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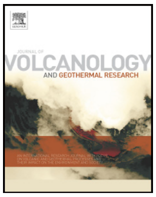

Update on the fluid geochemistry monitoring time series for geothermal systems in Dominica, Lesser Antilles island arc: 2009–2017

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ABSTRACT

With updated geochemical and isotopic compositions obtained over the period 2009 to 2017, this study presents revised fluid characterizations for the active volcanic-hydrothermal systems on the island of Dominica in the Lesser Antilles, which were first reported in 2011. Hydrothermal waters of Dominica cover a wide spectrum of pH, temperatures and chemical composition. The pH of the thermal waters ranges from acidic to neutral (pH values of 1–7.8) and the waters are predominantly Na-SO_4 in character (Na = 14–2127 mg/L; SO_4 = 1–1725 mg/L), likely formed as a result of dilution of acidic H_2S-rich gases in near surface oxygenated groundwater, and have experienced limited water-rock interaction. The geochemical composition of the waters for most of the hydrothermal systems studied indicate no significant changes, with the exception of the Boiling Lake, which experienced a short (~6 week) episode of instability in November 2016 which appeared to be associated with a small mud-rich explosion. Unlike the last such event in December 2004, which was reported to be earthquake-triggered, this event is possibly the consequence of a moderate-sized landslide into the lake. The lake draining episodes have been accompanied by changes in composition between Na-SO_4 and Na-Cl, which is attributed to hydrothermal fluid contributions from two different aquifers: a shallower acid-sulphate hydrothermal aquifer and a deeply-sourced brine aquifer.

Reservoir temperatures determined by quartz geothermometers have not changed significantly over the monitoring period, suggesting steady-state degassing of the magma chambers. In two areas, temperatures have increased: Watten Waven (from 83–90 °C to 89–139 °C) and Sulphur Springs (from 145–152 °C to 93–243 °C). The elevated reservoir temperatures have affected the isotopic composition of the waters ($\delta^{18}O = -5.7$ to 9.1‰ and $\delta D = -8$ to 20.5‰), that reflect a dominantly meteoric source, with boiling/degassing and evaporation also playing an important role. The time series data suggests that some hydrothermal areas are experiencing increased steam evaporation over time whereas other waters are becoming more meteoric. The $\delta^{13}C_{DIC}$ is decoupled from the deuterium and oxygen-18 isotopes and shows very little variation over time, but a broad range in values from −11 to +5‰. The dominant process contributing to $\delta^{13}C_{DIC}$ is degassing of primarily magmatic CO_2, as exhibited by the bubbling pools. Hydrothermal streams have experienced mixing with biogenic CO_2 sources, including plant respiration and methanogenesis. The slight variations observed from site to site are likely a consequence of fractional degassing of the magma chamber during exsolution of CO_2. Over the sampling period 2014–2017, the temperatures and $\delta^{13}C$ values do not change, which suggests a current steady-state of degassing.

1. Introduction

Dominica is part of the Lesser Antilles volcanic arc and is home to nine young volcanic complexes, of which seven major andesitic-dacitic volcanic centers have been active since the late Pleistocene (Fig. 1) (Lindsay et al., 2005). Four of these centers have associated active geothermal areas that have been routinely monitored since 2000 by the UWI Seismic Research Centre (SRC) and since 2013 by Union College (Fig. 1). Volcano hydrothermal monitoring provides information on temperature, origin, and temporal changes in chemical composition of volcanic fluids and informs on potential volcanic hazards to which the public may be exposed. Geochemical data collected between 2000 and 2006, showed that the hydrothermal waters of Dominica are predominantly acid-sulphate in character, and are of primarily meteoric origin (Joseph et al., 2011). Stable isotopic composition

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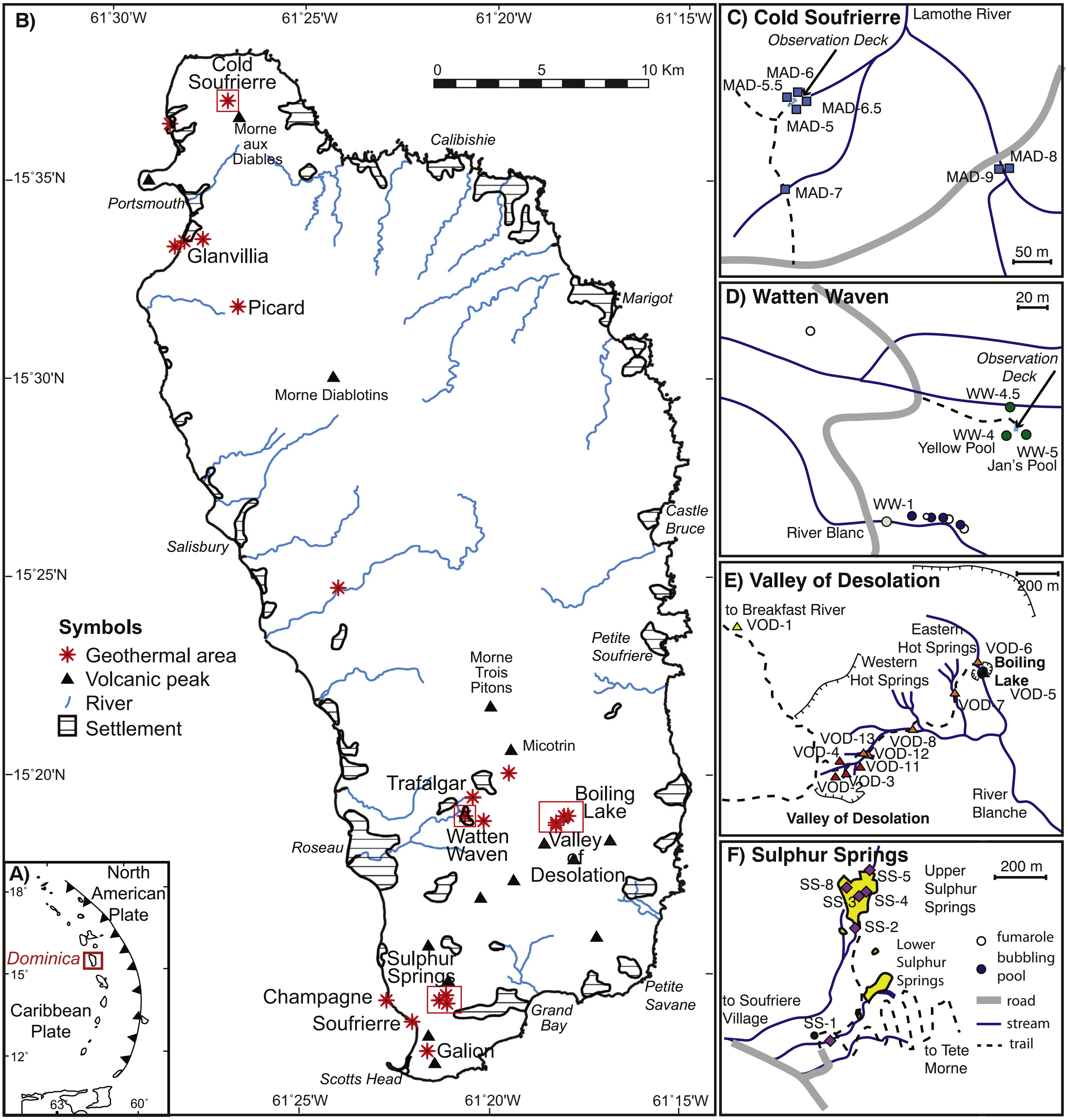

Fig. 1. A) Inset map of the Lesser Antilles showing the location of Dominica; and B) a map of Dominica (modified from Smith et al., 2013) highlighting geothermal areas (springs, fumaroles, bubbling pools) sampled. Sketch maps of the four major geothermal areas monitored by the UWI-SRC showing sample locations in this study are shown for: C) Cold Soufrière; D) Watten Waven; E) Valley of Desolation/Boiling Lake; and F) Sulphur Springs.

(deuterium and oxygen-18), determined in 2002, show that they have been affected by evaporation, water-rock interaction with the host lithology, and possible ^{18}O exchange between the thermal waters with dissolved CO_2.

The most prominent volcanic feature of Dominica is the Boiling Lake, a vigorously bubbling hot (80–90 °C), saline-rich volcanic lake characterized by a strongly degassing plume (Fig. 2A). Situated within two kilometers of the Valley of Desolation, the Boiling Lake is a ~50 m × 60 m crater lake with a depth of 12–15 m. It is believed to have formed as a result of a phreatic or phreatomagmatic explosion, similar to that which occurs in the nearby Valley of Desolation (Fournier et al., 2009; Lindsay et al., 2005). Over the last 200 years of documented history the lake has exhibited at least eight periods of instability sometimes involving rapid draining and refilling, which is accompanied by a cessation of hydrothermal activity (Fournier et al., 2009; Lindsay et al., 2005). In December 2004, the lake's water level dropped by ~8–10 m (Fig. 2C) and the temperature at the water's edge fell to <30 °C. This was followed by a period during which the hydrothermal activity and water levels fluctuated significantly over a period of approximately four months until normal activity resumed in late April 2005 (Joseph

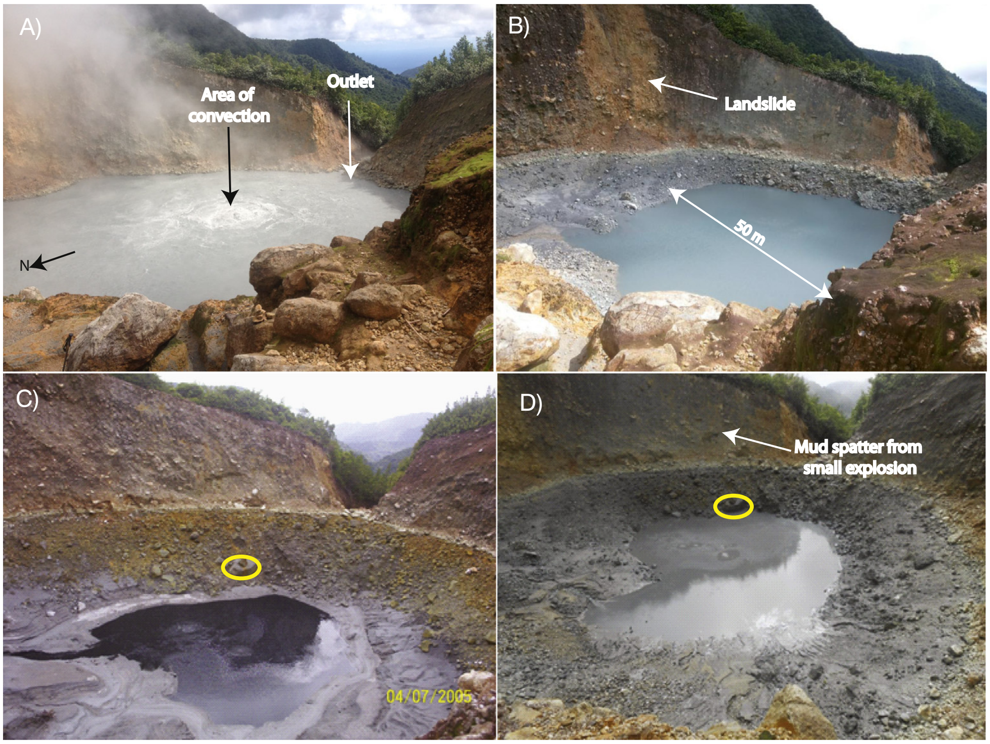

Fig. 2. A) View of Boiling Lake during normal activity displaying vigorous convection due to degassing. B) View of the Boiling Lake in November 2016, showing no convection and a lake level drop of several meters. Note the mud splatter on the flanks of the crater, hypothesized to be the result of a small explosion or phreatic eruption. C) View of the lake bed of the Boiling Lake on April 7, 2005 (Photo courtesy A. James), following the December 2004 lake draining event. D) View of the lake bed of Boiling Lake on November 17th, 2016 (photo courtesy of S. Durand), following the mid-November 2016 lake draining event. For comparison between the lake shore morphologies, a boulder embedded near the lake bottom has been circled in yellow.

et al., 2011). The most recent episode of instability was reported on November 8, 2016 (Fig. 2B) and lasted for a period of approximately six weeks before the lake resumed its normal activity (Durand, 2017). Mud spatter on the crater walls suggests that the drainage event was accompanied by a small mud-rich explosion (Fig. 2B) (Durand, 2016). The Valley of Desolation and Boiling Lake is a popular tourist attraction and concerns for public safety warrants that it is monitored closely for such changes in activity due to the potential risks of phreatic activity and the sudden fatal release of CO_2, as has been observed in the past (Bell, 1946; Elliot, 1938; Nicholls, 1880).

In this paper, new data on the chemical and isotopic composition of the hydrothermal systems of Dominica, including the first carbon isotope measurements, is presented as a component of the comprehensive volcanic monitoring program conducted on the island by the SRC. With updated and new geochemical and isotopic data from four hydrothermal areas (Penville 'Cold Soufrière', Watten Waven, Sulphur Springs, and Boiling Lake/Valley of Desolation) on the island for the period 2009 to 2017, we re-evaluate the characteristics of these systems, last reported in 2011, and compute revised reservoir temperatures using silica-based geothermometry. We also describe the temporal changes in the chemistry of the Boiling Lake and discuss implications for the evolution of the volcanic hydrothermal system and potential for future volcanic unrest.

2. Previous work

Dominica is made up of predominantly andesitic and dacitic volcanic rocks along with their weathered products (Lindsay et al., 2005; Smith et al., 2013). All of the seven volcanoes active in the last 100 ka are considered likely to erupt again, given the widespread geothermal activity and shallow seismicity (Joseph et al., 2011; Lindsay et al., 2003), as well as recent eruptive history (Frey et al., 2018). More than 30 geothermal and hydrothermal areas have been identified throughout the island and off-shore (Smith et al., 2013) and initial characterization of the most prominent hydrothermal fields was done by Joseph et al. (2011) and is summarized here. Hydrothermal activity at the Cold Soufrière, Morne aux Diables (MAD) in northern Dominica (Fig. 1C) manifests as vigorously bubbling pools and "frying pan" features with temperatures of 23 °C to 28 °C and strongly acidic pH of 1–2. These waters are Na-SO_4 type in composition. The lack of heat is a consequence of its location in a steep terrain, where the meteoric recharge is supplied to the hydrothermal system at a lower elevation than the area overlying the upflow zone (Bogie et al., 1987).

Hydrothermal activity in the Watten Waven/Micotrin center (Fig. 1D) manifests in the form of bubbling pools and hot/warm springs of Na-SO_4 type composition with temperatures up to 99 °C and pH values of 1–5 (Joseph et al., 2011). The Plat Pays Volcanic Centre in southern Dominica (Fig. 1) hosts the hydrothermal areas of Galion, Sulphur Springs (Fig. 1F) and underwater diffuse emissions at Champagne Springs. Hot springs of pH value 1–3 with Na-SO_4 type composition and low-temperature fumaroles (90–100 °C) are present in these areas. The fumaroles are particularly abundant at Sulphur Springs, with more than a dozen vents typically active. Hydrothermal fluid discharges in the Valley of Desolation (VOD) and Boiling Lake areas (Fig. 1E) are in the form of numerous hot springs, bubbling pools and fumaroles. Thermal waters in the VOD generally have temperature in the range 74 °C to 98 °C and pH values of 1 to 4, with a predominantly Na-SO_4 composition (Joseph et al., 2011). Acid-sulphate waters are likely derived from the CO_2-H_2S rich steam up-flow, generated by boiling of meteoric waters, which partially condenses and dissolves in shallow groundwater (Joseph et al., 2011).

The Boiling Lake exhibits prolonged periods of long-term depth stability with water temperatures of 80 to 90 °C, pH values 4–6 and highly saline ($Cl = 2000–6000$ mg/L, $SO_4 = 1500–4000$ mg/L, and $TDS = 6800–14{,}200$ mg/L) Ca/Na-Cl or Na-SO_4 waters (Fournier et al., 2009; Joseph et al., 2011; Lasne and Traineau, 2005). Percolation of hot gases occurs through the water and vigorous gas upwelling (predominantly H_2O, CO_2, and H_2S) takes place in the lake's center (Fig. 2A) promoting a continuous convection cell. During periods of short-term crises, the lake undergoes successive draining and refilling with neutral cool water (pH value 7, temperature of 18–21 °C) of Na-Cl type composition (Cl of 2274 mg/L and TDS 2817 mg/L). The source of the lake's chloride water is believed to be derived from brines from a deep-seated hydrothermal reservoir, which is diluted by meteoric water in the shallow aquifer (Joseph et al., 2011). Prefeasibility studies for geothermal exploration carried out in 2005 and 2008, also supported the existence of a high temperature (200–300 °C) geothermal reservoir with neutral sodium chloride waters in the areas of the Boiling Lake, with bicarbonate waters (Ca-Na-HCO_3 type and Na-HCO_3-SO_4 type) and acid-sulphate waters observed in the VOD (Lasne and Traineau, 2005; Traineau et al., 2008).

The lake is hypothesized to be suspended above the water table by the buoyancy of rising steam bubbles, during its normal steady state with periods of instability being attributed to external perturbations triggered by landslides and/or regional seismicity (Fournier et al., 2009). These perturbations result in a disruption to the uprising gas bubbles, causing the water of the lake to drain back down into the underlying aquifer to remain at the level of the natural meteoric water table. While direct sampling of gases from the central fumarole in Boiling Lake is not possible, Di Napoli et al. (2013) was able to use a Multi-component Gas Analyzer System (Multi-GAS) to measure the composition of the volcanic gas plume issuing from the lake. No notable SO_2 is present in the gases, confirming that there was no rapid oxidation of H_2S occurring in the plume. Plume characteristic ratios of CO_2/H_2S (5.2 ± 0.4) and H_2O/CO_2 (31.4 ± 6), with an air free calculated volcanic gas composition of ~96.3% H_2O, 3.1% CO_2 and 0.6% H_2S. These ratios are within the range of published gas compositions for more magmatically derived gases in the Lesser Antilles region, such as Soufrière of Guadeloupe (Allard et al., 2014; Brombach et al., 2000). These results support a volcanic derivation for the gases from the Boiling Lake, and only a marginal role played by interaction with lake waters (gas scrubbing).

The risk of a phreatic or phreatomagmatic eruption from the VOD/Boiling Lake is considered to be the most likely scenario for future volcanic activity on the island (Lindsay et al., 2005). Researchers recently conducted an investigation of the hydrothermal alteration of dacitic rocks in the VOD and its effect on degassing and phreatic eruption (Mayer et al., 2017). Their results show that alteration leads to a decrease in both strength and permeability of the rocks, as well as an increasing abundance of the clay mineral content. Alteration effects may in turn inhibit degassing at the surface, resulting in an increased potential for pressurization in the subsurface, which can lead to phreatic eruptions (Browne and Lawless, 2001; Montanaro et al., 2016). The possibility of these events occurring with little to no warning further increases the hazard potential of such eruptions from the VOD to people who may be in close proximity to the area.

3. Sampling and analytical methodology

Sampling of thermal waters from the hydrothermal areas described above took place during the period 2009–2017, with a total of 121 water samples collected for this study: 28 from the Penville Cold Soufrière, 35 from Watten Waven/Micotrin, 23 from Sulphur Springs, 26 from the Valley of Desolation, and 9 from the Boiling Lake (Fig. 1C–F). At each location, samples were collected for alkalinity, cation, anion, trace elements and isotope analyses. Water temperature, pH, pressure, conductivity, total dissolved solids, and salinity were measured in situ using a ProDSS Multi-parameter Water Quality Meter (YSI).

Water samples were filtered on site through a 0.20 μm cellulose acetate filter into 60 mL Nalgene™ HDPE sterile sample bottles for cation and anion analyses, as well as deuterium and oxygen isotope analyses and 50 mL polypropylene Falcon™ conical centrifuge tubes for alkalinity analyses. Samples for trace element analysis were acidified with 1–2 drops of 70% HNO_3. Raw water samples for carbon isotopes of DIC were collected in 12 mL Exetainer vials, poisoned with $HgCl_2$, and capped without headspace.

Ion concentrations were analyzed using Dionex Ion Chromatographs (ICS-2100, anions; DX-500, cations) at Union College. Anions were eluted with an AS19 column using potassium hydroxide as the eluent and the cations using a CS16 column and methanesulfonic acid. Multi-ion standards were prepared by pipetting appropriate volumes from single ion standards to analyze for F, ClO_2^-, Cl^-, NO_2^-, ClO_3^-, Br^-, NO_3^-, SO_4^{2-}, PO_4^{2-}, and Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, respectively. Four dilutions to this standard (1:2, 1:5 and 1:10) were made to calibrate the chromatographs over an order of magnitude change in concentration. Trace element analyses of acidified samples were performed using the Elan 6100 DRC quadrupole ICP-MS at Union College. Standard solutions of varying concentration were prepared by pipetting appropriate volumes of 1000 ppm single element standards into a 100 mL volumetric flask containing 7 mL of high-purity concentrated nitric acid and diluted to volume with 18.2 mOhm deionized water. One hundred microliters of 0.5 ppm internal standard solution containing Be, Ga, Y, In, Re, Bi, and Th was added to each blank, standard and sample tube for every 10 mL of sample volume. To check accuracy, the composition of a standard river water SLRS-6 was monitored several times during each run. In general for abundant elements such as Si (>1 ppb), our analyses match the reference concentrations within 5%.

Total alkalinity was analyzed based on methods described in Bouillon et al. (2012) using a MetrOhm 888 Titrando™ autotitrator and 869 compact sample changer with 0.1 mol/L HCl as titrant; reproducibility was typically better than ± 6 μmol kg^{-1} based on replicate analyses of an in-house standard. CO2SYS software (Lewis et al., 1998) was used to calculate DIC values using TA, pH, temperature, and salinity in conjunction with the thermodynamic constants outlined by Millero (1979).

Oxygen isotope values were measured on a Thermo Gas Bench II connected to a Thermo Delta Advantage isotope ratio mass spectrometer (IRMS) in continuous flow mode at Union College. For analysis, 0.5 mL of sample was transferred to a 12 mL Exetainer vial previously flushed with 0.5% CO_2 and was allowed to equilibrate for at least 24 h. Three in-house laboratory standards were used for isotopic corrections, and to assign the data to the appropriate isotopic scale using linear regression. These standards were calibrated directly to VSMOW (0.0‰) and SLAP (−55.50‰). The in-house standards have $\delta^{18}O$ values that range from −0.6‰ to −16.52‰. The combined uncertainty (analytical uncertainty) for $\delta^{18}O$ is $<\pm 0.06$‰ (SMW), based on internal tap water standards.

Deuterium isotopes were analyzed on a Thermo TC/EA (High Temperature Conversion Elemental Analyzer) at 1425 °C connected via a ConFlo IV to the same IRMS mentioned above. Each sample was analyzed six times by injecting 100 mL into the TC/EA using a CombiPAL autosampler. To remove the memory effect, only the last four analyses of each sample were averaged. Three in-house standards were used for isotopic corrections, and to assign the data to the appropriate isotopic scale using linear regression. These standards were calibrated directly to VSMOW (0.0‰) and SLAP (−427.5‰). The in-house standards have δD values that range from −4.5‰ to −121.4‰. The combined uncertainty (analytical uncertainty) for δD is $<\pm 1$‰ (VSMOW), based on internal tap water standards.

Samples for carbon isotopes of DIC were measured on the Gas Bench and IRMS mentioned above. For analysis, various amount of sample (based on DIC content) was added to pre-flushed 12 mL Exetainers with 20 μL H_3PO_4 (100%). Analysis and data correction followed Gillikin and Bouillon (2007) and Assayag et al. (2006). Solid reference standards (LSVEC, NBS-18, and NBS-19) were used for isotopic corrections, and to assign the data to the appropriate isotopic scale using linear regression. The following values were used for $\delta^{13}C$: LSVEC: −46.6‰, NBS-18: −5.014‰, and NBS-19: +1.95‰. The combined uncertainty (analytical uncertainty) for $\delta^{13}C$ is $<\pm 0.1$‰ (VPDB), based on NBS-19 standards.

Table 1
Temperature, pH and composition of major chemical species of the sampled hydrothermal waters from Dominica.

Site	Location	Date (m/d/y)	T (°C)	pH	Concentrations (mg/L)												
					Li	Na	K	Mg	Ca	SiO_2	F	Cl	Br	SO_4	HCO_3	NO_3	TDS
Mome aux Diablest	Eric's pool (MAD-5)	12/02/09	25	2.0	n.a.	36	8	7	26	n.a.	0.03	29	0.15	126*	0.00	n.a.	232
Mome aux Diablest	Eric's pool (MAD-5)	01/29/10	22	2.0	n.a.	23	8	4	5	n.a.	0.00	15	1.14	56*	0.00	n.a.	112
Mome aux Diables	Eric's pool (MAD-5)	04/10/13	17	4.0	n.a.	49	9	9	30	n.a.	0.03	30	0.05	168*	0.00	n.a.	295
Mome aux Diables	Eric's pool (MAD-5)	06/22/14	24	2.2	0.02	34	5	9	44	75	0.04	30	0.10	171*	0.00	0.00	368
Mome aux Diables	Eric's pool (MAD-5)	06/01/15	24	2.0	0.05	64	10	19	134	50	0.00	33	0.00	485*	0.00	0.31	796
Mome aux Diables	Eric's pool (MAD-5)	06/20/16	25	3.2	0.01	25	3	5	23	32	0.02	26	0.10	92*	0.00	0.02	206
Mome aux Diables	Eric's pool (MAD-5)	06/24/17	24	2.3	0.01	22	3	5	17	29	0.02	27	0.09	79*	0.00	0.09	182
Mome aux Diables	MAD-5.5	06/01/15	24	2.0	0.05	61	10	20	136	49	0.00	33	0.11	488*	0.00	0.01	797
Mome aux Diables	MAD-5.5	06/21/16	27	2.3	0.02	31	5	8	41	39	0.05	26	0.09	160	0.00	0.01	310
Mome aux Diables	MAD-5.5	06/24/17	24	2.2	0.01	22	3	5	17	29	0.02	26	0.09	72	0.00	0.05	174
Mome aux Diables	MAD-6	06/22/14	24	2.7	0.00	19	2	9	25	55	0.02	19	0.10	135	0.00	0.00	245
Mome aux Diables	MAD-6	06/01/15	23	2.3	0.00	25	3	13	37	32	0.03	23	0.12	162	0.00	0.15	295
Mome aux Diables	MAD-6	06/20/16	25	3.1	0.00	19	2	7	20	26	0.01	19	0.11	90	0.00	0.05	183
Mome aux Diables	MAD-6	06/24/17	24	3.1	0.00	17	2	6	16	23	0.01	19	0.11	73	0.00	0.01	156
Mome aux Diables	MAD-6.5	06/21/16	25	1.4	0.02	27	8	11	38	33	0.00	16	0.06	170	0.00	0.40	304
Mome aux Diables	MAD-6.5	06/24/17	24	1.4	0.01	18	6	8	25	24	0.00	13	0.05	110	0.00	0.03	205
Mome aux Diablest	Nancy's pool (MAD-7)	01/29/10	22	1.0	n.a.	18	12	5	8	n.a.	0.05	8	2.00	66	0.00	n.a.	119
Mome aux Diables	Nancy's pool (MAD-7)	06/22/14	25	5.1	0.00	17	2	6	9	24	0.02	27	0.15	41	6.34	0.03	129
Mome aux Diables	Nancy's pool (MAD-7)	06/01/15	25	4.9	0.00	19	2	6	9	30	0.01	28	0.18	26	20.49	0.01	140
Mome aux Diables	Nancy's pool (MAD-7)	06/20/16	25	5.1	0.00	18	2	5	9	27	0.01	27	0.00	38	6.57	0.00	128
Mome aux Diables	Nancy's pool (MAD-7)	06/24/17	24	1.5	0.00	18	6	8	25	29	0.00	13	0.00	109	0.00	0.00	209
Mome aux Diables	MAD-8	06/22/14	23	5.7	0.02	30	3	5	10	19	0.01	42	0.15	35	19.48	0.03	149
Mome aux Diables	MAD-8	06/01/15	23	5.2	0.07	71	7	9	21	24	0.01	91	0.40	65	51.98	0.25	302
Mome aux Diables	MAD-8	06/20/16	24	5.6	0.02	34	3	5	12	24	0.01	45	0.19	36	30.30	0.09	167
Mome aux Diables	MAD-9	06/22/14	23	3.9	0.01	19	2	5	10	34	0.02	26	0.08	49	0.00	0.02	145
Mome aux Diables	MAD-9	06/01/15	23	5.2	0.06	71	6	9	21	24	0.01	91	0.40	69	45.45	0.18	302
Glanvillia	Picard warm spring (PC-1)	04/10/13	47	7.0	n.a.	29	6	4	26	n.a.	0.00	30	0.42	0	127.38	4.02	148
Glanvillia	Picard warm spring (PC-1)	06/17/17	39	7.0	0.01	25	3	6	23	149	0.02	26	0.08	2	116.96	0.66	283
Micotrin	MI-4	06/24/14	26	7.3	0.01	14	2	6	30	29	0.10	7	0.00	15	127.32	0.28	154
Micotrin	MI-4	06/01/15	24	7.1	0.01	14	2	6	27	28	0.12	8	0.02	8	125.53	0.14	144
Micotrin	MI-4	06/19/16	25	7.1	0.01	14	2	5	29	29	0.09	8	0.02	9	125.16	0.29	147
Micotrin	MI-4	06/13/17	21	6.5	0.00	6	1	1	7	16	0.03	5	0.02	1	31.69	0.32	50
Micotrint	Micotrin warm springs (MI-5)	01/30/10	31	5.0	0.00	18	4	5	n.a.	n.a	0.04	12	0.07	35	7.580	n.a.	74
Micotrint	Micotrin warm springs (MI-5)	09/04/13	35	7.0	0.00	27	7	13	43	n.a	0.07	12	1.42	93	128.45	5.17	240
Micotrin	Micotrin warm springs (MI-5)	06/19/14	32	6.0	0.03	22	3	13	56	44	0.07	9	0.01	33	236.15	0.02	275
Micotrin	Micotrin warm springs (MI-5)	06/01/15	33	5.8	0.03	24	3	14	57	n.a	0.08	9	0.02	18	246.29	0.04	234
Micotrin	Micotrin warm springs (MI-5)	06/20/16	31	6.3	0.03	23	5	11	48	40	0.06	12	0.02	15	222.66	0.30	244
Micotrin	Micotrin warm springs (MI-5)	06/15/17	32	6.0	0.03	23	3	13	58	52	0.07	9	0.02	24	256.89	0.03	286
Watten Wavent	Yellow Pool (WW-4)	01/30/10	92	4.0	n.a.	28	8	6	21	n.a	0.08	10	0.17	119*	0.00	n.a.	368
Watten Waven	Yellow Pool (WW-4)	04/08/13	86	6.0	n.a.	14	6	4	17	n.a	0.20	12	n.a.	70*	0.00	0.20	123
Watten Waven	Yellow Pool (WW-4)	06/20/14	92	3.2	0.04	29	9	15	59	67	0.08	7	0.02	252*	0.00	0.00	438
Watten Waven	Yellow Pool (WW-4)	06/01/15	90	2.8	0.11	40	14	27	116	85	0.20	8	0.03	458*	0.00	0.01	748
Watten Waven	Yellow Pool (WW-4)	06/20/16	95	3.6	0.04	30	6	7	30	56	0.03	7	0.03	178	0.00	0.02	314
Watten Waven	Yellow Pool (WW-4)	06/15/17	78	3.7	0.02	17	5	7	33	38	0.03	7	0.02	221	0.00	0.06	328
Watten Waven	WW-4.5	06/01/15	26	6.5	0.01	18	4	11	32	28	0.04	11	0.01	80	80.00	0.16	209
Watten Waven	WW-4.5	06/20/16	31	5.5	0.02	14	3	9	33	34	0.02	7	0.04	107	33.96	0.01	212
Watten Waven	WW-4.5	06/19/17	26	3.8	0.01	8	2	3	11	23	0.01	7	0.02	66	0.00	0.02	120
Watten Waven*	Jan's pool (WW-5)	01/30/10	47	4.0	n.a.	22	47	6	22	n.a	0.10	10	n.a.	96*	16.480	0.17	203
Watten Waven	Jan's pool (WW-5)	04/08/13	86	6.0	n.a.	13	46	6	33	n.a	0.49	9	2.30	81*	41.80	n.a.	205
Watten Waven	Jan's pool (WW-5)	06/20/14	81	3.0	0.06	26	8	15	58	68	0.07	7	0.00	243*	0.00	0.02	357
Watten Waven	Jan's pool (WW-5)	06/01/15	69	2.8	0.10	38	13	27	112	103	0.21	9	0.04	442*	0.00	0.13	745
Watten Waven	Jan's pool (WW-5)	06/20/16	90	3.6	0.04	30	6	7	31	55	0.03	6	0.03	183	25.41	0.02	362
Watten Waven	Jan's pool (WW-5)	06/15/17	59	3.7	0.02	16	4	8	33	51	0.03	7	0.02	136	0.00	0.06	259
Watten Waven	River Blanc (WW-1)	06/20/14	28	7.7	0.01	14	3	7	22	22	0.04	7	0.00	41	76.25	0.18	141
Watten Waven	River Blanc (WW-1)	06/01/15	27	7.3	0.01	16	4	9	25	31	0.04	9	0.02	45	81.89	0.12	171
Watten Waven	River Blanc (WW-1)	06/20/16	27	7.5	0.01	14	3	7	25	31	0.03	7	0.02	42	78.67	0.16	158
Watten Waven	River Blanc (WW-1)	06/15/17	28	6.8	0.06	28	5	6	21	35	0.04	30	0.12	48	53.65	0.00	189
Trafalgar	TR-2	06/20/14	39	7.8	0.20	77	17	49	81	61	0.20	86	0.23	78	448.73	0.15	644
Trafalgar	TR-2	06/01/15	39	7.6	0.20	80	17	50	85	53	0.20	81	0.23	67	497.78	0.32	643
Trafalgar	TR-2	06/20/16	40	7.0	0.21	82	16	50	89	62	0.21	88	0.24	74	493.00	0.00	673
Trafalgar	TR-5	06/20/14	29	6.6	0.07	36	8	26	44	39	0.12	38	0.10	36	248.00	0.27	335
Trafalgar	TR-5	06/01/15	30	6.5	0.09	46	10	34	55	42	0.14	50	0.10	34	311.22	0.27	417
Trafalgar	TR-5	06/14/17	28	6.4	0.07	30	7	18	34	42	0.11	32	0.09	24	185.41	0.53	268
Sulphur Springs*	Nico's spring	01/30/10	83	2.0		95	11	n.a.	24	n.a.	1.01	98	2.01	123	0.00	0.07	354
Sulphur Springs	SS-4	06/24/14	97	6.4	0.22	181	15	104	183	150	0.19	8	0.00	1218	0.00	0.02	1859
Sulphur Springs	SS-4	06/01/15	60	2.7	0.21	198	13	102	225	139	0.33	5	0.00	1349	0.00	0.02	2032
Sulphur Springs	SS-4	06/20/16	97	4.2	0.02	33	4	15	47	48	0.16	12	0.04	255	0.00	0.06	414
Sulphur Springs	SS-4	06/13/17	91	6.6	0.29	161	6	147	187	n.a	0.00	3	0.01	1590	0.00	0.03	2094

Table 1 (*continued*)

Site	Location	Date (m/d/y)	T (°C)	pH	Concentrations (mg/L)												
					Li	Na	K	Mg	Ca	SiO_2	F	Cl	Br	SO_4	HCO_3	NO_3	TDS
Sulphur Springs	SS-1	06/24/14	39	6.3	0.16	144	13	56	138	107	0.05	200	0.80	592	0.00	0.03	1251
Sulphur Springs	SS-1	06/01/15	36	4.2	0.15	147	12	59	142	96	0.07	173	0.65	635	13.26	0.07	1265
Sulphur Springs	SS-1	06/20/16	42	2.8	0.16	135	11	66	151	115	0.16	130	0.54	1047	0.00	0.02	1656
Sulphur Springs	SS-1	06/13/17	42	3.7	0.15	115	8	54	119	105	0.06	104	0.44	701	0.00	0.04	1207
Sulphur Springs	SS-2	06/24/14	32	2.5	0.08	99	8	55	151	453	0.11	10	0.03	772	0.00	0.00	1549
Sulphur Springs	SS-2	06/01/15	29	2.4	0.11	145	9	75	190	105	0.00	10	0.03	1041	0.00	0.00	1575
Sulphur Springs	SS-2	06/20/16	36	2.5	0.05	63	4	39	117	103	0.29	11	0.04	551	0.00	0.03	888
Sulphur Springs	SS-2	06/13/17	36	2.7	0.07	82	5	43	123	164	0.19	13	0.04	619	0.00	0.01	1049
Sulphur Springs	SS-3	06/24/14	51	6.7	0.05	65	6	28	74	71	0.30	13	0.03	310	120.85	0.00	568
Sulphur Springs	SS-3	06/01/15	52	6.3	0.06	100	9	35	86	72	0.46	14	0.03	426	93.08	0.00	742
Sulphur Springs	SS-3	06/20/16	95	4.6	0.02	59	4	13	40	70	0.24	12	0.04	204	32.80	0.00	402
Sulphur Springs	SS-3	06/13/17	50	6.2	0.04	55	4	20	55	59	0.19	13	0.04	283	32.80	0.02	489
Sulphur Springs	SS-5	06/24/14	40	6.9	0.06	59	6	26	69	64	0.33	14	0.03	163	154.43	0.00	467
Sulphur Springs	SS-5	06/01/15	91	7.3	0.09	93	9	37	88	75	0.49	15	0.03	203	414.06	0.00	617
Sulphur Springs	SS-5	06/20/16	30	5.0	0.01	26	3	12	38	41	0.13	12	0.04	164	15.94	0.08	296
Sulphur Springs	SS-5	06/13/17	37	7.0	0.04	50	4	19	51	55	0.23	14	0.04	155	154.43	0.13	375
Sulphur Springs	SS-8	06/20/16	97	2.6	0.27	207	9	165	271	191	0.00	6	0.02	1725*	0.00	0.01	2575
Sulphur Springs	SS-8	06/13/17	76	3.5	0.13	162	9	128	0	168	0.19	9	0.04	832*	0.00	0.01	1309
Valley of Desolation*	Boiling Lake (VOD-5)	01/31/10	84	5.0	n.a.	169	187	19	0	n.a.	0.09	51	0.51	359*	0.00	0.00	786
Valley of Desolation	Boiling Lake (VOD-5)	04/11/13	82	7.0	n.a.	183	194	21	0	n.a.	1.72	342	4.06	164*	0.00	0.00	748
Valley of Desolation	Boiling Lake (VOD-5)	05/15/15	83	5.0	0.05	51	7	15	91	n.a.	0.10	234	6.59	71	0.00	0.00	476
Valley of Desolation	Boiling Lake (VOD-5)	06/21/15	82	3.5	1.85	2127	542	39	647	250	0.00	4627	15.43	51	0.00	0.00	8300
Valley of Desolation	Boiling Lake (VOD-5)	05/10/16	86	3.4	2.40	982	248	15	344	121	0.00	2344	6.56	71	0.00	0.06	4134
Valley of Desolation	Boiling Lake (VOD-5)	06/23/16	89	3.8	3.86	1585	391	19	564	178	0.93	3853	13.40	56	0.00	1.31	6665
Valley of Desolation*	Boiling Lake (VOD-5)	12/15/16	77	n.m.	n.a.	818	180	11	238	153	0.60	1807	5.40	82	0.00	0.00	3295
Valley of Desolation*	Boiling Lake (VOD-5)	01/10/17	82	n.m.	n.a.	1110	268	15	364	175	0.50	2586	7.30	71	0.00	0.00	4597
Valley of Desolation	Boiling Lake (VOD-5)	06/16/17	89	3.9	3.32	1104	299	19	345	159	0.48	1708	9.41	894	0.00	0.10	4542
Valley of Desolation*	Bubbling Pool 1 (VOD 4)	01/31/10	87	1.0	n.a.	31	13	9	7	n.a.	0.13	5	n.a.	110*	0.00	n.a.	175
Valley of Desolation	Bubbling Pool 1 (VOD 4)	04/11/13	84	6.0	0.00	25	8	10	16	n.a.	0.07	8	0.06	120*	0.00	0.00	187
Valley of Desolation	Bubbling Pool 1 (VOD 4)	06/21/15	74	2.2	0.08	51	10	90	194	137	0.00	3	0.01	922*	0.00	0.00	1408
Valley of Desolation	Bubbling Pool 1 (VOD 4)	06/23/16	90	2.2	0.03	26	11	32	112	150	0.00	5	0.02	443*	0.00	0.22	779
Valley of Desolation	Bubbling Pool 1 (VOD 4)	06/16/17	79	3.7	0.03	39	9	7	54	90	0.03	4	0.02	233*	0.00	0.01	436
Valley of Desolation*	Bubbling Pool 2 (VOD-2)	01/31/10	74	5.0	n.a.	29	8	9	31	n.a.	0.11	7	0.23	159	1.910	n.a.	244
Valley of Desolation	Bubbling Pool 2 (VOD-2)	06/21/15	93	6.0	0.01	25	5	13	42	53	0.03	5	0.01	168	34.20	0.00	311
Valley of Desolation	Bubbling Pool 2 (VOD-2)	06/23/16	88	2.5	0.14	111	21	50	238	186	0.00	6	0.06	991*	0.00	0.15	1604
Valley of Desolation	Bubbling Pool 2 (VOD-2)	06/16/17	99	3.2	0.04	67	13	16	96	128	0.04	5	0.02	427*	0.00	0.06	752
Valley of Desolation	VOD-3 (pool)	06/18/15	82	2.8	0.02	53	10	30	123	200	0.14	5	0.02	518*	0.00	0.45	939
Valley of Desolation	VOD-3 (pool)	06/20/16	93	n.m.	0.01	30	4	17	92	50	0.07	6	0.02	347	0.00	0.39	547
Valley of Desolation	VOD-3 (pool)	06/13/17	69	3.6	0.02	25	5	12	67	62	0.09	5	0.01	310	0.00	0.01	486
Valley of Desolation	VOD-7	06/18/15	41	6.5	0.03	40	6	18	50	58	0.08	11	0.02	218	52.00	0.00	402
Valley of Desolation	VOD-7	06/20/16	n.m.	n.m.	0.02	27	4	11	36	31	0.03	9	0.01	160	0.00	0.00	278
Valley of Desolation	VOD-7	06/13/17	40	6.6	0.03	32	5	12	37	46	0.03	13	0.01	166	0.00	0.02	311
Valley of Desolation	VOD-8	06/18/15	37	4.3	0.05	68	11	24	72	71	0.11	45	0.04	304	55.64	0.09	596
Valley of Desolation	VOD-8	06/20/16	37	6.3	0.04	48	7	18	56	53	0.05	26	0.03	238	41.14	0.06	446
Valley of Desolation	VOD-8	06/13/17	37	4.6	0.05	47	8	16	52	60	0.07	37	0.04	256	0.00	0.69	477
Valley of Desolation	VOD-11 (pool)	06/20/16	93	2.7	0.03	94	12	21	86	138	0.10	5	0.02	478*	0.00	0.07	835
Valley of Desolation	VOD-11	06/13/17	99	2.4	0.05	46	9	27	69	139	0.00	2	0.06	365*	0.00	0.02	658
Valley of Desolation	VOD-12	06/20/16	47	4.7	0.01	20	4	11	39	46	0.04	7	0.01	166	0.00	0.03	293
Valley of Desolation	VOD-12	06/13/17	49	3.9	0.01	20	4	11	39	49	0.04	8	0.01	194	0.00	0.04	325
Valley of Desolation	VOD-13	06/20/16	39	3.9	0.01	29	4	13	54	56	0.07	6	0.01	270	0.00	0.00	432
Trail to Valley of Desolation	VOD-1 (Breakfast River)	06/18/15	21	7.6	0.00	9	2	5	11	21	0.02	6	0.01	17	51.23	0.00	89
Trail to Valley of Desolation	VOD-1 (Breakfast River)	06/20/16	21	7.7	0.00	9	1	4	11	21	0.02	6	0.02	17	46.21	0.00	84
Trail to Valley of Desolation	VOD-1 (Breakfast River)	06/13/17	21	7.3	0.00	8	1	3	9	19	0.02	6	0.01	18	30.49	0.04	74
Inlet to Boiling Lake	VOD-6	06/18/15	21	3.9	0.00	11	2	5	20	26	0.04	6	0.01	97	0.00	0.07	167

n.a. = not analyzed.
n.m. = not measured.
* = corrected using the AquaChem groundwater software package.
‡ = wet season sample.

4. Results

The temperature, pH, and composition of major chemical species of the sampled waters are presented in Table 1. Stable carbon ($\delta^{13}C$), oxygen ($\delta^{18}O$) and hydrogen (δD) isotope data are shown in Table 2.

4.1. Chemical composition of waters

Hydrothermal waters of Dominica cover a wide spectrum of pH, temperatures and chemical composition. The pH of the waters ranges from acid to neutral (1–7.8). Surface temperatures range from ambient

Table 2
Stable carbon ($\delta^{13}C$), oxygen ($\delta^{18}O$) and hydrogen (δD) isotope data for hydrothermal waters from Dominica.

Sample	Date (m/d/y)	d^{13}C	d^{18}O water (VSMOW)	Corrected SD (VSMOW)
Valley of Desolation				
VOD-1 (Breakfast River)	06/18/15	-10.26	-2.51	-4.20
VOD-1 (Breakfast River)	06/20/16	-8.96	-2.51	-3.50
VOD-1 (Breakfast River)	06/13/17	-11.02	-2.50	-3.21
Bubbling Pool 2 (VOD-2)	11/17/02	N/A	-0.86	-3.44
Bubbling Pool 2 (VOD-2)	11/17/02	N/A	-0.83	-3.48
VOD-2	06/18/15	N/A	1.01	1.43
VOD-2	06/20/16	-3.86	7.52	20.50
VOD-2	06/13/17	-4.50	4.88	14.13
VOD-3 (pool)	06/18/15	-3.90	4.45	10.58
VOD-3 (pool)	06/20/16	-2.97	-0.49	0.20
VOD-3 (pool)	06/13/17	-4.19	-0.54	0.30
Bubbling Pool (VOD-4)	11/17/02	N/A	10.67	14.53
Bubbling Pool (VOD-4)	11/17/02	N/A	10.57	14.55
VOD-4	06/18/15	-3.88	9.10	17.91
VOD-4	06/20/16	-3.81	3.70	10.90
VOD-4	06/13/17	-4.06	1.48	3.79
VOD-7	06/18/15	N/A	-0.92	-5.27
VOD-7	06/20/16	4.91	-1.78	-2.90
VOD-7	06/13/17	2.49	-1.67	-3.29
VOD-8	06/18/15	N/A	-0.27	-3.82
VOD-8	06/20/16	-4.37	-1.34	-2.80
VOD-8	06/13/17	-11.06	-1.43	-2.94
VOD-11	06/20/16	-3.98	7.64	19.00
VOD-11	06/13/17	-4.14	6.53	16.11
VOD-12	06/20/16	-3.54	-1.52	-1.40
VOD-12	06/13/17	-5.60	-1.82	-2.57
VOD-13	06/20/16	-4.69	-0.60	1.10
VOD-13	06/13/17	-1.84	2.26	2.61
EHS VoD	11/17/02	N/A	-1.30	-4.48
EHS VoD	11/17/02	N/A	-1.29	-4.87
Boiling Lake				
Boiling Lake	11/17/02		6.05	6.46
Boiling Lake	11/17/02		6.00	7.36
VOD-5 (Boiling Lake)	05/01/15	N/A	7.98	12.05
VOD-5 (Boiling Lake)	06/01/15	N/A	8.60	13.05
VOD-5 (Boiling Lake)	06/20/16	-3.44	6.44	10.00
VOD-5 (Boiling Lake)	06/13/17	-3.64	4.73	6.14
Sulphur Springs				
Sulphur Springs	11/19/02	N/A	4.62	7.18
Sulphur Springs	11/19/02	N/A	4.60	6.96
SS 1	06/24/14	-5.34	-1.28	-6.50
SS-1	06/01/15	N/A	-1.11	-3.47
SS-1	06/20/16	N/A	-1.31	-5.00
SS-1	06/13/17	N/A	-1.71	-6.10
SS 2	06/24/14	-22.63	2.74	2.63
SS-2	06/01/15	N/A	4.46	8.43
SS-2	06/20/16	N/A	-0.13	-1.70
SS-2	06/13/17	N/A	2.11	2.72
SS 3	06/24/14	2.07	-0.93	-4.47
SS-3	06/01/15	4.01	0.58	-1.30
SS-3	06/20/16	-1.43	-0.87	-8.00
SS-3	06/13/17	-0.16	-1.22	-5.54
SS 4	06/24/14	-3.45	6.99	8.33
SS-4	06/01/15	-2.17	8.51	13.59
SS-4	06/20/16	-2.27	-2.18	-5.70
SS-4	06/13/17	-2.23	7.91	12.79
SS 5	06/24/14	1.51	-2.15	-6.01
SS-5	06/01/15	2.58	-1.51	-5.19
SS-5	06/20/16	N/A	-2.52	-6.60
SS-5	06/13/17	2.71	-2.52	-6.33
SS-6	06/01/15	-2.27	8.55	13.50
SS-8	06/20/16	-3.59	3.24	-3.20
SS-8	06/13/17	-2.14	6.18	8.36
Micotrin/Watten Waven				
MI-4	06/24/14	0.61	-2.30	-5.04
MI-4	06/01/15	-3.43	-2.22	-4.40
MI-4	06/19/16	2.08	-2.31	-4.20
MI-4	06/13/17	-6.04	-2.45	-3.14
MI-5	06/24/14	-2.09	-2.32	-4.48
MI-5	06/01/15	-2.03	-2.26	-4.05
MI-5	06/19/16	-2.72	-2.35	-4.20
MI-5	06/13/17	-2.15	-2.42	-4.30
TR-2	06/24/14	-0.08	-2.18	-6.85
TR2	06/01/15	-0.41	-1.97	-4.47
TR-2	06/20/16	-0.32	-2.15	-5.60
TR-5	06/24/14	-4.85	-2.04	-5.61
TR 5	06/01/15	-4.51	-1.98	-3.30
TR-5	06/20/16	-4.48	-2.14	-4.10
TR-5	06/19/17	-6.13	-2.13	-4.05
WW-1	06/24/14	-1.06	-2.25	-8.06
WW-1	06/01/15	3.67	-2.01	-2.85
WW-1	06/20/16	3.57	-2.19	-2.80
WW-1	06/19/17	1.10	N/A	-2.04
Yellow Pool (WW-4)	11/20/02	N/A	-1.47	-4.65
Yellow Pool (WW-4)	11/20/02	N/A	-1.46	-4.71
WW 4	06/24/14	-2.12	-0.47	0.85
WW-4	06/01/15	-2.74	1.09	7.06
WW-4	06/20/16	-2.52	0.19	4.70
WW-4	06/19/17	-2.27	-1.50	0.68
WW-4.5	06/01/15	-9.54	-1.62	0.00
WW-4.5	06/20/16	-1.36	-1.34	2.10
WW-4.5	06/19/17	-6.21	-1.51	1.19
Jan's pool (WW-5)	11/20/02	N/A	-1.62	-4.21
Jan's pool (WW-5)	11/20/02	N/A	-1.75	-4.79
WW 5	06/24/14	-3.25	-0.04	1.41
WW-5	06/01/15	-2.58	0.62	5.72
WW-5	06/20/16	-2.27	-0.06	3.40
WW-5	06/19/17	-2.33	-1.57	0.42
PC-1	06/17/17	-21.74	-2.23	-4.41
Morne aux Diables				
Eric's pool (MAD-5)	11/18/02	N/A	-2.57	-6.08
Eric's pool (MAD-5)	11/18/02	N/A	-2.55	-5.80
MAD 5	06/24/14	N/A	-2.54	-5.47
MAD-5	06/01/15	-4.63	-3.08	-2.03
MAD-5	06/21/16	-4.71	-2.58	-3.80
MAD-5	06/24/17	-5.06	-2.58	-4.23
MAD-5.5	06/01/15	-5.23	-3.04	-1.20
MAD-5.5	06/21/16	-5.14	-2.96	-2.30
MAD-5.5	06/24/17	-5.18	-2.53	-3.56
MAD 6	06/24/14	-4.71	-2.09	-3.84
MAD-6	06/01/15	-4.99	-2.08	-0.37
MAD-6	06/21/16	-4.81	-2.30	-1.70
MAD-6	06/24/17	-5.50	-2.30	-2.29
MAD-6.5	06/21/16	-4.81	-5.70	3.00
MAD-6.5	06/24/17	-4.98	-4.86	1.06
Nancy's Pool (MAD-7)	11/18/02	N/A	-4.37	1.29
Nancy's Pool (MAD-7)	11/18/02	N/A	-4.43	1.02
MAD 7	06/24/14	-8.86	-2.64	-4.26
MAD-7	06/01/15	-8.09	-2.21	-2.57
MAD-7	06/21/16	-7.61	-2.33	-3.00
MAD 8	06/24/14	-3.82	-2.46	-3.99
MAD-8	06/01/15	-2.75	-2.17	-3.02
MAD-8	06/21/16	-2.76	-2.41	-4.20
MAD 9	06/24/14	N/A	-1.93	-2.94
MAD-9	06/01/15	-3.50	-2.25	-3.01

to near boiling (17–99 °C). Total dissolved solids were low to high (TDS = 50–8300 mg/L), with overall higher concentrations found in the waters of Sulphur Springs (354–2575 mg/L) and the Boiling Lake (476–8300 mg/L). Most waters had relatively low concentrations of Na^+ (14–207 mg/L), with the exception of the Boiling Lake whose Na^+ concentrations were higher, ranging from 51 to 2127 mg/L over the monitoring period. Ca^{2+} concentrations for the sampled waters were also low (5–271 mg/L), with the Boiling Lake again having higher overall concentrations in the range 91–647 mg/L. K^+ concentrations for the hydrothermal waters were very low (1–47 mg/L), with the Boiling Lake again having higher concentrations in the range 7–299 mg/L. The waters were generally richer in SO_4^{2-} (1–1725 mg/L) and Cl (2–200 mg/L) than meteoric water, with water from the Boiling Lake having a higher range in Cl concentrations of 51–4627 mg/L than found in other areas. HCO_3^- values were very low (0–414 mg/L) with higher concentrations seen at Trafalgar Falls in the range of 185–498 mg/L.

Cl-SO_4-HCO_3 ternary plots are used to characterize and classify the waters from each location (Fig. 3). The hydrothermal waters of the Cold Soufrière (Fig. 3A) are predominantly acid-sulphate, with a few samples being more Cl-rich. Watten Waven (Fig. 3B) waters are acid-sulphate, with a few classified as steam-heated condensates due to higher bicarbonate. The Sulphur Springs (Fig. 3C) waters are all predominantly Na-SO_4 type steam heated/condensates. Waters from the Cold Soufrière had temperatures of 17 °C to 27 °C, and pH in the range 1 to 5.7. Water temperatures of Sulphur Springs ranged from 36 °C to 97 °C and pH from 2 to 6.9. The waters with the higher pH values contained black filamentous algae. Water samples from the main geothermal area at Watten Waven had temperatures in the range 47 °C to 95 °C, and pH values of 2.8 to 6.

In the wider catchments around the hydrothermal areas of the Cold Soufrière and Watten Waven/Micotrin (Fig. 1C–D), peripheral waters were sampled to compare their composition and assess potential hydrothermal input. The Picard warm spring in Glanvillia (Fig. 1) is associated with the MAD complex that also hosts the Cold Soufrière. The Picard warm spring has temperatures of 39 °C to 47 °C and pH of 7 with a Ca-Na-HCO_3 composition (Fig. 3A). Micotrin warm springs, River Blanc and the Trafalgar Falls are all associated with the Watten Waven/Micotrin complex and all reflect Ca-Na-HCO_3 type compositions. These peripheral waters show distinctly different chemical characteristics from hydrothermal waters in the same catchments and are more meteoric in character, likely due to dilution.

The hydrothermal waters from the VOD range in temperature from 37 °C to 99 °C and pH from 1 to 6.5, and display a Na-SO_4 type composition. The waters of the Boiling Lake show composition types of steam heated/condensates Na-SO_4 (Fig. 3D) with temperatures of 82 °C to 84 °C, and pH of 5 to 7 during the period 2010 to 2013. In June 2015, there was a notable increase in Cl concentrations from 234 to 4627 mg/L, with levels of SO_4 remaining at low concentrations (15 mg/L). The low SO_4 concentrations contrast sharply with the high SO_4 values (1830–4200 mg/L) from 2000 to 2003, prior to the lake draining event. The lake's water from 2013 to 2017 reflects a Na-Cl type composition, with temperatures of 83 °C and pH decreasing to 3.5. Unlike what was observed in the 2004 lake draining event, there was not a substantial change in composition during the period November to December 2016 when the lake experienced a six-week period of instability. The Breakfast River is the last major freshwater stream on the trail to the VOD/Boiling Lake and is used for geochemical and isotopic comparison with the hydrothermal data in this study (Fig. 1E). The water from Breakfast River has a Ca-Na-HCO_3 type composition (Fig. 3D) with the dominant cations of Ca and Na at very low concentrations of 9–11 mg/L and 8–9 mg/L, respectively. Bicarbonate concentrations are also low in the range 30–51 mg/L.

Fig. 4 shows a spider plot of the concentration of several main elements from each hydrothermal area in Dominica, normalized to local meteoric water (freshwater streams on the east coast of Dominica with no hydrothermal input). Breakfast River is also included for reference as a meteoric water source in relatively close proximity to a major hydrothermal area (VOD/Boiling Lake), which does not show evidence of significant hydrothermal input. It is observed that each hydrothermal area has its own distinct signature with respect to its chemical composition, with the Cold Soufrière (MAD) having the lowest concentration of elements measured. This is in keeping with its characterization as reflecting diffuse gas emissions through surface streams and pools of dominantly meteoric origin (stable isotope composition close to the GMWL), which are located high above the hydrothermal aquifer (Joseph et al., 2011). It can also be observed that the Boiling Lake shows a unique chemical composition that does not follow any of the trends in the chemical composition seen for any of the other hydrothermal areas, including the nearby Valley of Desolation. Concentrations for all elements, with the exception of Mg and SO_4, are much higher for the Boiling Lake than for any other monitored hydrothermal feature across the island. The composition of the Boling Lake in 2000 (dashed black line) is broadly similar to the composition in 2017 (black line), with the exception of SO_4, which decreases by more than an order of magnitude. Sulphur Springs shows a marked increase in Mg and Ca concentration in comparison to other hydrothermal areas.

Fig. 5 shows a time series, from 2000 to 2017, comparing pH with the concentration of total dissolved solids (TDS) for a representative water sample from each main hydrothermal area in Dominica. As a consequence of fluctuations in ion concentration due to seasonality, only samples from the dry season (April–June) have been plotted. In all areas but the Boiling Lake, the variation in TDS is predominantly controlled by the abundance of SO_4. At Boiling Lake, SO_4 dominates the TDS prior to the 2004 lake draining event, after which both Cl and SO_4 are the main contributors to TDS. Na and Cl are the predominant ions, reflecting the brine character of the lake (Fig. 3D), post 2004. For thermal waters of the Cold Soufrière (MAD-7, Fig. 5A), Watten Waven (WW-4, Fig. 5C), Valley of Desolation (VOD-2, Fig. 5E), and Boiling Lake (Fig. 5F), we see an inverse relationship between pH and ion concentration since 2000. The peripheral waters from the flanks of Micotrin (Fig. 5B) show little variation in pH (~6) or TDS and are only slightly warmer (31–33 °C) than local meteoric water. At Sulphur Springs (Fig. 5D), the sample shown (SS-4) is located at the steep slope of the main deposit. The pH and TDS fluctuate over time, but there is no apparent correlation, contrary to the observations at the other hydrothermal areas. SS-4 also shows significant fluctuations in temperature, from 97 °C when the water is close to neutral to 60 °C when the water is acidic.

4.2. Isotope geochemistry

The hydrothermal waters in Dominica exhibit a range in stable isotopic composition ($\delta^{18}O$, δD and $\delta^{13}C_{DIC}$) that is a function of the specific geothermal area and geothermal feature sampled. The values also show temporal changes since initial analysis in 2002. From June 2014 to June 2017, the overall range in $\delta^{18}O$ is from −5.70 to 9.10‰ and δD is from −8.00 to 20.50‰ (Table 2; Fig. 6), which is slightly broader than, but similar to the range measured by Joseph et al. (2011) in 2002. Because local streams are affected by evaporation, a local meteoric water line has not been established in Dominica and waters are compared to the global meteoric water line (GMWL). In previous work by Govender et al. (2013), a local meteoric water line ($\delta D = 7.79\ \delta^{18}O + 10.85$) was established for southwestern Puerto Rico, which experiences similar atmospheric conditions as Dominica. This local meteoric water line is very similar to the GMWL ($\delta D = 8.17\ \delta^{18}O + 11.27$) that is referenced in this study. The meteoric stream Breakfast River, is shifted ~1‰ lighter in $\delta^{18}O$ compared GMWL and has an isotopic composition of $\delta^{18}O = -2.5$‰ and $\delta D = -3.6$‰. The relatively high δD compositions of the meteoric waters in Dominica are a function of its low latitude and altitude.

The majority of samples from the Cold Soufrière (acid-sulphate composition, but low temperature ~25 °C) plot <1‰ more negative than the GMWL, but several of the vigorously bubbling pools show a negative $\delta^{18}O$ shift up to 5‰, atypical of hydrothermal systems (Fig. 6). In the Watten Waven region, samples that are predominantly bicarbonate, with some SO_4, from the warm springs draining Micotrin and the area around Trafalgar Falls, as well as the River Blanc, appear to be meteoric in origin, unaffected by degassing, evaporation or significant water-rock interaction and plot in a cluster along the GMWL (Fig. 6) and do not change year to year (Fig. 7A). In contrast, the acid-sulphate hot pools at Watten Waven display variation over time. In November 2002, samples plot on the GMWL as do samples from June 2017. The 2017 samples show ~5‰ heavier shift in deuterium along the GMWL. However, between 2013 and 2015 (all June samples), the Watten Waven pools display a positive isotopic enrichment, with a slope of 4.4. In 2015 when the isotopic composition is heaviest, the Watten Waven pools had their lowest recorded pH – 2.8, as well as highest amount of TDS, with Li, Mg, Ca, and SO_4 abundances more than twice as high as measured in other years.

Samples from the Sulphur Springs area span a broad chemical (Fig. 3C) and isotopic range (Fig. 6). The stagnant pool at the top of the cliff-side deposit has a meteoric isotopic signature, whereas the trail streams are slightly enriched in heavier isotopes compared to the GMWL. Significant isotopic enrichment (up to 8.55‰ for $\delta^{18}O$ and 13.5‰ for δD) is seen in several of the bubbling pools along the cliff-side deposits, as well as the stream at the base of the deposit (SS-2; Fig. 7B). Individual samples define linear arrays with an average slope of 1.85 and intercept the meteoric water line at −6‰ for δD and −6‰ for $\delta^{18}O$, analogous to the isotopic composition of most of the Dominica hydrothermal water samples. Like Watten Waven, the hotter samples ($T > 50$ °C) appear to be changing over time, along a linear array. In this case, the pools are becoming more isotopically enriched. Interestingly, the stream at the base of the deposit which drains the hot pools and steam vents does not show the same trend, with identical isotopic compositions in 2014 and 2017, but is relatively enriched in 2015 and is relatively depleted in 2016 along the same linear array.

The VOD acid-sulphate waters are also characterized by a broad range in stable isotopic composition (Fig. 6). For comparison, Breakfast River defines a trend parallel to the GMWL, with <1‰ negative $\delta^{18}O$, likely defining the local meteoric water line. The VOD streams located between the Valley of Desolation and Boiling Lake (Fig. 1E) have a very similar isotopic composition and show subtle shifts over the monitoring period. In 2015, the waters show a slight positive $\delta^{18}O$ shift of ~1‰ compared to the GMWL, but in 2017 the streams plot on the GMWL (Fig. 7C). One of the streams in the Valley of Desolation plots on the GMWL with the trail streams, whereas the other streams have slightly heavier $\delta^{18}O$ and δD. The hot bubbling pools in VOD are the most isotopically enriched waters in Dominica (>10‰ for $\delta^{18}O$ and >20‰ for δD). The hot pool data defines a slope of 2.6, which intersects the meteoric water line at the same isotopic composition as the trail streams. The isotopic composition of the pools is changing over time, but is becoming progressively more depleted, unlike what is observed at Sulphur Springs.

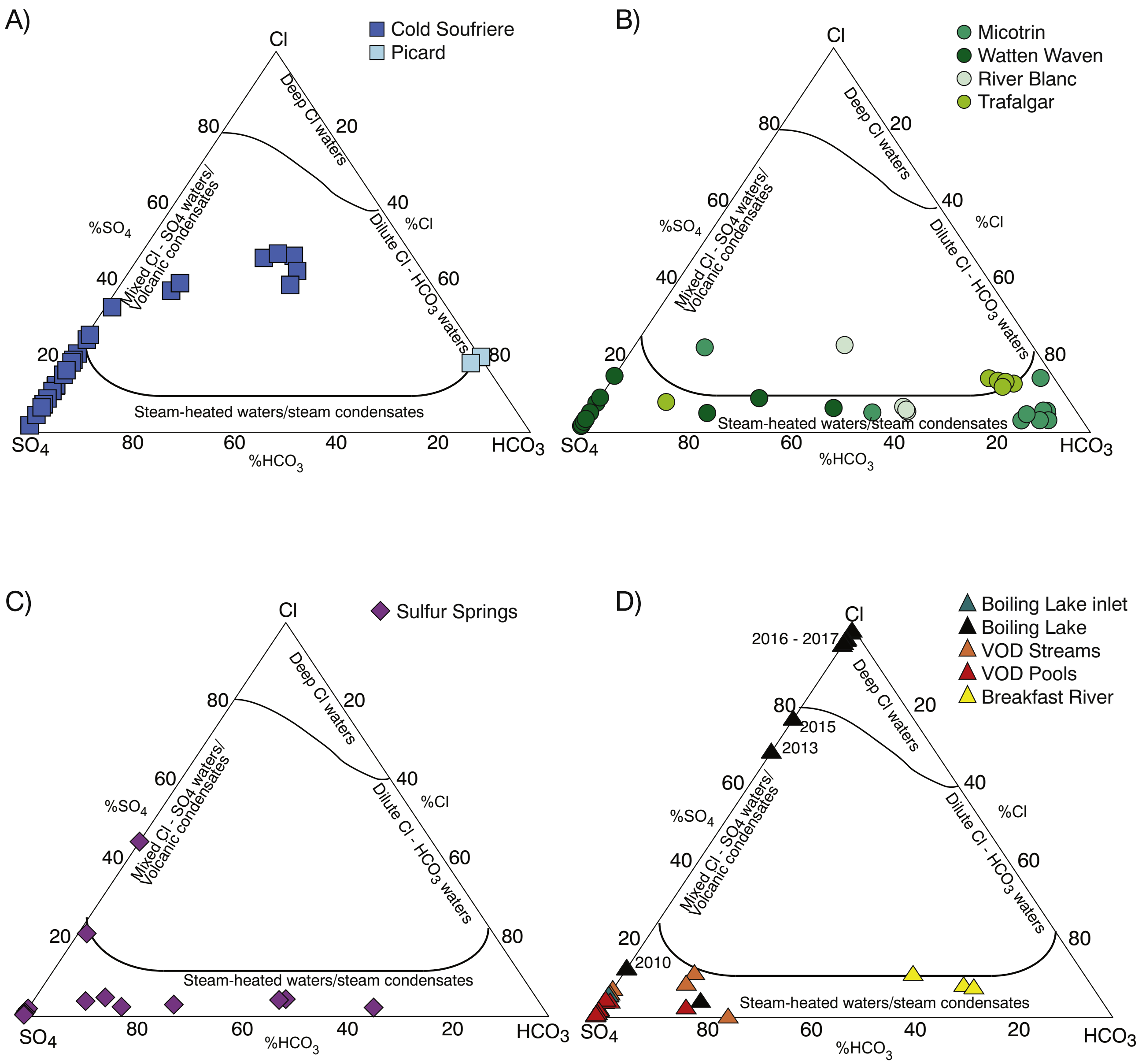

Fig. 3. Cl-SO_4-HCO_3 ternary diagrams for the four major geothermal areas display a variety of water types for the monitoring period 2009–2017: (A) northern Dominica – Cold Soufrière and Picard; (B) Watten Waven/Micotrin; (C) Sulphur Springs; and (D) Valley of Desolation/Boiling Lake.

One pool has values peaking at >10‰ for $\delta^{18}O$ and 14.5‰ for δD in 2002 and dropping by 8‰ for $\delta^{18}O$ and >10‰ for δD by 2017. Collectively, all features in the VOD area show a trend towards lighter isotopic values in the last few years compared to previous measurements.

Despite its Na-Cl composition since 2004, the Boiling Lake exhibits a similar slope (1.97) to the nearby acid-sulphate VOD pools (2.6). Boiling Lake waters did not record quite as extreme isotopic variations as the VOD pools, peaking at 8.6‰ for $\delta^{18}O$ and 13.05‰ for δD in 2015, before falling below 2002 levels in 2017 (Fig. 7C). The similarity in the isotopic composition of Boiling Lake in 2002, with its higher SO_4 concentrations and acid-sulphate composition, compared to 2017 with its Na-Cl water composition and much lower SO_4 content, is striking. Because the Boiling Lake isotopic compositions show a similar slope and are changing in a similar way to the Valley of Desolation pools, the cause of the isotopic enrichment is likely the same and *not* composition dependent.

Prior to this study, $\delta^{13}C_{DIC}$ had only been reported for 11 meteoric streams (Rivé et al., 2013) and six hydrothermal features (Pedroni et al., 1999) in Dominica. The meteoric streams have $\delta^{13}C_{DIC,}$ ranging from −14 to −10‰, whereas the fumaroles recorded −4 to −1.8‰. The waters sampled in the hydrothermal areas from 2014 to 2017 in this study display a broad range in $\delta^{13}C_{DIC,}$ from −11 to +5‰ (Table 2, Fig. 8). Unlike the deuterium-oxygen isotopic values, there is very little $\delta^{13}C_{DIC}$ year to year variation among samples from each hydrothermal area. In general, the vigorously bubbling hot pools in all locations, as well as the Boiling Lake, show a very restricted range of ~2‰ $\delta^{13}C_{DIC}$, with very similar values compared to the fumaroles (that are likely recording the most magmatic end-member) and differing slightly from site to site (Fig. 8). Water from pools in the Cold Soufrière are slightly isotopically lighter (−5.5 to −4.6‰) than the hot pools of VOD (−4.5 to −3.0‰) and Boiling Lake (−3.6 to −3.4‰). Hot pools at Watten Waven (−3.3 to −2.3‰) and bubbling vents at Sulphur Springs (−3.5 to −2.2‰) are slightly heavier, analogous to the fumarole gas measurements (Fig. 8).

Several of the streams in the hydrothermal areas have lighter $\delta^{13}C$ values (−4 to −11‰) than the pools and fumaroles, suggesting mixing with sources of lighter, biogenic $\delta^{13}C$ in addition to magmatic gases. However, several of the streams also have significantly heavier $\delta^{13}C_{DIC}$ than the fumaroles or bubbling pools, documenting positive $\delta^{13}C_{DIC}$ shifts up to +5‰. These streams have a higher pH (6.2–7.7) and are classified as bicarbonate waters, often depleted in SO_4, compared to nearby geothermal features. Most strikingly, the water in several of these features appears black in color due to a filamentous algae-like substance in the water.

4.3. Geothermometry

The Na, K, Mg ternary diagram of Giggenbach (1988) can be used to discriminate mature waters (waters that have attained equilibrium with a primary silicate host lithology), thus providing indications of the suitability of the waters for the application of cation geothermometry for estimating reservoir temperatures. It can also help to identify immature waters, waters affected by mixing with shallow waters or re-equilibration along their circulation path and other shallow effects. The resulting Na, K, Mg equilibrium diagrams for geothermal waters of the Cold Soufrière, Sulphur Springs and Watten Waven/Micotrin (Fig. 9) show that the waters plot in the immature waters field, indicating that these fluids have not attained equilibrium with the host rocks and the use of cation geothermometers are not suitable for estimating aquifer temperatures. This is consistent for thermal waters of these areas sampled over the time period 2000 to 2006 (Joseph et al., 2011).

Thermal waters of the VOD (Fig. 9) also plot in the immature waters field reflecting a lack of equilibrium with the host rocks. This is the same tendency observed in earlier years of monitoring (Joseph et al., 2011). However, the water of the Boiling Lake has reflected changes in maturity over the more recent monitoring period, moving from an immature state in 2010 towards partial maturity in 2017 (Fig. 9). It is noted that changes towards partial maturity occurs when the water composition is more Na-Cl type in character and more representative of the fluids from the deeper brine, as compared to Na-SO_4 that is more characteristic of the shallow hydrothermal aquifer. This pattern of activity has also been observed from previous monitoring data.

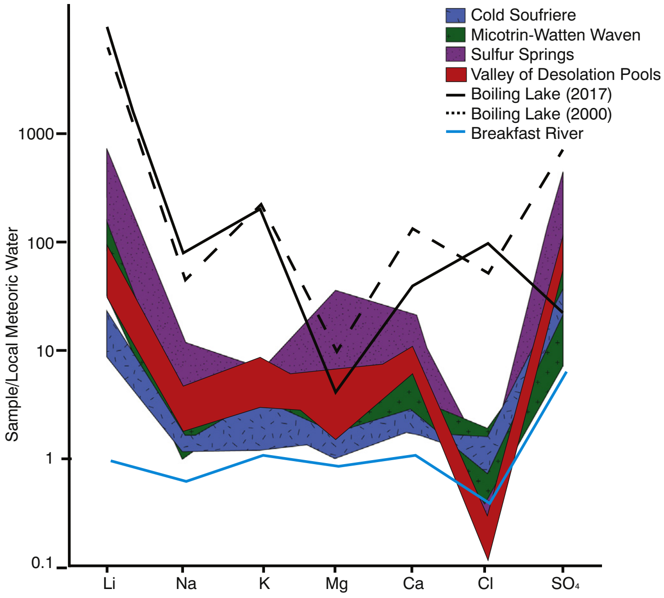

Fig. 4. A spider plot of the major ions in the Dominica hydrothermal waters (2017) normalized to average meteoric water from eastern Dominica shows the enrichment of most ions compared to local meteoric water and a distinct chemical signature for each hydrothermal area, particularly Boiling Lake. The composition of Boiling Lake in 2000 (dashed line) shows a significantly higher SO_4^{2-} concentration compared to 2017.

We employ silica-based geothermometers (see equations in Table 3), which provide a useful alternative for comparing potential changes to the reservoir temperatures over time (Taran et al., 2008). Acidic hydrothermal waters in this type of volcanic setting are partially equilibrated with Al-silicate alteration minerals at temperatures close to quartz temperatures. As a result, quartz geothermometers (quartz and quartz-steam loss; Fournier, 1977) are used to obtain inferred temperatures of equilibrium for the hydrothermal waters from the various geothermal systems across the island (Table 3). It should be noted that silica geothermometry can be affected by precipitation of the dissolved silica and/or dilution by relatively cold shallow aquifers of the thermal fluids during ascent to the surface, thereby leading to an underestimation of equilibrium temperatures (Tassi et al., 2010). For this reason, the quartz derived equilibrium temperatures for the geothermal reservoirs should be interpreted as minimum temperatures. However, there is no more suitable thermometer for immature waters. Subsurface equilibrium temperatures of 70 °C–122 °C are calculated for the Cold Soufrière, which is similar to previously reported silica thermometry temperatures of 101–102 °C (Joseph et al., 2011). It was found that equilibrium temperatures for Watten Waven have increased from 83 to 90 °C to 89–139 °C, whereas Sulphur Springs shows an increase in temperature range from 145 to 152 °C to 93–243 °C. Equilibrium temperatures of 81–180 °C was obtained for the VOD, for which no previously reported quartz temperatures are available. The Boiling Lake had equilibrium temperatures of 154–196 °C, generally consistent with previously reported temperatures of 187–203 °C (Joseph et al., 2011). The change in chemical composition of the Boiling Lake to a more Na-Cl water type during the period 2015 to 2017 suggests that the Na/K geothermometer (Fournier, 1979), used for calculating equilibrium for mature waters, may be useful for interpreting reservoir temperature for this feature. Na/K geothermometry calculated for samples

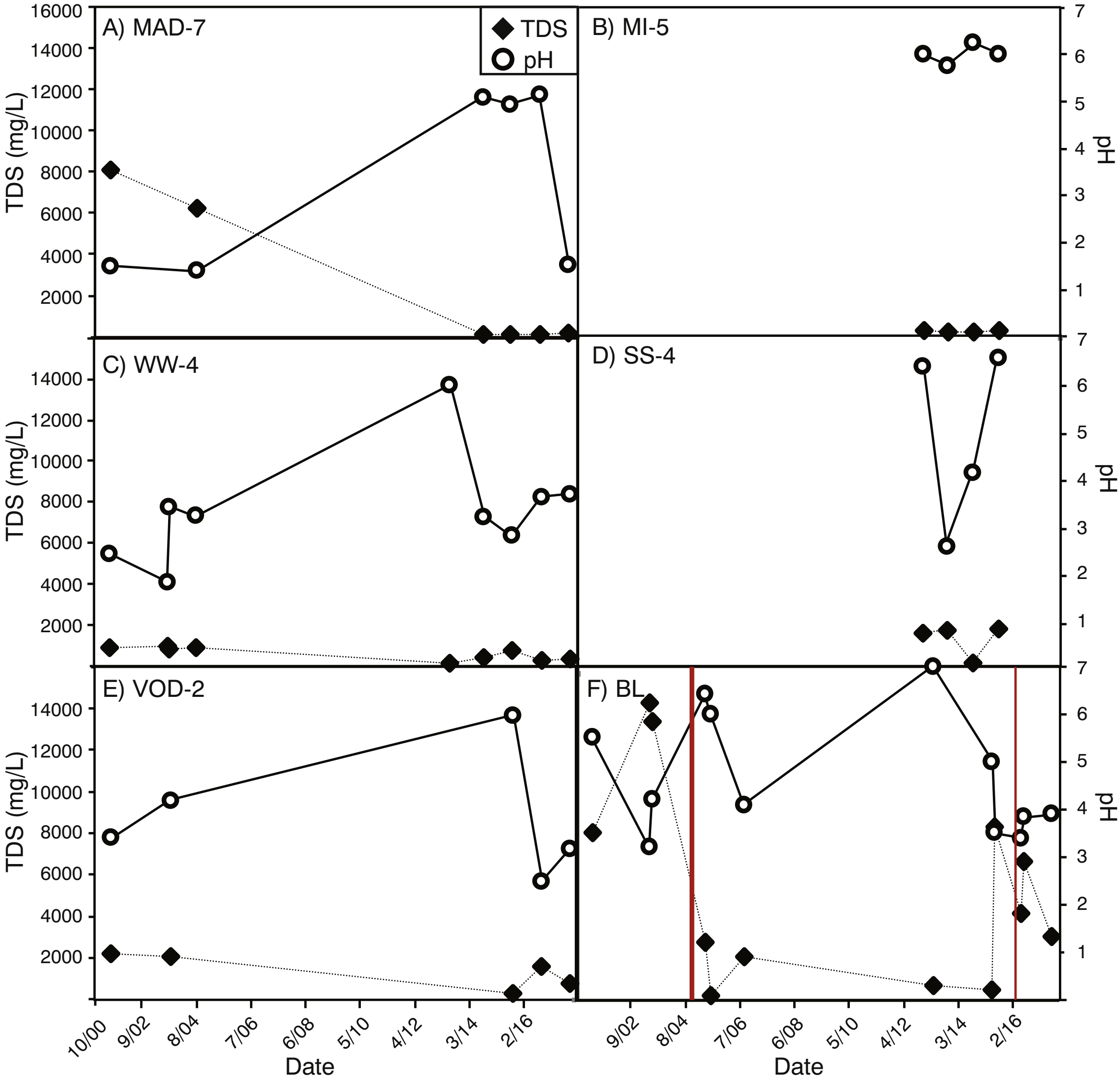

Fig. 5. Plot of pH and TDS (total dissolved solids) for representative samples from 2000 to 2017. There is a strong inverse correlation seen in MAD-7 (A), WW-4 (C), VOD-2 (E), and Boiling Lake (F). The samples from Micotrin (B) and Sulphur Springs (D) do not show the same pattern. The red lines in (E) correspond to the lake draining events.

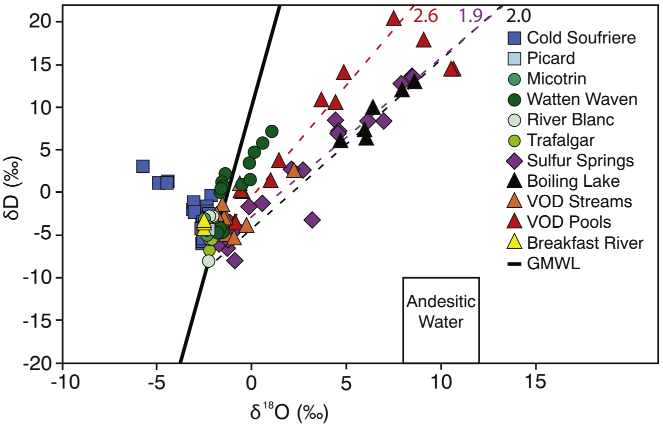

Fig. 6. δD vs. δ^{18}O plot for hydrothermal waters of Dominica, with respect to the global meteoric water line (GMWL) and the composition of andesite waters (Taran et al., 1989). The hydrothermal waters are primarily of meteoric origin. Several Cold Soufrière waters reflect low temperature exchange with CO_2. Many of the high temperature samples likely experienced varying degrees of surface evaporation and/or mixing with steam from a deeper boiling reservoir (Sulphur Springs, Valley of Desolation, Boiling Lake) and slopes of dashed lines are indicated.

collected during this period indicate higher equilibrium temperatures of 295–320 °C.

5. Discussion

5.1. Insights from the geochemistry of the hydrothermal waters

The inverse relationship observed between pH and TDS for thermal waters of the Cold Soufrière, Watten Waven and Valley of Desolation (Fig. 5) is in response to the concentrations of the dominant anion SO_4^{2-} (and/or Cl^-, as is the case for the Boiling Lake). The apparent lack of correlation between pH and TDS at Sulphur Springs, as compared to the other areas on Dominica, could be attributed to the ephemeral nature of the water features sampled in this much drier hydrothermal field. The main deposit at Sulphur Springs is an un-vegetated steep slope (~20°) that is subject to frequent slumps and landslides during high precipitation events, so the location of the surface vents and pools is dynamic. Thus, many of the surface pools and streams sampled at Sulphur Springs are small and short-lived features with much more localized variation in chemical composition due to the seasonal variability of rainfall and groundwater. While attempts were made to consistently sample the same features during each field season, it was more

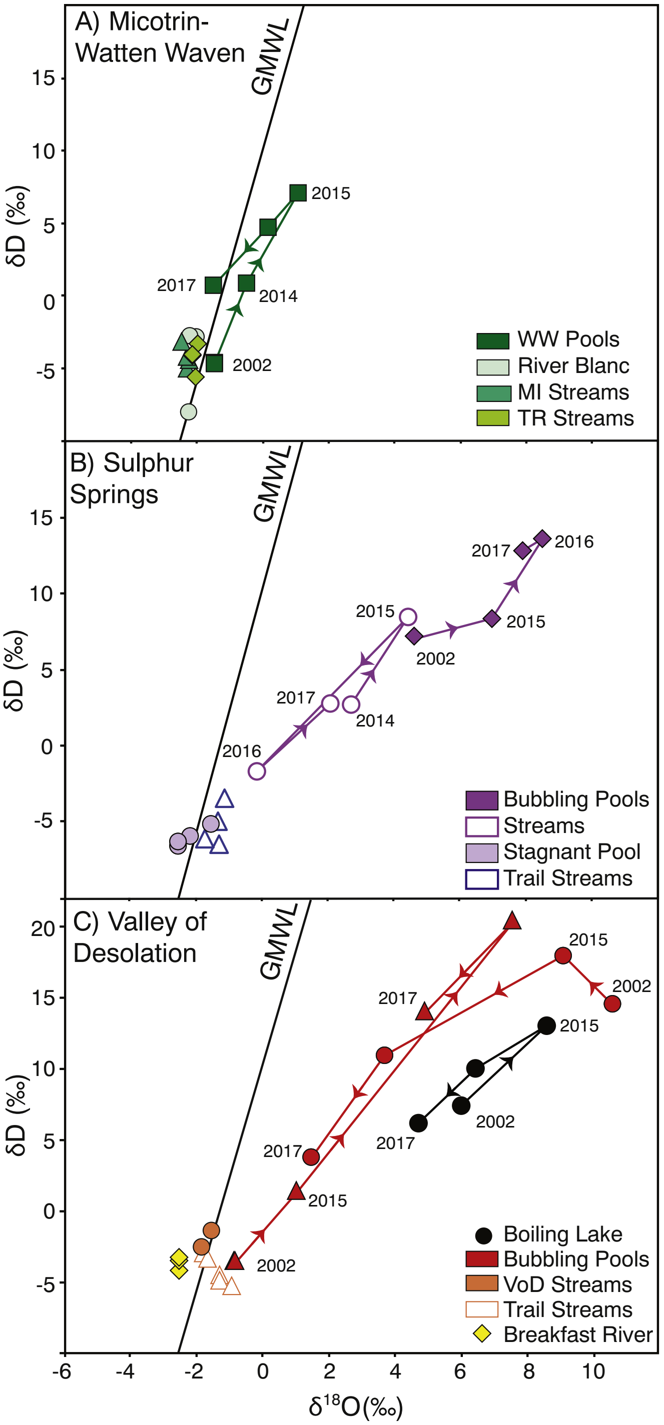

Fig. 7. δD vs. $\delta^{18}O$ plot for individual hydrothermal waters of Dominica display variation from 2002 to 2017. Colors indicate different features as shown in the legend and different symbols are indicative of individual samples. In general, the streams have a meteoric signature, whereas pools reflect dynamic processes. A) The bubbling pools of Watten Waven were isotopically heaviest in 2015, but then experienced a negative δD and $\delta^{18}O$ shift. B) At Sulphur Springs, several of the pools display a trend towards isotopically heavier signatures over time. C) In contrast, bubbling pools from the Valley of Desolation and Boiling Lake appear to be becoming less enriched with time and more meteoric-like.

challenging to do this at Sulphur Springs compared to the other hydrothermal areas on island, which exhibit more long-lived permanent features. The near-neutral pH values recorded during the sampling period at SS-4 may be a consequence of sample location or increased acid neutralization by mineral-fluid interactions which is supported by the higher concentrations of Mg observed at Sulphur Springs. The Cl concentrations are very low (<12 mg/L), so a more neutral deeper Na-Cl brine contribution is not viable. Another potential source of the neutral waters is extremophile microorganisms. The Sulphur Springs locations which have near neutral pH are classified as bicarbonate waters and uniquely feature black filamentous-like algae. In similar studies, extremophile microorganisms like algae have been found in hydrothermal waters (e.g. Coman et al., 2013; Stetter, 1999). These extremophiles likely exhibit chemo-lithoautotrophic mode of nutrition, using inorganic redox reactions to serve as energy sources and H_2 and CO_2 to build up organic cell material (Stetter, 1999), thereby affecting the water chemistry. The diversity of microorganisms that can inhabit sulphuric-acid-buffering springs is limited and previous work demonstrated that a high concentration of crenarchaeol bacteria in hot springs correlated to an increased pH in the spring (Costa et al., 2009). In Dominica, other areas with the black organic material (VOD-7 eastern hot springs and MI-4) all have pH >6.5 and $\delta^{13}C_{DIC}$ >2‰.

The predominantly steam heated Na-SO_4 type water compositions of the thermal springs of the Cold Soufrière, Sulphur Springs, Watten Waven and the VOD are generally formed as a result of the near-surface oxidation of magmatic H_2S to H_2SO_4 in shallow ground waters (Joseph et al., 2011; Rouwet et al., 2009; Taran et al., 2008). The chemical composition of these immature waters is thought to be a result of the complex processes of mineral-water equilibration-re-equilibration on different levels between the aquifer and the surface, with variable amounts of dilution by meteoric water as a major contributing factor. This is reflected in the distinct chemical signatures from each hydrothermal system, as seen for the thermal waters (Fig. 4). The higher chloride content in the Ca-Na-Cl waters of the Valley of Desolation area, supports the concept of a Cl-rich magmatic contribution that is more representative of a deep parent water, as proposed by Joseph et al. (2011).

The modest enrichments in most cations and anions at the Boiling Lake as compared to other hydrothermal waters of Dominica (Fig. 4), could be a result of increased leaching of the host dacites by acid condensates (Bernard et al., 2004; Giggenbach, 1991) or reflect continuous evaporation of water at high temperature, with limited meteoric water recharge. However, the most notable characteristic of the lake's chemistry is that, unlike any of the other hydrothermal areas, the thermal water shows temporal changes in composition between the spectrums of Na-SO_4 and Na-Cl (Figs. 3D, 4). This range in temporal compositions can also be seen from previous monitoring data (Joseph et al., 2011) and is indicative of a significant hydrothermal fluid contribution (deeply-sourced brine aquifer), partially mitigated by the presence of solute from a shallower acid-sulphate hydrothermal aquifer. We propose that the balance between the contributions from these two distinct hydrothermal sources fluctuates over time and results in changes in the overall chemical composition of the lake's water at the surface. This is similar to the effects seen at the crater lake of Kelud volcano in Java, Indonesia where a deep system of neutral alkali-chloride fluids at high temperature (250 °C) and a shallow Ca/Mg-SO_4 aquifer at lower temperature both feed the volcanic lake (Bernard and Mazot, 2014). Other volcanic lakes exhibiting analogous geochemical characteristics to the Boiling Lake include El Chicòn, Mexico (Rouwet et al., 2008) and Mt. Pinatubo, Philippines after the 1991 eruption (Stimac et al., 2004). The thermal waters of both of these crater lakes also show influences from two aquifers; a shallow acid-sulphate aquifer and a deeper near-neutral saline aquifer, feeding the lakes.

At Kelud volcano the 1990 eruption cleared the vent beneath the lake and allowed the ascent of the deep Na-Cl fluids towards the surface. For the Boiling Lake, we propose that the main mechanism regulating the exchange between the two hydrothermal sources is a temporal variation in the porosity and size of the fractures of the conduit beneath the lake. Earthquake-induced static strain is believed to affect the porosity and size of the fractures in the conduit of the Boiling Lake conduit extending to considerable depths (Feuillet et al., 2011). This mechanism

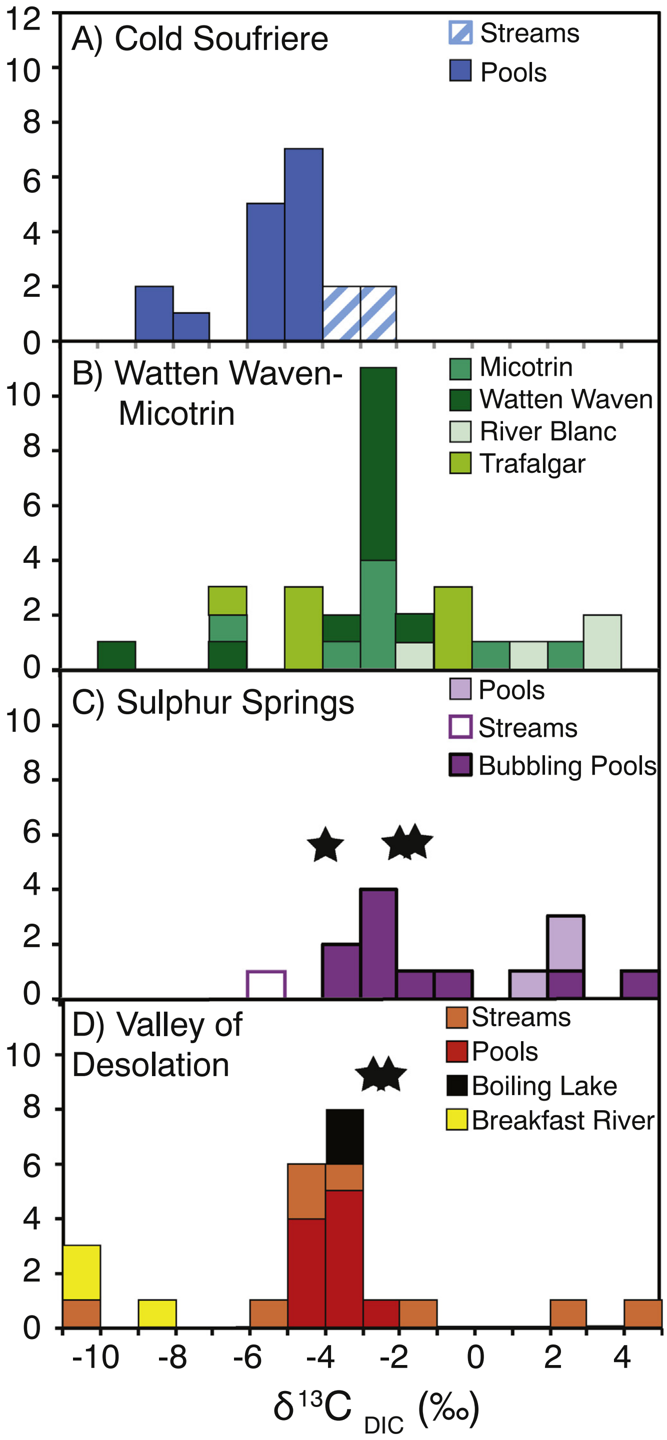

Fig. 8. Values of $\delta^{13}C_{DIC}$ for hydrothermal waters (this study) are shown as bars and fumaroles are denoted as stars (Pedroni et al., 1999). A) The pools of the Cold Soufrière are isotopically lighter than the streams. B) The pools at Watten Waven have a restricted range of $\delta^{13}C_{DIC}$ at −3‰, whereas the streams are quite variable. C) Most of the waters associated with hydrothermal vents at Sulphur Springs have very similar $\delta^{13}C_{DIC}$ compared to the fumaroles, with a few exceptions discussed in the text. D) Boiling Lake and most pools in the Valley of Desolation have similar $\delta^{13}C_{DIC}$ compared to the fumaroles in the Valley, with a few outliers, including Breakfast River, the meteoric stream and a stream draining the eastern hot springs of VOD.

is also thought to play a role in the draining and refilling of the lake during periods of instability, as seen during the lake crisis on 25 December 2004, following a 6.3 Mw regional earthquake on 21 November 2004. Opening and closing of these cracks could allow for the increased brine upflow, or the brine sealing off, from the deeper reservoir into the shallower sulphate dominant hydrothermal aquifer.

5.2. The Boiling Lake 2016 "crisis"

The episode of instability reported on November 8, 2016, was not associated with any known regional seismicity as compared to the lake draining event of December 2004. However, evidence provided from photographs taken of the lake (Fig. 2B) as well as observations provided by local tour guides and staff of the Forestry Division of Dominica (Durand, 2016), have indicated a fairly recent moderate-sized landslide took place at the lake, prior to the draining that was observed on November 8, 2016, with material from the sides of the crater slumping into the lake and partially covering the lake bed. The differences in morphology of the lake bed can clearly be seen from photographs taken of the 2004 and 2016 draining episodes (Fig. 2C–D). The overall visible effects of the landslide into the lake appear to be a filling-in of the lake bed and a gentling of the slopes of the walls of the lake. Lack of any regional or local seismicity and evidence of the recent landslide suggests that this may have be the "trigger" of this particular event, as compared to the earthquake-triggered December 2004 event. The proposed landslide mechanism resulted in a more short-lived period (six weeks) of instability at the lake in 2016, as compared to a much longer duration (~six months) seen in the December 2004 to May 2005 event. The possibility of a sufficiently large perturbation inside the lake, such as a landslide, causing the lake to drain was proposed by Fournier et al. (2009) following their modelling of the lake dynamics. They proposed that the geometry of the lake-conduit system provides a mechanism for instability with a denser liquid lake overlying a bubbly fractured permeable conduit. The downward flow of bubble-free water into the vent can vertically displace steam bubbles, following a sufficiently large perturbation inside the lake, causing downward flow of bubble-free water into the vent that vertically displaces the steam bubbles. If this increased flow is faster than the ascent speed of the fastest bubbles, all bubbles will be forced downward and the total upward drag force will be reduced as the bubbles compress causing the lake to drain.

5.3. Constraints on origins of the hydrothermal waters from stable isotopes

The hydrothermal waters of Dominica are predominantly of local meteoric origin (Fig. 6), but several have been affected by boiling/degassing, evaporation, and water-rock interaction, as described below. Samples from the Cold Soufriere are the only ones to exhibit a negative ^{18}O shift relative to the meteoric water line. Joseph et al. (2011) attributed the negative shift to either ^{18}O exchange between the thermal waters with dissolved CO_2, which is the dominant gas in the system, or low temperature mineral dissolution and secondary minerals precipitation. However, the alteration minerals found at the Cold Soufriere do not include clays (Smith et al., 2017), which tend to absorb heavy oxygen (Taran et al., 1998), so mineralization at the surface is unlikely to be responsible for the negative ^{18}O shift observed. However, mineralization at depth is still a possibility. Interestingly, the negative ^{18}O shift has become less pronounced over time, with samples plotting closer to the GMWL, perhaps indicating a decrease in CO_2 flux.

In the other hydrothermal areas, most waters are either very similar to meteoric water or display positive linear arrays, with a slope of ~1.9 to 2.6. The samples that deviate from the GMWL and form these trends are typically hotter ($T > 70$ °C) and have been classified as acid-sulphate, except for the Boiling Lake. In other systems, positive isotopic enrichment of hydrothermal waters has been attributed to (1) water-rock interaction (Craig, 1963), (2) mixing of meteoric groundwater with high temperature "andesitic-waters" from depth, (Giggenbach, 1992; Taran et al., 1989); and (3) evaporation at the surface or subsurface (Giggenbach and Stewart, 1982), or some combination thereof. In Dominica, the first two possibilities are unlikely. Water-rock interaction results in a positive ^{18}O enrichment, with virtually no change in

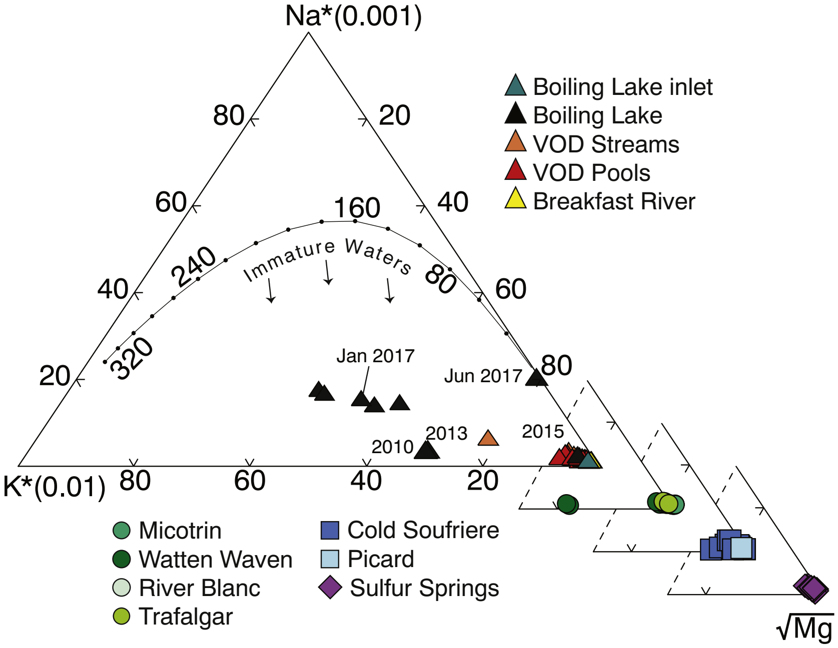

Fig. 9. Na-K-Mg equilibrium diagrams (from Giggenbach, 1988) for hydrothermal waters for the period 2009–2017. With the exception of several samples from the Boiling Lake, all waters are immature and therefore not in equilibrium with the host rock. The water immaturity precludes the use of cation reservoir thermometers and silica thermometers are used.

deuterium composition due to the high concentration of oxygen in rocks compared to hydrogen, as noted by Craig (1963). The positive slopes recorded by the Dominica hydrothermal waters preclude this process as a primary driver. The possibility of a significant component of isotopically enriched magmatic fluids (Fig. 6) is also unlikely, given the much higher δD values in the Dominica waters; a mixing line between the “andesitic waters” field and the GMWL would not adequately explain the linear trends observed. In addition, because the hypothesized “andesitic waters” are derived from seawater, they typically contain a high Cl concentration. All of the Dominica waters have concentration of Cl < 100 mg/L, with the exception one stream at Sulphur Springs (100–200 mg/L) and Boiling Lake (>2000 mg/L). Magmatic fluid contributions may still play some role in Dominican waters, but such contributions must be minor enough to be masked by dilution with meteoric water and/or overshadowed by the effects of evaporation.

The enrichment in both $\delta^{18}O$ and δD is most likely caused by evaporation. Craig (1963) observed slopes of ~3 in acidic geothermal waters and attributed it to non-equilibrium evaporation of steam at elevated temperatures. Giggenbach and Stewart (1982) showed that surface evaporation from steam-heated pools yielded a slightly steeper slope of 3.6. Subsequent work has demonstrated and quantified the effects of humidity on isotopic enrichment, particularly in lakes (e.g. Gibson and Edwards, 2002; Varekamp and Kreulen, 2000), and slopes of 3–5 are generally attributed to surface evaporation effects.

The slightly shallower nature of the Dominica isotopic enrichments (slopes of 1.9 to 2.6) suggests that surface evaporation alone cannot explain the trend. Similar shallow slopes in acid-sulphate pools in Sulphur Springs, St. Lucia (1.4; Barrett and Joseph, 2018), Poas, Costa Rica (1.0–1.9; Rowe, 1994) and Wairakei, New Zealand and El Tatio, Chile (1.5–1.6; Giggenbach and Stewart, 1982) were explained by the contribution of D-depleted steam from high temperature boiling (~230 °C) from a deep chloride-rich reservoir. The reservoir temperatures obtained by silica geothermometry for Sulphur Springs, Valley of Desolation, and Boiling Lake give maximum values of 180–243 °C. These temperatures are slightly lower than those proposed by Giggenbach and Stewart (1982), but silica thermometry typically underestimates reservoir temperatures and more likely represents discharge temperatures (Tassi et al., 2010). Consideration of Na/K geothermometry for the Boiling Lake, however, gives higher equilibrium temperatures of 295–320 °C for the period 2015–2017, which may be more representative of the deeper Na-Cl reservoir associated with this feature. If the Boiling Lake continues to reflect a predominantly Na-Cl composition in the future, this may be the better option for the monitoring of subsurface temperature change, particularly during times of unrest.

The combination of surface evaporation and steam from reservoir boiling is consistent with the chemistry of the Dominica hydrothermal waters that show isotopic enrichment, which are classified as steam heated Na-SO_4 type water with low Cl concentrations (<100 mg/L), as well as the elevated reservoir temperatures. When the Boiling Lake transitioned from Na-SO_4 to Na-Cl composition after the lake draining event in 2004, the isotopic composition was unaffected. Pre-2004, it is plausible that steam or vapors separated from the deeper boiling reservoir and mixed with the overlying acid sulphate waters that filled the lake. When the source of the lake waters transitioned to the deeper reservoir, the water and vapor phases were no longer separated, both emanating from a deeper Na-Cl brine. If this is the case, the proportion of steam relative to water must have increased post-2004, as the deeper Na-Cl brine would be isotopically depleted compared to the steam.

The hydrothermal waters at Watten Waven do not show significant deviation from the GMWL, likely owing to their lower reservoir temperature (calculated 89–139 °C with silica thermometry). However, the 2017 samples show a positive deuterium shift of ~5‰ compared to the 2002 samples (Fig. 7A). This could be the result of increased fractionation between H_2S and water, which would enrich δD without affecting $\delta^{18}O$ (Richet et al., 1977), but is more likely a consequence of seasonality, as the 2002 samples were collected in November near the end of the rainy season, whereas most of the samples in the 2014–2017 period were collected in the dry season (April–June). Joseph et al. (2013) showed that hydrothermal waters sampled in Sulphur Springs, St. Lucia in June (dry) versus November (rainy) had parallel trends, but that the November samples were affected by dilution and recorded lower deuterium by ~6‰. The slight co-variant negative isotopic trend of both δD and $\delta^{18}O$ from 2015 to 2017 (Fig. 7A) may indicate less surface evaporation over the time period.

Table 3
Measured discharge temperatures and inferred reservoir temperatures for Dominica hydrothermal waters (°C).

Site	Location	Date (m/d/y)	Surface temperature (°C)	T_{OZ}[a]	T_{OZ}[b]
Mome aux Diables	Eric's pool (MAD-5)	06/22/14	24	122	120
Mome aux Diables	Eric's pool (MAD-5)	06/01/15	24	102	102
Mome aux Diables	Eric's pool (MAD-5)	06/20/16	25	82	85
Mome aux Diables	Eric's pool (MAD-5)	06/24/17	24	78	82
Mome aux Diables	MAD-5.5	06/01/15	24	101	102
Mome aux Diables	MAD-5.5	06/21/16	27	91	93
Mome aux Diables	MAD-5.5	06/24/17	24	78	82
Mome aux Diables	MAD-6	06/22/14	24	106	106
Mome aux Diables	MAD-6	06/01/15	23	82	85
Mome aux Diables	MAD-6	06/20/16	25	74	78
Mome aux Diables	MAD-6	06/24/17	24	69	74
Mome aux Diables	MAD-6.5	06/21/16	25	83	86
Mome aux Diables	MAD-6.5	06/24/17	24	70	75
Mome aux Diables	Nancy's pool (MAD-7)	06/22/14	25	70	75
Mome aux Diables	Nancy's pool (MAD-7)	06/01/15	25	79	83
Mome aux Diables	Nancy's pool (MAD-7)	06/20/16	25	75	79
Mome aux Diables	Nancy's pool (MAD-7)	06/24/17	24	78	82
Mome aux Diables	MAD-8	06/22/14	23	61	67
Mome aux Diables	MAD-8	06/01/15	23	70	75
Mome aux Diables	MAD-8	06/20/16	24	70	75
Mome aux Diables	MAD-9	06/22/14	23	85	88
Mome aux Diables	MAD-9	06/01/15	23	70	75
Micotrin	MI-4	06/24/14	26	78	82
Micotrin	MI-4	06/01/15	24	77	81
Micotrin	MI-4	06/19/16	25	78	82
Micotrin	MI-4	06/13/17	21	55	62
Micotrin	Micotrin warm springs (MI-5)	06/19/14	32	96	97
Micotrin	Micotrin warm springs (MI-5)	06/20/16	31	92	94
Micotrin	Micotrin warm springs (MI-5)	06/15/17	32	104	104
Watten Waven	Yellow Pool (WW-4)	06/20/14	92	116	115
Watten Waven	Yellow Pool (WW-4)	06/01/15	90	128	125
Watten Waven	Yellow Pool (WW-4)	06/20/16	95	107	107
Watten Waven	Yellow Pool (WW-4)	06/15/17	78	89	92
Watten Waven	Jan's pool (WW-5)	06/01/15	69	139	134
Watten Waven	Jan's pool (WW-5)	06/20/16	90	139	134
Watten Waven	Jan's pool (WW-5)	06/15/17	59	106	106
Trafalgar	TR-2	06/20/14	39	111	111
Trafalgar	TR-2	06/01/15	39	104	105
Trafalgar	TR-2	06/20/16	40	112	111
Trafalgar	TR-5	06/20/14	29	91	93
Trafalgar	TR-5	06/01/15	30	94	96
Trafalgar	TR-5	06/20/16	30	99	100
Trafalgar	TR-5	06/14/17	28	94	96
Sulphur Springs	SS-4	06/24/14	97	161	153
Sulphur Springs	SS-4	06/01/15	60	156	149
Sulphur Springs	SS-4	06/20/16	97	100	101
Sulphur Springs	SS-1	06/24/14	39	141	136
Sulphur Springs	SS-1	06/01/15	36	135	131
Sulphur Springs	SS-1	06/20/16	42	145	139
Sulphur Springs	SS-1	06/13/17	42	140	135
Sulphur Springs	SS-2	06/24/14	32	243	219
Sulphur Springs	SS-2	06/01/15	29	140	135
Sulphur Springs	SS-2	06/20/16	36	139	134
Sulphur Springs	SS-2	06/13/17	36	167	157
Sulphur Springs	SS-3	06/24/14	51	119	117
Sulphur Springs	SS-3	06/01/15	52	120	118
Sulphur Springs	SS-3	06/20/16	95	118	117
Sulphur Springs	SS-3	06/13/17	50	110	109
Sulphur Springs	SS-5	06/24/14	40	114	113
Sulphur Springs	SS-5	06/01/15	91	122	120
Sulphur Springs	SS-5	06/20/16	30	93	95
Sulphur Springs	SS-5	06/13/17	37	106	106
Sulphur Springs	SS-8	06/20/16	97	177	166
Sulphur Springs	SS-8	06/13/17	76	168	159
Valley of Desolation	Roiling Lake (VOD-5)	06/21/15	82	196	181
Valley of Desolation	Roiling Lake (VOD-5)	05/10/16	86	162	154
Valley of Desolation	Roiling Lake (VOD-5)	06/23/16	89	172	162
Valley of Desolation	Roiling Lake (VOD-5)	12/15/16	77	162	154
Valley of Desolation	Roiling Lake (VOD-5)	01/10/17	82	171	161
Valley of Desolation	Roiling Lake (VOD-5)	06/16/17	89	165	156
Valley of Desolation					
Valley of Desolation	Rubbling Pool 1 (VOD 4)	06/21/15	74	155	148

Table 3 (*continued*)

Site	Location	Date (m/d/y)	Surface temperature (°C)	T_{OZ}[a]	T_{OZ}[b]
Valley of Desolation	Rubbling Pool 1 (VOD 4)	06/23/16	90	161	153
Valley of Desolation	Rubbling Pool 1 (VOD 4)	06/16/17	79	131	128
Valley of Desolation	Rubbling Pool 2 (VOD-2)	06/21/15	93	101	105
Valley of Desolation	Rubbling Pool 2 (VOD-2)	06/23/16	88	175	164
Valley of Desolation	Rubbling Pool 2 (VOD-2)	06/16/17	99	151	145
Valley of Desolation	VOD-3 (pool)	06/18/15	82	180	168
Valley of Desolation	VOD-3 (pool)	06/20/16	93	102	102
Valley of Desolation	VOD-3 (pool)	06/13/17	69	112	111
Valley of Desolation	VOD-7	06/20/16	n.m.	81	84
Valley of Desolation	VOD-8	06/18/15	37	119	117
Valley of Desolation	VOD-8	06/20/16	37	104	105
Valley of Desolation	VOD-8	06/13/17	37	110	110
Valley of Desolation	VOD-11	06/20/16	93	156	148
Valley of Desolation	VOD-11	06/13/17	99	156	149
Valley of Desolation	VOD-12	06/20/16	47	98	99
Valley of Desolation	VOD-12	06/13/17	49	101	102
Valley of Desolation	VOD-13	06/20/16	39	107	107
Valley of Desolation	VOD-13	06/13/17	94	140	135
Trail toVOD	VOD-1 (Rreakfast River)	06/18/15	21	65	71
Trail toVOD	VOD-1 (Rreakfast River)	06/20/16	21	65	71
Trail toVOD	VOD-1 (Rreakfast River)	06/13/17	21	61	67
Inlet to Roiling Lake	VOD-6	06/18/15	21	74	78

n.m. = not measured.

[a] Quartz, no steam-loss (Fournier, 1977) Geothermometer Temperature (°C) = 1309/ (5.19-log S) - 273.15 (S represents silica concentration as SiO_2 in mg/kg).

[b] Quartz steam-loss (Fournier, 1977) Geothermometer Temperature (°C) = 1522/ (5.75-log S) - 273.15 (S represents silica concentration as SiO_2 in mg/kg).

5.4. Record of magmatic CO_2

The broad range of $\delta^{13}C_{DIC,}$ (−11 to +5‰, Table 2) in Dominica's hydrothermal waters suggests that multiple factors likely play a role. Unlike the deuterium and oxygen isotopes, which reflect meteoric origin (with steam and evaporation effects) and no obvious contribution from magmatic or andesitic waters, the range in carbon isotopes suggests the dominant process is degassing of CO_2 of primarily magmatic origin, with modification or contamination by other sources of CO_2 in some samples. The majority of samples, and all of the vigorously bubbling pools, have $\delta^{13}C$ ratios between −8 and −2‰, which is consistent with the range documented at N-MORBs (Taylor, 1986 and references therein). These values are also consistent with the $\delta^{13}C$ isotope ratios measured in gases from several Dominican fumaroles (Fig. 8, Pedroni et al., 1999). A similar study of hydrothermal waters and fumaroles at La Soufriere, Guadeloupe yielded $\delta^{13}C$ isotope ratios of −18.11‰ to −2.11‰ and −3.19‰ (gas), respectively (Ruzie et al., 2013). At low pH and high temperatures, magmatic CO_2 is dissolved in meteoric water and there is very little carbon isotope fractionation (<1‰), as DIC is dominated by H_2CO_3. The slight variations observed from site to site are likely a consequence of fractional degassing of the magma chamber, which occurs during the exsolution of CO_2. The pools with the highest $\delta^{13}C$ isotope values are located in the Cold Soufriere (−4 to −8‰), where CO_2 degassing is vigorous and the depth to the magma chamber is assumed to be greater based on the cool water temperatures (<30 °C). Therefore, some of the range in fractionation/$\delta^{13}C$ ratios of the pools could reflect varying depths to the magma reservoir. Over the four-year sampling period (2014–2017), the surface temperatures and $\delta^{13}C$ values did not change, which suggests a current steady-state of degassing. Given the consistency with the documented $\delta^{13}C$ gas values, it may be possible to use the $\delta^{13}C$ of the hydrothermal pools as a proxy for degassing. Magmatic unrest, which could include magma replenishments to the system and/or magma migration, could affect the degassing rate, and in turn the fractionation of $\delta^{13}C$. For those areas with slightly lighter $\delta^{13}C$ values (i.e. Cold Soufriere), a transition to heavier $\delta^{13}C$ values like that of the Dominican fumaroles (−1.81 to −4.01‰), could indicate a change in the underlying magmatic system. Therefore, analysis of $\delta^{13}C$ from hydrothermal waters, which began in 2013, should continue to be part of an island-wide monitoring strategy.

Many of the streams in the hydrothermal systems have more depleted $\delta^{13}C$ values than those recorded in the pools (Fig. 8), suggesting mixing from another source. For comparison, Rivé et al. (2013) analyzed 11 larger meteoric rivers from across the island, which yielded $\delta^{13}C$ values between −10 and −14‰, consistent with the lightest values observed in the hydrothermal streams. Sources of crustal CO_2 include marine limestone (+2 to −2‰), organic sediments (−20 to −40‰) and air (−7.5‰). The limestone and air would not shift the $\delta^{13}C$ to lighter values. Organic sediments are not significant in the hydrothermal streams, therefore the streams likely reflect a biologic influence. Vegetation sampled on nearby Guadeloupe had an average $\delta^{13}C$ value of organic carbon of −29 ± 4‰, dominated by C3 vascular plants (Rivé et al., 2013), which is similar to the vegetation in Dominica. If magmatic and biogenic CO_2 are considered the only possible sources of carbon in the hydrothermal streams and we use the mass balance equation proposed by Rivé et al. (2013), the proportion of carbon derived from the magma reservoir is 50–100%, with subordinate contributions from biogenic sources. Rivé et al. (2013) proposed a similar magmatic contribution for the Trafalgar and Roseau Rivers, which are larger rivers in the Watten Waven-Micotrin watershed.

The presence of heavy $\delta^{13}C$ (>−2‰) in waters is unusual. The most commonly invoked source is limestones (+2 to −2‰). However, this is extremely unlikely in Dominica, as >95% of the island is volcanic and carbonates have only been mapped in a narrow band on the western coast of Dominica (Smith et al., 2013). Another possible explanation is evaporation. In a global study on lakes, Horton et al. (2016) noted the co-variance of $\delta^{18}O$ and $\delta^{13}C$ and documented the isotopic fractionation relationship in evaporation experiments. Given the evidence for evaporation seen in the $\delta^{18}O$ and δD (Fig. 6), this would appear plausible. However, the samples that show evidence of evaporation (bubbling pools in VOD and Sulphur Springs, Boiling Lake) have $\delta^{13}C$ values of −2 to −4‰ (Fig. 8) and lack the $\delta^{13}C$ enrichment seen in the lower temperature streams. Furthermore, some of the bicarbonate hydrothermal streams are just a few meters from hydrothermal vents that are acid-sulphate waters that have a higher temperature, lower pH and higher TDS, with significantly higher concentrations of SO_4. The notable feature about the $\delta^{13}C$ enriched streams is their black color, derived from a filamentous substance in the water, suggestive of a biologic origin, as opposed to a chemical precipitate. Therefore, the most likely explanation for the heavy isotopic values stems from a biologic fractionation process that preferentially incorporates ^{12}C, which can also affect the pH and chemistry of the water. Methanogenesis of bacteria causes a large kinetic fractionation effect, resulting in enrichment in $\delta^{13}C$ in the host water and has been suggested to explain carbon isotopic enrichment in lakes (e.g. Talbot and Kelts, 1986; Lamb et al., 2000; Zhu et al., 2013). This process seems plausible for the Dominican streams and warrants further investigation.

6. Conclusions

Time series monitoring of geothermal fluids is important for detecting changes to these systems for volcanic surveillance and for understanding the processes that lead to chemical and isotopic variation. Although the hydrothermal areas on Dominica show broad similarities, each region has a unique character, reflecting complex processes of mineral-water equilibration-re-equilibration, evaporation and degassing, and variable amounts of dilution by meteoric water. Thermal water of the Cold Soufrière, Sulphur Springs, Watten Waven and the VOD generally have Na-SO_4 type water compositions, whereas the waters of the Boiling Lake show compositions between the spectrums of Na-SO_4 and Na-Cl. Continued long term geochemical monitoring can help to identify changes to these systems and their possible causes, or allow for the detection of precursory volcanic activity. Monitoring of the water composition of thermal features in the VOD and the Boiling Lake since 2001 has shown that during periods of crisis at the lake, which are accompanied by changes in activity and water composition (but not changes in deuterium and oxygen isotopes), hydrothermal activity at the nearby VOD and the geochemistry of the sampled thermal features have not been affected. This suggests that the hydrothermal reservoir of the Boiling Lake is more localized and is not directly connected to that of the VOD, although they may have shared an aquifer prior to the 2004 lake draining event.

The geochemical composition of thermal waters of the Cold Soufrière, Sulphur Springs, Watten Waven/Micotrin and the VOD sampled over the period 2009 to 2017 show that the waters are still "immature", indicating that they have not attained equilibrium with the host reservoir rocks. This suggests that the limited degree of water-rock interaction in their respective hydrothermal aquifers has not changed significantly since the start of regular monitoring in 2000 up to the 2017 monitoring campaign. Therefore, the calculation of reservoir temperatures through the use of cation geothermometry is not a reliable monitoring tool, but we show the utility of using silica thermometers in conjunction with deuterium and oxygen isotopes. The linear array and isotopic enrichment of the time series isotopic data compared to the GMWL for several hydrothermal areas (Sulphur Springs, VOD, and Boiling Lake) is indicative of significant evaporation and steam heating at elevated reservoir temperatures. Although the silica thermometry provides minimum temperatures, two areas appear to have experienced an increase in reservoir temperature since monitoring commenced; Watten Waven, where temperatures rose from 90 °C to 139 °C and Sulphur Springs, where temperatures have increased from 152 °C to 243 °C. The higher temperatures in the reservoir beneath Sulphur Springs have led to increasing isotopic enrichments over time. Continued monitoring of these sites is needed to see if this trend persists and what the possible implications are with respect to volcanic activity.

Unlike the other hydrothermal areas, the Boiling Lake has shown compositional changes over time and more water-rock interaction. The partial maturity reflected by the waters of the Boiling Lake is more representative of the fluids from a brine, sourced from a deeper mature aquifer, which contributes fluids to the shallow hydrothermal acid-sulphate aquifer. The balance between the contributions from these two sources can be monitored over time with geochemistry and the more mature NaCl-type composition provides a more robust evaluation of reservoir temperature. Since monitoring began in 2002, the quartz geothermometry does not indicate a significant change in reservoir temperature, suggesting no increased magmatic input to the hydrothermal reservoirs of these systems. The trend towards isotopically lighter values of deuterium and oxygen would in fact suggest the opposite; that the amount of steam fractionation from aquifer boiling may be decreasing due to falling reservoir temperatures. Therefore, silica thermometry may not be as sensitive an indicator of changing aquifer conditions and monitoring the deuterium and oxygen isotopic values is a better tool for assessing change.

Although $\delta^{13}C_{DIC}$ had not previously been analyzed in Dominican hydrothermal waters, it shows promise as an additional monitoring tool. Because of its low solubility in hydrothermal systems, the exsolution of CO_2 may be able to capture changes in the magma reservoir, such as injection of more volatile-rich magmas. The $\delta^{13}C_{DIC}$ values for bubbling pools were very similar to that of Dominican fumaroles, suggesting little fractionation occurs in these systems and therefore the pools are a window to deep-seated magma degassing of CO_2. Other studies have documented that a shift towards more positive $\delta^{13}C_{DIC}$ may be correlated with an influx of magma and increase in eruption frequency (Chiodini et al., 2011). The baseline $\delta^{13}C_{DIC}$ values that we have established for each hydrothermal system over the last four years will allow for future assessment of potential changes to the system, which may signify volcanic unrest.

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