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Chemical and isotopic characteristics of geothermal fluids from Sulphur Springs, Saint Lucia

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ABSTRACT

Sulphur Springs is a vigorous, geothermal field associated with the active Soufrière Volcanic Centre in southern Saint Lucia, Lesser Antilles island arc. The 'Sulphur Springs Park' is an important tourist attraction (touted as the 'world's only drive-through volcano') with some of the hot pools being developed into recreational pools. Some 200,000 people visit the park each year. Since 2001, the hydrothermal fluids of Sulphur Springs have been sampled as part of an integrated volcanic monitoring programme for the island. Gas and water samples were analysed to characterise the geochemistry of the hydrothermal system, and to assess the equilibrium state and subsurface temperatures of the reservoir. This has also enabled us, for the first time, to establish baseline data for future geochemical monitoring.

The gases are of typical arc-type composition, with N_2 excess and low He and Ar content. The dry gas composition is dominated by CO_2 (ranging from 601–993 mmol/mol), with deeper magmatic sourced H_2S-rich vapour undergoing boiling and redox changes in the geothermal reservoir to emerge with a hydrothermal signature in the fumarolic gases. Fluid contributions from magmatic degassing are also evident, mainly from the moderate to high contents of HCl and deeply-sourced H_2S gas, respectively. Sulphur Springs hydrothermal waters have acid-sulphate type compositions ($SO_4 = 78$–4008 mg/L; pH = 3–7), and are of primarily meteoric origin which have been affected by evaporation processes based on the enrichment in both $\delta^{18}O$ and δD ($\delta^{18}O = -1$ to 15‰ and $\delta D = -9$ to 14‰ respectively) in relation to the global meteoric water line (GMWL). These waters are steam-heated water typically formed by absorption of H_2S-rich gases in the near surface oxygenated groundwaters. Reservoir temperatures calculated from the evaluation of gas equilibria in the CO_2–CH_4–H_2 system reveal higher temperatures (190 to 300 °C) than those derived from quartz geothermometry (95 to 169 °C), which appeared to be affected by dilution with meteoric waters. Generally, no significant variations in fluid geochemistry of the hydrothermal system were observed between 2001 and 2006, and we propose that there were no changes in the state of volcanic activity during this period.

1. Introduction

While geochemical monitoring of volcanic-hydrothermal systems is commonly practiced at many volcanoes around the world, it is only recently that it was implemented as part of the ongoing volcanic surveillance programme of the University of the West Indies (UWI) Seismic Research Centre (SRC) for the English-speaking islands of the Lesser Antilles. This has, in general, primarily been due to a lack of financial and human resources in the region. In the French islands, geothermal monitoring of the volcanic-hydrothermal systems of La Soufrière (Guadeloupe) and Mt. Pelée (Martinique) has proven to be an important tool in volcanic surveillance and geothermal exploration (Bigot and Hammouya, 1987; Bigot et al., 1994; Brombach et al., 2000; Komorowski et al., 2002). The need to improve the understanding of, and provide baseline geochemical data for other poorly studied volcanoes in the Lesser Antilles was clearly recognised, and in November 2000 a geochemical monitoring programme in Dominica was initiated by the SRC. The data obtained from that study provided the first time-series observations used for the purpose of volcano monitoring, and permitted the characterisation of the geothermal fluids associated with volcanoes of Dominica (Joseph et al., 2011). The use of geochemical monitoring of springs, fumaroles, and bubbling gases in providing information about the hydrology of a geothermal system and conditions of the reservoir, has been recognised by many other researchers. This is especially important in the context of establishing baseline studies for future monitoring and understanding of the hydrothermal system during periods of quiescence (Rouwet et al., 2009b).

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In Latin America, several pioneering studies related to baseline geochemical monitoring of the fluids associated with volcanoes have been conducted. Amongst them are Giggenbach et al. (1990), who commenced a chemical surveillance programme of Nevado del Ruiz, Colombia in September 1985, three months prior to the major eruption that led to heavy loss of life. Their research revealed that the fumarolic discharges in September were essentially magmatic in composition with an increasing hydrothermal component up until the eruption. Fischer et al. (1997), began a sampling programme of fumarolic gases and spring discharges at Galeras volcano, Colombia over the period 1988 to 1995 when it had reactivated. Their study indicated that sampling of thermal springs for the evaluation of the extent, maturity and duration of hydrothermal activity at active volcanoes provided a good indicator for the possibility of sector collapse, unrelated to changes in actual magmatic activity. It also demonstrated how long-term chemical surveillance of springs and fumaroles makes a significant contribution to understanding volcanic activity, magma degassing and the sources of magmatic and hydrothermal volatiles. Initial geochemical studies of magmatic hydrothermal systems for use in volcanic surveillance have been conducted at Rincon de la Vieja volcano, Costa Rica, and in Northern Chile at the Arica-Parinacota, Tarapacá and Antofagasta regions, and Lascar volcano (Tassi et al., 2005, 2009, 2010); at Tacaná volcano, Mexico-Guatemala and El Chichón, Mexico (Rouwet et al., 2009a, 2009b; Tassi et al., 2003); at Puracé volcano and Cumbal volcano in Colombia (Sturchio et al., 1993; Lewicki et al., 2000); and San Vincente, El Salvador (Aiuppa et al., 1997).

The Sulphur Springs geothermal field, located in the Soufrière Volcanic Centre (SVC) in the south of Saint Lucia (Fig. 1), is one site that was chosen to initiate the geochemical monitoring programme in Saint Lucia in 2001. Sulphur Springs has been incorporated into a Park that is managed by the Soufrière Foundation and visited by locals and tourists all year round, with an average of 200,000 visitors per year. The physical dangers associated with the geothermal activity at Sulphur Springs have been demonstrated by historical occurrences of landslides, small phreatic and hydrothermal eruptions that eject ash into the surrounding atmosphere and by people falling into boiling mud pools. Several thermal pools at the site have been developed for recreational use including bathing, and the application of mud masques, as well as for therapeutic applications.

With the exception of geochemical data obtained from geothermal feasibility studies at Sulphur Springs, limited data is available on the evolution over time of the fluid composition of the hydrothermal system. This study presents an extensive description of the present-day manifestations and provides a data set to define the baseline for future geochemical monitoring, through the undertaking of time series monitoring of gas and water chemistry over the period 2001 to 2006. In this paper we (a) describe the chemical and isotopic compositional features of the hydrothermal fluids of Sulphur Springs; (b) revaluate the reservoir temperatures and state of equilibrium on the basis of gas and solute geothermometry; and (c) and look at the implications of geochemical surveillance on the overall volcano monitoring efforts in Saint Lucia.

2. Geological setting

2.1. Geology

The island of Saint Lucia, located in the southern region of the Lesser Antilles, is one of the larger islands of the arc, with an area of approximately 610 km^2. The most pronounced topographic feature is the N–S trending axial range with the highest mountain, Mount Gimie (950 m), located in the south-western part of the range (Fig. 1). Saint Lucia is made up almost entirely of volcanic rocks, but only one volcano, the Soufrière Volcanic Centre (SVC) in the southwest of the island, is considered to be potentially active (Lindsay et al., 2005). The youngest age dates available for large pyroclastic eruptions at the SVC are 20,000 years B.P. (Schmitt et al., 2010). Several lava domes and explosion craters have, however, formed since then

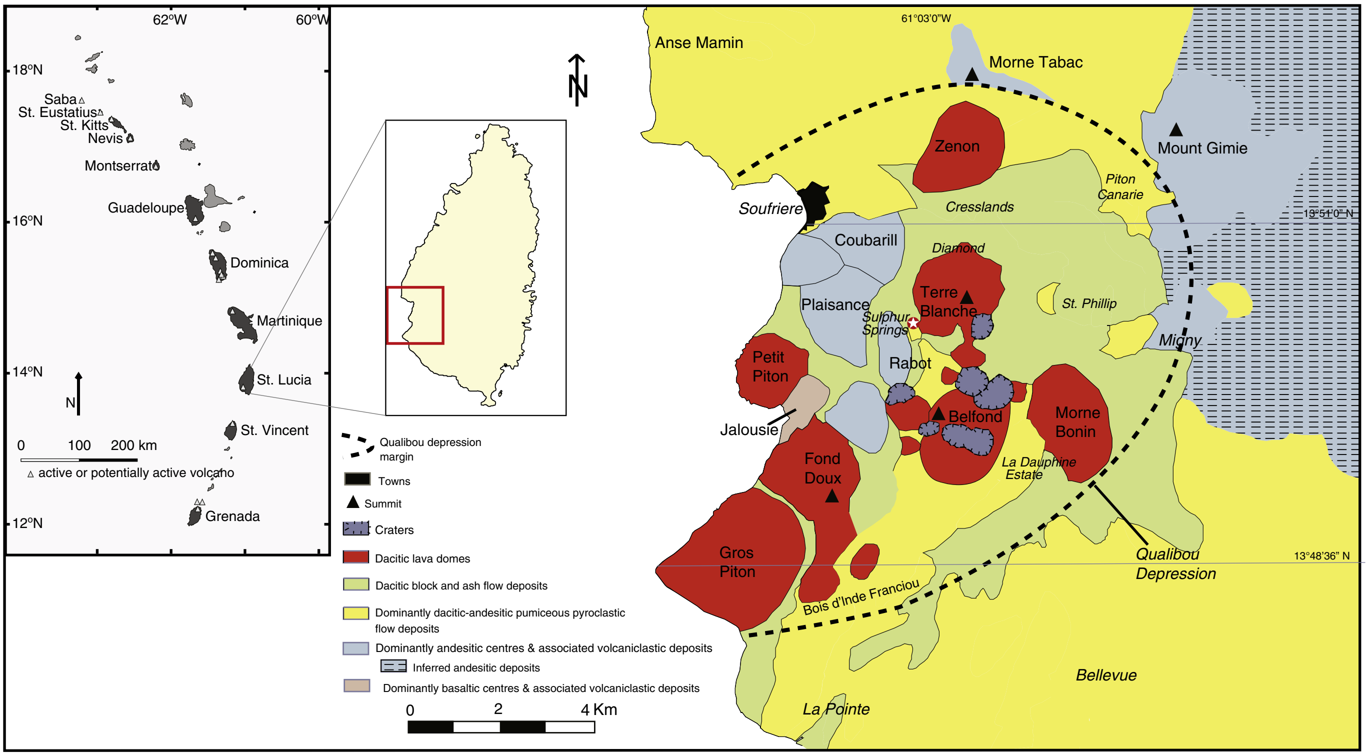

Fig. 1. Map of Lesser Antilles showing the location of Saint Lucia (left), and map of Saint Lucia showing an outline of the Qualibou Depression and main vents of the Soufriere Volcanic Centre (right).

(e.g. Belfond: 13.6 ± 0.4 ka; Terre Blanche: 15.3 ± 0.4 ka; Schmitt et al., 2010), which, together with the occurrence of occasional swarms of shallow earthquakes and vigorous hot spring activity in southern Saint Lucia, indicates that this area is still potentially active and could generate volcanic eruptions in the future. Volcanic activity on Saint Lucia is monitored by the Seismic Research Centre of the University of the West Indies (UWI) in Trinidad. There is a network of six telemetered seismometers, one continuous GPS station and several benchmarks used for ground deformation monitoring on the island.

2.2. Geothermal activity

There are several areas of fumarolic and hot spring activity associated with the Soufrière Volcanic Centre. The main site of geothermal activity occurs at the well-known Sulphur Springs area (Fig. 1). Thermal manifestations at Sulphur Springs include features such as boiling springs and pools, fumaroles with strong gas flux, hot ground, and extensive rock alteration (Fig. 2). Thermal springs are present at Diamond and Cresslands (Fig. 1), which are located about 200–300 m from the northern and eastern base, respectively of the Terre Blanche dome (Wohletz et al., 1986). Several other sites of geothermal activity can be found in southern Saint Lucia, amongst them are the warm springs at Jalousie, and underwater gas vents offshore between Anse Mamin and Soufrière Bay (Fig. 1) (Lindsay et al., 2005). Newman (1965) reported an area of intensely hydrothermal clayey ground about 1.6 km to the south of Piton Canaries (Fig. 1), however, this is most likely an area of hydrothermal activity that is no longer active.

2.3. Seismic activity

A continuous seismic monitoring programme was established in Saint Lucia in 1982 by the SRC. This network facilitated the identification of at least four swarms of shallow earthquakes in the last 30 years. These occurred in 1986, 1990, 1999 and 2000, and at least three of these seem to have been triggered by a larger tectonic earthquake (1990, 1999, and 2000) (Lindsay et al., 2005). The most recent swarm occurred between July 2000 and January 2001. Neither of the more recent shallow ($\leq$30 km) earthquake swarms in Saint Lucia for which we have good seismograph data (1990 and 2000) was directly related to the area of most recent volcanic activity, the Soufrière Volcanic Centre (Lindsay et al., 2002). In fact, some of the earthquakes of these swarms were located beneath older basaltic centers that have previously been considered ‘dead’ (e.g. Mt. Gomier and Morne Caillandre/Victorin). The two main swarms of shallow earthquakes in 1990 and 2000 displayed a similar pattern: a single large shock was followed by a sequence of gradually diminishing smaller shocks, a pattern typical of tectonic earthquake sequences (Lindsay et al., 2002). However, the epicentres of the “aftershocks” did not cluster around the epicentre of the main shock, which is not typical of tectonic earthquakes. The earthquakes that occurred in Saint Lucia in 1990 and 2000 therefore have characteristics of both volcanic and tectonic earthquakes which make them difficult to interpret. The most likely interpretation of the recent swarms is that several near plate boundary intraplate earthquakes of magnitude $>\sim3$ occurred, triggering seismic activity on nearby near-surface faults (Lindsay et al., 2002). This would explain the shallow depth of the earthquakes, and the fact that the “aftershocks” do not cluster around the epicentre of the main shock.

3. Sulphur Springs geothermal field

3.1. Reservoir characteristics

Sulphur Springs is the surface manifestation of a sub-surface geothermal field. Early descriptions of activity at Sulphur Springs were given by Lafort de Latour (1787) and Hovey (1905) and the first detailed study of the area was made by Robson and Willmore (1955). More recent studies of the Sulphur Springs area have been directed towards evaluating its potential as a geothermal power source (Greenwood and Lee, 1976; Lee and Greenwood, 1976; Merz and McLellan, 1977; Williamson and Wright, 1978; Williamson, 1979; AQUATER, 1982; Ander et al., 1984; L.A.N.L, 1984; Gandino et al., 1985; Battaglia et al., 1991; GI, 1991; GENZL, 1992). While the area was found to have significant geothermal potential and several exploratory boreholes exist, to date no successful exploitation has taken place, and with its appointment as a World Heritage Site this appears to be unlikely in the near future.

The geochemistry of the thermal waters at Sulphur Springs, based on these periodic investigations, was found to be acid-sulphate in character, with the waters having relatively low pH, high SO_4 and low Cl, while divalent and trivalent cations (Ca, Mg, Al, Fe) dominated over Na and K, and trace elements identified were Ba, Cd, Co, Cr, Mo, Ni, Rb, Sb, Se, Zn (Goff and Vuataz, 1984; GI, 1991). The subsurface reservoir temperature was estimated to be 280 °C based on the empirical gas geothermometer of D'Amore and Panichi (1980).

In 1986 a geothermal feasibility study of the SVC was jointly conducted by the United Nations Revolving Fund for Natural Resources Exploration (UNRFNRE) and the United States Agency for International Development (USAID). As a result of analysing geothermal fluids collected from drill wells it was reported that the geothermal reservoir was a vapour-dominated system with an estimated temperature of 292 °C (UNRFNRE, 1989). The report indicated that hydrogen chloride (HCl) was present in the condensed steam and its concentration increased with time suggesting the presence of a boiling brine in the deep reservoir, that might be partially influenced by sea water recharge (GI, 1991). The heat source for the Sulphur Springs geothermal system was speculated to be the cooling magma body responsible for the young volcanism of the Soufrière Volcanic Centre (Wohletz et al., 1986; Wohletz and Heiken, 1987).

More recently, geochemical and microbiological investigations at Sulphur Springs have been undertaken in the context that its sulphur-rich environment can be used as a possible Martian analogue (Greenwood et al., 2002, 2005; Greenwood, 2004). Preliminary geochemical, spectral, and biological surveys investigating jarosite mineralisation and the effects of microbial activity on element cycling and isotopic fractionations have been the primary focus of these studies as a comparison with the formation of jarosite on Mars.

3.2. Surface features

The main area of the Sulphur Springs geothermal field is comprised of numerous hot springs, bubbling mud pools, boiling springs, and fumaroles in an area of strongly argillic altered rock approximately 200 m × 100 m in size (Fig. 2b). Many fumaroles have temperatures of up to 100 °C or hotter, with temperatures of up to 172 °C being recorded on occasion (Lindsay, 2001). There is an extensive area of hydrothermally altered ground together with stunted vegetation on the flanks of Terre Blanche, indicating that this area was once geothermally active. The features sampled at Sulphur Springs during this study are described below and shown in Fig. 2a, b.

3.2.1. Painted pool

Painted Pool is a cloudy-grey coloured pool situated upstream from a small tributary to the Sulphur Springs River that lies below the first lookout as you enter the Park by road (Fig. 2b). Just uphill from the pool is a hydrothermally altered orange coloured clayey cliff face. The pool itself is ~4 m × 3 m in size. The geothermal activity at this feature is usually fairly intense, with water spouting at the centre of the pool, reaching to a height of ~0.3 m. Strong degassing is observed from the pool. The water level is generally low (depth of ~0.5 m), and the pool appears dark grey/black in colour.

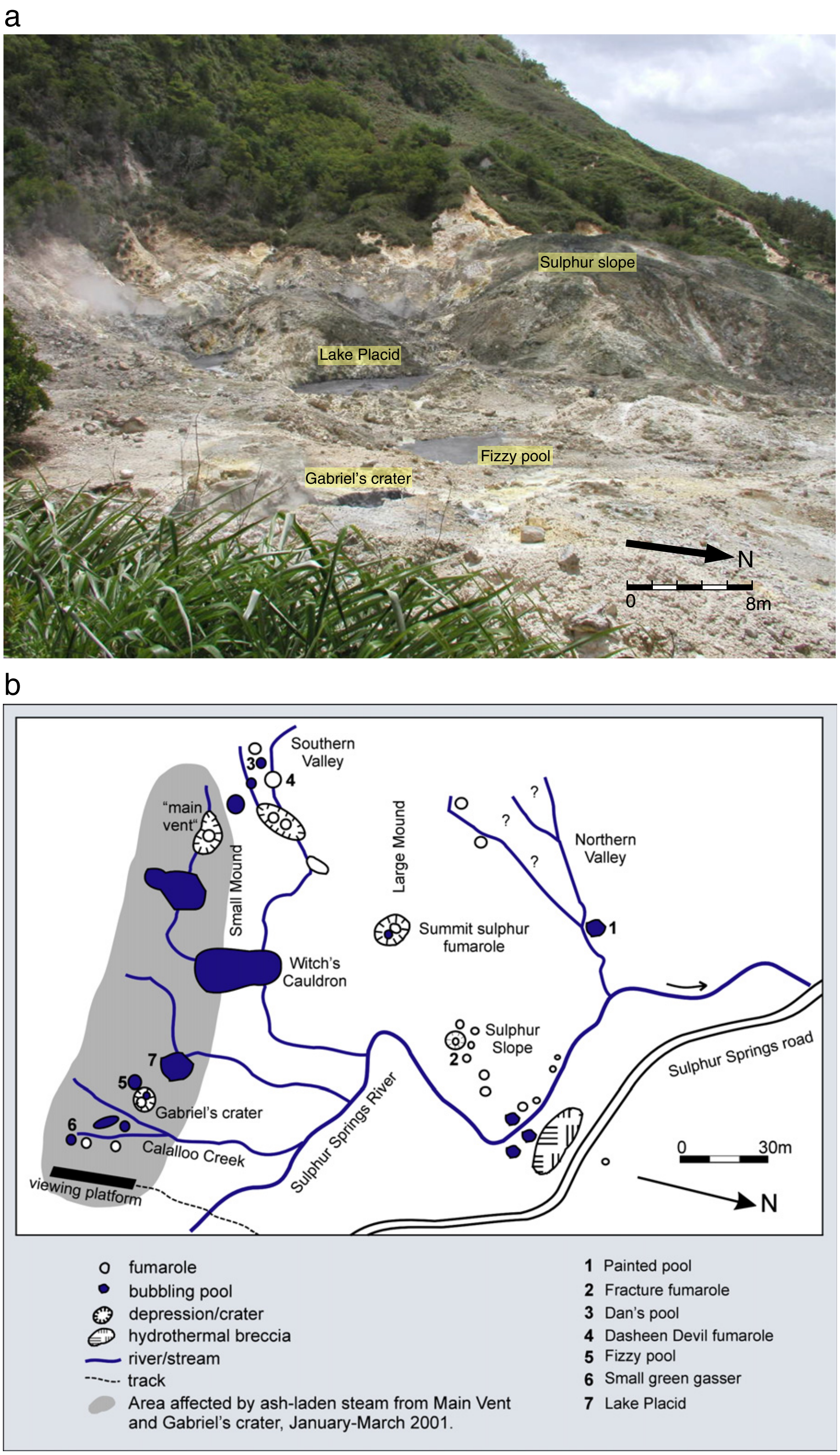

Fig. 2. (a) Features sampled at the Sulphur Springs geothermal field; and (b) map of the Sulphur Springs geothermal field with sample sites identified.

3.2.2. Fracture fumarole

This fumarole is situated in a highly active area as indicated by the presence of numerous small fumaroles and holes in the slope (Fig. 2a, b). It is a strongly degassing fumarole located along a fracture in the slope and was ~0.3 m × 0.3 m in diameter in 2001. Over the monitoring period several small landslides occurred, which buried many of the smaller fumaroles that were observed in this area. By 2006 only two main fumaroles were left uncovered and the gas vent for Fracture Fumarole was ~0.10 m in diameter.

3.2.3. Small Green Gasser

This feature is located at the base of a little amphitheatre at the top of a small stream below the viewing platform (Fig. 2b). The geothermal activity displayed by this feature increased over the monitoring period. The feature had grown from ~0.05 m to ~0.15 m during the study period, with an adjacent pool of roughly the same size developing alongside it that had not previously existed in 2001. The water appears black/blackish grey in colour. The area above and around this feature appears to be showing increased geothermal activity.

3.2.4. Lake Placid

This feature is situated along one of the tributaries of the Sulphur Springs River. It is roughly oblong in shape and in 2001 measured ~8 m × 5 m in size (Fig. 2a, b). By 2006 the feature had increased to ~9 m × 7 m in size as a result of landslides along its northern banks. The lake exhibited fairly vigorous degassing during the study period, with the water appearing dark grey in colour.

3.2.5. Fizzy Pool

This feature is an oval-shaped pool ~3 m × ~2.5 m in size (Fig. 2 a, b). The rocks surrounding the pool were stained green in November 2002, however this staining was not observed in subsequent years. It is located adjacent to a feature called Gabriel's Crater, an active vent that erupted ash-laden steam during the period January–March 2001. The water in the Fizzy Pool is usually very effervescent with constant passive degassing, and appears milky grey in colour. There was a wide fluctuation in the water temperature over the monitoring period.

4. Sampling and analysis

Sampling of gas and thermal waters at Sulphur Springs took place during the period 2001–2006. A total of 25 sets of water samples were collected. Each water sample comprised three aliquots (for cation, anion and isotope analyses). A total of 11 gas samples were collected over the sampling period.

4.1. Water sampling and analysis

Filtered (0.45 μm) samples (for anion analysis) and filtered acidified (with HNO_3 1:1) samples (for cation and SiO_2 analyses) were collected and stored in individual polyethylene bottles. Unfiltered water samples were stored in glass Quorpak bottles for stable isotope analyses. Outlet temperatures (±0.1 °C) and pH (±0.1 units) were determined in the field using a thermocouple meter (Omega HH509), and pH meter (Hach Sension 1) respectively. Water samples collected in 2002 were analysed at the NERC Isotope Geosciences Laboratory (NIGL) in Keyworth, Nottingham, UK for $\delta^{18}O$ and δD values of water using internal standards calibrated against international reference materials VSMOW, SLAP, and GISP with an analytical precision of ±0.05‰ for $\delta^{18}O$, and ±1.0‰ for δD. Isotope determinations were performed following standard procedures outlined in Gonfiantini (1981). $\delta^{18}O$ analysis was performed using an Isoprep 18 CO_2/H_2O equilibration system coupled to a SIRA 10 split-flight mass spectrometer. δD analysis was performed using a continuous flow EuroPyrOH-3110 system coupled to a Micromass Isoprime Mass Spectrometer.

All other water analyses were carried out at the University of the West Indies in Trinidad, using standard procedures outlined in the Standard Methods for the Examination of Water and Wastewater, 21st edition (Eaton et al., 2005), as follows:

(1) Mg, Ca, Fe, Al, Na, and K by atomic absorption spectrophotometry and/or flame photometry; using a Varian AA800 Atomic Absorption Spectrophotometer, and a Jenway (PFP 7) Flame Photometer respectively.
(2) F, Cl, Br, SO_4, by ion chromatography; using a Dionex DX-100 Ion Chromatograph and an AS14 column.
(3) SiO_2 by visible spectrophotometry; using a Bran and Luebbe Autoanalyzer (Multitest MT19)
(4) HCO_3 was analysed volumetrically by titration with 0.1 N HCl.

Accuracy and precision of the measures were computed by analysing certified reference materials and by performing several replicas and dilutions on samples. The relative errors for all analysed elements were ≤10%. The ionic balances were calculated from the water analyses and only those with ≤10% maximum residuals are presented in Table 1.

4.2. Gas sampling and analysis

The gas samples were collected from bubbling springs and fumaroles in evacuated Giggenbach flasks equipped with a Teflon stopcock and containing approximately 50 ml of 5 N NaOH solution. The samples were analysed at the Volcanic and Hydrothermal Fluid Analysis

Table 1
Chemical composition of thermal waters from Sulphur Springs (concentrations in mg/L).

Feature	Date	pH	T (°C)	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Fe^{3+}	IA^{3+}	F^-	CI^-	Br^-	SO_4^{-2}	HCO_3^-	SiO_2	TDS
Fizzy pool	4/15/2001	6.5	70.0	0.0	15	112	4	71	0	44	5	102	0	238	14	n.m	591
Fizzy pool	11/14/2002	61	73.2	n.m	55	27	5	61	22	65	1	87	13	303	n.d.	n.m	655
Fizzy pool	5/26/2003	3.6	41.5	n.m	82	26	2	90	16	69	1	165	0	299	n.d.	n.m	752
Fizzy pool	11/412003	3.5	43.8	n.m	87	29	1	31	16	75	8	115	18	237	n.d.	n.m	625
Fizzy pool	3/17/2005	3.5	64.8	n.m	89	24	3	90	19	53	15	136	12	329	n.d.	n.m	771
Fizzy pool	5/22/2006	1.9	41.6	n.m	36	10	3	13	15	98	10	102	0	220	n.d.	222	729
Lake Placid	4/15/2001	6.7	77.0	0.0	18	115	4	68	0	15	6	79	0	222	13	n.m	527
Lake Placid	11/14/2002	7.2	83.5	n.m	41	25	5	204	1	84	8	128	2	552	28	n.m	1063
Lake Placid	11/4/2003	6.6	74.4	n.m	77	19	15	289	1	76	18	271	8	622	111	n.m	1557
Lake Placid	5/26/2003	4.8	71.6	n.m	134	32	12	110	1	16	6	105	3	470	n.d.	n.m	918
Lake Placid	3/17/2005	6.5	84.7	n.m	159	102	14	44	39	48	10	111	0	423	183	n.m	954
Lake Placid	5/22/2006	6.4	69.6	n.m	88	39	10	4	0	1	6	83	0	184	n.d.	102	523
Painted pool	4/15/2001	6.7	84.0	0.0	100	141	35	426	0	45	10	212	0	1220	110	n.m	2187
Painted pool	11/14/2002	7.3	89.0	n.m	48	70	72	275	10	97	5	206	3	956	171	n.m	1739
Painted pool	5/26/2003	7.2	81.4	n.m	247	384	13	1313	1	36	1	24	6	4008	146	n.m	6117
Painted pool	11/4/2003	6.6	84.8	n.m	164	26	123	807	0	81	3	62	45	2331	113	n.m	4433
Painted pool	3/17/2005	6.5	88.2	rim	161	23	79	496	1	48	6	190	1	1670	116	n.m	2674
Painted pool	5/21/2006	6.5	87.0	n.m	172	41	83	181	4	1	4	106	0	1061	162	56	1710
Small green gasser	4/15/2001	7.1	93.3	0.6	54	48	8	110	0	14	4	55	68	333	26	n.m	695
Small green gasser	11/14/2002	7.3	95.2	n.m	66	64	16	154	1	72	0	132	1	600	n.d.	n.m	1166
Small green gasser	5/26/2003	7.3	89.4	n.m	145	65	3	131	1	18	2	92	8	379	244	n.m	861
Small green gasser	11/4/2003	7.3	89.5	n.m	332	123	4	255	1	17	3	50	26	758	37	n.m	2383
Small green gasser	3/17/2005	7.3	96.7	n.m	138	37	14	118	0	17	2	93	1	358	201	n.m	789
Small green gasser	5/22/2006	3.8	86.3	n.m	37	30	1	8	0	0	6	25	0	79	n.d.	88	281

n.m = not measured n.d. = not detected.

Laboratory, University of New Mexico, USA using gas chromatography techniques outlined in Zimmer et al. (2004). A Gow Mac (600) Gas Chromatograph fitted with both TCD and FID detectors, using Chrom Perfect software, to assess the head space gas species He, H_2, O_2, Ar, N_2, CH_4, and CO. He, H_2, and O_2 were analysed with Ar carrier gas; and Ar, N_2, CH_4 and CO were analysed with H_2 carrier gas.

Wet chemistry techniques were used for the analysis of acidic gases CO_2, H_2S, and HCl, trapped in the alkaline solution. Acidimetric titration with 0.1 N HCl was conducted for CO_2 as CO_3^{2-}, titration with 0.01 N thiosulphate was used to evaluate S_{tot} (which is assumed to be entirely composed of H_2S), and titration with 1 N $AgNO_3$ was used for HCl.

5. Water chemistry

5.1. Chemical composition of thermal waters

The temperature, pH, and composition of the major chemical species in the thermal waters from Sulphur Springs are reported in Table 1. Oxygen and hydrogen stable isotope data are shown in Table 2. The temperatures of the geothermal water samples at Sulphur Springs (excluding the recreational sites) ranged from 65 to 97 °C, with the temperature of individual features showing a variation of only ~10 °C between seasonal sampling periods. The exception to this was Fizzy Pool, which displayed a wider temperature range of 41 °C–73 °C over the monitoring period. The pH of the features sampled was generally neutral to acidic (pH = 3–7), with the exception of Fizzy Pool whose recorded pH was 1.9 in 2006 (Table 1). The total dissolved solids content was mainly moderate to high (TDS = 280–6117 mg/L), with most waters having relatively low to moderate concentrations of Na (14–333 mg/L), K (10–384 mg/L), and Ca (4–1313 mg/L). The waters generally had low concentrations of HCO_3 (<250 mg/L), relatively high concentrations of SO_4 (78–4008 mg/L), and lower concentrations of Cl (24–271 mg/L).

The classification of the waters from Sulphur Springs based on their relative amounts of Cl–SO_4–HCO_3, Na–SO_4–Mg and Mg–Ca–Na is shown in Fig. 3. The waters are generally Na/Ca–SO_4 steam-heated acidic waters, resulting from the condensation of acid hydrothermal gases (principally H_2S, and CO_2) into near-surface oxygenated waters. There is also a positive correlation between SO_4 and Ca concentrations and TDS (Fig. 4a, b), suggesting that the composition of the thermal waters have possibly been influenced by the leaching of pyroclastic rocks containing gypsum and/or anhydrite (Taran et al., 1998; Taran and Peiffer, 2009; Mohammadi et al., 2010). Additionally, the SO_4/Ca mole ratios in the geothermal waters ranged from ~1–18, providing evidence that the SO_4 composition in the waters is not only influenced by the

Table 2
Stable isotopic composition of thermal waters from Sulphur Springs.

Sample ID	Feature	Date	$\delta^{18}O$ VSMOW	δD VSMOW
P1	Fizzy Pool	11/14/2002	+8.44	6
P1	Fizzy Pool	11/14/2002	+8.46	7
P6	Lake Placid	11/14/2002	+14.79	14
P6	Lake Placid	11/14/2002	+14.83	14
P7	Small green gasser	11/14/2002	−1.20	−9
P7	Small green gasser	11/14/2002	−1.23	−9
P12	Painted pool	11/14/2002	+9.91	4
P12	Painted pool	11/14/2002	+9.86	4
SU3[a]		Jun-01	+0.99	−6
SU4[a]		Jun-01	÷14.40	13
SU9[a]		Jun-01	+11.75	8
SU12[a]	King Louis bath	Jun-01	−2.64	−11
SU13[a]	Platform pool	Jun-01	−2.30	−11
SS1[a]	Platform pool	Nov-00	−2.97	16
SS2[a]	King Louis bath	Nov-00	−3.12	19
SS3[a]		Nov-00	+5.80	−9
SS4[a]		Nov-00	+10.50	−1
SS6[a]	Lake Placid	Nov-00	+12.20	2
SS7[a]	Bridge Pool	Nov-00	−0.40	−14

[a] Data from Greenwood (2004).

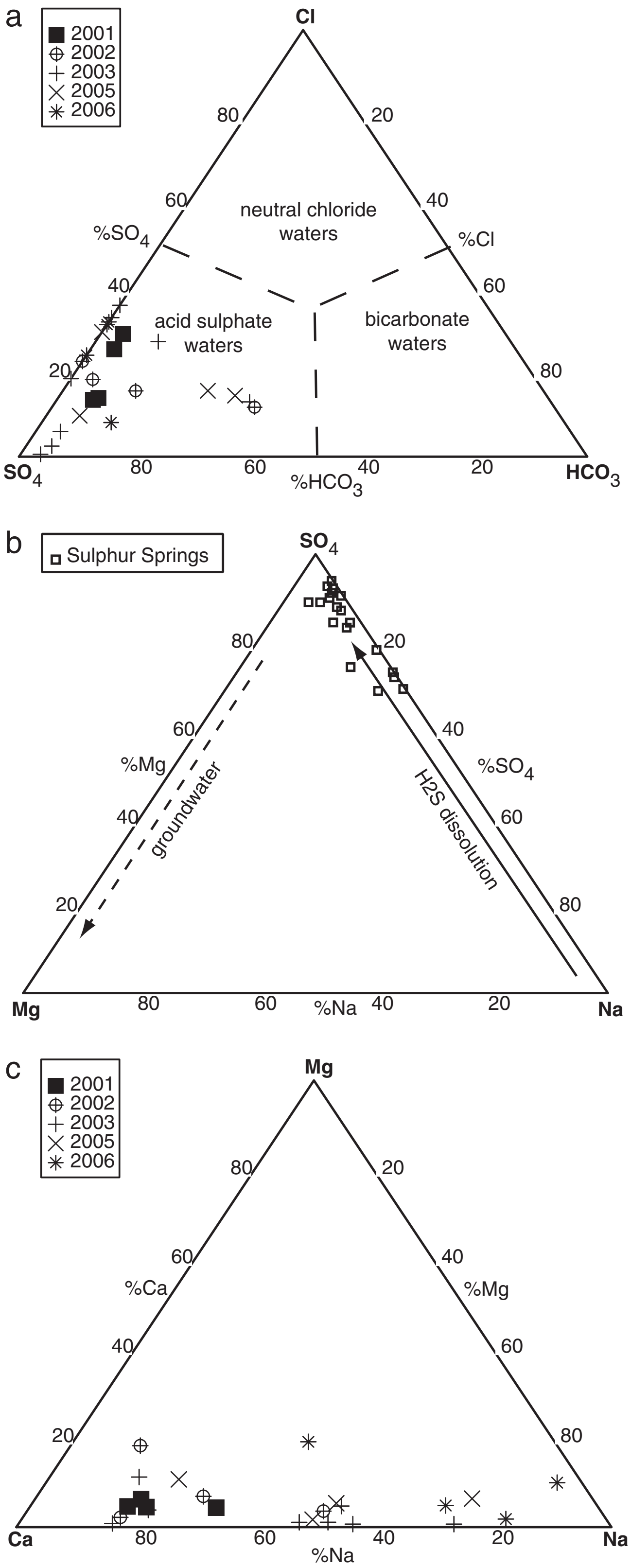

Fig. 3. (a) Cl–SO_4–HCO_3; (b) Na–SO_4–Mg; and (c) Mg–Ca–Na ternary diagrams for hydrothermal water samples from Sulphur Springs.

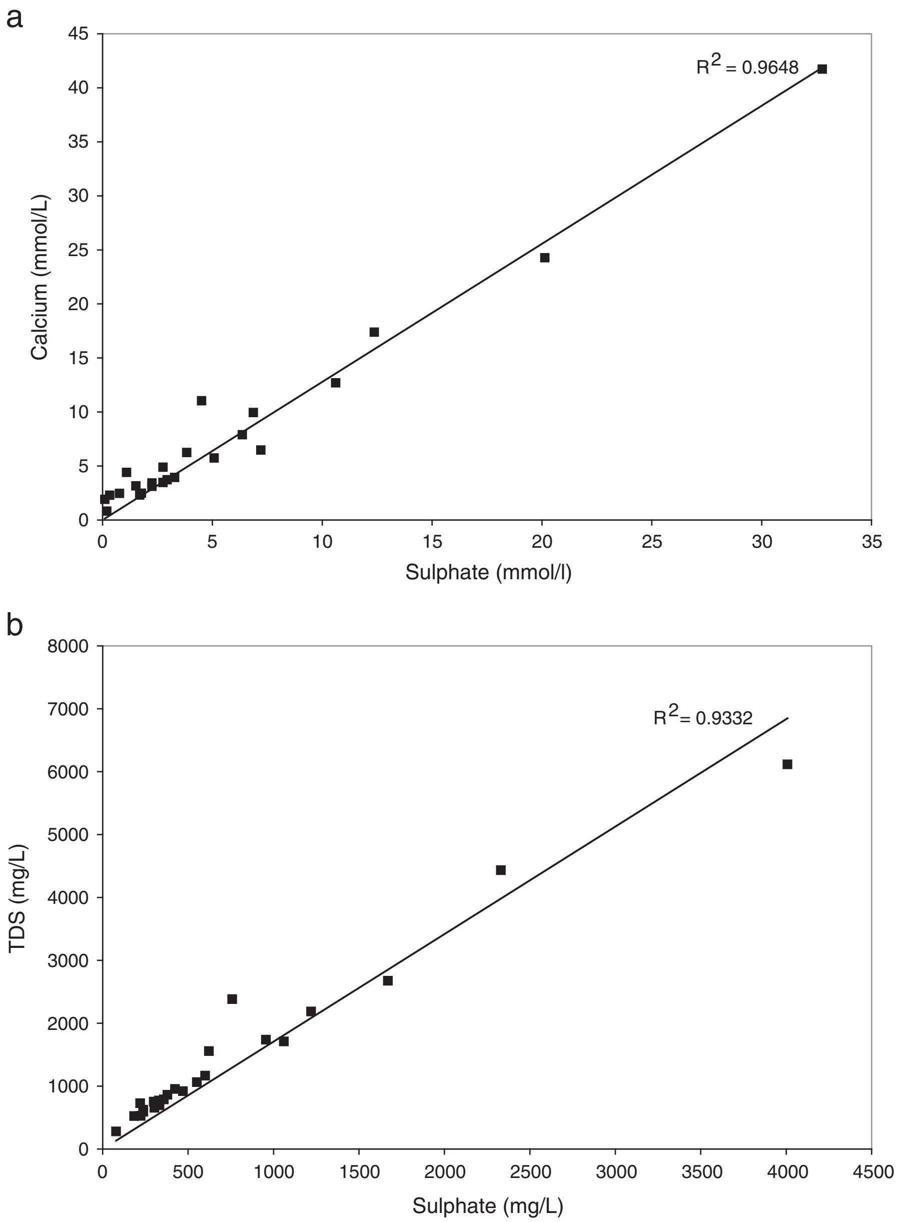

Fig. 4. (a) Ca vs. SO_4 concentrations (b) TDS vs. SO_4 concentrations and (c) TDS vs. Ca concentrations for the Sulphur Springs geothermal water samples (2000–2006). Note the linear correlation on these diagrams.

leaching of surrounding pyroclastic rocks, but also by the contribution of sulphur from the hydrothermal gases.

5.2. $\delta^{18}O$ and δD of thermal waters

The stable isotope contents for the hydrothermal waters of Sulphur Springs range from −1.2 to 14.8‰ for $\delta^{18}O$ and from −8.8 to −14.1‰ for δD (Table 2). Comparison of these values to the Global Meteoric Water Line (GMWL) shows an enrichment of both ^{18}O and D with respect to meteoric waters (Fig. 5). An overall positive $\delta^{18}O$ and δD shift is commonly seen in thermal waters, and has been attributed to evaporation taking place at shallow depth and/or on the surface, at temperatures ranging from 70 °C to 90 °C (Craig, 1963; Clark and Fritz, 1997). The initial origin of these waters is meteoric, since the lines extend from the local meteoric water isotopic composition.

It was also noted that samples taken in June 2001 by Greenwood (2004) show an almost identical trend of isotopic deviation as the samples taken in November 2002 for our study (Fig. 5). However, the samples taken by Greenwood (2004) in November 2000 lie on a different isotopic trend line, which demonstrated that seasonal variations in stable isotopic composition occur at Sulphur Springs. This suggests that the hydrothermal waters of Sulphur Springs are subject to mild dilution by local groundwaters, with no significant alteration of their original chemistry (Majumdar et al., 2009).

5.3. Water-rock equilibrium state and geothermometry

The Na–K–Mg diagram of Giggenbach (1988) can be used to obtain Na–K and K–Mg equilibrium temperatures of fully equilibrated waters. The relative Na–K–Mg compositions of the thermal waters from Sulphur Springs when plotted in the equilibrium diagram (Fig. 6), show that the samples lie in the 'immature waters' field.

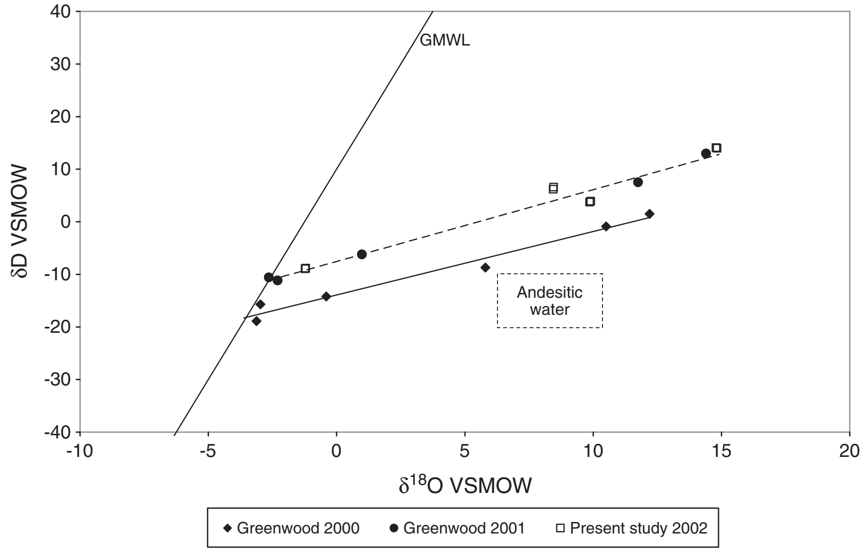

Fig. 5. δD vs. δ^{18}O plot for geothermal waters of Sulphur Springs. The waters are primarily of meteoric origin but have been affected by high temperature exchange and mixing with volcanic fluids. Also shown are the global meteoric water line (GMWL) and the composition of andesitic waters (Taran et al. 1989).

This indicates that the fluids appear to be primarily controlled by mineral-solution equilibria involving the host lithology (Giggenbach, 1988), involving isochemical leaching of a host rock still rich in Mg. This implies that there is no equilibrium between the waters and the alteration phases, resulting in a 'young' and 'immature' host rock–water equilibrium, which makes these waters unsuitable for the evaluation of meaningful Na–K and K–Mg equilibrium temperatures. The use of silica geothermometers (quartz, quartz-steam loss and chalcedony) may provide more reasonable reservoir temperature estimations because of the non-equilibrium conditions, as compared to other cation geothermometers (Shakeri et al., 2008; Matlu and Kilic, 2009; Mohammadi et al., 2010).

The computed equilibrium temperatures for hydrothermal systems of Sulphur Springs using silica geothermometers (Fournier, 1977) are listed in Table 3. The quartz geothermometers generally yielded higher reservoir temperatures (95 °C–169 °C) as compared to the chalcedony geothermometer (64 °C–147 °C). However, it was found that quartz equilibrium temperatures were influenced by lower Cl^- concentrations, suggesting that the geothermometers are affected by the dilution of the hydrothermal fluids with meteoric waters (Tassi et al., 2010; Joseph et al., 2011). Hence, the quartz derived reservoir temperatures for the Sulphur Springs geothermal system should also be interpreted as minimum temperatures.

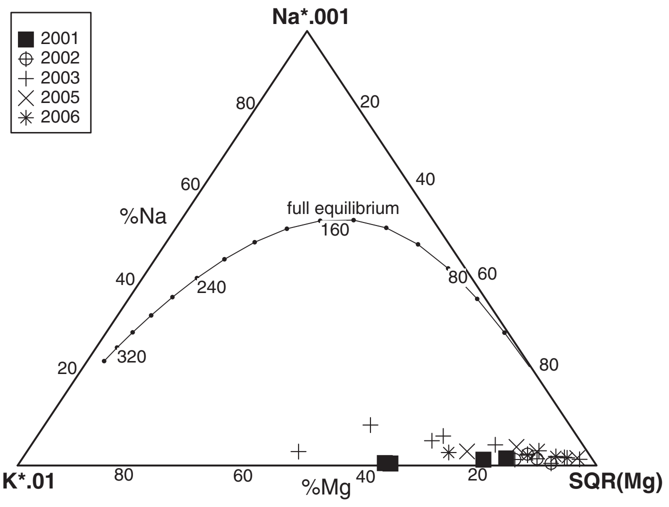

Fig. 6. Na, K, Mg trilinear equilibrium diagram (based on Giggenbach, 1988) for the geothermal water samples of Sulphur Springs (2000–2006).

Another useful geothermometer, often referred to as a "geo-indicator", is the K–Mg–Ca geothermometer proposed by Giggenbach and Goguel (1989) (Fig. 7). This cross-plot juxtaposes the K–Mg geothermometer with a measure of the partial pressure of CO_2 based upon equilibrium between K-feldspar, calcite and K-mica on one side and dissolved Ca^{+2} and K^+ on the other according to Eq. (1):

$$\text{Ca–Al}_2\text{–silicate} + \text{K-feldspar} + CO_2 \leftrightarrow \text{K-mica} + \text{calcite} \qquad (1)$$

The purpose of the plot is to determine the partial pressure of CO_2 at the "last temperature" when the water was in equilibration with the rock, as determined by the K–Mg geothermometer. Samples from Sulphur Springs are plotted using the K–Mg–Ca geo-indicator (Fig. 7), where it is observed that most samples plot below the full equilibrium line in the calcite field, implying that CO_2 content of the rising fluid is influenced by rock alterations resulting in calcite formation, rather than by mineral-solution equilibrium. Samples plotting above the full equilibrium line have CO_2 contents too low to induce rock alterations as expressed in Eq. (1), implying that the CO_2 contributing to magmatic fluids has been affected by dilution with meteoric waters. Two samples plot below the lower boundary for calcite formation indicating that the fluids may have risen too fast for calcite alteration to take place.

Table 3

Measured discharge temperatures and inferred reservoir temperatures, Sulphur Springs thermal waters (°C).

Feature	Site	Surface temperature	T Chalcedony	T QZ[a]	T QZ[b]
Fizzy Pool	Sulphur Springs	42	147	169	159
Lake Placid	Sulphur Springs	70	96	124	122
Painted pool	Sulphur Springs	87	64	95	97
Small green gasser	Sulphur Springs	86	88	116	115

Note: Geothermometers are from Fournier (1977).

[a] Quartz, no steam-loss.

[b] Quartz steam-loss.

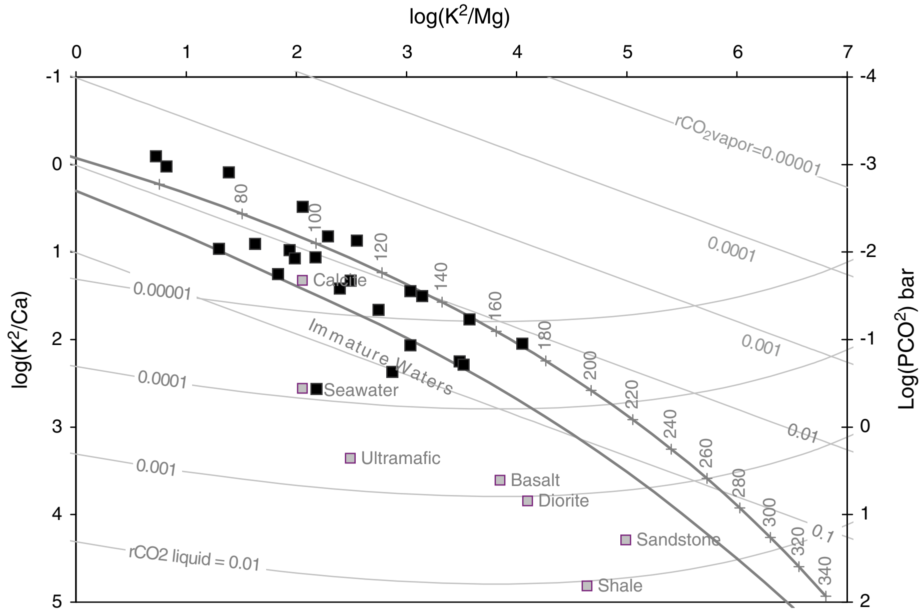

Fig. 7. Plot of log (K_2/Mg) vs. log (K_2/Ca), used to evaluate the PCO_2 of geothermal liquids. The stability fields of calcite, the full equilibrium line, and the dissolution lines of basalt, sandstone and shale are also shown.
From Giggenbach, 1988.

6. Gas chemistry

6.1. Chemical composition of gases

The chemical composition of the dry gas fraction of the hydrothermal gases of Sulphur Springs, expressed in mmol/mol, is reported in Table 4. Composition of the dry gas fraction is dominated by CO_2 (601–993 mmol/mol), followed by the acidic species H_2S (2–190 mmol/mol) and HCl (5–198 mmol/mol). Smaller amounts of N_2 (1–85 mmol/mol) and H_2 (3–41), O_2 (0–30 mmol/mol) were also found. Very low Ar (<1.8 mmol/mol) (with the exception of one sample from Small Green Gasser in 2002), He ($<3\times10^{-4}$ mmol/mol) and CO ($<1\times10^{-2}$ mmol/mol) contents are also observed.

The relative abundances of N_2, He and Ar can be used to determine the contributions of fluids from various source regions (i.e. meteoric, magmatic, or crustal) to the gases, as a function of tectonic setting (Giggenbach, 1996). Additionally, reactions between the hydrothermal fluids and the surrounding rocks can result in the production of H_2, H_2S, and CO_2 in the hydrothermal reservoir (Chiodini and Marini, 1998). The compositions of the gases from Sulphur Springs are plotted in the context of N_2–He–Ar and Ar–H_2S–CH_4 ternary diagrams to examine contributions from various fluid source regions (Fig. 8). The gases generally have N_2/Ar ratios (>100) that are typically associated with arc-type settings, and attributed to the addition of N_2 to the mantle wedge from subducted oceanic sediments (Giggenbach, 1996; Snyder et al., 2003).

Some samples show significant contamination from the atmosphere, as seen by the shift towards the air and air saturated groundwater (ASW) compositions (Fig. 8a). This can also be observed by comparison of the N_2/O_2 ratios of the samples with that of air. For example, the May 2003 fracture fumarole sample has a N_2/O_2 ratio of 3.71, which is very close to 3.97 (the N_2/O_2 ratio of air), and indicates that it has been affected by air-contamination. This type of contamination is usually a result of sampling related to weak gas flux, however, some fumaroles, such as from the Tolbachik scoria scones, Kamchatka, do naturally emit air-contaminated gases (Zelenski and Taran, 2012).

6.2. Gas geothermometry

A thermodynamic evaluation of gas equilibria in the CO_2–CH_4–H_2 system was done for the gases of Sulphur Springs, based on its usefulness in providing information on the thermodynamic conditions dominating at depth (Tassi et al., 2010; Vasseli et al., 2010). Thermodynamic conditions of the CO_2–CH_4–H_2 equilibria in the hydrothermal system

Table 4
Gas composition of thermal features from Sulphur Springs (mmol/mol total gas).

Feature	Date	T (°C)	CO_2	H_2S	HCl	He	H_2	Ar	O_2	N_2	CH_4	CO
Dasheen Devil fumarole	04/15/01	137.6	992	7	n.d.	0.0004	5	0.01	0.00	1.6	1.0	0.01
Fizzy pool	04/15/01	70.0	993	3	n.d.	0.0003	5	0.01	0.00	1.4	0.8	0.00
Fizzy pool	05/26/03	41.5	706	190	6	n.d.	25	n.d.	6.13	61.8	4.7	n.d.
Fizzy pool	11/04/03	43.8	795	151	23	n.d.	5	1.83	3.56	19.2	0.8	n.d.
Fracture fumarole	04/15/01	96.6	993	4	n.d.	0.0003	5	0.01	0.00	1.4	0.9	0.01
Fracture fumarole	05/26/03	95.1	658	147	41	n.d.	3	n.d.	30.25	119.8	0.5	n.d.
Fracture fumarole	11/03/03	92.6	672	159	66	n.d.	11	n.d.	5.66	84.9	1.7	n.d.
Small green gasser	04/15/01	93.3	992	4	n.d.	0.0003	6	0.00	0.02	1.6	1.0	0.00
Small green gasser	11/15/02	95.2	558	179	113	n.d.	41	13.06	4.11	85.3	6.7	n.d.
Small green gasser	05/26/03	89.4	601	144	198	n.d.	38	0.05	0.00	12.6	6.0	n.d.
Small green gasser	11/04/03	89.5	678	164	48	n.d.	40	0.72	0.38	63.6	6.3	n.d.

n.d. = not detected.

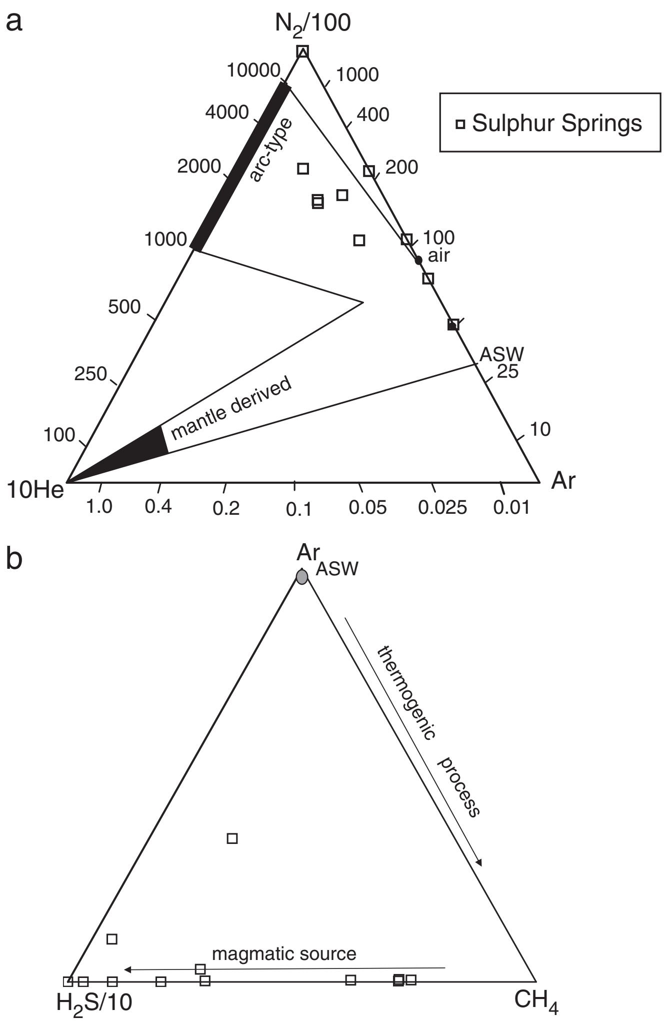

Fig. 8. (a) Ar–N_2–He and (b) CH_4–Ar–H_2S ternary diagrams for hydrothermal gases of Sulphur Springs.

can be shown by the log (X_{H2}/X_{Ar^*}) vs. log (X_{CH4}/X_{CO2}) diagram (Giggenbach and Goguel, 1989; Giggenbach, 1993), where the vapour–liquid equilibrium grid at R_H ranging from −3.6 to −3.0 and temperatures in the interval of ~150–350 °C are depicted (Fig. 9). R_H is a measure of redox potential evaluating the ratio of fugacities of H_2 and H_2O ($R_H = f\,H_2/f\,H_2O$) in order to investigate the predominant redox conditions within the reservoir (Giggenbach, 1987; Taran et al., 2002). The Ar* values, used in Fig. 9, take into consideration the part of Ar related to atmospheric contamination by subtracting a value equal to $O_2/22$ from the Ar concentration of the sample i.e. $Ar^* = Ar–(O_2/22)$. The $O_2/22$ values correspond to the amounts of Ar added by atmospheric contamination, because O_2 is completely absent in pristine hydrothermal fluids and only occurs as the result of shallow level atmospheric contamination (Vaselli et al., 2010). This correction assumes that O_2 is completely absent in the reservoir. $R_H = \log (fH_2/fH_2O)$, is a measure of the redox potential of fugacities of H_2 and H_2O used in order to investigate the predominating conditions within the reservoir. The redox conditions of most hydrothermal fluids are controlled by the FeO/$FeO_{1.5}$ buffer ($R_H = -2.8$). Values of R_H close to −2.8 are found for vapour-dominated systems, whereas values below −2.8 are considered oxidising conditions and are characteristic of geothermal systems. Gases collected from Sulphur Springs plot above the liquid equilibrium curve and appear to be produced by boiling of a liquid phase at temperatures ranging from ~190 °C to 300 °C, with all except one sample plotting at $R_H = < -3.0$ (Fig. 9).

7. Discussion

7.1. Inferences from the composition of thermal waters of Sulphur Springs

The thermal waters of Sulphur Springs are steam-heated acid-sulphate type in character, likely formed by dilution of acidic hydrothermal fluids with oxygenated meteoric waters (Henley and Stewart, 1983). The likely origin of the Ca enriched acid-SO_4 water is the result of the absorption of a H_2S-enriched steam into a shallow aquifer of meteoric origin. The Ca is contributed by the leaching of pyroclastic rocks containing gypsum and/or anhydrite, as well as from the dissolution of limestone inter-bedded with the volcanic rocks, which make up the host lithology (Ander et al., 1984; Wohletz and Heiken, 1987). The relatively high temperatures and acidic waters facilitate enhanced rock dissolution and fluid–rock interaction at depth; thereby further influencing the measured chemical composition of the waters, and releasing Ca by reaction with the limestone rocks. The geochemistry of the thermal waters and gases, and the reservoir temperature (190–300 °C as estimated by gas geothermometry) of Sulphur Springs is consistent with previous structural, petrological, and deep resistivity studies of the geothermal field (Williamson, 1979; Gandino et al., 1985; Wohletz et al., 1986). These studies proposed the existence of fissures that connect a deeper reservoir (at a depth of ~1000–1500 m, and temperature of 220–250 °C), with a groundwater aquifer at an estimated depth of 350–450 m (Fig. 10).

$\delta^{18}O$ and δD values also provide additional evidence that the waters are of primarily meteoric origin, but have been affected by boiling and surface evaporation processes (White, 2005). This type of interaction is common in other similar geothermal systems such as Miravalles, Costa Rica (Gherardi et al., 2002) and Onikobe, Japan (Pang, 2006).

7.2. Origin of geothermal gases of Sulphur Springs

The dominance of CO_2 over S and HCl in the Suphur Springs gases indicates a strong hydrothermal signature for the geothermal system (Fischer et al., 1997). The gas composition is also affected by minor atmospheric and magmatic components (Fig. 8), although typical magmatic gas species (SO_2 and HF) were not detected. This is not surprising, as abundant groundwater or surface waters are known to scrub magmatic gases in volcanic systems (Symonds et al., 2001). Relatively high concentrations of the acidic gas species H_2S and HCl, however, clearly indicate that gases are affected by contributions from a high-temperature source (Fig. 8b). In systems where the gas: water ratio increases from 0.008 to 1.7, temperature increases, pH decreases more drastically, and the less soluble H_2S gas is exsolved from the aqueous phase (Symonds et al., 2001). This may account for the presence of relatively high concentrations of H_2S in the gases of Sulphur Springs. The presence of a low, but significant, Cl content in the low-temperature fumaroles of Sulphur Springs may be explained by a simple mixing model, which takes into account single-step steam separation from a partially condensed mixture of magmatic gas and meteoric water, and the partitioning of Cl between steam and water (Taran et al., 1997); or as was observed at El Chichón Volcano, Mexico where it was attributed to droplets of saline waters in the collecting bottles (Taran et al., 1998). Additional evidence of volatile contributions from a deeper high temperature source is provided by $^3He/^4He$ ratios of geothermal gases for Sulphur Springs of 4.8–5.2R_A (Van-Soest et al., 1998), where R_A = air $^3He/^4He$. These R_A values indicate a significant mantle-derived component of He.

The dominance of CO_2 in the hydrothermal gases (>60% of the dry gas fraction) may be a result of contributions from several sources. CO_2 is derived from a partly magmatic origin; produced by thermal alteration of carbonate rocks and minerals (Marziano and Gaillard, 2006); from the degradation of organic matter within sedimentary

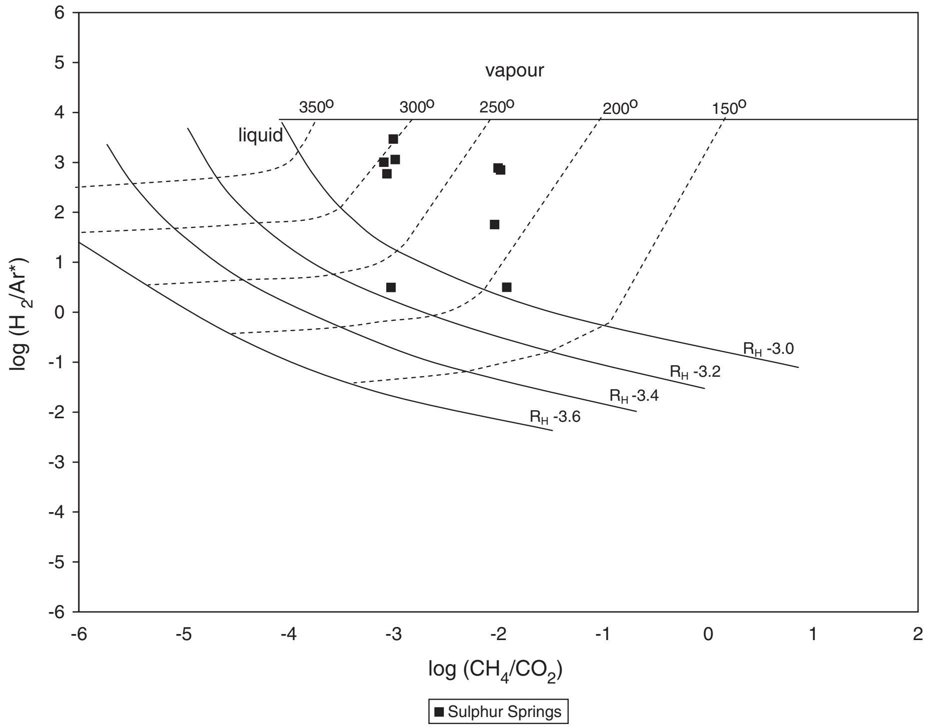

Fig. 9. Binary diagram of log (H_2/Ar*) vs. log (CH_4/CO_2). Ar* = Ar-O_2/22; RH = log (H_2/H_2O) (Giggenbach, 1987).

rocks; and from solutes in meteoric waters (conversion of HCO_3^-(aq) to CO_2(g) on boiling) (Nicholson, 1993).

7.3. Implications for volcanic monitoring

This study provides the first baseline dataset for geochemical monitoring of the Sulphur Springs, Saint Lucia geothermal system (Fig. 10), and complements a similar study that was conducted in the neighbouring island of Dominica (Joseph et al., 2011). Our research suggests that equilibrium temperatures for the Sulphur Springs geothermal system calculated from the evaluation of the H_2/Ar*–CH_4/CO_2 gas ratios (190–300 °C) are higher than those obtained by quartz geothermometry (90–169 °C). The under-estimated temperatures are likely due to the possible non-attainment of the equilibrium implied by the silica geothermometers, as well as the loss of silica by precipitation and/or dilution by the shallow aquifers during ascent to the surface (Tassi et al., 2010; Joseph et al., 2011). Additionally, it is likely that actual reservoir temperatures may exceed those estimated from gas geothermometry due to changes in the chemistry of the hydrothermal fluids resulting from secondary gas–water–rock interactions. This

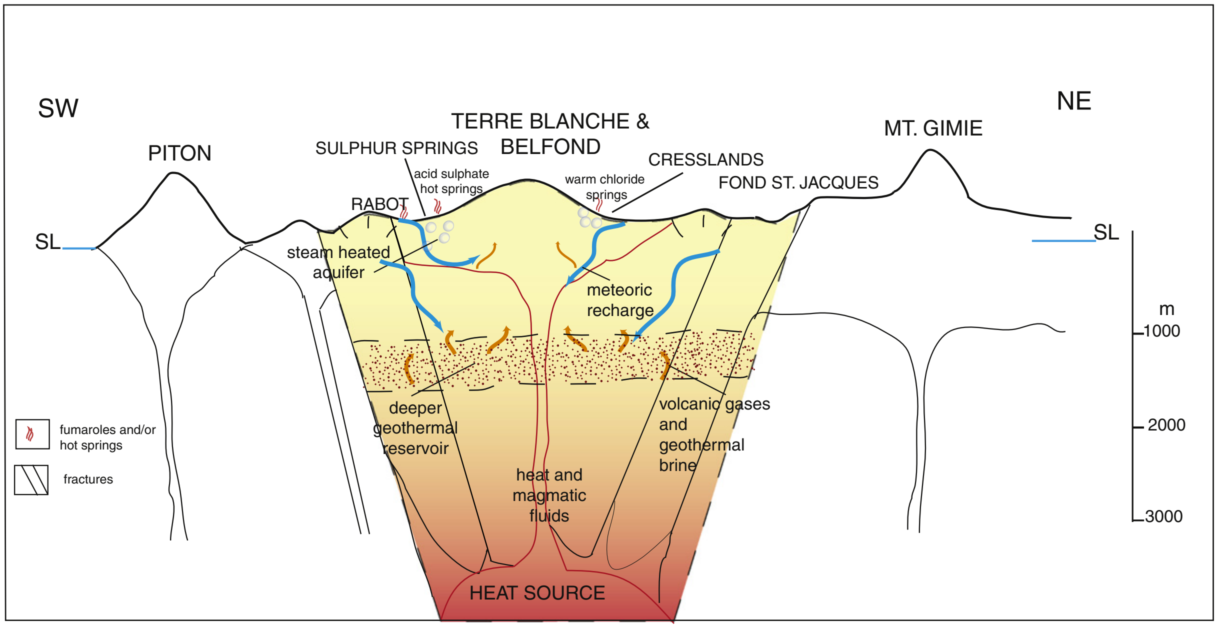

Fig. 10. Schematic cross section of the Qualibou Depression.
Modified after Wohletz et al., 1986.

relationship was also observed for geothermal systems in Dominica (Joseph et al., 2011), which shared the acid-sulphate character of the Sulphur Springs geothermal system.

It is clear from the isotopic data that the water in the hydrothermal system is primarily derived from meteoric input. This implies that any magmatic fluid contribution may be masked by dilution as it ascends to the surface (Fig. 10). The main implication of this is that it reduces our ability to detect changes in chemical composition of the hydrothermal fluids that may be related to precursory volcanic activity. Most of the observed chemical changes over this monitoring period may be attributed to an adjustment in the dynamic circulation of the hydrothermal fluids to the surface, and the results of argillic alterations occurring due to prolonged interaction with strongly acid fluids in the hydrothermal system. There is need for a multi-disciplinary approach to volcanic monitoring in Saint Lucia, with seismic and ground deformation surveillance providing important information in the overall monitoring efforts. This may enable the distinction of temporal changes in the chemical composition of the hydrothermal fluids due to periodic fluxes in fluid transfer and gas–water–rock interaction, as compared to more permanent changes associated with magmatic input to the system.

The lack of significant changes in the chemical composition of gas at the Sulphur Springs geothermal system over the monitoring period suggests that there was no increase in magmatic input during this time. Furthermore, the earthquake swarm that occurred between July 2000 and January 2001, around the time of the start of this study did not provide sufficient geophysical evidence of intrusion of fresh magma in the upper part of the hydrothermal system. Magmatic input to the volcanic system would likely be manifested by changes in gas geochemistry of fumaroles at Sulphur Springs. Fumarolic composition is expected to change from predominantly hydrothermal in character to a more hydrothermal-magmatic composition, with increases in SO_2 being apparent, as was observed at Turrialba volcano, Costa Rica(Vaselli et al., 2010). The possibility of small to medium phreatic eruptions with few geochemical precursors cannot be excluded, as evidenced by the phreatic event from Gabriel's Crater in 2001. This behaviour is comparable to that observed at other volcanoes with hydrothermal systems of similar character e.g. Turrialba in Costa Rica (Vasseli et al., 2010), and Galeras in Colombia (Fischer et al., 1997).

Phreatic eruptions occur when sub-surface geothermal waters are heated to temperatures above their boiling point and flash to steam when they come into contact with nearby magma. Likely precursors of phreatic explosions may include anomalous seismicity, ground deformation, changes in the gas flux, chemistry and temperature of fumaroles and thermal springs (Barberi et al., 1992). An underestimation of the subsurface temperature of the geothermal fluids may therefore result in reduced ability to interpret the likelihood of phreatic events occurring at Sulphur Springs. However, the use of gas geothermometry on fluid samples from Sulphur Springs collected in this study have yielded temperatures consistent with other methods (UNRFNRE, 1989; GI, 1991), and is therefore considered to be a reasonably reliable monitoring tool. Bearing in mind the uncertainty in the absolute values for equilibrium temperatures and their dependence of the buffer used for the calculation, monitoring the relative changes though time in estimated temperatures would provide insights into potential changes in the geothermal system. Measures taken to minimize the potential risk of phreatic events to staff and visitors at Sulphur Springs include forbidding of walking in the geothermal field; and limiting the group size and time spent at viewing platforms that are located in closer proximity to the field. It is clear that continued geochemical monitoring is necessary to develop an understanding of processes occurring in the geothermal system, and to survey the level of volcanic degassing for both volcanic surveillance and public safety.

8. Conclusions

Sulphur Springs is the main site of geothermal activity in Saint Lucia. This study interprets the first comprehensive time series data set of geochemical composition of thermal springs and gases emitted at the site. These data will serve as the baseline for future and continued geochemical monitoring. The thermal waters are acidic steam-heated $Ca–SO_4$ type, thought to be generated by the absorption of a $H_2S–CO_2$ enriched steam into shallow groundwaters that has promoted leaching of the Ca from surrounding pyroclastic rocks containing anhydrite, and the dissolution of carbonate rocks making up the host lithology. The overall composition of the thermal waters reveals that they have not attained chemical equilibria with the host lithology. As a result of their immaturity and high acidity the calculation of reservoir equilibria temperatures using typical solute geothermometers are unreliable.

The hydrothermal gases have typical arc-type N_2/Ar ratios, and have a significant ASW component. However, a magmatic contribution to the gases is evidenced by relatively high proportions of H_2S and HCl. Geothermometric calculations of reservoir temperatures from $H_2/Ar^*–CH_4/CO_2$ gas ratios give a range of 190–300 °C, generally consistent with temperature calculations of 292 °C on fluids obtained from borehole sampling (UNRFNRE, 1989), and 280 °C as estimated from gas geothermometers (GI, 1991) from previous studies. There is no evidence from this study of changes to the Sulphur Springs geothermal system between the period 2001 and 2006.

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