



Helium isotope systematics of volcanic gases and thermal waters of Guadeloupe Island, Lesser Antilles



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ABSTRACT

The island of Guadeloupe is located in the middle of the 850 km long Lesser Antilles island arc. Present-day volcanic and geothermal activity is concentrated in two systems both located in the southwestern part of the island (Basse Terre): the La Soufrière volcanic complex and the Bouillante hydrothermal system, some 20 km to the northwest of the volcano. We report here the largest isotopic data set for helium isotopes in hydrothermal gases and waters from both systems, acquired between 1980 and 2012. $^3\text{He}/^4\text{He}$ ratios in the fumarolic gases of La Soufrière volcano have been quite homogeneous and stable over the last thirty years. The average ratio of $8.2 \pm 0.2 R_a$ confirms that the volcano is tapping a MORB-like mantle source. In contrast, the nearby Bouillante geothermal system displays a much lower $^3\text{He}/^4\text{He}$ ratio ($4.5 \pm 0.1 R_a$). He–C elemental and isotopic relationships show that both systems are actually fed by the same magmatic source, and that their marked difference in $^3\text{He}/^4\text{He}$ results from the ^4He contamination of the Bouillante deep aquifer by the surrounding wallrock. This conclusion is strengthened by the spatial distribution of $^3\text{He}/^4\text{He}$ ratios which shows that La Soufrière fumaroles and the Bouillante geothermal system are the two end-members of a spatial trend of decreasing $^3\text{He}/^4\text{He}$ ratio with distance from La Soufrière summit dome, implying an increasing addition of radiogenic ^4He from the host rocks away from the present-day active volcanic edifice.

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1. Introduction

Guadeloupe island belongs to the Lesser Antilles island arc, the active volcanic chain generated by the subduction of the Atlantic seafloor beneath the Caribbean plate (MacDonald et al., 2000). It is located in the middle of the arc, just south of the island of Montserrat. Present-day volcanism in Guadeloupe is active in Basse-Terre, the western part of the territory (Fig. 1). There, volcanic activity started some 3 million years ago (Briden et al., 1979; Samper et al., 2007). It migrated southward over time to give birth, some 200,000 years ago, to the Grande Découverte–La Soufrière volcanic complex (Boudon et al., 1989). The last eruption, in 1530 AD (Boudon et al., 2008), built the 0.05 km³ andesitic lava dome of La Soufrière volcano, the highest landmark (1430 m asl) in Guadeloupe. Since then, intense hydrothermal activity has persisted at La Soufrière, including six phreatic eruptive phases. Volcanic gases are persistently released as fumaroles on and around the lava dome (Brombach et al., 2000; Ruzié et al., 2012) and as dissolved and/or bubbling gases in thermal springs around the volcanic edifice (Villemant et al., 2005; Ruzié et al., 2013).

Thermal manifestations are also widespread in the Bouillante area located on the coast some 20 km to the northwest of La Soufrière, including hot springs, fluids from geothermal wells, gas bubbling at sea (off the coastal area of Pointe Lézarde) and a deep submarine hot spring (–23 m) at the base of Ilet Pigeon (Fig. 1). The chemical composition of the thermal springs indicates a marked difference between both systems: the thermal springs of La Soufrière edifice are characteristics of young and shallow groundwaters of meteoric origin interacting with high temperature volcanic rocks and gases (Brombach et al., 2000). In contrast, Bouillante thermal waters, which have been studied intensively for their geothermal potential (Cormy et al., 1970; Demians D'Archambaud and Surcin, 1972, 1976; Sanjuan et al., 1999; Brombach et al., 2000), originate from a deeper, more mature aquifer with a marked Na–Cl composition showing the influence of marine waters. This deep aquifer is exploited for generating electricity by a geothermal power plant located on the coast and plans for future extension are being considered.

Helium isotopes are a powerful indicator of the extent of the mantle-derived contribution to crustal fluids (Ballentine et al., 2002). Their ratio varies by more than three orders of magnitude in terrestrial samples. This results from the distinct origins of ^3He (essentially primordial) and ^4He (produced by the radioactive decay of U and Th) and their contrasted proportions in the Earth's reservoirs. When referred to the

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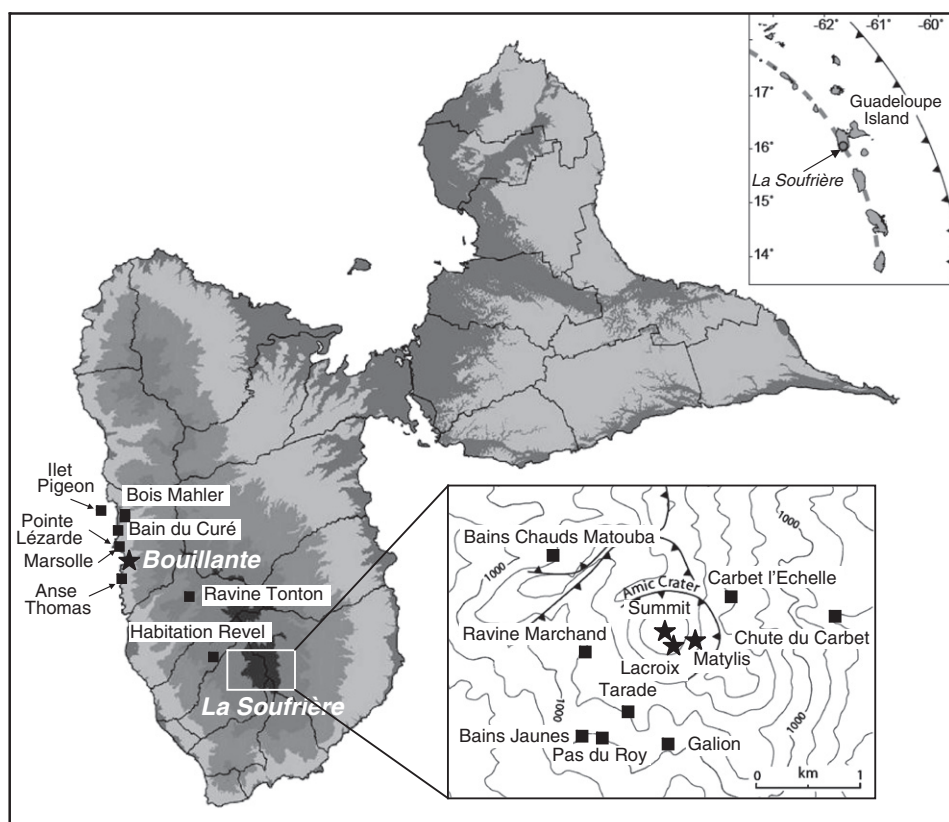


Fig. 1. Location map of the sampling points.

atmospheric ratio ($R_a = 1.38 \times 10^{-6}$), typical $^3\text{He}/^4\text{He}$ ratios vary from $<0.05 R_a$ in the continental crust to $8 \pm 1 R_a$ on average in MORB-type upper mantle, and up to $\sim 40\text{--}50 R_a$ in products of plume-related ocean islands, such as Hawaii and Iceland (Ballentine and Burnard, 2002; Graham, 2002; Stuart et al., 2003). Furthermore, helium closely follows carbon dioxide during magma degassing and the $\text{CO}_2/{}^3\text{He}$ ratio of volcanic gases is one important complementary indicator of their origin (Sano and Marty, 1995; Allard et al., 1997; Marty and Tolstikhin, 1998).

Previous studies of helium isotopes in Guadeloupe (van Soest et al., 1998; Pedroni et al., 1999; Ruzié et al., 2012, 2013) have concentrated mostly on La Soufrière system and have shown that the volcano is tapping a MORB-like source with $^3\text{He}/^4\text{He}$ values around $8 R_a$. In contrast, two results from the Bouillante geothermal power plant (van Soest et al., 1998; Pedroni et al., 1999) indicate a much lower $^3\text{He}/^4\text{He}$ value ($4.5 R_a$), raising interrogations as to whether the Bouillante hydrothermal system is fed by a magmatic source distinct from that of La Soufrière. Here, we report the results of a study conducted from 1980 to 2012, covering the two systems of La Soufrière and Bouillante and comprising a total of 92 samples from 20 sites, including both free gases (fumaroles, gas bubbles, geothermal wells) and dissolved gases in hot springs. Some of the gas samples were also analysed for their carbon isotope ratio. The aim of this study was to investigate the helium isotope composition of the main geothermal manifestations of Basse-Terre (Guadeloupe), to map their spatial distribution, to study their temporal variability and to gain deeper insight into the source of the volcanic gases.

2. Sampling and methods

Our data set goes back to 1980 when the Lacroix fumaroles (now extinct) were sampled for the first time for helium isotopes (Allard, 1983;

Allard et al., 1983). Our first extensive survey of the helium isotopic composition of the gases and hot springs was performed in 1995. The following campaigns took place in 1996, 1999, 2006 and 2012. Water samples for helium isotopes were collected in standard refrigeration grade 3/8" copper tubes equipped with metal clamps at both ends. The tubes were flushed with the water prior to closure using either the natural water flow or a peristaltic pump connected with Tygon tubing. Fumarolic gases were collected in copper tubes or pre-evacuated glass flasks with stopcocks. When present, gas bubbles in water were also collected in the same way using an inverted funnel. Prior to 2000, He analyses were performed at LSCE-Saclay using a VG-3000 mass spectrometer (Jean-Baptiste et al., 1992) and on a MAP-215-50 mass spectrometer with simultaneous helium and neon isotope determination afterwards (Jean-Baptiste et al., 2010). Gas samples were directly connected to the high-vacuum inlet system of the mass spectrometer. Helium and neon dissolved in the water samples were first extracted under vacuum into sealed glass tubes. Typical ^4He and ${}^{20}\text{Ne}$ blanks are 5×10^{-10} and 3×10^{-10} cm^3 STP for the mass spectrometer inlet, and 2×10^{-9} and 1×10^{-9} cm^3 STP for the extraction system, respectively. For gases, analytical uncertainties on R/R_a and helium mixing ratio are ± 0.08 and 0.1 ppm, respectively. Analytical precision on helium and neon concentrations and on $^3\text{He}/^4\text{He}$ ratios in water samples is better than 0.8%. Helium concentrations and isotopic ratios were corrected for the atmospheric air component using the measured ${}^{20}\text{Ne}/^4\text{He}$ ratio (when available) assuming a pure atmospheric origin for neon (Hilton, 1996). For the earlier samples for which no neon data were available, the helium volcanic component dissolved in water was obtained by subtracting the atmospheric air component at the solubility equilibrium (Weiss, 1971; Jean-Baptiste et al., 2009), and, for gas samples, from the measured co-amount of incondensable gases assumed to be entirely atmospheric in origin. Comparison of the results given by both methods for waters (Table 2) shows that using the solubility

data to derive the atmospheric component gives acceptable results as long as the helium excess in the sample is large enough (in practice, greater than 50%).

CO₂ concentration in volcanic gases was determined at Palermo University using a Perkin Elmer AutoSystem XLClarus 500 gas chromatograph equipped with a thermal conductivity detector (HWD). $\delta^{13}\text{C}$ measurements were also performed at Palermo University using a Finnigan Delta Plus mass spectrometer, with an accuracy of $\pm 0.1\text{‰}$.

3. Results

3.1. Free gases

Gas results are given in Table 1. Volcanic gases were repeatedly sampled from the South Crater, the most active fumarolic vent at the top of La Soufrière lava dome, and from the Matylis fumarolic field extending at the base of the dome on a major volcano-tectonic fault (Ty Fault) cutting the southeast flank of the volcanic edifice. Gases were also sampled at Bains Chauds Matouba, a bubbling hot spring located on a former crater rim some 1.5 km to the northwest of the dome (Fig. 1). Gases representative of the Bouillante geothermal system were sampled at the well head of the geothermal power plant and off the shoreline of Pointe Lézarde (Fig. 1): in this latter area, degassing occurs over a wide area, with gas bubbles rising intermittently and randomly from the seafloor. These bubbles were collected on their way to the surface by scuba diving.

3.1.1. La Soufrière system

The air-corrected $^3\text{He}/^4\text{He}$ values for La Soufrière gas samples are quite homogeneous and quite stable over time (Fig. 2). The average value of $8.2 \pm 0.2 R_a$ is in good agreement with the results already published by van Soest et al., 1998 (7.94–7.96 R_a); Pedroni et al., 1999

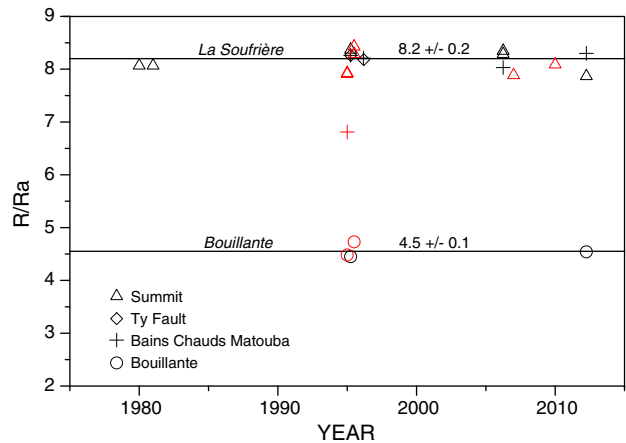


Fig. 2. $^3\text{He}/^4\text{He}$ time-series in the volcanic gases (in red: data from Van Soest et al., 1998; Pedroni et al., 1999; Ruzié et al., 2012; in black: this work).

(8.32–8.46 R_a) and Ruzié et al., 2012 (7.9–8.1 R_a) and evidences a MORB-type mantle source feeding the volcanic system. As classically observed in arc-related fluids (Fischer and Marty, 2005), the mean value of $(\text{CO}_2/^3\text{He})$ ratios, $(11.2 \pm 2.7) \times 10^9$, is ~ 5 times higher than the MORB value of $(2 \pm 1) \times 10^9$ (Marty and Jambon, 1987; Marty and Tolstikhin, 1998), due to the addition of slab-derived carbon supplied by sedimentary marine carbonate and organic matter. The mean $\delta^{13}\text{C}$ value of the volcanic CO₂, $(-3.2 \pm 0.3)\text{‰}$, is also significantly higher than the MORB value of $(-6.5 \pm 2)\text{‰}$ (Javoy et al., 1986; Marty and Jambon, 1987; Sano and Marty, 1995), indicating that the carbonate carbon component ($\delta^{13}\text{C} \sim 0\text{‰}$) is predominant over the organic carbon component ($\delta^{13}\text{C} \sim -30 \pm 10\text{‰}$ —Hoefs, 1980; Sano and

Table 1

Helium and carbon isotopic compositions of the volcanic gases of Guadeloupe. Words and numbers in italic refer to literature data.

Site	Date	T°C	CO ₂ mol%	⁴ He/ ²⁰ Ne	(He) _c ppmv	³ He/ ⁴ He (R/Ra) _m	³ He/ ⁴ He (R/Ra) _c	CO ₂ / ^{(³He)_c}	$\delta^{13}\text{C}$ ‰	References
South Crater (fum-AN9)	03/1995	98.0	90.6		6	8.23	8.4	13.3	-3.2	This work
South Crater (fum-AN2)	03/1995	97.7				7.63	7.83		-3.2	This work
South Crater	1995	94				7.93	7.94	11.5	-3.2	Van Soest et al., 1998
South Crater	1995	94				7.91	7.96	11.7	-3.1	Van Soest et al., 1998
South Crater	06/1995	108	99		4.95	8.31	8.32	17.4	-3.01	Pedroni et al., 1999
South Crater	06/1995	108	65		6.35	8.46	8.46	8.8	-3.02	Pedroni et al., 1999
South Crater (fum-AN2)	02/1996	97.3	92.2			7.17			-3.2	This work
South Crater (fum-AN2)	01/1999	98.9	92.1		9.7					This work
South Crater (fum-AN2)	03/2006	108.5	66.9	10.7	5.3	8.16	8.38	11.2		This work
South Crater (fum-AN2)	03/2006	108.5	66.6	38.9	5.4	8.26	8.32	10.8		This work
South Crater	2007				5.32		7.8			Ruzié et al., 2012
South Crater	2010				6.78		7.6			Ruzié et al., 2012
South Crater	03/2012	107.6	67.3	18.3	6.2	7.78	7.90	10.1		This work
Lacroix fumarole	01/1980	103.8	80.0		8.3	8.06	8.10	8.7	-3.7	This work
Lacroix fumarole	04/1981	97.8	73.8		7.7	8.10	8.10	8.6	-3.9	This work
Ty Fault (Matylis)	03/1995	97.5	89.6			7.98	8.26		-2.8	This work
Ty Fault (Matylis)	02/1996	96.4				8.18	8.18		-3.2	This work
Ty Fault (Matylis)	02/1996					7.86				This work
Ty Fault (Matylis)	01/1999	96.6	88.3		6.7					This work
Bain Chaud Matouba	1985		5.13							Fabriol and Ouzounian, 1985
Bain Chaud Matouba	03/1995	59.9	1.04		10.5	4.56	8.26	0.16	-6.0	This work
Bain Chaud Matouba	1995	55.5				3.27	6.81			Van Soest et al., 1998
Bain Chaud Matouba	02/1996	58.6	7.9			4.47			-11.3	This work
Bain Chaud Matouba	01/1999	58.6								This work
Bain Chaud Matouba	03/2006	58.5	3.87	0.67	6.1	4.69	8.03	0.98		This work
Bain Chaud Matouba	03/2012	58.5		0.60	8.5	4.43	8.30			This work
Bouillante BO2	1991		93.6		40				-2.6	Abou Akar et al., 1992
Bouillante (Pte Lézarde)	03/1995				494	4.41	4.45			This work
Bouillante BO4	03/1995								-3.4	This work
Bouillante	1995	55.5				4.46	4.48		-2.9	Van Soest et al., 1998
Bouillante	06/1995		38		203	4.72	4.73	0.29	-2.43	Pedroni et al., 1999
Bouillante BO4	01/1999		90.4							This work
Bouillante BO6	11/2012		94.3	31.87	26.2	4.50	4.53	5.80		This work

Marty, 1995). The gases from the Bains Chauds Matouba hot spring were not taken into account in the calculation of the ($\text{CO}_2/{}^3\text{He}$) and $\delta^{13}\text{C}$ mean values because of their peculiar composition (low CO_2 and

very high N_2 concentrations) which indicates a strong CO_2 elemental and isotopic fractionation during previous gas–water separation (Ruzi e et al., 2013).

Table 2

Helium isotope data for the geothermal waters of Guadeloupe: $(\text{R/Ra})_c$ is the helium isotopic ratio corrected for the atmospheric air component using the measured ${}^{20}\text{Ne}/{}^4\text{He}$ ratios (when available). $(\text{R/Ra})_{ex}$ is the helium isotopic ratio determined by subtracting the atmospheric air component (assumed to be at the solubility equilibrium) – see text. Numbers in italic refer to literature data.

Site	Date	Temperature (°C)	Conductivity ($\mu\text{S}-25^\circ\text{C}$)	pH	$[{}^4\text{He}]$ $\times \text{E} + 8 \text{ cm}^3/\text{g}$	$[{}^3\text{He}]$ $\times \text{E} + 14 \text{ cm}^3/\text{g}$	$[{}^{20}\text{Ne}]$ $\times \text{E} + 8 \text{ cm}^3/\text{g}$	$(\text{R/Ra})_{\text{meas}}$	$(\text{R/Ra})_{\text{ex}}$	$(\text{R/Ra})_c$
Carbet l'Echelle	03/1995	23.0	1410	5.51	28.92	268.19		6.72	7.8	
Carbet l'Echelle	01/1996	23.2			27.20	233.85		6.23	7.2	
Carbet l'Echelle	01/1999	22.4	1920	5.44	25.68	246.30		6.95	8.2	
Carbet l'Echelle	03/2006	21.2	936	5.19	18.3	159.10	14.5	6.30	8.0	7.76
Galion	03/1995	42.5	1200	4.80	8.55	58.52		4.96	8.7	
Galion	01/1996	42.9			5.82	38.15		4.75		
Galion	01/1999	41.9	1557	4.95	5.81	42.98		5.36		
Galion	03/2006	44.2	1890	4.93	5.29	35.99	7.2	4.93		7.55
Galion-1	03/2012	47.9	2047	4.29	5.49	44.46	4.78	5.87		7.57
Galion-2	03/2012	47.9	2047	4.29	5.20	41.67	4.62	5.81		7.54
Ravine Marchand	03/2006	45.3	1220	5.30	13.6	120.30	9.6	6.41	8.8	7.81
Ravine Marchand-1	03/2012	44.6	1105	5.29	23.0	233.86	6.08	7.37	8.8	7.91
Ravine Marchand-2	03/2012	44.6	1105	5.29	22.9	232.21	5.99	7.35	8.7	7.88
Tarade	03/1995	34.7	1185	6.02	6.62	21.74		2.38		
Tarade	01/1996	33.1			6.45	26.08		2.93	6.8	
Tarade	01/1999	33.2	1492	5.98	4.98	16.08		2.34		
Tarade	03/2006	36.8	1540	5.87	4.93	16.53	13.4	2.43		7.49
Tarade-1	03/2012	41.5	1645	5.97	5.52	23.73	12.4	3.12		7.13
Tarade-2	03/2012	41.5	1645	5.97	5.51	24.01	12.2	3.16		7.10
Tarade-3	03/2012	41.6	1534	5.97	6.04	30.29	11.8	3.63		7.15
Tarade-4	03/2012	41.6	1534	5.97	6.28	33.37	11.6	3.85		7.15
Pas du Roy	03/1995	31.8	1023	5.65						
Pas du Roy	03/2006	33.5	990	5.46	5.74	22.89	14.5	2.89		7.66
Pas du Roy-1	03/2012	34.6	1018	5.59	5.43	19.18	14.1	2.56		6.98
Pas du Roy-2	03/2012	34.6	1018	5.59	5.25	17.53	14.0	2.42		6.90
Bains Jaunes (main)	03/1995	28.9	745	5.09	5.58	11.47		1.49		
Bains Jaunes (main)	01/1999	27.9	789	5.15	4.24	9.01		1.54		
Bains Jaunes (main)	03/2006	29.8	720	5.26	4.03	6.06	14.4	1.09		6.59
Bains Jaunes (main)	03/2012	35.3	780	5.35	4.01	6.26	13.7	1.13		7.19
Bains Jaunes (side)-1	03/2012	29.4	725	4.43	4.43	8.47	14.6	1.39		6.11
Bains Jaunes (side)-2	03/2012	29.4	725	4.51	4.51	8.64	14.9	1.39		6.08
Bains Chauds Matouba	03/1995	59.9	649	5.57	6.56	31.23		3.45	6.8	
Bains Chauds Matouba	01/1996	58.6			7.65	47.19		4.47	7.9	
Bains Chauds Matouba	01/1999	58.6	1197	5.93	5.12	20.28		2.87		
Bains Chauds Matouba	03/2006	58.5	1696	5.50	7.11	40.03	13.8	4.08	7.7	8.67
Bains Chauds Matouba-1	03/2012	58.5	1014	5.50	6.90	38.38	13.5	4.03	7.8	8.58
Bains Chauds Matouba-2	03/2012	58.5	1014	5.50	5.95	28.98	13.2	3.53	8.1	8.99
Chute du Carbet	03/1995	45.7	0.623	6.63	14.70	97.17		4.79	6.3	
Chute du Carbet	01/1996	45.6			20.10	127.87		4.61	5.5	
Chute du Carbet	01/1999	45.5	1700	6.62	8.50	45.75		3.90	6.6	
Chute du Carbet	03/2006	45.0	1414	6.34	15.4	106.90	13.2	5.03	6.5	6.39
Chute du Carbet-1	03/2012	43.8	909		16.2	114.64	14.4	5.13	6.6	6.59
Chute du Carbet-2	03/2012	42.5	875		14.6	99.79	14.0	4.95	6.5	6.49
Chute du Carbet-3	03/2012	41.8	806		8.43	45.85	13.7	3.94	6.8	6.59
Chute du Carbet-4	03/2012	41.8	806		9.61	55.04	14.3	4.15	6.6	6.57
Habitation Revel	03/1995	33.6	180	6.66	4.40	20.28		3.34		
Habitation Revel	01/1999	31.4	260	6.72	7.76	30.52		2.85	5.2	
Habitation Revel	03/2006	25.2	298	6.43	11.9	67.33	15.4	4.10	5.9	5.81
Habitation Revel-1	03/2012	32.7	284	6.53	15.9	97.88	15.0	4.46	5.8	5.72
Habitation Revel-2	03/2012	32.7	284	6.53	13.8	81.11	15.3	4.26	5.7	5.75
Ravine Tonton	03/1995	39.2	125	7.60	23.06	135.88		4.27	5.0	
Anse Thomas	03/1995	85.3	18,400	7.55	9.64	38.98		2.93	3.5	
Anse Thomas-1	03/2012	72.5	19,300	6.80	28.1	163.99	10.9	4.23	4.6	4.72
Anse Thomas-2	03/2012	72.5	19,300	6.80	25.5	145.33	11.5	4.13	4.6	4.69
Bouillante BO4	03/1995	33.5	19,600		439.20	2685.01		4.43	4.46	
Bain du Cur�e	03/1995	40.3	223	7.13	7.26	21.84		2.18	3.8	
Bain du Cur�e	01/1999	39.6	223		6.03	15.39		1.85		
Bain du Cur�e-1	03/2012	40.7	319		6.90	21.84	15.2	2.29	4.3	4.59
Bain du Cur�e-2	03/2012	40.7	319		6.96	21.59	15.7	2.25	4.2	4.64
Marsolle	03/1995	46.3	528	7.03	10.30	41.50		2.92	4.2	
Marsolle-1	03/2012	47.2	839	7.05	11.9	53.45	15.3	3.26	4.4	4.66
Marsolle-2	03/2012	47.2	839	7.05	11.2	48.92	15.1	3.17	4.4	4.61
Bois Mahler	03/1995	36.3	227	7.25	8.05	25.44		2.29	3.8	
Bois Mahler	01/1999	33.8	227		6.70	20.99		2.27	4.6	
Bois Mahler-1	03/2012	36.2	310		8.07	29.51	17.2	2.65	4.5	5.23
Bois Mahler-2	03/2012	36.2	310		8.27	29.99	17.4	2.63	4.4	5.11
Ilet Pigeon	03/1995	49.5	28,500	7.88	7300.00	33,143.46		3.29	3.29	

3.1.2. Bouillante system

Helium isotope composition of the gases from the Bouillante geothermal area is also stable over time (Fig. 2). Although their carbon isotopic composition differs only slightly from that of La Soufrière gases, with a mean $\delta^{13}\text{C}$ value of $(-3.0 \pm 0.4) \text{‰}$, their $^3\text{He}/^4\text{He}$ ratio ($4.5 \pm 0.1 R_a$) is much lower. This strong helium isotope contrast between both systems thus raises the question of the possibility of a different magmatic source feeding the geothermal reservoir (see discussion § 4).

3.2. Thermal springs

Thermal spring results are given in Table 2. Their location is shown in Fig. 1. Most groundwaters in La Soufrière area have transit times of a few months only (Pascaline et al., 1982; Bigot et al., 1994). Because of this low residence time and of the low tritium (Pascaline et al., 1982) and high helium contents of the waters, the tritiogenic ^3He contribution to the measured $^3\text{He}/^4\text{He}$ ratio is negligible. Our results are in excellent agreement with those published by Ruzié et al., 2013. Helium isotope data are plotted in Fig. 3. Thermal springs in the close vicinity of the volcano plot along a line the slope of which defines a $^3\text{He}/^4\text{He}$ ratio which is in close agreement with that of the summit fumaroles. More distant springs are characterized by lower $^3\text{He}/^4\text{He}$ values, thus displaying a decreasing trend with distance from the volcanic axis. Helium isotope results for the thermal springs in the Bouillante area indicate a $^3\text{He}/^4\text{He}$ ratio which is fully consistent with that of the free gases sampled at the geothermal station and in the marine bubbles off Pointe Lézarde. The lowest $^3\text{He}/^4\text{He}$ of the whole data set ($3.3 R_a$), coinciding with the highest helium concentration ($7.3 \times 10^{-5} \text{ cm}^3 \text{ STP/g}$), is found in the small submarine hot spring located at -23 m off Ilet Pigeon, a tiny island located a few kilometres to the NE of the Bouillante power station. It also corresponds to the sampling point which is the most distant from La Soufrière volcanic centre.

4. Discussion

$^3\text{He}/^4\text{He}$ ratios for La Soufrière clearly fall in the MORB range and thus indicate a MORB-type mantle source feeding the volcanic system.

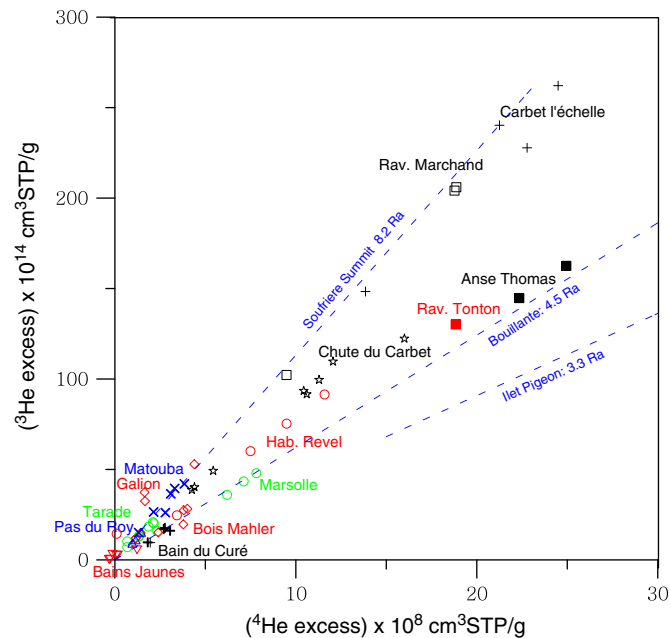


Fig. 3. Relationship between the non-atmospheric ^3He and ^4He concentrations in hot spring waters. The non-atmospheric component is obtained by subtracting the dissolved air component (calculated using the neon concentration or the solubility value when no neon is available – see text) from the measured concentrations.

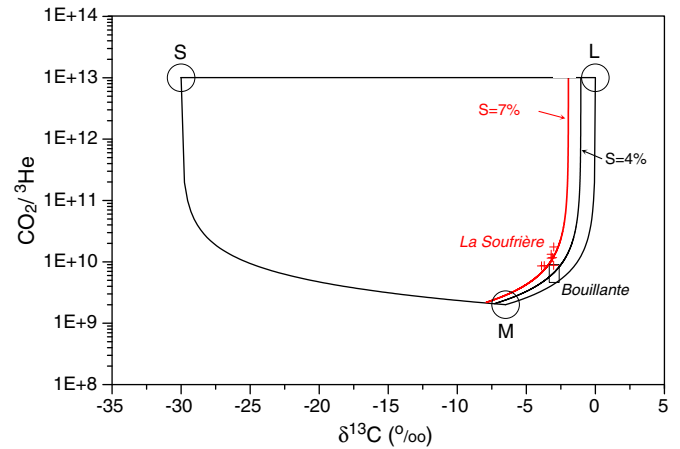


Fig. 4. $(\text{CO}_2/{}^3\text{He})$ vs $\delta^{13}\text{C}$ diagram for summit fumaroles and Bouillante gases in relation to the three major end-members contributing to He and CO_2 in geothermal fluids (M represents the upper mantle end-member, L and O represent the marine carbonate-limestone and organic material, respectively). The black rectangle represents the mean of the $(\text{CO}_2/{}^3\text{He})$ and $\delta^{13}\text{C}$ values for the Bouillante system deduced from our CO_2 , helium and $\delta^{13}\text{C}$ data (see Table 1).

Fig. 4 displays the $(\text{CO}_2/{}^3\text{He})$ vs $\delta^{13}\text{C}$ data for the summit fumaroles of La Soufrière and for the Bouillante gases in relation to the three major end-members contributing to He and CO_2 in volcanic and geothermal fluids (Sano and Marty, 1995): M represents the upper mantle end-member with $(\text{CO}_2/{}^3\text{He})_M = (2 \pm 1) \times 10^9$ (Marty and Jambon, 1987) and $\delta^{13}\text{C}_M = (-6.5 \pm 2) \text{‰}$ (Javoy et al., 1986; Marty and Jambon, 1987; Sano and Marty, 1995); L represents the sedimentary carbonate-limestone end-member with $(\text{CO}_2/{}^3\text{He})_L \approx 1 \times 10^{13}$ (Sano and Marty, 1995; Kulongoski et al., 2013) and $\delta^{13}\text{C}_L = 0 \text{‰}$; and S the sedimentary organic end-member with $(\text{CO}_2/{}^3\text{He})_S \approx 1 \times 10^{13}$ (Sano and Marty, 1995; Kulongoski et al., 2013) and $\delta^{13}\text{C}_S \approx (-30 \pm 10) \text{‰}$ (Hoefs, 1980; Sano and Marty, 1995). The $(\text{CO}_2/{}^3\text{He})$ value of most crustal CO_2 -rich continental gases is in the range 10^{12} – 10^{14} (O'Nions and Oxburgh, 1988). Therefore, the adopted value of 10^{13} for the L and S end-members is not well constrained. However, as already noted by Sano and Marty (1995), assuming either 10^{12} or 10^{14} does not significantly change the proportion of CO_2 derived from each of the three end-members (Fig. 4).

The respective proportions M, L and S can be calculated from the following set of equations:

$$(\delta^{13}\text{C}) = M(\delta^{13}\text{C})_M + L(\delta^{13}\text{C})_L + S(\delta^{13}\text{C})_S \quad (1)$$

$$(^3\text{He}/\text{CO}_2) = M(^3\text{He}/\text{CO}_2)_M + L(^3\text{He}/\text{CO}_2)_L + S(^3\text{He}/\text{CO}_2)_S \quad (2)$$

$$L + M + S = 1. \quad (3)$$

For La Soufrière, the calculated mixing coefficients are $M = 18 \pm 1\%$, $L = 75 \pm 5\%$ and $S = 7 \pm 4\%$, in agreement with typical values for volcanic arcs (Oppenheimer et al., 2013). For the Bouillante area, the mixing proportions are $30 \pm 1\%$, $66 \pm 4\%$ and $4 \pm 3\%$, respectively. The difference with La Soufrière system is almost entirely due to the lower $(\text{CO}_2/{}^3\text{He})$ ratio (5.8×10^9). The validity of the $(\text{CO}_2/{}^3\text{He})$ – $\delta^{13}\text{C}$ mixing diagram is based on the assumption that CO_2 and He are not fractionated during their transport to the Earth's surface. However, CO_2 and He have a highly contrasted solubility in groundwater and this assumption is not always valid; for instance, in the Kusatsu-Shirane volcanic area, Sano et al. (1994) observed a positive correlation between the temperature of the fumaroles and hot springs and the $(\text{CO}_2/{}^3\text{He})$ ratio: $(\text{CO}_2/{}^3\text{He})$ values varied by a factor 2 for a temperature

range 23 °C–102 °C, even though the $\delta^{13}\text{C}$ was not affected, thus showing that elemental fractionation due to physico-chemical processes affecting CO_2 may be important. In La Soufrière fumaroles however, the temperature range is much narrower (94 °C–108.5 °C), therefore such an effect is not expected to be seen. Nevertheless, in the Bouillante area in particular, the physico-chemical interaction between magmatic CO_2 and the inorganic marine carbon system may decrease the $(\text{CO}_2/{}^3\text{He})$ ratio due to the partial transformation of magma-derived CO_2 into marine bi-carbonate and carbonate, as observed for instance by Pedroni et al. (1999) for the gases of a Bouillante thermal spring (Table 1) with a $(\text{CO}_2/{}^3\text{He})$ value as low as 0.3×10^9 and a high helium content of 204 ppm. Taking account of this potential influence, the $(\text{CO}_2/{}^3\text{He})$ - $\delta^{13}\text{C}$ diagram suggests that the proportion of MORB-type upper mantle end-member in the Bouillante gases is about the same as in La Soufrière fumaroles. Therefore, the strong difference in the $({}^3\text{He}/{}^4\text{He})$ ratio between both systems clearly points to an additional radiogenic ${}^4\text{He}$ component in the Bouillante geothermal reservoir.

This can be further investigated by plotting $({}^3\text{He}/{}^4\text{He})$ ratios as a function of $\delta^{13}\text{C}$ (Fig. 5), using the additional Eq. (4) for helium isotopes:

$$R \left({}^3\text{He}/\text{CO}_2 \right) = M R_M \left({}^3\text{He}/\text{CO}_2 \right)_M + L R_L \left({}^3\text{He}/\text{CO}_2 \right)_L + S R_S \left({}^3\text{He}/\text{CO}_2 \right)_S \quad (4)$$

where R_M , R_L , and R_S are the ${}^3\text{He}/{}^4\text{He}$ ratios of the three end-members. R_M value is taken equal to $8.25 R_a$, and R_L and R_S are $<0.05 R_a$. Using the S value determined above ($S = 7\%$), the calculated values of M and L for La Soufrière are 17% and 76% respectively, in excellent agreement with the values determined from the $(\text{CO}_2/{}^3\text{He})$ vs $\delta^{13}\text{C}$ diagram. On the contrary, the ${}^3\text{He}/{}^4\text{He}$ ratio of the Bouillante system clearly departs from the mixing curve (Fig. 5), demonstrating that the lower ${}^3\text{He}/{}^4\text{He}$ ratio is due to the addition of extraneous radiogenic helium, presumably from the surrounding host rocks. Such a subsurface crustal contamination has been observed in many instances (see Gasparon et al., 1994 and references therein) and is also responsible for the decreasing trend in the $({}^3\text{He}/{}^4\text{He})$ values of volcanic gases which is classically observed away from the main conduit of volcanic edifices (Sano et al., 1984, 1995). Fig. 6 shows that such a spatial trend also characterizes all measured fluids in Guadeloupe. It also shows that the low $({}^3\text{He}/{}^4\text{He})$ values observed for the Bouillante hydrothermal system are consistent with this spatial trend. This strengthens our view, based on the $(\text{CO}_2/{}^3\text{He})$ vs $\delta^{13}\text{C}$ and $({}^3\text{He}/{}^4\text{He})$ vs $\delta^{13}\text{C}$ relationships, that La Soufrière and Bouillante systems, despite their marked hydrogeological differences, are fed by the same magmatic source, and that the strong contrast in

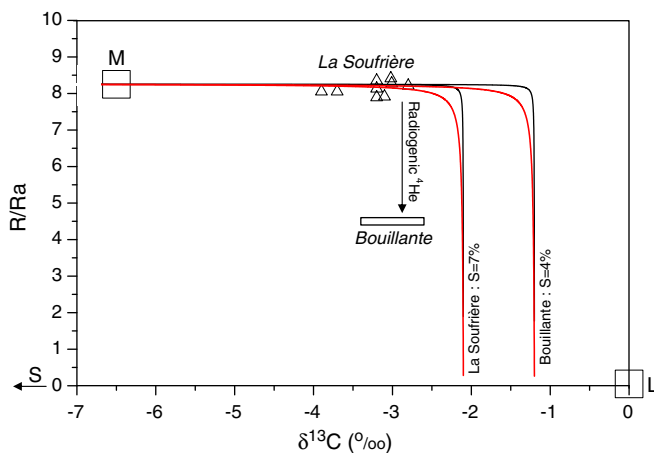


Fig. 5. $({}^3\text{He}/{}^4\text{He})$ vs $\delta^{13}\text{C}$ diagram for summit fumaroles and Bouillante gases in relation to the three major end-members contributing to He and CO_2 in geothermal fluids (M represents the upper mantle end-member, L and O represent the marine carbonate-limestone and organic material, respectively). The black rectangle represents the $({}^3\text{He}/{}^4\text{He})$ - $\delta^{13}\text{C}$ domain for Bouillante (see Table 1).

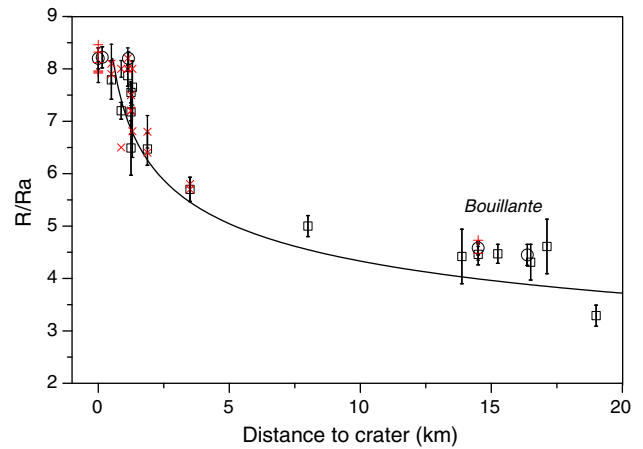


Fig. 6. Decreasing trend of the ${}^3\text{He}/{}^4\text{He}$ ratios with distance to the crater for gases (black circles) and waters (black squares). In red, literature data for gases (+) by Van Soest et al., 1998; Pedroni et al., 1999; Ruzié et al., 2012 and for waters (x) (Ruzié et al., 2013).

the ${}^3\text{He}/{}^4\text{He}$ values between both systems has to be ascribed to radiogenic helium contamination by the surrounding wallrock.

5. Conclusions

A substantial number of samples were collected over the last thirty years from the volcanic and geothermal manifestations of Guadeloupe in order to study their helium and carbon isotope geochemistry. Based on this data set, our main conclusions are as follows:

${}^3\text{He}/{}^4\text{He}$ values in the fumarolic gases around La Soufrière volcano are quite homogeneous and have remained quite stable over the sampling period (1980–2012). The average value of $8.2 \pm 0.2 R_a$ indicates that the volcano is tapping a MORB-like source.

In contrast, the ${}^3\text{He}/{}^4\text{He}$ values for the Bouillante deep geothermal reservoir ($4.5 \pm 0.1 R_a$) are strikingly lower.

He–C relationships strongly suggest that both systems are fed by the same magmatic source, the marked difference in their ${}^3\text{He}/{}^4\text{He}$ being due to radiogenic ${}^4\text{He}$ accumulation from the host rock in the confined Bouillante deep aquifer.

This conclusion is strengthened by the spatial distribution of the ${}^3\text{He}/{}^4\text{He}$ ratio for all studied sites, which shows that La Soufrière volcano and the Bouillante geothermal system are the two end-members of a spatial decreasing trend for ${}^3\text{He}/{}^4\text{He}$ ratios with distance from La Soufrière dome, due to an increasing radiogenic ${}^4\text{He}$ contamination by the host rock away from the volcanic axis.

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