicating that the water in this geothermal system is mainly meteoric in origin. However, water-rock interaction cannot be excluded. The waters from the Penville cold soufrière show a less common 'negative shift'. This shift may be a result of ^{18}O exchange between the thermal waters with dissolved CO_2 , which takes place during equilibration in systems with high ratios of CO_2 to water (Clark and Fritz, 1997; Negrel et al., 1999). ^{18}O exchange between the waters and CO_2 is not surprising as CO_2 is the major gas, other than steam, in the hydrothermal fluids and comprises $\geq 70\%$ of the total dry gas for the cold soufrière gases (Table 3). A negative $\delta^{18}\text{O}$ shift may also be a result of interaction between water and hydrated secondary minerals derived from silicate minerals, which also takes place at low temperatures (Clark and Fritz, 1997).

6. Gas chemistry

6.1. Chemical composition of gases

The compositions of major chemical species found in the dry gas fraction of the hydrothermal gases of Dominica, expressed in mmol/

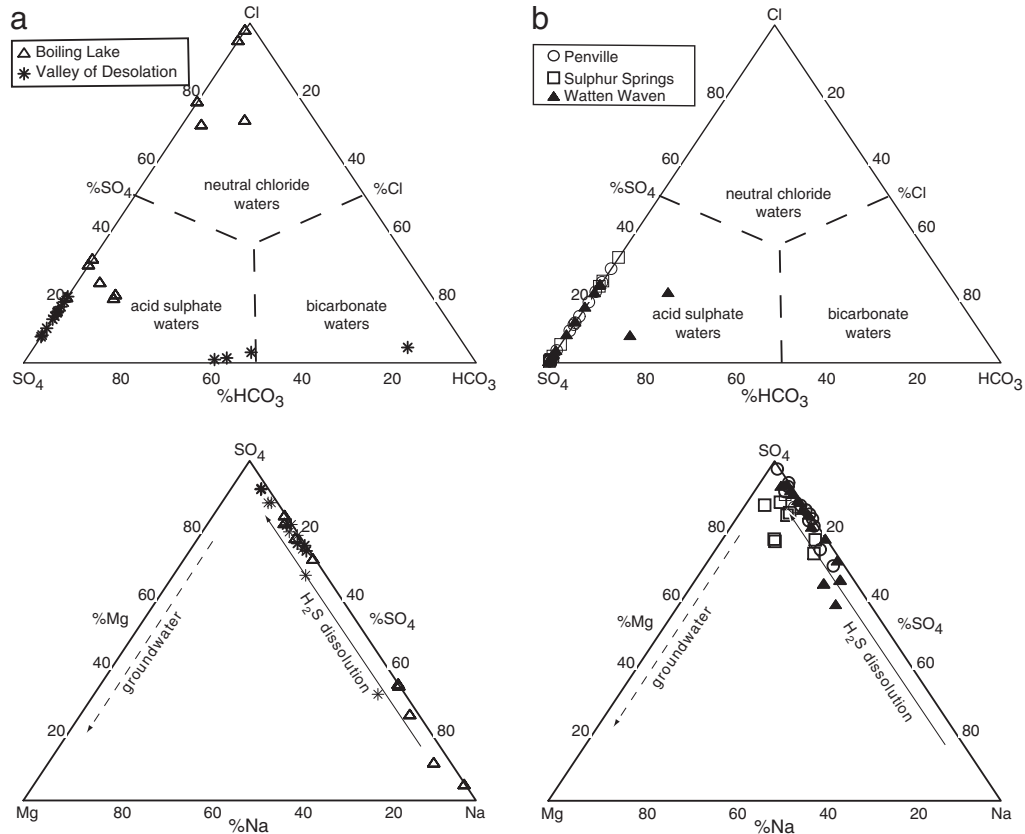


Fig. 3. Cl–SO₄–HCO₃ and Na–SO₄–Mg ternary diagrams for hydrothermal water samples from (a) Valley of Desolation/Boiling Lake; and (b) Sulphur Springs, Watten Waven, and Penville for the period 2000–2006, depicting their associated water types.

mol, are presented in Table 3. Composition of the dry fraction in all gas samples is dominated by CO₂ (492–993 mmol/mol) and H₂S (1.5–354 mmol/mol), with smaller amounts of HCl (0–46 mmol/mol, with one exception of a sea water contaminated sample from Champagne), and N₂ (4–121 mmol/mol) contents. Very low H₂ (<82 mmol/mol), O₂ (<24 mmol/mol), Ar (<16 mmol/mol), He (<0.9 mmol/mol.) and CO (<×10⁻³ mmol/mol) contents were observed. The very low

carbon monoxide concentrations are possible because of its high solubility in shallow aquifers to form HCOOH (Shock, 1993). The relatively high concentrations of the atmospheric-related compounds, i.e., O₂ and Ar (>3 mmol/mol and >7 mmol/mol respectively) in some samples, were likely caused by air entrainment during the gas sampling related to weak gas flux.

7. Discussion

7.1. Origin of thermal waters in Dominica

Thermal springs of Dominica are generally formed as a result of dilution of fluids from hydrothermal systems, with meteoric waters. The typically steam-heated acid-sulphate type character of the discharged waters can be explained by the O₂-driven oxidation of H₂S to H₂SO₄ in the near surface oxygenated ground waters (Henley and Stewart, 1983). Shallow waters of meteoric origin are likely heated by H₂S-rich vapour coming from depth, and forced to boil on their own (Arnorsson, 1985; Arnorsson and Gunnlaugsson, 1985). Na is released by intense leaching of host rocks, and Mg is depleted by incorporation into clay minerals (Giggenbach, 1988, 1991a). Their measured composition is derived from the balance between the meteoric water composition and the deep end-member.

The water of the Boiling Lake, characterised by a Na–Cl (SO₄) composition with moderate to high TDS concentrations, at times plots in the intermediate position between the mature and immature water fields (Fig. 5a), indicating a significant hydrothermal fluid contribution partially mitigated by the presence of solute from secondary gas-water–rock interactions. This marked enrichment in Cl content (Table 1) may be explained by inputs of the deep brine derived from the boiling process of a meteoric-originated hydrothermal aquifer that is fed by deep fluids (Tassi et al., 2005), and/or seawater

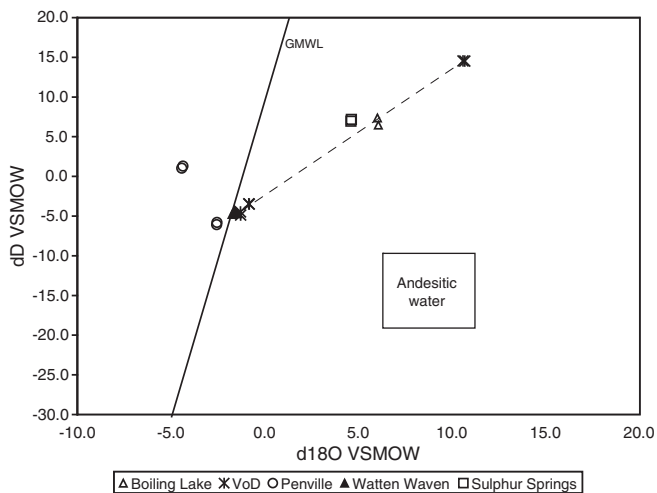


Fig. 4. δD vs. δ¹⁸O plot for hydrothermal waters of Dominica. The waters are primarily of meteoric origin but have been affected by a number of factors including evaporation processes, and low temperature exchange with CO₂ and/or silicate alteration minerals. Also shown are the global meteoric water line (GMWL), the composition of arc-type magmatic waters (Giggenbach, 1992), and the composition of andesitic waters (Taran et al., 1989).

Table 3
Gas composition of hydrothermal features from Dominica (mmol/mol dry gas).

Location	Feature	Date	T (°C)	CO ₂	H ₂ S	HCl	He	H ₂	Ar	O ₂	N ₂	CH ₄	CO	Total
Champagne	Underwater vent (f)	11/25/00	48.0	934	2	3	0.029	0.01	1.654	0.24	59	1.61	0.0001	1002
Champagne	Underwater vent (f)	04/20/01	45.0	762	28	182	0.008	0.00	2.888	3.81	47	1.78	0.0001	1028
Galion	Side fumarole (f)	05/31/03	80.0	672	174	5	0.011	11.52	7.412	8.57	121	0.02	n.d	1000
Galion	Top fumarole (f)	04/18/01	96.0	937	7	n.d.	0.003	4.67	0.027	3.70	55	0.02	0.0013	1007
Galion	Top fumarole (f)	11/06/03	98.3	721	186	4	0.003	8.56	0.442	0.00	80	0.00	n.d	1000
Penville	Eric's pool (s)	05/29/03	24.9	731	181	46	0.007	0.01	0.052	0.00	35	6.61	n.d	1000
Penville	Eric's pool (s)	11/06/03	25.4	746	177	3	0.020	0.00	7.173	6.25	60	0.00	n.d	1000
Sulphur Springs	Bubb. Sulphur hole 1(s)	11/26/00	97.4	977	7	n.d.	0.000	14.75	0.032	0.00	8	0.13	0.0005	1007
Sulphur Springs	Bubb. Sulphur hole 1(s)	04/18/01	96.0	986	9	5	0.001	2.35	0.067	0.00	6	0.01	0.0005	1009
Sulphur springs	Bubb. Sulphur hole 1(s)	11/19/02	97.4	777	109	4	0.000	0.04	0.000	23.89	86	0.00	n.d	1000
Sulphur springs	Bubb. Sulphur hole 1(s)	11/07/03	83.0	769	161	6	0.002	5.63	0.000	0.00	58	0.05	n.d	1000
Valley of Desolation	Bubbling Pool 1(s)	05/30/03	84.3	492	354	18	0.000	81.68	0.323	0.00	52	2.16	n.d	1000
Valley of Desolation	Bubbling Pool 1(s)	11/08/03	57.0	800	165	8	0.000	3.33	0.595	1.08	22	0.08	n.d	1000
Valley of Desolation	Bubbling Pool 1(s)	11/08/03	57.0	719	141	8	0.000	4.41	0.000	10.58	116	0.12	n.d	1000
Valley of Desolation	Bubbling Pool 2 (s)	11/25/00	80.7	976	15	n.d.	0.913	0.00	0.118	0.00	22	0.66	0.0085	1015
Valley of Desolation	Bubbling Pool 2 (s)	04/21/01	90.0	965	108	23	0.000	7.50	0.036	0.02	4	0.15	0.0023	1108
Valley of Desolation	Bubbling Pool 2 (s)	05/30/03	86.8	714	199	16	0.000	45.41	0.119	0.00	25	1.16	n.d	1000
Valley of Desolation	EHS Small stream fumarole (f)	05/30/03	96.6	502	329	22	0.000	54.94	1.575	0.00	90	0.30	n.d	1000
Valley of Desolation	EHS Vig. Bubb. Spring (s)	11/25/00	95.8	965	24	24	0.474	0.00	0.041	0.01	11	0.14	0.0029	1024
Watten Waven	Jan's pool (s)	05/29/03	91.2	784	186	3	0.005	6.18	0.182	0.00	20	0.70	n.d	1000
Watten Waven	Jan's pool (s)	11/05/03	43.0	689	157	3	0.007	7.91	16.902	20.35	105	0.88	n.d	1000
Watten Waven	Small spouter (s)	11/26/00	94.7	983	5	n.d.	0.000	3.05	0.091	0.01	13	0.34	0.0007	1005
Watten Waven	Small spouter (s)	04/19/01	94.0	993	13	n.d.	0.002	1.522	0.057	0.01	5	0.14	0.0005	1013

n.a : not analysed; n.d.: not detected; f= fumarole; s = spring.

contamination. However, additional studies involving the use of conservative elements such as Li/Cl or B/Cl ratios would have to be conducted to verify the reservoir source. The relatively high pH (5.5–8.1) in the waters of the VoD and Boiling Lake (Table 1) suggests the occurrence of prolonged water–rock interaction, and the low to moderate concentrations of HCO₃ (15–671 ppm) may be produced by CO₂ dissolution and bicarbonate conversion in an almost neutral environment, as is similarly observed for the waters of Agua Calientes, Costa Rica (Tassi et al., 2005).

δ¹⁸O and δD values also provide additional evidence that the deep fluids are of primarily meteoric origin. The distinct isotope enrichment in both δ¹⁸O and δD for thermal waters of the VoD, Boiling Lake and Sulphur Springs systems (Fig. 4) indicate that the discharged waters seem to be affected by surface evaporation processes (White, 2009). These evaporation processes, however, may mask any isotopic signature deriving from magmatic waters represented by the ‘andesitic waters’ field (Taran et al., 1989; Giggenbach, 1992). Others, such as the waters of the Penville cold soufrière, have been affected by low temperature exchange with CO₂ and/or hydrated silicate alteration minerals. The absence of any appreciable δ¹⁸O positive shift in the waters from Watten Waven suggests that the hydrothermal fluid had a relatively short residence time in the geothermal reservoir; this has also been observed for the waters from the Bouillante geothermal reservoir in Guadeloupe (Brombach et al., 2000).

7.2. The Boiling Lake “crisis”

The Boiling Lake generally exhibits a stable water level and temperature (~90 °C), which is occasionally interrupted by brief periods of instability involving rapid filling and draining of the lake and changes in water temperature. The most recent of these crises occurred during the period December 2004 to April 2005, and is described by Fournier et al. (2009). Water from the lake sampled prior to the crisis period (30 May 2003), was compared with water collected during the crisis (11 February 2005), as well as post crisis (25 August 2006) (Table 1). The pH of the water changed from its normal acidic state to a more neutral composition with the onset of the crisis. Concentrations of chloride in the water decreased from 6008 to 2274 ppm and sulphate from 1830 to 127 ppm respectively. Total Dissolved Solid (TDS) decreased from 13,382 to 4526 ppm, implying strong dilution by fresh water. Chloride,

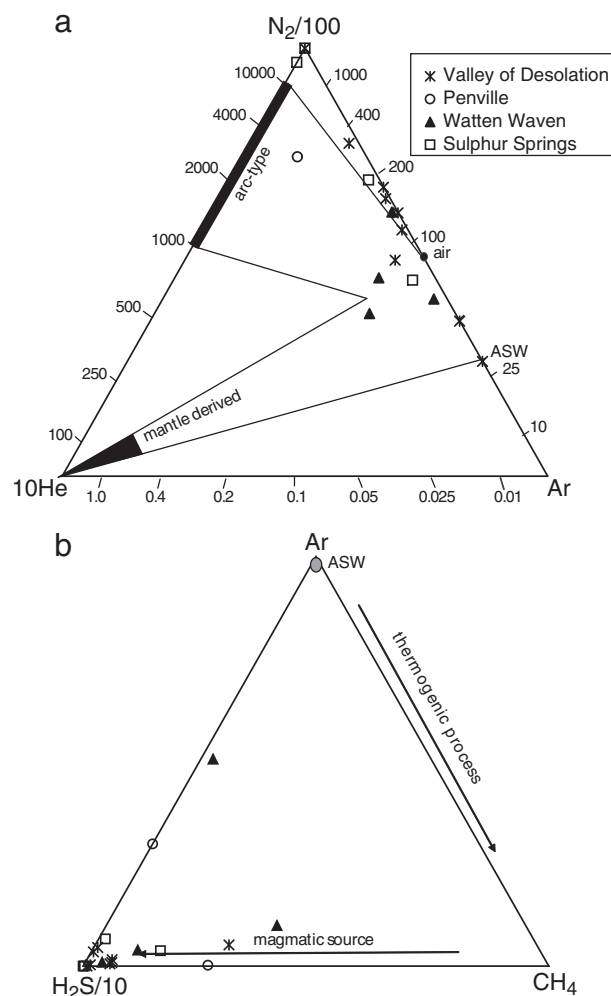


Fig. 5. (a) Ar–N₂–He and (b) CH₄–Ar–H₂S ternary diagrams for hydrothermal gases of Dominica.

sulphate and TDS continued to decrease until 25 August 2006, when concentrations started increasing. The evidence of fresh water input provided by the chemical composition of the water supports the concept that the Boiling Lake is suspended above the water table by the buoyancy of rising steam bubbles as proposed by Fournier et al. (2009) in their conceptual model.

The increase in temperature, and change in chemistry to a more acid-sulphate type character when normal geothermal activity resumes is likely the result of heating of the shallow aquifer by the acidic fluids sourced from the boiling of a deep-seated hydrothermal system.

7.3. Origin of geothermal gases in Dominica

The fumarolic composition of Dominica gases is mainly affected by a hydrothermal component, with a minor surficial (mainly atmospheric) component, and a subordinate magmatic component. Different contributions from the two sources give rise to changes in the relative abundances of the gas compounds. The hydrothermal magmatic gases are then discharged at the surface, interacting with shallow meteoric water and undergoing partial condensation of water vapour. The main characteristic feature of the gases associated with the hydrothermal systems of Dominica is the lack of magmatic-related gas compounds (HCl, HF, and SO₂). This may be associated with the high solubility of these gas species, whose behaviour is significantly affected by the interaction between the uprising deep fluids and the shallow liquid-dominated environment in the hydrothermal systems.

While it is clear that the gases sampled in this study were equilibrated with the liquid phase (Fig. 7), some “hydrothermally” equilibrated gas samples from Penville and the VoD contain noticeably “magmatic” HCl concentrations (Table 3). This has also been observed for hydrothermal discharges of El Chicon Volcano, Mexico where high HCl content in the vapours were reported (Taran et al., 1998). The increased Cl content in the gas condensates was attributed to droplets of saline water in the sampling flasks, which may have also occurred with some of the samples in this study.

Evidence of contributions to the hydrothermal fluids from deeper source components are indicated by the significant N₂-excess (from subducted oceanic sediments) (Fischer and Marty, 2005) observed for the discharges from Sulphur Springs, Watten Waven, and VoD (Fig. 5a); as well as the relatively high proportions of H₂S likely contributed from a deep magmatic related component (Fig. 5b). The MORB-like helium R/Ra ratios of 7.2 to 8.6 in the hydrothermal gases of Dominica provide evidence of deep fluid contributions (Van-Soest et al., 1998; Pedroni et al., 1999).

7.4. Gas geochemistry

Investigation of hydrothermal fluids at convergent plate boundaries reveals that they are generally associated with three possible source components; a meteoric component, represented by atmospheric gases (N₂, O₂, Ar) released from air saturated groundwater (ASW); a magmatic component from magma degassing, rich in CO₂, sulphur gas compounds and HCl; and a crustal component, showing relatively high concentrations of CH₄ and radiogenic He (Giggenbach, 1996). Circulating fluids also react with embedding rocks, under reducing conditions, to produce H₂, H₂S and CO₂ in the hydrothermal reservoir (Giggenbach, 1991b; Chiodini and Marini, 1998). The ultimate source of N₂, CO₂ and water of gases discharging in subduction zone settings generally is a mixture of gases derived from the mantle wedge, the overlying crust and the subducted lithospheric plate which is capped with altered oceanic crust and seafloor sediments (Hilton et al., 2002; Fischer, 2008).

The hydrothermal fluids of Dominica are examined in the context of ternary diagrams, to investigate the contributions of fluids from the source regions described above (Fig. 5). Gases discharging in volcanic arcs have relatively high N₂/He (1000–10,000) and N₂/Ar (> 100)

ratios compared to gases released from hot spots or rift environments (Giggenbach, 1996). The source of the elevated N₂ contents is thought to be sediments from the subducted oceanic crust (Sano et al., 2001; Fischer et al., 2002), although contributions from the overlying crust have also been identified (Snyder et al., 2003). Most Dominica samples show significant atmospheric contamination as indicated by shifts towards the air and ASW compositions, but generally have N₂/Ar ratios typical of arc-type gases suggesting N₂ addition from subducted sediments as also suggested by Brombach et al. (2000) (Fig. 5a).

Two samples from Sulphur Springs and one from the VoD show an even greater enrichment in N₂, which place them out of the mixing zone between arc-type and atmospheric end members. One possible explanation for this is that the N₂ content contributing to the increased ratio is controlled by a local process, as is the case for Cerro Prieto, Mexico where Norman et al. (2001) proposed a mechanism for enriching fluids in N₂ and Ar that involves wall-rock boiling and bubble trapping to sequester these species, then solution of bubbles at times of elevated pressure and temperature that occurs when fractures close. The relatively high concentrations of H₂S (Fig. 5b) indicates a contribution from a deep magmatic source based on its dependence on a high temperature; however, typical magmatic gases (SO₂ and HCl) appear to be efficiently removed by gas–water interactions (Giggenbach, 1996). Two samples from the VoD show enrichment in He that we attribute to analytical error incurred during the re-evaluation of the samples for He, where all of the H₂ was not removed before they were re-analysed.

7.5. Geothermometry

7.5.1. Water geothermometry

Geothermometers outlined in Giggenbach (1988) provide simultaneous comparison of the temperature dependence of the concentration quotients Na/K and K/Mg, which are controlled in fully equilibrated geothermal liquids by mineral-solution equilibrium involving albite, K-feldspar, illite, chlorite, and a silica mineral (either chalcedony or quartz). The resulting Na, K, Mg equilibrium diagrams for geothermal water samples from the Boiling Lake and Valley of Desolation (Fig. 6a), and Sulphur Springs, Watten Waven, and Penville systems (Fig. 6b) over the period 2000–2006 show that the samples plot in the immature waters field, indicating that the fluids are not in equilibrium with the host lithology (Giggenbach, 1988). Hence, the use of Na, K, and Mg geothermometers for estimating subsurface temperatures is not appropriate for these systems.

While the use of silica geothermometers (quartz, quartz-steam loss and chalcedony) may be accepted as more reasonable than those of the other cation geothermometers to estimate reservoir temperatures for immature waters (Gokgoz and Taran, 2006; Shakeri et al., 2008; El-Fiky, 2009; Matlu and Kilic, 2009), this type of approach was not found to be a reliable indicator for thermal waters of Dominica. The computed reservoir temperatures for hydrothermal systems of Dominica using silica geothermometers (Fournier, 1977) are listed in Table 4. The quartz geothermometers yielded subsurface temperatures of 187 °C–203 °C for the Boiling Lake; 145 °C–152 °C for Sulphur Springs; 83 °C–90 °C for Watten Waven; and ~102 °C for the Penville cold soufrière. Chalcedony geothermometers yielded lower temperatures in comparison, which were even lower than the measured temperatures in some instances e.g. Watten Waven (Table 4). In general lower SiO₂ equilibrium temperatures (Table 4) is seen to be related to lower Cl⁻ concentrations (Table 1), suggesting that the silica geothermometers are affected by mixing of hydrothermal fluids with shallow waters (Tassi et al., 2010), a process that likely controls most of the Dominica springs.

7.5.2. Gas geothermometry

The use of gas ratios to estimate reservoir temperatures at depth has proven useful for many geothermal systems (Giggenbach and Goguel, 1989; Chiodini and Marini, 1998). We examined the CO₂–

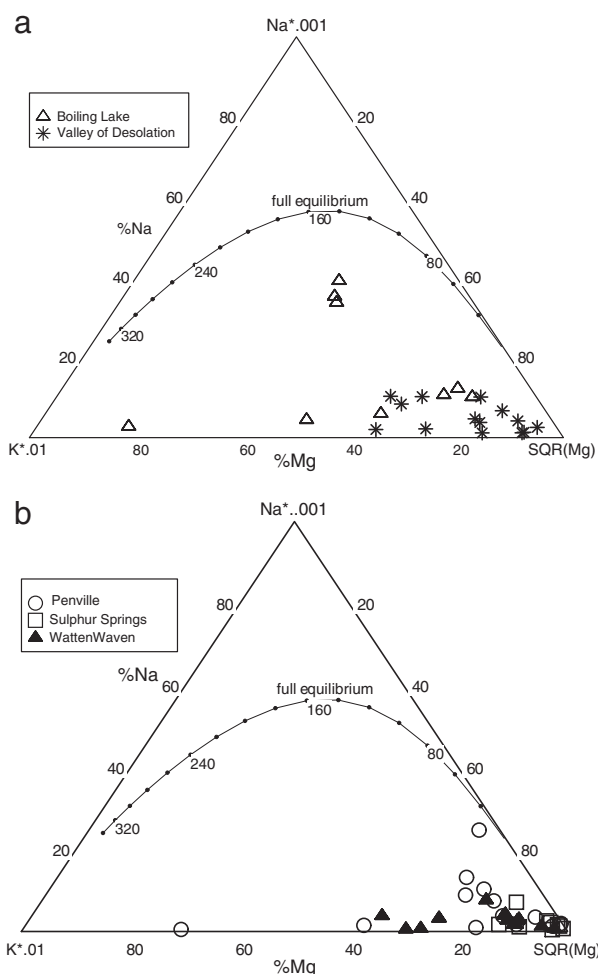


Fig. 6. Na–K–Mg equilibrium diagrams (from Giggenbach, 1988) for hydrothermal water samples from (a) Valley of Desolation/Boiling Lake; and (b) Sulphur Springs, Watten Waven, and Penville for the period 2000–2006. The geothermal systems of Dominica appear to be ‘immature’ and in a state of disequilibrium with the host lithology.

CH₄–H₂ system for the hydrothermal gases of Dominica. Thermodynamic conditions of the CO₂–CH₄–H₂ equilibria in the hydrothermal system can be shown by the log(*X*_{H₂}/*X*_{Ar*}) vs. log(*X*_{CH₄}/*X*_{CO₂}) diagram (Giggenbach, 1993; Giggenbach et al., 1993), where the vapour–liquid equilibrium grid at *R*_H ranging from –3.6 to –3.0 and temperatures in the interval of ~175–350 °C are reported (Fig. 7). *R*_H is a measure of redox potential evaluating the ratio of fugacities of H₂ and H₂O (*R*_H = log(*f* H₂/*f* H₂O)) in order to investigate predominating redox conditions within the reservoir (Giggenbach, 1987; Taran et al., 2002). For most hydrothermal fluids the redox state is controlled by FeO/FeO_{1.5} and hematite–fayalite–quartz assemblages, *R*_H values are temperature independent at –2.8. For vapour dominated geothermal systems values of *R*_H close to –2.8 are found. Values above –2.8 are considered to be typical of reducing conditions and are found in high-temperature (about 800 °C) volcanic gases (Taran et al., 2002) whereas values below –2.8 are considered oxidising conditions and are characteristic of geothermal systems. The part of Ar related to air entered in the system at shallow depth (or during sampling) is eliminated by subtracting a value equal to O₂/22 from the Ar concentration of the sample, i.e. assuming that no O₂ is present in the reservoir (Tassi et al., 2010). It should be noted that the two geothermometers, i.e. H₂/Ar and CH₄/CO₂, have different kinetics, thus the dispersions of the data points in Fig. 7 may also be affected by their different approaches to equilibrium.

Table 4
Measured discharge temperatures and inferred reservoir temperatures, Dominica hydrothermal waters (°C).

Feature	Site	Surface temperature	T Chalcedony	T QZ ^a	T QZ ^b
Boiling Lake	Valley of Desolation	84	186	203	187
Nico's spring	Sulphur Springs	62	126	152	145
Jan's pool	Watten Waven	90	56	87	90
Ellie's pool	Watten Waven	39	52	83	86
Fred's pool	Penville	27	71	101	102

Note: geothermometers are from Fournier (1977).

^a Quartz, no steam-loss.

^b Quartz steam-loss.

The CO₂–CH₄–H₂ grid of the gas samples show that the Sulphur Spring gases seem to be produced by boiling of a liquid phase at temperatures of ~300–350 °C and *R*_H > –3.0, indicating conditions more oxidising than those of the rock buffer (FeO–FeO_{1.5}) typically observed in hydrothermal environments (Giggenbach, 1987). One Sulphur Spring sample plotted above the vapour equilibration line indicating gas equilibration in a vapour phase at temperatures above 350 °C. It therefore suggests that the redox conditions of the gases are affected by contributions from the internal reactions among the gas species, commonly ones including H₂S and SO₂. Samples from Galion equilibrate at temperatures of ~250–300 °C attained at *R*_H ranging between –3.4 and –3.6. With the exception of one sample that equilibrates at a temperature of ~200 °C, the Watten Waven gases show temperatures of ~260–300 °C, and *R*_H ranging between –3.0 and –3.2. Most of the VoD gas samples equilibrate at temperatures ranging between ~250 and 325 °C, and *R*_H > –2.8, however, two samples plot far from any reasonable equilibrium conditions suggesting that any deep fluid contributions may have been masked by boiling of shallow aquifers (Tassi et al., 2010). This also appears to be the case for the Champagne hydrothermal gases, and one of the Penville samples. The other Penville gas sample equilibrates at a temperature of ~170 °C and *R*_H = –3.2, indicating that the fluid reservoir may be cooler than that of the other systems. The gas samples from VoD, Champagne, and Penville that show lowered or no reasonable equilibrium temperatures all show very low H₂ concentrations (Table 3), in comparison to the other gas samples, and this is believed to have affected the calculated CO₂–CH₄–H₂ temperatures. This may result from secondary oxidation reactions produced by fluid–rock redox processes that are able to consume H₂, thereby affecting the calculated equilibrium temperatures.

During a geophysical and geochemical survey conducted in Dominica during the period 1982–85 by the Bureau de Recherches Géologiques et Minières (BRGM), equilibrium temperature ranges of 230 °C–240 °C for Watten Waven, and 300 °C–320 °C for Sulphur Springs were obtained (GI, 1991). While the equilibrium temperatures found for the gases of Sulphur Springs (~300–350 °C) derived from the evaluation of the H₂/Ar*–CH₄/CO₂ gas ratios in this study are comparable to those estimated by the BRGM, temperatures for the Watten Waven (~260 °C–300 °C) gases are slightly higher. This difference in temperature for the Watten Waven gases may be a result of magmatic input to the hydrothermal system after 1985; however, this cannot be assessed due to the lack of fluid geochemical data for the island. The BRGM also used rectangle array and low frequency magnetotelluric techniques to identify potential geothermal reservoirs at both sites lying at depths of 700 m–1500 m. It is therefore likely that the depths of these reservoirs have not changed significantly since the 1980s.

7.6. Implications for volcano monitoring

Equilibrium temperatures of Dominica geothermal systems (~170 °C–350 °C) derived from evaluation of the H₂/Ar*–CH₄/CO₂

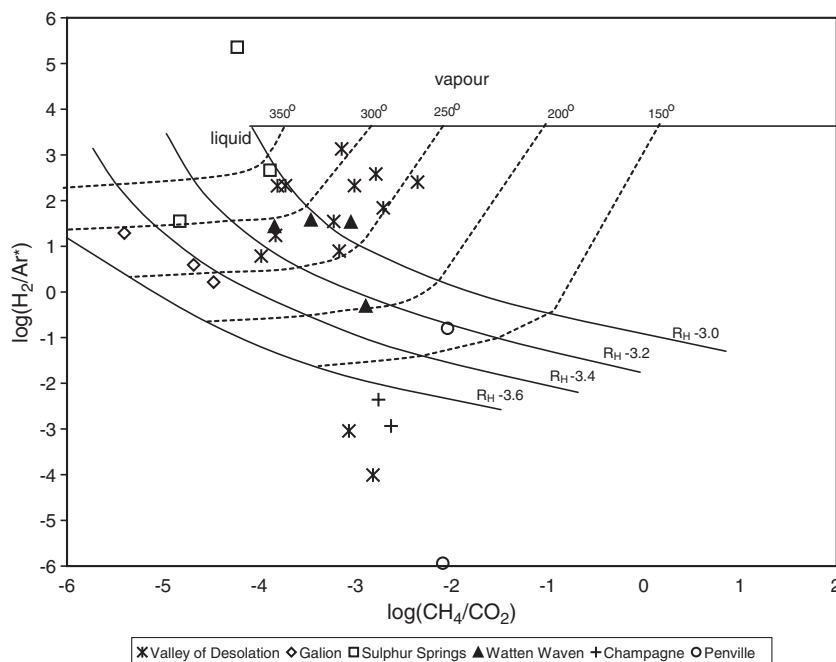


Fig. 7. Binary diagram of $\log(\text{H}_2/\text{Ar}^*)$ vs. $\log(\text{CH}_4/\text{CO}_2)$. $\text{Ar}^* = \text{Ar}-\text{O}_2/22$; $R_H = \log(\text{H}_2/\text{H}_2\text{O})$ (Giggenbach, 1987).

gas ratios indicate higher temperatures than those obtained from quartz geothermometers (~ 80 – 200 °C). It is possible that the underestimated temperatures indicated by the silica geothermometer results from possible non-attainment of the equilibrium implied by the geothermometer. In addition, if precipitation of the dissolved silica and/or dilution by relatively cold shallow aquifers were to happen during the ascent of the thermal fluid, the reservoir temperatures would be underestimated (Tassi et al., 2010). Secondary gas–water–rock interactions likely affect the chemistry of hydrothermal fluids of Dominica, and it is likely that actual reservoir temperatures may surpass those estimated by gas geothermometry.

Water isotopes of hydrothermal fluids from Dominica clearly indicate that there is a dominance of a meteoric component in the hydrothermal systems. This suggests that either the flux of magmatic fluids entering the hydrothermal systems is not high enough to dominate the signal, or the thickness of hydrothermal reservoirs is sufficient to buffer any magmatic inflow. A similar situation was observed for La Soufrière in Guadeloupe (Brombach et al., 2000), and Soufrière Hills Volcano in Montserrat before the eruption in 1995 (Chiodini et al., 1996). This directly impacts the possibility of detecting changes in chemical composition of the hydrothermal fluids that may be associated with precursory volcanic activity in Dominica. Hence, other precursory indicators, including surface deformation of the volcanic edifice, and an increase in the number of volcanic earthquakes indicating fracturing between the degassing magma body and the hydrothermal system, will need to be carefully monitored to distinguish between permanent changes due to magmatic input and changes induced by surficial (hydrothermal and meteoric) components during fluid transfer to the surface.

Re-activation of any of Dominica's volcanic systems due to magmatic input will probably be manifested in changes in fluid chemistry. Changes in fumarolic activity and composition may be more obvious than changes in the chemistry of acidic springs with the hydrothermal gas composition characterised by the presence of H_2O , CO_2 , H_2S , and, to a very minor extent, HCl and HF ; changing to a more hydrothermal/magmatic composition, with the appearance of SO_2 and a significant increase of HCl and HF as was observed for Turrrialba volcano, Costa Rica (Vasseli et al., 2010).

8. Conclusions

Hydrothermal manifestations in Dominica are mainly distributed within the four main areas investigated in this paper. These hydrothermal systems do not appear to be derived from a single geothermal reservoir, but may be related to distinct systems diluted to different extents by shallow aquifers. The chemistry of the thermal discharges of Dominica indicates steam-heated acidic-sulphate waters produced by the mixing between shallow groundwaters heated by rich sulphur-bearing gases coming from depth. The composition of the thermal waters reveals that they have not reached chemical equilibrium with the host rocks, and their immaturity and high acidity have therefore made the temperatures inferred from geothermometer data unreliable. Hydrothermal gases generally have N_2/Ar ratios typical of arc-type gases. Geothermometric calculations of reservoir temperatures from $\text{H}_2/\text{Ar}^*-\text{CH}_4/\text{CO}_2$ gas ratios give a range of 170 °C to 350 °C, generally consistent with calculations done by the BRGM over the period 1982–85 of ~ 260 – 350 °C (G.I., 1991). These fluids are generally characteristic of young active volcanic systems with a likely contribution of magmatic fluids to the hydrothermal systems. No significant variations in water and gas chemistry of the hydrothermal systems were observed during the study period, with the exception of the Boiling Lake during the crisis in 2004–2005, and we infer that there have not been any drastic changes in the status of volcanic activity during this time.

The unusual activity observed at the Boiling Lake is based on the concept that the Lake is suspended above the water table by the buoyancy of rising steam bubbles. The geometry of the lake-conduit system is believed to provide a mechanism for instability, with a denser liquid lake overlying a bubbly fractured permeable conduit (Fournier et al., 2009). Following a sufficiently large perturbation inside the lake or conduit (e.g. landslide or regional seismic activity) or changes to the water table, downward flow of bubble-free water into the vent can vertically displace steam bubbles. If this increased flow is faster than the rise speed of the fastest bubbles, all bubbles will be forced downward and the total upward drag force will be reduced as the bubbles compress; a positive feedback mechanism is initiated causing the lake to drain until its surface is at the level of the local water table (Fournier et al., 2009).

Our investigation reveals that there are limitations in using geochemistry as a tool for volcano monitoring in Dominica. The buffering action of the hydrothermal aquifers on the magmatic component of the thermal discharges significantly affects their surface composition and can lead to underestimation of reservoir temperatures, and directly impacts the possibility of detecting changes in chemical composition of the hydrothermal fluids that may be associated with precursory volcanic activity. However, continued chemical monitoring of the thermal discharges would provide valuable information towards understanding the dynamic processes occurring in the hydrothermal systems, and help determine if their compositional evolution is a reliable precursor to volcanic activity. This is particularly important when it is considered that seven of the potentially active volcanic centres lie in the southern half of the island within 10 km of the capital, Roseau.

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