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

Erouscilla P. Joseph a,⁎, Nicolas Fournier b, Jan M. Lindsay c, Richard Robertson a, Denise M. Beckles d

⁎ Corresponding author. Tel.: +1 868 662 4659x36; fax: +1 868 662 9293.
E-mail address: pjoseph@uwiseismic.com (E.P. Joseph).


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A B S T R A C T

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 N2 excess and low He and Ar content. The dry gas composition is dominated by CO2 (ranging from 601–993 mmol/mol), with deeper magmatic sourced H2S-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 H2S gas, respectively. Sulphur Springs hydrothermal waters have acid-sulphate type compositions (SO4 = 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 δ18O and δD (δ18O = −1 to 15‰ and δD = −9 to 14‰ respectively) in relation to the global meteoric water line (GMWL). These waters are steam-heated water typically formed by absorption of H2S-rich gases in the near surface oxygenated groundwaters. Reservoir temperatures calculated from the evaluation of gas equilibria in the CO2–CH4–H2 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.

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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, geochemical 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).
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 (Aluppa 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 geochemical 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) reevaluate the reservoir temperatures and state of equilibrium on the basis of gas and solute geothermometry; and (c) 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 km². 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 south-west 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.
interpretation of the recent swarms is that several near plate bound-
earthquakes which make them difficult to interpret. The most likely
classification of shallow swarms is that they are related to the area of
most recent volcanic activity, 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 Dia-
mond 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.

2.2. Geothermal activity

There are several areas of fumarolic and hot spring activity associ-
ated with the Soufrière Volcanic Centre. The main site of geothermal
activity occurs at the well-known Sulphur Springs area (Fig. 1). Ther-
mal manifestations at Sulphur Springs include features such as boiling
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(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 identifi-
cation 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 earth-
quake (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 (< 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 tecton-
ic 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 bound-
ary intraplate earthquakes of magnitude ≥3 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 geo-
thermal 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 di-
rected 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; Gl, 1991; GENZL, 1992). While the area
was found to have significant geothermal potential and several explora-
 tors 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 SO4 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, Rh, Sb, Se, Zn (Goff and Vuataz, 1984; Gl, 1991). The subsurface
reservoir temperature was estimated to be 280 °C based on the em-
pirical gas geothermometer of D’Amore and Panichi (1980).

In 1986 a geothermal feasibility study of the SVC was jointly con-
ducted 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 col-
lected 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 in-
creased with time suggesting the presence of a boiling brine in the
deep reservoir, that might be partially influenced by sea water rechage
(Gl, 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 geo-
chemical, 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 com-
prised of numerous hot springs, bubbling mud pools, boiling springs,
and fumaroles in an area of strongly argillic altered rock approxi-
mately 200 m x 100 m in size (Fig. 2b). Many fumaroles have tempera-
atures 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 x 3 m in size. The geothermal activity
at this feature is usually fairly intense, with water spouting at the cen-
tre 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.

(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.
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 an adjacent pool of roughly the same size developing alongside it that had not previously existed in 2001. The water temperature fluctuated 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 HNO₃ 1:1) samples (for cation and SiO₂ analyses) were collected and stored in individual polyethylene bottles. Unfiltered water samples were stored in glass Quorpak bottles for stable isotope analyses.

Table 1

<table>
<thead>
<tr>
<th>Feature</th>
<th>Date</th>
<th>pH</th>
<th>T (°C)</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Fe³⁺</th>
<th>Al³⁺</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>Br⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
<th>SiO₂</th>
<th>TDS</th>
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<td>5/21/2006</td>
<td>6.5</td>
<td>87.0</td>
<td>n.m</td>
<td>172</td>
<td>41</td>
<td>83</td>
<td>181</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>106</td>
<td>0</td>
<td>1061</td>
<td>162</td>
<td>56</td>
</tr>
<tr>
<td>Small green gasser</td>
<td>11/14/2002</td>
<td>7.3</td>
<td>95.2</td>
<td>n.m</td>
<td>66</td>
<td>64</td>
<td>16</td>
<td>154</td>
<td>1</td>
<td>72</td>
<td>0</td>
<td>132</td>
<td>1</td>
<td>600</td>
<td>n.d.</td>
<td>1166</td>
</tr>
<tr>
<td>Small green gasser</td>
<td>5/26/2003</td>
<td>7.3</td>
<td>89.4</td>
<td>n.m</td>
<td>145</td>
<td>65</td>
<td>3</td>
<td>131</td>
<td>1</td>
<td>18</td>
<td>2</td>
<td>92</td>
<td>8</td>
<td>379</td>
<td>244</td>
<td>n.m</td>
</tr>
<tr>
<td>Small green gasser</td>
<td>11/4/2003</td>
<td>7.3</td>
<td>89.5</td>
<td>n.m</td>
<td>332</td>
<td>123</td>
<td>4</td>
<td>255</td>
<td>1</td>
<td>17</td>
<td>3</td>
<td>50</td>
<td>26</td>
<td>758</td>
<td>37</td>
<td>n.m</td>
</tr>
<tr>
<td>Small green gasser</td>
<td>3/17/2005</td>
<td>7.3</td>
<td>96.7</td>
<td>n.m</td>
<td>138</td>
<td>37</td>
<td>14</td>
<td>118</td>
<td>0</td>
<td>17</td>
<td>2</td>
<td>93</td>
<td>1</td>
<td>358</td>
<td>201</td>
<td>n.m</td>
</tr>
<tr>
<td>Small green gasser</td>
<td>5/22/2006</td>
<td>3.8</td>
<td>86.3</td>
<td>n.m</td>
<td>37</td>
<td>30</td>
<td>1</td>
<td>8</td>
<td>0</td>
<td>6</td>
<td>25</td>
<td>0</td>
<td>79</td>
<td>n.d.</td>
<td>88</td>
<td>281</td>
</tr>
</tbody>
</table>

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, H2,

O2, Ar, N2, CH4, and CO. He, H2, and O2 were analysed with Ar carrier

gas; and Ar, N2, CH4 and CO were analysed with H2 carrier gas.

Wet chemistry techniques were used for the analysis of acidic

gases CO2, H2S, and HCl, trapped in the alkaline solution. Acidimetric

titration with 0.1 N AgNO3 was used for evaluation S\text{tot} (which is assumed to be

entirely composed of H2S), and titration with 1 N AgNO3 was used for

HCl.

5. Water chemistry

5.1. Chemical composition of thermal waters

The temperature, pH, and composition of the major chemical spe-
cies in the thermal waters from Sulphur Springs are reported in
Table 2. Oxygen and hydrogen stable isotope data are shown in
Table 1. The temperatures of the thermal water samples at Sul-

phur Springs (excluding the recreational sites) ranged from 65 to

97 °C, with the temperature of individual features showing a vari-
ation of only ~10 °C between seasonal sampling periods. The excep-
tion 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 HCO3 (<250 mg/L), relatively high concentrations of SO4 (78–

4008 mg/L), and lower concentrations of Cl (24–138 mg/L).

The classification of the waters from Sulphur Springs based on their
relative amounts of Cl–SO4–HCO3, Na–SO4–Mg and Mg–Ca–Na is shown in
Fig. 3. The waters are generally Na/Ca–SO4 steam-heated acidic
waters, resulting from the condensation of acid hydrothermal gases
(principally H2S, and CO2) into near-surface oxygenated waters. There
is also a positive correlation between SO4 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 SO4/Ca mole
ratios in the geothermal waters ranged from ~1–18, providing evidence
that the SO4 composition in the waters is not only influenced by the

Table 2

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Feature</th>
<th>Date</th>
<th>δ18O VSMOW</th>
<th>δD VSMOW</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Fizzy Pool</td>
<td>11/14/2002</td>
<td>+8.44</td>
<td>6</td>
</tr>
<tr>
<td>P1</td>
<td>Fizzy Pool</td>
<td>11/14/2002</td>
<td>+8.46</td>
<td>7</td>
</tr>
<tr>
<td>P6</td>
<td>Lake Placid</td>
<td>11/14/2002</td>
<td>+14.79</td>
<td>14</td>
</tr>
<tr>
<td>P6</td>
<td>Lake Placid</td>
<td>11/14/2002</td>
<td>+14.83</td>
<td>14</td>
</tr>
<tr>
<td>P7</td>
<td>Small green gasser</td>
<td>11/14/2002</td>
<td>−1.20</td>
<td>9</td>
</tr>
<tr>
<td>P7</td>
<td>Small green gasser</td>
<td>11/14/2002</td>
<td>−1.23</td>
<td>9</td>
</tr>
<tr>
<td>P12</td>
<td>Painted pool</td>
<td>11/14/2002</td>
<td>+9.91</td>
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</tr>
<tr>
<td>P12</td>
<td>Painted pool</td>
<td>11/14/2002</td>
<td>+9.86</td>
<td>4</td>
</tr>
<tr>
<td>SU3*</td>
<td>Jun-01</td>
<td></td>
<td>+0.99</td>
<td>6</td>
</tr>
<tr>
<td>SU4*</td>
<td>Jun-01</td>
<td></td>
<td>+14.40</td>
<td>13</td>
</tr>
<tr>
<td>SU9*</td>
<td>Jun-01</td>
<td></td>
<td>+11.75</td>
<td>8</td>
</tr>
<tr>
<td>SU12*</td>
<td>King Louis bath</td>
<td>Jun-01</td>
<td>−2.64</td>
<td>11</td>
</tr>
<tr>
<td>SU13*</td>
<td>Platform pool</td>
<td>Jun-01</td>
<td>−2.30</td>
<td>11</td>
</tr>
<tr>
<td>SS1*</td>
<td>Platform pool</td>
<td>Nov-00</td>
<td>−2.97</td>
<td>16</td>
</tr>
<tr>
<td>SS2*</td>
<td>King Louis bath</td>
<td>Nov-00</td>
<td>−3.12</td>
<td>19</td>
</tr>
<tr>
<td>SS3*</td>
<td>Nov-00</td>
<td>+5.80</td>
<td>−9</td>
<td></td>
</tr>
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<td>SS4*</td>
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<td>+10.50</td>
<td>−1</td>
<td></td>
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<tr>
<td>SS6*</td>
<td>Nov-00</td>
<td>+12.20</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>SS7*</td>
<td>Bridge Pool</td>
<td>Nov-00</td>
<td>−0.40</td>
<td>−14</td>
</tr>
</tbody>
</table>

* Data from Greenwood (2004).
leaching of surrounding pyroclastic rocks, but also by the contribution of sulphur from the hydrothermal gases.

5.2. $\delta^{18}O$ and $\delta^D$ 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 $\delta^D$ (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 $\delta^D$ 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.
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.

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 CO2 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):

\[
\text{Ca-Al}_2\text{-silicate} + \text{K-feldspar} + \text{CO}_2 \leftrightarrow \text{K-mica} + \text{calcite}
\]

The purpose of the plot is to determine the partial pressure of CO2 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 CO2 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 CO2 contents too low to induce rock alterations as expressed in Eq. (1), implying that the CO2 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>
<thead>
<tr>
<th>Feature</th>
<th>Site</th>
<th>Surface temperature</th>
<th>T Chalcedony</th>
<th>T QZa</th>
<th>T QZb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fizzy Pool</td>
<td>Sulphur Springs</td>
<td>42</td>
<td>147</td>
<td>169</td>
<td>159</td>
</tr>
<tr>
<td>Lake Placid</td>
<td>Sulphur Springs</td>
<td>70</td>
<td>96</td>
<td>124</td>
<td>122</td>
</tr>
<tr>
<td>Painted pool</td>
<td>Sulphur Springs</td>
<td>87</td>
<td>64</td>
<td>95</td>
<td>97</td>
</tr>
<tr>
<td>Small green gasser</td>
<td>Sulphur Springs</td>
<td>86</td>
<td>88</td>
<td>116</td>
<td>115</td>
</tr>
</tbody>
</table>

Note: Geothermometers are from Fournier (1977).

\( ^a \) Quartz, no steam-loss.

\( ^b \) Quartz steam-loss.
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 CO2 (601–993 mmol/mol), followed by the acidic species H2S (2–190 mmol/mol) and HCl (5–198 mmol/mol). Smaller amounts of N2 (1–85 mmol/mol) and H2 (3–41) were found. O2 (0–30 mmol/mol), Ar (<1.8 mmol/mol) (with the exception of one sample from Small Green Gasser in 2002), He (<3×10^-4 mmol/mol), and CO (<1×10^-2 mmol/mol) contents are also observed.

The relative abundances of N2, 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 H2, H2S, and CO2 in the hydrothermal reservoir (Chiodini and Marini, 1998). The compositions of the gases from Sulphur Springs are plotted in the context of N2–He–Ar and Ar–H2S–CH4 ternary diagrams to examine contributions from various fluid source regions (Fig. 8). The gases generally have N2/Ar ratios (>100) that are typically associated with arc-type settings, and attributed to the addition of N2 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 N2/O2 ratios of the samples with that of air. For example, the May 2003 fracture fumarole sample has a N2/O2 ratio of 3.71, which is very close to 3.97 (the N2/O2 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 cones, Kamchatka, do naturally emit air-contaminated gases (Zelenski and Taran, 2012).

6.2. Gas geothermometry

A thermodynamic evaluation of gas equilibria in the CO2–CH4–H2 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 CO2–CH4–H2 equilibria in the hydrothermal system (Fig. 7). The stability fields of calcite, the full equilibrium line, and the dissolution lines of basalt, sandstone and shale are also shown. From Giggenbach, 1988.

Fig. 7. Plot of log (K2/Mg) vs. log (K2/Ca), used to evaluate the PCO2 of geothermal liquids. The stability fields of calcite, the full equilibrium line, and the dissolution lines of basalt, sandstone and shale are also shown.


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

<table>
<thead>
<tr>
<th>Feature</th>
<th>Date</th>
<th>T (°C)</th>
<th>CO2</th>
<th>H2S</th>
<th>HCl</th>
<th>He</th>
<th>H2</th>
<th>Ar</th>
<th>O2</th>
<th>N2</th>
<th>CH4</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dasheen Devil fumarole</td>
<td>04/15/01</td>
<td>137.6</td>
<td>992</td>
<td>7</td>
<td>n.d.</td>
<td>0.0004</td>
<td>5</td>
<td>0.01</td>
<td>0.00</td>
<td>1.6</td>
<td>1.0</td>
<td>0.01</td>
</tr>
<tr>
<td>Fizzy pool</td>
<td>04/15/01</td>
<td>70.0</td>
<td>993</td>
<td>3</td>
<td>n.d.</td>
<td>0.0003</td>
<td>5</td>
<td>0.01</td>
<td>0.00</td>
<td>1.4</td>
<td>0.8</td>
<td>0.00</td>
</tr>
<tr>
<td>Fizzy pool</td>
<td>05/26/03</td>
<td>41.5</td>
<td>706</td>
<td>190</td>
<td>6</td>
<td>n.d.</td>
<td>25</td>
<td>n.d.</td>
<td>6.13</td>
<td>61.8</td>
<td>4.7</td>
<td>n.d.</td>
</tr>
<tr>
<td>Fizzy pool</td>
<td>11/04/03</td>
<td>43.8</td>
<td>795</td>
<td>151</td>
<td>23</td>
<td>n.d.</td>
<td>5</td>
<td>1.83</td>
<td>3.56</td>
<td>19.2</td>
<td>0.8</td>
<td>n.d.</td>
</tr>
<tr>
<td>Fracture fumarole</td>
<td>04/15/01</td>
<td>96.6</td>
<td>993</td>
<td>4</td>
<td>n.d.</td>
<td>0.0003</td>
<td>5</td>
<td>0.01</td>
<td>0.00</td>
<td>1.4</td>
<td>0.9</td>
<td>0.01</td>
</tr>
<tr>
<td>Fracture fumarole</td>
<td>05/26/03</td>
<td>95.1</td>
<td>658</td>
<td>147</td>
<td>41</td>
<td>n.d.</td>
<td>3</td>
<td>n.d.</td>
<td>30.25</td>
<td>119.8</td>
<td>0.5</td>
<td>n.d.</td>
</tr>
<tr>
<td>Fracture fumarole</td>
<td>11/03/03</td>
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<td>672</td>
<td>159</td>
<td>66</td>
<td>n.d.</td>
<td>11</td>
<td>n.d.</td>
<td>5.66</td>
<td>84.9</td>
<td>1.7</td>
<td>n.d.</td>
</tr>
<tr>
<td>Small green gasser</td>
<td>04/15/01</td>
<td>93.3</td>
<td>992</td>
<td>4</td>
<td>n.d.</td>
<td>0.0003</td>
<td>6</td>
<td>0.00</td>
<td>0.02</td>
<td>1.6</td>
<td>1.0</td>
<td>0.00</td>
</tr>
<tr>
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<td>11/15/02</td>
<td>95.2</td>
<td>558</td>
<td>179</td>
<td>113</td>
<td>n.d.</td>
<td>41</td>
<td>13.06</td>
<td>4.11</td>
<td>85.3</td>
<td>6.7</td>
<td>n.d.</td>
</tr>
<tr>
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<td>05/26/03</td>
<td>89.4</td>
<td>601</td>
<td>144</td>
<td>198</td>
<td>n.d.</td>
<td>38</td>
<td>0.05</td>
<td>0.00</td>
<td>12.6</td>
<td>6.0</td>
<td>n.d.</td>
</tr>
<tr>
<td>Small green gasser</td>
<td>11/04/03</td>
<td>85.5</td>
<td>678</td>
<td>164</td>
<td>48</td>
<td>n.d.</td>
<td>40</td>
<td>0.72</td>
<td>0.38</td>
<td>63.8</td>
<td>6.3</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

n.d. = not detected.
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-SO₄ water is the result of the absorption of a H₂S-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., 1983; 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).

δ¹⁸O 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 CO₂ over S and HCl in the Sulphur 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 (SO₂ 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 H₂S 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 H₂S gas is exsolved from the aqueous phase (Symonds et al., 2001). This may account for the presence of relatively high concentrations of H₂S 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., 1998); 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 4.8–5.2RA (Van-Soest et al., 1998), where RA = air ³He/⁴He. These RA values indicate a significant mantle-derived component of He.

The dominance of CO₂ in the hydrothermal gases (>60% of the dry gas fraction) may be a result of contributions from several sources. CO₂ 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
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. 9. Binary diagram of log (H$_2$/Ar*) vs. log (CH$_4$/CO$_2$). Ar* = Ar–O$_2$/2; RH = log (H$_2$/H$_2$O) (Giggenbach, 1987).](image)

![Fig. 10. Schematic cross section of the Qualibou Depression. Modified after Wohletz et al., 1986.](image)
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 SO₂ 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 (Vaselli 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 hydrothermal 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 hydrothermal 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–SO₄ type, thought to be generated by the absorption of a H₂S–CO₂ 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 N₂/Ar ratios, and have a significant ASW component. However, a magmatic contribution to the gases is evidenced by relatively high proportions of H₂S and HCl. Geothermometric calculations of reservoir temperatures from H₂/Ar*–CH₄/CO₂ 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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