

Evolution of fluid geochemistry at the Turrialba volcano (Costa Rica) from 1998 to 2008

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Abstract Turrialba (10°02'N, 83°45'W) is a 3,349-m high stratovolcano belonging to the Holocene “Cordillera Central” volcanic belt of Costa Rica. The summit consists of three EW-oriented craters (East, Central, and West). Since its last eruptive phase (1864–1866), the Central and West craters have displayed modest fumarolic activity, with outlet temperatures clustering around 90°C. In 2001, seismic swarms, ground deformation, and increasing fumarolic activity occurred. From 2005 to 2008, new fumarolic vents opened between and within the Central and West craters, and along the western and southwestern outer flanks of the volcanic edifice. These physical changes

were accompanied by a drastic modification in the gas chemistry that can be divided in three stages: (1) hydrothermal (from 1998 to autumn 2001), characterized by the presence of H₂O, CO₂, H₂S, and, to a very minor extent, HCl and HF; (2) hydrothermal/magmatic (autumn 2001–2007), with the appearance of SO₂ and a significant increase of HCl and HF; and (3) magmatic-dominated (2007–2008), characterized by increased SO₂ content, SO₂/H₂S > 100, and temperatures up to 282°C. Accordingly, gas equilibrium in the CO₂-CH₄-H₂ system suggests a progressive evolution of the deep fluid reservoir toward higher temperatures and more oxidizing conditions. The chemical–physical modifications of Turrialba in the last decade can be interpreted as part of a cyclic mechanism controlling the balance between the hydrothermal and the magmatic systems. Nevertheless, the risk of rejuvenation of the volcanic activity cannot be excluded, and an appropriate seismic, ground deformation, and geochemical monitoring program is highly recommended. Turrialba lies at a distance of 35 and 15 km from San José and Cartago, respectively, the two largest cities in Costa Rica.

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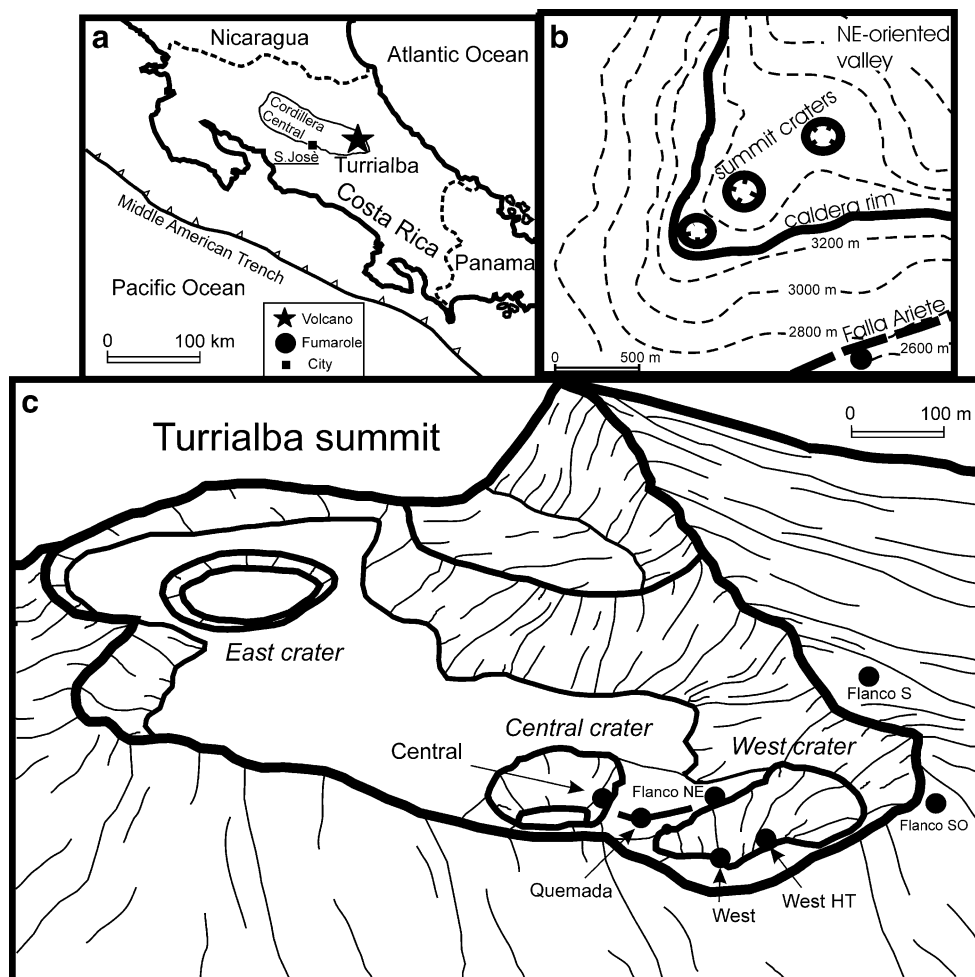
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Introduction

Turrialba (10°01'N, 83°45'E, 3,349 m a.s.l.) is an active stratovolcano and belongs to the Holocene “Cordillera Central” volcanic belt (Fig. 1a), formed by the subduction of the Cocos Plate beneath the Caribbean Plate (Carr and Stoiber 1990). Turrialba (“The white tower”) is 10 km NE Irazu volcano, and its products (mainly basalts, basalt andesites, andesites, and dacites) overlie the Tertiary sedi-

Fig. 1 **a** Location map of Turrialba volcano in the Cordillera Central (Costa Rica). **b** Schematic map showing the summit craters of Turrialba and Falla Ariete. **c** Location of the fumaroles sampled in this study



ments of the Limón Basin and a 2.1-Ma old andesitic lava flow (Bellon and Tournon 1978; Gans et al. 2003; Soto 1988; Tournon 1984). After a major erosional period interrupted by minor volcanic events (at about 12,000 B.P.; Lachniet and Seltzer 2002; Orvis and Horn 2000; Reagan et al. 2006; Soto 1988), volcanic activity at Turrialba resumed at about 9,000 years B.P. with the emplacement of andesite to dacite lavas. A Plinian eruption occurred at about 1,970 years B.P. with an estimated volume of ca. 0.2 km^3 (Reagan et al. 2006). The last eruptive event (1884–1886 A.D.) at Turrialba produced ash fall deposits and some minor pyroclastic surges (e.g., Reagan et al. 2006 and references therein). The onset of this eruptive phase was preceded by several months of intense fumarolic activity (González-Viquez 1910). Since then, the volcano has been in a continuous state of passive degassing through fumarolic activity.

The summit area of Turrialba consists of three craters (West, Central, and East craters), but only the West and East craters have active fumaroles (Fig. 1b, c). The southern flank of Turrialba volcano opens to the Central Valley, where more than 50% of the Costa Rican population

resides. Because of its proximity to major urban centers (San José and Cartago) and its record of explosive activity (Reagan et al. 2006), Turrialba poses a serious volcanic hazard (Duarte 1990; Clark et al. 2006; Reagan et al. 2006; Pavanelli et al. 2009).

In 2000, seismic swarms followed by an increase in fumarole degassing occurred (e.g., Barboza et al. 2000, 2003; Fernandez et al. 2002; Vaselli et al. 2002; Mora et al. 2004). New fumarolic vents at the summit and on the western outer flank also became active. These changes were accompanied by important variations in the chemical compositions of the fumarolic gases (appearance of SO_2 , HCl , and HF ; Tassi et al. 2004b; Vaselli and Tassi 2007).

In the present paper, the geochemical and isotopic (helium and carbon) compositions of the fumarolic discharges of Turrialba in the period 1998–2008 are presented and discussed in order to delineate the complex relationships between the surficial (hydrothermal) and deep-seated (magmatic) fluid reservoirs. A more effective seismic, ground deformation, and geochemical monitoring program at Turrialba will aid in assessing its present state

and the potential risk to the Costa Rica economy and population.

The Turrialba fumarolic discharges from 1998 to 2008

From 1998 to 2000, the crater summit contained two small active fumarolic fields: one (hereafter, Central fumarole) located in the inner SW flank of the Central crater and the other one (hereafter, West fumarole) in the northern rim of the West crater (Fig. 2a). Fumarolic outlet temperatures clustered around 90°C (approximately boiling temperature at 3,000 m). In April 2002, a 4-m wide fracture (named Quemada) opened between the West and the Central craters (Fig. 2b), discharging fluids at 90°C (Tassi et al. 2004b). This event coincided with a significant increase of the flux from the Central fumarole. Contemporaneously, new fumarolic vents and cracks (Fig. 2c, d) opened in the N and S outer flanks of the West crater and within the Central crater. In June 2005, the fumarolic activity dramatically

changed as new fractures opened along the N inner flank of the West crater discharging fluids at 90–92°C. At the same time, propagating south from the Turrialba summit at an elevation of 2,700 and 2,600 m, $\leq 40^\circ\text{C}$ and $< 90^\circ\text{C}$, new fumaroles formed along the NE-SW-oriented regional fault system named Falla Ariete (Figs. 1b and 2e). In summer of 2007, the active summit craters had a further overall increase in the fumarolic emissions, and a high flux fumarole (hereafter, West HT fumarole) began to discharge from the floor of the West crater. In March 2008, a radial fracture system in the outer southern (Flanco SO and Flanco S fumaroles) and inner northern (Flanco NE fumarole) flanks (Fig. 2f) took place with fluid discharge to 92°C. This intense fumarolic activity caused a volcanic plume up to 1 km high that was occasionally visible from San José (OVSICORI-UNA 2008). The acidic gas species of the fumarolic-induced plume initiated damage to the vegetation. The inhabitants living in small villages and farmhouses located in the SW sector of the volcano frequently reported eye irritation and breathing problems.

Fig. 2 **a** Aerial view of the East, Central, and West craters of Turrialba summit in 1998. The *blue circles* indicate the Central and West small fumarolic fields. **b** The Quemada fumarole. It formed in April 2002 between the Central and West craters. **c** The new fumarolic vents between the Central and West craters (June 2007). **d** Fumarolic cracks in the inner N flank of West crater. **e** The Falla Ariete fumaroles (March 2008). **f** Radial fumarolic fractures in the S and SW flanks of the West crater (March 2008)



Gas sampling and analytical methods

The gas samples were collected from (1) the West fumarole, from February 1998 to May 2008 (21 samples); (2) the Central fumarole, from February 1999 to March 2008 (19 samples); (3) the West HT fumarole, from September 2007 to May 2008 (six samples); (4) the Quemada fracture, in April 2002; (5) the Flanco NE, Flanco SO, and Flanco S fumaroles, in March 2008; and (5) the Falla Ariete fumarole, in November 2007 and March 2008 (Tables 1 and 2).

To collect the fumarolic gases, a titanium tube was inserted into the gas outlet and connected to pyrex glass dewars to transfer the sample into pre-weighed and pre-evacuated 50-mL thorium-tapped flasks containing 20 mL of 0.15 M Cd(OH)₂ and 4 M NaOH suspension. Water vapor and acidic gas compounds, i.e., CO₂, SO₂, HCl, and HF, dissolved into the alkaline solutions, whereas H₂S formed insoluble CdS. Low-solubility gases (N₂, H₂, O₂, CO, He, CH₄, Ar, Ne, and light hydrocarbons) were collected in the headspace of the sampling flasks. Occasionally, condensates and fumarolic gas were collected into vacuum gas vials for the analysis of oxygen and hydrogen isotopes in the water vapor and carbon isotopes in CO₂, respectively. The condensation device consisted of a series of two glass bulbs immersed in ice (Vaselli et al. 2006). The residual inorganic compounds stored in the sampling tube headspace were analyzed by gas-chromatography (Shimadzu 15A) equipped with a thermal conductivity detector. Organic gas species were analyzed using a Shimadzu 14A following the procedure described by Tassi et al. (2004a). The caustic solution, separated from the solid phase by centrifugation, was used for the analysis of (1) CO₂ by automatic titration with 0.1 N HCl, (2) F⁻ and Cl⁻ by ion chromatography, and (3) SO₂, as SO₄²⁻ after oxidation with H₂O₂, by ion chromatography (Methrom 761). Solid CdS was dissolved with H₂O₂, and the resulting SO₄²⁻ was analyzed chromatographically for determination of the H₂S concentration. Eventually, the extraction of S⁰ from the residual precipitate was performed with CCl₄. The extracted S⁰ was then oxidized to SO₄²⁻ with I₂ as carrier and KBrO₃ as oxidizing agent and analyzed by ion chromatography (Montegrossi et al. 2001; Tassi et al. 2004a; Vaselli et al. 2006). Analytical precision was <1% for major components and <5% for minor and trace compounds.

The ¹⁸O/¹⁶O and ²H/¹H ratios (expressed as δ¹⁸O and δD permill V-SMOW, respectively) were determined with a Finnigan Delta Plus XL mass spectrometer according to standard protocols. Oxygen isotopes were analyzed by using the CO₂-H₂O equilibration method (Epstein and Mayeda 1953). Hydrogen isotopic ratios were measured on H₂ obtained after the reaction of 10 μL of water with

metallic Zn at 550°C (Coleman et al. 1982). The experimental error was ±0.1‰ and ±1‰ for δ¹⁸O and δD values, respectively, using EEZ-3 and EEZ-4 as internal standards that were previously calibrated vs. V-SMOW and SLAP reference standards.

The ¹³C/¹²C ratios in CO₂ (expressed as δ¹³C-CO₂ permill V-PDB) were determined with a Finnigan Delta S mass spectrometer after a two-step extraction and purification procedures of the gas mixtures by using liquid N₂ and a solid-liquid mixture of liquid N₂ and tri-chloro-ethylene (e.g., Evans et al. 1998; Vaselli et al. 2006). Internal (Carrara and San Vincenzo marbles) and international (NBS18 and NBS19) standards were used for estimating the external precision. The analytical error and the reproducibility are ±0.05‰ and ±0.1‰, respectively.

The ³He/⁴He ratios (expressed as R/R_{air}, where R is the measured ³He/⁴He ratio, and R_{air} is that of the air: 1.39 × 10⁻⁶; Mamyrin and Tolstikhin 1984) were analyzed on a VG 5400 Rare Gas Mass Spectrometer fitted with a Faraday cup (resolution of 200) and a Johnston electron multiplier (resolution of 600) following the procedure described by Poreda and Farley (1992). Analytical error for R/R_{air} determination is ≤0.3% using Rochester, NY air and a secondary standard of Yellowstone Park gas (MM= 16.5 × air; Craig et al. 1978).

Results

Chemical gas composition

Apart from the West HT fumarole, which had outlet temperatures up to 282°C (February 2008), the temperature of Turrialba fumaroles ranged from 86°C (Central fumarole, November 2001) to 94°C (Falla Ariete fumarole, March 2008). Table 1 displays the chemical composition of the main and trace gas components (in micromoles per mole) as “dry” (i.e., water-free) gas fraction because fluids discharged from the low-temperature Turrialba fumaroles have likely suffered steam condensation at the surface. The gas/vapor ratios are extremely variable, ranging from 0.012 (West fumarole, February 2000) to 11.7 (Central fumarole, April 2004; Table 1). The main gas compound of the dry gas fraction was CO₂, whose concentrations ranged from 423,158 (Falla Ariete fumarole, March 2008) to 990,009 (West fumarole, April 2003) μmol/mol. The fumaroles of the summit crater also had significant concentrations of H₂S (from 86 to 68,598 μmol/mol), HCl (from 98 to 21,555 μmol/mol), and HF (from 2 to 23,761 μmol/mol). Sulfur dioxide, detected for the first time at the Central fumarole in November 2001, varied from 14 (West fumarole, April 2003) to 387,582 (West HT fumarole, January 2008) μmol/mol. At the Falla Ariete fumarole, N₂

was the most abundant residual gas (from 182 and 461,165 $\mu\text{mol/mol}$), followed by H_2 (from 21 and 13,612 $\mu\text{mol/mol}$), whereas the concentrations of the acidic gases were below detection ($<1 \mu\text{mol/mol}$), with the exception of H_2S whose concentration in March 2008 was up to 3,408 $\mu\text{mol/mol}$. At the crater fumaroles, the concentrations of the atmospheric-related compounds, i.e., O_2 , Ar, and Ne, were relatively low, slightly exceeding 2,000, 200, and 0.33 $\mu\text{mol/mol}$, respectively. The relatively high concentrations of these compounds measured at the Central fumarole between August 2002 and November 2003 (up to 21,513, 1,238, and 1 $\mu\text{mol/mol}$, respectively) were likely caused by air entrainment during the gas sampling related to the weak gas flux. Strong atmospheric contribution also occurred at the Falla Ariete fumarole, especially in November 2007, when this new fumarole had O_2 , Ar, and Ne concentrations of 107,079, 3,583, and 5.13 $\mu\text{mol/mol}$, respectively. The concentrations of CO at the West HT fumarole were relatively high (from 44.1 to 99.5 $\mu\text{mol/mol}$), whereas the other crateric fumaroles and Falla Ariete had content up to 11.9 $\mu\text{mol/mol}$. Helium concentrations were generally low ($<58 \mu\text{mol/mol}$). Methane was the most abundant organic gas at both the crater (up to 5.29 $\mu\text{mol/mol}$) and the Falla Ariete fumaroles (up to 23.06 $\mu\text{mol/mol}$). Significant concentrations of light alkanes (C_2H_6 and C_3H_8 , up to 2.584 and 0.573 $\mu\text{mol/mol}$, respectively) and light alkenes (C_2H_4 , C_3H_6 , and iso- C_4H_8 , up to 0.078, 0.083, and 1.583 $\mu\text{mol/mol}$, respectively) were measured. Heavier organic species (C_{4+}), not reported in the present paper, had very low concentrations (Tassi et al. 2004b), below the detection limit (0.001 $\mu\text{mol/mol}$) in most samples.

Steam and gas isotopic composition

The values of $\delta^{18}\text{O}$ and δD in the steam and those of $\delta^{13}\text{C}$ in CO_2 and R/R_{air} (Tassi et al. 2004b and present work) are reported in Table 2. The $\delta^{18}\text{O}$ values varied between -13.6‰ (Central fumarole, April 2003) and -1.1‰ (West fumarole, April 2004) V-SMOW, whereas those of δD ranged from -94.3‰ (Central fumarole, April 2003) to -55.1‰ (West fumarole, February 1998) V-SMOW. The $\delta^{13}\text{C}$ - CO_2 values of the low-temperature fumaroles ($<94^\circ\text{C}$) ranged from -4.8‰ (Central fumarole, February 1999) to -1.8‰ (West fumarole, July 2007) V-PBD. The high-temperature fumarole (West HT) had $\delta^{13}\text{C}$ - CO_2 values significantly more positive than those of the other fumarolic discharges (up to -0.2‰ V-PBD). Turrialba fumaroles showed extremely high R/R_{air} values (between 7.32 and 7.71), representing the highest values recorded in the Nicaragua and Costa Rica segment of the Central America volcanic arc (e.g., Snyder et al. 2001, 2003; Tassi et al. 2004b; Shaw et al. 2003, 2006) and similar to values

measured at Pacaya, Mombacho (e.g., Garofalo et al. 2006), and Poas (e.g., Shaw et al. 2003).

Discussion

Fluid source regions

The chemistry of the Turrialba crater fumaroles mainly relates to (1) degassing from an active magmatic system, producing SO_2 -rich fluids, and (2) fluids from a hydrothermal zone, where high-temperature gas–water–rock interactions generate the reduced reactive gases, H_2S , H_2 and, at a lesser extent, HCl and HF (e.g., Giggenbach 1987, 1996; Martini 1993). The hypocenters of the seismic events of the last decade suggest a magmatic source at a depth of 4–6 km (Barboza et al. 2003). The outlet temperatures of most of the crater fumaroles, at the boiling temperature of pure water at the altitudes of 3,000 m (approximately 90°C), may suggest the presence of a shallow aquifer. Water–gas interactions and cooling-induced re-equilibration mechanisms (e.g., Giggenbach 1996; Symonds et al. 2001) likely play an important role in modifying the chemical features of the ascending fluids. Such processes can explain the low concentrations of CO, likely resulting by hydrolysis processes in low-temperature fumaroles (Table 1). Time-dependent dissolution of CO in NaOH could also explain the lack of CO in the headspace of the sampling flasks (Giggenbach and Matsuo 1991; Arnósson et al. 2006). The West HT fumarole, characterized by the highest gas flux, outlet temperature, and CO concentrations (Table 1), was less affected by the shallow level water–gas interactions. Besides decreasing the concentrations of the most soluble gas compounds, a shallow aquifer added atmospheric-related compounds to the fumarolic feeding system. The high N_2/Ar ratios (up to 1,945) measured in all the crater fumaroles indicated that N_2 had a non-atmospheric origin. Strong N_2 -excess occurs in gas discharges from other geothermal and volcanic centers of Central America (Giggenbach 1997a; Snyder et al. 2003), likely related to thermal decomposition of organic material buried in the subducted sediments (Matsuo et al. 1978). This process can also produce light hydrocarbons, as suggested by the low ($<1,000$) $\text{CH}_4/(\text{C}_2\text{H}_6+\text{C}_3\text{H}_8)$ ratios (Whiticar and Suess 1990). The presence of unsaturated organic gas species, such as C_2H_4 and C_3H_6 , suggests that the organic source evolved at relatively high temperature and characterized by redox conditions more oxidizing than those typical of a hydrothermal environment (e.g., Capaccioni et al. 1993, 2004). The helium isotopic signature (Table 2), closely resembling that of mantle-related He in subduction zones (Poreda and Craig 1989), confirmed the strong relation existing between the crater fumaroles and the magmatic

Table 1 Outlet temperatures (°C), chemical compositions, and gas/vapor ratios of the Turrialba fumaroles

Sample	Date	T (°C)	CO ₂	HCl	HF	SO ₂	H ₂ S	S	N ₂	CH ₄	Ar	O ₂	Ne	H ₂	He	CO	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	i-C ₄ H ₈	Gas/H ₂ O
West	Feb. 1998 ^a	91	964,039	220	15	ND	10,438	ND	23,932	0.38	56	56	0.062	422	20	0.1	0.032	ND	0.012	0.012	0.036	0.019
West	Feb. 2009 ^a	90	973,313	438	25	ND	4,206	ND	20,165	2.15	134	53	0.128	844	18	ND	ND	ND	0.026	0.040	0.347	0.020
West	Feb. 2000 ^a	92	957,053	175	21	ND	4,387	43.7	34,171	1.21	203	115	0.331	1,407	29	ND	0.150	0.040	0.047	0.078	0.004	0.012
West	Feb. 2001 ^a	92	979,013	359	10	ND	2,048	12.0	14,493	0.60	80	802	0.048	566	17	ND	0.042	0.078	ND	0.083	ND	0.022
West	Sep. 2001 ^a	90	991,744	98	6	ND	493	12.0	5,336	0.36	8	46	0.005	2,251	6	ND	0.045	0.008	0.022	0.021	0.019	0.044
West	Nov. 2001 ^a	88	990,403	125	7	ND	677	8.6	6,098	0.31	9	65	0.007	2,600	6	ND	0.040	0.007	0.022	0.021	0.019	0.054
West	Jan. 2002 ^a	90	993,433	410	29	ND	280	12.4	4,040	0.37	7	35	0.005	1,749	4	ND	0.054	ND	0.012	0.017	0.051	0.055
West	Feb. 2002 ^a	90	987,414	1,623	85	ND	253	8.8	9,539	0.22	18	263	0.010	786	9	ND	0.025	ND	0.013	0.007	0.012	0.060
West	Mar. 2002 ^a	90	985,647	2,372	113	ND	375	10.9	9,735	0.39	16	210	0.012	1,516	4	0.1	0.050	ND	0.029	0.037	0.032	0.049
West	Apr. 2002 ^a	90	995,794	443	23	ND	700	4.8	2,232	0.22	4	16	0.004	780	3	ND	0.023	ND	0.012	0.010	0.009	0.068
West	Sep. 2002	89	993,480	502	139	349	962	1.9	2,876	0.53	10	56	0.009	1,617	3	0.3	1.302	ND	0.073	0.136	0.071	0.064
West	Apr. 2003	88	997,508	524	114	514	1,086	0.3	182	0.03	1	1	ND	411	1	0.1	0.087	ND	0.033	0.063	0.004	0.062
West	Apr. 2004	90	986,419	691	182	10,296	808	3.1	1,042	0.05	2	9	0.001	545	2	0.1	0.005	ND	0.022	0.053	0.009	0.057
West	Dec. 2004	90	977,243	714	170	8,844	10,255	11.8	2,594	0.07	8	96	0.007	521	26	0.1	0.012	0.001	0.020	0.038	0.007	0.060
West	Apr. 2005	90	993,698	294	221	1,848	2,411	2.8	1,144	0.05	3	28	0.002	287	3	0.1	0.007	0.003	0.015	0.037	0.007	0.054
West	May 2007	91	963,683	5,437	480	24,293	1,405	0.8	2,795	0.09	4	10	0.002	1,886	2	2.7	0.009	0.002	0.004	0.015	0.044	0.068
West	Jun. 2007	90	979,451	3,454	267	9,620	1,822	0.7	3,091	0.01	3	19	0.002	1,582	2	3.9	0.012	0.002	0.003	0.012	0.013	0.079
West	Jul. 2007	92	817,767	8,113	566	166,882	768	0.8	3,400	0.01	4	25	0.003	2,298	3	4.9	0.008	0.002	0.003	0.012	0.010	0.069
West	Sep. 2007	92	801,556	8,829	3,243	179,316	716	0.8	3,862	0.01	4	16	0.002	2,290	3	6.4	0.007	0.002	0.004	0.012	0.010	0.068
West	Mar. 2008	92	729,372	8,312	20,048	195,043	35,774	2.0	6,258	0.05	10	14	0.006	13,612	4	11.9	0.028	0.007	0.004	0.015	0.042	0.061
West	May 2008	92	684,646	7,403	10,484	227,914	62,601	1.6	1,362	0.04	4	45	0.002	5,529	8	9.5	0.026	0.014	0.002	0.007	0.118	0.067
Central	Feb. 1999 ^a	89	929,114	801	4	ND	13,157	ND	54,490	2.43	94	1,720	0.242	214	37	ND	0.902	0.068	ND	ND	0.529	0.022
Central	Feb. 2001 ^a	90	946,772	315	2	ND	798	10.6	43,577	0.84	198	2,016	0.294	259	2	ND	ND	ND	ND	ND	ND	0.021
Central	Sep. 2001 ^a	89	991,283	170	6	ND	574	15.8	5,525	0.38	12	66	0.006	2,341	7	ND	0.051	0.009	0.028	0.024	0.029	0.224
Central	Nov. 2001 ^a	86	880,751	378	12	104,022	3,606	43.9	9,053	0.73	16	93	0.009	2,021	4	ND	0.008	ND	ND	ND	0.007	2.002
Central	Feb. 2002 ^a	89	906,650	2,406	28	73,639	1,632	20.0	13,207	0.75	38	280	0.031	2,096	3	0.7	0.017	ND	0.005	0.005	0.016	0.269
Central	Apr. 2002 ^a	89	904,552	1,540	166	83,969	2,968	20.8	4,645	0.68	9	10	0.010	2,114	7	0.4	0.003	0.001	0.002	0.001	0.003	0.321
Central	Aug. 2002	88	898,959	14,665	1,603	2,534	512	2.6	71,444	0.58	303	3,318	0.244	2,650	28	5.9	0.075	ND	ND	ND	0.466	0.026
Central	Apr. 2003	88	661,740	5,892	593	7,357	2,229	8.9	287,601	0.17	1,238	21,513	1.011	2,786	24	7.9	0.261	ND	ND	ND	1.583	0.079
Central	Nov. 2003	89	947,644	359	32	17,209	568	1.9	30,940	0.13	118	916	0.063	2,203	8	2.0	0.007	0.001	0.004	0.006	0.021	1.553
Central	Dec. 2003	89	956,348	265	25	17,225	454	1.4	22,650	0.05	111	842	0.064	2,071	7	1.4	0.002	ND	0.001	0.001	0.004	2.572
Central	Feb. 2004	88	954,768	295	27	20,763	941	1.1	20,472	0.17	52	557	0.034	2,116	6	1.5	0.007	0.001	0.002	0.006	0.005	2.550
Central	Apr. 2004	90	967,687	275	22	18,279	1,269	1.4	10,154	0.19	28	251	0.017	2,030	2	0.6	0.012	0.004	0.001	0.003	0.007	11.74
Central	Aug. 2004	90	934,079	1,973	93	36,720	750	4.3	24,245	0.11	65	91	0.038	1,937	40	2.5	0.055	0.006	0.014	0.026	0.079	0.172
Central	Feb. 2005	89	882,060	1,912	139	49,293	265	7.1	63,903	0.18	179	160	0.099	2,036	32	6.0	0.136	0.016	0.040	0.074	0.200	0.157
Central	Apr. 2005	89	900,600	1,512	114	90,090	3,350	3.7	2,772	0.12	9	8	0.006	1,530	8	2.5	0.004	0.000	0.001	0.002	0.002	0.208
Central	May 2007	90	864,030	6,540	835	123,980	1,208	0.3	1,654	0.04	2	9	0.001	1,738	1	3.6	0.009	0.002	0.001	0.004	0.038	0.145

Central	Jun. 2007	90	900,633	4,241	467	87,859	3,915	0.3	1,300	0.03	1	1	0.001	1,579	1	2.5	0.004	0.001	0.002	0.008	0.007	0.160
Central	Jul. 2007	91	868,631	8,506	1,019	117,992	1,071	0.6	1,300	0.03	1	6	0.001	1,464	1	9.2	0.003	0.001	0.003	0.012	0.002	0.179
Central	Mar. 2008	90	680,835	5,097	5,844	287,906	14,184	2.7	3,891	0.35	5	4	0.003	2,563	2	1.5	0.014	0.003	0.003	0.008	0.029	0.100
West HT	Sep. 2007	185	718,620	21,555	5,252	237,768	512	1.5	4,822	2.70	3	17	0.002	11,366	9	70.9	0.014	0.003	0.001	0.007	0.060	0.126
West HT	Nov. 2007	261	639,644	8,234	9,145	333,045	2,643	2.6	378	1.10	1	1	0.001	6,894	2	51.8	0.003	0.002	0.001	0.011	0.032	0.126
West HT	Jan. 2008	236	581,311	8,939	14,647	387,582	2,192	3.2	183	0.92	1	2	0.001	5,086	2	44.1	0.001	0.001	0.001	0.017	0.007	0.160
West HT	Feb. 2008	282	597,534	10,060	23,761	359,682	2,329	2.4	672	0.56	0.4	1	0.001	5,848	4	82.5	0.006	0.005	0.001	0.019	0.049	0.196
West HT	Mar. 2008	278	647,213	9,727	19,227	313,801	2,547	1.8	678	0.21	0.3	1	0.001	6,701	3	99.5	0.009	0.006	0.001	0.021	0.047	0.226
West HT	May 2008	237	663,740	7,798	12,867	300,092	9,004	0.6	285	0.02	0.2	1	ND	6,121	1	90.5	0.008	0.006	0.001	0.023	0.040	0.227
Falla Ariete	Nov. 2007	90	423,158	ND	ND	ND	ND	ND	461,145	23.06	8,214	107,079	5.130	357	5	ND	ND	ND	ND	ND	ND	0.031
Falla Ariete	Mar. 2008	94	934,682	659	133	ND	3,408	ND	56,606	10.38	452	3,583	0.281	423	5	ND	2.584	ND	0.267	0.005	ND	0.064
Fianco S	Mar. 2008	92	823,105	6,025	6,595	93,359	62,134	2.2	8,712	2.20	8	3	0.005	42	6	4.8	0.040	0.001	0.004	0.003	0.030	0.056
Fianco SO	Mar. 2008	90	845,460	4,056	3,444	65,045	68,598	1.2	13,258	3.33	15	60	0.009	47	9	3.3	0.087	0.001	0.009	0.006	0.040	0.049
Fianco NE	Mar. 2008	90	840,015	5,874	4,115	74,518	63,455	1.5	11,884	3.14	14	58	0.009	51	8	3.5	0.077	0.001	0.008	0.006	0.035	0.051
Quemada	Apr. 2002 ^a	90	970,169	120	9	22,037	286	2.9	6,880	0.32	23	80	0.015	1,289	4	ND	0.048	ND	0.010	0.027	0.028	0.096

Gas concentrations are in micromoles per mole

ND not detected

^a Part of these data is from Tassi et al. (2004b)

system at the Turrialba volcano. Small reductions in the He isotopic ratio may reflect residence time in a crustal setting and/or interaction with “sub-volcanic” crustal rock to release small amounts of ⁴He. However, the dominance of mantle input, even in the distal Falla Ariete fumaroles ($R/R_{air}=7.71$), argues that a common deep source feeds both the crater and peripheral gas discharges. The $\delta^{13}C-CO_2$ values, especially at the West HT fumarole, were significantly more positive (up to -0.2% V-PDB) than those of CO_2 from mantle degassing that range between -3% and -7% V-PDB (e.g., Javoy et al. 1982; Rollinson 1993). This isotopic signature, consistent with that measured in other volcanoes of Costa Rica, Nicaragua, Honduras, and Salvador, likely reflected the carbon-rich nature of the sediments on the subducting Cocos plate at which, according to Shaw et al. (2003), important, though subordinate, contributions by the organic sediments (approximately 9%) and mantle wedge (approximately 9%) were added (Snyder et al. 2001; Leeuw et al. 2007). As shown in Fig. 3, this hypothesis was supported by the $CO_2/{}^3He$ ratios (up to 28.6×10^9 ; Table 1), up to ten times higher than that of MORB (Des Marais and Moore 1984; Marty and Jambon 1987) and similar to the “end-member” ratios measured at the Pacaya and Mombacho volcanoes (Snyder et al. 2001, 2003). Conversely, the $CH_4/{}^3He$ ratios from 1.6×10^3 and 1.9×10^5 (Table 1) are extremely low when compared with other Central American volcanic and geothermal settings (from 10^6 to 10^8 ; Snyder et al. 2003). Ratios for abiogenic CH_4 , produced by reduction of C-bearing gas species (Giggenbach 1997b), are $<1 \times 10^6$ (Poreda et al. 1988). Therefore, CH_4 production at the Turrialba volcano is likely related to a different source than that of the other light alkanes, whose genesis can be attributed to thermocatalytic reactions involving organic matter-bearing sediments.

Temporal and spatial evolution of the fumarolic fluid chemistry

In the last decade, increased seismic activity and ground deformation episodes have signaled at the Turrialba volcanic system an increase of heat flux from depth that has caused an over-pressurization of the hydrothermal reservoir (Barboza et al. 2003).

As reported by Tassi et al. (2004b), strong changes of the geochemical features of the crater fumaroles, mainly the concentrations of the acidic gas species, have accompanied the visual and geophysical observations. As shown in Fig. 4, the temporal patterns of the S_{tot}/CO_2 ratio at the West and the Central fumaroles suggest three distinct phases of activity: (1) synchronous decreasing trends (from February 1998 to September 2001), (2) a wide peak at the Central fumarole ratios and no specific trend at the West

Table 2 $\delta^{13}\text{C}$ in CO_2 (permil V-PDB), R/R_{air} , $\text{CO}_2/{}^3\text{He}$, and He/Ne values of Turrialba fumaroles and Isotopic composition ($\delta^{18}\text{O}$ and δD expressed as permil V-SMOW) of the fumarole condensates

Sample	Date	R/R_{air}	$\text{CO}_2/{}^3\text{He}$ ($\times 10^9$)	He/Ne	δD	$\delta^{18}\text{O}$	$\delta^{13}\text{C-CO}_2$
West	Feb. 1998				-55.1	-4.8	
West	Feb. 1999	7.33	5.2	144			-2.7
West	Feb. 2000						-3.1
West	Feb. 2001						-3.0
West	Feb. 2002						-2.7
West	Mar. 2002				-93.2	-12.5	-2.8
West	Apr. 2002						-2.8
West	Apr. 2003				-72.2	-9.1	-3.4
West	Apr. 2005	7.32	28.6	1,496	-63.5	-2.6	-2.3
West	May 2007				-64.2	-1.1	-2.2
West	Jun. 2007						-1.4
West	Jul. 2007						-1.8
West	Mar. 2008	7.66	17.6	680			-1.7
Central	Feb. 1999						-4.8
Central	Sep. 2001	7.48	13.9	1,078			-3.0
Central	Nov. 2001						-2.7
Central	Feb. 2002				-69.5	-8.8	-2.6
Central	Apr. 2002						-2.2
Central	Apr. 2003				-94.3	-13.7	
Central	Apr. 2004						-2.5
Central	Apr. 2005				-68.5	-3.2	
Central	May 2007				-65.9	-3.0	
Central	Mar. 2008						-3.1
West HT	Feb. 2008						-0.4
West HT	Mar. 2008	7.58	21.2	5,571			-0.2
West HT	May 2008						-0.4
Falla Ariete	Mar. 2008	7.71	17.4	18			-2.8
Flanco S	Mar. 2008						-2.5
Flanco SO	Mar. 2008						-2.8

fumarole (from November 2001 to September 2002), and (3) synchronous increasing trends in both the Central and West fumaroles (up to May 2008). The evolution of the $S_{\text{tot}}/\text{CO}_2$ ratio, also observed in the $(\text{HCl}+\text{HF})/\text{CO}_2$ ratio (Fig. 5), likely result from the evolution of the fluid source of the fumarolic discharges. In the first period, the crater fumaroles had a CO_2 - and $\text{H}_2\text{S}(\text{CH}_4)$ -dominated composition, typically characterizing volcanic emissions in the hydrothermal stage. The beginning of the intermediate period (November 2001) corresponds to the appearance of SO_2 at the Central fumarole (Table 1). This represents an important event because the presence of SO_2 is typically a diagnostic component of high-temperature fumaroles (and a rejuvenation of magmatic activity?), as this soluble and reactive gas compound is rapidly buffered by liquid-dominated systems feeding low-temperature ($<100^\circ\text{C}$) gas discharges (e.g., Gerlach and Nordlie 1975; Giggenbach et al. 1986; Giggenbach 1987), such as those of the Turrialba crater. In February 2002, the CO/CH_4 ratio of the Central

fumarole increased by more than one order of magnitude (Table 1), as the more oxidizing conditions and increased heat flux related to magmatic fluids overwhelmed the previous “hydrothermal signature” of the crater fumaroles (e.g., Giggenbach et al. 1986; Giggenbach 1987). Therefore, the compositional evolution of the Turrialba gas discharges was likely caused by strong inputs of magmatic gases such as SO_2 into the hydrothermal reservoir. The increasing seismic activity also indicates enhanced fluid circulation (Barboza et al. 2003). At this stage, the Central fumarole was the only site where these changes were evident. In September 2002, SO_2 was also detected at the West fumarole (Table 1), and from 2002, the concentrations of the sulfur gas species at both the West and the Central fumaroles have increased, suggesting a progressive increase of magmatic-related fluid contribution. In the same year, new fractures opened in the summit area, i.e., Quemada (Figs. 1c and 2b). New fractures successively opened in the summit area and along the outer flanks, emitting fluids with

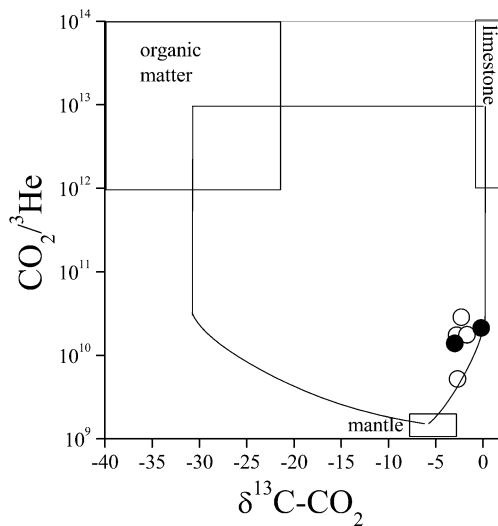


Fig. 3 $\text{CO}_2/{}^3\text{He}$ vs. $\delta^{13}\text{C-CO}_2$ diagram for the Turrialba fumarolic gases. The “organic matter,” “limestone,” and “mantle” fields as defined by Sano and Marty (1995)

a chemical composition similar to that of the West and Central fumaroles (Table 1). Despite the overall increased flux from the Turrialba fumarolic field, the outlet temperature of the two monitored fumaroles did not significantly change from near boiling temperatures. However, the temperature of the West HT fumaroles has shown a sharp increase from June 2007 to February 2008, from 130°C (E. Fernández, personal communication) to 282°C (Table 1), the highest temperature recorded at Turrialba volcano from 1982 (Cheminée et al. 1982) to the present. Two parameters directly related to magmatic degassing such as $\text{SO}_2/\text{H}_2\text{S}$ and HF/HCl ratios (e.g., Gerlach and Nordlie 1975;

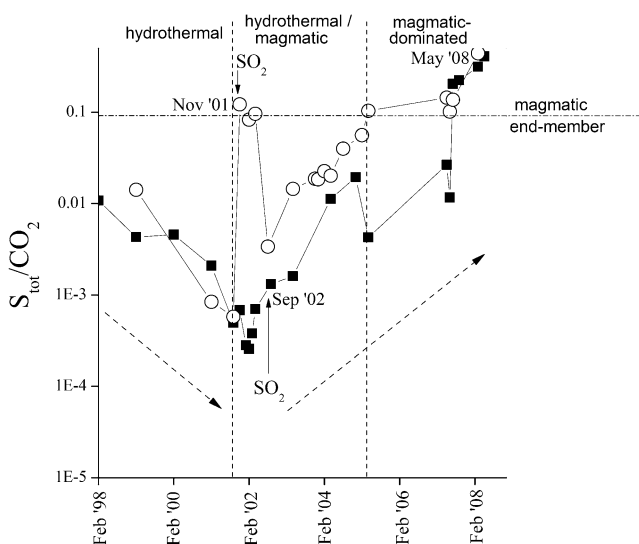


Fig. 4 $S_{\text{tot}}/\text{CO}_2$ vs. time diagram in the Central (open circle) and West (closed square) fumaroles at Turrialba volcano. $S_{\text{tot}}=\text{SO}_2+\text{H}_2\text{S}$

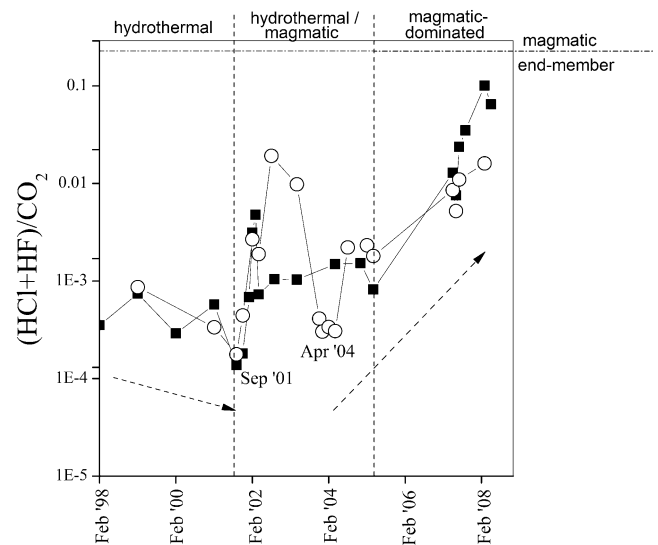


Fig. 5 $(\text{HCl}+\text{HF})/\text{CO}_2$ vs. time diagram. Symbols as in Fig. 4

Giggenbach 1987) were occasionally >100 and up to 2, respectively.

In November 2007, the distal fumarole of Falla Ariete (Figs. 1b and 2e) consisted of atmospheric-related compounds and relatively low concentrations of CO_2 and H_2 (423,158 and 357 $\mu\text{mol}/\text{mol}$, respectively), likely released from a boiling shallow aquifer conductively heated from depth. By March 2008, the composition of this gas discharge had completely changed, now dominated by CO_2 with subordinate H_2S , indicating that the contribution from the main hydrothermal-magmatic system had significantly increased.

The distribution of the δD and $\delta^{18}\text{O}$ values for the samples collected from 1998 to 2004 (Fig. 6) seems to define an evaporation trend (slope of approximately 5), suggesting a major contribution resulting from the boiling of a meteoric-originated aquifer. The δD and $\delta^{18}\text{O}$ values of local meteoric water likely correspond to those measured at the West (March 2002) and Central (April 2003) fumaroles, significantly more negative than those suggested by Tassi et al. (2004b) on the basis of the isotopic signature of Costa Rican surface waters (Lachniet and Patterson 2002). Gases sampled in 2005 and 2007 tend to follow a mixing trend between a meteoric and an “andesitic” (Taran et al. 1989; Giggenbach 1992) end-member. This evidence is consistent with the progressive input of magmatic fluids into the hydrothermal system and/or input of fluids that have equilibrated their oxygen at high temperature (>400°C) with andesitic rocks. No significant variations of either the $\delta^{13}\text{C-CO}_2$ and R/Ra values were recorded, probably because these two compounds are typically not affected by interactions with the shallow environment and displayed a clear magmatic-dominated isotopic signature since the beginning of the geochemical monitoring (Table 2).

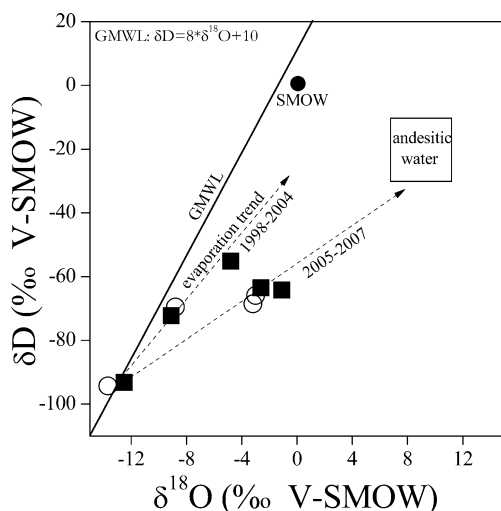


Fig. 6 δD vs. $\delta^{18}O$ binary for the condensates from the Central and West fumaroles at Turrialba volcano. Symbols as in Fig. 4. The “andesitic water” field (Taran et al. 1989; Giggenbach 1992) and the global meteoric water line (GMWL; Craig 1961) are also reported

Temporal changes of the thermodynamic conditions at depth

The hydrothermal-magmatic fluid reservoir of the Turrialba volcano has changed in the last decade to produce dramatic compositional variations of the fumarolic fluids through time. At Turrialba, CO_2 , one of the most commonly adopted geoindicators for geothermal systems (e.g., Giggenbach 1991; Chiodini and Marini 1998), cannot be used for geothermometric estimations because the shallow aquifer has likely interacted strongly with this relatively soluble compound. Conversely, chemical equilibrium in the CH_4 - CO_2 - H_2 system for both the liquid and vapor phases can provide useful information on the temporal evolution of the thermodynamic conditions dominating at depth.

Assuming that the CH_4 - CO_2 pair ratio in the gas phase is controlled by the following equilibrium:



in the equilibrated vapor:

$$\log(CH_4/CO_2)_V = 2 \log f_{H_2O} + 4R_H - \log K_{eq} \quad (2)$$

where $\log f_{H_2O} = 4.9 - 1,820/T$, $R_H = \log(H_2/H_2O)$, and T is in K (Giggenbach 1987).

Therefore, the dependence of the $\log(CH_4/CO_2)_V$ values on temperature and R_H can be expressed as follows:

$$\log(CH_4/CO_2)_V = 4R_H + 5,181/T(K) \quad (3)$$

At equilibrium, the $\log(CH_4/CO_2)_V$ values are related to their aqueous counterparts through the expression:

$$\log(CH_4/CO_2)_V = \log(CH_4/CO_2)_L + \log(B_{CH_4}/B_{CO_2}) \quad (4)$$

where B_{CO_2} and B_{CH_4} are the vapor/liquid distribution coefficients of CO_2 and CH_4 , respectively. The B_{CO_2} and B_{CH_4} values at different temperatures are calculated on the basis of the solubility data of Wilhelm et al. (1977) using the polynomial equations reported by Sepulveda et al. (2007).

At equilibrium, the relation between the $\log(CH_4/CO_2)_L$ values and thermodynamic conditions can be obtained by inserting Eq. 2 into Eq. 4, as follows:

$$\log(CH_4/CO_2)_L = 4R_H + 5181/T + \log(B_{CO_2}) - \log(B_{CH_4}) \quad (5)$$

If we assume that (a) Argon in hydrothermal fluids is of atmospheric origin (e.g., Sano et al. 2001), based on the $^{40}Ar/^{36}Ar$ ratio (not reported), i.e., equal to 296 (Nier 1950), and (b) is controlled by the equilibrium between the atmosphere and air-saturated water ($\log r_{Ar} = -6.52$, where r_{Ar} is the Ar mol-ratio), Giggenbach (1991) suggested that at equilibrium, H_2 concentrations were related to R_H by the following equation:

$$\log(H_2/Ar)_V = R_H - \log r_{Ar} \quad (6)$$

The relation between the $\log(H_2/Ar)_V$ and $\log(H_2/Ar)_L$ values is analogous to that expressed by Eq. 2. Therefore, the behavior of the $\log(H_2/Ar)_L$ values at various R_H values can be described by the expression:

$$\log(H_2/Ar)_L = R_H - \log(B_{H_2}) - \log r_{Ar} \quad (7)$$

where the vapor/liquid distribution coefficients B_{H_2} and B_{Ar} were calculated from the same data sources used for those of CO_2 and CH_4 .

In Fig. 7, the $\log(H_2/Ar^*)$ vs. $\log(CH_4/CO_2)$ grid (Giggenbach and Goguel 1989; Giggenbach 1993) is constructed on the basis of Eqs. 3, 5, 6, and 8 at R_H equal to 3.4 and 3.6. The Ar^* values, used in Fig. 7 instead of the Ar concentrations, were calculated as follows:

$$Ar^* = Ar - (O_2/22) \quad (8)$$

The $O_2/22$ values correspond to the amounts of Ar added by atmospheric contamination, because O_2 is completely absent in pristine hydrothermal fluids and only occurs as the result of shallow level atmospheric contamination.

Gases collected from the Central and the West fumaroles prior to 2001, before the detection of SO_2 , plot along the liquid equilibrium curve at temperatures $\leq 300^\circ C$ and $R_H = -3.6$ (Fig. 7). Similar conditions also control the

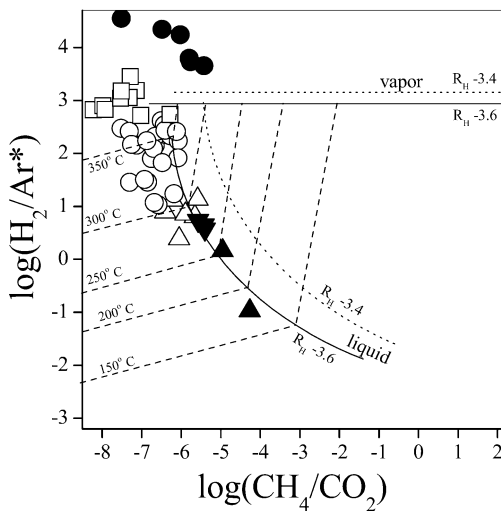


Fig. 7 $\log(\text{H}_2/\text{Ar}^*)$ vs. $\log(\text{CH}_4/\text{CO}_2)$ diagram for the Turrialba fumarolic gases (West and Central fumaroles from 1998 to February 2001: *open up triangle*; West and Central fumaroles from September 2001 to April 2005 and Quemada fumarole: *open circle*; West and Central fumaroles from April 2005 to May 2008: *open square*; West HT fumaroles: *closed circle*; Falla Ariete fumaroles: *closed up triangle*; Flanco S, Flanco SO, and Flanco NE fumaroles: *closed down triangle*. $\text{Ar}^* = \text{Ar} - \text{O}_2/22$; $R_H = \log(\text{H}_2/\text{H}_2\text{O})$ (Giggenbach 1987)

fumarole fluids in the outer flanks of the volcano in 2008 (Flanco S, Flanco SO, and Flanco NE; Figs. 1c and 2f). Such redox conditions are significantly more oxidizing than those of the $\text{FeO}/\text{FeO}_{1.5}$ buffer ($R_H = -2.8$), the most typical redox buffer in hydrothermal environments (Giggenbach 1987). The distribution of the gases sampled between November 2001 and April 2005 in the same sites and at the Quemada fracture (Figs. 1c and 2b) indicates higher equilibrium temperatures (up to about 370°C) and more oxidizing conditions ($R_H < -3.6$) with respect to the prior period (Fig. 7). Equilibrium conditions of the fluids collected in 2007–2008 are even more extreme, especially those of the West HT fumarole that seems to attain supercritical conditions, i.e., not controlled by the boiling of a liquid phase. It is worth noting that the evolution of the equilibrium temperatures indicated by the $\text{CO}_2\text{-CH}_4\text{-H}_2$ geothermometer is consistent with the changes observed in both the acidic gas species and the isotopic values ($\delta^{18}\text{O}$ and δD) of the steam over the last decade.

Chemical equilibrium involving light alkanes, such as the reactions between saturated–unsaturated pairs, can also apply to geothermometry (e.g., Capaccioni and Mangani 2001; Taran and Giggenbach 2003; Tassi et al. 2005). Dehydrogenation process of the C_3 alkane (propane) to produce its homologous alkene (propene) is described by the following reaction:



In the equilibrated vapor, the temperature dependence of Eq. 9 is (Capaccioni et al. 2004):

$$\log(\text{C}_3\text{H}_6/\text{C}_3\text{H}_8)_V + \log(\text{H}_2) = 7.15 - 6,600/T \tag{10}$$

By considering that $\log f\text{H}_2\text{O} = 4.9 - 1,820/T$ (Giggenbach 1987), the relation between the $\log(\text{C}_3\text{H}_6/\text{C}_3\text{H}_8)$ values and temperature and R_H values is obtained from Eq. 10, as follows:

$$\log(\text{C}_3\text{H}_6/\text{C}_3\text{H}_8)_V = 2.25 - R_H - 4,780/T \tag{11}$$

The solubility behavior of C_3H_8 and C_3H_6 in response to vapor–liquid phase changes was nearly identical (Tassi et al. 2007); therefore, it is reasonable to assume that:

$$\log(\text{C}_3\text{H}_6/\text{C}_3\text{H}_8)_V = \log(\text{C}_3\text{H}_6/\text{C}_3\text{H}_8)_L \tag{12}$$

Figure 8 shows the $\log(\text{C}_3\text{H}_6/\text{C}_3\text{H}_8)$ values plotted vs. temperature (°C) estimates from the $\text{CO}_2\text{-CH}_4\text{-H}_2$ system. All the gas samples, with the exception of that from the Falla Ariete fumarole, cluster far from the equilibrium curve $R_H = -3.6$. This suggests that the $\text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_8$ conversion was efficiently controlled at higher oxidizing conditions (e.g., by the $\text{SO}_2\text{-H}_2\text{S}$ redox pair) than those that control the $\text{CO}_2\text{-CH}_4\text{-H}_2$ equilibrium.

The $\text{SO}_2\text{-H}_2\text{S}$ redox pair is considered the most reliable buffer system in a magmatic-dominated environment (e.g., Giggenbach 1996). The R_H and temperature values in a vapor phase depends on the $\log(\text{SO}_2/\text{H}_2\text{S})$ values, as follows:

$$\log(\text{SO}_2/\text{H}_2\text{S}) = -3R_H - 1.24 - 8,924/T \tag{13}$$

By combining Eqs. 11 and 13 at $\text{SO}_2/\text{H}_2\text{S} = 100$, an equilibrium curve matching most of the Turrialba crater gas samples was generated. Adopting the same $\text{SO}_2\text{-H}_2\text{S}$

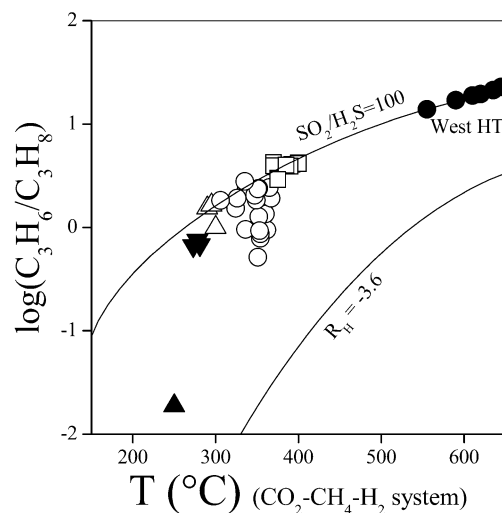


Fig. 8 $\log(\text{C}_3\text{H}_6/\text{C}_3\text{H}_8)$ vs. equilibrium temperature (°C) in the $\text{CO}_2\text{-CH}_4\text{-H}_2$ system. Symbols as in Fig. 7

redox buffer, the equilibrium temperatures of the gases from the West HT fumaroles ranged between 550°C and 650°C (Fig. 8).

In summary, during the last decade, three different stages of activity can be distinguished at Turrialba volcano (Figs. 4 and 5): (1) “hydrothermal” (1998 to autumn 2001), characterized by relatively low fumarolic emission from the summit crater. During this period, the magmatic fluids completely dissolved into the main hydrothermal reservoir, with the exception of the low-solubility compounds, i.e., He and CO₂ that showed magmatic isotopic signatures in the surface emissions. A shallow meteoric-originated aquifer maintained the outlet temperature of the fumaroles at <90°C or approximately boiling at this altitude; (2) “hydrothermal-magmatic” (autumn 2001 to 2007), marked by a progressive increase of the fumarolic flux accompanied by seismic activity and ground deformation. At this stage, an increasing magmatic contribution increased the temperature of the hydrothermal system, and the redox conditions became more oxidizing. Accordingly, the hydrothermal aquifer was not able to efficiently buffer SO₂. Despite the strong compositional changes of the fumarolic fluids, their outlet temperature was still controlled by the presence of a shallow aquifer; (3) “magmatic-dominated” (2007 to 2008), defined by a dramatic increase of the fumarolic discharge rate at the crater and the opening of new vents even in areas distant from the crater summit (i.e., Falla Ariete area). The magmatic-related contribution to the crater fumaroles largely exceeded that of the hydrothermal fluids. An extended vapor reservoir overlying the hydrothermal aquifer was likely present. The shallow meteoric aquifer was partially consumed and disappeared in some zones of the crater, i.e., at the conduit feeding West HT, as the heat flux increased from the deep magmatic/hydrothermal environment.

Conclusions

The drastic changes of the fluid geochemistry that occurred in the last decade at the Turrialba volcano, coupled with those shown by the geophysical and morphological observations, suggest a risk of a rejuvenation of the volcanic activity even though the seismic activity recorded prior to 2001 (OVSICORI-UNA 1998, 1999, 2000, 2001) has not apparently reflected any significant magma movements. The recorded evolution of the Turrialba volcano could be part of a cycle regulating the balance between the hydrothermal and the magmatic systems. According to this hypothesis, during periods of relatively low fumarolic emission (“hydrothermal” stage), the boiling of the hydrothermal aquifer, heated by ascending magmatic fluids, progressively causes overpressure at depth, eventually opening new pathways that allow rising fluids to dissipate the energy excess (“hydrothermal-

magmatic” and then “magmatic-dominated” stages). In this current phase (2007–2008), the occurrence of small-to-medium phreatic eruptions cannot be excluded.

Such cyclic behavior in the fumarolic activity of Turrialba mimics that of other volcanoes worldwide, e.g., Galeras (Fischer et al. 1996), Showa-Shinzan (Symonds et al. 1996), Vulcano Island (Capasso et al. 1999), Poàs (Vaselli et al. 2003), and El Chichon (Tassi et al. 2003). To the best of our knowledge, this “pulsing trend” involving the presence and the temporal increase of magmatic species in the fumarolic discharges was not recorded at Turrialba after the 1864–1866 explosive event. The complete consumption of the hydrothermal reservoir, although unlikely, could drastically change this scenario. The magmatic system, no longer buffered by an overlying liquid-dominated system, could directly begin eruptive activity. However, lack of information about the eruptive style of this volcanic system, previously considered of secondary risk relative to the Costa Rica other volcanoes, i.e., Poàs and Irazu, makes a reliable prediction of the events difficult. Our data suggest that the geochemical monitoring of the Turrialba volcano should be broadened to include not only the crater fumaroles but also the distal gas discharges (Falla Ariete fumaroles). Further efforts should initiate a periodic inventory of the diffuse gas (CO₂) emissions from the soil of the outer flanks of the volcanic edifice, as these may link to increased fracturing of the volcanic edifice. The gas emanations data should be coordinated with improved geophysical measurements such as a new seismic array and high definition global positioning system permanent station. In these recently awakened volcanic systems such as Turrialba, both the local authorities and the international scientific community should focus their attention on the evolution of the hydrothermal system and how it relates to possible volcanic activity.

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