Carbon and helium isotopes in thermal springs of La Soufrière volcano (Guadeloupe, Lesser Antilles): Implications for volcanological monitoring

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ABSTRACT

La Soufrière (Guadeloupe, Lesser Antilles) is one of the most active and dangerous volcanoes of the Lesser Antilles arc. The renewal of the volcanic activity at La Soufrière requires replenishment of the volatile-poor andesitic stored magma with more primitive, volatile-rich basaltic magma. This event will trigger early release of large quantities of highly volatile species, like CO₂ and helium, in the hydrothermal system. To use these precursors, first their baseline abundances and their behaviour in the hydrothermal system must be known during the current phase of dormancy. In this study, we have combined a previous systematic investigation of noble gases with carbon data of hydrothermal fluids flowing out of La Soufrière.

The results for dissolved gases reveal that an intense interaction between rising magmatic volatiles and groundwaters currently takes place at La Soufrière. We show that the pristine magmatic composition, with a $\delta^{13}\text{C}_{\text{CO}_2}$ value of $-3.19 \pm 0.03\text{‰}$, a $^3\text{He}/^4\text{He}$ ratio of $8.1 \pm 0.2 R_a$ and a $\text{CO}_2/{}^3\text{He}$ ratio of $1.03 \pm 0.18 \times 10^{10}$, may vary during the ascent of magmatic fluids due to either fractionation or mixing processes with meteoric water and/or an organic component. Here, we provide a baseline for CO₂ and helium isotopes at each monitored spring and describe the superficial processes affecting both elemental and isotopic ratios.

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1. Introduction

The most recent eruptive activity at La Soufrière (Guadeloupe Island, Lesser Antilles) was a phreatic eruption in 1976–77 (Feuillard et al., 1983; Komorowski et al., 2005). That event led to the evacuation of 73,000 people living in the vicinity of the volcano for six months. La Soufrière remains one of the most active and dangerous volcanoes of the Lesser Antilles arc and the potential for any new unrest raises concerns regarding the safety of the growing population (Komorowski et al., 2005).

The Volcanological and Seismological Observatory of Guadeloupe (hereafter OVSG) monitors the volcano through a broad geophysical and geochemical network. Monthly hydrothermal fluid sampling provides information on the temporal changes in the magmatic system (OVSG-IPGP, 1978–2012). In fact, the well-established hydrothermal system of La Soufrière continually incorporates the rising magmatic fluids degassed by the magma chamber. However, superficial hydrothermal processes (e.g.: late degassing, mixing, water–

rock interactions) can affect those deep fluids (Federico et al., 2002; Di Napoli et al., 2009).

In this study, we focus on the processes affecting each hydrothermal manifestation located on the volcano using both CO₂ and helium and their isotopes, as tracers. Our aim is to refine our understanding of the hydrothermal system, which plays a critical role in the activity of La Soufrière. Carbon dioxide is the least soluble species in magmas (Dixon and Stolper, 1995). Therefore, the deep exsolution of this species and its low solubility in hydrothermal systems imply that carbon systematics is ideally suited to monitor the magmatic component injected into the system. However, CO₂ exsolution, precipitation as calcite and biogenic contributions can disturb its budget. Therefore, a second tracer, which is not affected by these processes, should be considered. Owing to their high incompatibilities in magma, low concentrations and unreactive nature, the noble gases measured in hydrothermal fluids supplement the information provided by the carbon data. Also, the $\text{CO}_2/{}^3\text{He}$ ratio can be used to distinguish between observed variations coming from the magmatic source and any variations due to the hydrothermal effects (e.g. Allard et al., 1997; Federico et al., 2002).

Here, we combine previous published noble gases data (Ruzié et al., 2012) with carbon data from hydrothermal springs and fumaroles sampled at the same time at La Soufrière over a 3 year period. Ruzié

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et al. (2012) focused on magmatic degassing processes through the use of noble gas tracers. No attention was given to the hydrothermal system. This decision was due to the fact that helium and neon have similar solubilities in water (e.g. Fernandez-Prini et al., 2003) which renders them inappropriate to describe the superficial processes such as degassing. By coupling carbon with helium/neon data, the range of solubilities increases, as well as the sensitivity to superficial processes. With both elemental and isotopic ratios, we propose a model of fluid circulation under the present non-eruptive conditions that could serve as a baseline for geochemical monitoring of the volcano.

2. Geological setting

2.1. Volcanological activity

The island of Guadeloupe is located in the Lesser Antilles island arc (Fig. 1A). La Soufrière volcano, located in the southern part of Basse-Terre, is the only active volcanic centre on the island. It is an andesitic explosive volcano with past activity characterised by Pelean and Plinian eruptions (Boudon et al., 1989). The last magmatic eruption occurred 560 years ago (Boudon et al., 2008).

Since 1635, only phreatic eruptions occurred in 1690, 1797–1798, 1836–1837, 1956, 1976–1977 (Komorowski et al., 2005). The triggering of the last phreatic eruption (1976–77) is still debated: aborted magmatic eruption (Feuillard et al., 1983; Villemant et al., 2005; Boichu et al., 2008, 2011) versus pure hydrothermal control (Zlotnicki et al., 1992). Recently, Ruzié et al. (2012) proposed that this last phreatic eruption was triggered by both: the emplacement of a new magma batch in the magmatic chamber around 1959–1962 followed by a progressive clogging of the hydrothermal system. This new scenario is based on the fact that the actual ^3He flux at the Central South Crater (CSC) Fumarole (0.02 mol/year) cannot be sustained since the last magmatic eruption. Ruzié et al. (2012) concluded that the actual magmatic chamber (located at 6 km depth) must be regularly fed by fresh basaltic magma batches.

After a period of relatively low activity (1984–1992), fumarolic manifestations increased in 1992 in a period also marked by a seismic crisis and the reactivation of two thermal springs (Zlotnicki et al., 1994; Boichu et al., 2011; OVSG-IPGP, 1978–2012). In 1998, the fumarolic

condensates became more acidic due to chlorine degassing as HCl. This was followed by reactivation of dome summit fumaroles at South Crater (1998), at Napoleon (2000), at Tarissan (2002) (Bernard et al., 2006; Nicollin et al., 2006, 2007) and more recently, Gouffre 1956 (2007), while the dome flank fumaroles at la Route de la Citerne progressively vanished (OVSG-IPGP, 1978–2012; Allard et al., 1998).

2.2. Hydrothermal system

The hydrothermal system of La Soufrière is composed of a main aquifer with restricted size delimited by the Amic caldera borders (Barat, 1986). This aquifer is fed by meteoric water percolating through recent pyroclastic deposits (Bigot et al., 1994b; Brombach et al., 2000; Pascaline et al., 1982; OVSG-IPGP, 1978–2012). The main aquifer is also subjected to a gas flux derived from an underlying degassing magma chamber (Villemant et al., 2005; Ruzié et al., 2012). The roof of this main aquifer is thought to be located at a depth of 500 m under the dome summit and its temperature is between 190°C and 260°C (Brombach et al., 2000). This main aquifer is therefore most likely continually boiling. These temperatures are also in good agreement with the hydrothermal mineral assemblages observed in debris avalanche deposits of La Soufrière (smectite + silica $\pm$ pyrite $\pm$ natrojarosite). This assemblage is formed at temperatures below 300°C (Salaün et al., 2011). The dome is made of unaltered massive andesite lava separated by major radial fractures as demonstrated by both electrical tomography (Nicollin et al., 2006) and VLF survey (Zlotnicki et al., 2006). Numerous low-density parts of highly hydrothermalized and unconsolidated materials (Lesparre et al., 2012) could also contain small shallow aquifers, feeding the thermal springs.

The distribution of the thermal springs on La Soufrière is controlled by geological structures (Fig. 1B). Seven thermal springs are located in the Amic Crater at high altitudes (1146–981 m) and at a maximum distance of 1.2 km from the lava dome: Ravine Marchand (RM3), Galion (GA), Galion Bas (GAB), Carbet-Echelle (CE), Bains Jaunes (BJ), Pas du Roy (PR) and Tarade (TA). One spring, Bains Chauds du Matouba (BCM), is located outside the Amic Crater but still in La Grande Découverte Caldera. Finally, two springs lie outside La Grande Découverte Caldera: one on the eastern flank of the volcano, Chute du Carbet (CC), at 2.1 km from the

Fig. 1. Sample location. A) Map of Lesser Antilles Arc. B) Structural map of La Grande Découverte/Soufrière volcanic complex showing the locations of the monitored thermal springs and South Crater (CSC) fumarole.

Table 1

Helium and carbon isotopic compositions of dissolved gases in La Soufrière volcano thermal springs.

Sample name	Sampling date	Sample type	Dome distance (m)	Alt. (m)	Temp. (°C)	pH	[R _m /R _a] ¹	σ	⁴ He/ ²² Ne	σ	[R _c /R _a] ²	σ	³ He (×10 ^{−14} ccSTP/g)	X _m ³	TDIC (mmol/l)	[TDIC _i] ⁴ (mmol/l)	δ ¹³ C ⁵ (‰)	CO ₂ / ³ He (×10 ¹⁰)
Bains Jaunes																		
GUA07_BJ	Jul-07	Ca-SO ₄ water	1200	981	31.4	5.6	1.02	0.10	3.0	0.2	–	–	7	12%	0.86		−5.10	29
GUA09_BJ	May-09				33.9	5.5	1.38	0.04	3.1	0.2	–	–	9	17%	1.56		−7.83	40
GUA10_BJ	Oct-10				29.4	5.4	1.40	0.06	2.9	0.1	–	–	8	17%	2.21		−4.97	59
Bains Chauds du Matouba																		
GUA07_BCM	Jul-07	Ca-SO ₄ water	1250	1055	58.5	5.9	4.38	0.31	5.1	0.3	8.0	0.8	102	99%	0.79		−10.04	1.7
Carbet Echelle																		
GUA07_CE	Jul-07	Ca-SO ₄ water	640	1146	20.9	5.4	6.61	0.45	12.3	0.8	8.1	0.6	162	100%	5.59	8.59	−2.87	12
GUA09_CE	May-09				20.3	5.4	6.55	0.11	13.6	0.7	8.2	0.2	176	100%	6.58	11.09	−2.80	14
Central South Crater Fumarole																		
GUA07_CSC	May-07	Fumarole	0	1476	120	0.7	7.80	0.20	442	3	7.9	0.2	^a	99%	^a		−3.17	1.2
GUA09_CSC	Oct-10				97.9	2.0	7.60	0.30	56.3	1.0	8.2	0.4	^b	100%	^b		−3.21	0.9
Chute du Carbet																		
GUA07_CC	Jul-07	Ca-Na-Cl water	2100	605	44.5	6.6	5.22	0.36	9.8	0.7	6.8	0.5	103	84%	3.24	3.74	−2.95	8.2
GUA10_CC	Oct-10				44.7	6.6	4.88	0.18	9.2	0.2	6.4	0.3	108	79%	3.89	4.80	−2.73	9.8
Galion bas																		
GUA07_GAB	Jul-07	Ca-SO ₄ water	760	1100	41.4	4.8	6.76	0.47	15.1	1.0	8.0	0.6	60	99%	7.45		−3.00	28
GUA09_GAB	May-09				41.6	4.7	5.27	0.10	8.2	0.4	7.3	0.2	37	90%	5.22		−3.00	32
GUA10_GAB	Oct-10				42.8	4.9	5.94	0.22	10.1	0.3	7.7	0.3	51	95%	–		–	–
Galion																		
GUA07_GA	Jul-07	Ca-SO ₄ water	760	1100	45.7	4.8	5.91	0.42	10.6	0.7	7.5	0.6	39	93%	8.97		−3.39	52
GUA09_GA	May-09				45.8	4.7	5.47	0.11	9.4	0.5	7.2	0.2	35	89%	7.43		−3.37	48
GUA10_GA	Oct-10				45.9	5.0	5.35	0.20	8.9	0.3	7.2	0.3	41	89%	–		–	–
Tarade																		
GUA09_TA	May-09	Ca-SO ₄ water	1000	1079	41.4	6.0	3.75	0.07	5.2	0.1	6.5	0.2	36	80%	4.36	6.36	−2.63	40
GUA10_TA	Oct-10				39.4	6.1	3.49	0.14	4.1	0.1	8.0	0.6	27	99%	2.98	3.98	−2.55	34
Pas du Roy																		
GUA07_PR	Jul-07	Ca-SO ₄ water	1200	1008	34.0	5.6	2.77	0.20	3.7	0.3	7.1	1.2	51	88%	3.28		−3.01	38
GUA09_PR	May-09				33.9	5.6	2.88	0.06	3.8	0.2	7.0	0.7	49	86%	3.26		−3.27	36
GUA10_PR	Oct-10				34.2	5.8	2.65	0.10	3.7	0.1	6.5	0.5	51	80%			–	–
Habitation Revel																		
GUA09_HR	May-09	Ca-Na-HCO ₃ water	3700	609	31.2	6.8	4.51	0.08	10.1	0.5	5.7	0.1	89	70%	2.83		−18.11	7.1
GUA10_HR	Oct-10				33.4	6.7	3.49	0.13	5.5	0.1	5.8	0.3	43	71%			–	–
Ravine Marchand 3																		
GUA07_RM3	Jul-07	Ca-SO ₄ water	950	1015	44.9	5.2	7.66	0.52	36.6	2.5	8.2	0.6	197	100%	3.81	10.81	−2.11	11
GUA09_RM3	May-09				48.4	5.2	7.54	0.13	43.1	1.3	8.0	0.1	211	99%	8.33		−3.19	8.9
GUA10_RM3	Oct-10				42.9	5.5	7.45	0.27	32.6	0.8	8.0	0.3	225	99%			–	–

1. R_m: ³He/⁴He ration measured; R_a: ratio of air (1.4 ×10⁻⁶).2. R_c: air corrected helium isotopic ratio, assuming all the neon is derived from air (Poreda and Craig, 1989).3. X_m: percent of the local magmatic end-member based on the calculation of Eq. (9).4. TDIC: TDIC corrected for the CO₂ degassing (see text for more details).

5. Accuracy is ±0.04‰ for TDIC greater than 2 mmol/l and ±0.20‰ for TDIC lower than 2 mmol/l. N.B.: For the gas samples accuracy is ±0.3‰.

^a GUA07_CSC (dry gas): [He] = 5.32 ppm, [CO₂] = 67.45%.^b GUA10_CSC (dry gas): [He] = 6.78 ppm, [CO₂] = 66.43%.

dome summit and one in the western part at 3.7 km (Habitation Revel – HR) (Table 1).

Three types of thermal waters are identified around La Soufrière dome (OVSG-IPGP, 1978–2012; Pascaline et al., 1982; Brombach et al., 2000; Villemant et al., 2005): a) Ca–SO₄ waters produced by mixing of meteoric water and rising magmatic fluids (BCM, BJ, PR, CE, GA, GAB, RM3, TA); b) Ca–Na–HCO₃ springs which are conductively heated (HR) and c) Ca–Na–Cl waters interpreted as a mixture of Ca–SO₄ waters and Na–Cl waters (CC) (Table 1).

Based on major elements and oxygen isotopes, Brombach et al. (2000) defined two settings of the thermal springs at La Soufrière: 1) a central area dominated by the ascent of steam which is extracted from the main aquifer. The steam feeds the summit fumaroles or dissolves in shallow aquifers and 2) an outer zone, where the groundwaters are heated through conduction. For the superficial aquifers hosted in the dome flanks, Villemant et al. (2005) developed a model of fluid circulation using chlorine concentration data recorded since 1979 by the OVSG. The evolution of the chlorine content seems to be related to the location of the springs: the magmatic chlorine signal, injected as pulses, get smoothed and delayed while the distance to the dome increases.

Finally, Van Soest et al. (1998) and Pedroni et al. (1999) reported carbon and noble gas data for springs and fumaroles from several islands of the Lesser Antilles. While their studies are useful at the scale of the arc, La Soufrière of Guadeloupe has been poorly sampled in terms of thermal springs. Therefore, a more detailed and focused study is needed to describe the interactions between the magmatic fluids and the superficial processes that could modify the pristine magmatic signal. We propose to improve our understanding of the

Fig. 2. Carbon and helium variations as a function of the dome distance. A) TDIC (Total Dissolved Inorganic Carbon), B) R_c/R_a ratio (R_c = [³He/⁴He]_{corrected}; R_a = [³He/⁴He]_{air} = 1.4 × 10^{−6}) and C) CO₂/³He versus distance from the dome. The TDIC concentrations and R_c/R_a ratio in thermal springs decrease with increasing distance from the dome centre. No trend seems to appear between CO₂/³He ratio as a function of the dome distance. RM3 = Ravine Marchand, GAB = Galion Bis, GA = Galion, CE = Carbet Echelle, CC = Chute du Carbet, BCM = Bains Chauds du Matouba, TA = Tarade, HR = Habitation Revel, BJ = Bains Jaunes and PR = Pas du Roy.

Fig. 3. Isotopic composition of dissolved CO₂ in thermal waters of La Soufrière vs. the corresponding TDIC (mmol/l). The Rayleigh distillation curve (1) is plotted in dashed line. The theoretical mixing curves between different end-members are plotted. The black solid curve (2) corresponds to a mixture between the local magmatic end-member (δ¹³C = −3.19 ± 0.03‰, TDIC = 10 mmol/l) and the meteoric water (δ¹³C = −8.0/−4.2‰, TDIC = 0.5 mmol/l). The grey lines (3 and 4) reflect a mixture between the magmatic end-member and the organic end-member (δ¹³C = −29/−24‰, TDIC_{soil} comprised between 0.47 and 1.56 mmol/l – Rivé et al., 2013).

hydrothermal system by coupling carbon and noble gas systematics under the present hydrothermal conditions.

3. Field and laboratory methods

In order to understand the superficial processes that could affect the magmatic signal, fluid samples for noble gas analyses were collected once per year (from 2007 to 2010) at 11 sites (Fig. 1B). In this study, we link to these samples to the corresponding carbon measurements.

3.1. Water samples

The water samples for total dissolved inorganic carbon measurements (hereafter TDIC which is defined as [H₂CO₃] + [HCO₃[−]] + [CO₃^{2−}]) were filtered in the field (filter size 0.2 mm) and collected using Labco 12 ml Exetainer vials with no headspace. The vials (hereafter storage vials) were then stored at 4 °C to limit bacterial development until their analysis. The method for TDIC and δ¹³C_{TDIC} value measurements in water has been published previously in detail by Assayag et al. (2006) and is summarised here. The TDIC is released from the sample as CO₂ by the H₃PO₄ acidification method as follows. Fifteen drops of H₃PO₄ are loaded in empty and uncapped 12-ml exetainers (hereafter analytical vial). The analytical vials are then isolated from the atmosphere by screwing a cap equipped with a septum on top of them. The analytical vials are then flushed with pure helium. A fixed quantity (2 or 5 ml depending on the TDIC concentration of the sample) of the natural water sample is extracted with a syringe from the storage vial through the septum. This is accomplished by injecting an equivalent volume of pure helium into the storage vial with a second syringe while the first syringe is used to sample the water. The water is then injected into the analytical vial. Equilibration between CO₂ in the gas phase and CO₂ dissolved in the liquid is obtained by shaking during a period of 15–25 h (see Assayag et al., 2006 for the original tests regarding equilibration time). Two sets of standards are prepared: the first set for concentration determination and the second set for δ¹³C determination. The first set of standard is prepared from an initial solution of NaHCO₃ (with a

known $\delta^{13}\text{C}$) that is then diluted by several factors. This is used for concentration determinations and corrections from non-linearity effects of the mass spectrometer (see details and Fig. 4 in Assayag et al., 2006). The second standard is then prepared with different CaCO_3 powders with known $\delta^{13}\text{C}$ -values. This set of standards is used for carbon isotope determination only. These two sets of standards are analysed before, in-between and after the unknowns to check for drifting analytical conditions of the gas chromatograph-isotope ratio mass spectrometer (GC-IRMS) system. The GC-IRMS system is a helium continuous flow mass spectrometer (GV AP2003©) equipped with a gas chromatograph (see description in Assayag et al., 2006). During the analysis, a fully automated autosampler equipped with a needle sequentially samples the gas ($\text{CO}_2 + \text{He} + \text{traces of water vapour and atmospheric gases}$) in the headspace of the analytical vials. This mixture is then purified to remove water vapour, separated with a GC column and admitted to the source of the mass spectrometer. Concentrations are obtained by comparison of sample height with those of the NaHCO_3 standards. $\delta^{13}\text{C}$ -values are obtained by first correcting the raw values from non-linearity effects and then comparing the corrected raw $\delta^{13}\text{C}$ values to those of the CaCO_3 standards. Details of the procedures can be found in Assayag et al. (2006). TDIC concentrations are obtained with a relative uncertainty of $\pm 10\%$. Analyses of a calcite standard (IAEA-CO-1) conducted during the period of this work and ran as an unknown were within analytical uncertainty of the accepted value ($+2.49\text{‰}/\text{VPDB}$) and reproducible to $\pm 0.04\text{‰}$ (1 s; $n = 16$) for TDIC greater than 2 mmol/l and $\pm 0.20\text{‰}$ (1 s; $n = 6$) for TDIC lower than 2 mmol/l.

The water samples dedicated to noble gas analyses were collected using copper tubes sealed at both ends by steel clamps after repeated tube flushing. The measurements were conducted on a Quadrupole Mass-Spectrometer (QMG220, Pfeiffer©) for helium and neon concentrations and a Noblesse mass-spectrometer (Nu Instruments©) for helium and neon isotopic ratios. The complete procedure is described in Ruzié et al. (2012).

3.2. Gas samples

The $\delta^{13}\text{C}_{\text{CO}_2}$ of CSC fumarole CO_2 is measured on the dry fraction of the fumarolic gases sampled in pyrex bottles filled with P_2O_5 . The CO_2 is purified both cryogenically and by circulation over CuO maintained at 250 °C (notably to remove H_2S). The $\delta^{13}\text{C}$ -value of the resulting purified CO_2 is measured with a dual inlet mass-spectrometer (ThermoFisher Delta Plus XP©) with a typical uncertainty of $\pm 0.03\text{‰}$.

For the noble gas systematics, CSC fumarole was collected twice in April 2007 and October 2010 using the routine method of the observatory (Ruzié et al., 2012). The samples were analysed for all the noble gas on the glass mass-spectrometer ARESIBO II.

4. Results

4.1. Carbon isotopes in fumaroles and springs

The $\delta^{13}\text{C}_{\text{TDIC}}$ values of La Soufrière hydrothermal water range from -18.11‰ (HR) to -2.11‰ (RM3) (Table 1). This range of values is similar to previously published data on La Soufrière (van Soest et al.,

1998; Pedroni et al., 1999; Rivé et al., 2013). The TDIC concentration of springs varies from 0.79 (BCM) to 8.97 (GA) mmol/l and decreases with increasing distance from the dome centre (Fig. 2A). The carbon isotopic composition ($\delta^{13}\text{C}$) as a function of the TDIC concentration is represented in Fig. 3. At high TDIC (>3 mmol/l), the spring data plot on a quasi-horizontal line anchored at the $\delta^{13}\text{C}$ value ($= -3.19 \pm 0.03\text{‰}$, $n = 2$) of the CO_2 degassed by the summit fumarole. The fumarolic $\delta^{13}\text{C}$ is compared to values measured in 1995 by Pedroni et al. (1999) and van Soest et al. (1998) (Table 2). We decided to consider our measurements in CSC fumarole as the isotopic signature of the local magmatic end-member. The low TDIC springs, <3 mmol/l, have lower $\delta^{13}\text{C}_{\text{TDIC}}$, down to -18‰ for HR. These low $\delta^{13}\text{C}_{\text{TDIC}}$ values are common in volcanic areas and reflect the contribution of soil respired- CO_2 derived from bacterial degradation of organic matter and plant root respiration (Chiodini et al., 2000; Cartwright et al., 2002; Inguaggiato et al., 2005). Recently, Rivé et al. (2013) estimated the organic component in Guadeloupe between -29.0 and -24.0‰ with TDIC between 0.47 and 1.56 mmol/l.

On a large scale, mixing modelling shows that all of the observed compositional range can be explained by variable contributions of a local magmatic component (LMC), diluted in the shallow groundwaters loaded with TDIC from the soil and/or air (Fig. 3). The $\delta^{13}\text{C}_{\text{TDIC}}$ value of meteoric water is unknown but can be calculated from the average atmospheric $\delta^{13}\text{C}$ value (-8.2 , see http://scrippsco2.ucsd.edu/data/atmospheric_co2.html) and appropriate carbon isotopic fractionation factors (Deines et al., 1974; Mook et al., 1974). In coastal areas, the pH of rainwater varies from 5.5 to 6.5 (Negrel et al., 1997 for French Guiana). At 20 °C, $\delta^{13}\text{C}_{\text{TDIC}}$ is enriched by $+0.2\text{‰}$ (at pH = 5.5) to $+4\text{‰}$ (at pH = 6.5) relative to CO_2 resulting in a range of DIC from -8 to -4.2‰ .

On a smaller scale, we note that some springs have $\delta^{13}\text{C}_{\text{TDIC}}$ higher than the range defined for magmatic component ($\geq -3.19 \pm 0.03\text{‰}$). Low TDIC values are systematically associated with high $\delta^{13}\text{C}_{\text{TDIC}}$ (Table 1). Degassing of CO_2 could be responsible for a decrease in TDIC and an increase in $\delta^{13}\text{C}$ -value. The magnitude of the carbon isotope fractionation during this loss depends on the speciation of the dissolved carbon species (H_2CO_3 , HCO_3^- , CO_3^{2-}), which is in turn dependent on the pH of the water and on temperature (Mook et al., 1974; Mook et al., 1975). At low pH, H_2CO_3 dominates and the bulk fractionation between CO_2 and TDIC ($\delta^{13}\text{C}_{\text{CO}_2\text{-TDIC}}$) is $+1.1\text{‰}$ at 25 °C. To assess the initial DIC content of the water, we have assumed conservation of alkalinity, this holds true if no carbonate minerals are precipitated or dissolved. Carbonated Saturation indexes are all below 1 showing the validity of this assumption (Rivé et al., 2013). For an open system degassing we may write a Rayleigh distillation law to describe the evolution of the isotopic composition of the DIC:

$$\delta^{13}\text{C}_{\text{DIC}}/\delta^{12}\text{C}_{\text{DIC}} = \alpha_{\text{CO}_2\text{-DIC}} * {}^{13}\text{C}_{\text{DIC}}/{}^{12}\text{C}_{\text{DIC}} \quad (1)$$

In dissolved state, TDIC can be in the form of dissolved CO_2 (H_2CO_3) or bicarbonate ions (HCO_3^-) or carbonate ion (CO_3^{2-}) whose relative concentrations depend on the solution pH. Thus, the general fractionation between DIC and CO_2 in gaseous state is a linear combination of fractionation between each ionic form of dissolved CO_2 and gaseous

Table 2
Helium and carbon elemental and isotopic compositions of CSC fumarole.

Ref.		Date	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	±	$^3\text{He}/^4\text{He}$ (Ra)	±	$\text{CO}_2/{}^3\text{He}$ ($\times 10^{10}$)	±
van Soest et al., 1998	n = 2	1995	-3.15	0.07	7.95	0.01	1.16	0.01
Pedroni et al., 1999	n = 2	1995	-3.02	0.01	8.40	0.10	1.29	0.62
This study	n = 2	2007 and 2010	-3.19	0.03	8.05	0.21	1.03	0.18
Average			-3.12	0.09	8.13	0.24	1.16	0.13

CO₂:

$$\text{DIC} * \alpha_{\text{CO}_2\text{-DIC}} = [\text{H}_2\text{CO}_3] * \alpha_{\text{CO}_2\text{-H}_2\text{CO}_3} + [\text{HCO}_3^-] * \alpha_{\text{CO}_2\text{-H}_2\text{CO}_3} + [\text{CO}_3^{2-}] * \alpha_{\text{CO}_2\text{-CO}_3^{2-}} \quad (2)$$

Here in all studied cases as pH is smaller than 7, [CO₃²⁻] is smaller than 1% and can be neglected in (2), in the DIC and alkalinity formulas. The CO₂ degassing causes pH to rise and the relative abundance of [H₂CO₃], [HCO₃⁻] and [CO₃²⁻] to change. Consequently the fractionation factor $\alpha_{\text{CO}_2\text{-DIC}}$ gets smaller as $\alpha_{\text{CO}_2\text{-HCO}_3^-}$ is smaller than $\alpha_{\text{CO}_2\text{-H}_2\text{CO}_3}$.

Letting K₁, be the equilibrium constant between H₂CO₃ and HCO₃⁻ and neglecting K₂, the equilibrium constant between HCO₃⁻ and CO₃²⁻, DIC can be expressed as a function of HCO₃⁻ according:

$$\text{DIC} = [\text{HCO}_3^-] \left(\frac{[\text{H}^+]}{K_1} + 1 \right) \quad (3)$$

Alkalinity is the sum of the bases relative to the reference state of H₂O and H₂CO₃, for pH below 9, it can be reduced to

$$\text{Alkalinity} = [\text{HCO}_3^-] \quad (4)$$

Therefore, along the CO₂ degassing path, pH can be recalculated using Eq. (3) and assuming constant alkalinity (no mineral precipitation nor mineral dissolution):

$$[\text{H}^+] \approx (\text{DIC}/\text{alkalinity} - 1) K_1 \quad (5)$$

Thus, inserting this equation into (1) we get,

$$\partial^{13}\text{C}_{\text{DIC}} / \partial \text{DIC} = \partial \text{DIC} / \partial \text{DIC} (\alpha_{\text{CO}_2\text{-H}_2\text{CO}_3} + \text{Alkalinity} / \text{DIC} (\alpha_{\text{CO}_2\text{-HCO}_3^-} - \alpha_{\text{CO}_2\text{-H}_2\text{CO}_3})) \quad (6)$$

assuming DIC $\approx$ ¹²C_{DIC}, the analytical solution is:

$$\text{Ln} \left[\frac{^{13}\text{C}_{\text{DIC}}}{^{13}\text{C}_{\text{DIC}_0}} \right] = \alpha_{\text{CO}_2\text{-H}_2\text{CO}_3} \text{Ln} [\text{DIC}/\text{DIC}_0] + \text{Alkalinity} [\alpha_{\text{CO}_2\text{-H}_2\text{CO}_3^-} - \alpha_{\text{CO}_2\text{-H}_2\text{CO}_3}] (1/\text{DIC}_0 - 1/\text{DIC}) \quad (7)$$

from which a $\delta^{13}\text{C}_{\text{DIC}}$ value can be computed from any given DIC. Conversely, the original DIC, before degassing CO₂, can be computed in order to have an original $\delta^{13}\text{C}_{\text{DIC}}$ consistent with that of measured for CO₂ rich samples ($\approx -3.2\%$). For RM3, CE, CC, and TA (i.e. sample with $\delta^{13}\text{C}_{\text{DIC}} > -3\%$), the calculated initial TDIC are given in Table 1.

4.2. Helium isotopes and heat flux

The helium isotopes in fluids of La Soufrière have already been investigated to impose new constraints on the ongoing magmatic degassing (Ruzié et al., 2012). The helium isotope data (³He/⁴He = R) are reported with respect to air (R_a) (where R_a = atmospheric ³He/⁴He = 1.4×10^{-6}). By measuring ⁴He/²²Ne ratios and assuming that the neon is purely derived from air or air saturated water (ASW), the atmospheric He contribution can be corrected and therefore we can calculate the ³He/⁴He_c according Eq. (8):

$$\left(\frac{^3\text{He}}{^4\text{He}} \right)_c = \left[\left(\frac{^3\text{He}}{^4\text{He}} \right)_m - \left(\frac{^3\text{He}}{^4\text{He}} \right)_{\text{air}} * r \right] / (1-r) \quad (8)$$

with $r = (^4\text{He}/^{22}\text{Ne})_{\text{air or asw}} / (^4\text{He}/^{22}\text{Ne})_m$, subscript “c” is the corrected value and “m” is the measured value. The (⁴He/²²Ne)_{air} ratio is 4.81 and (⁴He/²²Ne)_{ASW} is 2.62, adjusted for He and Ne solubility variations in water and assuming a recharge temperature of 20 °C.

The magmatic signal is clearly recorded in the summit fumarole of CSC [³He/⁴He = 8.1 ± 0.2 R_a, n = 2]. This ratio is similar to the global MORB range (³He/⁴He = 8 ± 1 R_a – Allègre et al., 1995) and previous regional studies of van Soest et al. (1998) and Pedroni et al. (1999). We observe that the R_c/R_a decreases with increasing distance from the dome, except at BJ (Fig. 2B). For this spring, the dilution of the magmatic signal is so significant that no correction can be reasonably applied, suggesting a significant contribution from an atmospheric component. The highest values recorded in the springs closest to the dome are similar to the fumarole value (Table 1).

The most radiogenic values are displayed in the most distant springs (HR and CC). Assuming the measured sample is the mixture of mantle and crust components with ³He/⁴He ratios of 8.1 and 0.05 R_a respectively, we can calculate the percentage of each component following Eq. (9):

$$R_c = 8.1 * X_M + 0.05 * (1 - X_M) \quad (9)$$

with X_M as the percentage of magmatic component in the sample. The magmatic component is the dominant component in all the samples (X_M = 71–100%). Note that two water samples (GUA07-CE and GUA07-RM3) have a corrected ³He/⁴He ratio larger than 8.1 R_a. We treat them as being derived from 100% magmatic component.

In order to impose new constraints on the hydrothermal system, we plot the correlation between the magmatic signal (X_M) and temperature in the springs (Fig. 4). A clear trend highlights the direct link between both heat and magmatic signal. Two springs do not fit the general trend: (1) the CE spring, which displays a pure magmatic signal (X_M = 100%) and low temperature (20.6 °C) and (2) the BCM spring, with high temperature (58.5 °C) and also a pure magmatic signal (X_M = 100%).

4.3. CO₂/³He ratio

The CO₂/³He is calculated from He and TDIC_i contents and the (³He/⁴He)_c ratios. At La Soufrière, CO₂/³He ratios range from 0.9 to 59×10^{10} (Table 1 and Fig. 5). The CSC fumarole (CO₂/³He = $1.03 \pm 0.18 \times 10^{10}$, n = 2) displays the lowest measured ratio and is in the arc worldwide range of Sano and Marty, 1995 ($1.5 \pm 1.1 \times 10^{10}$). All samples display CO₂/³He ratio greater than the range of MORB ($2 \pm 1 \times 10^9$, – Marty and Tolstikhin, 1998). This is

Fig. 4. The magmatic signal vs. in-situ temperature measurements. The grey area highlights a positive trend between both parameters. It emphasizes the direct link existing between heat flux and magmatic flux. CE and BCM springs are clearly decoupled from that trend (see text for more details) *: data from van Soest et al. (1998).

Fig. 5. Plots of $\text{CO}_2/{}^3\text{He}$ ratio vs. ${}^3\text{He}$ (ccSTP/g) and TDIC_i (mmol/l). (A) The samples with the lowest $[{}^3\text{He}]$ content display the highest $\text{CO}_2/{}^3\text{He}$ (except BCM – see section 4.2.4). As a result, we attribute elemental fractionation processes to solubility controlled phase-separation with the main aquifer. In order to test this assumption, we model open-degassing processes (Rayleigh distillation). Solubility data for carbon and helium are calculated from Fernandez-Prini et al. (2003). We modelled two degassing processes at 190 °C and 260 °C, the upper and lower limits of temperature of the main aquifer proposed by Brombach et al. (2000). Model 1: The $[{}^3\text{He}]_0$ concentration considered is ten times enriched than the highest concentration measured in RM3. Model 2: We consider a $[{}^3\text{He}]_0$ twice lower than Model 1. (B) There is no clear correlation between $\text{CO}_2/{}^3\text{He}$ and TDIC_i , indicating that CO_2 loss does not significantly affect the $\text{CO}_2/{}^3\text{He}$ values.

presumably due to the addition of either slab-derived carbon (Marty et al., 1989; Sano and Marty, 1995) as discussed later.

The higher ratios are measured in the thermal springs (up to 59×10^{10} , BJ). The $\text{CO}_2/{}^3\text{He}$ ratio of hydrothermal waters does not seem to be related to the summit distance (Fig. 2C), but affected by superficial processes, whose amplitudes may vary from one spring to another. These could be physical/chemical processes, which occur in the hydrothermal system, such as late degassing or dilution (e.g. Barry et al., 2013). Surface contamination (soil, biology) is ruled out by $\delta^{13}\text{C}$ arguments for most of springs with the exception of HR, BCM and BJ (Fig. 3). Finally, the ratio versus ${}^3\text{He}$ concentration and TDIC for all the fluid samples is plotted in Fig. 5. Fluid samples with $<50 \times 10^{-14}$ ccSTP/g H_2O clearly display the highest measured $\text{CO}_2/{}^3\text{He}$ values (Fig. 5A). The lack of correlation between $\text{CO}_2/{}^3\text{He}$ ratio and TDIC shows that CO_2 loss does not affect the elemental ratio (Fig. 5B).

5. Discussion

5.1. The local magmatic end-member at La Soufrière

The supply of the La Soufrière hydrothermal system with deep magmatic fluids is clearly indicated by the composition of the dissolved gases in the thermal waters. CO_2 and helium isotopic data support this hypothesis and reveal that the hydrothermal system is supplied by a CO_2 -rich magmatic component, sampled by fumaroles ($n = 2$) with a $\delta^{13}\text{C}_{\text{CO}_2}$ value of $-3.19 \pm 0.03\text{‰}$, a ${}^3\text{He}/{}^4\text{He}$ ratio of $8.1 \pm 0.2 R_a$ and a $\text{CO}_2/{}^3\text{He}$ ratio of $1.03 \pm 0.18 \times 10^{10}$. These values are compared to previous publications in Table 2 (van Soest et al., 1998; Pedroni et al., 1999). No significant changes are recorded since 1995.

Although the helium isotopic data are in the range of MORB, the carbon isotopic signature is higher than the generally accepted MORB range [$-3.68 \pm 0.14\text{‰}$ – Javoy and Pineau, 1991]. However such a ${}^{13}\text{C}$ value is common in other hydrothermal systems of volcanic arc areas for example, Central Italy (Chiodini et al., 2000), Popocatepetl (Inguaggiato et al., 2005) or in Japan (Sano et Marty, 1995). This ${}^{13}\text{C}$ positive shift can be explained by the carbon isotope fractionation between CO_2 and carbon dissolved in the magma. Such a possibility has been largely demonstrated in MORB where this fractionation is as

high as 4‰ at 1200 °C in favour of CO_2 (Javoy et al., 1978; Matthey, 1991 and Cartigny et al., 1998). But in arc magmas, due to the lower C solubility in more acidic magmas, the co-degassing of water and the lower temperature and pressure of volatile degassing, a comparatively reduced carbon isotope ${}^{13}\text{C}$ -enrichment of CO_2 is expected since most of the carbon initially dissolved in the magma would be degassed as CO_2 . Consequently the degassed CO_2 inherits the C isotope composition of the initial magma. Only in such circumstances, the C isotope difference between the CO_2 emitted at La Soufrière ($-3.19 \pm 0.03\text{‰}$) and the “canonical” mantle range ($\sim -4\text{‰}$) may be interpreted in terms of magmatic source components. A classical approach used to assess carbon provenance at subduction zones is the three-component mixing model of Sano and Marty (1995). We apply this model only for the gas sample because the high-temperature volcanic gases are less affected by elemental and isotopic fractionations than groundwaters, as we will show below. Based on He–C characteristics, samples can be described in terms of carbon mixtures derived from three end-members: limestone and/or marine carbonate (including slab carbonates) (L), the mantle (M) and sedimentary organic C (S). Using the following Eqs. (10)–(12), the relative contributions (expressed as fractions, f) from the various sources can be determined:

$$\left({}^{13}\text{C}/{}^{12}\text{C}\right)_{\text{meas.}} = \left({}^{13}\text{C}/{}^{12}\text{C}\right)_{\text{M}} f_{\text{M}} + \left({}^{13}\text{C}/{}^{12}\text{C}\right)_{\text{L}} f_{\text{L}} + \left({}^{13}\text{C}/{}^{12}\text{C}\right)_{\text{S}} f_{\text{S}} \quad (10)$$

$$1/\left({}^{12}\text{C}/{}^3\text{He}\right)_{\text{meas.}} = f_{\text{M}}/\left({}^{12}\text{C}/{}^3\text{He}\right)_{\text{M}} + f_{\text{L}}/\left({}^{12}\text{C}/{}^3\text{He}\right)_{\text{L}} + f_{\text{S}}/\left({}^{12}\text{C}/{}^3\text{He}\right)_{\text{S}} \quad (11)$$

$$f_{\text{M}} + f_{\text{L}} + f_{\text{S}} = 1 \quad (12)$$

taking the $\delta^{13}\text{C}_{\text{CO}_2}$ values of -4‰ , 0‰ and -30‰ for M, L, and S and ${}^{12}\text{C}/{}^3\text{He}$ ratios of 1.5×10^9 , 1×10^{13} , 1×10^{13} for M, L and S, respectively. The carbon isotopic signature and the $\text{CO}_2/{}^3\text{He}$ ratio degassed at La Soufrière possibly reflects a mantle contribution of 15% and a (L + S) contribution of 85% ($=76\% + 9\%$, respectively) in the magma source beneath Guadeloupe. These values are in the range determined by van Soest et al. (1998) for the northern part of the Lesser Antilles arc. The calculated ratio $(\text{L} + \text{S}) / \text{M} = 5.7$ is within the range of global average for arcs (6.0 ± 2.4 – Sano and Marty, 1995).

However, the major issue of concern with the methodology of Sano and co-workers is the selection of the end-member values (van Soest et al., 1998; Hilton et al., 2002). For example, the C-isotopic composition of sediments can be altered during subduction (Ohmoto, 1986). A second issue is the role of the superficial contamination by soil or organic matter as illustrated in this study by HR ($\delta^{13}\text{C}_{\text{TDIC}} = -18.11\%$) and BCM ($\delta^{13}\text{C}_{\text{TDIC}} = -10.04\%$). We will discuss this aspect later.

5.2. The superficial hydrothermal processes

5.2.1. Fumarole and CE spring fed by the vapour phase produced by the boiling aquifer

We suggest that the summit fumaroles are directly fed by the vapour produced during the boiling of the main aquifer. This suggestion is supported by the noble gas pattern recorded in the CSC fumarole, which indicated mixing between meteoric water at 20 °C and the local magmatic component (Ruzié et al., 2012).

Considering both the location of CE (altitude = 1146 m) and its helium–carbon data ($^3\text{He}/^4\text{He} = 8.0 \pm 0.1\text{R}_a$ and $\delta^{13}\text{C} = -2.84 \pm 0.03\%$), we propose that the spring might be fed by the same ascending gas as the fumarole, which could partially condense in its small superficial aquifer. However, the temperature and magmatic signal of CE do not fall within the range of our dataset average (Fig. 4). The spring records a pure helium magmatic input ($X_m = 100\%$) associated with a low temperature (only 20.6 °C).

To evaluate the maximum temperature increase in the thermal spring, we have to quantify the heat transfer between rising magmatic gases from the main aquifer and a shallow aquifer. A budget of the heat advectively transported by the gas flux gives an estimate of the maximum temperature increase of the shallow aquifer. We assume that the fumarole gases made of water (95%), CO_2 (3.5%) and H_2S (1.5%) (Bernard et al., 2006; Bagnato et al., 2009, OVSG-IPGP, 1978–2012) get totally dissolved into the aquifer water and consequently we are able to compute the quantity of heat released by the cooling of the gas phase from 190–260 °C to the spring temperature assuming first steam cooling, then steam liquefaction to water, and finally water cooling. Using thermodynamical data (the heat capacity C_p for vapour phase = $2.040 \text{ kJ K}^{-1} \text{ kg}^{-1}$ and that for liquid phase = $4.180 \text{ kJ K}^{-1} \text{ kg}^{-1}$) and the enthalpy of water ($\Delta H = 2,257 \text{ kJ/kg}$), we get a thermal input of 12 kJ in the meteoric water. This energy can heat the water by at max 3 °C. As a consequence the input of magmatic volatiles in spring waters may not be associated with a significant water temperature increase.

5.2.2. Springs fed by water affected by an open-degassing process

The residual water of the boiling process that provides the steam to the fumaroles can be mixed with meteoric water in smaller shallow aquifers. It seems that the TA, GA, GAB, PR and RM3 springs could all be the result of this process. To test this assumption, we first modelled the evolution of $\text{CO}_2/^3\text{He}$ ratio of the residual water during an open-system degassing process (Fig. 5) using the Rayleigh distillation Eq. (13),

$$\left(\text{CO}_2/^3\text{He}\right)_{\text{water}} = \left(\text{CO}_2/^3\text{He}\right)_0 * f^{[(S_{\text{He}}/S_{\text{CO}_2})-1]} \quad (13)$$

where f is the ratio between $[^3\text{He}]_{\text{water}}/[^3\text{He}]_0$. Solubility data for helium (S_{He}) and CO_2 (S_{CO_2}) are calculated at the temperature between 190 °C and 260 °C using data from Fernandez-Prini et al. (2003). The $\text{CO}_2/^3\text{He}$ ratio of CSC fumarole (1.03×10^{10}) is chosen as representative of deep, non-fractionated gas (Federico et al., 2002). For a degassing of 97–99%, we obtain ratios between 25 and 60×10^{10} , close to the measured ratios (Fig. 5A). The thermal springs GA, GAB, TA and PR seem to be fed by the residual water of an open degassing process, which is then mixed with small amounts of meteoric water in their respective shallow aquifers.

Using this model, we can see that the water feeding RM3 is less affected by the degassing than the other springs (degassing of ~89%). RM3 displays a pure helium magmatic isotopic signal ($^3\text{He}/^4\text{He} = 8.0 \text{ R}_a$) with low correction for helium ($7 \pm 1\%$) and the highest ^3He concentration measured in water samples ($2.25 \times 10^{-12} \text{ ccSTP/g}$) (Table 1). The $\delta^{13}\text{C}$ in 2007 was -2.11% and in 2009 -3.19% . The latter value is exactly the isotopic value of the summit fumarole. It is difficult to explain the discrepancy between those two values. It could reflect a sampling issue for carbon or the fact that the source was affected by late degassing processes in 2007. The last assumption could also explain the increase of ^3He from 1.97 to $2.25 \times 10^{-12} \text{ ccSTP/g}$ between 2007 and 2010. We suggest that this spring could sample water closer to the water of main aquifer, with minimal dilution in term of TDIC and helium by meteoric water and no addition of radiogenic helium.

5.2.3. Springs affected by mixing processes

HR and CC display quite homogeneous $\text{CO}_2/^3\text{He}$ ratios ($7.2\text{--}9.1 \times 10^{10}$) and ^3He concentrations ($0.43\text{--}1.0 \times 10^{-12} \text{ ccSTP/g}$) (Table 1 and Fig. 5A). However, significant variations are observed in the helium and carbon isotopic ratios due to different mixing processes.

The C-isotopic ratio of TDIC for CC displays a signal ($\delta^{13}\text{C}_{\text{TDIC}} = -2.84 \pm 0.16\%$) close to magmatic signal and the helium isotopic ratio, ($^3\text{He}/^4\text{He})_c = 6.6 \pm 0.2 \text{ R}_a$ is clearly affected by the addition of radiogenic helium. The addition of ^4He could have occurred during water–rock interactions facilitated by a lower ^3He input (Fig. 5A) and by a long residence time of water in the shallow aquifer (Ruzié et al., 2012). The residence time has been estimated from tritium data to be about 10 years (Pascaline et al., 1982). This is longer than the average residence time of three months as inferred for the other springs (Pascaline et al., 1982; Bigot et al., 1994a; Villemant et al., 2005).

HR spring has a $\delta^{13}\text{C}_{\text{TDIC}}$ value of -18.11% and a helium isotopic ratio of $^3\text{He}/^4\text{He} = 5.7 \pm 0.1\text{R}_a$. The tritium data do not support a long residence time in that aquifer (Pascaline et al., 1982) and this spring receives a similar ^3He input than CC (Fig. 5A). We assume then the isotopic values of helium are not influenced by the addition of radiogenic helium produced from water–rock interactions. Combining this with the carbon isotopes, we have built a mixing model of two component end-members (organic and magmatic) that could explain the isotopic ratios. We have plotted $\delta^{13}\text{C}$ vs. helium isotope ratio (Fig. 6). Theoretical mixing curves were constructed using $\delta^{13}\text{C}_{\text{TDIC}} = -3.19\%$ and $^3\text{He}/^4\text{He} = 8.1 \text{ R}_a$ for the magmatic end-member and $\delta^{13}\text{C}_{\text{TDIC}} = -29\text{--}24\%$ (Rivé et al., 2013) and $^3\text{He}/^4\text{He} = 1 \text{ R}_a$ for the organic end-member. The helium in the organic end-member is assumed to be air-derived (Inguaggiato et al., 2005). The curvature of the mixing line is defined by the ratio $K = (C/\text{He})_{\text{mag}}/(C/\text{He})_{\text{org}}$. From Fig. 6, we see that one quarter of the isotopic composition of HR is magmatic ($K = 0.25$) in relation to its setting far from the dome (3.7 km). The isotopic signatures of both carbon and helium are therefore strongly influenced by the organic end-member.

5.2.4. Bains Chauds du Matouba

BCM thermal spring (1055 m) is located at 1.25 km from the dome centre, outside the Amic Crater but still within the Grande Découverte Caldera (Fig. 1). The helium signature is magmatic ($^3\text{He}/^4\text{He} = 8.0 \pm 0.8\text{R}_a$) despite a $\delta^{13}\text{C}$ value (-10%) which does not share this characteristic. The $\text{CO}_2/^3\text{He}$ ratio (2×10^{10}) is close to that of fumaroles ($1.03 \pm 0.18 \times 10^{10}$). This spring also records the highest temperature (58.5 °C) suggesting a new feeding pathway in comparison with other springs (Fig. 4).

Here, our data are compared to a previous study. According to van Soest et al. (1998), the thermal water had a $\text{CO}_2/^3\text{He}$ ratio of 5×10^{10} with a low ^3He concentration ($0.26 \times 10^{-12} \text{ ccSTP/g}$) and a more radiogenic helium isotopic ratio ($^3\text{He}/^4\text{He} = 6.8 \text{ R}_a$) (Fig. 3). These results differ from the observations made in the present study.

Fig. 6. $\delta^{13}\text{C}$ vs. $^3\text{He}/^4\text{He}$ diagram. Combining the helium and carbon isotopic data illustrates that the measured values can be explained by mixing of two end-members. The mixing equation proposed by Langmuir et al. (1978) uses three end-members: magmatic ($\delta^{13}\text{C} = -3.19\text{‰}$ and $^3\text{He}/^4\text{He} = 8 R_a$), meteoric ($\delta^{13}\text{C} = -8.6\text{‰}$ and $^3\text{He}/^4\text{He} = 1 R_a$ or) and organic ($\delta^{13}\text{C} = -29\text{--}24\text{‰}$ and $^3\text{He}/^4\text{He} = 1 R_a$). The set of equations was solved by introducing a K constant, defined as $K = (C/\text{He})_{\text{mag}} / (C/\text{He})_{\text{org}}$. When $K = 1$, the mixing is a straight line in our diagram. When $K > 1$ or $K < 1$, the mixing line between the two end-members becomes a hyperbola.

In this particular spring, we observe small rising bubbles of N_2 (OVSG-IPGP, 1978–2012). As CO_2 is 40 times more soluble in water than helium at 58.5°C (Fernandez-Prini et al., 2003), the rising N_2 -bubbles concentrate helium, producing an elemental fractionation with CO_2 . For noble gas measurements, we collected a sample lighter than the others (1.95 g versus an average of 2.20 g for similar volumes). We therefore think that this gaseous phase was sampled too. This would account for the difference between the measured ^3He concentration

(1.02×10^{-12} ccSTP/g) and $\text{CO}_2/{}^3\text{He}$ compared to those of van Soest et al. (1998). Considering both helium and carbon isotopes (Fig. 6), we observe that the BCM signature can result from the same mixing as the HR spring ($K = 0.25$), with a higher contribution of the magmatic fraction.

Finally, we propose that the small aquifer of this spring could be heated by conduction as suggested by Brombach et al. (2000) and fed by a diffusive flux of gas through fractures. Moreover, this spring seems to be disconnected from the main aquifer, as it has shown no geochemical changes since 1979 (OVSG-IPGP, 1978–2012; Villemant et al., 2005). In the shallow aquifer, a late-stage formation of N_2 -bubbles could induce late-stage fractionation between CO_2 and helium.

5.3. Implications for volcano monitoring

Our survey of hydrothermal springs sets a first baseline for helium and carbon concentrations and isotopic variations during the current period of quiescence. Assuming that renewal of volcanic activity at La Soufrière requires partial replenishment of stored volatile-poor andesitic magma by volatile-rich basaltic magma (Ruzié et al., 2012), we argue that a more extensive release of heat, CO_2 and helium gases in the shallow hydrothermal system would be triggered by this event. We could expect therefore to measure higher concentrations of these species as well as a temperature increase in both fumaroles and thermal springs. The present study highlights that the fumaroles are probably the most effective way to quickly monitor a change in the magmatic input (Fig. 7). The magmatic volatiles sampled by groundwaters appear to change from their pristine magmatic compositions as a result of various processes such as dilution, solubility-controlled fractionation mechanisms and mixing (Fig. 7). Therefore, springs that are least affected by such superficial processes should be carefully monitored. Based on our investigation, only RM3 spring fulfils these conditions during the present dormancy.

6. Conclusion

In this study, we provide a complete baseline of both carbon and helium data of La Soufrière through a systematic geochemical investigation of hydrothermal fluids. We also refine our understanding of the

Fig. 7. Interpretative model of hydrothermal fluid flowpaths in La Soufrière. The schematic cross-section depicts the interaction between meteoric water and deep rising magmatic fluids. The variable helium and carbon isotopic compositions of the gas phase feeding thermal springs are interpreted as resulting from physical processes such as dilution, Rayleigh distillation and late degassing. See text for further details.

Guadeloupe hydrothermal system. Assuming that the chemistry of both helium and carbon is the result of a variable mixture of three components: a deep magmatic gas phase, meteoric water and a contribution of biogenic end-member, we propose how superficial processes affect each spring. The spring waters of La Soufrière can be classified into four groups:

- 1) thermal springs fed by a mix of meteoric water with residual water of an open-degassing of the main aquifer (GA, GAB, PR, TA, RM3);
- 2) a vapour phase produced by the open-degassing of the main aquifer feeding fumaroles (CSC) or condensing in shallower water table (CE);
- 3) thermal springs fed by the non-boiling portion of the main aquifer and then submitted to different mixing processes (HR, CC);
- 4) thermal spring fed by gas diffusing through fractures and affected by late-stage air-bubbles formation (BCM).

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