



The Geothermal Resource in the Guanacaste Region (Costa Rica): New Hints From the Geochemistry of Naturally Discharging Fluids

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The Guanacaste Geothermal Province (GGP) encompasses the three major volcanoes of northern Costa Rica, namely from NW to SE: Rincón de la Vieja, Miravalles, and Tenorio. The dominant occurrence of (i) SO₄-rich acidic fluids at Rincón de la Vieja, (ii) Cl-rich mature fluids at Miravalles, and (iii) HCO₃⁻-rich and low-temperature fluids at Tenorio was previously interpreted as due to a north-to-south general flow of thermal waters and a magmatic gas upwelling mostly centered at Rincón de la Vieja, whereas Miravalles volcano was regarded as fed by a typical geothermal reservoir consisting of a highly saline Na-Cl aquifer. The uniformity in chemical and isotopic (R/Ra and δ³⁴S) compositions of the neutral Cl-rich waters suggested to state that all the thermal discharges in the GGP are linked at depth to a single, regional geothermal system. In this scenario, the thermal manifestations related to Tenorio volcano were regarded as a distal and diluted fluid outflow. In this study, a new gas geochemical dataset, including both chemical and isotopic (δ¹³C-CO₂ and R/Ra) parameters of fluid discharges from the three volcanoes, is presented and discussed. Particular attention was devoted to the Tenorio thermal manifestations, since they were poorly studied in the past because this area has been considered of low geothermal potential. The aim is to provide insights into the magmatic-hydrothermal fluid circulation and to verify the spatial distribution of the heat fluid source feeding the fluid manifestations. According to this new dataset, CO₂, i.e., the most abundant dry gas in the fluid manifestations, is mostly produced by limestone, whereas the mantle CO₂ contribution is ≤3.3%. Strongly acidic gas compounds from magma degassing were absent in the discharged fluids, being scrubbed by secondary processes related to prolonged fluid-rock interactions and mixing with shallow aquifers. Our results only partially confirm the previously depicted model, because the geochemical and isotopic features (e.g., relatively high concentrations of temperature-dependent gases and high R/Ra values) shown by fluids seeping out from the southern sector of Tenorio volcano are more representative of medium-to-high enthalpy volcanic systems than those typically occurring in distal areas. This implies that the geothermal potential in the south of the GGP is higher than previously thought.

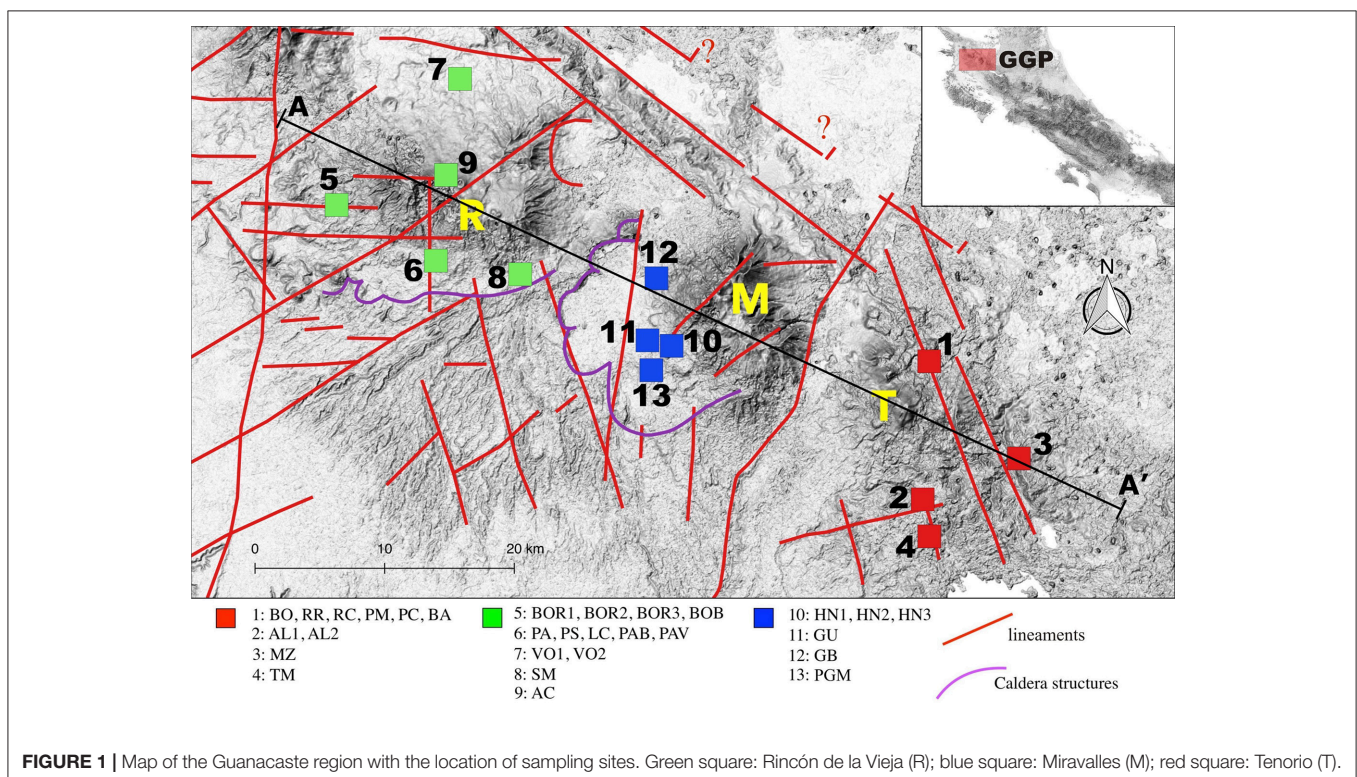
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INTRODUCTION

Actions aimed to the evaluation of the sustainable potential of geothermal fluid reservoirs can provide fundamental information for minimizing the financial risk related to the exploitation activity of such natural resources. Geochemical prospections, coupled with geophysical measurements, are considered useful tools to investigate the chemical-physical features of hot, deep aquifers at relatively low cost (e.g., Giggenbach, 1991), especially for developing countries poor in conventional energy sources, such as carbon, oil, and natural gases. The geothermal potential in the Guanacaste Geothermal Province (GGP), northern Costa Rica, has been investigated since the early 1970's (Ferguson and Alfonso, 1977; Gardner and Corrales, 1977). There are three stratovolcanoes in this region, namely from NW to SE: Rincón de la Vieja, Miravalles, and Tenorio. In the last centuries, phreatic and phreatomagmatic eruptions frequently occurred at Rincón de la Vieja (e.g., Barquero and Segura, 1983; Boudon et al., 1996; Kempter et al., 1996), whereas at Miravalles and Tenorio (**Figure 1**) no historical eruptions were recorded (Mainieri et al., 1985; Alvarado, 2000). GGP shows numerous thermal fluid discharges, e.g., fumaroles, steam-heated soils, low-to-high temperature SO_4^- and Cl^- rich springs, and CO_2 -rich bubbling pools (Giggenbach and Corrales, 1992; Gherardi et al., 2002; Tassi et al., 2005), which, as commonly occurs in a volcanic environment, are related to a hydrothermal-magmatic source. The spatial distribution of neutral, geothermal-type Cl^- -rich water discharges, locally known as *salitrales*, and acidic SO_4^{2-} -rich springs produced

by interaction of meteoric water and hydrothermal gases, was interpreted as an evidence for the presence of a single contiguous geothermal reservoir beneath the GGP (Giggenbach and Corrales, 1992). The Cl^- concentration and temperature of this deep aquifer were estimated at $\sim 3,500$ mg/L and $\sim 250^\circ\text{C}$, respectively (Giggenbach and Corrales, 1992; Gherardi et al., 2002). A similar temperature was also found in fluids from other exploited geothermal systems of Central America, such as those located in Salvador (Ahuachapan and Berlin), whose Cl^- concentrations at the beginning of the exploitation where up to 9,000 and 11,000 mg/L, respectively (D'Amore and Mejia, 1999). The temperature hypothesized for the GGP reservoir, supported by calculations based on water isotopes and the contents of the main anions (Cl^- and SO_4^{2-}), were consistent with those measured on the fluids discharged from the geothermal wells along the SW slope of the Miravalles volcano (Gherardi et al., 2002). According to this scenario, the area named Las Pailas (on the NW flank of Rincón de la Vieja volcano; #6 in **Figure 1**) and the inner zone of the Miravalles caldera were regarded as the areas most affected by deep fluid upwelling, whereas the thermal manifestations located within the SE portion of GGP, corresponding to Tenorio volcano, were considered as distal fluid outflow (**Figure 1**). These indications gave a pulse to the development of the geothermal fluid exploitation at Miravalles (Vallejos-Ruiz et al., 2005), as well as the prospection at Rincón de la Vieja (Molina and Martí, 2016, and references therein) where the geothermal fluid exploitation is still at the preliminary stage.

In the present study, the chemical and isotopic ($\delta^{13}\text{C}\text{-CO}_2$ and R/Ra) composition of the GGP fluid discharges, with a special



focus on those related to Tenorio volcano, is reported. At the light of this robust geochemical database, integrated with data from literature, the primary sources and secondary chemical-physical processes controlling the fate of the hydrothermal fluids are investigated. A critical revision of the hydro-geochemical conceptual models proposed for GGP by the previous authors is carried out, providing new insight into the geothermal potential of this region.

REGIONAL SETTING AND VOLCANIC ACTIVITY

Costa Rica has a complex geology, related to the presence of three tectonic plates (Caribbean, Cocos and Nazca), the Panama microplate and an uncertain number of tectonic terranes (Alvarado and Cárdenes, 2016). These slabs are separated by a zone of diffusive deformation named Central Costa Rica Deformed Belt (CCRBBD) and are bound to the southwest by the Middle America Trench (MAT; Montero et al., 2017). The magmatic arc, which is located ~150 km northeast of MAT, consists of (i) two active volcanic ranges, namely Cordillera Central (CC) and Cordillera de Guanacaste (CG), and (ii) two extinct ranges, i.e., Cordillera de Tilarán-Aguacate (CAG) and Cordillera de Talamanca (CT) (Alvarado and Cárdenes, 2016).

The Cordillera de Guanacaste (NW Costa Rica) was formed about 0.6 Ma and comprises four stratovolcanic complexes (1,500–2,000 m high): Orosí-Cacao, Rincón de la Vieja-Santa María, Miravalles-Zapote, and Tenorio-Montezuma (Chiesa et al., 1994). A series of E-W-trending lineament were identified between Orosí-Cacao and Rincón de la Vieja volcanoes, whereas secondary lineaments showing a different trend (NNE-SSW, N-S-, and NNW-SSE) were recognized along the eastern flank of Miravalles volcano, as well as at Rincón de la Vieja and Tenorio volcanoes (Chavarría et al., 2010) (**Figure 1**).

Rincón de la Vieja is the largest volcano of the Cordillera de Guanacaste, with an estimated volume of 130 km³ (Carr, 1984). It is a complex andesitic stratovolcano consisting of an elongated, arcuate NW-SE trending of nine coalescing pyroclastic cones, spreading over an 8-km long axis (Chiesa et al., 1994). The maximum elevation (Santa María cone) is 1916 m a.s.l. The last plinian eruption occurred 3.5 ka (Alvarado et al., 1992), whereas the historical activity was characterized by the occurrence of frequent phreatic and phreato-magmatic eruptions from the Active Crater (Tristan, 1921; Barquero and Segura, 1983). Since 1991, 20 phreatic eruptions, producing ash deposits and debris-flows, occurred (OVSICORI-UNA, 1998), while a transition to a phreato-magmatic activity took place in 1995 (OVSICORI-UNA, 1995). Intense phreatic activity was recorded in August–September 2011, February–April 2012, September 2014, February 2015, March 2016, February–October 2017 (OVSICORI-UNA, 2011, 2012, 2014, 2015, 2016, 2017).

Miravalles is the highest volcano of the Cordillera de Guanacaste (2028 m a.s.l.). This andesitic stratovolcano pertains to the Miravalles-Zapote complex, whose activity started with the edification of the Guayabo volcano (1.17–1.0 Ma; Alvarado and Gans, 2012). The latter was destroyed by the following

explosive activity (1.5 and 0.6 Ma) giving rise to the formation of the 15 km wide Guayabo caldera (Chiesa et al., 1992). The latter hosts Cabro Muco volcano (0.57–0.28 Ma), in the eastern sector, and Zapote and Miravalles volcanoes (<0.28 Ma) in the northern sector (Chiesa et al., 1992; Alvarado and Gans, 2012). Tephrochronology data suggested that an important eruptive event occurred at about 5050 BC, whilst local witnesses reported a volcanic event on the 14th of September 1946 in the SW flank of Miravalles.

Tenorio-Montezuma, in the south-easternmost part of the Cordillera de Guanacaste, is a basaltic-andesitic volcanic complex, consisting of NNW-ESE-oriented volcanic structures, including pyroclastic cones and two twin-craters (Tenorio and Montezuma) (Alvarado, 1993). An andesitic dome field (Bijagua) grew over a relatively old volcanic center in the northern flank of Tenorio (Chiesa et al., 1994). Little is known about the geology of this intensely forested area. The andesitic and basaltic lavas of Monteverde (2.17–1.92 Ma) are the basement of the Tenorio edifice that developed during two main eruptive phases, dated 0.74–0.54 and 0.37–0.26 Ma, respectively (Alvarado and Gans, 2012). The occurrence of a caldera in the southern flank was hypothesized by ICE (Instituto Costarricense de Electricidad) and ENEL (Italian Board of Electricity) (ICE, 1990), although Alvarado and Gans (2012) suggested that the depression should be regarded as a northernmost branch of the Arenal graben. No historical volcanic activity has likely occurred at Tenorio-Montezuma. Notwithstanding, a legend, not supported by scientific investigation, speaks of an eruption that occurred in 1816 (Alvarado, 1993).

PREVIOUS GEOTHERMAL PROSPECTION AND EXPLOITATION

A pre-feasibility study carried out in 1976 in the Miravalles area suggested the presence of a geothermal reservoir with temperature ~240°C (Gardner and Corrales, 1977). From 1977 to 1986, new exploratory activities, including the drilling of eight wells, provided the first insights into the geochemical features of the liquid-dominated system, i.e., neutral pH and a typical Na⁺-Cl⁻ composition (Giggenbach and Corrales, 1992; Gherardi et al., 2002). The chemical and isotopic composition of fluid discharges from the GGP sampled between 1982 and 1988, allowed the construction of a hydro-geochemical model of the hydrothermal system (Giggenbach and Corrales, 1992). A geophysical prospection carried out by ICE and ELC (Electroconsult) between 1989 and 1991 (ICE, 1991), revealed areas of great interest for geothermal fluid exploitation along the slopes of Rincón de la Vieja, Miravalles, and Tenorio volcanoes. From 1994 to 2004, 5 geothermal power plants were installed in the Miravalles area, amounting for a maximum sustainable capacity of 163.5 MW (Sánchez-Rivera and Vallejos-Ruiz, 2015). Then, ICE focused its attention on the Rincón de la Vieja area, especially on the westernmost flank of this volcano (Las Pailas and Borinquen hydrothermal areas), where the occurrence of a number of fumaroles, silicified rocks, soils and thermal springs clearly indicated a significant thermal anomaly (Molina and

Marti, 2016). At Las Pailas, a first geothermal plant (Unit I; 41.5 MW) was installed in 2011, whereas a second unit (55 MW) is planned to be placed to the east of Unit I, in 2018. At Borinquen, the construction of two units (55 MW each) is planned for 2023–2024 (ICE, 2014; Sánchez-Rivera and Vallejos-Ruiz, 2015), following the indication of a recent study (Molina and Marti, 2016) suggesting the occurrence of an aquifer at a temperature $\geq 220^{\circ}\text{C}$ located at <3 km depth.

In the Tenorio area, preliminary geothermal prospection, carried out by ICE in 1987–1991, recognized an area of geothermal interest on the southern flank of the volcano (Mayorga, 2009). According to this indication, in 1999, two exploratory wells, PGT-1 and PGT-2, were drilled down to 2,473 m and 1,345 m depth, respectively (Mayorga, 2009). Unfortunately, the low temperature of the discharged water ($<160^{\circ}\text{C}$), the low permeability and the proximity of a protected area (Tenorio Volcano National Park) discouraged the development of geothermal exploitation (Mayorga, 2009). New preliminary geochemical prospecting activities, carried out since 2008 in a 198 km² wide area that includes the northern Tenorio Volcano National Park section and a zone located east of Bijagua (Figure 1), did not provide promising results (Sánchez-Rivera and Vallejos-Ruiz, 2015).

MATERIALS AND METHODS

Gases were collected during 4 campaigns (April 2000, March 2005, February 2009, and February 2017) from thermal manifestations located in the surroundings of Rincón de la Vieja, Miravalles, and Tenorio volcanoes (Figure 1).

Gases from fumaroles were collected using a sampling line consisting of a 1 m-long titanium tube ($\varnothing = 2.5$ cm) and pyrex glass dewared pipes connected to pre-weighed and pre-evacuated 50-mL glass Thorion[®]-tapped flasks filled with 20 mL of a 4N NaOH and 0.15M Cd(OH)₂ suspension (Montegrossi et al., 2001). Bubbling gases were sampled using a funnel up-side-down positioned above the bubbles and connected to the soda flasks using a silicon tube. Water vapor and CO₂, dissolved in the alkaline solution, whereas H₂S formed insoluble CdS. Low-solubility gas species (N₂, O₂, CO, H₂, He, Ar, CH₄, and light hydrocarbons) were trapped in the flask headspace. Dry gases (for the analysis of the ¹³C/¹²C ratios in CO₂ and He isotopes) were collected using a water-cooled condenser connected to the soda flask sampling line.

Inorganic (N₂, Ar, O₂, H₂, He, and CO) and organic (CH₄, C₂H₆, C₃H₈, and C₆H₆) gases were analyzed at the Laboratory of Fluid Geochemistry of the University of Florence (Italy) by gas chromatography (GC; Shimadzu 15A, Shimadzu 14, and Thermo Focus). The liquid and the solid phases of the suspension were separated by centrifuge, to analyze for CO₂ in the form of CO₃²⁻ by acidimetric titration (AT; Metrohm Basic Titrino). The CdS precipitate was dissolved by oxidation with H₂O₂ in order to analyze H₂S as SO₄²⁻ by ion chromatography (IC; Methrom 761). The analytical error for GC, AT and IC analyses was $<5\%$.

The analysis of ¹³C/¹²C of CO₂ (expressed as $\delta^{13}\text{C-CO}_2$ ‰ vs. V-PDB) was carried out at the laboratory of Stable

Isotopes of CNR-IGG (Pisa, Italy) using a Finnigan MAT252 mass spectrometer after standard extraction and purification procedures of the gas mixtures (Evans et al., 1988) performed at the Department of Earth Sciences of Florence (Italy). Carrara and San Vincenzo marbles, as well as international NBS18 and NBS19 standards, were used to estimate the external precision. The analytical error and the reproducibility were ± 0.05 and $\pm 0.1\%$, respectively.

The R/Ra (where R is the ³He/⁴He measured ratio and Ra is the ³He/⁴He ratio in the air: 1.39×10^{-6} ; Mamyrin and Tolstikhin, 1984) and ⁴He/²⁰Ne ratios were determined at the INGV laboratories in Palermo (Italy) by separately introducing He and Ne into a split-flight-tube mass spectrometer (GVI Helix SFT) after performing standard purification procedures (Rizzo et al., 2015). The analytical error was $\pm 1\%$. The measured R/Ra values were corrected for air contamination using the ⁴He/²⁰Ne ratios (Poreda and Craig, 1989), as follows:

$$R_c/R_a = [(R/R_a) - r]/(1 - r) \quad (1)$$

where $r = (^4\text{He}/^{20}\text{Ne})_{\text{air}}/(^4\text{He}/^{20}\text{Ne})_{\text{meas}}$, the $(^4\text{He}/^{20}\text{Ne})_{\text{air}}$ ratio being that in the atmosphere (0.318; Ozima and Posodek, 1983) and the $(^4\text{He}/^{20}\text{Ne})_{\text{meas}}$ ratio that measured in the gas sample.

RESULTS

Chemical Composition

The chemical compositions of gases collected in 2000, 2009, 2015, and 2017 from the GGP are reported in Table 1, whereas the location of the fluid discharges is shown in Figure 1. Data from literature of some of these thermal fluid discharges from Rincón de la Vieja and Miravalles that were sampled in 1984 and 1987 (BOR1 and PA; Giggenbach and Corrales, 1992), as well as in 1998, 1999, and 2001 (BOR1 and PA; Tassi et al., 2005), are also reported. The dataset also includes the chemical composition of gases collected from different sites within GGP in 1987 and 1990 (MZ, TM, and GB; Giggenbach and Corrales, 1992), 1998 (GB; Gherardi et al., 2002), 1999, 2001, and 2002 (BOR2, BOB, LC, PAB, PAV, VO2, SM, and AC; Tassi et al., 2005), as well as that of gases from exploitation wells of the Miravalles geothermal plant (PGM01, PGM05, PGM10, PGM11, PGM12, PGM17, PGM31, and PGM49; Gherardi et al., 2002).

The thermal manifestations consist of bubbling and boiling pools with temperatures ranging from 21 to 99°C. The chemical composition of the dry fraction of the fluids (the concentrations of steam were mostly controlled by the liquid phase at the surface) was dominated by CO₂ (up to 996 mmol/mol), followed by N₂ (from 2 to 53 and mmol/mol). The concentrations of H₂S and CH₄ ranged widely (from 0.075 to 17 and from 0.071 to 20, respectively), while those of H₂ were relatively high (up to 4.8 mmol/mol) with the exception of those (from 0.0013 to 0.0085 mmol/mol) measured in the gases from the NE flank of Tenorio volcano (BO, RR, RC, PM, PC and BA; Figure 1). Oxygen and Ar varied from 0.019 to 0.79 and from 0.015 to 0.44 mmol/mol, respectively, whereas CO and He were ≤ 0.054 and ≤ 0.0068 mmol/mol, respectively. The Miravalles thermal discharges were characterized by relatively high concentrations of ethane (C₂H₆;

TABLE 1 | Outlet temperature (°C), chemical and stable isotope ($\delta^{13}\text{C}\text{-CO}_2$, in ‰ vs. V-PDB; R/Ra; R/Ra) composition of fumaroles from GGP.

	Date	T °C	CO ₂	H ₂ S	N ₂	CH ₄	Ar	O ₂	H ₂	He	CO	C ₂ H ₆	C ₃ H ₈	C ₃ H ₆	C ₆ H ₆	$\delta^{13}\text{C}\text{-CO}_2$	R/Ra	$\frac{^4\text{He}}{^{20}\text{Ne}}$	$\frac{\text{CO}_2}{^3\text{He} \times 10^9}$	L	S	M
1	Borbollones	BO	2017	96	993	3.5	2.5	9.6	0.620	0.31	0.0069	0.0012	0.00061	1.2	0.025	1.2	6.21	21	96	87	11	1.5
	Borbollones	BO	2015	93	992	2.2	3.720	0.072	0.092	0.0052	0.0027	0.00065	8.2	1.3	0.0072	0.84	3.41					
	Borbollones	BO	2000	94	993	3.1	2.310	0.052	0.49	0.0057	0.0010	0.00076	1.0	0.39	0.029	0.92	4.29					
	Rio Roble	RR	2017	27	995	2.3	2.1	1.1	0.045	0.069	0.0019	0.0002	0.00028	0.29	0.038	0.39	4.61					
	Rio Roble	RR	2000	21	993	2.9	2.8	1.2	0.069	0.80	0.0013	0.0003	0.00042	0.23	0.054	0.41	2.80					
	Rio Celeste	RC	2017	61	995	1.1	3.6	0.45	0.051	0.095	0.0085	0.0013	0.00022	0.85	0.096	0.21	4.30	16	124	85	14	1.2
	Rio Celeste	RC	2000	58	995	1.3	3.4	0.37	0.054	0.46	0.0078	0.0012	0.00020	0.21	0.031	0.28	4.68					
	Pozo de la muerte	PM	2000	80	991	4.1	3.7	1.5	0.071	0.57	0.0017	0.0011	0.0044	0.75	0.090	0.18	3.01					
	Pozo Celeste	PC	2000	83	996	0.35	2.0	6.5	0.048	0.74	0.0024	0.0005	0.00019	0.55	0.29	0.040	3.77					
	Bambú	BA	2000	36	995	1.3	3.4	1.6	0.081	0.12	0.0014	0.0012	0.00026	0.78	0.17	0.0066	5.44					
2	Altomassiss 1	AL1	2017	72	987	8.3	4.6	0.38	0.026	0.015	0.14	0.0022	0.0036	6.7	1.8	0.033	1.5	31	45	90	6.5	3.3
	Altomassiss 1	AL1	2015	81	988	6.9	4.2	0.23	0.039	0.037	0.10	0.0018	0.0031	5.1	2.0	0.029	1.8	25	56	91	6.4	2.7
	Altomassiss 2	AL2	2017	74	989	7.1	3.1	0.35	0.039	0.021	0.11	0.0021	0.0038	7.4	1.6	0.035	2.1					
	Altomassiss 2	AL2	2015	70	989	8.0	2.9	0.29	0.028	0.028	0.096	0.0023	0.0041	6.0	1.5	0.032	1.9					
3	Montezuma*	MZ	1987	62	987	1.5	9.0	1.5	0.21	0.99		0.00040					2.22					
4	Tierra Morenas*	TM	1987	91	986	1.6	8.9	2.9	0.11	0.70		0.0026										
5	Borinquen1	BOR1	2017	83	980	9.1	6.5	0.075	0.18	0.15	3.9	0.0018	0.0015	2.9	0.56	0.091	1.3	11	110	93	5.4	1.3
	Borinquen1	BOR1	2015	94	981	8.8	6.3	0.071	0.16	0.31	3.7	0.0021	0.0012	2.6	0.61	0.085	1.1	12	82	92	6.0	1.8
	Borinquen1***	BOR1	2001	96	980	2.4	16	0.010	0.32	0.62	0.078	0.00050	0.0053	0.90	0.34	0.31	1.11					
	Borinquen1***	BOR1	1999	96	987	0.45	8.7	0.028	0.16	0.0020	3.5	0.0014	0.0012	27	26	1.4	0.89	8	134	96	2.8	1.1
	Borinquen1*	BOR1	1987	96	933	35	27	0.61	0.36		4.1	0.0030										
	Borinquen2***	BOR2	1999	75	986	0.28	12	0.038	0.26	0.0049	1.7	0.0028		11	1.6	0.22	5.0					
	Borinquen3	BOR3	2017	97	972	9.5	13	0.10	0.25	0.11	4.8	0.0023	0.0026	2.3	0.76	0.11	2.1					
	Borinquen Barro**	BOB	1999	95	951	23	19	0.16	0.34	0.014	7.3	0.0026	0.012	5.1	2.5	0.14						
	Borinquen Barro***	BOB	2001	96	976	3.1	16	0.012	0.30		4.7	0.00026	0.014	1.8	0.95	0.13	1.1					
6	Pailas de Agua	PA	2017	83	984	1.5	12	0.39	0.19	0.12	1.3	0.0018	0.00081	1.9	0.62	0.032	1.7	18	84	90	7.8	1.8
	Pailas de Agua***	PA	1999	96	990	0.13	8.2	0.029	0.19	0.19	1.0	0.0022	0.0018	7.9	0.70	0.029	2.7					
	Pailas de Agua***	PA	1998	93	991	0.080	7.1	0.030	0.16		1.1	0.0015	0.00055	1.5	0.57	0.025	2.3					
	Pailas de Agua*	PA	1984	98	950	24	18	0.36	0.25	2.3	5.3	0.013						13	89			
	Pailas seca	PS	2017	83	990	1.1	6.2	0.41	0.11	0.14	1.5	0.0026	0.0028	6.5	0.66	0.031	2.4					
																	2.05					

(Continued)

TABLE 1 | Continued

		Date	T °C	CO ₂	H ₂ S	N ₂	CH ₄	Ar	O ₂	H ₂	He	CO	C ₂ H ₆	C ₃ H ₈	C ₃ H ₆	C ₆ H ₆	d ¹³ C-CO ₂	Rc/Ra	⁴ He/ ²⁰ Ne	CO ₂ / ³ He x 10 ⁹	L	S	M
Lago Caliente***	LC	1999	86	991	0.012	7.2	0.025	0.13	0.014	1.2	0.0023	0.00073	4.6	0.75	0.050	1.5	-0.68						
Lago Caliente***	LC	1998	94	992	0.016	7.9	0.024	0.15		0.26	0.0018	0.00077	0.50	0.26	0.019	1.7							
Pailas de Barro***	PAB	1999	89	905	11	70	0.37	1.3	1.8	11	0.0019	0.0047	35	8.2	0.85	37	-0.63	4.12	3	83	96	1.8	1.8
Pailas de Volcancito***	PAV	1999	99	983	0.87	12	0.84	0.18	0.39	2.8	0.0018	0.0020	6.7	1.4	0.19	5.6	-0.64	4.00	12	99	97	1.9	1.5
Volcancito1	VO1	2017	53	977	0.075	22	0.51	0.44	0.18		0.0026		0.71				-3.78						
Volcancito2***	VO2	1999	59	974	0.084	25	0.60	0.49	0.23		0.0037		0.83										
Santa Maria***	SM	1999	37	990	0.003	10	0.013	0.22	0.0030	0.0018	0.00039		9.9	0.91	0.13	0.86	-1.49	4.86	2	377	95	4.9	0.4
Active crater***	AC	2002	76	980	14	3.1	0.00006	0.019	0.38	0.21	0.0031	0.0033	0.0002	0.005		0.073							
Hornillas1	HN1	2017	82	985	11	1.8	1.9	0.036	0.059	0.61	0.00025	0.046	45	4.9	0.085	15	-2.02						
Hornillas1	HN1	2015	97	982	15	1.6	1.2	0.035	0.028	0.54	0.00037	0.054	43	6.9	0.090	12	-2.71						
Hornillas1	HN1	2009	58	980	12	4.7	1.7	0.11	0.019	1.5	0.0019	0.0021	58	11	0.21	75	-1.82	3.24	15	113	93	5.8	1.3
Hornillas2	HN2	2017	83	980	16	2.2	1.6	0.036	0.062	0.27	0.00076	0.031	53	6.1	0.089	11	-2.68						
Hornillas2	HN2	2009	71	960	17	21	1.5	0.33	0.62	0.097	0.00097	0.00077	19	4.4	0.069	6.0							
Hornillas2	HN2	2015	71	963	16	19	1.4	0.31	0.57	0.091	0.00091	0.00075	67	11	0.11	18	-2.36						
Hornillas3	HN3	2009	56	985	7.4	4.9	1.8	0.089	0.79	0.47	0.0026	0.00010	8.5	2.9	0.064	3.5							
Guayacac	GU	2015	97	986	2.6	9.4	1.5	0.11	0.19	0.20	0.00049	0.014	9.3	1.5	0.029	1.9	-1.43						
Guayabal*	GB	1990	70	982	0.50	15	1.1	0.30	1.4		0.0027							7.20	8	36			
Guayabal**	GB	1998	64	995	0.04	4.3	1.1	0.11	0.37		0.0004												
Geothermal well**	PGM05	1998	n.d.	960	20	18	0.59	0.29	0.015	1.3	0.0028												
Geothermal well**	PGM11	1998	n.d.	978	11	10	0.39	0.18	0.015	0.88	0.0021												
Geothermal well**	PGM49	1998	n.d.	845	25	129	0.12	0.29	0.015	0.80	0.037												
Geothermal well**	PGM01	1998	n.d.	970	14	14	0.19	0.16	0.11	1.6	0.0058												
Geothermal well**	PGM17	1998	n.d.	947	16	34	1.6	0.11	0.29	1.2	0.0073												
Geothermal well**	PGM12	1998	n.d.	948	16	34	0.79	0.11	0.010	0.65	0.0095												
Geothermal well**	PGM31	1998	n.d.	969	18	12	0.30	0.085	0.12	0.25	0.0093												
Geothermal well**	PGM10	1998	n.d.	932	8.5	58	0.58	0.32	0.015	1.0	0.0075												

⁴He/²⁰Ne and CO₂/³He ratios, as well as %L, %S, and %M values are also reported. Concentrations are in mmol/mol, except for those of light hydrocarbons (C₂H₆, C₃H₈, C₃H₆, and C₆H₆) that are in μmol/mol. Data from *Giggenbach and Corrales (1992), **Gherardi et al. (2002), and ***Tassi et al. (2005) are also reported.

up to 67 $\mu\text{mol/mol}$), propane (C_3H_8 ; up to 11 $\mu\text{mol/mol}$), and benzene (C_6H_6 ; up to 75 $\mu\text{mol/mol}$) with respect to those of the other thermal manifestations (≤ 8.2 , ≤ 2.0 , and ≤ 2.4 $\mu\text{mol/mol}$, respectively). Minor amounts (≤ 0.21 $\mu\text{mol/mol}$) of propene (C_3H_6) were also measured.

$\delta^{13}\text{C}\text{-CO}_2$ and Rc/Ra Values

The $\delta^{13}\text{C}\text{-CO}_2$ and Rc/Ra values of gases from the GGP are listed in **Table 1**. Data from literature (Tassi et al., 2005) of Rincón de la Vieja thermal manifestations are also reported. The $\delta^{13}\text{C}\text{-CO}_2$ values of gases from the N flank of Tenorio (**Figure 1**) were significantly more negative (from -5.44 to -2.80‰ vs. V-PDB) with respect to those from the other thermal discharges (from -2.71 to -1.16‰ vs. V-PDB). The Rc/Ra values of gases from Rincón de la Vieja volcano ranged from 3.55 to 4.66, whereas that measured in HN1 gas (Miravalles volcano) was slightly lower (3.24). On the contrary, significantly higher Rc/Ra values were measured at Tenorio, especially in the AL1 gases (7.11 and 7.07, respectively).

DISCUSSION

Gas Sources and Secondary Chemical-Physical Processes

The isotopic ratios of He in hydrothermal gas discharges from different geodynamic settings are helpful to evaluate the contribution of mantle- and crust-related fluids (e.g., Polyak and Tolstikhin, 1985). The R/Ra values of gases released along convergent plate boundaries may vary between 3 and 8, depending on the degree of crustal contamination affecting the mantle source (Poreda and Craig, 1989; Hilton et al., 2002). The Rc/Ra values measured in the GGP gases (**Table 1**) fall within such range (**Table 1**). The highest mantle He contribution observed in the study area was found in GB (Miravalles), as already highlighted by previous data (Poreda and Craig, 1989), and, surprisingly, in AL (Tenorio) gases. It is worth noting that gas discharges from the same area, such as Borinquen and Las Pailas (**Figure 1**), i.e., located close to each other, were characterized by relatively strong differences in Rc/Ra values, suggesting that the hydrothermal fluids uprising from the deep reservoirs were affected by variable inputs of crustal gases at a local scale. The $\delta^{13}\text{C}\text{-CO}_2$ values showed overlapping ranges between mantle and crustal CO_2 (Sherwood Lollar et al., 1997). Thus, this geochemical parameter cannot clearly distinguish gases from these two sources. The $\delta^{13}\text{C}\text{-CO}_2$ values of most GGP gases, being higher than those that characterize mantle gases (from -7 to -3‰ vs. V-PDB) (Pineau and Javoy, 1983), may be interpreted as due to interactions of limestone with the hydrothermal/magmatic fluids, as also observed in other volcanic systems such as Vulcano Island (Tedesco and Nagao, 1996), Mt. Vesuvius (Chiodini et al., 2001), and Nysiros (Brombach et al., 2003). The $\delta^{13}\text{C}\text{-CO}_2$ values of the gases from the NE sector of Tenorio volcano (**Figure 1**), which were slightly more negative, may imply (i) a pure mantle CO_2 source or (ii) a contribution of ^{12}C -enriched CO_2 ($\leq -20\text{‰}$ vs. V-PDB) from degradation of organic matter (O'Leary, 1988; Hoefs, 2009). These values may also be related to $^{13}\text{C}\text{-}^{12}\text{C}$ fractionation processes due to interactions with shallow aquifers and/or

carbonate precipitation/dissolution (Venturi et al., 2017, and references therein). Useful insights into the origin of CO_2 of the GGP gases are provided by combining $\delta^{13}\text{C}\text{-CO}_2$ values and $\text{CO}_2/{}^3\text{He}$ ratios (Marty and Jambon, 1987; O'Nions and Oxburgh, 1988). As shown in **Figure 2**, all the gases from the three volcanic systems of GGP displayed a strong CO_2 -excess (1–2 orders of magnitude) with respect to mantle, mostly due to CO_2 production from limestone and/or marine carbonate. As suggested by Sano and Marty (1995), the relative contribution of carbon from mantle degassing (M), limestone (L), and/or organic-rich sediments (S) can be computed, as follows:

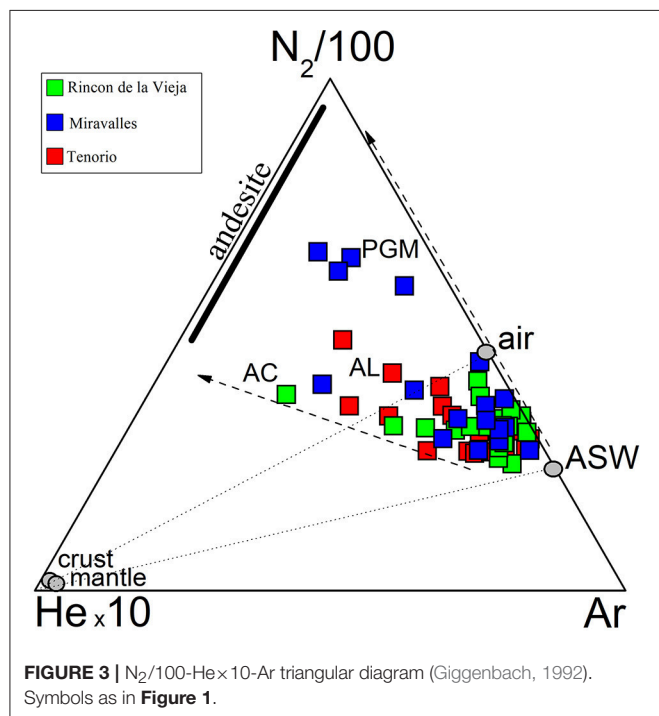
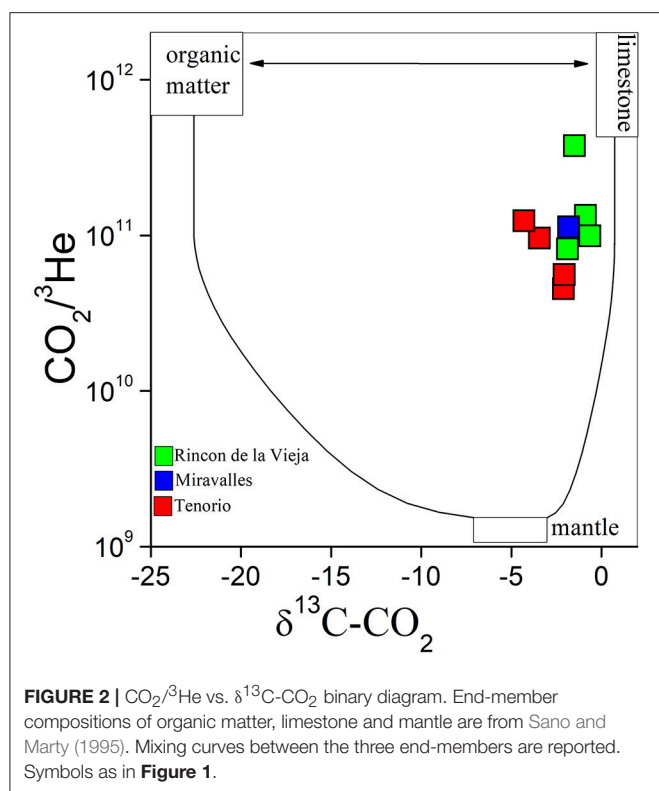
$$M + S + L = 1 \quad (2)$$

$$(\delta^{13}\text{C} - \text{CO}_2)_{\text{meas}} = M(\delta^{13}\text{C} - \text{CO}_2)_{\text{MORB}} + L(\delta^{13}\text{C} - \text{CO}_2)_{\text{Lim}} + S(\delta^{13}\text{C} - \text{CO}_2)_{\text{Sed}} \quad (3)$$

$$1/(\text{CO}_2/{}^3\text{He})_{\text{meas}} = M/(\text{CO}_2/{}^3\text{He})_{\text{MORB}} + L/(\text{CO}_2/{}^3\text{He})_{\text{Lim}} + S/(\text{CO}_2/{}^3\text{He})_{\text{Sed}} \quad (4)$$

Equations (3, 4) were solved considering the following data: $(\delta^{13}\text{C}\text{-CO}_2)_{\text{MORB}} = -6.5\text{‰}$, $(\delta^{13}\text{C}\text{-CO}_2)_{\text{Sed}} = -30\text{‰}$, $(\delta^{13}\text{C}\text{-CO}_2)_{\text{Lim}} = 0\text{‰}$, $(\text{CO}_2/{}^3\text{He})_{\text{MORB}} = 1.5 \times 10^9$, $(\text{CO}_2/{}^3\text{He})_{\text{Sed}} = 1 \times 10^{13}$ and $(\text{CO}_2/{}^3\text{He})_{\text{Lim}} = 1 \times 10^{13}$. According to these calculations (**Table 1**), the highest mantle CO_2 fraction (3.3%) was measured at Altomassisi (AL, Tenorio), whereas those of the other emissions ranged from 0.4 to 1.8%. As already shown in **Figure 2**, limestone was by far the most abundant crustal carbon source (from 85 to 87%), with variable contribution from organic-rich sediments (from 1.8 to 14%). As already reported by Shaw et al. (2003) on the basis of the $\text{CO}_2\text{-He}$ systematics of various thermal fluid discharges from volcanoes and geothermal systems in the Costa Rica and Nicaragua regions including Rincón de la Vieja and Miravalles volcanoes, the fluids from the study area were characterized by a relatively high L/S average ratio (21.7), i.e., strongly higher than the worldwide arc L/S average value (6.0 ± 0.38 ; Sano and Williams, 1996), possibly due to the carbonate-rich composition of the Cocos Plate subducting sedimentary material (Patino et al., 2000; Saginor et al., 2013). Similar features were also observed in fluids from the Chilean Southern and Central Volcanic Zones (CVZ and SVZ) (Ray et al., 2009; Benavente et al., 2013, 2016).

The N_2/Ar ratios of most GGP gases were comprised between those of Air Saturated Water (ASW) and air (**Figure 3**), likely due to atmospheric gas contribution from shallow aquifers in contact with the uprising hydrothermal fluids. In contrast, gases from (i) the Miravalles geothermal gases (GW), (ii) the active crater (AC) of Rincón de la Vieja, and (iii) AL were marked by a significant N_2 -excess (**Figure 3**). The GW gases were expected to show a limited interaction with the shallow environment, being preserved by the tubing of the wells, whereas the low air contamination of AC was likely related to a strong magmatic fluid inputs, considering that this gas collected from a high-flux emission at the border of the hyperacidic and extremely active crater lake of Rincón de la Vieja (Tassi et al., 2005). The high N_2/Ar ratios of the AL gases were surprising since these gas emissions were apparently similar to the other hydrothermal discharges, i.e., low flux bubbling pools with a relatively low ($<100^\circ\text{C}$) outlet temperature (**Table 1**). Such a

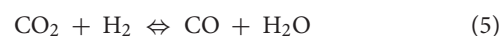


N_2 -excess, as well as the relatively high Rc/Ra values and H_2 and CO concentrations (Table 1), clearly distinguish the AL gases from those emitted on the northern flank of Tenorio volcano (Figure 1). A similar chemical composition was also

shown by the TM boiling pools (Table 1; Giggenbach and Corrales, 1992), which are located relatively close to the AL discharges (Figure 1). These compositional features suggest that gases from this area were characterized by a relatively high contribution of a deep gas component, a peculiarity that may be related to the occurrence of tectonic structures able to favor the uprising of deep fluids. Unfortunately, the promising indications provided by gas geochemistry cannot be supported by the poorly developed studies on the local structural setting, since, to date, the intense vegetation and the relatively low temperatures of the fluids exploited during the preliminary geothermal prospection (Mayorga, 2009) discouraged appropriate investigations.

Gas Geothermometry

Temperature- and redox-sensitive compounds of waters and gases from volcanic systems are commonly used as geoindicators for fluid reservoirs (e.g., Giggenbach, 1991, and references therein). Geothermometers can provide reliable results when (i) the chemical reactions among the species considered for the geothermometric computations have attained equilibrium within the reservoirs, and (ii) no significant compositional changes have occurred during the uprising of fluids toward the surface. According to these assumptions, the composition of fluids exploited from geothermal wells, rapidly uprising through tubing that prevent the contact between the hydrothermal fluids and the external environment, tends to strictly reflect the chemical-physical conditions at the fluid source. On the contrary, secondary processes, such as cooling, steam condensation, mixing with shallow aquifers, and air contamination may affect fluids feeding the natural emissions, modifying the chemical features they have acquired at depth. For example, water vapor concentrations of deep-originated gases discharged from bubbling and boiling pools, such as those of the present study, are strongly depending on condensation processes occurring close to the surface, to shallow depth. Therefore, gas geothermometry was preferably carried out in the $\text{CO}_2\text{-CO-H}_2\text{-CH}_4$ system. Among these gas compounds, CO and H_2 have a similar rapid kinetics in response to changes of the chemical-physical conditions (Giggenbach, 1987, 1996; Chiodini et al., 1993), e.g., during the fluid uprising toward the surface. Thus, the following pressure-independent chemical reaction was considered:



The dependence on temperature of reaction (5) in the vapor phase is given by:

$$\log(X_{\text{CO}}/X_{\text{CO}_2})_{\text{V}} = 2.49 - 2248/T + R_{\text{H}} \quad (6)$$

whereas in the liquid phase is, as follows:

$$\log(X_{\text{CO}}/X_{\text{CO}_2})_{\text{L}} = 2.49 - 2248/T + R_{\text{H}} + \log(B_{\text{CO}_2}) - \log(B_{\text{CO}}) \quad (7)$$

where T is in K, X_{CO} and X_{CO_2} are the molar fractions of CO_2 and CO , respectively, B_{CO_2} and B_{CO} are the vapor/liquid distribution coefficients of CO_2 and CO , respectively, whereas

R_H is $\log(X_{H_2}/X_{H_2O})$ (Giggenbach, 1980, 1987). Assuming that Ar concentrations are fixed by the equilibrium between the atmosphere and air saturated water (ASW) (Giggenbach, 1991), the dependence of H_2 on R_H in the two phases can also be described by the following equations:

$$\log(X_{H_2}/X_{Ar^*})_V = R_H + 6.52 - \log(B_{Ar}) \quad (8)$$

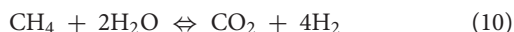
and

$$\log(X_{H_2}/X_{Ar^*})_L = R_H + 6.52 - \log(B_{H_2}) \quad (9)$$

where X_{H_2} , X_{Ar^*} , B_{Ar^*} , and B_{H_2} are the molar fractions and the vapor/liquid distribution coefficients of Ar* and H_2 , respectively. The X_{Ar^*} values, computed by $Ar^* = X_{Ar} - (X_{O_2}/22)$ considering that hydrothermal fluids are O_2 -free, was used instead of the X_{Ar} to minimize the effects on hydrothermal fluids of air contamination at the surface. Assuming that the R_H values were controlled by the rock redox buffer system proposed by D'Amore and Panichi (1980) (DP), the combination of Equations (6–9) allowed to construct liquid-vapor equilibrium grid reported in **Figure 4**. Gases from Rincón de la Vieja and Miravalles plot within and out of the liquid-vapor grid, and their apparent equilibrium temperatures ranges from $\sim 180^\circ$ to $>300^\circ\text{C}$. Gases from the northern sector of Tenorio seem to indicate lower equilibrium temperatures (130 – 180°C). The strong scattering of these data suggests that secondary processes likely controlled H_2 and CO. Interactions with shallow aquifers, which are typically rich in free O_2 , may have dramatically changed the redox conditions acting on the uprising fluid, severely affecting the behavior of these reduced gas species. Moreover, CO tends to dissolve in liquid water to form $HCOOH$ (Shock, 1993).

On the contrary, the AL gases, which cluster close to the vapor equilibrium curve at 240 – 250°C (**Figure 4**), seem to have maintained the chemical composition attained at depth. This is consistent with the relatively high fraction of mantle He and CO_2 (**Table 1**) and the high N_2/Ar ratios (**Figure 3**) of these gases. The H_2/Ar values of the AL gases were similar to those measured by Giggenbach and Corrales (1992) in the TM gas emission (**Table 1**), located in the same area (**Figure 1**). However, those authors surprising interpreted these data as evidence of low-temperature conditions.

To complete the geothermometric estimations in the CO_2 - CO - H_2 - CH_4 system, we hypothesized that the CH_4 concentrations were controlled by the Sabatier reaction, as follows:



Considering that $\log(f_{H_2O}) = 4.9 - 1820/T$ (Giggenbach, 1987), the dependence on temperature and R_H of the X_{CH_4}/X_{CO_2} log-ratios in the vapor and liquid phases can be expressed, as follows:

$$\log(X_{CH_4}/X_{CO_2})_V = 4R_H + 5181/T \quad (11)$$

and

$$\begin{aligned} \log(X_{CH_4}/X_{CO_2})_L &= 4R_H + 5181/T + \log(B_{CO_2}) \\ &\quad - \log(B_{CH_4}) \end{aligned} \quad (12)$$

where B_{CH_4} is the vapor/liquid distribution coefficient of CH_4 .

The $\log(X_{H_2}/X_{Ar^*})$ vs. $\log(X_{CH_4}/X_{CO_2})$ diagram (**Figure 5**) was constructed on the basis of Equations (8–12) and assuming that the R_H values were regulated the DP redox buffer system. It confirms a strong chemical disequilibrium of the gases from

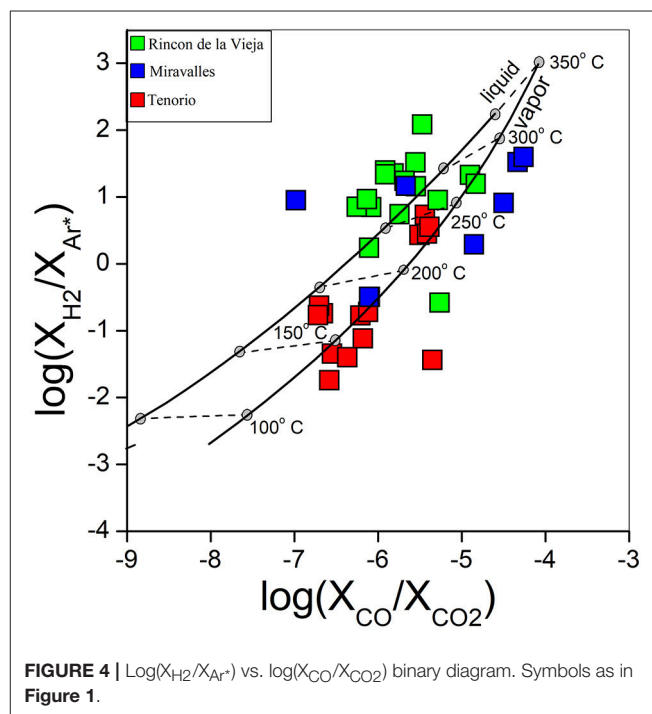


FIGURE 4 | $\log(X_{H_2}/X_{Ar^*})$ vs. $\log(X_{CO}/X_{CO_2})$ binary diagram. Symbols as in **Figure 1**.

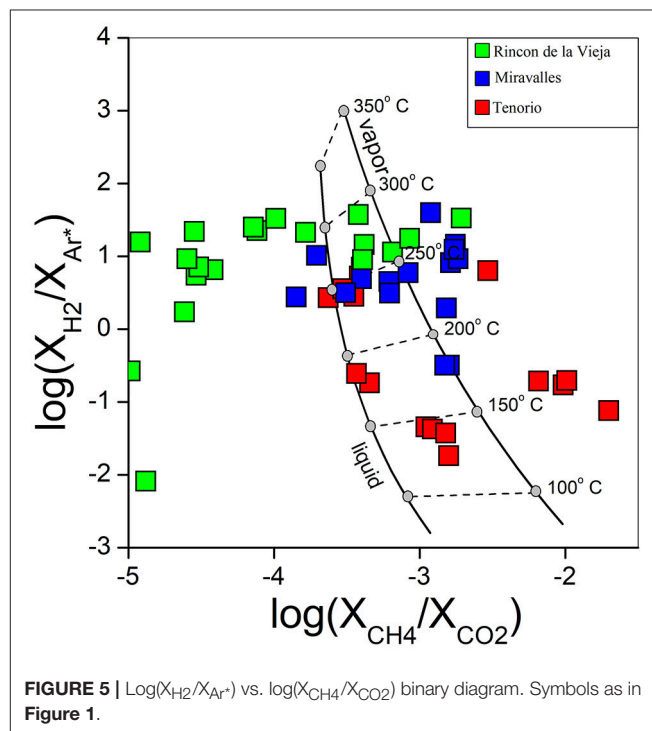
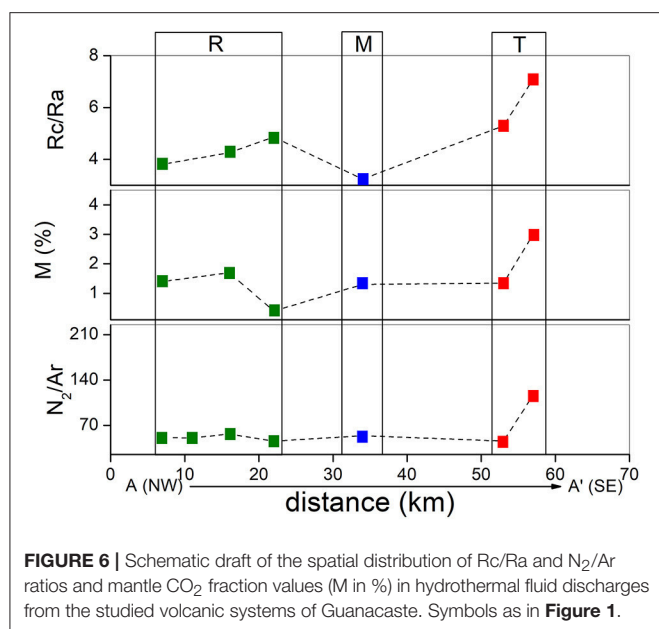


FIGURE 5 | $\log(X_{H_2}/X_{Ar^*})$ vs. $\log(X_{CH_4}/X_{CO_2})$ binary diagram. Symbols as in **Figure 1**.



the three volcanoes, which is consistent with the large variations of the Rc/Ra values measured in gas emissions from the same volcanic system (i.e., Rincón de la Vieja, **Table 1**). AL gases are the only exception, their equilibrium temperatures were the same as those indicated by the H_2 - CO pair. It is worth noting that the AL calculated temperatures were consistent with those hypothesized for the geothermal reservoir associated with the Miravalles volcano (Gardner and Corrales, 1977). It is worth noting that the CH_4 - CO_2 ratios of the AL gases were one order of magnitude lower than those of the TM and MZ gases (Giggenbach and Corrales, 1992) (**Figure 1**), suggesting a large chemical heterogeneity even at a relatively small spatial scale. The X_{H_2}/X_{Ar*} and X_{CH_4}/X_{CO_2} ratios of the Miravalles geothermal gases show strong variations (~ 1 log-unit; **Figure 5**), although supposedly less affected by the influence of the shallow environment. Comparable results were also found by Gherardi et al. (2002), who suggested that the fluids from Miravalles suffered the influence of fluid reinjection.

CONCLUSIONS

The occurrence of a strong heat source, demonstrated by the numerous thermal manifestations of GGP, and the abundant meteoric water recharge characterizing the volcanic chain of Guanacaste explain the high geothermal potential of this region. The chemical and isotopic features of the discharged fluids are dictated by the interaction of the uprising hydrothermal fluids and shallow aquifers. At a first approximation, the highest deep-originated fluid contribution can be recognized at the active crater of the Rincón de la Vieja volcano, where

phreatic and phreato-magmatic eruptions frequently occur, and progressively decreases with increasing distance from this site. Carbon dioxide production from limestone seems the main source for this gas, possibly related to carbonate assimilation at the magmatic source and/or due to interaction of carbonate-rich rocks and the hydrothermal fluids. The geochemical features of the fluids exploited from Miravalles correspond to those typically found in the surroundings of active volcanic systems, i.e., Na-Cl brines produced by prolonged fluid-rock interactions and dissolution of magmatic gases into a well-developed hydrothermal aquifer. The concentrations of minor reduced gases, such as CO , H_2 , and CH_4 were likely controlled by chemical reactions occurring within the hydrothermal deep fluid source, although the chemical composition attained at depth was strongly modified by secondary processes resulting in a large scattering of the chemistry of the surficial manifestations. According to the scenario suggested by Giggenbach and Corrales (1992), the Tenorio thermal discharges would represent the distal fluid outflow of the regional geothermal reservoir. The new geochemical evidences reported in the present study significantly modify this schematic model. As shown in **Figure 6**, the relatively high contribution of CO_2 from the mantle (M in %), as well as the high Rc/Ra and N_2/Ar ratios shown by the fluid discharges located in the southern sector of Tenorio volcano with respect to those from Miravalles and Rincón de la Vieja, suggest a high-temperature source in this area. This implies that, although the preliminary geochemical prospections carried out in the 1990's produced discouraging results, an important geothermal resource is hosted in this peripheral zone of GGP, where local tectonics favor the uprising of hot fluids minimizing their cooling and mixing with crustal and atmospheric gases. In light of this hypothesis, which needs to be supported by geophysical prospection activities and accurate investigations of the geologic and tectonic settings, promising results are expected to be obtained by extending the exploitation activity to the south of the Miravalles geothermal plant. Accordingly, the geothermal potential of GGP should likely be regarded as higher than previously thought.

AUTHOR CONTRIBUTIONS

FT: field campaigns, gas analysis, manuscript preparation; OV, GB, FC, and JdM: field campaigns, manuscript preparation; GP: gas analysis, manuscript preparation; SV: manuscript preparation.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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