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RESEARCH ARTICLE

Fumarolic gases at Mombacho volcano (Nicaragua): presence of magmatic gas species and implications for volcanic surveillance

K. Garofalo · F. Tassi · O. Vaselli · A. Delgado-Huertas · D. Tedesco · M. Frische · T. H. Hansteen · R. J. Poreda · W. Strauch

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Abstract Mombacho is a deeply dissected volcano belonging to the Quaternary volcanic chain of Nicaragua. The southern, historic collapse crater (El Crater) currently hosts a fumarolic field with a maximum temperature of 121°C. Chemical and isotopic data from five gas-sampling field campaigns carried out in 2002, 2003 and 2005 highlight the presence of high-temperature gas components (e.g. SO_2, HCl and HF), which indicate a significant contribution of juvenile magmatic fluids to the hydrothermal system feeding the gas discharges. This is strongly supported by the mantle-derived helium and carbon isotopic signatures, although the latter is partly masked by either a sedimentary subduction-related or a shallow carbonate component. The observed chemical and isotopic composition of the Mombacho fluids seems to indicate that this volcanic system, although it has not experienced eruptive events during the last centuries, can be considered active and possibly dangerous, in agreement with the geophysical data recorded in the region. Systematic geochemical monitoring of the fumarolic gas discharges, coupled with a seismic and ground deformation network, is highly recommended in order to monitor a possible new eruptive phase.

Keywords Nicaragua · Mombacho volcano · Fumarolic gases · Geochemical monitoring · Fluid geochemistry · Isotope geochemistry

Introduction

Assessing potential volcanic hazard in order to mitigate the risk of expected losses (such as lives, property, goods and so forth) in a given area and in a specific given

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K. Garofalo (✉) · M. Frische · T. H. Hansteen
SFB 574, IFM-GEOMAR,
Wischhofstraße 1-3,
24148 Kiel, Germany
e-mail: kgarofalo@ifm-geomar.de

F. Tassi · O. Vaselli
Department of Earth Sciences,
University of Florence,
Via G. La Pira 4,
50121 Florence, Italy

O. Vaselli
CNR-IGG Institute of Geosciences and Earth Resources,
Via G. La Pira 4,
50121 Florence, Italy

A. Delgado-Huertas
Estación Experimental de Zaidín, CSIC,
Prof. Albareda 1,
18008 Granada, Spain

D. Tedesco
Department of Environmental Sciences,
Second University of Naples,
Via Vivaldi 43,
81100 Caserta, Italy

D. Tedesco
CNR National Research Council,
Institute of Environmental Geology and Geo-Engineering,
Piazzale A. Moro,
00100 Roma, Italy

R. J. Poreda
Department of Earth and Environmental Sciences,
227 Hutchinson Hall,
Rochester, NY 14627, USA

W. Strauch
INETER, Instituto Nicaragüense de Estudios Territoriales,
Frente a Policlínica Oriental,
2110 Managua, Nicaragua

period, generally requires long-term monitoring programs. The precursors of eruptive events may be caused by the movement of deep-seated magma, tectonic activity (producing crustal deformation) and unloading of the magmatic system due to mass wasting (Sigurdsson et al. 2000). As the emplacement of volatile-oversaturated magma is often accompanied by degassing, the onset of renewed magmatic activity should lead to detectable changes in the physical-chemical features of the fluid phases (e.g. Gerlach and Nordlie 1975; Giggenbach 1987). Thus, the monitoring of the chemical and isotopic composition of gas discharges is a useful tool to assess the state of any volcanic system.

Mombacho volcano (Nicaragua) is located close to the city of Granada and is surrounded by several small villages. It represents a realistic threat to more than 90,000 people, with regard to two possible types of hazard: (1) debris avalanches and lahars originating from a fragile sector of the volcanic edifice (van Wyk de Vries and Francis 1997; Vallance et al. 2001) and (2) eruptive events. This volcanic system is characterized by persistent fumarolic activity; however, as no eruptions have occurred in historical times, a resumption of eruptive activity at Mombacho is considered unlikely (van Wyk de Vries and Francis 1997; Havlíèek et al. 1998; Vallance et al. 2001). Although several geologic and structural maps of the area have been produced (Hradecký 1988; van Wyk de Vries 1993; van Wyk de Vries and Francis 1997; Havlíèek et al. 1998), detailed information about its past and present activity, i.e. volcanic succession reconstruction, dating of volcanic deposits and long-term geochemical and geophysical measurements, is lacking.

In this study, based on five sampling campaigns (in 2002, 2003 and 2005), we investigate the chemical and isotopic composition of the fumarolic gas discharges from the southern collapse crater (El Crater; van Wyk de Vries and Francis 1997) of Mombacho and assess the likelihood of renewed eruptive activity. For this reason, we focus on (1) investigating the physical-chemical conditions acting on the deep fluid reservoirs and (2) evaluating the utility of the geochemical data in terms of monitoring to assess Mombacho's state of activity.

Geological setting and past volcanic activity

The Quaternary volcanic chain (Cordillera de los Marrabios) of Nicaragua is related to the subduction of the Cocos plate beneath the Caribbean plate along the Middle America trench, at a rate of ~8 cm/year (DeMets 2001; La Femina et al. 2002) at an angle of about 80° (Protti et al. 1995). This active volcanic range rises from the Nicaraguan Depression, a large NW–SE trending graben hosting the largest lakes (Nicaragua and Managua) and cities (Managua, xLeon and Granada) of the country (Fig. 1a). The Nicaraguan Depression is bordered by Tertiary volcanic rocks to the east (Central American Highlands) and by Upper Cretaceous-Miocene sedimentary rocks to the west (Pacific Coastal Plain; Fig. 1a). The marine sedimentary sequences rarely crop out outside the domain of the Pacific Coastal Plain. Nevertheless, they are considered to underlie the Quaternary volcanic rocks (Los Marrabios, Las Sierras formations) in the Nicaraguan Depression (McBirney and Williams 1965; Weinberg 1992; Ehrenborg 1996; Elming et al. 2001; Fig. 1a). The Quaternary volcanic range consists of an alignment of shield and stratocone volcanoes and ignimbrite complexes at various stages of evolution. Shield volcanoes are commonly associated with major regional fault systems, whereas the stratocone volcanoes are often related to thin-skinned volcano-tectonic compressive structures (van Wyk de Vries 1993).

Mombacho (11.83 N, 85.98 W; 1,350 m asl) is a basaltic-andesitic stratocone volcano located in the southwestern edge of the Nicaraguan Depression (Fig. 1a). The volcano lies on the Quaternary ignimbrites erupted from the Las Sierras Caldera surrounding Masaya volcano (Las Sierras Formation) and Tertiary igneous and sedimentary rocks (van Wyk de Vries 1993; van Wyk de Vries and Francis 1997). Volcanic activity at Mombacho is characterized by numerous lava flows, whose composition is mainly andesite to basaltic andesite, and explosive events producing pyroclastic flows and ash-fall deposits (Hradecký 1988; Havlíèek et al. 1998). Mombacho volcanic edifice has experienced at least three voluminous debris avalanche episodes. The first failure occurred between 20,000 and 1,000 years ago, and affected the southeastern sector of the volcanic edifice. This was followed by a second event (Las Isletas failure; van Wyk de Vries and Francis 1997) to the NE. The third collapse (El Crater failure) destroyed the south side of the edifice in A.D. 1570, producing a debris avalanche that covered the indigenous village of Mombacho and killed 400 people (Incer 1995; Vallance et al. 2001). During the A.D. 1570 collapse, a horseshoe-shaped crater (1.5 km wide and 700 m deep) was formed (van Wyk de Vries and Francis 1997) and presently encompasses a wide fumarolic field.

Sampling procedures and analytical methods

Gas sampling

The main fumarolic field of Mombacho volcano consists of several fluid discharges (fumaroles, bubbling gas in boiling pools and hot springs) and covers an area of about 200 m^2 within the SE crater (Fig. 1b). Low-flux fumarolic emissions and steaming grounds are also present on the

N–NE flank of the volcano (Fig. 1b), especially after heavy rains. Gas sampling was performed during five field campaigns: (1) mid of November 2002 (beginning of the dry season), (2) end of November 2002, (3) March–April 2003 (middle of the dry season), (4) July 2003 (end of the dry/ beginning of the rainy season) and (5) March–April 2005 (middle of the dry season). In addition to gas samples, in April 2005 two cold-water springs (T=20 and 27°C) at the top of the volcano and a thermal spring (T=41°C) in the southern collapse crater (Fig. 1b) were sampled for oxygen and hydrogen isotopic analysis. Gases were collected at four sampling sites: (1) F1 fumarole (85°58.476′ N, 11° 49.875′ W NAD27 central coordinates; 689 m asl), characterized by a relatively constant outlet temperature (ca. 120°C) during the whole sampling period; (2) F2 fumarole (85°58.477′ N, 11°49.875′ W NAD27 central coordinates; 689 m asl), a hiss-jet gas discharge which formed in the late 1980s (Global Volcanism Program 1980, 1982, 1988, 1991, 1994) that has an outlet temperature similar to that of the F1 fumarole; (3) BP1 and (4) BP2 boiling pools, located a few meters from the F1 fumarole. In 2002, the gas flux from the F2 fumarole was particularly strong, which made it difficult to collect samples. In 2003 and 2005, the gas flow rate from this fumarole had decreased significantly.

Pre-evacuated 60 ml glass flasks filled with 20 ml of a 4N NaOH and 0.15 M $Cd(OH)_2$ solution (Giggenbach and Gougel 1989; Montegrossi et al. 2001) were used on line with (1) a quartz-glass pipe and dewar tubes, and (2) silicone/tygon tubes connected to a plastic funnel, to sample gases from fumarolic vents and boiling pools, respectively. During sampling, CO_2, SO_2, HCl and HF dissolve into the alkaline solution, water vapor condenses, elemental sulfur precipitates and H_2S reacts with Cd^{2+} to form insoluble CdS, allowing the residual gases (N_2, O_2, CO, H_2, He, Ar, Ne, CH_4 and light hydrocarbons) to concentrate in the head-space. Three aliquots of the discharging fluids were also collected to determine: (1) $\delta^{13}C$–CO_2 values by 50 ml pre-evacuated flasks, (2) $^3He/^4He$, $^{40}Ar/^{36}Ar$ and $^4He/^{20}Ne$ isotopic ratios by a pre-evacuated 100-ml glas flask filled with 40 ml of a 4N NaOH solution and (3) HF content and $\delta^{18}O$– and δD–H_2O values by condensation with a quartz-glass water-cooled condenser.

Gas chemical analysis

The inorganic residual gases were analysed by a gas-chromatograph (Shimadzu 15a) with a thermal conductivity detector (TCD). Methane and light hydrocarbons were analysed with a Shimadzu 14a gas-chromatograph with a Flame Ionization Detector (FID). CO was converted to CH_4 at 400°C, using a Shimadzu MTN-1 methanizer (Tassi 2004), and analysed by gas-chromatography (FID detector). Following the analysis of the residual gases, the alkaline solution was centrifuged in order to separate the solid

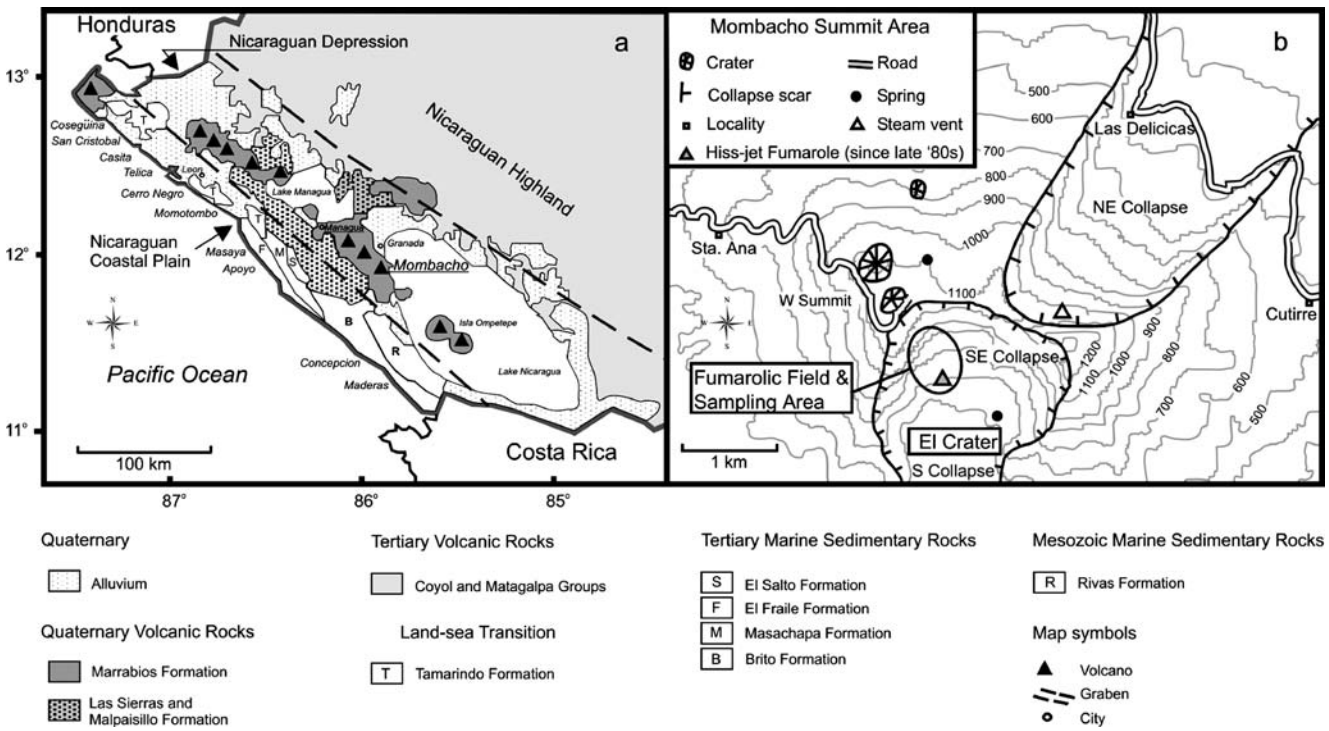

Fig. 1 **a** Schematic geological map of Nicaragua (modified after Van Wyk de Vries 1993) and **b** location of the fumarolic field on the summit area of Mombacho volcano (modified after Van Wyk de Vries and Hernandez 1994)

precipitate. The supernatant was used for: (1) CO_3^{2-} analysis (for CO_2 content) by titration with 0.5N HCl solution; (2) SO_4^{2-} analysis, after oxidation with H_2O_2 (for SO_2 content), by ion-chromatography (Dionex DX100); (3) Cl^- analysis (for HCl content) by ion-chromatography. The solid precipitate was oxidized with H_2O_2 to dissolve CdS. The resulting solution was centrifuged and separated from the residual solid and then used for SO_4^{2-} analysis by ion-chromatography for the determination of H_2S. S^0 was extracted from the residual solid with CCl_4 and oxidized to S_2I_2 with the addition of KI. Sulfur of S_2I_2 was oxidized to SO_4^{2-} by $KBrO_3$ and finally analysed by ion-chromatography (Montegrossi et al. 2001). F^- analysis (for HF determination) was performed in the condensate by ion-chromatography. Analytical error is <5% for the main gas components and <10% for minor and trace gas compounds.

Isotope geochemistry analysis

The $^{13}C/^{12}C$ isotopic ratio of CO_2 (expressed as $\delta^{13}C$‰ V-PDB) was determined with a Finningan Delta S mass spectrometer after standard extraction and purification procedures of the gas mixture (Evans et al. 1988). Internal (Carrara and San Vincenzo marbles) and international (NBS18 and NBS19) standards were used for the estimation of external precision. Analytical error is ±0.05‰. The reproducibility of δ-values for C is ±0.1‰. Oxygen and hydrogen isotope compositions were determined on the condensates by Delta Plus XL and MAT 251 (Finningan) mass spectrometers. Oxygen isotopes were analysed by using the CO_2–H_2O equilibration method (Epstein and Mayeda 1953). Hydrogen isotope measurements were carried out on H_2 after the reaction of 10-μl water sample with 0.3 g of metallic zinc at 500°C, according to the analytical procedure described by Coleman et al. (1982). EEZ-3 and EEZ-4 internal standards were calibrated vs. V-SMOW and SLAP reference standards. The analytical error for $\delta^{18}O$ and δD values is ±0.1 and ±2‰, respectively.

$^3He/^4He$, $^{40}Ar/^{36}Ar$ and $^4He/^{20}Ne$ isotopic ratios were determined using a VG5400 gas mass spectrometer following the procedure of Poreda and Farley (1992). The analytical error for the $^3He/^4He$ ratio is about 0.3%, while those for both the $^{40}Ar/^{36}Ar$ and $^4He/^{20}Ne$ isotope ratios is 0.2%.

Chemical and isotopic composition of gases

Gas chemistry

The chemical composition of the gas discharges studied during this work is reported in Tables 1 and 2. Steam was the main component of the gas samples ranging between 800,000 and 990,000 μmol/mol, followed by CO_2 (up to 163,000 μmol/mol) and H_2S (500–16,200 μmol/mol). The presence of SO_2 (6–7,800 μmol/mol), HCl (2–240 μmol/mol) and HF (up to 5 μmol/mol) is worthy of note, as this is typical of high-temperature gases. H_2 and N_2 are the most abundant compounds (up to 17,160 and 4,000 μmol/mol, respectively) among the non-condensable gases, whilst CH_4, He, and CO are characterized by abundances up to 1.1, 1 and 0.03 μmol/mol, respectively. Several light hydrocarbon compounds, whose total content (ΣC_2-C_6) does not exceed 0.25 μmol/mol, were also detected (Table 2). Aside from samples no. 4 and 13, which are likely to have been air-contaminated during sampling, Ar and Ne contents are up to 7.7 and 0.005 μmol/mol, respectively (Table 1), indicating that the Mombacho gases are only slightly affected by meteoric-related contributions.

Carbon, oxygen, hydrogen and noble gas isotopic composition

Table 1 shows $\delta^{13}C$–CO_2, $\delta^{18}O$ and δD in water vapor data, $^{40}Ar/^{36}Ar$, $^4He/^{20}Ne$, $^{20}Ne/^{36}Ar$ and R/Ra ($R=^3He/^4He_{sample}$ and $Ra=^3He/^4He_{air}$, the latter being 1.39×10^6; Mamyrin and Tolstikhin 1984) ratios for the samples collected. The $\delta^{13}C$–CO_2 values, determined on selected samples, are between 0.67 and 1.83‰ V-PDB, a range commonly ascribed to CO_2 production by thermo-metamorphic processes of marine carbonate rocks (e.g. Rollinson 1993).

The values of $\delta^{18}O$ and δD ratios in fumarolic condensates range from +3.5 to +9.3 and from −15.1 to +11.9‰ V-SMOW, respectively. The $\delta^{18}O$ and δD ratios of water samples collected from three springs located in the area (Fig. 1b) were taken as reference for local precipitation. Their $\delta^{18}O$ (−6.0, −6.1 and −6.4‰ V-SMOW) and δ^2H (−40.4, −39.7 and −37.9‰ V-SMOW) values are consistent with those calculated using the relationship between the isotopic composition of precipitation at their latitude and altitude (Bowen and Wilkinson 2002), i.e. $\delta^{18}O=-6.5$‰ and $\delta^2H=-41.7$‰ V-SMOW. Steam samples in the $\delta^{18}O$–δD diagram (Fig. 2), plot far from both the local (LMWL) and global (GMWL) meteoric water lines (Craig 1961; IAEA 2004; IAEA/WMO 2004). The relatively high δD values appear to exclude a significant contribution of "arc-related water" (Taran et al. 1989; Giggenbach 1992) derived from the magmatic source. Thus, the enrichment of both ^{18}O and ^2H (Fig. 2) is likely to be due to evaporative fractionation of locally heated meteoric water, which strongly contributes to Mombacho fumarolic discharges.

The $^{40}Ar/^{36}Ar$ and $^{20}Ne/^{36}Ar$ ratios (297 and 0.68, respectively) are close to that of air-saturated water at 25°C (295 and 0.15, respectively), suggesting a meteoric origin

Table 1 Outlet temperatures (in °C) and chemical and isotopic composition of the fumarolic discharges from Mombacho volcano

No.	Sample	Date	T°C	CO_2	HCl	HF	SO_2	H_2S	S	H_2O	N_2	CH_4	Ar	O_2	Ne	H_2	He	CO	$\delta^{18}O$	δD	$\delta^{13}C$	R/Ra	$^{40}Ar/^{36}Ar$	$^{4}He/^{20}Ne$	$^{20}Ne/^{36}Ar$
1	F2	Mid-Nov 2002	120.6	8815	26.61	ND	81.95	1774	0.213	987072	63.04	0.201	1.249	0.335	0.0010	2166	0.105	0.001							
2	F1	Mid-Nov 2002	119.2	24616	1.814	ND	20.74	2177	0.268	971681	312.7	0.106	6.218	80.36	0.0032	1103	0.467	0.008							
3	F2	Mid-Nov 2002	115.6	28826	2.239	ND	40.93	2315	0.413	965735	319.4	0.245	6.407	77.03	0.0034	2677	0.092	0.002	7.7	4.9	1.83				
4	F1	End-Nov 2002	119.6	36702	4.305	ND	61.20	1908	0.477	953499	4057	0.192	87.25	1168	0.0352	2513	0.352	0.039	7.9	9.3	1.64				
5	F1	End-Nov 2002	119.6	26566	2.339	ND	8.312	528.9	0.259	970289	74.30	0.307	1.456	8.293	0.0010	2521	0.031	0.002							
6	F2	End-Nov 2002	116.0	24172	239.2	ND	7881	1095	0.341	963896	94.91	0.219	1.955	13.66	0.0014	2605	0.041	0.002							
7	F1	Mar 2003	115.0	20575	2.243	0.150	6.074	1294	0.552	977889	184.2	0.030	3.994	44.27	0.0035	1950	0.299	0.001	5.2	−7.5					
8	F2	Mar 2003	118.0	21831	2.380	1.494	145.0	1845	0.176	973625	43.25	0.231	0.892	3.825	0.0008	2503	0.048	0.001							
9	BP1	Mar 2003	94.2	59053	5.245	3.293	319.6	4648	0.387	930333	224.4	0.172	4.397	56.99	0.0028	5351	0.069	0.003	9.3	11.6	0.67				
10	BP2	Mar 2003	93.7	60202	7.520	4.722	560.0	4906	0.370	927609	209.3	0.279	4.161	26.37	0.0034	6471	0.114	0.034							
11	F2	Apr 2003	118.4	163171	10.70	ND	81.49	16199	1.185	802923	401.6	1.067	7.761	39.68	0.0053	17162	0.988	0.018	4.9	−4.9					
12	F1	Jul 2003	118.0	56149	56.70	ND	17.83	2026	0.215	939155	65.94	0.223	1.298	0.830	0.0010	2527	0.029	0.002	5.4	2.4					
13	F1	Apr 2005	116.4	35518	7.678	4.000	3275	4324	0.567	951793	782.4	0.096	16.96	114.9	0.0102	4164	0.208	0.003	3.5	−15.1		7.62	297	70.4	0.68

Gas contents are in µmol/mol. $\delta^{13}C$ in CO_2 (‰V-PDB), $\delta^{18}O$ and δD (‰V-SMOW), R/Ra, $^{40}Ar/^{36}Ar$ and $^{4}He/^{20}Ne$, $^{20}Ne/^{36}Ar$ ratios are presented for a selected number of fumarolic samples
ND not detected

of these two gas species. The slight Ne excess is possibly due to the higher efficiency of neon, compared with that of argon, to be transferred to the gas phase during boiling and steam–gas–water separation (Ballentine et al. 1991). The R/Ra ratio measured on sample no. 13 (7.62 Ra) is similar to those previously measured (7.6–7.7 Ra; Shaw et al. 2003; Snyder et al. 2003) and represents one of the highest values found in Central American volcanoes (Shaw et al. 2003). This high ratio is similar to that measured in the Mid-Ocean Ridge Basalts (MORB=8±1 Ra; Farley and Neroda 1998) and indicates a significant contribution of mantle-derived helium (≈95%).

Discussion

Origin of gases

The chemical and isotopic composition of fumaroles sampled at Mombacho volcano is unlike that commonly found in extinct volcanic systems. The presence of highly acidic gas compounds (i.e. SO_2, HCl and HF) can only be ascribed to a high-temperature fluid source, which is in agreement with the mantle signature of the helium isotopic ratio. Furthermore, the $CO_2/^3He$ ratio (7.6×10^9) is within a factor of 5 of MORB magmatic fluids (2×10^9; Marty and Jambon 1987) and within the range of values measured in hot springs and geothermal wells along the volcanic axis of Central America (varying between 2.55×10^9 and 617×10^9; Snyder et al. 2001). This suggests that the relatively positive values of $\delta^{13}C$ of CO_2 (Table 1) may originate from a mantle source locally modified by carbonate-rich sediments carried by the subducting Cocos plate, and/ or from shallow sedimentary rocks and secondary processes, as is suggested for other Central American and arc-type volcanoes (Patino et al. 2000; Snyder et al. 2001; Shaw et al. 2003; Sumino et al. 2004; Notsu et al. 2005). A meteoric water vapor source indicates that the water table is close to the surface, which is also supported by the low temperatures of the fumaroles (<121°C; Table 1). The large variability in SO_2, HCl and HF measured in F1 and F2 fumaroles over a short time period (i.e. samples no. 1–6; Table 1) may be due to scrubbing processes, which would be significant for these highly soluble compounds (Giggenbach 1992; Symonds et al. 2001). Gas scrubbing depends on a number of parameters (precipitation rate, thickness of the shallow aquifer, flux rate of ascending fluids, etc.) and, as already observed in other volcanic systems (e.g. Poas volcano, Vaselli et al. 2003), may show rapid variations with local conditions. Part of the SO_2, HCl and HF variability in the samples from the two bubbling springs (samples no. 9 and 10; Table 1), could be due to water droplets that entered the glass vials during sampling.

Table 2 Outlet temperatures (in °C) and hydrocarbons composition of the fumarolic discharges from Mombacho volcano

No.	Sample	Date	T°C	C_2H_6	C_2H_4	C_3H_8	C_3H_6	i-C_4H_{10}	n-C_4H_{10}	i-C_4H_8	C_6H_6
1	F2	Mid-Nov 2002	120.6	0.00653	0.00065	0.00196	0.00310	ND	0.00243	0.00310	0.00745
2	F1	Mid-Nov 2002	119.2	0.00356	0.00044	0.00083	0.00146	ND	ND	0.01392	0.00566
3	F2	Mid-Nov 2002	115.6	0.00819	0.00139	0.00339	0.00357	ND	ND	0.00779	0.00970
4	F1	End-Nov 2002	119.6	0.00759	ND	ND	0.00595	ND	ND	0.00282	0.01002
5	F1	End-Nov 2002	119.6	0.00764	0.00083	0.00190	0.01419	ND	ND	0.00361	0.00403
6	F2	End-Nov 2002	116.0	0.00744	0.00095	0.00166	0.00280	ND	ND	0.00809	0.00902
7	F1	Mar 2003	115.0	0.00086	0.00010	0.00055	0.00021	0.00070	ND	0.00203	0.00130
8	F2	Mar 2003	118.0	0.00727	0.00089	0.00326	0.00477	0.00140	0.00217	0.00586	0.01109
9	BP1	Mar 2003	94.2	0.06866	0.03179	0.00395	0.00913	0.00423	0.00310	0.03890	0.02937
10	BP2	Mar 2003	93.7	0.07959	0.02986	0.00859	0.01148	0.00369	0.00302	0.02201	0.03490
11	F2	Apr 2003	118.4	0.04833	0.00794	0.01676	0.02381	ND	ND	0.05097	0.06191
12	F1	Jul 2003	118.0	0.00086	0.00032	0.00022	0.00038	ND	ND	0.00044	0.00082
13	F1	Apr 2005	116.4	0.00167	0.00018	0.00069	0.00109	0.000279	0.00033	0.00021	0.00235

Gas contents are in μmol/mol
ND not detected

This process cannot have significantly affected the composition of the gases however, since SO_3^2, which can only be derived from gaseous SO_2, was consistently the prevailing sulfur compound in the NaOH solution. The low CO abundance (<0.039 μmol/mol) can be ascribed to hydrolysis processes that favour the production of formic acid (Shock 1993). A similar process was invoked to justify the relatively low CO contents from other geothermal and volcanic gas discharges (i.e. Tatio geothermal field, Larderello geothermal field, El Chichon volcano, Rincon de la Vieja volcano, etc.) where ascending hot fluids interact with a shallow water table (e.g. Tassi et al. 2003; 2005a,b). As shown by the (H_2+HCl)-(SO_2+H_2S)-(CO_2+CH_4) ternary diagram (Fig. 3), H_2 and HCl are significantly enriched with respect to other active volcanoes in Central America, e.g. Poas, Irazu, San Cristobal and Momotombo (Martini 1996) and Cerro Negro (Garofalo et al., unpublished data). Such a feature, commonly ascribed to chemical reactions in presence of a liquid phase at a relatively high temperature (Martini 1993), suggests that a large amount of heat from depth is transferred to the meteoric-related hydrothermal aquifer. The O_2/Ar and O_2/Ne ratios (up to 13 and 25,476 respectively) are lower than those of the air-saturated water (ASW; Fig. 4) due to O_2 consumption by redox reactions among gas compounds and during fluid–rock interactions. This further indicates that the atmospheric-related compounds are added to the system as dissolved phases that mix with the ascending hot fluids. The N_2/100-Ar-10×He ternary diagram (Fig. 5), which shows fields for gases associated with basaltic magmatism ("mantle") and convergent plate boundaries ("arc-type") fields (Kita et al. 1993; Giggenbach 1996), shows that the N_2/Ar ratios plot between those of air and ASW, indicating an atmospheric origin for N_2. Helium, however, is supplied by a non-atmospheric (mantle) source, which is supported by the helium isotopic ratio.

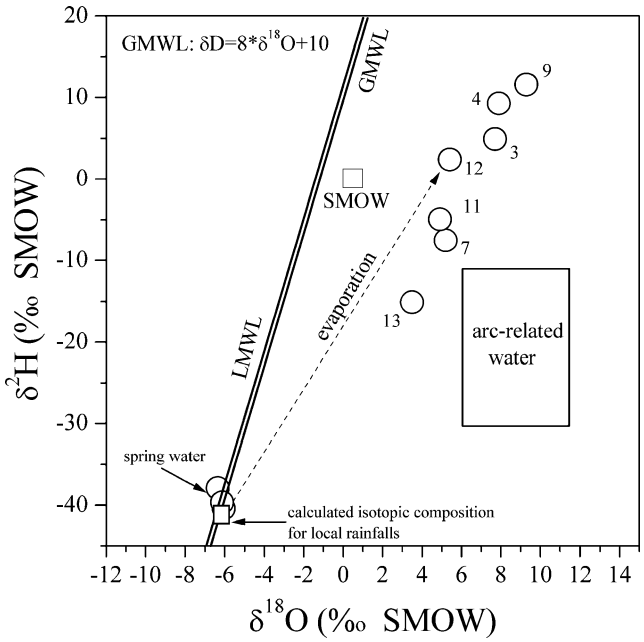

Fig. 2 $\delta^{18}O$–δD diagram for gas and spring water samples from Mombacho volcano. The "arc-related water" field (Taran et al. 1989; Giggenbach 1992), the Local and Global Meteoric Water Lines (LMWL, IAEA 2004 and IAEA/WMO 2004; GMWL, Craig 1961) and the calculated composition (Bowen and Wilkinson 2002) for local precipitation at Mombacho are also shown

The organic gas fraction is minor. However, the relatively high abundances of hydrocarbons of the alkenes group (Fig. 6), which are systematically observed in fumaroles from active volcanic areas (Capaccioni et al. 1995), are considered a feature of gas species produced at medium-to-high temperatures. In particular, the presence of ethane, C_2H_4 (Table 2), whose production is negligible at T <300°C (Capaccioni et al. 2004; Tassi 2004), points to the existence of a high-temperature reservoir.

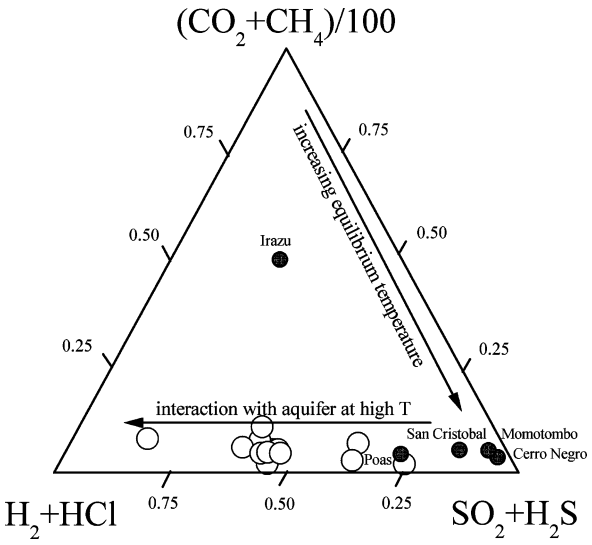

Fig. 3 (SO_2+H_2S)–(CO_2+CH_4)/100–(H_2+HCl) ternary diagram for gas samples from Mombacho volcano (*open circles*). Composition of gas samples from Poas, Irazu, San Cristobal and Momotombo (Martini 1996) and Cerro Negro (Garofalo et al., unpublished data) are also presented

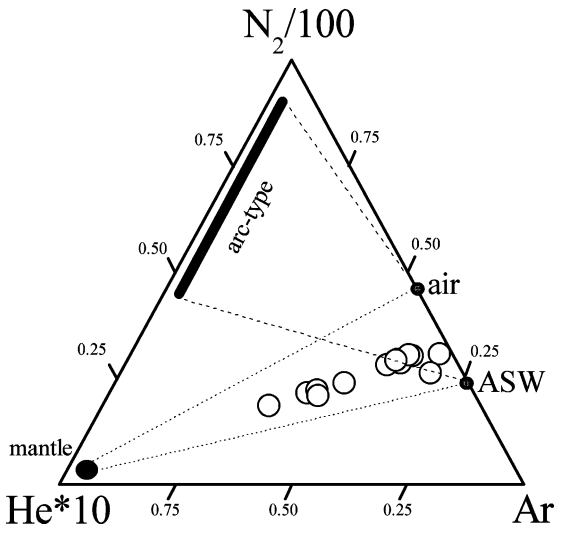

Fig. 5 Ar-N_2/100-He×10 ternary diagram for gas samples from Mombacho volcano. Air and air saturated waters (ASW) compositions, convergent plate boundaries ("arc-type") and "mantle" fields (Giggenbach 1996) are also reported

Geothermometry

The chemical composition of gases provides reliable estimates of temperature conditions acting on fluids at depth. The thermodynamic reaction between the CH_4 and CO_2 redox pair, which is characterized by slow kinetics, may form the basis for a "deep" geothermometer, which is only to a very small extent affected by re-equilibration as the physical-chemical parameters change during fluid upflow (Giggenbach 1987). However, the CH_4/CO_2 ratio depends on gas-liquid separation during secondary boiling and condensation processes, due to the different vapor-liquid partitioning coefficients of CH_4 and CO_2 (Chiodini and Marini 1998) and therefore, the CH_4–CO_2 geothermometer may be strongly affected by the presence of a liquid phase, i.e. a boiling aquifer at a shallow depth. In contrast, since H_2 is characterized by low solubility and Ar is essentially derived from air-saturated water, the H_2–Ar pair may represent a more suitable geothermometer for two-phase hydrothermal systems. Assuming that redox conditions are controlled by the FeO–$FeO_{1.5}$ buffer system

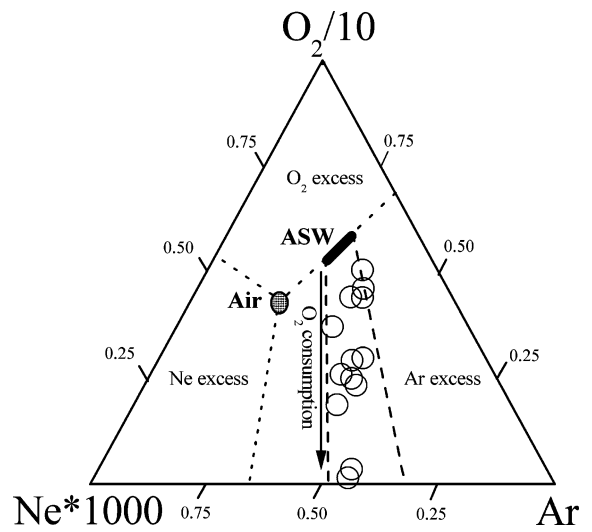

Fig. 4 Ar-O_2/10-Ne×1,000 ternary diagram for gas samples from Mombacho volcano. Air and air saturated waters (ASW) compositions are reported

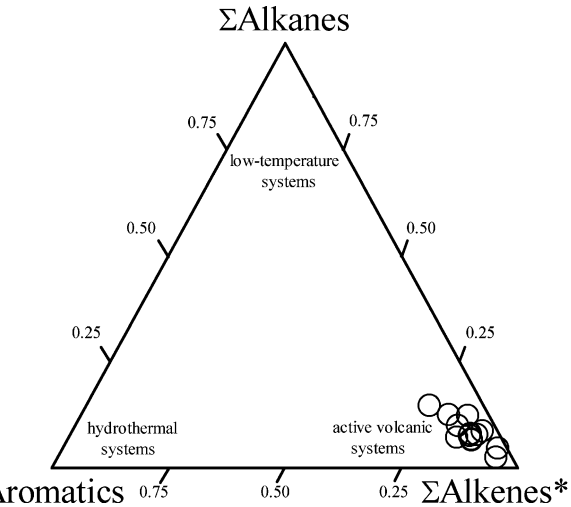

Fig. 6 ΣAlkene×10-ΣAlkanes-ΣAromatics ternary diagram for gas samples from Mombacho volcano. ΣAlkanes is the sum of C_2–C_4 alkanes (CH_4 is not included). The gas fields for low temperature systems, hydrothermal systems and active volcanic systems (Capaccioni et al. 1995) are approximately indicated

(Giggenbach 1987), the temperature dependence of the H_2/Ar ratio is given by (Giggenbach 1991b):

$$T(^{\circ}\mathrm{C}) = 70 \times [2.5 + \log(H_2/\mathrm{Ar})] \quad (1)$$

Equilibrium temperatures for Mombacho gases from Eq. (1) range between 363 and 416°C. Samples no. 2, 3, 4, 11 and 13 were not included in the geothermometric calculation as their relatively high Ar contents (up to 87.25 μmol/mol), are likely a result of contamination by air (Table 1). The calculated temperatures are well above the typical temperature range for a liquid-dominated system (up to 350°C). The H_2–Ar geothermometer refers to the last-attained equilibrium temperatures, since H_2 reacts almost instantaneously to physical-chemical changes (Giggenbach 1987). These high temperatures may be due to the rapid transfer of heat and high-temperature compounds from the deep magmatic-related system to the shallow meteoric aquifer. This mechanism, which is consistent with the presence of the highly soluble compounds (i.e. SO_2) in the gas discharges, may cause H_2 overproduction and, consequently, high H_2–Ar equilibrium temperatures.

The chemical characteristics of the organic gas fraction can provide further insights into the physical-chemical features of the source region of the fumarolic fluids. As shown by the extremely low $CH_4/(C_2H_6+C_3H_8)$ ratios (between 2 and 206), the production of hydrocarbon gas compounds at Mombacho is mainly related to thermogenic processes; any significant contribution of organic gases from bacterial activity can be excluded (e.g. Oremland et al. 1987; Whiticar and Suess 1990). Therefore, the relative abundance of these compounds in the fumarolic discharges reflects the composition established at depth; i.e. under hydrothermal-magmatic conditions. Among the numerous chemical reactions involving light hydrocarbons, the dehydrogenation processes of alkanes to produce their homologous alkenes (i.e. ethane-ethene, propane-propene) are particularly suitable to investigate the thermal and redox conditions of hydrothermal reservoirs in volcanic systems (e.g. Seewald 1994; Capaccioni and Mangani 2001). Moreover, these light hydrocarbon pairs are characterized by similar vapor-liquid distribution coefficients (Lide 2001) and a relatively high chemical inertness. This allows us to neglect the complex effects induced by secondary processes (i.e. phase changes) that affect the H_2–CO_2–CO–CH_4–H_2O system (Tassi et al. 2005b).

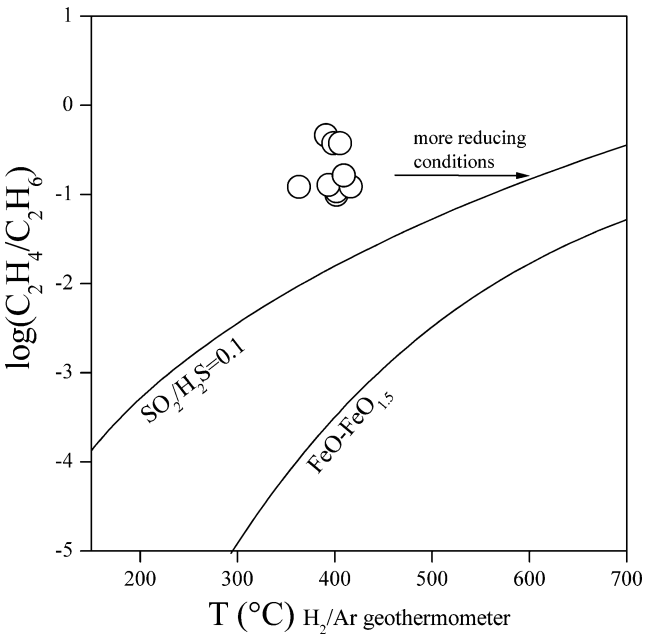

Fig. 7 $\mathrm{Log}(C_2H_4/C_2H_6)$ vs. H_2/Ar-calculated temperature (°C; Chiodini et al. 2001) binary diagram for the Mombacho gas discharges (*open symbols*). *Solid lines* represent the positions of the FeO–$FeO_{1.5}$ and SO_2–H_2S redox buffer systems (Giggenbach 1987)

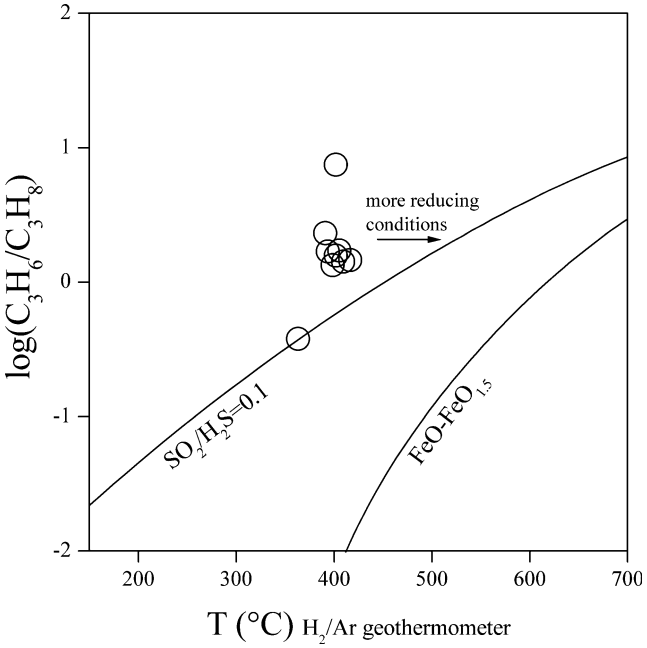

Fig. 8 $\mathrm{Log}(C_3H_6/C_3H_8)$ vs. H_2/Ar-calculated temperature (°C; Chiodini et al. 2001) binary diagram for the Mombacho gas discharges (*open symbols*). *Solid lines* represent the positions of the FeO–$FeO_{1.5}$ and SO_2–H_2S redox buffer systems (Giggenbach 1987)

De-hydrogenation reactions involving the C_2 and C_3 alkene-alkane pairs are given by:

$$C_2H_6 \leftrightarrow C_2H_4 + H_2 \quad (2)$$

and

$$C_3H_8 \leftrightarrow C_3H_6 + H_2 \quad (3)$$

The temperature dependences of the equilibrium constants for these reactions are given by (Capaccioni et al. 2004):

$$7.43 - 7,809/T = \log(C_2H_4/C_2H_6) + \log fH_2 \quad (4)$$

and

$$7.15 - 6,600/T = \log(C_3H_6/C_3H_8) + \log fH_2 \quad (5)$$

Since Eqs. (4) and (5) depend on both $f(H_2)$ and temperature, it is possible to determine $f(H_2)$ and, consequently, the redox conditions governing reaction (2) and (3), by referring to the equilibrium temperatures calculated with the H_2–Ar geothermometer. In the $\log(C_2H_4/C_2H_6)$ vs. H_2–Ar temperature diagram (Fig. 7), the solid lines represent the theoretical equilibrium composition of a gas coexisting with an aqueous phase in a system controlled by the FeO–$FeO_{1.5}$ or the SO_2–H_2S (for SO_2/H_2S=0.1) redox buffer systems. The plot indicates that the Mombacho gases cluster in an area of unrealistic redox oxidizing conditions. More reducing equilibrium conditions would correspond to higher temperatures. The C_3H_6–C_3H_8 pair (Fig. 8) provides similar indications, although the equilibrium, at fixed redox conditions, is apparently achieved at lower temperatures than those of the C_2H_4–C_2H_6 pair. This difference is likely due to the faster kinetics of reaction (3), owing to a lower activation energy (Lide 2001), compared to that of reaction (2), the latter responding more slowly to temperature and pressure changes during the uprising of hot fluids. Such a chemical evolution of ascending fluids within a highly dynamic fluid circulation pathway is considered to typify active volcanic systems (Taran and Giggenbach 2003).

Conclusions

Nicaragua's active volcanoes such as Telica, San Cristobal, Cerro Negro, Masaya and Momotombo, have been the focus of scientific investigation owing to their frequent eruption. Mombacho is currently considered an extinct volcano, and has therefore received much less attention. Although the recent history of this volcano testifies that gravitational events are the most probable hazard, the chemical and isotopic gas composition data presented here suggest that eruptive activity could resume. The presence of high-temperature compounds in fumaroles, whose outlet temperatures do not exceed 121°C, is consistent with a mantle helium and carbon isotopic signature. The fumarolic system reflects a balance between hot fluids, related to an active magmatic system, and a shallow, water-dominated environment fed by meteoric waters. A perturbation such as an increase in the heat input from depth, variation in the water table thickness, regional seismic events, etc., could modify this balance and, consequently, lead to an eruption.

This geochemical study of the Mombacho fumarolic field is a starting-point for a medium- to long-term geochemical monitoring program, which, coupled with seismic and GPS measurements, is a reliable method by which to evaluate the short-term evolution of magmatic activity at Mombacho. Mombacho volcano should be included among the potentially dangerous volcanoes of Nicaragua and fully considered when planning scientific programs devoted to the mitigation of volcanic hazards.

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