Origin, composition and evolution of fumarolic fluids of subduction zone volcanoes in Nicaragua

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Der Dekan

Hiermit erkläre ich, dass die vorliegende Abhandlung, abgesehen von der Beratung durch meine akademischen Lehrer, nach Inhalt und Form meine eigene Arbeit darstellt. Ferner habe ich weder diese noch eine ähnliche Arbeit an einer anderen Abteilung oder Hochschule im Rahmen eines Prüfungsverfahrens vorgelegt.

Kristin Garofalo

Preface

This thesis comprises three independent manuscripts that are prepared for submission to international journals. They may therefore be subject to revision. Each publication contains its own abstract, introduction, sampling and analytical methods description, data presentation, discussion, conclusion, and reference list.

The three papers are:

The fumarolic gas discharges at Mombacho Volcano (Nicaragua): presence of magmatic gas species and implications for a volcanic surveillance. In revision for publication in *Bulletin of Volcanology*
K. Garofalo, F. Tassi, O. Vaselli, A. Delgado-Huertas, M. Frische, T.H. Hansteen, D. Tedesco, R.J. Poreda, W. Strauch

Past and present chemical and isotopic composition of high temperature fumarolic gases of Momotombo volcano, Nicaragua. To be submitted to *Journal of Volcanology and Geothermal Research*
K. Garofalo, F. Tassi, O. Vaselli, A. Delgado-Huertas, M. Frische, T.H. Hansteen, D. Tedesco, R.J. Poreda

Geochemistry and flux estimation of magma-derived volatile trace elements from the high-temperature fumarolic field of Momotombo volcano (Nicaragua). To be submitted to *Journal of Volcanology and Geothermal Research*
K. Garofalo, F. Tassi , O. Vaselli, M. Frische, T.H. Hansteen, D. Garbe-Schönberg

For these publications I carried out four field campaigns in Nicaragua with durations between three and five weeks, including extensive sampling. I conducted measurement campaigns for wet chemical and stable isotopes analysis (δ^{18}O-δD-H_2O, δ^{13}C-CO_2) processed and interpreted the data and prepared the manuscripts. This thesis is focussed on the chemistry and stable isotope composition of fumarolic emissions.

In addition to the work presented in this thesis, I contributed to the following publications:

1. M. Frische, K. Garofalo, T.H. Hansteen, R. Borchers, J. Harnisch (2006) A volcanic contribution of stable halogenated compounds? *Environmental Science and Pollution Research, 8pp.* DOI: http://dx.doi.org/10.1065/espr2006.01.291

2. M. Frische, K. Garofalo, T.H. Hansteen, R. Borchers (2006) Fluxes and origin of halogenated trace gases from Momotombo volcano (Nicaragua). *Geochemistry Geophysics Geosystems* in press

3. M. Frische, K. Garofalo, T.H. Hansteen, R. Borchers. Variations of alkylhalide emissions from fumaroles in Nicaragua: Dynamics of quiescent degassing volcanoes. Submitted to *Geophysical Research Letters*

4. K. Garofalo, T.H. Hansteen, M. Frische, F. Tassi, O. Vaselli, W. Strauch (2004) Geochemical and isotopic study of fumarolic emissions from three Nicaraguan Volcanoes. IAVCEI General Assembly in Pucon, Chile, abs vol

5. K. Garofalo, T.H. Hansteen, M. Frische, F. Tassi, O. Vaselli, W. Strauch (2003) Geochemical and isotopic study of fumarolic emissions from three Nicaraguan Volcanoes. IAVCEI 8th Field Workshop Volcanic Gases, abs vol

6. B. Galle, T.H. Hansteen, M. Frische, K. Garofalo, W. Strauch (2003) An estimate of the SO_2 emissions from four volcanoes in Nicaragua, made using mini-DOAS spectroscopy. IAVCEI 8th Field Workshop Volcanic Gases, abs vol

Zusammenfassung

Das Hauptaugenmerk dieser Doktorarbeit ist die von Fumarolen freigesetzten Volatile und Gase still und passiv entgasender Vulkane. Ziel während vier Geländekampagnen und wiederholter Beprobung fumarolischer Gase der nicaraguanischen Vulkane Mombacho und Momotombo war es, ein besseres Verständnis der Prozesse, die innerhalb ihrer Vulkan-Magma-Systeme auftreten, zu erlangen.

Mombacho ist ein wenig untersuchter, stark zerklüfteter Stratovulkan. Nachdem er in den letzten Jahrhundertern nicht eruptierte, gilt Mombacho im Allgemeinen als erloschen. Diese Arbeit stellt die erste umfassende Studie über fumarolische Gase von Mombacho dar. Die auftretenden fumarolischen Emissionen beinhalten sauere Gas-Spezies wie SO_2, HCl und HF. Des weiteren treten verhältnismäßig hohe Gehalte an H_2 auf, was sehr ungewöhnlich für solch Niedrigtemperatur Austritte ist. Außerdem impliziert das Verhältnis von $^3He/^4He$ (7.62Ra) Werte, die mit dem Mantel in Verbindung gebracht werden können. Die Isotopen Zusammensetzung des Wasserdampfs ($\delta^{18}O$-δD-H_2O) weißt zudem auf Interaktionen mit einem flachen meteorischen Aquifer hin. Die Kombination von chemischen und isotopischen Daten bringen deshalb den Beweis für Hochtemperatur Bedingungen im flachen Untergrund. Dies wiederum bedeutet, das der Vulkan Mombacho nicht als erloschen bezeichnet werden kann und das die Möglichkeit besteht, daß er in Zukunft wieder aktiv wird und eruptieren könnte.

Momotombo auf der anderen Seite ist ein aktiver Vulkan im Vulkanbogen von Nicaragua. Er ist durchgehend fumarolisch aktiv seit seiner letzten Eruption im Jahr 1905 und setzt Gase mit hohen Temperaturen frei. Die hohe Austrittstemperatur von über 776°C geht auf ein flachen magmatischen Körper innerhalb des Vulkangebäudes zurück. Die ausgetretenen Gase zwischen 2002 und 2003 waren reich an CO_2- und SO_2 und weisen $^3He/^4He$- (6.29-5.44Ra) und $\delta^{13}C$-CO_2 (-2.63 to -3.24‰ V-PDB) - Werte auf, die mit Inselbogen-Mantel assoziiert sind, sowie $\delta^{18}O$-δD-H_2O- und $\delta^{34}S$-SO_2 (6.3-7.1‰ V-CDT) - Signaturen aus dem magmatischen Inselbogen. Die Charakteristik dieser chemischen und isotopischen Daten deuten auf Fluid Separation aus einer relativ unentgasten Magmafraktion hin. Die Änderung der Chemie und Isotopie der Gase zwischen März 2002 und Juli 2003 weisen auf die Öffnung tiefliegender Wegbarkeiten hin, welche das Entgasen tief sitzender magmatischer Quellen erleichtert. Die chemische und isotopische Zusammensetzung der Gase von Momotombo hat sich zusätzlich noch über die letzten 20 Jahre wesentlich verändert. Die Unterschiede zwischen der Gasfreisetzung 2002-2003 und in den achtziger Jahren letzten Jahrhunderts

scheint auf das Entgasen verschiedener Magmaschübe (nicht entgast gegen entgast) und gravierenden Änderungen in den Interaktionen zwischen magmatischem und hydrothermalem System zurückzuführen zu sein. Im Einzelnen haben hydrothermale Fluide sehr stark zu der Zusammensetzung der 80er Jahre Gase beigetragen, während in 2002-2003 keine nachweisliche Wechselwirkung zwischen dem magmatischen und hydrothermalen System stattfand. Die magmatischen Gase von 2002-2003 wurden nur durch flache meteorische Verdünnung beeinflußt, welche von der Menge des saisonalen Niederschlages abhängig ist. Diese herausgearbeiteten Unterschiede weisen auf grundsätzliche Änderungen in den Wechselwirkungen zwischen dem magmatischen und hydrothermalen System irgendwann zwischen den späten 80er Jahren und 2002 hin. Dies könnte auf das Austrocknen des hydrothermalen Systems oder auf seine hydrologische Isolierung vom Hauptmagmakörper, welcher die Fumarolen im zentralen Krater speist, zurückzuführen sein.

Spurenelement-Konzentrationen in den Emissionen von Momotombo zeigen ihre komplexe Abhängigkeit von magmatischer Gaschemie, Emissionstemperatur, Verdünnungseffekten, Gas-Säure-Gesteins Wechselwirkungen, und chemische sowie physikalische Prozessen während des Gasaufstiegs. Das beobachtete starke Auftreten von Tl, Bi, As, Se, Mo, Sb, Hg, Au, W, Pb, Cd, Sn in den Gas-Austritten spiegelt wahrscheinlich den magmatischen Ursprung der fumarolischen Gase des Vulkans Momotombo wieder. Abschätzungen für Flüsse einiger dieser hochvolatilen und potentiell gefährlichen Spurenmetalle magmatischen Ursprungs zeigen, das Momotombo nur eine unwichtige Quelle für Verunreinigungen der Atmosphäre darstellt.

Zusammenfassend kann man feststellen, das diese Arbeit bewiesen hat, das die kombinierte Analyse von chemischen und isotopischen Signaturen fumarolischer Gasemissionen ein gewichtiges Werkzeug ist um die komplexen Prozesse innerhalb passive entgasender Vulkane zu entschlüsseln und die Bedeutung vulkanischer Gasfreisetzung in die Atmosphäre zu erforschen.

Abstract

Volatiles and gases discharged from fumaroles at passively degassing volcanoes are the focus of this thesis. During four field campaigns, fumarolic gases from the two Nicaraguan volcanoes Mombacho and Momotombo were repeatedly collected with the objective of gaining a better understanding of processes occurring within their volcano-magma-systems.

Mombacho is a poorly studied, highly dissected stratocone volcano that is generally considered extinct because it has not erupted during the last centuries. This study represents the first comprehensive fumarolic gas study of Mombacho. The fumarolic emissions contain acid gas species like SO_2, HCl, and HF and comparatively high amounts of H_2, which are unusual for such low temperature (<120ºC) discharges. The $^3He/^4He$ ratio (7.62Ra) indicates mantle-related values. The isotopic composition of water vapor ($\delta^{18}O$-δD-H_2O) indicates interaction with a shallow meteoric–aquifer. The combined chemical and isotopic data thus provide evidence for high-temperature conditions in the shallow subsurface. This suggests that Mombacho volcano should not be considered extinct, and could re-awaken and erupt in the future.

Momotombo is an active volcano of the Nicaraguan volcanic arc. It is in a persistent state of fumarolic activity since its last eruption in 1905 and discharges gases at high temperatures. The high emission temperatures of up to 776ºC result from a shallow magmatic body within the volcanic edifice. The gases venting in 2002-2003 were CO_2- and SO_2-rich and show arc-mantle $^3He/^4He$ (6.29-5.44Ra) and $\delta^{13}C$-CO_2 (-2.63 to -3.24‰ V-PDB) values and arc-magmatic $\delta^{18}O$-δD-H_2O and $\delta^{34}S$-SO_2 (6.3-7.1‰ V-CDT) signatures. These chemical and isotopic characteristics indicate fluid separation from relatively undegassed magma batches. A change in chemistry and isotopic composition of the gases between March 2002 and July 2003 indicates the opening of deep pathways that favor the degassing of a deeper-sited magmatic source. The chemistry and isotopic compositions of the gases at Momotombo have additionally changed considerably over the last 20 years. The differences between gas emissions in 2002-2003 and in the 1980s appear to be related to degassing of different magma batches (undegassed vs degassed) and major changes in the interaction between the magmatic and hydrothermal systems. In particular, hydrothermal fluids were contributing strongly to the '80s gases, while in 2002-2003 no evident interaction occurred between the magmatic and the hydrothermal systems. The 2002-2003 magmatic gases were only affected by shallow meteoric dilution, which depends on the amount of seasonal precipitation. These differences point to major changes in the type of interaction between the magmatic and the hydrothermal

systems sometime between the late ‘80s and 2002, and could indicate a dry-out of the hydrothermal system, or its hydrological isolation from the main magmatic body sustaining the central crater fumaroles.

Trace element concentrations in Momotombo emissions reflect their complex dependence on magmatic gas chemistry, emission temperatures, dilution processes, gas-acid-rock interaction, and chemical and physical processes during gas ascent. The observed high abundances of Tl, Bi, As, Se, Mo, Sb, Hg, Au, W, Pb, Cd, Sn in the gas emissions probably reflect their magmatic origin in the fumarolic gases at Momotombo. Flux estimates for some of these highly volatile and potentially harmful trace metals of magmatic origin show that Momotombo is only a minor source of pollutants in the atmosphere.

In conclusion, the combined analysis of chemical and isotopic signatures of fumarolic gas emissions has proven to be a powerful tool for deciphering the complex processes inside passively degassing volcanoes and for exploring the importance of volcanic discharges into the atmosphere

Contents

Chapter 4 **58**

- Geochemistry and flux estimation of magma-derived volatile trace elements from the high-temperature fumarolic field of Momotombo volcano (Nicaragua)-

Chapter 1

General Introduction

1.1 Introduction

Subduction zones are the sites where oceanic lithosphere, together with oceanic sediments and porewater is transferred into the mantle and partly recycled to the surface through arc volcanism. Volatiles play a key role in the origin of arc volcanism, as they are transferred from the subducting slab to the mantle wedge, inducing melting of mantle peridotite. The volatile content of the magmas determine the style of activity (e.g. explosiveness of eruptions) and the type of material erupted at arc volcanoes. During explosive eruptions the released volatiles and fine-grained material may be injected into the stratosphere and influence its chemistry. However, smaller eruptions and passive degassing are by far more frequent in the lifetime of a volcano. Several recent studies indicate that large amounts of volatiles are released during non-eruptive periods, in continuous quiescent phases of magma degassing. The gas release can occur by advection through open craters, fractures, or via diffuse degassing through large areas of permeable ground.

Degassing can be either a pre-eruptive, eruptive or a post-eruptive phenomenon and be prolonged in time. In either way, volcanoes discharge large amounts of acid gases and potentially harmful metals into the surrounding environment and into the troposphere.

Three distinctive modes of degassing can be detected at the surface: open vent degassing, soil degassing and fumarolic degassing. Open vent degassing implies that the volcanic system is open and in direct contact with the atmosphere. In this case it is possible that magma is present in the volcanic conduit, and emissions of volcanic gas plumes are frequent. The gas plume is transported in the prevailing wind direction, and gradually diffuses into the surrounding atmosphere, where the local atmospheric circulation controls its further behavior. Such emissions are mostly studied by optical remote sensing techniques (COSPEC, OP-FTIR, Mini-DOAS) or passive impregnated filter packs (e.g. McGonigle and Oppenheimer 2003). Reliable results can generally be obtained for species like SO_2 that do not have high atmospheric background values. The ratios between SO_2 and other major components in the gas phase can be measured with FTIR. Extensive studies of open vent degassing have been conducted at many volcanoes, and continuous monitoring of plume emissions have shown variations that correlate with changes in volcanic and earthquake activity.

Soil degassing is a diffuse type of emission that mostly occurs through the volcano flanks, where the porosities are comparatively elevated. CO_2, He, H_2 and Rn are the common gases studied by this method, since they are relatively little affected by adsorption by water circulating in the system and usually have low background contents in the atmosphere and aerated soil zone.

Fumaroles are punctual emission sources of gas and occur along fissures in the ground through which gases escape to the surface. Extensive fumarole fields generally develop where the magmatic conduit is sealed. Fumaroles allow for the direct measurement of the physical (e.g. temperature, total gas flux) and chemical parameters of the emissions (e.g. Symonds et al. 1993). So far it is only possible to determine the bulk chemistry and isotopic characteristics of the volcanic emissions through the direct collection of fumarolic fluids. The gases, having the dynamic nature of fluids, respond rapidly to changes in the volcano-magma-system and thus provide an important tool for monitoring volcanic activity. Understanding the origin and behavior of volatiles in arc volcanism can therefore provide important insights into recycling processes operating in subduction zones and into the interaction between volcanoes and the surrounding systems (crust, hydrosphere, atmosphere).

1.2 Study area

Nicaragua has an area of 129,494 km^2 and is thus the largest country in Central America, extending 490 km E-W and 470 km N-S at its widest points. Nicaragua is divided into three major regions: the Pacific coast, the Central Highlands - a cooler highland plateau in the center of the country that is crossed by mountain ranges - and the Nicaraguan Depression, a stretch of low-lying hot land, between the Central Highlands and the Pacific Costal Plain. The Nicaraguan Depression is a 50-km-wide SE-NW-trending fault-bounded depression, extending from El Salvador to the Caribbean cost of Costa Rica (Weyl 1980) whose origin has been long debated (e.g. McBirney and Williams 1965; Weinberg 1992). The Nicaraguan Depression hosts the active volcanic front (Cordillera los Marrabios) and the two major lakes of the country (lake Nicaragua and lake Managua). This fertile ground is the site of most major Nicaraguan cities, including Managua, Leon and Granada.

1.2.2 The Quaternary volcanism of the Cordillera de los Marrabios

The present volcanism of Nicaragua results from the subduction of the Cocos Plate beneath the Caribbean Plate along the Middle America trench at a rate of ~8cm/yr (e.g. DeMets 2001). The Cocos plate descends northeastwardly underneath the Pacific margin of Nicaragua at an angle of about 80º (Protti at al. 1995), reaching a depth of 200 km beneath the active volcanic chain 150-190 Km away from the trench (Hernandez et al. 1994).

The Nicaraguan volcanic belt consists of 18 main volcanic centres, many of them active, spaced ~25 km apart from each other (Stoiber et al. 1986). The chain of volcanoes extends through the country along the western edge of the Nicarguan Depression, reaching its highest point of 1,745 m a.s.l. at San Cristobal volcano. The volcanic chain is characterized by an alignment of stratocone and shield volcanoes and ignimbrite complexes that represent the youngest structural surfaces located within the Nicaragua Depression.

1.3 Scope and organization of the thesis

The goal of this thesis is to provide a better understanding of the processes occurring inside selected volcano-magma-systems and to assess the importance of quiescent volcanic degassing as a source of pollutants in the atmosphere. The thesis is divided into three chapters that have been written as stand-alone scientific papers. The first paper is currently in review at *Bulletin of Volcanology*. In this paper fumarolic gases are analyzed in order to assess the current activity state of Mombacho volcano. A clear magmatic chemical signature is found in the emissions that may suggest a re-awakening of Mombacho. The second paper will be submitted to *Journal of Volcanology and Geothermal research*. In this paper fumarolic gases from Momotombo volcano are analyzed for their major components and stable isotopic signature. A comparison of these new data with older data from the 1980s reveals major changes in the volcano-magma-system. Most prominently, a dry-out of the hydrothermal system and repeated input of volatiles from fresh magma batches probably occurred between the 1980s and 2002, and between February 2003 and July 2003. The third paper will also be submitted to *Journal of Volcanology and Geothermal research*. This paper concerns trace element geochemistry, explores trace metal discharges from Momotombo volcano and evaluates the influence of seasonal changes on fumarole chemistry. Furthermore, flux estimates of potentially harmful compounds of magmatic origin are determined.

References

DeMets C (2001) A new estimate for present-day Cocos-Caribbean plate motion: Implications for slip along the Central American volcanic arc. Geophys Res Lett 28: 4043-4046

Hernandez Z, Atakan K, Havskov J (1994) Seismicity and tectonics near Managua, Nicaragua, in Report 1-16. Reduction of Natural Disasters in Central America Establishment of Local and Regional Data Centers: CEPREDENAC/Institute of Solid Earth Physics, Bergen, Norway.

McGonigle AJS, Oppenheimer C (2003) Optical sensing of volcanic gas and aerosol emissions. In Oppenheimer C, Pyle DM, Barclay J (eds) Volcanic Degassing. Geol Soc Spec Publ 213: 149-168

McBirney AR, Williams H (1965) Volcanic history of Nicaragua. Berkeley and Los Angeles, University of California press, pp 1-65

Protti M, Guendel F, McNally K (1995) Correlation between the age of the subducting Cocos plate and the geometry of the Wadati-Benioff zone under Nicaragua and Costa Rica. In Mann P (eds) Geologic and Tectonic Development of the Caribbean Plate Boundary in Southern Central America. Geol Soc Am, Boulder, CO. 309–326

Stoiber RE, Williams S and Huebert BJ (1986) Sulfur and halogen gases at Masaya caldera complex, Nicaragua: total flux and variations with time. J Geophys Res 91: 12,215- 12,231

Symonds RB, Rose WI, Bluth GJS, Gerlach TM (1993) Volcanic gas studies: Methods, results and applications. In: Carroll MR, Holloway JR (eds) Volatiles in Magmas. Rev Mineral 30: 1-66

Weinberg RF (1992) Neotectonic development of Nicaragua. Tectonics 11: 1010 –1017

Weyl R (1980) Geology of Central America. Berlin, Borntreager, 371 pp

Chapter 2

The fumarolic gas discharges at Mombacho Volcano (Nicaragua): presence of magmatic gas species and implications for a volcanic surveillance

The fumarolic gas discharges at Mombacho Volcano (Nicaragua): presence of magmatic gas species and implications for a volcanic surveillance

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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 works carried out in 2002, 2003 and 2005 highlight the presence of high-temperature components (e.g. SO_2, HCl and HF), ongoing for significant contribution of juvenile magmatic fluids to the hydrothermal system feeding the gas discharges. This is strongly supported by the mantle-related helium and carbon isotopic signatures, although the latter is partly masked by either a sedimentary subduction-related or a shallow carbonatic component. The observed chemical and isotopic composition of the Mombacho fluids, that are in agreement with the geophysical data, recorded in the region, 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. Therefore, a systematic geochemical monitoring of the fumarolic gas discharges, coupled with an adequate seismic and ground deformation network, is highly recommended to assess the possible onset of a new eruptive phase.

Keywords: *Nicaragua - Mombacho volcano - Fumarolic gases - Geochemical monitoring - Fluid geochemistry - Isotope geochemistry*

2.1 Introduction

Assessing the potential volcanic hazard, in terms of risk mitigation for expected losses (such as lives, properties, goods and so forth) in a given area and in a specific given period, generally requires long-time monitoring programs. The precursors of eruptive events are still poorly known, since several causes may be responsible, including movements of deep-seated magmas, tectonic activity producing crustal deformation and unloading of the magmatic system due to mass wasting (e.g. 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 may be regarded as a useful tool to assess the state of any volcanic system.

Mombacho volcano (Nicaragua) is located close to the city of Granada surrounded by several small villages. It represents a realistic threat to more than 90,000 people, in relation to two possible types of hazards: i) debris avalanches and lahars originating from a fragile sector of the volcanic edifice (Wyk de Vries and Francis 1997; Vallance et al. 2001) and ii) eruptive events. This volcanic system is characterized by a persistent fumarolic activity, however, by considering that no eruptions are supposed to have occurred in historical times, a resumption of eruptive activity at Mombacho has been considered unlikely (van Wyk de Vries and Francis 1997; Havlíèek et al. 1998;

Vallance et al. 2001). Although several maps of the area were produced (Hradecky 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, still lacks.

In this study, based on five sampling campaigns carried out in 2002, 2003 and 2005 we point out that 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 shows clear evidences that this volcanic system cannot be considered extinct. For this reason, we focus our study to i) investigate on the physical-chemical conditions acting on the deep fluid reservoirs and ii) evaluate the usefulness of the geochemical parameters for a more intense monitoring program to assess the Mombacho's state of activity.

2.2 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/yr (De Mets 2001; La Femina et al. 2002) at an angle of about 80º (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, Leon 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 a.s.l.) is a basaltic-andesitic stratocone volcano located in the south-western edge of the Nicaraguan Depression (Fig. 1a). It is built upon a wide base of subsidiary cones and it is built onto the Quaternary ignimbrites erupted from the Las Sierras Caldera surrounding Masaya volcano (Las Sierras Formation) and the Tertiary igneous and sedimentary rocks (van Wyk de Vries 1993; van Wyk de Vries and Francis 1997). Volcanic activity at Mombacho was characterized by numerous lava flows (related to andesite to basaltic andesite and minor basalts) and explosive events producing pyroclastic flows and ash-fall deposits (Hradecky 1988; Havlíèek et al. 1998). On the other hand, Mombacho volcanic edifice has experienced at least three voluminous debris avalanche episodes. The first failure occurred between 20,000 and 1,000 years ago. It affected the South-eastern sector of the volcanic edifice and it 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; van Wyk de Vries and Francis 1997) completely destroyed the South side of the edifice in 1570 A.D., producing a debris avalanche that covered the indigenous village of Mombacho and killed 400 people (Incer 1995; van Wyk de Vries and Francis 1997; Vallance et al. 2001). During the 1570 A.D. collapse, a horseshoe shape crater (1.5 km wide and 700 m deep) was formed (van Wyk de Vries and Francis 1997) and presently comprises a relatively wide fumarolic field.

2.3 Sampling procedures and analytical methods

2.3.1 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 some tens of square meters within the SE crater (Fig. 1b). Low-flux fumarolic emissions and steaming grounds are also recognizable on the N-NE flank of the volcano (Fig. 1b), especially after heavy rains. Gas samplings were performed during five field campaigns: i) mid of November 2002 (beginning of the dry season), ii) end of November 2002, iii) March-April 2003 (middle of the dry season), iv) July 2003 (end of the dry/ beginning of the rainy season) and v) March-April 2005 (middle of the dry season). In addition to gas samples, in April 2005 two cold water springs (T = 20°C and 27°C) seeping out at

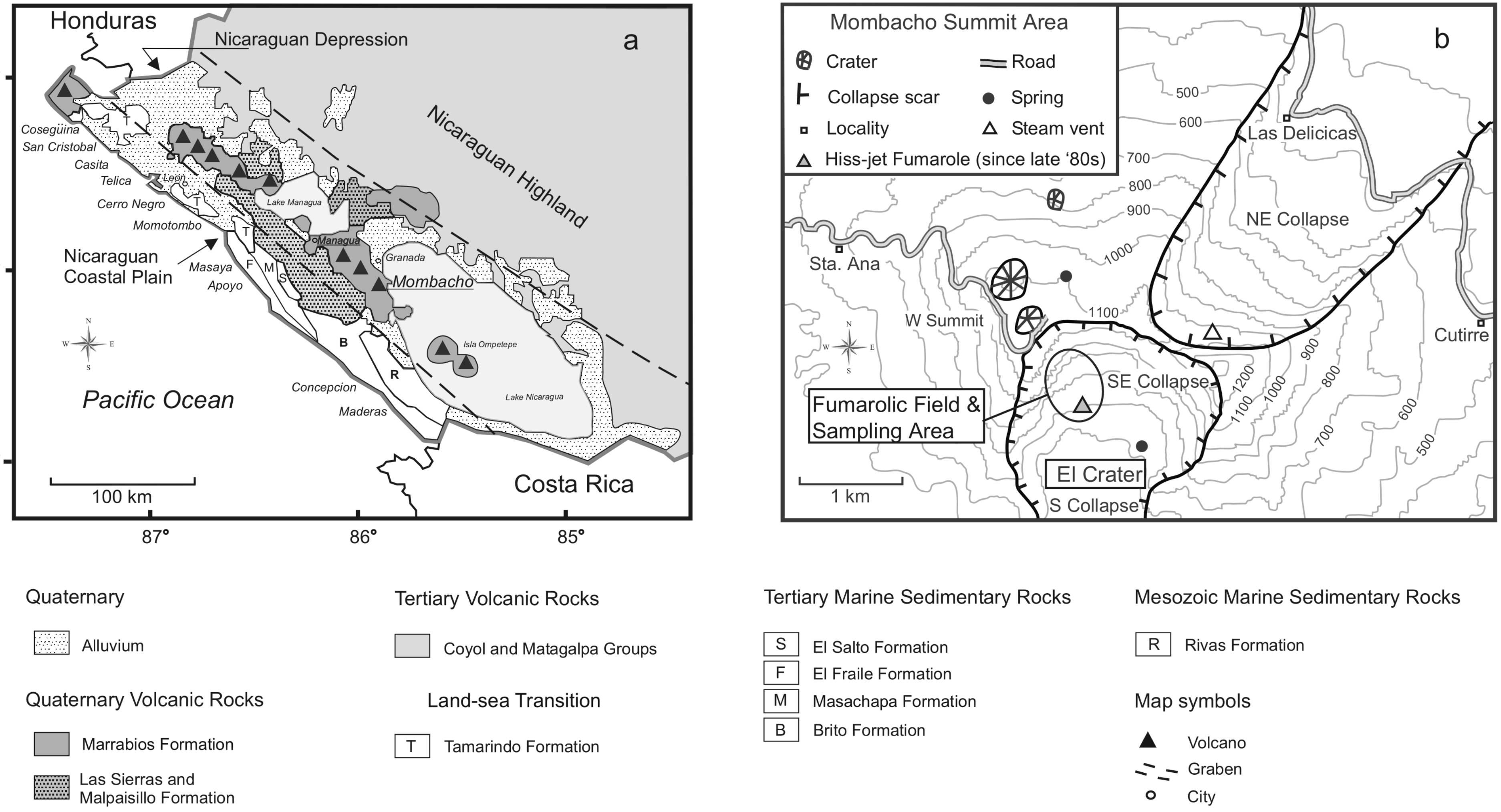

Fig. 1 a) Schematic geological map of Nicaragua (modified after Van Wyk de Vries 1993) and **b)** location of the fumarolic field on the summit area of Mombacho volcano (modified after Wyk de Vries and Hernandez 1994) the top of the volcano and a thermal spring (T = 41°C) located in the southern collapse crater (Fig. 1b) were sampled for oxygen and hydrogen isotopic analysis. Gases were collected at four sampling sites: i) F1 fumarole (85°58.476' N, 11°49.875' W NAD27 central coordinates; 689 m a.s.l.), characterized by a relatively constant outlet temperature (ca. 120°C) during the whole sampling period; ii) F2 fumarole (85°58.477' N, 11°49.875' W NAD27 central coordinates; 689 m a.s.l.), a recently (late eighties) born hiss-jet gas discharge (Global Volcanism Program: SEAN Bulletin 1980, 1982, 1988; BGVN 1991, 1994) that has an outlet temperature similar to that of the F1 fumarole; iii) BP1 and iv) BP2 boiling pools, located a few meters from the F1 fumarole. It is worthy to note that in 2002 the gas flux of F2 fumarole was particularly strong, which made difficult to collect samples. Conversely, in 2003 and 2005, the gas flow rate had significantly decreased.

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: i) $\delta^{13}C\text{-}CO_2$ values by 50 mL pre-evacuated flasks, ii) $^{3}He/^{4}He$, $^{40}Ar/^{36}Ar$ and $^{4}He/^{20}Ne$ isotopic ratios by a pre-evacuated 100 mL glass flask filled with 40 mL of a 4N NaOH solution and iii) HF content and $\delta^{18}O$- and $\delta D\text{-}H_2O$ values by condensation with a quartz-glass water-cooled condenser.

2.3.2 Gas chemical analysis

The inorganic residual gases were analyzed by a gas-chromatograph (Shimadzu 15a) with a thermal conductivity detector (TCD). Methane and light hydrocarbons were analyzed with a Shimadzu 14a gas-chromatograph with a Flame Ionization Detector (FID). CO was converted to CH_4 at 400 °C, by using a Shimadzu MTN-1 methanizer (Tassi 2004), and analyzed by gas-chromatography (FID detector). Following the analysis of the residual gases, the alkaline solution was centrifuged in order to separate the solid precipitate. The supernatant was used for: i) CO_3^{2-} analysis (for CO_2 content) by titration with 0.5N HCl solution; ii) SO_4^{2-} analysis, after oxidation with H_2O_2 (for SO_2 content), by ion-chromatography (Dionex DX100); iii) 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 analyzed 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.

2.3.3 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 analyzed 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%.

2.4 Chemical and isotopic composition of gases

2.4.1 Gas chemistry

The chemical composition of the gas discharges studied during this work is reported in Table 1 and Table 2. Steam is always the main component with contents 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 variable amounts of SO_2 (6–7,800 μmol/mol), HCl (2-240 μmol/mol) and HF (up to 5 μmol/mol) are worthy of note, as they are 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 incondensable gases, whereas 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, have also been detected (Table 2). Setting aside samples # 4 and 13, likely to be 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.

2.4.2 Carbon, oxygen, hydrogen and noble gas isotopic composition

The $\delta^{13}C$-CO_2 values and those of $\delta^{18}O$ and δD in water vapour are listed in Table 1, together with the $^{40}Ar/^{36}Ar$, $^{4}He/^{20}Ne$, $^{20}Ne/^{36}Ar$ and R/Ra (R=$^{3}He/^{4}He_{sample}$ and Ra=$^{3}He/^{4}He_{air}$, the latter being 1.39*10^{6}; Mamyrin and Tolstikhin 1984) ratios. The $\delta^{13}C$-CO_2 values, determined on selected samples, are between 0.67 and 1.83 ‰ V-PDB, that are commonly ascribed to CO_2 production by thermometamorphic processes of marine carbonate rocks (e.g. Rollinson 1993).

The values of $\delta^{18}O$ and δD ratios in fumarolic condensates vary 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 $\delta^{2}H$ (-40.4, -39.7 and -37.9 ‰ V-SMOW) values are consistent with those calculated by using the relationship that links the isotopic composition of precipitation to their latitude

Table 1. Outlet temperatures (in °C) and chemical and isotopic composition of the fumarolic discharges from Mombacho volcano. 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 fumarolic samples; n.d. – not detected

#	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-'02	120.6	8815	26.61	n.d.	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-'02	119.2	24616	1.814	n.d.	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-'02	115.6	28826	2.239	n.d.	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-'02	119.6	36702	4.305	n.d.	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-'02	119.6	26566	2.339	n.d.	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-'02	116.0	24172	239.2	n.d.	7881	1095	0.341	963896	94.91	0.219	1.955	13.66	0.0014	2605	0.041	0.002							
7	F1	Mar-'03	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-'03	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-'03	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-'03	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-'03	118.4	163171	10.70	n.d.	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-'03	118.0	56149	56.70	n.d.	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-'05	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

Table 2. Light hydrocarbon compositions (μmol/mol) of the fumarolic discharges from Mombacho volcano. n.d. – not detected

#	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-'02	120.6	0.00653	0.00065	0.00196	0.00310	n.d.	0.00243	0.00310	0.00745
2	F1	mid Nov-'02	119.2	0.00356	0.00044	0.00083	0.00146	n.d.	n.d.	0.01392	0.00566
3	F2	mid Nov-'02	115.6	0.00819	0.00139	0.00339	0.00357	n.d.	n.d.	0.00779	0.00970
4	F1	end Nov-'02	119.6	0.00759	n.d.	n.d.	0.00595	n.d.	n.d.	0.00282	0.01002
5	F1	end Nov-'02	119.6	0.00764	0.00083	0.00190	0.01419	n.d.	n.d.	0.00361	0.00403
6	F2	end Nov-'02	116.0	0.00744	0.00095	0.00166	0.00280	n.d.	n.d.	0.00809	0.00902
7	F1	Mar-'03	115.0	0.00086	0.00010	0.00055	0.00021	0.00070	n.d.	0.00203	0.00130
8	F2	Mar-'03	118.0	0.00727	0.00089	0.00326	0.00477	0.00140	0.00217	0.00586	0.01109
9	BP1	Mar-'03	94.2	0.06866	0.03179	0.00395	0.00913	0.00423	0.00310	0.03890	0.02937
10	BP2	Mar-'03	93.7	0.07959	0.02986	0.00859	0.01148	0.00369	0.00302	0.02201	0.03490
11	F2	Apr-'03	118.4	0.04833	0.00794	0.01676	0.02381	n.d.	n.d.	0.05097	0.06191
12	F1	Jul-'03	118.0	0.00086	0.00032	0.00022	0.00038	n.d.	n.d.	0.00044	0.00082
13	F1	Apr-'05	116.4	0.00167	0.00018	0.00069	0.00109	0.000279	0.00033	0.00021	0.00235

and altitude (Bowen and Wilkinson 2002), i.e. $\delta^{18}O$=-6.5 ‰ and $\delta^{2}H$=-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 seem also to exclude any significant contribution of "arc-related water" (Taran et al. 1989; Giggenbach 1992) related to the magmatic source. Thus, the enrichment of both ^{18}O and ^{2}H (Fig. 2) is likely to be due to evaporative fractionation of locally heated meteoric water, which strongly contributes to Mombacho fumarolic discharges.

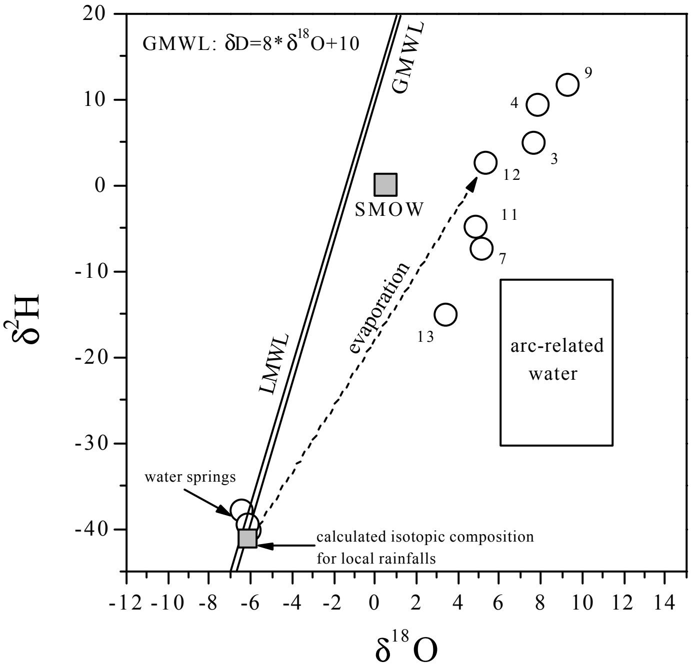

Fig. 2 $\delta^{18}O$-δD diagram for gas and spring water samples from Mombacho volcano. The "arc-related water" field (Taran et al. 1989; Giggenbach 1992), the Local and Global Meteoric Water Lines (LMWL; IAEA 2004 and IAEA/WMO 2004. GMWL; Craig 1961) and the calculated composition (Bowen and Wilkinson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

The $^{40}Ar/^{36}Ar$ 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 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 # 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). Such result confirms the presence of a significant fraction of mantle-derived helium (≈95 %) when compared with that measured in the Middle Oceanic Ridge Basalts (MORB=8±1 Ra; Farley and Neroda 1998).

2.5 Discussion

2.5.1 Origin of gases

The chemical and isotopic composition of fumaroles sampled at Mombacho volcano can be considered extremely different from that commonly found in extinct volcanic systems. The presence of highly acidic gas compounds (i.e. SO_2, HCl and HF) can indeed only be ascribed to a high-temperature fluid source, in agreement with the mantle signature of the helium isotopic ratio. Furthermore, the $CO_2/^3He$ ratio ($7.6x10^9$) is within a factor of 5 of MORB magmatic fluids ($2x10^9$; Marty and Jambon 1987) and it is in the range of values measured in hot springs and geothermal wells along the volcanic axis of Central America (varying between $2.55x10^9$ and $617x10^9$; Snyder et al. 2001). This suggests that the relatively positive values of $\delta^{13}C$ of CO_2 (Table 1) possibly originate from a mantle source locally modified by carbonate-rich sediments carried by the subsiding Cocos plate, and/ or from shallow sedimentary rocks and secondary processes as also 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-originated water vapor indicates that a water table is present close to surface, as also supported by the low temperatures of the fumaroles (<121°C; Table 1). According to the presence of a shallow aquifer, the large changes of SO_2, HCl and HF contents measured in F1 and F2 fumaroles in a short time period (i.e. samples # 1-6; Table 1) may be possibly due to scrubbing processes, whose influence is particularly strong for these highly soluble compounds (Giggenbach 1992; Symonds et al. 2001). Gas scrubbing depends indeed on a large number of parameters (precipitation rate, thickness of the shallow aquifer, flux rate of ascending fluids, etc.) and, as already observed in other volcanic systems (i.e. Poas volcano; Vaselli et al. 2003), may show rapid variations in relation to local conditions. Anyway, it cannot be excluded that part of the SO_2, HCl and HF from the two bubbling springs (samples # 9 and 10; Table 1), could be due to water droplets entered the glass vials during sampling. Nevertheless, this process cannot be considered able to have significantly affected the composition of the gases since SO_3^{2-}, which can only derive from gaseous SO_2, was found to be always the prevailing sulfur compound in the NaOH solution. The low CO abundance (<0.039 µmol/mol) can be ascribed to hydrolysis processes that favor the production of formic acid (Shock 1993). A similar process was already 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 chemical feature, commonly ascribed to chemical reactions in presence of a liquid phase at relatively high temperature (e.g. Martini 1993), suggests that at Mombacho a huge amount of heat is released from depth and enters the

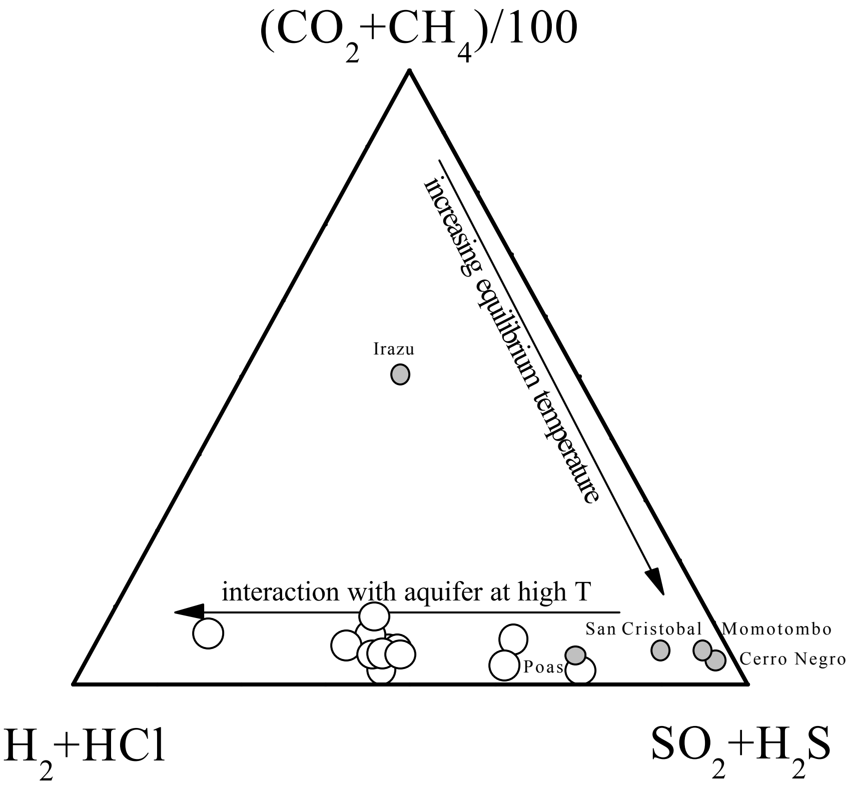

Fig. 3 (SO_2+H_2S)-(CO_2+CH_4)/100-(H_2+HCl) ternary diagram for gas samples from Mombacho volcano (open circles). Composition of gas samples from Cerro Negro, Irazu, Poas (Garofalo et al. unpublished data) and Momotombo volcanoes (Chapter 3) are also presented

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 into meteoric waters that mix with the ascending hot fluids. The N_2/100-Ar-10*He ternary diagram (Fig. 5), where basaltic magmatism ("mantle") and convergent plate boundaries ("arc-type") fields are also reported (Kita et al. 1993; Giggenbach 1996), shows that the N_2/Ar ratios plot between those of the air and ASW, pointing to an almost complete atmospheric origin for N_2. On the contrary, helium is mainly related to a non-atmospheric (mantle) source, as also indicated by the helium isotopic ratio.

As already mentioned, the organic fraction only forms a minor part of the gas composition. However, the relatively high abundances of hydrocarbons pertaining to the alkenes group (Fig. 6), being systematically observed in fumaroles from active volcanic areas (Capaccioni et al. 1995), are to be considered a peculiar feature of gas species produced at medium-to-high temperatures. In particular, the presence of ethene (Table 1), whose production is negligible at T <300 °C (Capaccioni et al. 2004; Tassi 2004), points out to the existence of a high-temperature reservoir.

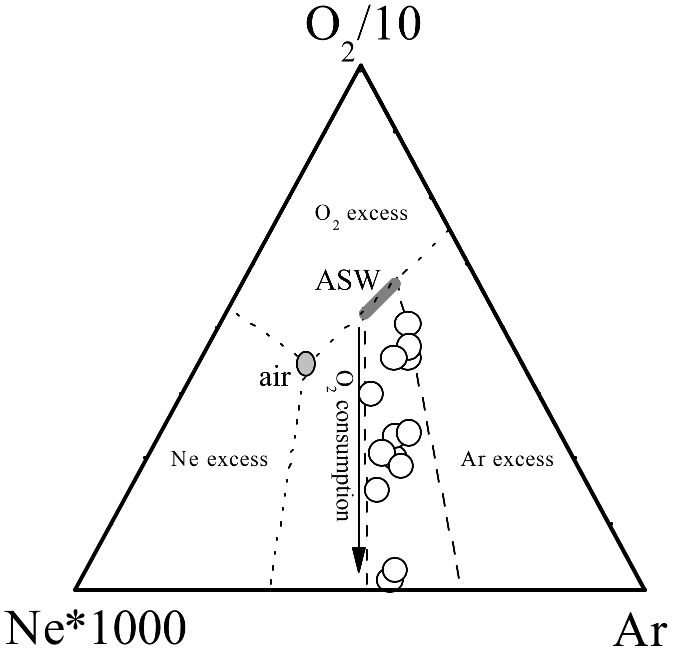

Fig. 4 Ar-O_2/10-Ne*1000 ternary diagram for gas samples from Mombacho volcano. Air and Air Saturated Waters (ASW) compositions are reported

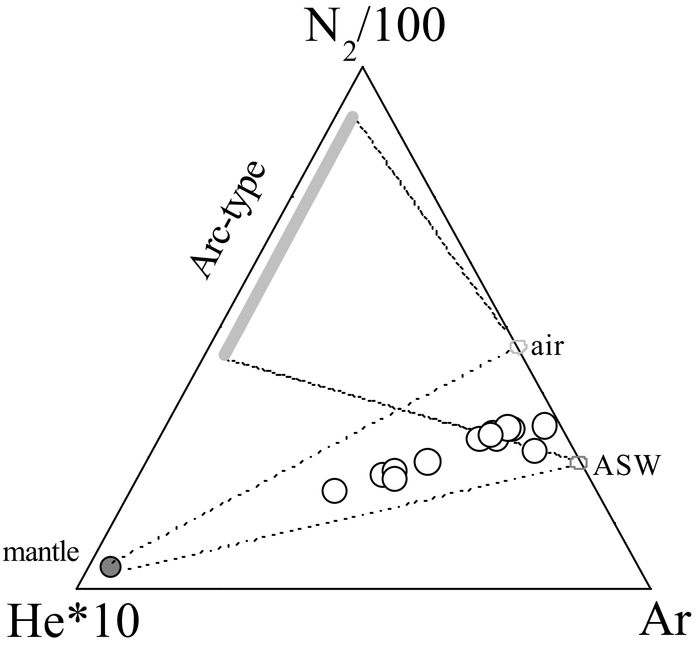

Fig. 5 Ar-N$_2$/100-He*10 ternary diagram for gas samples from Mombacho volcano. Air and Air Saturated Waters (ASW) compositions, convergent plate boundaries ("Arc-type") and "mantle" fields (Giggenbach 1996) are also reported

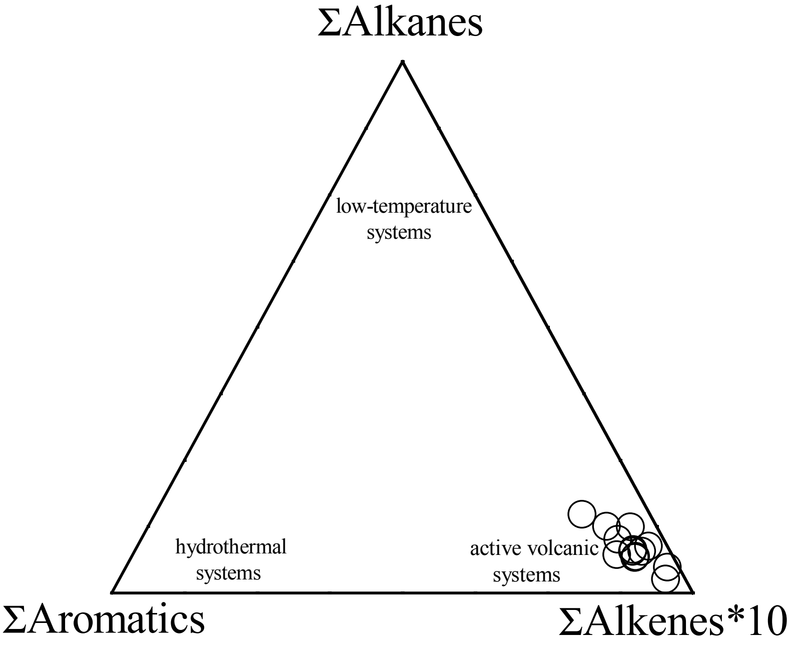

Fig. 6 ΣAlkene*10-ΣAlkanes-ΣAromatics ternary diagram for gas samples from Mombacho volcano. The gas fields for low temperature, hydrothermal and active volcanic systems (Capaccioni et al. 1995) are also reported

2.5.2 Geothermometry

The chemical composition of gases provides reliable estimations of temperature conditions acting on fluids at depth. The thermodynamic reaction between the CH_4 and CO_2 redox pair, being characterized by a slow kinetics, may form the basis for a "deep" geothermometer, which is only to a very low extent affected by re-equilibration as the physical-chemical parameters change during fluid uprising (Giggenbach 1987). Nevertheless, the CH_4/CO_2 ratio depends on gas-liquid separation during secondary boiling and condensation processes, due to the different vapor-liquid partitioning coefficient of CH_4 and CO_2 (Chiodini and Marini 1998). 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, the H_2-Ar pair may represent a suitable geothermometer for two-phase hydrothermal systems, since H_2 is characterized by low solubility and Ar is essentially derived from air-saturated water. By assuming that redox conditions are controlled by the FeO-$FeO_{1.5}$ buffer system (Giggenbach 1987), the temperature dependence of the H_2/Ar ratio is given by (Giggenbach 1991):

$$T(°C) = 70*[2.5+\log(H_2/Ar)] \qquad \mathit{(1)}$$

Equilibrium temperatures for Mombacho gases from equation *(1)* range between 363 and 416 °C. Samples # 2, 3, 4 and 13 were not included in the geothermometric calculation for their relatively high Ar contents (up to 87.25 μmol/mol), possibly related to some, although minimum, air-contamination (Table 1). It is worthy to note that the calculated temperatures are well above the typical temperature range for a liquid-dominated system, which is comprised in an interval of about 100-350 °C. These results are even more relevant, if we consider that the H_2-Ar geothermometer refers to the last-attained equilibrium temperatures, since H_2 reacts almost instantaneously to the physical-chemical changes (Giggenbach 1987). Such results can be possibly explained by considering that, at Mombacho, heat and high-temperature compounds are very rapidly transferred from the deep magmatic-related system up to the shallow meteoric-originated aquifer. This mechanism, which is consistent with the presence of the highly soluble compounds (i.e. SO_2) in the gas discharges, may cause a 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 indicated 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 is likely to well represent the composition established at depth; i.e. at hydrothermal-magmatic conditions. Among the numerous chemical reactions involving light hydrocarbons, dehydrogenation processes of alkanes to produce their homologous alkenes (i.e. ethane-ethene, propane-propane) 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 very similar vapour-liquid distribution coefficients (CRC 2001) and a relatively high chemical inertness. This is a particular advantage since it allows us to neglect the complex effects induced by secondary processes (i.e. phase changes) that rather affect the H_2-CO_2-CO-CH_4-H_2O system (Tassi et al. 2005b).

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

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

and

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

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

$$7.43-8{,}809/T = \log(C_2H_4/C_2H_6)+\log fH_2 \qquad (4)$$

and

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

Since equations *(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 temperatures 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-$FeO_{1.5}$ and the SO_2-H_2S (for $SO_2/H_2S=0.1$) redox buffer

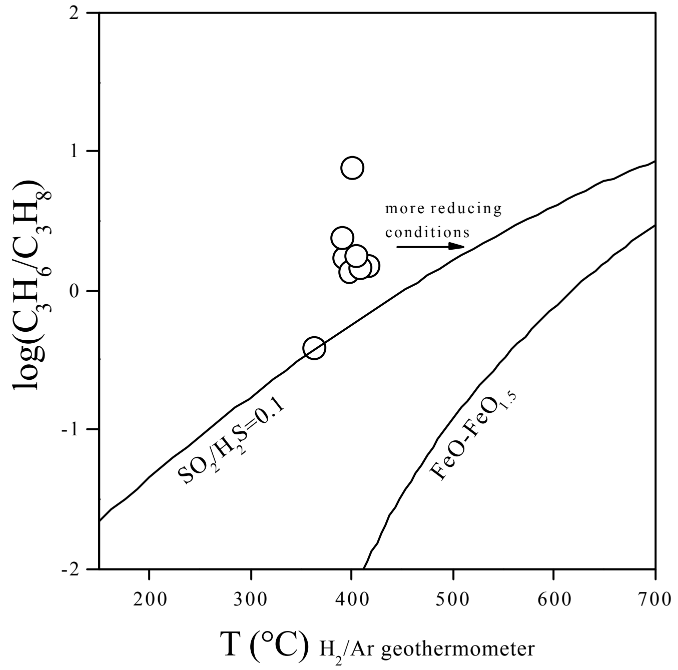

Fig. 7 Log(C_2H_4/C_2H_6) vs. H_2/Ar-calculated temperature (°C) (Chiodini et al. 2001) binary diagram for the Mombacho gas discharges. Solid lines represent the positions of the FeO-Fe$O_{1.5}$ and SO_2-H_2S redox buffer systems (Giggenbach 1987)

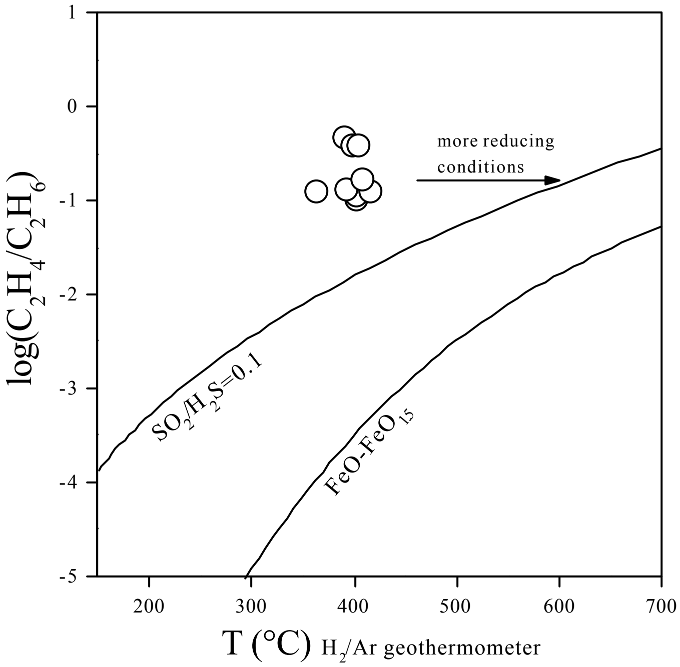

Fig. 8 Log(C_3H_6/C_3H_8) vs. H_2/Ar-calculated temperature (°C) (Chiodini et al. 2001) binary diagram for the Mombacho gas discharges. Solid lines represent the positions of the FeO-Fe$O_{1.5}$ and SO_2-H_2S redox buffer systems (Giggenbach 1987)

systems. The plot indicates that the Mombacho gases are well clustered in an area that corresponds to unrealistic oxidizing conditions. More reducing equilibrium conditions would correspond to higher equilibrium 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. Such difference is likely due to the faster kinetics of reaction *(3)*, that is characterized by a lower activation energy (CRC 2001), compared to that of reaction *(2)*, the latter responding more slowly to temperature and pressure changes during the uprising of hot fluids. Such chemical evolution of ascending fluids within a highly dynamic fluid circulation pathway is considered to generally typify active volcanic systems (Taran and Giggenbach 2003).

2.6 Conclusions

Nicaragua is a famous and attractive region for its active volcanoes such as Telica, San Cristobal, Cerro Negro, Masaya and Momotombo. They are of high interest for the international scientific community and are often taken as the best examples of the intense eruptive activity characterizing Central America. In this context, Mombacho, currently considered an extinct volcano, has played a secondary role, partly explaining the scanty information about its volcanological features. The results of our geochemical investigation should change this perspective. Although the recent history of this volcano testifies that gravitational events have to be considered as the most probable hazard, chemical and isotopic gas composition suggests that a possible resuming of eruptive activity cannot be excluded. The presence of high-temperature compounds in fumaroles, whose outlet temperatures do not exceed 121°C, is consistent with the mantle helium and carbon isotopic signature. This is clear evidence that the behaviour of this volcano strongly depends on the balance between hot fluids, likely related to an active magmatic system, and a shallow, water-dominated environment, mainly fed by meteoric waters. We suggest that even a limited perturbation, e.g. increase of the heat input from depth, variation in the water table thickness, regional seismic events, etc., could modify the precarious equilibrium of this volcano and, consequently, lead to an eruption whose intensity is difficult to be evaluated without a proper geochemical, volcanological and petrological investigation.

Thus, this first geochemical study of the Mombacho fumarolic field is of particular importance and should be regarded as a starting-point for a medium- to long-term geochemical monitoring program, which, coupled with the continuation and the development of the existing seismic and GPS measurements, represents the most reliable way to evaluate the short-term evolution of Mombacho volcanic activity. As a consequence, Mombacho volcano has to be included among the active volcanoes of Nicaragua and fully considered when planning scientific programs devoted to the mitigation of volcanic hazards.

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References

Ballentine CJ, O’Nions RK, Oxburgh, ER, Horvath F, Deak J (1991) Rare-gas constraints on hydrocarbon accumulation, crustal degassing and groundwater-flow in the Pannonian Basin. Earth Planet Sci Lett 105: 229-246

Bowen GJ, Wilkinson B (2002) Spatial distribution of delta O-18 in meteoric precipitation. Geology 30: 315-318

Capaccioni B, Martini M, Mangani F (1995) Light hydrocarbons in hydrothermal and magmatic fumaroles: hints of catalytic and thermal reactions. Bull Volcanol 56: 593-600

Capaccioni B, Mangani F (2001) Monitoring of active but quiescent volcanoes using light hydrocarbon distribution in volcanic gases: the results of 4 years of discontinuous monitoring in the Campi Flegrei (Italy). Earth Planet Sci Lett 188: 543-555

Capaccioni B, Taran Y, Tassi F, Vaselli O, Mangani F, Macias JL (2004) Source conditions and degradation processes of light hydrocarbons in volcanic gases: an example from El Chichón volcano (Chiapas State, Mexico). Chem Geol 206: 81-96

Chiodini G, Marini L (1998) Hydrothermal gas equilibria: The H_2O-H_2-CO_2-CO-CH_4 system. Geochim Cosmochim Acta 62: 2673-2687

Chiodini G, Marini L, Russo M (2001) Geochemical evidence for the existence of high-temperature hydrothermal brines at Vesuvio volcano, Italy. Geochim Cosmochim Acta 65: 2129-2147

Coleman ML, Shepherd TJ, Durham JJ, Rouse JE, Moore GR (1982) Reduction of water with zinc for hydrogen isotope analysis. Anal Chem 54: 993-995

Craig H (1961) Isotopic variations in meteoric water. Science 133: 1702-1703

CRC (2001) Handbook of chemistry and physics. 82nd, Lide DR (eds), CRC press, Boca Raton, Florida, USA

DeMets C (2001) A new estimate for present-day Cocos-Caribbean plate motion: Implications for slip along the Central American volcanic arc. Geophys Res Lett 28: 4043-4046

Ehrenborg J (1996) A new stratigraphy for the Tertiary volcanic rocks of the Nicaraguan Highland. Geol Soc Am Bull 108: 830-842

Elming SA, Layer P, Ubieta K (2001) A palaeomagnetic study and age determinations of Tertiary rocks in Nicaragua, Central America. Geophys J Int 147: 294-309

Epstein S, Mayeda TK (1953) Variation of the ^{18}O/^{16}O ratio in natural waters. Geochim Cosmochim Acta 4: 213-224

Evans WC, White LD, Rapp JB (1988) Geochemistry of some gases in hydrothermal fluids from the Southern Juan-De-Fuca-Ridge. J Geophys Res 93: 15305-15313

Farley KA, Neroda E (1998) Noble gases in the Earth's mantle. Annu Rev Earth Planet Sci 26: 189-218

Gerlach TM, Nordlie BE (1975) The C-O-H-S gaseous system, part II: temperature, atomic composition and molecular equilibria in volcanic gases. Am J Sci 275: 377-395

Giggenbach WF (1987) Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand. Appl Geochem 2: 143-161

Giggenbach WF (1991) Chemical techniques in geothermal exploration. In: Application of Geochemistry in Geothermal Reservoir Development. UNITAR, New York, pp 253-273

Giggenbach WF (1992) Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin. Earth Planet Sci Lett 113: 495-510

Giggenbach WF (1996) Chemical composition of volcanic gases. In: Scarpa M and Tilling RJ (eds) Monitoring and mitigation of Volcanic Hazards. Springer-Verlag, Berlin Heidelberg, pp 221-256

Giggenbach WF, Gougel RL (1989) Method for the collection and analysis of geothermal and volcanic water and gas samples. NZ-DSIR Report, CD 2387, 53

Global Volcanism Program (1980) Volcanic Activity Reports, SEAN Bulletin 05: 12. http://www.volcano.si.edu

Global Volcanism Program (1982) Volcanic Activity Reports, SEAN Bulletin 07:03. http://www.volcano.si.edu

Global Volcanism Program (1988) Volcanic Activity Reports, SEAN Bulletin 13: 01. http://www.volcano.si.edu

Global Volcanism Program (1991) Volcanic Activity Reports, BGVN 16:02. http://www.volcano.si.edu

Global Volcanism Program (1994) Volcanic Activity Reports, BGVN 19:11. http://www.volcano.si.edu

Hradeck□ P (1988) Geológia del Volcán Mombacho y sus alrededores. Archive INETER, Managua, Nicaragua

Havlíèek P, Hradecký P, Mlèoch B, Novák Z, Staník E, Šebesta J, Buitrago N, Navarro M (1998) Estudio geologico para reconocimiento de riesgo natural y vulnerabilidad geologica en el area de masaya Y Granada. Servicio Geologico Checo-Instituto Nicaraguense de Estudios Territoriales Praha Managua.

IAEA (2004) Isotope Hydrology Information System, ISOHIS Database. http://isohis.iaea.org

IAEA/WMO (2004) Global Network of Isotopes in Precipitation, GNIP Database. http://isohis.iaea.org

Incer J (1995) Geografía dinámica de Nicaragua. Managua, p 169

Kita I, Nitta K, Nagao K, Taguchi S, Koga A (1993) Difference in N2/Ar ratio of magmatic gases from northeast and southwest Japan: New evidence for different state of plate subduction. Geology 21: 391-394

La Femina PC, Dixon TH, Strauch W (2002) Bookshelf faulting in Nicaragua. Geology 30: 751-754

Mamyrin BA, Tolstikhin IN (1984) Helium isotopes in nature. In: Fyfe WS (eds) Development in geochemistry. Elsevier, Amsterdam, pp 1- 273

Martini M (1993) Water and fire: Vulcano island from 1977-1991. Geochem J 27: 297-303

Martini M (1996) Chemical characters of the gaseous phase in different stages of volcanism: precursors and volcanic activity. In: Scarpa M and Tilling RJ (eds) Monitoring and mitigation of Volcanic Hazards. Springer-Verlag, Berlin Heidelberg, pp 199-219

Marty B, Jambon A (1987) C/3He in volatile fluxes from the Solid Earth - Implications for Carbon geodynamics. Earth Planet Sci Lett 83: 16-26

McBirney AR, Williams H (1965) Volcanic history of Nicaragua. Berkeley and Los Angeles, University of California press, pp 1-65

Montegrossi G, Tassi F, Vaselli O, Buccianti A, Garofalo K (2001) Sulfur species in volcanic gases. Anal Chem 73: 3709-3715

Notsu K, Sugiyama K, Hosoe M, Uemura A, Shimoike Y, Tsunomori F, Sumino H, Yamamoto J, Mori T, hernandez PA (2005) Diffuse CO_2 efflux from Iwojima volcano, Izu-Ogasawara arc. Japan. J Volcanol Geotherm Res 139: 147-161

Oremland RS, Miller LG, Whiticar MJ (1987) Sources and flux of natural gases from Mono Lake, California. Geochim Cosmochim Acta 51: 2915-2929

Patino LC, Carr MJ, Feigenson MD (2000) Local and regional variations in Central American arc lavas controlled by variations in subducted sediment input. Contrib Mineral Petrol 138: 265-283

Poreda RJ, Farley KA (1992) Rare-gases in Samoan Xenoliths. Earth Planet Sci Lett 113: 129-144

Protti M, Guendel F, McNally K (1995) Correlation between the age of the subducting Cocos plate and the geometry of the Wadati- Benioff zone under Nicaragua and Costa Rica. In: Mann P (eds) Geologic and Tectonic Development of the Caribbean Plate Boundary in Southern Central America. Boulder, Geol Soc Am Spec Issue 295: 309-326

Rollinson H (1993) Using geochemical data. Longman, London, UK, pp 1-352

Seewald JS (1994) Evidence for metastable equilibrium between hydrocarbons under hydrothermal conditions. Nature 370: 285-287

Shaw AM, Hilton DR, Fischer TP, Walker JA, Alvarado GE (2003) Contrasting He-C relationship in Nicaragua and Costa Rica: insights into C cycling through subduction zones. Earth Planet Sci Lett 214: 499-513

Shock LE (1993) Hydrothermal dehydration of aqueous organic compounds. Geochim Cosmochim Acta 57: 3341-3349

Sigurdsson H, Houghton B, Rymer H, Stix J, McNutt S (2000) Encyclopedia of Volcanoes, Academic Press, New York

Snyder G, Poreda R, Hunt A, Fehn U (2001) Regional variations in volatile composition: Isotopic evidence for carbonate recycling in the Central American volcanic arc. Geochem Geophys Geosyst 2, DOI 10.1029/2001GC000163

Snyder G, Poreda R, Fehn U, Hunt A (2003) Sources of nitrogen and methane in Central American geothermal settings: Noble gas and ^{129}I evidence for crustal and magmatic volatile components. Geochem Geophys Geosyst 4, DOI 10.1029/2002GC000363

Sumino H, Notsu K, Nakai S, Sato M, Nagao K, Hosoe M, Wakita H (2004) Noble gas and carbon isotopes of fumarolic gas from Iwojima volcano, Izu-Ogasawara arc, Japan: implications for the origin of unusual arc magmatism. Chem Geol 209: 153-173

Symonds RB, Gerlach TM, Reed MH (2001) Magmatic gas scrubbing: implications for volcano monitoring. J Volcanol Geotherm Res 108: 303-341

Taran YA, Giggenbach WF (2003) Geochemistry of light hydrocarbons in subduction-related volcanic and hydrothermal fluids. In: Simmons SF and Graham IJ (eds) Volcanic, geothermal, and ore-forming fluids: rulers and witnesses of processes within the Earth. Littleton, Colo: Soc Econ Geol Spec Publ 10, pp 61-74

Taran YA, Pokrovsky BG, Esikov AD (1989) Deuterium and oxygen-18 in fumarolic steam and amphiboles from some Kamchatka volcanoes: "andesitic waters". Doklady Akademii nauk SSSR 304: 440-443

Tassi F, Vaselli O, Capaccioni B, Nencetti A, Montegrossi G, Macias JL, Magro G (2003) Chemical composition of fumarolic gases and spring discharges from El Chichon volcano, Chiapas, Mexico: causes and implications of the changes detected over the period 1998-2000. Special Issue of J Volcanol Geoth Res 123: 105-121

Tassi F (2004) Fluidi in ambiente vulcanico: Evoluzione temporale dei parametri composizionali e distribuzione degli idrocarburi leggeri in fase gassosa. Ph.D. thesis, Department of Earth Science, University of Florence, Italy, pp 1-356

Tassi F, Martinez C, Vaselli O, Capaccioni B, Viramonte J (2005a) The light hydrocarbons as new geoindicators of equilibrium temperatures and redox conditions of geothermal fields: evidence from El Tatio (northern Chile). Appl Geochem 20: 2049-2062

Tassi F, Vaselli O, Capaccioni B, Giolito C, Duarte E, Fernandez E, Minissale A, Magro G (2005b) The hydrothermal-volcanic system of Rincon de la Vieja volcano (Costa Rica): a combined (inorganic and organic) geochemical approach to understanding the origin of the fluid discharges and its possible application to volcanic surveillance. J Volcanol Geotherm Res 148: 315-333

Vallance JW, Schilling SP, Devoli G (2001) Lahar hazards at Mombacho Volcano, Nicaragua. Open-File Rep, US Geol Surv 01-455

van Wyk de Vries B (1993) Tectonics and magma evolution of Nicaraguan volcanic systems. Ph.D. thesis, Department of Earth Sciences, The Open University, UK, pp. 1- 328

van Wyk de Vries B, Hernandez P (1994) Map of Mombacho summit area. Global Volcanism Program, Volcanic Activity Reports, BGVN 19:11

van Wyk de Vries B, Francis PW (1997) Catastrophic collapse at stratovolcanoes induced by gradual volcano spreading. Nature 387: 387-390

Vaselli O, Tassi F, Montegrossi G, Duarte E, Fernandez E (2003) Poas volcano (Costa Rica): fumarole migration and chemical variation from 1998 to 2001. Special Memory of the Geol Soc of London (UK) 213: 247-262

Weinberg RF (1992) Neotectonic development of western Nicaragua. Tectonics 11: 1010-1017

Whiticar MJ, Suess E (1990) Hydrothermal hydrocarbon gases in the sediments of the King-George Basin, Bransfield Strait, Antarctica. Appl Geochem 5: 135-147

Chapter 3

Past and present chemical and isotopic composition of high temperature fumarolic gases of Momotombo volcano, Nicaragua

Past and present chemical and isotopic composition of high temperature fumarolic gases of Momotombo volcano, Nicaragua

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Abstract

Five fumaroles in the crater area of the Nicaraguan volcano Momotombo, discharging gases at temperatures between 368°C and 776°C, were repeatedly sampled during 2002-2003. The chemical composition and stable isotope signatures of the gases have changed considerably during the last 20 years. The 2002-2003 emissions are characterized by generally lower temperatures and lower H_2O (83-92 mol%) contents with respect to the past. Furthermore the fumarolic discharges are characterized by higher C_{tot} (55,000 μmol/mol) and S_{tot} (35,000 μmol/mol) coupled by generally lower Cl (6,000-200 μmol/mol) contents, which result in higher SO_2 (60,000-4,500 μmol/mol), SO_2/H_2S (4) and SO_2/HCl molar ratios (>> 3). The high-temperature gases at F9 (776-737°C) and F7 (616-600°C) have arc mantle $\delta^{13}C-CO_2$ (-3.24 to -3.02‰ V-PDB) and $^3He/^4He$ (6.29Ra) values, and arc magmatic $\delta^{18}O-\delta D-H_2O$ (averaging $\delta^{18}O$ = +6.20‰ and δD = -11‰ V-SMOW) and $\delta^{34}S-SO_2$ signatures (6-7‰ CDT). The lower temperature gases, collected at the peripheral fumaroles F4, F5 and F15 (F4 = 368°C, F5 = 594°C, F15 = 478-472°C) show generally higher water contents and higher proportions of CH_4 and non-methane hydrocarbons. The isotopic composition of the gases at F15 ($\delta^{13}C-CO_2$ = -2.63‰ PDB, $\delta^{18}O-H_2O$ = +1.4‰ and $\delta D-H_2O$ = -15.7‰ V-SMOW, and $^3He/^4He$ = 5.44Ra) possibly indicates limited interaction of the gases with crustal material or marginal hydrothermal cells.

The chemistry and the isotopic signature of the 2002-2003 gases suggest venting of a relatively undegassed magma batch and limited meteoric dilution and is probably best explained by opening of a new fracture system during the repeated seismic events that have occurred at the volcano since 1996. Long-term chemical and isotopic variations (‘80s-2002) seem to be coupled to main changes in the interaction between the magmatic and hydrothermal system.

Keywords: *Nicaragua - Momotombo volcano - Fumarolic gases - Fluid geochemistry - Isotope geochemistry – Temporal evolution*

3.1 Introduction

Long-lived high temperature (>500°C) fumarolic fields are an atypical feature of basaltic volcanoes (e.g. Allard and Sabroux 1980; Taran et al. 1995) and are especially rare during non-eruptive periods (Giggenbach 1996). Such fumaroles are usually associated with felsic magmatism, and commonly with the presence of a growing lava dome (i.e. Augustine, Alaska: Symonds et al. 1990; Shawa-Shizan, Satsuma Iwojima, Japan: Shinohara et al. 1993; Hedenquist et al. 1994; Merapi, Indonesia: Allard and Sabroux 1980; Symonds et al. 1987; White Island, New Zealand: Giggenbach 1987). An example of a basaltic-andesitic volcano that does have a long-lived fumarolic field is Momotombo volcano (Nicaragua). Its crater fumaroles are in a persistent state of degassing since the last eruption in 1905 (Smithsonian Institution 1980-1989; 1990-2003; INETER 2000-2005).

In the last two decades (late ‘70s-2000) Momotombo has experienced repeated events of temperature increase at the crater’ fumaroles (Smithsonian Institution 1980-1989; 1990-2000). Between 1973 and 1978 the temperature rose abruptly from 230 to 750°C, further increased to 904°C in 1986 (Allard 1986; Allard and Sabroux 1980; Smithsonian Institution 1983; 1995; Menyailov et al. 1986; Quisefit et al. 1989; Martini 1991) and rose further to 933°C in May-June 2000 - the maximum temperature ever recorded at Momotombo (INETER 2000; Smithsonian Institution 2000). This coincided with intense seismic activity underneath the volcano possibly accompanied by fluid (magma, hot water, steam) migration to a shallower level, or vesiculation (gas exsolution) of a magma batch proximal to the surface (Tenorio et al. 2000; Smithsonian Institution 2000). After this last restless period Momotombo has shown episodic moderate-to-intense seismic activity and temperature oscillations at the crater fumaroles around a maximum of about 750°C (Smithsonian Institution 2003; INETER 2000-2005). The presence of high temperature (HT) fumaroles associated with permanent degassing and a non-eruptive behavior is explainable by the presence of a magmatic intrusion a few hundred meters below the crater bottom (Allard 1986; Allard and Sabroux 1980; Menyailov et al. 1986; Gemmel 1987; Martini et al. 1991). The presence of a magmatic source at such shallow level potentially minimizes any substantial interaction of the gas with crustal materials and favors the venting of juvenile gases at the surface (e.g. Symonds et al. 1993). The permanence of the system in this HT degassing regime will be strongly dependent on magma supply rates and/or the efficiency of convective magma movements in promoting mass exchange between shallow and deeper magma reservoirs (e.g. Williams-Jones 2003).

At Momotombo volcano we have studied, during four field campaigns in 2002 and 2003, the origin and causes of passive degassing into the atmosphere. In particular we sampled fumarolic gases and condensates from Momotombo volcano in order to: 1) document the present chemical and isotopic composition of Momotombo's fumarolic discharges and 2) constrain changes in the volcano-magma-system over the last 20 years. In a companion paper (Chapter 4) we examine the processes responsible for the abundances of trace elements in the present gas discharges, and provide a record of the emission rates for some potentially harmful metals and metalloids at Momotombo.

3.2 Geological setting and volcanological history

Momotombo volcano (12.423°N, 86.540°W, 1,258 m asl) is a basaltic-andesitic composite volcano that rises on the NW shore of Lake Managua (Fig. 1a).

Three principle stratigraphic sequences cover the Quaternary-Middle Miocene period (McBirney and Williams 1965; Van Wyk de Vries 1993; BID-ENEL 1995; Hradecky et al. 2001): 1) the first principle sequence consists of the (a) volcanic sequences corresponding to the Quaternary andesitic-basaltic volcanism of Momotombo volcano itself and the nearby andesitic-dacitic Monte Galan and La Guatusa (Cordillera de los Marrabios), (b) the stratigraphically lower/older andesitic-dacitic deposits produced by highly explosive phreato-magmatic activity related to the Malpaisillo Ignimbrite (Pleistocene), erupted from the Malpaisillo caldera located ca. 30 km N-NE from Momotombo, and (c) the andesitic-dacitic products of the ending phase of the Tertiary volcanism of the Upper Coyol Group (Pliocene-Miocene). The latter two products are inter-fingered together and can occur simultaneously with the second and third principle sequences: 2) the continental volcano-sedimentary sequence Tamarindo Formation (Upper Miocene) and 3) the marine sedimentary sequences El Salto (Pliocene) covering the deeper El Fraile Formation (Miocene). The sedimentary deposits in the Nicaraguan depression are estimated to be 2000 m thick.

The volcanic history of Momotombo can be dated to 4,500 B.P. and divided into two main evolutionary stages (Kirianov et al. 1988; Hradecky et al. 2001; Menyailov et al. 1986): 1) the construction of the edifice of “Momotombo Viejo“ (Old Momotombo) that was suddenly interrupted at the beginning of the second millennium by a strong Plinian eruption and 2) renewed activity after some centuries of pause that produced a new central cone in the old crater and resulted in the present Somma-Vesuvius type structure (“Momotombo Actual”) (Present Momotombo).

The historic eruptive activity of Momotombo can be traced back to the time of the Spanish conquest of Nicaragua (1524), since then it has erupted ca. 15 times (Global Volcanism Program). According to the historical descriptions all the eruptions were of moderately explosive character (VEI 2-3), punctuated by occasional large explosive ones (VEI $\geq$ 4; Global Volcanism Program). A large explosive eruption (VEI 4) occurred in 1605-1606 when the colonial city of León (Viejo), the former capital of the country, was destroyed. Momotombo erupted last in 1905, producing a lava flow that spilled over the NE rim of the crater reaching the northern foot of the volcano. Since that time the volcano has been persistently degassing through strong fumarolic activity (INETER 2000-2005; Smithsonian Institution 1980-1989, 1990-2003).

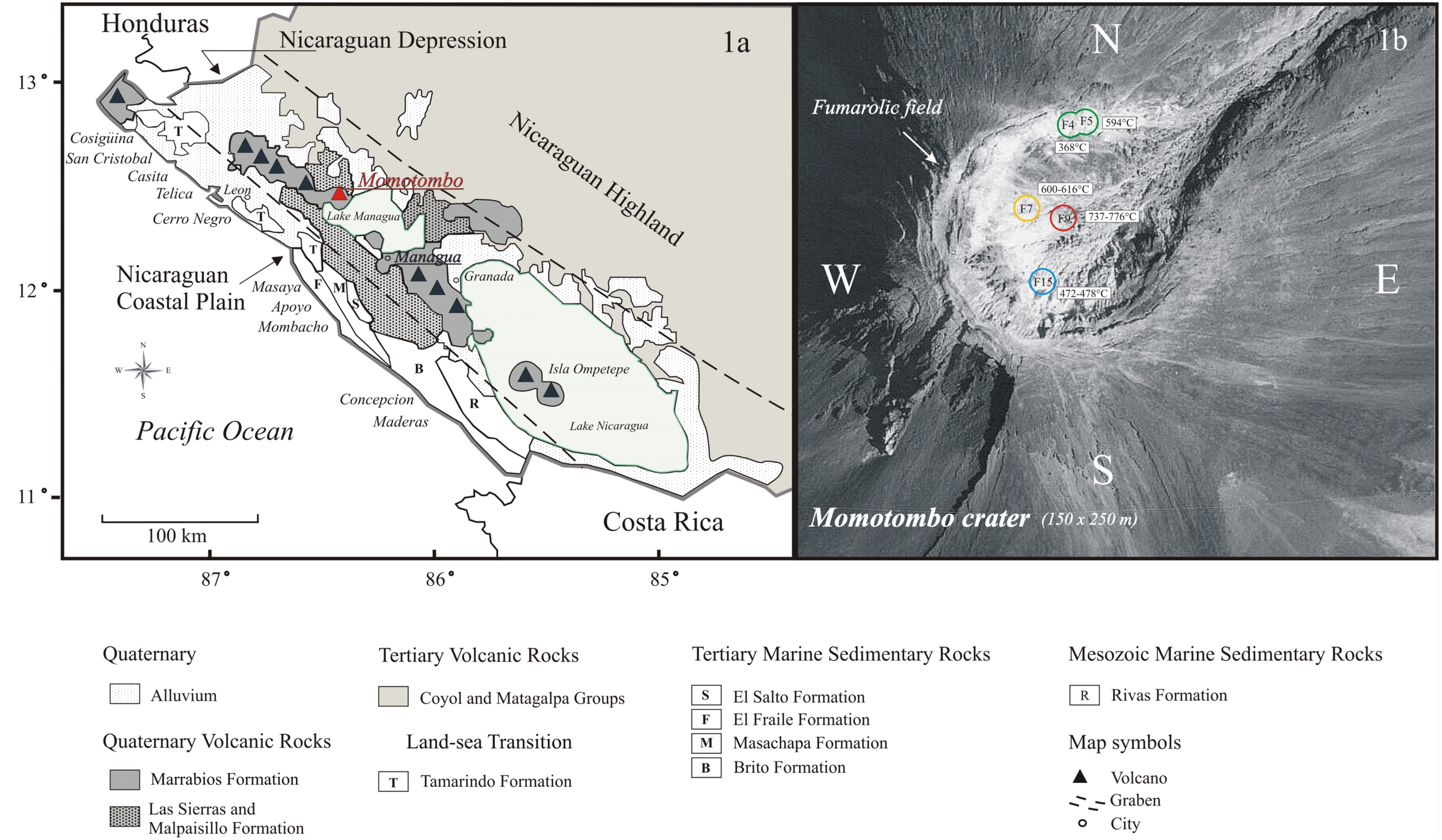

Fig. 1 a) Schematic geological map of Nicaragua (modified after Van Wyk de Vries 1993) and **b)** Summit area of Momotombo and location of sampling points (photo courtesy of INETER)

3.3 Sampling sites and field observations

The fumarolic activity is confined to the summit area, where gases are emitted from vents controlled by a system of concentric fissures along the subsided crater floor of 150 x 250 m (Menyailov et al. 1986). The fumarolic field can be divided into four main areas (Fig. 1b): 1) the inner crater area to the west, where the higher temperature fumaroles F9 (776-737°C) and F7 (616-600°C) are located; 2) the internal rim wall, where the fumarole F15 (472-478 °C) occurs on the S-SW side; 3) the peripheral upper north crater rim where there are fumaroles, including F4 (368°C) and F5 (594°C), which generally show lower emission rates and 4) the W-NW crater rim wall, where the fumaroles are quite inaccessible, and were not sampled for safety reasons, since an intense alteration characterizes this sector of the crater rim.

The fumaroles F9 and F7 were repeatedly sampled at seasonal intervals during 2002-2003. F9 is at present the highest temperature fumarole of the field. In 2002, the internal fumarolic vent wall at F9 site was glowing to red-hot. While sampling it was common that molten sulfur was suddenly flowing out of the fumarole vents, especially at the F7 site. Bluish and greenish flows were glowing in the night in the crater area, indicating that sulfur was melting. We assume that the deposited sublimates occurring all over the fumarole area were burning at contact with the hot flow's surface, giving that characteristic light not visible during daylight.

Fumarole F15 and F4, F5 located at the marginal fumarolic fields tended to be intermittent and for this reason they were not regularly sampled.

3.4 Sampling and analysis

3.4.1 Gas sampling

Fluid samples were collected by inserting an assembled Qz-glass sampling train 30-40 cm deep into the fumaroles. The sampling train consists of a tube, a pipe and Dewar tubes to which end a sampling bottle is attached. Depending on the parameters to be examined the sampling bottle is: 1) a pre-evacuated 50 mL flask, for determination of the $\delta^{13}C\text{-}CO_2$ value of the gas; 2) an evacuated glass bottle partially filled with 4 N NaOH and 0,15 M $Cd(OH)_2$ alkaline solution (Giggenbach and Gougel 1989;

Montegrossi et al. 2001) to measure the amount of incondensable species (N_2, O_2, CO, H_2, CH_3, Ar, He, Ne and light hydrocarbons) accumulated in the headspace, the quantity of acid species (CO_2, SO_2, HCl, HF) dissolved into the alkaline solution (as CO_3^{2-}, SO_3^{2-}, Cl^-, F^-, respectively), the amount of H_2S precipitated as CdS, and the content of native S^0 and the fraction of H_2O_v condensed. Consequently, it is also possible to determine the distinct isotopic composition of SO_2, H_2S and S^0 ($^{34}S/^{32}S$ ratio) in this sample; 3) an evacuated glass bottle partially filled with 4 N NaOH solution, to determine the helium isotopic composition ($^3He/^4He$).

Replacing the Dewar tubes with a Qz-glass water-cooled condenser two aliquots of water condensates were collected in either 25 mL HPTF bottles, for main anions and metals analysis along with trace elements quantification (Chapter 4); or 40 mL dark-glass bottles, to determine the oxygen and hydrogen isotopic composition of water ($\delta^{18}O$- and δD-H_2O).

3.4.2 Chemical and isotopic analyses

The composition of the non-condensable gas fraction was analyzed by gas chromatography. The inorganic compounds, except for CO, were determined by a Shimadzu 15a gas-chromatographer equipped with a thermal conductivity detector (TCD). The light hydrocarbons including methane, and CO previously converted to CH_4 at 400°C by a Shimadzu MTN-1 methanizer (Tassi 2004), were analyzed with a Shimadzu 14a gas-chromatographer equipped with a Flame Ionization Detector (FID). After the quantification of the fix gases, wet-chemical laboratory work was conducted to analyze the alkaline solution. Following the three-step procedure described by Montegrossi et al. (2001), the alkaline solution was centrifuged: 1) the supernatant (SO_2-aliquot) was separated from the solid precipitate and analyzed for a) CO_3^{2-} (for CO_2 content) by titration with 0.5N HCl solution; b) SO_4^{2-}, deriving from the oxidation of SO_3^{2-} with H_2O_2 (for SO_2 content), by ion-chromatography (Dionex DX100); c) Cl^- (for HCl content) by ion-chromatography. 2) The solid precipitate was oxidized with H_2O_2 to dissolve CdS. The resulting solution (H_2S aliquot) was centrifuged, separated from the residual solid and analyzed for SO_4^{2-} by ion-chromatography to determine the original H_2S amount. 3) S^0 was extracted from the residual solid with CCl_4 and oxidized to S_2I_2 with the addition of KI (S^0 aliquot). Sulfur of S_2I_2 was oxidized to SO_4^{2-} by $KBrO_3$ and finally analyzed by ion-chromatography.

Analytical error is < ±5% for the main gas components and < ±10% for minor and trace gas compounds.

Stable isotope analyses were performed on selected samples and the obtained results are given in Table 1. The $^{13}C/^{12}C$ isotopic ratio of CO_2 was determined with a Finningan Delta S mass spectrometer after standard extraction and purification of the gas mixture (Evans et al. 1988) and is expressed in $\delta^{13}C$ ‰ V-PDB notation. Analytical error is ±0.05‰, while the reproducibility of δ-values for C is ±0.1‰.

The oxygen and hydrogen isotopic compositions of the H_2O condensate samples were determined by Finningan Delta Plus XL and Finnegan MAT 251 mass spectrometers and expressed respectively as $\delta^{18}O$ and δD ‰ V-SMOW. Oxygen isotopes ratios were analyzed using the CO_2-H_2O equilibration method (Epstein and Mayeda 1953). Hydrogen isotopes ratios were instead measured on H_2 produced by the reaction of 10 μL water condensate sample with 0.3 g of metallic zinc at 500°C, following the directions given by Coleman et al. (1982). The analytical error for $\delta^{18}O$ and δD values is ±0.1 and ±2‰, respectively.

The sulfur isotopic composition ($^{34}S/^{32}S$) of SO_2 and H_2S was determined on $BaSO_4$ quantitatively precipitated by adding $BaCl_2$ to the corresponding SO_4-bearing aliquots (derived from the separation and oxidation of the alkaline solution), previously acidified to pH< 2. The barium sulfate precipitate was washed with Millipore water, filtered and dried. $^{34}S/^{32}S$ ratios were analyzed by combustion isotope ratio-monitoring mass spectrometry (Coleman and Moore 1978). After total conversion of $BaSO_4$ to SO_2 with an elemental analyzer, the samples, international (NBS-127, IAEA-S1 and CP-1) and internal (EEZ-8) standards were measured by a Finnegan MAT 251 mass spectrometer. Data are reported in $\delta^{34}S$ notation as permil (‰) variations from the Vienna Cañon Diablo Troilite standard (V-CDT) in Table 1. The analytical error for $\delta^{34}S$ is ±0.2‰.

$^{3}He/^{4}He$ ratios were measured following the procedure of Poreda and Farley (1992) and determined with a VG5400 gas mass spectrometer. The analytical error for the $^{3}He/^{4}He$ ratio is about ±0.3%.

3.5 Composition of the fumarolic emissions

3.5.1 Chemical composition of the gases

The emission temperatures and chemical compositions of the gas discharges are reported in Table 1-2. Emission temperatures generally decreased between 2002 and 2003 at the different sampling spots. The main fumarolic gas compound is H_2O, which occurs in average contents of 830,000 μmol/mol at F9, 870,000 μmol/mol at F7 and 900,000 μmol/mol at F15 and 900,000-920,000 μmol/mol at F4-F5. CO_2 is the second most abundant gaseous species, with measured concentrations of 80,000-200,000 μmol/mol at F9, 35,000-180,000 μmol/mol at F7, 55,000-89,000 μmol/mol at F15 and F4, and 50,000 μmol/mol at F5. The CO_2 contents increased between 2002 and 2003. The sulfur species SO_2, H_2S and S^0 are present in variable amounts in HT and LT fumaroles, with SO_2 being always the dominating species (up to 62,000 μmol/mol at F9; 44,000 μmol/mol at F7; 28,000 μmol/mol at F5; 27,000 μmol/mol at F15; and 9,500 μmol/mol at F4). The SO_2/H_2S ratio was quite stable at values of 4 at F9, and 3-11 at F15 and F5, while it varied significantly at F7 with maximum values of up to 86. However, the highest values at F7 are probably artifacts, related to sulfur deposition and flows of molten sulfur associated with this fumarole. At F9 and F7 elemental sulfur occurs in the range 0.100-0.900 μmol/mol while F15, F5 and F4 show contents lower then 0.100 μmol/mol, which is compatible with the lower gas flux at these fumaroles and makes sulfur transport less efficient in the gas stream. The acid gas HCl shows an apparent seasonal variation with generally lower concentrations in November 2002 (end of the rainy season; e.g. 600-3,000 μmol/mol at F9) compared to those in July 2003 (end of the dry and beginning of the rain season; e.g. 6,000 μmol/mol at F9). In contrast HF, occurring at the 10s to few 100s of μmol/mol level, seems to vary unsystematically within the set of samples analyzed. The HCl/HF ratios at F9 (79) and F7 (100) were higher in July 2003 than in Mar/Apr'02, Nov-'02 and Mar-'03 when the observed values varied between 8 to 22.

CO contents show a generally scattered variation at the different fumaroles and vary between 174 μmol/mol at F9 (#2) and 0.1 μmol/mol at F4 (#24). This scattered distribution may be ascribed to hydrolysis processes that favor the production of formic acid in the alkaline solution (Symonds et al 1993).

Among the incondensable gases H_2 tends to be more abundant then N_2 when N_2/Ar ratios are >> 84 (Air) and decreases in the order F9 > F7 > F5 > F15 > F4 from about

Table 1. Outlet temperatures (in °C) and chemical and isotopic composition of the fumarolic discharges from Momotombo volcano. Gas contents are in µmol/mol. $\delta^{13}C$ in CO_2 (‰V-PDB), $\delta^{18}O$ and δD in H_2O (‰V-SMOW), $\delta^{32}S$ in SO_2 and H_2S (‰V-CDT) and R/Ra ratios are presented for selected fumarolic samples; n.d. – not detected, n.a. – not analyzed

Sample ID	Fumarole	mm/year	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	N_2/Ar	N_2/He	$\delta^{18}O$	δD	$\delta^{13}C$	$\delta^{34}S$-SO_2	$\delta^{34}S$-H_2S	R/Ra
Locality: 086°32.330´ W 12°25,385´ N, 1237 m a.s.l.																										
1	F9	Mar-02	776	85490	857	38.73	29654	6681	0.188	871471	444	0.022	0.639	n.d.	0.0006	5285	0.111	78.13	695	3983						
2	F9	Apr-02	761	168660	2477	111.93	59619	16599	0.542	739698	1046	0.176	2.952	n.d.	0.0026	11612	0.231	173.7	354	4529						
3	F9	Nov-02	763	79393	2820	n.a.	22027	5951	0.320	885424	495	0.002	4.999	3.640	0.0022	3874	0.083	7.292	99	5938						
4	F9	Nov-02	760	257241	1409	n.a.	61884	17581	0.563	645324	1749	0.022	15.062	3.972	0.0132	14746	0.348	44.54	116	5033						
5	F9	Nov-02	760	94474	3168	n.a.	23264	6975	0.540	866698	526	0.005	4.389	0.325	0.0033	4885	0.173	5.077	120	3033			-3.08			
6	F9	Nov-02	760	35458	610	n.a.	4544	1239	0.165	951025	4878	0.017	51.008	991	0.0335	1202	0.036	1.546	96	1.E+05						
7	F9	Nov-02	761	113314	781	94.38	30050	9106	0.202	838410	778	0.027	4.856	0.247	0.0033	7452	0.132	9.540	160	5904	6.16	-12.32				
8	F9	Mar-03	741	89466	306	18.45	26749	4804	0.570	873834	754	0.014	7.121	32.38	0.0053	4018	0.217	10.42	106	3484	6.30	-21.80				
9	F9	Jul-03	739	203812	6324	79.83	34649	7820	0.111	741324	504	0.006	1.496	1.496	0.0010	5479	0.090	5.085	337	5614				6.3	5.4	
10	F9	Jul-03	737	147277	6185	78.08	25123	7475	0.154	808555	453	0.005	1.327	7.588	0.0011	4830	0.074	16.02	341	6092	6.79	-13.52				
Locality: 086°32.337´ W 12°25.396´ N, 1240 m a.s.l.																										
11	F7	Nov-02	615	34641	281	n.a.	8394	131	0.175	955645	231	0.003	2.489	1.036	0.0013	673	0.062	1.102	93	3737						
12	F7	Nov-02	615	89501	1063	n.a.	25010	6902	0.541	875281	535	0.005	3.000	0.313	0.0022	1700	0.130	3.724	178	4116						
13	F7	Nov-02	615	97706	595	n.a.	26439	21782	0.451	850633	722	0.004	7.209	0.227	0.0040	2111	0.202	2.605	100	3585						
14	F7	Nov-02	615	64548	480	n.a.	9153	159	0.155	924056	389	0.001	3.445	0.096	0.0019	1211	0.072	0.980	113	5390						
15	F7	Nov-02	616	85927	593	66.04	15113	176	0.147	895264	1313	0.002	14.653	4.980	0.0074	1528	0.094	0.927	90	13905	6.21	-16.55				
16	F7	Mar-03	614	105003	557	56.92	24467	4866	0.334	861884	1583	0.006	18.075	76.796	0.0092	1470	0.133	17.02	88	11910						6.29
17	F7	Jul-03	600	182228	27608	276.1	37848	8920	0.168	740514	450	0.003	1.432	0.703	0.0008	2152	0.107	1.719	314	4213						
18	F7	Jul-03	600	110979	2172	21.72	23952	3667	0.213	854671	3144	0.005	14.227	80.803	0.0090	1292	0.050	4.291	221	63283			-3.24	7.1	5.3	
Locality: 086°32.283´ W 12°25.391´ N, 1230 m a.s.l.																										
19	F15	Nov-02	475	89323	378	n.a.	26630	4716	0.050	877914	464	0.176	0.995	0.052	0.0007	566	0.107	6.512	466	4344	1.49	-25.83				5.44
20	F15	Nov-02	472	57942	244	n.a.	17913	2752	0.074	920177	428	0.115	1.113	0.261	0.0009	534	0.105	5.487	384	4089			-2.63			
21	F15	Nov-02	478	54843	738	79.20	1659	1243	0.097	940840	252	0.041	0.733	0.083	0.0005	344	0.060	0.657	343	4180						
22	F15	Nov-02	478	79696	221	23.70	15991	4998	0.087	898125	408	0.029	0.897	0.076	0.0007	535	0.097	0.775	455	4196						
Locality: 086°32.313´ W 12°25.460´ N, 1224 m a.s.l.																										
23	F5	Apr-02	594	49921	623	32.83	27585	2473	0.056	918213	270	0.002	0.184	n.d.	0.0001	875	0.073	7.264	1467	3690						
Locality: 086°32.313´ W 12°25.460´ N, 1224 m a.s.l.																										
24	F4	Nov-02	368	86986	519	n.a.	9418	2313	0.094	900672	81.7	0.001	0.988	1.057	0.0006	8.62	0.018	0.091	83	4636			-3.06			

Table 2. Light hydrocarbon compositions (nmol/mol) of the fumarolic discharges from Momotombo volcano. n.d. – not detected

Sample ID	Fumarole	mm/year	T(°C)	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8	C_5H_{12}	C_5H_{10}	C_6H_{14}	C_7H_{16}	C_9H_{20}	C_6H_6	C_7H_8	Alkanes	Alkenes	Aromatics	Σ Hydrocarbons
Locality: 086°32.330´ W 12°25,385´ N, 1237 m a.s.l.																					
1	F9	Mar-02	776	21.9	0.65	2.10	n.d.	0.44	0.31	0.94	0.90	n.d.	0.06	0.46	n.d.	0.40	0.05	2.38	3.47	0.45	28.2
2	F9	Apr-02	761	176	1.77	13.6	n.d.	2.72	0.73	3.76	3.13	n.d.	n.d.	n.d.	n.d.	1.39	0.14	5.63	20.1	1.53	203
3	F9	Nov-02	763	2.19	4.56	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.35	n.d.	4.56	n.d.	0.35	7.10
4	F9	Nov-02	760	21.5	60.6	19.0	7.45	11.8	n.d.	10.4	n.d.	n.d.	n.d.	n.d.	n.d.	1.16	n.d.	68.0	41.2	1.16	132
5	F9	Nov-02	760	4.88	8.62	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.27	n.d.	8.62	n.d.	0.27	13.8
6	F9	Nov-02	760	17.1	24.6	n.d.	n.d.	n.d.	n.d.	11.9	n.d.	n.d.	n.d.	n.d.	n.d.	1.00	n.d.	24.6	11.9	1.00	54.6
7	F9	Nov-02	761	27.2	29.7	6.34	6.75	2.80	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.00	n.d.	36.5	9.14	7.00	79.8
8	F9	Mar-03	741	14.0	13.1	2.60	2.31	11.2	n.d.	17.2	n.d.	n.d.	n.d.	n.d.	n.d.	0.34	n.d.	15.4	31.0	0.34	60.7
9	F9	Jul-03	739	5.98	0.69	1.30	n.d.	0.21	n.d.	0.57	n.d.	n.d.	n.d.	n.d.	n.d.	0.15	n.d.	0.69	2.08	0.15	8.90
10	F9	Jul-03	737	5.31	0.50	0.99	n.d.	n.d.	n.d.	0.99	n.d.	n.d.	n.d.	n.d.	n.d.	0.13	n.d.	0.50	1.98	0.13	7.93
Locality: 086°32.337´ W 12°25.396´ N, 1240 m a.s.l.																					
11	F7	Nov-02	615	3.45	7.94	2.83	0.30	7.97	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.77	n.d.	8.24	10.8	1.77	24.3
12	F7	Nov-02	615	5.37	27.2	12.4	1.16	24.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.72	n.d.	28.3	37.0	0.72	71.4
13	F7	Nov-02	615	4.26	14.6	5.62	1.16	21.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.40	n.d.	15.8	26.6	4.40	51.1
14	F7	Nov-02	615	0.64	0.72	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	0.72	n.d.	0.06	1.43
15	F7	Nov-02	616	2.00	9.01	n.d.	n.d.	n.d.	n.d.	25.0	n.d.	n.d.	n.d.	n.d.	n.d.	0.23	n.d.	9.01	25.0	0.23	36.3
16	F7	Mar-03	614	6.01	3.86	0.98	1.04	2.15	n.d.	12.5	n.d.	n.d.	n.d.	n.d.	n.d.	0.79	n.d.	4.91	15.6	0.79	27.3
17	F7	Jul-03	600	2.60	n.d.	n.d.	n.d.	n.d.	n.d.	0.83	n.d.	n.d.	n.d.	n.d.	n.d.	0.10	n.d.	n.d.	0.83	0.10	3.54
18	F7	Jul-03	600	4.52	1.24	1.42	0.11	0.51	n.d.	0.88	n.d.	n.d.	n.d.	n.d.	n.d.	0.20	n.d.	1.35	2.81	0.20	8.88
Locality: 086°32.283´ W 12°25.391´ N, 1230 m a.s.l.																					
19	F15	Nov-02	475	176	721	12.9	244	192	54.6	68.0	9.39	2.15	6.63	1.61	4.68	70.3	15.1	1042	275	85.4	1578
20	F15	Nov-02	472	115	634	10.9	379	344	136	293	32.1	6.88	21.3	1.72	4.71	56.9	13.2	1208	655	70.1	2049
21	F15	Nov-02	478	40.7	14.1	3.76	5.42	8.36	n.d.	10.4	n.d.	n.d.	n.d.	n.d.	n.d.	1.06	n.d.	19.5	22.5	1.06	83.73
22	F15	Nov-02	478	29.0	7.56	1.05	1.97	2.88	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.37	n.d.	9.54	3.93	1.37	43.82
Locality: 086°32.313´ W 12°25.460´ N, 1224 m a.s.l.																					
23	F5	Apr-02	594	1.97	0.34	0.27	0.17	0.16	0.05	0.18	0.38	n.d.	0.01	n.d.	n.d.	0.13	0.01	0.95	0.60	0.14	3.66
Locality: 086°32.313´ W 12°25.460´ N, 1224 m a.s.l.																					
24	F4	Nov-02	368	0.53	4.26	0.30	2.50	1.25	1.98	1.60	0.19	0.25	0.25	0.02	n.d.	0.16	0.22	9.20	3.40	0.38	13.51

15,000 to 9 µmol/mol, which is compatible with the decrease of emission temperatures. Momotombo gases show high relative N_2 contents with N_2/Ar ratios up to 1,467 and N_2/He ratios of 3,000-137,000. He contents are below the 1 ppmv level: 0.07-0.3 µmol/mol at F9, 0.05-0.2 µmol/mol at F7, 0.06-0.1 µmol/mol at F15 and 0.07 µmol/mol at F5 and 0.02 µmol/mol at the lowest temperature fumarole F4 (#24).

In the $N_2/100$-Ar-10*He ternary diagram (Giggenbach 1996) (Fig. 2), the Momotombo gases plot within the typical field of "arc volcanism" (Kita et al. 1993; Giggenbach 1996) suggesting an almost complete magmatic origin for the N_2, which was probably added to the magma source by subducted marine sediments. Exceptions are a) sample #6 which is air contaminated, b) samples from Nov-'02 and Mar-'03 (with the exception of the ones from F15) that show generally lower N_2/Ar ratios (84-200) and point to a significant contribution of meteoric N_2 and Ar from ASW (Air saturated water: N_2/Ar = 38.4 and low He concentrations), and c) sample #18 which shows an apparent "N_2 excess".

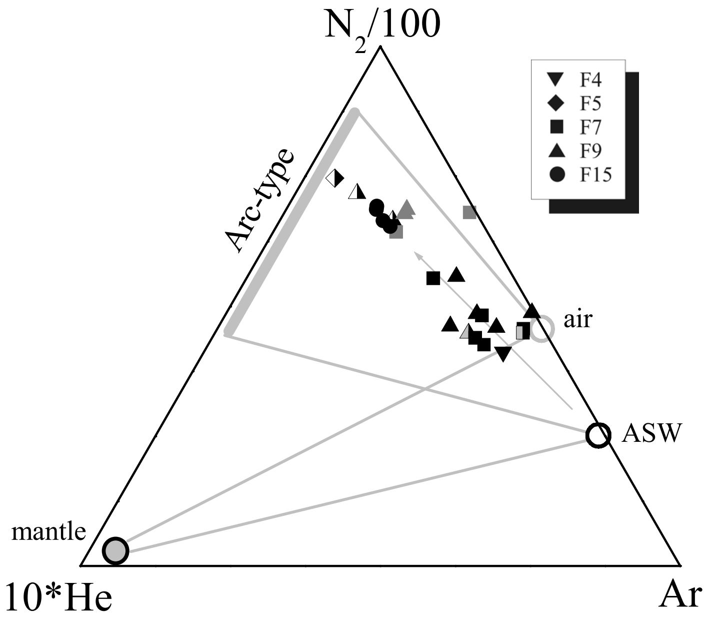

Fig. 2 Ar-N2/100-He*10 ternary diagram for gas samples from Momotombo volcano. Air and Air Saturated Water (ASW) compositions, convergent plate boundaries ("Arc-type") and "mantle" fields (Giggenbach 1996) are also shown. The symbols adopted here are used also in the graphs that follow. The different colours distinguish the sampling periods: black-white for March-April 2002 (middle of the dry season), black for November 2002 (end of the rainy season), black-gray for February-March 2003 (middle of the dry season) and gray for July 2003 (end of the dry season)

Excess amounts of N_2, associated to high CH_4, were noticed in geothermal gases from the Momotombo Power Plant by Snyder et al. (2003), and were supposedly derived from "metamorphic processes" involving a shallow sedimentary source. We think that the N_2 excess presented by sample #18 is not referable to a shallow meta-sedimentary N_2 source but to a scarce He contribution to the gas discharge. In fact the organic fraction of the gases is low, typically below 0.2 ppmv, and just occasionally reaches concentrations of up to 2 ppmv at F15 (#19, #20) (Table 2). CH_4 and C_6H_6 are ubiquitous and occur at ppbv levels with maximum values of respectively some 100s and 10s of nmol/mol at F15 (#19 and #20). The other hydrocarbons show a restricted spectrum at the HT fumaroles F9, F7 and F5 (generally only C_2-C_3 chains) and a broader one at the lower temperature fumaroles F15 and F4 (usually the whole range of C_2-C_9 alkanes and C_2-C_5 alkenes), with commonly highest contents at the intermediate temperature fumarole F15. Alkenes are more abundant at the high temperature fumaroles F9 (except in November) and F7 while non methane-alkanes are generally higher at the fumaroles F5, F4 and F15, where emission temperatures are less then 600ºC. These trends reflect the lower stability of higher hydrocarbons and alkanes, with respect to alkenes, with increasing temperature (e.g. Capaccioni et al. 1993). The extremely low $CH_4/(C_2H_6+C_3H_8)$ ratios (between 0.1 and 99) indicate that production of hydrocarbon compounds at Momotombo is related to thermogenic processes involving decomposition of low amounts of organic matter (e.g. Oremland et al. 1987).

3.5.2 Carbon, oxygen, hydrogen, sulfur and noble gas isotopic compositions

The $\delta^{13}C$-CO_2 values and those of $\delta^{18}O$ and δD in water vapor are listed in Table 1, together with the $\delta^{34}S$-H_2S-SO_2 values and $^3He/^4He$ ratios. The $\delta^{13}C$-CO_2 values, determined on selected samples from various fumaroles are between -2.63 at F15 (#21) and -3.06 to -3.24‰ V-PDB at F4 (#24), F9 (#5) and F7 (#18) suggest a primary arc-mantle origin of CO_2 ($\delta^{13}C$ = -3 to -8‰ PDB; e.g. Rollinson 1993), with possible small contributions of thermogenic CO_2 from a shallow sedimentary source.

The values of $\delta^{18}O$ and δD of the water condensates from 2002 to 2003 vary from +1.49 to +6.79‰ and from -12.32 to -25.83‰ V-SMOW, respectively. The fumarolic discharges (#7, #8, #10, #15, #19) show relatively heavy oxygen and hydrogen isotopic compositions with respect to the local precipitation. In the $\delta^{18}O$-δD diagram (Fig. 3) our

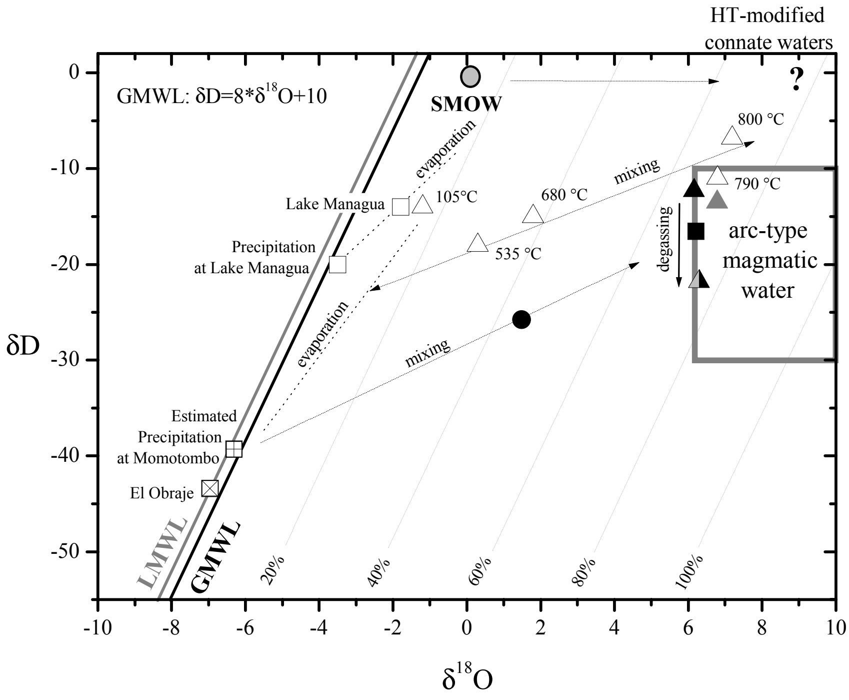

Fig. 3 $\delta^{18}O$-δD (SMOW) diagram for gases and a cold well-water sample (El Obraje) from Momotombo volcano. The "arc-type magmatic water" field (Taran et al. 1989; Giggenbach 1992), the Local and Global Meteoric Water Lines (LMWL; IAEA 2004 and IAEA/WMO 2004. GMWL; Craig 1961) and the calculated composition (Bowen and Wilkinson 2002) for local precipitation at Momotombo are also shown. The percentages indicate the fraction of magmatic water contributing to the fumarolic gases (Giggenbach 1992). The different lines are self-explanatory. The white symbols are use here and in the following graphs to indicate bibliographic data: square - for water samples; triangle - for fumarolic gas samples. Bibliographic data are from Allard (1983) and Menyailov et al. (1986)

(Craig 1961; IAEA 2004; IAEA/WMO 2004). We assume that the $\delta^{18}O$ and δD values of the precipitation at Momotombo is slightly heavier (-6.31 and -39.3‰ SMOW, respectively) than that of the cold well-water El Obraçe (-6.96 and -43.4‰ V-SMOW, respectively) sampled at the periphery of the volcano because the recharge altitude (Bowen and Wilkinson 2002) of the El Obraçe water is higher (1580 m) than that of Momotombo, indicating a probable origin from higher lands at the eastern border of the Nicaraguan Graben.

Momotombo HT gases are characterized by heavy sulfur isotopic compositions (#9 and #18) (Table 1). Measured $\delta^{34}S$-SO_2 values (F9= +6.3 and F7= +7.1‰ relative to V-CDT) are within the reported range of "arc-type" SO_2 (+5 to +7‰ CDT). The $\delta^{34}S$-H_2S values of +5.4‰ (F9) and +5.3‰ (F7) (V-CDT) are higher than the typical value of -8 to -3‰

CDT of volcanic H_2S (e.g. Ohmoto and Rye 1979; Rollison 1993), but similar to those from HT fumaroles at the arc-type volcanoes Showashizan (Ohmoto and Rye 1979) and Satsuma-Iwojima, Japan (Shinohara et al. 1993).

The $^3He/^4He$ ratio was measured on two samples (#16 and #19) from fumarole F7 (6.29Ra) and F15 (5.44Ra). Assuming that the $^3He/^4He$ ratio of the highest temperature fumarole F9 has not changed substantially from the value of 7.0Ra reported by Shaw et al. (2003), we detect a temperature dependence in the He isotope composition at the fumarolic field of Momotombo. We can expect that the path length of the gases discharging at the fumaroles changes and that the $^3He/^4He$ ratio decreases as the gas emission points move further away from the main magmatic intrusion. The lower $^3He/^4He$ ratio at F15 is associated with high He/Ne = 150 and $^4He/^{20}Ne = 375$ ratios and indicates a dilution by radiogenic crustal He. Varying degrees of crustal contamination could reflect the different ages of the fumaroles' rock substratum. The more altered conditions of the rocks at F7 and F15 with respect to F9 and the different distribution of REE in the gas condensates (Chapter 4) possibly indicate that F9 is located on products of the 1905 eruption while F7 and F15 are located on older material of "Momotombo Actual" (geologic map; Hradecky et al. 2001).

3.6 Discussion

Although the combined high temperatures of the fumaroles and the episodic intense seismic activity have not been connected with any evident external perturbation of the Momotombo system (e.g. eruption), the detected evolution of gas chemistry points to changes in degassing mechanisms. One of the main points emerging from this study is a substantial difference in chemical and isotopic composition between the 2002-2003 and 1980s fumarolic discharges (data from Allard (1983), Bernard (1985), Menyailov et al. (1986) and Martini (1996)). We will discuss the possible processes responsible for these changes in order to highlight how the Momotombo system has evolved through time. Another outcome of this study is that also seasonal variations in gas chemistry occurred during the four field campaigns in 2002 and 2003 and we will discuss these short-term variations as well.

3.6.1 Chlorine vs. Sulfur-rich gases

The chemical composition of the HT gases discharged at Momotombo in 2002-2003 (737-776ºC) differs from that in the ‘80s (790-863ºC) (Allard 1983; Bernard 1985; Menyailov et al. 1986; Martini 1996), both with respect to bulk chemical compositions and element ratios. The 2002-2003 discharges are characterized by H_2O/CO_2 ratios << 27, C_{tot} >> 50,000 µmol/mol, S_{tot} ~ 35,000 µmol/mol, $SO_2/H_2S = 4$, HCl/SO_2 << 0.3, and variable HCl/HF ratios, while the ‘80s gases are represented by H_2O/CO_2 >> 25, C_{tot} << 50,000 µmol/mol, S_{tot} < 16,000 µmol/mol, SO_2/H_2S ~ 1.5, HCl/SO_2 > 0.3, HCl/HF = 10-130 (Bernard 1985; Menyailov et al. 1986; Martini 1996).

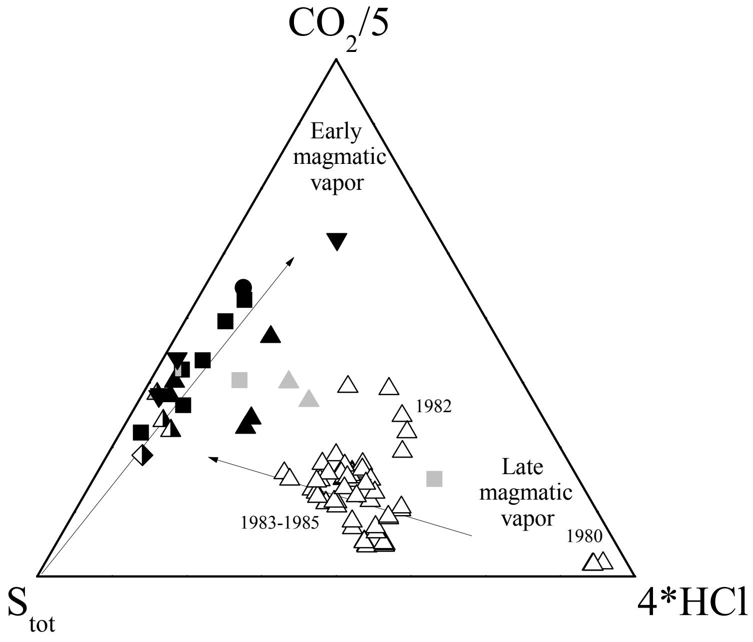

Fig. **4a** $4*HCl-CO_2/5-S_{tot}$ triangular plot (Giggenbach 1996) for gas samples from Momotombo volcano. White triangles indicate the composition of the gases discharged at the fumaroles in the ‘80s (Allard 1983; Bernard, 1985, Menyailov et al. 1986)

In the triangular diagrams $4*Cl-CO_2/5$-Stot (Giggenbach 1996) (Fig. 4a), $F*100-S_{tot}-Cl*10$ (Fig. 4b) it is evident that the 2002-2003 HT gases are generally CO2-sulfur-rich (only the group of samples from Jul-03 seems to deviate somewhat from this general trend) while the ones from the ‘80s are relatively Cl- to Cl-F-rich (µmol/mol average contents of the 1980 and 1985 gases: H_2O = 97,500-93,000, CO_2 = 14,500-37,000, S_{tot} =

6,500-16,000, HCl = 28,000-3,000 and HF = 2,500-140; Bernard 1985; Menyailov et al. 1986). Based on the solubility sequence of C < S < Cl < H_2O < F in basaltic melts (Carroll and Webster 1994; Giggenbach 1996) the 2002-2003 gas compositions indicate

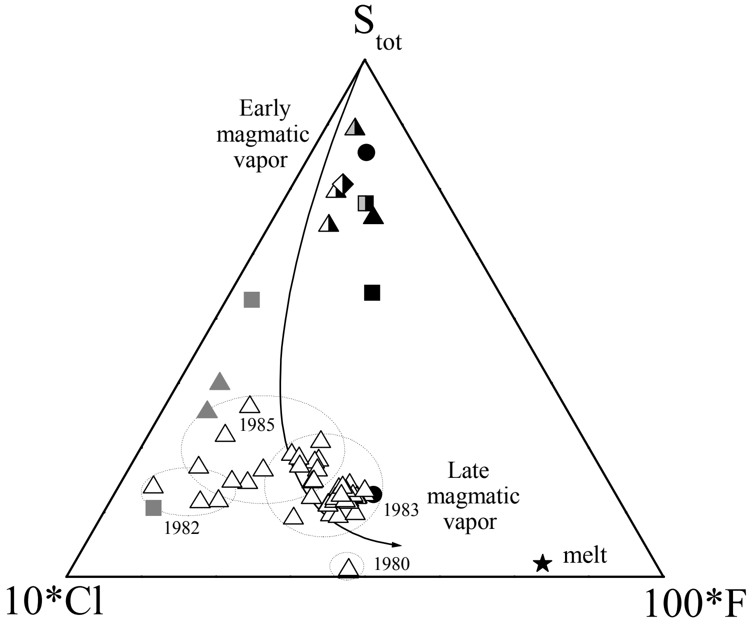

Fig. 4b 100*F- S_{tot} -10*Cl triangular plot for gas samples from Momotombo volcano. The initial melt ratios are fixed at representative values of melt inclusions in olivine phenocrysts from young mafic tephra in Nicaragua (F = 0.02 wt.%, Cl =0.09 wt.%, S = 0.11 wt%; Sadofsky et al. 2004, 2006). The curved line approximates the evolution of exolved magmatic gases with time, from "early" to "late vapor" with the transition from fresh magma to degassed magma. White triangles indicate the composition of the gases discharged at the fumaroles in the '80s (Bernard 1985; Menyailov et al. 1986)

a major contribution from a relatively undegassed magma (Fig. 4a-b). On the contrary, the chemical characteristics of the gases in the '80s suggest a derivation from a more outgassed magma batch, i.e. possibly a remnant batch from the 1905 activity. Such post-eruptive gas emissions are usually characterized by halogen-rich and sulfur-poor compositions, related to increased degrees of magma degassing (Stoiber and Rose 1970; Symonds et al. 1993; Aiuppa et al. 2004).

Following this line of reasoning, we can discard an input of fresh magma into the system during the '70s-'80s, and exclude this as a mechanism responsible for the intense seismic activity and rapid increase in the fumaroles' temperature recorded at the volcano in the same period (Smithsonian Institution 1980-1989). Thus, these events were more likely caused by the passive migration of a pre-existing and partially-degassed magma batch from an intermediate to a near-surface level, where it started to degas its residual fraction of dissolved volatiles (e.g. Symonds et al. 1990; Giggenbach 1996). This probably occurred together with the exsolution of aqueous and maybe non-silicate fluids from the magma (e.g. Shinohara 1994, Hedenquist and Lowenstern 1994). Magma migration towards the surface was likely the consequence of depressurization (removal of hydrostatic load) of the magma chamber, induced by the intense exploitation of geothermal fluids in the late `70s (Martini et al. 1991). Thus the chemical compositions of 2002-2003 gas discharges probably indicate that a pristine magma pulse entered the system only during year 2000, when an intense seismic activity was recorded underneath the volcano and the emissions reached the maximum temperature of 933 °C, the highest ever recorded at the Momotombo fumarolic field (Sismos y Volcanes de Nicaragua 2000; BGVN 2000).

3.6.2 Shallow vs. deeper contributions

Fresh magma supply to the volcanic system in 2000 is further supported by the more typical "arc-mantle" $\delta^{13}C$-CO_2 values (-8 to -3‰ PDB; e.g. Rollinson 1993) of the 2002-2003 HT emissions (-3.06 and -3.24‰ V-PDB) with respect to the past ones (-0.5 to +2.2‰ PDB; Allard 1983; Menyailov et al. 1986). In the triangular diagram H_2O/1000-CO_2/100-2000*He (Giggenbach 1996) (Fig. 5) the 2002-2003 gases describe two dilution trends at near-constant CO_2/He ratios (ca. 750,000 and 2,000,000).

The CO_2/He ratios of the 2003 Momotombo gases are higher then the typical "arc-type" value of 65,000-900,000 indicated by Giggenbach (1996). This feature and the "arc mantle" $\delta^{13}C$-CO_2 values of the emissions indicate the degassing of an extremely CO_2-rich magma at Momotombo, which production could be related to the high sedimentary subduction input in Nicaragua (Patino et al. 2000). Shaw et al. (2003) assign 87% of the total carbon at Momotombo to the limestone and carbonates derived from the incoming plate in the subduction zone. The highest CO_2/He ratio (~ 2,000,000) is associated with the most negative $\delta^{13}C$-CO_2 value (-3.24‰ V-PDB) and the highest HCl/HF (80-100) ratios (Fig 4b) at F9 and F7 in Jul-'03 (#9-10, #17-18). This could be related to the opening of new fracture during the occurrence of tectonic earthquakes in May-June 2003 (INETER 2003a; 2003b) and the degassing of a deeper sited gas-rich magma batch.

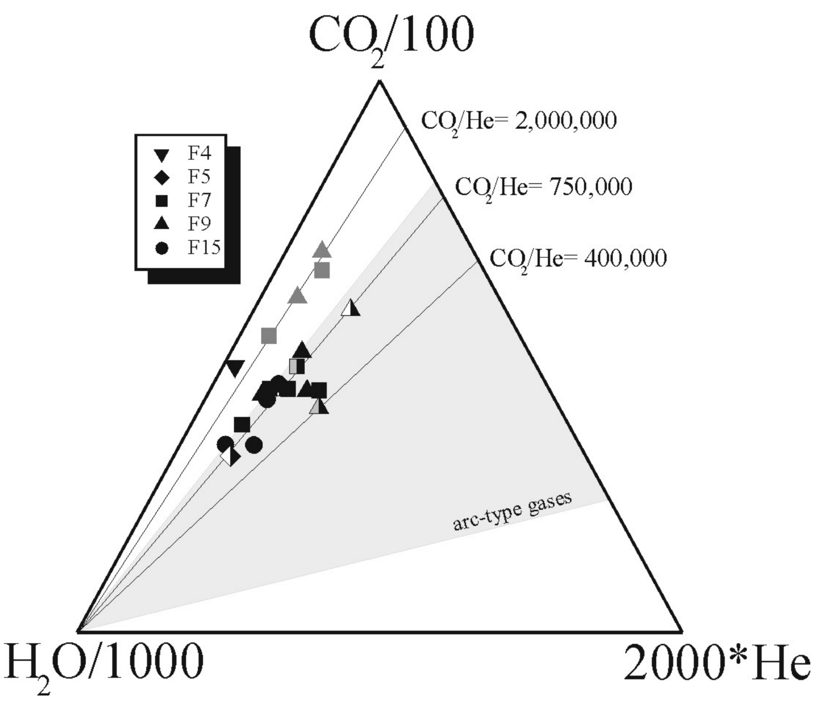

Fig. 5 2000*He-CO_2/100-H_2O/1000 ternary diagram (Giggenbach 1996) for gas samples from Momotombo volcano. Sample #4, which was affected by a sampling problem (lost solution) and #6 and #11, which are partly air contaminated were not plotted in the graph

Consequently the high CO_2/He ratio of the Momotombo gases could result from the higher solubility of He in CO_2-rich basaltic melts (e.g. Carroll and Webster 1994).

Protracted degassing leads to a decline in CO_2 and an increase of He in the gas emissions (e.g. Nuccio and Paonita 2001) and could account for the lower CO_2/He ratios (400,000) measured at F9 in Mar-'03 (#8). Similarly the lower CO_2 contents and higher $\delta^{13}C$-CO_2 values in the '80s discharges could indicate a derivation from a degassed magma, negligible magmatic input, and predominant contribution of thermogenic CO_2 from a shallow sedimentary source, possibly from marine carbonates present in the Nicaraguan Depression, as already suggested by Allard (1980) and Menyailov et al. (1986). Additionally CO_2 isotope fractionation could occur as the raising magmatic gases interact with water present in the system. This appears to be the most likely mechanism, as isotopic exchange between CO_2 and carbon-bearing ions and molecules coexisting in hydrothermal fluids could partly cause the more positive $\delta^{13}C$-CO_2 in the '80s gases (e.g. Faure 1986).

Also the isotopic signature of the water vapor differs significantly in the two periods. In 2002-2003 the $\delta^{18}O$-δD values of the water condensates indicate varying degrees of magma degassing and mixing between the local precipitation and "arc-type magmatic water" (Taran et al. 1989; Giggenbach 1992) (Fig. 3). Following Giggenbach (1992), we estimate that the magmatic water fraction is about 70-80% at the HT fumaroles F7 and F9 and about 50% at the lower temperature fumarole F15. The meteoric dilution of the magmatic gases occurs at high levels of the system and the sample from Jul-'03 (#10) (end of the dry season) appears to be the least diluted and shows the highest magmatic water content. δD-H_2O values show the same systematic variations through time as the CO_2/He ratios and further support the suggestions advanced above: a decrease in δD-H_2O and CO_2/He between Nov-'02 (#7) and Mar-'03 (#8) reflects the progressive degassing of the main, possibly small, magma batch sustaining the fumaroles, while successive simultaneous δD-H_2O and CO_2/He increase in Jul-'03 (#10) points to the degassing of a fresh magma batch.

The water vapor discharged at the fumaroles in the '80s (Allard 1983; Menyailov et al. 1986) is enriched in ^{2}H and shows higher δD-H_2O values than today (Fig. 3). If this signature is not a sampling artifact (evaporation at $T < 250°C$ enrich the condensate in deuterium; O'Neil 1986), which would be a quite odd coincidence, it points to a strong contribution from a heavy isotopic end-member to the magmatic vapors. The origin of such a diluting heavy end-member is difficult to identify, since both kinetic fractionation effects and D-enriched parent components (connate water, lake water, mid-low altitude recharges or exsolved saline fluids) could concur in producing this isotopic signature. Anyway magma intruding in a cold environment produces thermal gradients that likely promote the convection and mixing of fluids present at different levels in the crust (e.g. Hedenquist and Lowenstern 1994), suggesting a possible multi-source origin for the D-enriched component. This D-enriched component, particularly present in the HT discharges, was possibly masking the degassed (D-depleted) signature of the magma batch sustaining the '80s fumarolic gases.

Today there is no need to recur to such a complex model to explain the H_2O isotopic composition of the emissions since it appears to be the product of binary mixing between magmatic gases and local precipitation. In fact the seasonal distribution of the precipitation determines the different H_2O contents of the discharges. Higher water contents are generally measured in the samples collected at the end of the rainy season (Nov-'02), while water contents are low in samples collected during (Mar-Apr '02/'03) and at the end of the dry season (Jul-'03), when meteoric contributions are negligible. Furthermore a decrease in water-soluble species (i.e. SO_2 and HCl; Table 1) from the HT (lower H_2O/CO_2 ratios) to the LT gases (higher H_2O/CO_2 ratios) is associated with this dilution trend (Fig. 6-7).

The '80s gases differ from the 2002-2003 gases also in sulfur content, SO_2/H_2S ratios and $\delta^{34}S$-SO_2-H_2S signatures. Our samples #9 and #18 show values of $\delta^{34}S$-SO_2-$H_2S_{739°C}$ = +6.3 and +5.4‰ V-CDT and $\delta^{34}S$-SO_2-$H_2S_{600°C}$ = +7.1 and +5.3‰ V-CDT while Menyailov et al. (1986) reported $\delta^{34}S$-SO_2-$H_2S_{790°C}$ = +5.9 and +2.0‰ CDT, $\delta^{34}S$-SO_2-$H_2S_{680°C}$ = +10.7 and +1.3‰ CDT, SO_2-$H_2S_{535°C}$ = +11.9 and +0.1‰ CDT for emissions at almost comparable temperatures. In particular, at present we measure higher $\delta^{34}S$-H_2S values and limited $^{34}S/^{32}S$ fractionation between SO_2 and H_2S. The equilibrium fractionation temperatures of $\delta^{34}S$-SO_2 relative to $\delta^{34}S$-H_2S (Ohmoto and Rye 1979) are abnormally high in 2003 (T = 2000°C for #9 and 1400°C for #18) and were considerably lower in 1982 (T = 690, 370 and 280°C), and are in both cases in strong disagreement with the measured emission temperatures. This presumably means that in both cases $^{34}S/^{32}S$ fractionation between SO_2 and H_2S was not an equilibrium process and that kinetic effects were important. For the HT fumarolic discharges the calculated $\delta^{34}S$ of total sulfur (Faure 1986) differs between the ‘80s and 2003 (+4.3 vs. +6.1‰, respectively) while for the lower temperature fumaroles the same values are observed (+6.9‰). Since isotope fractionation depends on bond strength, and the preferential partitioning of ^{34}S decreases in the order $SO_4^{2-} > SO_3^{2-} > SO_2 > S_x \sim H_2S \sim HS^- > S^{2-}$ (Ohmoto and Rye 1979), the ^{34}S depletion in 1982 could be the product of kinetically controlled ^{34}S subtraction by sulfate phases, while ^{34}S enrichment in 2003 could result from subtraction of ^{32}S by sulfide phases or recycling of previously subtracted ^{34}S- rich phases.

On the one hand, a variation in the redox state (composition, temperature, pressure) of a magma batch, in our case induced by the proposed new magma input in 2000 and 2003, inevitably affects the sulfur solubility and speciation (S^{6+}/S^{2-}, $^{34}S/^{32}S$) in the melt (Faure 1986) and thereby the equilibrium bulk and isotopic composition of the separating sulfur-gases. On the other hand, kinetic fractionation processes dominate during gas ascent to the surface and influence the subsurface deposition of ^{32}S-rich elemental sulfur or metal-sulfides and/or ^{34}S-rich metal-sulfates in response to changes in T and fO_2 conditions (Ohmoto and Rye 1979; Rye 1993). Another, even more common process is the chemical and isotopic fractionation that occurs in the SO_2-H_2S-SO_4-S^0 system during gas-water interaction and breakdown reactions (Ohmoto and Rye 1979; Rollison 1993; Rye 1993).

Although we do not have any information on the sulfur systematics of Momotombo primary and derived products, we interpret the different sulfur features of the ‘80s and 2003 gases to originate from both deep magmatic and shallow-level secondary processes.

3.6.3 Hydrothermal contribution vs. meteoric dilution

So far we have shown that the diverse isotope characteristics of the ‘80s and 2002-2003 emissions cannot be fully explained by derivation from outgassed and undegassed magma batches, respectively. The isotopic studies indicate a different contribution of non-magmatic/ hydrothermal fluids to the gas emissions and a change in interaction between the magmatic system and the surrounding environment sometime in the period between the ‘80s and 2002. In particular we note a different distribution of SO_2 and HCl with varying H_2O contents between the ‘80s and 2002-2003 discharges. The 2002-2003 gases show decreasing SO_2 and HCl contents with increasing water content (Fig. 6-7).

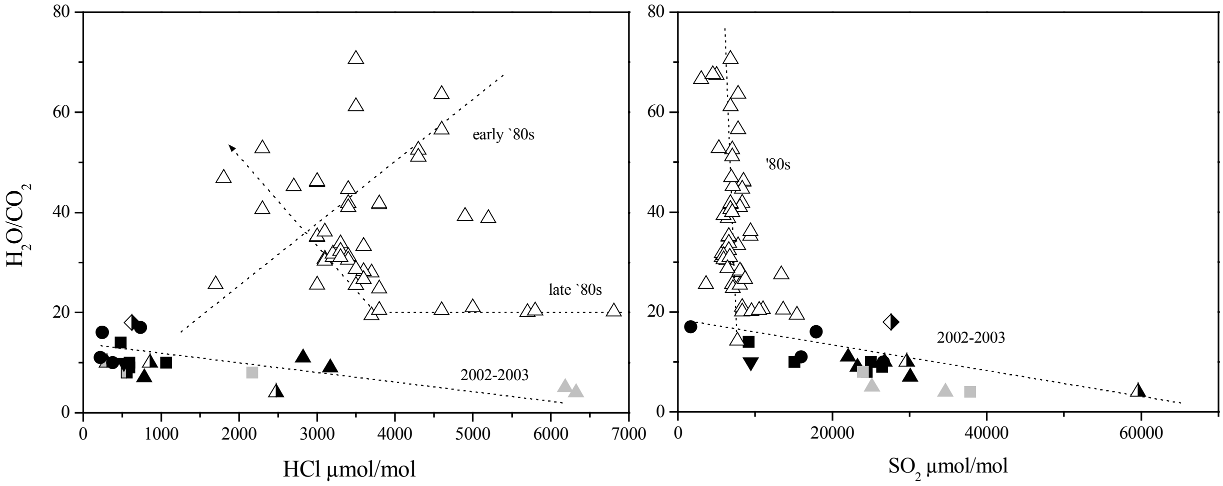

Fig. 6-7 HCl-H_2O/CO_2 and SO_2-H_2O/CO_2 binary diagram. Sample #4, which was affected by a sampling problem (lost solution) and #6 and #11, which are partly air contaminated were not plotted in the graph. White triangles indicate the composition of the gases discharged at the fumaroles in the ‘80s (Bernard 1985; Menyailov et al. 1986)

This can be explained by dilution since during interaction between magmatic gases and free water in the system SO_2 is easily hydrolyzed to $HSO_4^-{}_{aq}$ or $SO_4^{2-}{}_{aq}$ and HCl to $Cl^-{}_{aq}$. On the contrary, the SO_2 and HCl variation trends with H_2O contents in the '80s gases are more readily explained by interaction with a hydrothermal system. On the one hand, an acidic boiling hydrothermal solution containing $Cl^-{}_{aq}$ will release HCl (Martini 1996; Symonds et al. 2001). This can explain the observed increase in HCl with increasing water content in the '80s gases. On the other hand, SO_2 is not likely re-degassed even from sulfate-rich solutions undergoing rapid and complete boiling, in which case SO_4^{2-} precipitates as (^{34}S-rich) sulfate minerals (Gerlach et al. 1996; Symonds et al. 2001; Ohmoto and Rye 1979). Furthermore, subtraction of SO_2 by hydrothermal solutions could also explain the lower than today S_{tot} amounts, SO_2/H_2S ratios and $\delta^{34}S$ values of the ‘80s emission.

The constant low SO_2 and increasing HCl values with increasing and higher than today H_2O contents in the ‘80s therefore indicate that hydrothermal processes were active in the past. In 2002-2003 instead no evident interaction takes place between the magmatic and the hydrothermal systems. The emitted gases are only affected by varying degrees of meteoric dilution at shallow levels. This could indicate a dry-out of the hydrothermal system or its isolation from the magmatic system sometime between the late ‘80s and 2002.

3.7 Conclusions

The volcanic gas collections in 2002-2003 have shown that considerable variations have occurred at Momotombo during the last 20 years. The composition of the gases venting at the fumaroles in 2002-2003 indicate clearly their derivation from relatively undegassed magma batches (repeated intrusive events) and can be considered representative of the early magmatic vapors discharged at Momotombo. Differently the ‘80s discharges are more representative for a more advanced stage of magmatic degassing.

The isotopic signature of $\delta^{13}C$-CO_2, $\delta^{18}O$-δD-H_2O and $\delta^{34}S$-SO_2-H_2S of the‘80s discharges cannot be “genetically” re-conducted to that of the 2002-2003 through a degassing process. In fact non-magmatic/hydrothermal fluids contribute strongly to the ‘80s discharges. This points to major changes in the type of interaction between the magmatic and the hydrothermal system, sometime between the late ‘80s and 2002. In particular hydrothermal processes were more important in the past and are partly responsible for the lower SO_2 and the higher HCl contents of the‘80s emissions. In fact it seems that HCl was partly contributed by the same acid boiling hydrothermal solution, which was subtracting the rising magmatic SO_2.

In 2002-2003 no evident interaction takes place between the magmatic and the hydrothermal system. The magmatic gases are only affected by shallow meteoric dilution, which depends on the amount of seasonal precipitation. This could indicate a dry-out of the hydrothermal system or its hydrological isolation from the main magmatic body sustaining the central crater fumaroles, sometime between the late ‘80s and 2002.

Furthermore the lower HCl contents measured in the 2002-2003 magmatic gases indicate that Momotombo occasionally emits HCl-rich gases, but this seems not to be the most general case.

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References

Aiuppa A, Burton M, Murè F, Inguaggiato S (2004) Intercomparison of volcanic gas monitoring methodologies performed on Vulcano Island, Italy. Geophys Res Lett 31-L02610 DOI 10.1029/2003GL018651

Allard P (1983) The origin of hydrogen, carbon, sulfur, nitrogen and rare gases in volcanic exhalations: evidence from isotope geochemistry. In: Tazieff H, Sabroux J-C (ed) Forecasting Volcanic Events. Elsevier, Amsterdam, pp 337-386

Allard P (1986) Géochimie isotopique et origine de l'eau, du carbone et du soufre dans les gaz volcaniques; zones de rift, marges continentales et arcs insulaires - Isotope geochemistry and origin of water, carbon, and sulfur of volcanic gases; rift zones, continental margins and island arcs. Ph.D. thesis, Université Paris VII, Paris, France, pp 1-107

Allard P, Sabroux JC (1980) Actividad volcánica del Momotombo, Nicaragua. INETER Informe Preliminar. http://www.ineter.gob.ni/geofisica/vol/momotombo/doc/allard1980.html

Bernard A (1985) Les mécanismes de condensation des gaz volcaniques. Ph.D. thesis, University of Brussels, Belgium (in French)

Bowen GJ, Wilkinson B (2002) Spatial distribution of delta O-18 in meteoric precipitation. Geology 30: 315-318

Capaccioni B, Martini M, Mangani F, Giannini L, Nappi G, Prati F (1993) Light hydrocarbons in gas-emissions from volcanic areas and geothermal fields. Geochem J 27: 7-17

Carroll MR, Webster JD (1994) Solubilities of sulfur, noble gases, nitrogen, chlorine, and fluorine in magmas. In: Carroll MR, Holloway JR (ed) Volatiles in Magmas. Rev Mineral: 30, Mineral Soc America, Washington DC, pp 231-279

Coleman ML, Moore MP (1978) Direct reduction of sulfates to sulfur-dioxide for isotopic analysis. Anal Chem 50: 1594–1595

Coleman ML, Shepherd TJ, Durham JJ, Rouse JE, Moore GR (1982) Reduction of water with zinc for hydrogen isotope analysis. Anal Chem 54: 993-995

Craig H (1961) Isotopic variations in meteoric water. Science 133: 1702-1703

Epstein S, Mayeda TK (1953) Variation of the 18O/16O ratio in natural waters. Geochim Cosmochim Acta 4: 213-224

Evans WC, White LD, Rapp JB (1988) Geochemistry of some gases in hydrothermal fluids from the Southern Juan-De-Fuca-Ridge. J Geophys Res 93: 15305-15313

Farley KA, Neroda E (1998) Noble gases in the Earth's mantle. Annu Rev Earth Planet Sci 26: 189-218

Faure G (1986) Principles of Isotope Geology. Second edition, John Wiley and Sons, New York, , pp 1-589

Gemmell JB (1987) Geochemistry of metallic trace elements in fumarolic condensates from Nicaraguan and Costa Rican volcanoes. J Volcanol Geotherm Res 33: 161-181

Gerlach TM, Westrich HR, Symonds RB (1996) Preeruption vapor in magma of the climactic Mount Pinatubo eruption: Source of the giant stratospheric sulfur dioxide cloud. In Newhall CG, Punongbayan RS (ed) Fire and mud: Eruptions and lahars of Mount Pinatubo, Philippines. Philippine Institute of Volcanology and Seismology, Quezon City and University of Washington Press, Seattle, pp 415-433

Giggenbach WF (1987) Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand. Appl Geochem 2: 143-161

Giggenbach WF (1991) Chemical techniques in geothermal exploration. In: D'Amore F (co-ordinator) Application of Geochemistry in Geothermal Reservoir Development. UNITAR, New York, pp 253-273

Giggenbach WF (1992) Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin. Earth Planet Sci Lett 113: 495-510

Giggenbach WF (1996) Chemical composition of volcanic gases. In: Scarpa M, Tilling RJ (ed) Monitoring and mitigation of Volcanic Hazards. Springer-Verlag, Berlin Heidelberg, pp 221-256

Giggenbach WF, Gougel RL (1989) Methods for the collection and analysis of geothermal and volcanic water and gas samples. NZ-DSIR Report, CD 2387, 53

Global Volcanism Program. Momotombo. Eruptive history. http://www.volcano.si.edu/world/volcano.cfm?vnum=1404-09=&volpage=erupt&VErupt=Y&VSources=Y&VRep=Y&VWeekly=N

Hedenquist JW, Aoki M, Shinohara H (1994) Flux of volatiles and ore-forming metals from the magmatic-hydrothermal system of Satsuma Iwojima volcano. Geology 22: 585–588

Hedenquist JW, Lowenstern JB (1994) The role of magmas in the formation of hydrothermal ore deposits. Nature 370: 519-527

Hradecky P, Mayorga E, Mrazova S, Novák Z, Havlicek P, Opletal M, Sebesta J, Sevcik J (2001) Estudio Geológico y Reconocimiento de las Amenazas Geológicas en el Volcán Momotombo, Nicaragua. Informe del Servicio Geológico Checo e Instituto Nicaraguense de Estudios Territoriales, Praga-Managua

IAEA (2004) Isotope Hydrology Information System, ISOHIS Database. http://isohis.iaea.org

IAEA/WMO (2004) Global Network of Isotopes in Precipitation, GNIP Database. http://isohis.iaea.org

INETER (2000-2005) Sismos y Volcanes de Nicaragua. Boletines Sismológicos, Vulcanológicos y Geológicos**,** Anual y Mensuales. http://www.ineter.gob.ni/geofisica/sis/bolsis/bolsis.html

INETER (2000). Actividad volcánica: Volcán Momotombo. Sismos y Volcanes de Nicaragua, Boletín Mensual de Junio 2000. http://www.ineter.gob.ni/ geofisica /boletin/2000/06/volcan-momotombo 0006.htm

INETER (2003a). Actividad Sísmica Tectónica: Volcan Momotombo. Sismos y Volcanes de Nicaragua, Boletín Mensual Mayo 2003. http://www.ineter.gob.ni/geofisica/boletin/2003/05/volcan-momotombo0305.htm

INETER (2003b). Lista de sismos registrados en 2003. Sismos y Volcanes de Nicaragua, Boletín Anual 2003. http://www.ineter.gob.ni/geofisica/boletin/2003/anual/lista-sismos2003.htm

Kirianov VY, Melekestsev IV, Ovsyannikov AA, Andreev VN (1988) Reconstruction of the eruptive activity of Momotombo volcano (Nicaragua) to assess volcanic hazards. Kagoshima International Conference on Volcanoes, Proceedings, pp 495-498

Kita I, Nitta K, Nagao K, Taguchi S, Koga A (1993) Difference in N_2/Ar ratio of magmatic gases from northeast and southwest Japan: New evidence for different states of plate subduction. Geology 21: 391-394

Mamyrin BA, Tolstikhin IN (1984) Helium isotopes in nature. In: Fyfe WS (eds) Development in geochemistry. Elsevier, Amsterdam, pp 1- 273

Martini M (1996) Chemical characters of the gaseous phase in different stages of volcanism: Precursors and volcanic activity. In: Scarpa M, Tilling RJ (eds) Monitoring and mitigation of Volcanic Hazards, Springer-Verlag, Berlin Heidelberg, pp 199-219

Martini M, Giannini L, Capaccioni B (1991) Geochemical and seismic precursors of volcanic activity. Acta Vulcanol 1: 7-11

McBirney AR, Williams H (1965) Volcanic history of Nicaragua. Univ Calif Pub Geo Sci 55: 1-65

Menyailov IA, Nikitina LP, Shapar VN, Pilipenko VP (1986) Temperature increase and chemical change of fumarolic gases at Momotombo Volcano, Nicaragua, in 1982-1985: Are these indicators of possible eruption? J Geophys Res 91: 12,199-12,214

Montegrossi G, Tassi F, Vaselli O, Buccianti A, Garofalo K (2001) Sulfur species in volcanic gases. Anal Chem 73: 3709-3715

Nuccio PM, Paonita A (2001) Magmatic degassing of multicomponent vapors and assessment of magma depth: Application to Vulcano Island (Italy). Earth Planet Sci Lett 93: 467-481

Ohmoto H, Rye RO (1979) Isotopes of sulfur and carbon. In: Barnes HL (eds) Geochemistry of Hydrothermal Ore Deposits. 2nd edition, John Wiley & Sons, New York, pp 509-567

O'Neil JR (1986) Theoretical and experimental aspects of isotopic fractionation. In: Valley JW, Taylor HP, O'Neil JR (eds) Stable Isotopes in High Temperature Geological Processes. Rev Min 16, Min Soc America, Washington DC, pp 1-40

Oremland RS, Miller LG, Whiticar MJ (1987) Sources and flux of natural gases from Mono Lake, California. Geochim Cosmochim Acta 51: 2915-2929

Patino LC, Carr MJ, Feigenson MD (2000) Local and regional variations in Central American arc lavas controlled by variations in subducted sediment input. Contrib Mineral Petrol 138: 265-283

Quisefit JP, Toutain JP, Bergametti G, Javoy M, Cheynet B, Person A (1989) Evolution versus cooling of gaseous volcanic emissions from Momotombo volcano, Nicaragua: Thermochemical model and observations. Geochim Cosmochim Acta 53: 2591-2608

Poreda RJ, Farley KA (1992) Rare-gases in Samoan Xenoliths. Earth Planet Sci Lett 113: 129-144

Rollinson H (1993) Using Geochemical Data: Evaluation, Presentation, Interpretation: Longman Scientific & Technical Ltd, Harlow, UK, pp 1-352

Rye RO (1993) The evolution of magmatic fluids in the epithermal environment: the stable isotope perspective. Econ Geol 88: 733-752

Sadofsky SJ, Hoernle K, van den Bogaard P (2004) Volatiles in Melt Inclusions from the Central American Volcanic Arc: Insights into Subduction-zone Volatile Cycling. 14th Annual Goldschmidt Conference Copenhagen, Denmark. J Conf Abs

Sadofsky SJ, Hoernle K, van den Bogaard P (2006) Subducted Water Beneath Costa Rica and Nicaragua: What Goes in Sometimes Comes out. Geology (in review)

Shaw AM, Hilton DR, Fischer TP, Walker JA, Alvarado GE (2003) Contrasting He-C relationship in Nicaragua and Costa Rica: insights into C cycling through subduction zones. Earth Planet Sci Lett 214: 499-513

Shinohara H, Giggenbach WF, Kazahaya K, Hedenquist JW (1993) Geochemistry of volcanic gases and hot springs of Satsuma-Iwojima, Japan: Following Matsuo. Geochem J 27: 271-285

Shinohara H (1994) Exsolution of immiscible vapor and fluid phases from a crystallizing silicate melt: Implications for chlorine and metal transport. Geochim Cosmochim Acta 58: 5215–5221

Smithsonian Institution (1980-1989) Momotombo. Scientific Event Alert Network (SEAN) Bulletin 05:07-14:04. http://www.volcano.si.edu/world/volcano.cfm?vnum=1404-09=&volpage=var&Verupt=Y&VSources=Y&Vrep=Y&VWeekly=N

Smithsonian Institution (1983) Momotombo. Scientific Event Alert Network (SEAN) Bulletin 08:05

Smithsonian Institution (1990-2000) Momotombo. Bulletin of the Global Volcanism Network (BGVN) 15:04- 28:09 http://www.volcano.si.edu/world/volcano.cfm?vnum=1404-09=&volpage=var&Verupt=Y&VSources=Y&Vrep=Y&VWeekly=N

Smithsonian Institution (1995) Momotombo. Bulletin of the Global Volcanism Network (BGVN) 20:04

Smithsonian Institution (2000) Momotombo. Bulletin of the Global Volcanism Network (BGVN) 25:06

Smithsonian Institution (2003) Momotombo. Bulletin of the Global Volcanism Network (BGVN) 28:09

Snyder G, Poreda R, Fehn U, Hunt A (2003) Sources of nitrogen and methane in Central American geothermal settings: Noble gas and ^{129}I evidence for crustal and magmatic volatile components. Geochem Geophys Geosyst 4, DOI 10.1029/2002GC000363

Stoiber RE, Rose WI (1970) The geochemistry of Central American volcanic gas condensates. Geol Soc Am Bull 81: 2891-2911

Symonds RB, Gerlach TM, Reed MH (2001) Magmatic gas scrubbing: implications for volcano monitoring. J Volcanol Geotherm Res 108: 303-341

Symonds RB, Rose WI, Bluth GJS, Gerlach TM (1993) Volcanic gas studies: Methods, results and applications. In: Carroll MR, Holloway JR (eds) Volatiles in Magmas. Rev Mineral: 30, Mineral Soc America, Washington DC, pp 1-66

Symonds RB, Rose WI, Gerlach TM, Briggs PH, RS Harmon (1990) Evaluation of gases, condensates, and SO2 emissions from Augustine volcano, Alaska: the degassing of a Cl-rich volcanic system. Bull Volcanol 52: 355–374

Symonds RB, Rose WI, Reed MH, Lichte FE, Finnegan DL (1987) Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia, Geochim Cosmochim Acta 51: 2083-2101

Taran Y, Hedenquist JW, Korzhinsky MA, Tkachenko SI, Shmulovic KI (1995) Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands. Geochim Cosmochim Acta 59: 1749-1761

Taran YA, Pokrovsky BG, Esikov AD (1989) Deuterium and oxygen-18 in fumarolic steam and amphiboles from some Kamchatka volcanoes: "Andesitic waters". Dokl Akad Nauk USSR 304: 440-443

Tassi F (2004) Fluidi in ambiente vulcanico: Evoluzione temporale dei parametri composizionali e distribuzione degli idrocarburi leggeri in fase gassosa. Ph.D. thesis, Department of Earth Science, University of Florence, Italy, pp. 1-356

Tenorio V, Strauch W, Barboza V, Malavassi E (2000) Evaluación Sísmica del Volcán Momotombo al 16 de Junio del 2000. Sismos y Volcanes de Nicaragua, Boletín mensual de Junio 2000. INETER. http://www.ineter.gob.ni/geofisica/boletin /2000/06/sismos-momotombo0006.htm van Wyk de Vries B (1993) Tectonics and magma evolution of Nicaraguan volcanic systems. Ph.D. thesis, Department of Earth Sciences, The Open University, UK, pp. 1- 328

Williams-Jones G, Rymer H, Rothery DA (2003) Gravity changes and passive SO_2 degassing at the Masaya caldera complex, Nicaragua. J Volcanol Geotherm Res 123: 137-160

Chapter 4

Geochemistry and flux estimation of magma-derived volatile trace elements from the high-temperature fumarolic field of Momotombo volcano (Nicaragua)

Geochemistry and flux estimation of magma-derived volatile trace elements from the high-temperature fumarolic field of Momotombo volcano (Nicaragua)

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Abstract

Water condensate samples collected from three prominent fumaroles in the crater area of Momotombo volcano at seasonal intervals during 2002-2003 were analysed for trace elements. The three fumaroles discharge gases at significantly different temperatures (F9 = 776-737°C, F7 = 616-600°C, F15 = 478-472°C). In order to give a broad overview of trace metal discharges at Momotombo volcano we explore (a) seasonal variations in gas composition, b) variations between different fumaroles, and c) long-term changes in trace metal emissions between the 1980s and 2002-2003.

The Momotombo condensate samples are rich in HCl (3000-9000 mg/L) and H_2SO_4 (1500-5000 mg/L), and show relatively high contents of HF (150-600 mg/L). Trace element contents vary strongly, and range from few 10s of ppt to several 100s of ppb; Mo, Ni and Zn occasionally reach the ppm level in some samples.

We find that seasonal variations in gas trace metal contents were dominated by meteoric water dilution between March 2002 and February 2003. The probable arrival of a new magma batch sometime between February 2003 and July 2003 appears to be associated with major change in main gas composition and to a concomitant sharp reduction in trace element concentrations. Inter-fumarole variations are functions of emission temperatures and host-rock compositions. Because most of the investigated trace elements are dominantly transported as Cl-complexes, the lower Cl contents and lower temperatures of the 2002-2003 gases relative to those of the ‘80s seams to be the main causes for the generally lower trace element abundances in the present-day emissions. In order to obtain information on the origin of the trace metals the gases, we calculated enrichment factors (E.F.) relative to Momotombo reference rock. We find that Tl, Bi, As, Se, Mo, Sb, Hg, Au, W, Pb, Sn are the most enriched elements in the 2002-2003 emissions and are likely to be of magmatic origin.

Emission rates calculated for selected trace metals during passive degassing were based on trace metal concentrations in condensates and combined SO_2 plume flux measurements. Fluxes are provided for some highly mobile and potentially harmful components released at Momotombo. In comparison to other Nicaraguan and worldwide volcanoes Momotombo appears to be a small source of pollutants to the atmosphere.

Keywords: *Nicaragua - Momotombo volcano - Fumarolic gases – Trace elements – Metals - Fluxes*

4.1 Introduction

Recent investigations indicate that volcanic emissions are a significant source of trace metals and metalloids in the atmosphere (e.g. Nriagu 1989; Nho et al. 1996; Hinkley et al. 1999; Delmelle 2003 and reference therein). During highly explosive eruptions volatiles and fine-grained material are injected at high altitudes into the stratosphere. But also small eruptions and passive degassing, both by far more common processes during the lifetime of a volcano, release volatiles into the troposphere (Nriagu 1989; Nho et al. 1996; Gautier and Le Cloarec 1998; Hinkley et al. 1999; Allard et al. 2000; Delmelle 2003). Thus significant amounts of volatiles are released through quiescent degassing during non-eruptive phases. Investigations of the passive degassing behavior of volcanoes is therefore essential for better understanding the links between volcanic emmisions and atmospheric loading.

Passive degassing can be a long-term feature of a volcano. One example is Momotombo volcano in Nicaragua, which is in a persistent state of degassing since its last eruption in 1905. Momotombo's crater region is characterized by a long-lived high temperature

(HT) fumarolic field which appears to be the surface manifestation of a magmatic intrusion at shallow levels in the volcanic edifice (e.g. Gemmel 1987), sustained by repeated events of fresh magma input (Chapter 3). In this companion paper we have recently documented the isotopic and major chemical composition of fumarolic emissions in 2002-2003. Our studies have shown that the magmatic gases discharged at the surface are mainly “juvenile” and are only moderately affected by meteoric dilution at shallow levels (Chapter 3). The Momotombo fumarolic field therefore yields optimal conditions for investigating the magmatic contribution of trace metals and metalloids to the atmosphere and their transport in the gaseous phase. However, meteoric dilution is not the only processes affecting the composition of the venting gases. Several 'volcanic' processes play an important role in the transport and deposition of trace metals and metalloids, and their fractionation during gas ascent to the surface. During magma ascent and depressurization some elements can partition preferentially into segregating hydrosaline or non-silcate fluids (Shinohara 1994; Hedenquist and Lowenstern 1994; Taran et al. 1995; Shmulovich and Churakov 1998). Furthermore gas-water-rock interaction can modify the composition of the raising fluids and contribute material to the emissions and cooling can cause phase separation and mineral deposition (e.g. Symonds et al. 1987; 1992; Quisefit et al. 1989; Symonds and Reed 1993; Taran et al. 1995; Churakov et al. 2000).

At Momotombo volcano we have studied the characteristics of passive degassing during four field campaigns in 2002 and 2003. In particular we have sampled fumarolic gases and water condensates from the volcano. In the companion paper (Chapter 3), we discuss the chemical and isotopic characteristics of the 2002-2003 fumarolic discharges, and evaluate changes in gas composition over the past 20 years. Here we examine 1) the processes responsible for the observed trace metal abundances in the 2002-2003 fumarolic discharges, 2) the causes for short-term variations in trace elements abundances between the four field campaigns in 2002-2003, 3) differences in the fumarolic discharges between 2002-2003 and the 1980s and further provide estimates of emission rates for some highly volatile and potentially harmful metals and metalloids particularly enriched in the Momotombo magmatic gases.

4.2 Sampling and chemical analyses

4.2.1 Samples collection

Samples were collected at three fumaroles (Fig 1) discharging gases at different temperatures in the 150 x 250 m wide crater of Momotombo volcano. During 2002-2003 F9 was the highest temperature fumarole of the field (T = 776-737°C), F7 was at intermediate temperatures (T = 615-600°C) located to the N-NW of F9, and F15 located at the W-SW inner crater wall was more peripheral and showed lower temperatures (T = 472-478°C). Water condensate samples were collected at seasonal intervals at F9 and F7, but only once at F15 in November 2002 when it was active before becoming completely sealed in 2003.

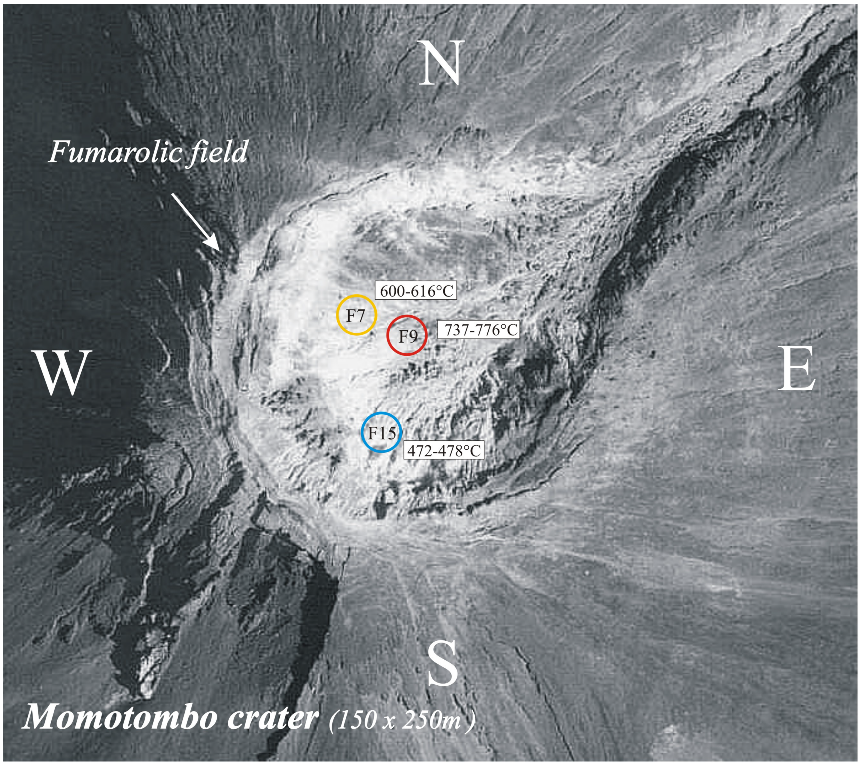

Fig. 1 Summit area of Momotombo and location of sampling points (photo courtesy of INETER)

Water condensate samples for main anions, metals analysis and trace element quantification were collected in 25 mL HPTF bottles at F9, F7 and F15 by inserting an assembled Qz-glass sampling train 30-40 cm deep into the fumarole's orifice. The sampling train consists of a tube, a pipe and Qz-glass water-cooled condenser. Care was taken to condense the gases efficiently in order to avoid partial loss of the more volatile species. Gas condensation was therefore promoted by using a water-cooled condenser connected to the sampling bottle trough a cavity in the bottle's cap. The sampling bottle was kept in a water bath and the departure of the incondensable gas fraction was allowed from another small cavity in the cap.

4.2.2 Chemical analyses

The major anions (F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}, and I^-) in condensates were analyzed by ion-chromatography (analytical error < ±5%) while the major alkaline and alkaline-earth metals (Na, K, Ca, Mg) were measured by atomic absorption spectrometry (AAS; analytical error < ±3.0%). Boron and NH_4 were analyzed in selected condensates by spectrophotometric technique (analytical error < ±10%). In some cases, when the of the sample was little, K, Ca, Mg, Al, and B were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The analytical precision for ICP-AES in terms of the relative standard deviation (RSD) of three replicate analyses was better than ±3% for most of the elements in all the samples.

Up to fifty-three trace elements among which Li, LILE (Rb, Cs, Sr, Ba, REE, Pb, Th and U), heavy metals (Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn), PGE (Ru, Rh, Pd, Pt), HFSE (Zr, Nb, Hf and Ta) and other transition elements (Y, Mo, Ag, Cd, W, Au, Hg), metalloids (As, Sb), basic metals (Ga, Sn, Bi, Tl) and non metals (Se) were simultaneously determined on fumarolic condensates (Table 1) with an AGILENT 7500c ICP-MS instrument. Sets of three calibration standard solutions were prepared in concentrations close to that expected for the elements in the samples. An internal standard (Re, In, Be at 50 ppb in HNO_3) was added to the samples, calibration standards and blanks to prevent instrumental deviation and compensate for physical interferences. Blanks, standards and a sample were run periodically throughout each analytical run for quality control.

Details of the analytical procedure have been described by Garbe-Schönberg (1993).

4.3 Composition of the fumarolic emissions

4.3.1 Composition of the fumarolic condensates

The chemical compositions of the fumarolic condensates collected at three fumaroles in 2002-2003 are presented in Table 1. The water condensate samples (#*n*c) are complementary to the gas #*n* in Table 2 (summary of Table 1 and Table 2 in Chapter 3) except for #8c, which is a stand-alone sample. All the condensates have pH ≈ 1 according to the pH indicator test measuring at 1 pH unit in the range of pH = 4-0. This generally low pH of the condensates is ascribed to the high amounts of dissolved acid gases in solution. These resulting concentration ranges in the condensates are 3000-9000 mg/L for Cl^-, 1500-5000 mg/L for SO_4^-, and lower amounts for F^- (150-600 mg/L), Br^- (3-20 mg/L), I^- (6-20 mg/L).

The total element distribution in the condensates varies in space, from fumarole to fumarole, and in time. At the highest temperature fumarole F9 (739-776°C) abundances in Jul-03 (#9c) were intermediate to the high values in Mar-02 and Feb-03 (#1c and 8c) and the low values in Nov-02 (#7c). Fumarole F7 (600-616°C) showed comparable element abundances in Nov-02 (#15c) and Jul-03 (#18c), which were generally lower (sometimes below detection limit) than in Mar-03 (#16c, the highest of this group). Elements abundances at F15 (472-478°C) in Nov-02 (#20c) are higher than those at F9 and F7 in the same period, and, except for few elements, always higher than at F7 (#15c, #16c, #18c).

The variation range of the dissolved elements in the 2002-2003 condensates is shown graphically in Fig. 2 together with available data from previous studies (e.g. Menyailov et al. 1986; Gemmel 1987; Quisefit et al. 1989). Please note that the present study adds a number of new elements to the already existing Momotombo condensed fumarolic gases database (i.e. B, I, Sr, V, Ga, Y, Zr Nb, Hf, Ta, W, Tl, Bi, Th, U, REE and indicative values for some PGEs). In Table 1 we also give the chemical composition of the last erupted material at Momotombo (1905), for later comparison purpose. This material is represented by the mean composition of three basaltic andesite lava samples

Table 2. Outlet temperatures (in °C) and chemical and isotopic composition of the fumarolic discharges from Momotombo (summary of Table 1 and Table 2 in Chapter 3). n.a. = not analyzed

Sample ID	Fumarole	mm/year	T(°C)	CO_2	HCl	HF	SO_2	H_2S	S	H_2O	N_2	Ar	O_2	Ne	H_2	He	CO	ΣC_1-C_9	$\delta^{18}O$	δD	$\delta^{13}C$	$\delta^{34}S$-SO_2	$\delta^{34}S$-H_2S	R/Ra
Locality: 086°32.330′ W 12°25,385′ N, 1237 m a.s.l.																								
1	F9	Mar-02	776	85490	857	38.73	29654	6681	0.188	871471	444	0.639	n.d.	0.0006	5285	0.111	78.13	0.028						
7	F9	Nov-02	761	113314	781	94.38	30050	9106	0.202	838410	778	4.856	0.247	0.0033	7452	0.132	9.540	0.203	6.16	-12.32	-3.08			
8	F9	Mar-03	741	89466	306	18.45	26749	4804	0.570	873834	754	7.121	32.38	0.0053	4018	0.217	10.42	0.007	6.30	-21.80				
9	F9	Jul-03	739	203812	6324	79.83	34649	7820	0.111	741324	504	1.496	1.496	0.0010	5479	0.090	5.085	0.132	6.79	-13.52		6.3	5.4	
Locality: 086°32.337′ W 12°25.396′ N, 1240 m a.s.l.																								
15	F7	Nov-02	616	85927	593	66.04	15113	176	0.147	895264	1313	14.653	4.980	0.0074	1528	0.094	0.927	0.036	6.21	-16.55				
16	F7	Mar-03	614	105003	557	56.92	24467	4866	0.334	861884	1583	18.075	76.796	0.0092	1470	0.133	17.02	0.027						6.29
18	F7	Jul-03	600	110979	2172	21.72	23952	3667	0.213	854671	3144	14.227	80.803	0.0090	1292	0.050	4.291	0.004			-3.24	7.1	5.3	
Locality: 086°32.283′ W 12°25.391′ N, 1230 m a.s.l.																								
20	F15	Nov-02	472	57942	244	n.a.	17913	2752	0.074	920177	428	1.113	0.261	0.0009	534	0.105	5.487	2.049	1.49	-25.83	-2.63			5.44

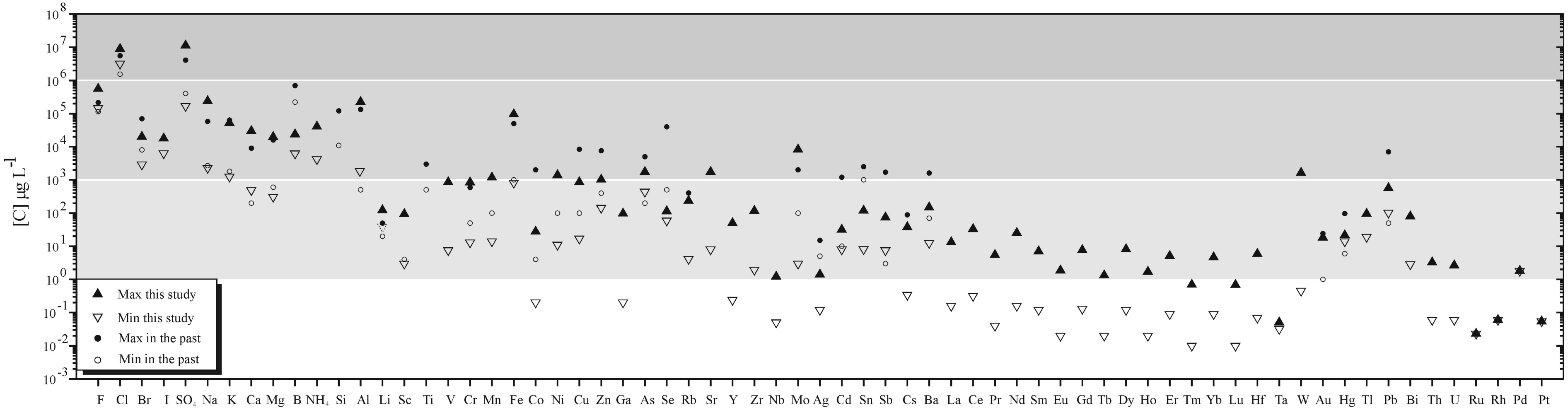

Fig. 2 Maximum and minimum concentrations of major, minor and trace elements measured in fumarolic condensates of Momotombo volcano

Table 1. Chemical composition of Momotombo fumarolic condensates, two glass samples (Hansteen and Haase unpubl data) and the 1905 basaltic andesite lava (average of three samples from Hoernle et al. in prep). n.d. not detected; n.a. not analyzed

Sample ID	1c	7c	8c	9c	15c	16c	18c	20c	Detection	TF1	TF2	Mo-1905
Type	Fumaroles								Limit	basaltic andesite		
Site	F9	F9	F9	F9	F7	F7	F7	F15	µg/l	Tephra fallout		Lava flow
Date	Mar-‘02	Nov-‘02	Feb-‘03	Jul-‘03	Nov-‘02	Mar-‘03	Jul-‘03	Nov-‘02		1905	1905	1905
T^{o}C	776	761	759	739	616	614	600	478				
I *	6.30	6.80	n.a.	n.a.	6.79	n.a	n.a	17.8				
F *	244	580	496	146	490	395	345	186				
Cl *	5989	8750	7803	7788	8020	7050	8153	3160				
Br *	7.6	7.4	2.90	n.r.	20.0	6.90	13.5	3.08				
SO_4 *	3185	3446	5006	4802	2500	1691	4035	2626				
B *	14.1	8.02	13.5	16.66	14.9	n.a.	22.01	6.67				25 $^{(1)}$
NH_4 *	n.a.	4.18	24.1	27.32	15.4	n.a.	13.82	40.8				
Na *	238	23.3	11.6	n.a	n.a	2.30	n.a.	18.55		n.a.	n.a.	9794
K *	48.2	10.7	11.6	6.13	1.79	1.26	3.99	4.70		n.a.	n.a.	3527
Ca *	221	17.8	30.0	16.24	1.38	1.22	2.17	21.6		n.a.	n.a.	67823
Mg *	11.0	1.60	3.60	4.45	0.310	0.58	0.46	4.70		n.a.	n.a.	28461
Al *	225	n.a.	n.a.	8.88	n.a.	n.a.	1.54	n.a.		n.a.	n.a.	46350
Li	104	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	10	5.89	6.32	7.72
Sc	93.7	n.d.	7.61	3.45	n.d.	n.d.	n.d.	n.d.	3	35.5	31.3	26.0
V	855	12.5	71.3	32.0	7.54	13.4	8.44	16.3	3	332	298	259
Cr	346	77.2	103	13.4	44.5	23.4	15.9	837	3	22.3	14.4	10.4
Mn	1188	28.4	192	321	18.0	58.2	14.4	222	3	n.a.	n.a.	1472
Fe	95675	1432	18830	8790	891	2082	816	5797	500	n.a.	n.a.	36680
Co	27.8	1.52	5.80	1.53	0.531	0.791	0.222	7.56	0.1	34.9	31.6	26.3
Ni	341	181	156	172	58.6	43.2	10.6	1383	0.1	12.2	11.0	8.7
Cu	857	17.1	317	55.6	35.8	89.0	28.0	223	1	170	143	145
Zn	1016	350	259	203	143	205	169	450	1	97.9	95.3	76.2
Ga	96.9	0.441	7.01	1.28	0.330	0.482	0.227	0.680	0.1	18.9	18.6	17.4
Rb	232	34.0	42.1	18.8	13.5	17.5	23.6	4.15	0.1	13.1	16.1	15.8
Sr	1725	40.7	329	81.6	15.0	31.7	7.99	96.7	1	472	490	464
Y	49.5	0.237	7.55	3.99	0.244	0.820	0.304	1.64	0.05	18.7	19.3	20.2
Zr	117	3.11	19.9	17.1	1.96	6.96	2.48	6.89	0.05	51.2	58.4	62.1
Nb	1.22	0.051	0.940	0.555	0.063	0.184	n.d	1.36	0.05	1.56	1.66	1.55
Mo	8315	18.0	249	50.5	16.8	34.5	26.2	2.99	1	0.662	0.729	0.756
Ag	0.153	0.133	n.d	0.151	0.121	1.43	0.692	n.d.	0.05	n.a.	n.a.	0.072 $^{(1)}$
Cd	31.7	15.6	11.1	9.76	13.6	24.4	7.73	19.8	1	n.a.	n.a.	0.14 $^{(1)}$
Sn	118	110	101	60.0	71.2	82.3	83.5	8.12	0.1	0.544	0.605	0.605
Sb	11.5	33.5	30.2	35.7	36.3	74.0	46.8	7.56	0.05	0.269	0.318	0.294
Cs	37.6	17.4	17.6	6.51	8.85	11.2	17.2	0.336	0.05	0.583	0.667	0.723
Ba	149	40.2	47.5	49.9	67.7	57.3	12.4	70.2	0.05	594	658	690
La	13.2	0.897	3.10	0.868	0.196	2.07	0.160	1.85	0.1	4.95	5.76	6.13
Ce	32.9	1.31	7.11	2.14	0.348	2.58	0.318	3.62	0.1	11.3	13.1	13.8
Pr	5.43	0.116	1.06	0.389	0.049	0.310	0.044	0.410	0.05	1.85	2.10	2.20
Nd	25.4	0.207	4.83	1.88	0.157	0.817	0.167	1.62	0.1	9.01	10.0	10.6
Sm	7.00	n.d.	1.26	0.520	n.d.	0.118	n.d.	0.361	0.1	2.58	2.76	3.01
Eu	1.85	0.020	0.445	0.172	n.d.	0.034	0.020	0.106	0.05	0.909	0.941	1.01
Gd	7.71	n.d.	1.41	0.566	n.d.	0.128	n.d.	0.365	0.1	3.06	3.16	3.36
Tb	1.33	n.d.	0.239	0.096	n.d.	0.019	n.d.	0.057	0.05	0.507	0.517	0.566
Dy	8.14	n.d.	1.52	0.655	n.d.	0.121	n.d.	0.341	0.1	3.24	3.28	3.60
Ho	1.69	n.d.	0.311	0.139	n.d.	0.025	n.d.	0.065	0.05	0.689	0.703	0.754
Er	5.08	n.d.	0.886	0.424	n.d.	0.086	n.d.	0.176	0.1	1.90	1.93	2.10
Tm	0.695	n.d.	0.130	0.067	n.d.	0.012	n.d.	0.023	0.05	0.293	0.299	0.317
Yb	4.66	n.d.	0.867	0.527	n.d.	0.094	n.d.	0.154	0.1	1.95	1.97	2.15
Lu	0.679	n.d.	0.122	0.080	n.d.	0.015	n.d.	0.020	0.05	0.302	0.307	0.327
Hf	5.85	0.088	0.703	0.433	0.086	0.229	0.075	0.222	0.05	1.56	1.71	1.93
Ta	0.032	n.d.	0.050	n.d.	n.d.	n.d.	n.d.	0.048	0.05	0.115	0.109	0.098
W	1646	3.63	73.1	5.41	0.663	2.95	6.71	0.446	0.1	0.165	0.184	0.219
Tl	73.8	57.5	53.9	47.0	68.8	94.6	54.1	19.2	0.05	0.077	0.091	0.101
Pb	349	329	299	272	308	570	313	103	0.1	2.38	2.61	2.52
Bi	9.14	6.13	21.8	12.1	12.6	80.3	11.4	2.87	0.05	n.a.	n.a.	0.033 $^{(1)}$
Th	3.27	n.d.	0.435	0.192	n.d.	0.065	n.d.	0.190	0.05	0.588	0.701	0.734
U	2.67	0.114	0.265	0.177	n.d.	0.063	n.d.	0.200	0.05	0.511	0.592	0.705
As	*915*	*1107*	*893*	*864*	*945*	*1727*	*866*	*443*	10	n.a.	n.a.	1.85 $^{(1)}$
Se	*114*	*n.d.*	*n.d.*	*96.0*	*59.4*	*n.d.*	*74.4*	*n.d.*	50	n.a.	n.a.	0.19 $^{(1)}$
Au	*18.2*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.05	n.a.	n.a.	0.00564 $^{(1)}$
Hg	*21.6*	*n.d.*	*n.d.*	*14*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	10	n.a.	n.a.	0.00478 $^{(1)}$
Ru	*0.023*	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	*0.05*	n.a.	n.a.	0.0065 $^{(1)}$
Rh	*0.060*	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	*0.05*	n.a.	n.a.	
Pd	*1.81*	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	*0.05*	n.a.	n.a.	0.0063 $^{(1)}$
Pt	*0.054*	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	*0.05*	n.a.	n.a.	0.004 $^{(1)}$

concentrations are in µg/l, except for the rock samples and when (*) concentration are ppm

Italicised: information values

Working detection limits (column 10). Detection limits for sample 1c are five times lower then the ones reported and valid for all the other condensate samples

^ indicates integration of data from different bibliographic sources: B and As from Patino et al. (2000); Ru is from JB1-standard and Ag, Cd, Bi, Se, As, Au, Hg, Pd and Pt from JB2-standard (Imai et al. 1995)

(SiO_2 = 52.57 wt%) (Hoernle et al. in prep) and two glass samples from a local tephra fallout (TF1 and TF2) (Hansteen and Haase unpubl data). For some elements whose abundances are unknown in the Momotombo reference rock (Se, Ag, Bi, Cd, Hg) we refer to the value reported for the geochemical standard JB-1 and JB-2 (Imai et al. 1995), being arc-basalts which are reasonably similar to the bulk Momotombo rock.

4.3.2 Main geochemical features of the gas emissions

Long- and short-term variations in the geochemical compositions of the fumarolic gases have been identified at Momotombo and already discussed in detail in Chapter 3. Here we summarize the most important results, since the trace elements distribution is strictly related and dependent on the major element composition of the gas. It is expected that processes responsible for variations in the major element composition of the gases will also be responsible for variations of the trace elements.

1. The 2002-2003 fumarolic emissions are CO_2- and S_{tot}-rich and indicate the degassing of a rather pristine magma (Fig 3a). On the contrary the ‘80s emissions were H_2O- and Cl-rich and probably derived from a more outgassed magma batch.
2. At least two events of renewed magma input to the volcano were identified between the late ‘80s and 2003. The first event was responsible for the higher CO_2 and S_{tot} contents in the 2002-2003 with respect to the ‘80s emissions (Fig 3a). The second event accounts for the increase in the CO_2/He ratio and the $\delta^{18}O$-δD-H_2O values from 2002 to 2003 (Fig 3b,c).
3. Both long- and short-term variations in the geochemical composition of the gases are largely induced by degassing processes and different amounts of mixing with meteoric water (2002-2003) and hydrothermal fluids (in the ‘80s) (Fig 3 c,d,e).
4. Non-magmatic/hydrothermal fluids contribute strongly to the ‘80s discharges. The 2002-2003 magmatic gases are only affected by shallow meteoric dilution, which depends on the amount of seasonal precipitation.
5. In the ‘80s the magmatic and the hydrothermal systems were strongly interacting, while in 2002-2003 no evident interaction took place between the two systems. This indicates a possibly dry-out of the hydrothermal system (or its

hydrologic separation from the magmatic system) sometime between the late ‘80s and 2002.

4.4 Fumarolic trace elements in space and time

The trace element contents of the fumarolic condensates are conveniently visualized and discussed using multi-element chondrite-normalized diagrams (Fig 4a,b). The multi-element distribution patterns are both sub-parallel to each other and to the pattern described by the reference Momotombo rock. This allows us to address several elements collectively. In the following discussion we will show how seasonal changes affect trace element concentration at individual fumaroles (F7 and F9) and illustrate how trace element concentrations can vary among different fumaroles.

4.4.1 Seasonal changes

We have sampled fumarole F9 and F7 repeatedly between March 2002 and July 2003. As Fig. 4a,b shows, the trace element concentration varies significantly between the different measurements. There are three principle parameters that can affect the trace element concentration: 1) changes in emission temperature alters the mobility of the trace elements, 2) meteoric water can lead to dilution, and 3) variations in gas chemistry.

Figure 5 show the average emission temperatures, average H_2O/CO_2 ratios, and average total trace element concentration through time for F9 and F7. Trace element concentrations decrease at F9 from Mar-02 to the lowest value in Nov-02. As November marks the end of the rainy season this is likely to be a seasonal effect and to result from gas dilution by meteoric precipitation, as already recognized for the main gas components (Chapter 3) (Fig 3d). Also the decrease in emission temperatures is consistent with this interpretation. During the dry months from Nov-02 to Feb-03 the H_2O/CO_2 ratios at F9 and F7 decrease. This indicates a decrease in meteoric dilution and is consistent with the observed increase in trace element concentrations. The emission temperatures did, however, decrease slightly during this period. But the temperatures obviously remained high enough that small temperature drops did not have a major

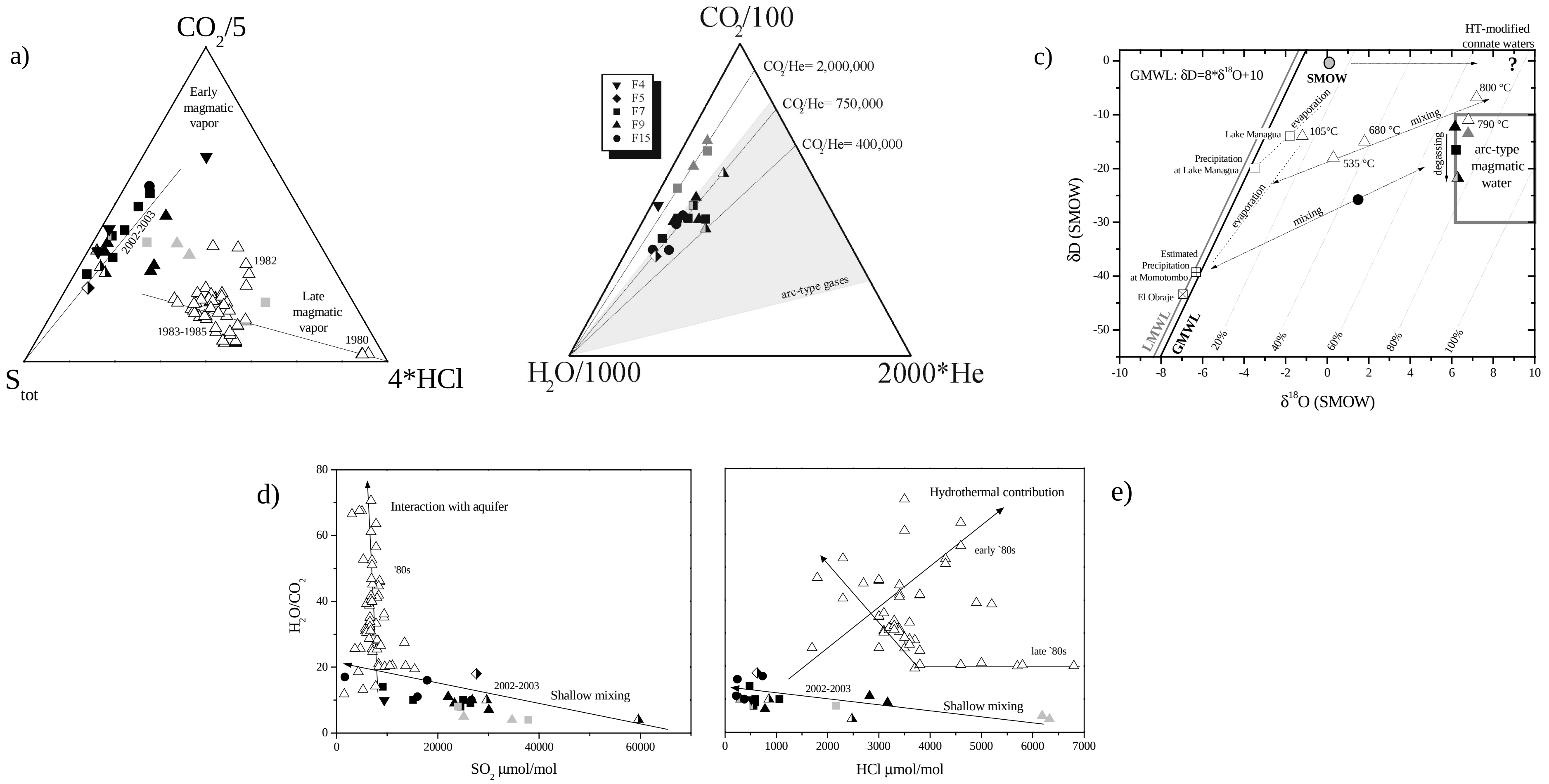

Fig. 3a-e Summary graphs showing the chemical and isotopic characteristics of Momotombo fumarolic gases in 2002-2003 and in the ‘80s (see text and Chapter 3)

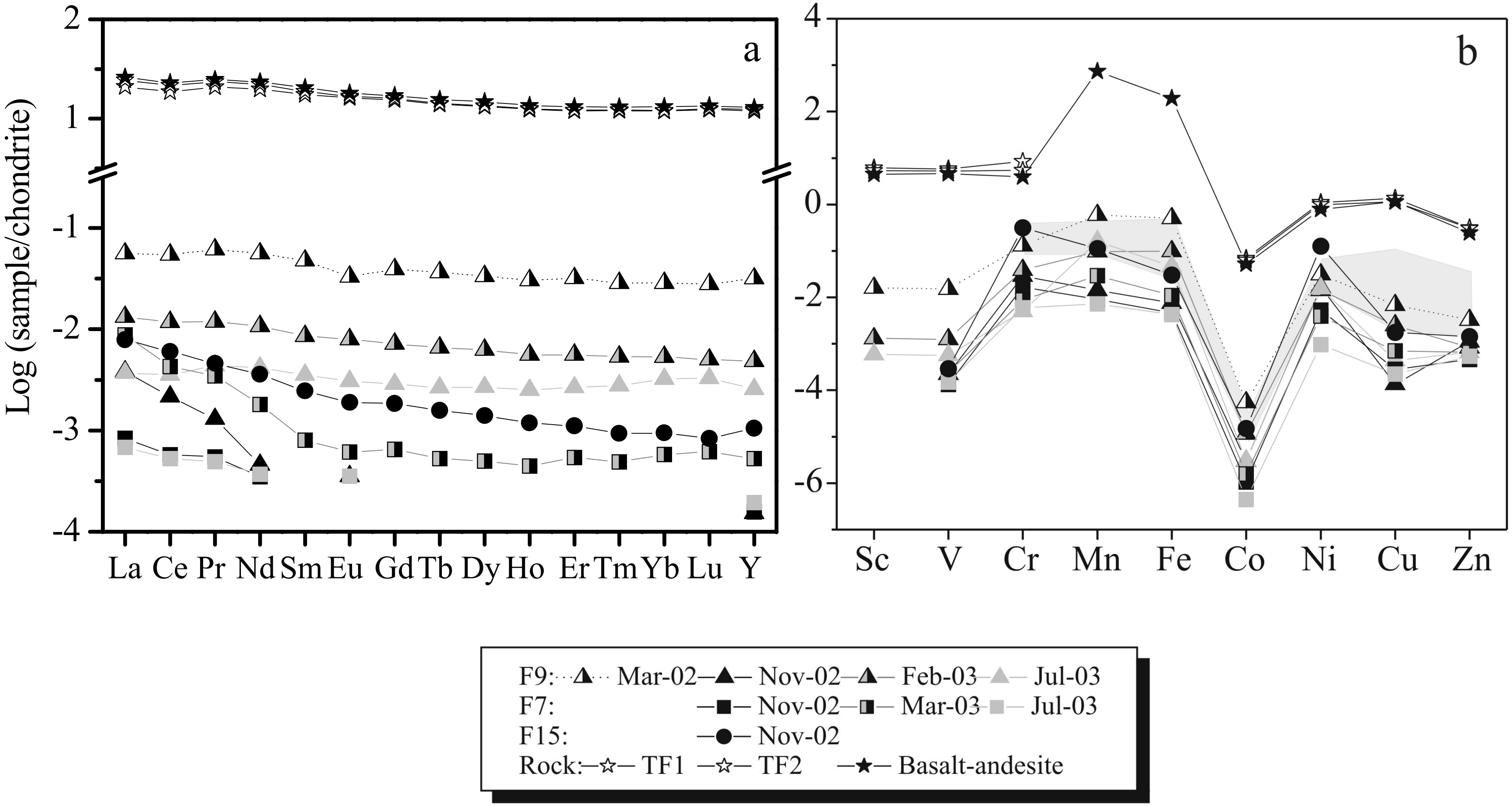

Fig. 4a-b Multi-element plots for condensate concentrations normalized to the Chondrite C1 values (Anders and Ebihara 1982). The symbols indicate the different fumaroles and the different color indicate the different sampling times: black-white and black-gray the middle of the dry season, black the end of the rainy/beginning of the dry season, gray the end of the dry/beginning of the rainy season effect. It therefore appears as if meteoric dilution is the dominant factor controlling trace element concentrations between Mar-02 and Feb-03. Trace element concentrations decreased again from Feb-03 to Jul-03 both at F9 and F7. This decrease cannot be explained by either dilution or temperature alone (note, however that the small drop in temperature is unlikely to compensate for the much smaller dilution of the gases). It therefore appears likely that the chemistry of the gases venting at F9 and F7 has changed during this period. Based on the major element geochemistry we have shown the likelihood of the arrival of a fresh magma between Mar-03 in Jul-03 (Chapter 3). The Jul-03 gases are CO_2-rich and CO_2 for its inherent thermodynamic stability hinders the development of gaseous metal-complexes (CRC 2001). Thus the "relatively dry" CO_2-rich gases discharged in Jul-'03 at F9 and F7 even though they are the most "primitive", show general low elemental concentrations. This is possibly imputable also to a deeper location of the degassing source and the chemical characteristics of the early magmatic vapors.

4.4.2 Inter-fumarole variations

In order to document and constrain variations between different fumaroles we now compare the different trace element concentration pattern at the fumaroles F7, F9, and F15 in November 2002. Emission temperatures varied among the fumaroles with F9 showing higher temperatures (~761°C) than F7 (~615°C) and F15 (478-472°C). Trace element concentrations are higher at F15 than at F9 and F7. As stated above, the low trace element contents of F9 and F7 are related to meteoric dilution. Although $\delta^{18}O$-δD-H_2O values in Nov-'02 indicate that the local precipitation contributes only smaller amounts (ca. 30%) to the total vapor discharged at F9 and F7 (ca. 70-80% is magmatic vapor) than to the peripheral LT fumarole F15 (ca. 50%) (Fig 3b), F15 shows the highest trace elements contents in this period. The differences in trace element contents among the three fumaroles can therefore not be explained by simple dilution and temperature effects. This could indicate i) an only partially primary magmatic origin of trace elements at F15 and/or, ii) particularly favorable chemo-physical conditions for high trace element occurrences in the volatile phase at F15 (e.g. acid disproportion, enhanced transport of elements in a vapor-rich phase, formation of organo-metallic complexes).

The wet and lower temperature conditions at F15 could favor the condensation of fumarolic fluids and the disproportion of SO_2 with the production of sulfuric acid. This would lower the pH-value of the fluids and render available a larger number of constituents from the rock (rock leaching).

The latter mechanism and an enhanced transport of elements in a vapor-rich phase (Williams-Jones et al. 2002), could explain the higher mobility of some heavy metals (e.g. Cr, Co, Ni, Cu, Zn) at F15 then at F9 and F7 during and at the end of the dry season (Fig 4b). Furthermore organo-metallic complexes are expected to play a significant role in transporting metals in the gaseous phase (Nriagu 1989, Shock and Koretsky 1995) at F15 where also the highest hydrocarbons, ammonia and iodine contents (Table 1 and Table 2) and the most consistent halocarbons abundances (Frische et al. 2006) are found. Although this whole group of species occurs in relatively low amounts at Momotombo (Chapter 3; Frische et al. 2006) some potential metal-carrier could be represented by anions derived from alkenes, halocarbons species and more rare halogens (e.g. iodine).

Although most trace element concentration patterns in the condensates mimic the trace element distribution of the wallrocks, some elements show different distributions relative to the rock. This is especially noticeable for the REE (Fig 4a) that show different mobility in the volatile phase at the different fumaroles. The contamination of the condensate by rock particle can be important at fumaroles showing sustained gas emissions. High S_0 contents in the gas samples at F9 and F7 (Table 2) are indicative for efficient transport of particulate matter in suspension in the gas stream. This could explain the rather smooth REE+Y patterns of the fumarolic fluids at F9 (exception for November) that replicate the rock trend. The discharges at F7 and F15 instead show a pronounce fractionation between the REE, with La/Sm >> 2.0, Sm/Nd << 0.31 and La/Yb >> 2.8 (rock ratios). This different REE distribution in the condensates at F9 and at F7-F15 could reflect the different age of the rocks. In particular the less altered stage of the rock substratum at F9 suggests the younger age of the rock (1905 lava) relative to that at F7 and F15. These last two fumaroles are possibly located on older, and likely more weathered and/or altered products of “Momotombo Actual” (geologic map; Hradecky et al. 2001). In addition the high temperatures and the dry-vapor gas emissions at F9 (exception in November) prevent the substantial disproportion and condensation of the acid gases (e.g. $SO_2 \rightarrow H_2SO_4$) and thus considerably decreases the

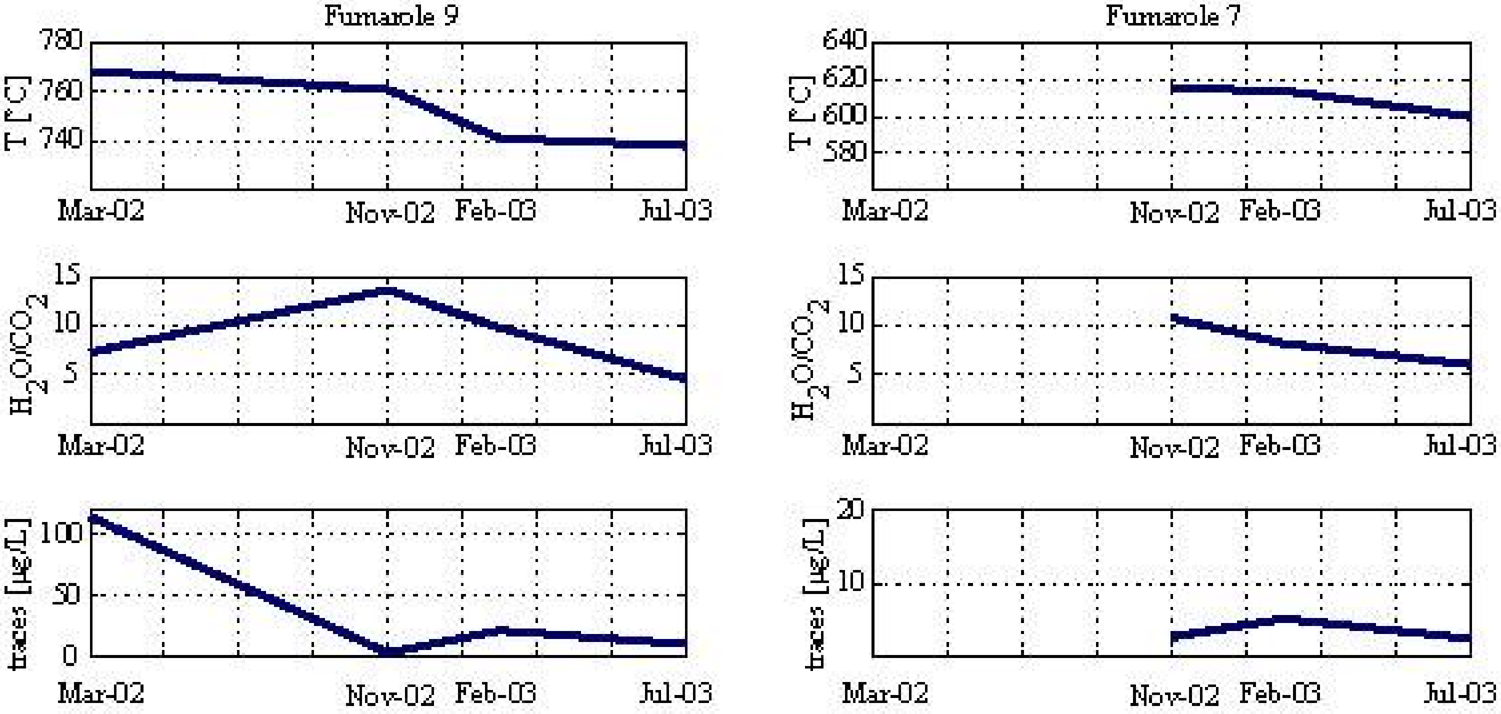

Fig. 5 Average emission temperatures, average H_2O/CO_2 ratios (Table 1 in Chapter 3) and total trace element concentration (Table 1 in Chapter 4) through time for F9 and F7 (see text)

aggressiveness of the fumarolic fluid (Ruaya and Seward 1987; Fulignati et al. 1999). The transition to a wet (F9 in November) and lower temperature environment (F15) favors the condensation of fumarolic fluids and the disproportion of the acid gases, resulting in a lowering of the pH in the fluids. Thus water-rock interaction processes are promote, and consequently rock leaching and REE mobilization (Fulignati et al. 1999). The LREE generally appear to be more mobile than the HREE at Momotombo. Since the mutual REE separation is mineral-controlled (Rollinson 1983), the acquired HREE-depleted signature of the fluid is possibly related to the presence of less alterable secondary minerals, which can fix the HREE into their structure.

The differences among the three fumaroles illustrates that trace element concentrations are dependent on numerous parameters. Not only temperature and dilution effects are important but also the main chemical composition of the gases and the interaction with and dissolution of wallrocks. Given this complexity we will next explore the possible origins of trace metals in the fumarolic gases.

4.4.3 Origin of trace elements

Contamination of the environment by harmful and potentially toxic pollutants introduced in the atmosphere by volcanic degassing has been evidenced at different volcanic locations (e.g. Parnell and Burke 1990, Zreda-Gostynska et al 1994, Delmelle et al 2002). Potentially harmful components can either be organic or inorganic with the latter being mostly transition metals and metalloids. Toxic compounds of particular environmental concern are those very mobile and volatile under normal environmental conditions.

In the fumarolic environment trace metals and metalloids are generally characterized by a relatively high mobility. During ascent to the surface the magmatic gas interacts with the surrounding environment (rock, hydrothermal fluids, water). The result of this interaction can be either enrichment or depletion of the trace element contents in the gases. Sources of trace metals in the fumarolic gases can be the rock minerals, sublimates deposited along the fumarolic conduit, hydrothermal solutions or degassingof the magmatic body. Constraining the origin of trace elements in fumarolic fluids is thus of primary importance in order to assess the consequences of magma degassing.

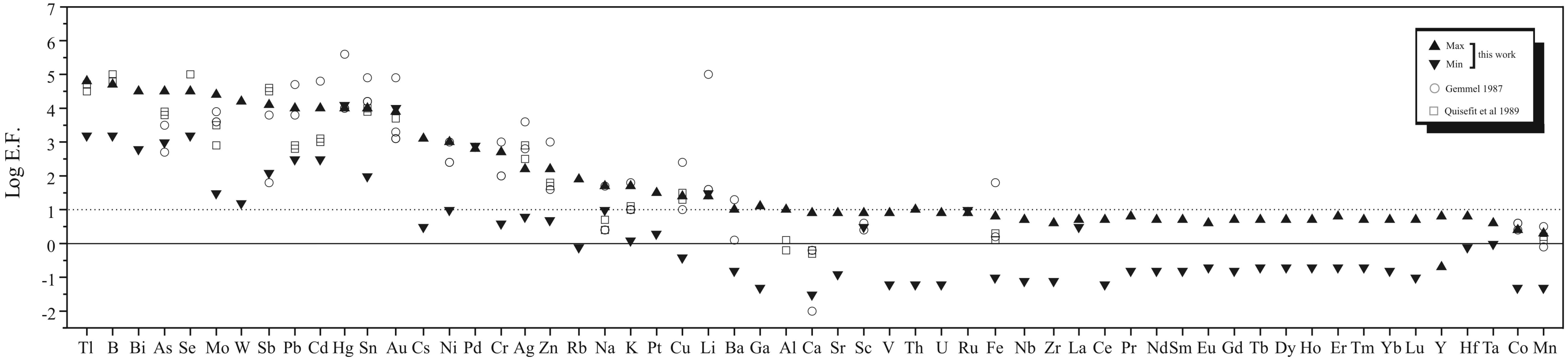

Fig. 6 Trace element enrichment factors range in the 2002-2003 fumarolic condensate from Momotombo. The enrichment factors range it is also shown for bibliografic data from the 80s. Note the logaritmic scale

Table 3 Enrichment factors and possible origin of trace element in the 2002-2003 Momotombo fumarolic gases

Log E.F.	Elements	Origin
Log $EF_{max-min}$ >> 1	B, Tl, Bi, As, Se, Mo, Sb, Hg, Au, W, Pb, Cd, Sn	Magma
-1≤ Log $EF_{max-min}$ ≤ 1	Al, Ca, Sr, Fe, Mn, Co, Th, U, Ba, REE, Y, Sc, V, Hf, Ta.	Rock
Log EF_{max} >>1 and Log EF_{min} ≤ 1	Cs, Ni, Cr, Cu, Ag, Rb, K, Na, Pt, Li	Multiple sources: magma and rock different behavior (volatilization and precipitation) with changing temperature of the emission

For these purposes we calculate the Enrichment Factor (E.F; Symonds et al. 1992) of the elements in the Momotombo fumarolic condensates (Fig 6). This parameter is helpful to constrain the origins of the elements in the fumarolic gases.

The Enrichment Factor is the ratio of the abundance of element (x_i) normalized to Mg in the condensate (c) and the abundance of (x_i) normalized to Mg in the reference rock (r). Mg is chosen as a normalization factor because it is quite immobile in the fumarolic environment (Symonds et al. 1992; Taran et al. 1995):

$$E.F._{xi} = (x_i / Mg)_c / (x_i / Mg)_r$$

On the base of the E.F. we can distinguish three groups of elements (Table 3):

a) highly enriched elements (Log $E.F._{\text{max-min}} >> 1$) likely originating from the magma, e.g. Tl, Bi, As, Se, Mo, Sb, Hg, Au, W, Pb, Cd, Sn;

b) not-enriched elements ($-1 \leq$ Log $E.F._{\text{max-min}} \leq 1$), deriving entirely from rock leaching or rock particle contamination, i.e. Al, Ca, Sr, Fe, Mn, Co, Th, U, Ba, REE, Y, Sc, V, Hf, Ta.

Within this last group:

Log $E.F._{\text{min}} < -1$ likely characterizes those elements forming secondary minerals (e.g. HREE) and

Log $EF_{\text{min}} = -1$ likely characterizes those elements contained in more resistant minerals or in the acid-leached rock residue (e.g Mn, Fe, Co, Sc, V, Sr, Ba. Hf, Nb, Zr, Th, U, LREE).

c) elements with E.F. in the whole range of Log $E.F._{\text{max}} >>1$ and Log $E.F._{\text{min}} \leq 1$ like Cs, Ni, Cr, Cu, Ag, Rb, K, Na, Pt, Li, derive from multiple sources (magma and rock). This distribution likely reflects their decreasing volatility, and consequent deposition, with decreasing emission temperatures.

4.5 Long-term changes in fumarole chemistry and implications for flux estimates

4.5.1 Long term variations: '80s vs 2002-2003 fumarolic discharges

Long-term changes in contents and E.F. of some elements emerge from comparison with previous data from the 1980s (e.g. Menyailov et al. 1986; Gemmel 1987; Quisefit et al. 1989). In particular in the 2002-2003 emissions Li, Ba, Cu, Zn, Sn, Ag, Pb, Sb and Au show lower contents and E.F. values then those in the past. Most of these elements are common constituents of (magmatic-) hydrothermal fluids (e.g. Pokrovki et al. 2005), which could be the origin of the higher contents in the ‘80s emissions. Furthermore, higher Cl and water vapor contributions in the ‘80s emissions (Fig 3e) could have enhanced the transport of these elements in the volatile phase (e.g. Williams-Jones et al. 2002; Pokrovki et al. 2005). In fact thermodynamic data (CRC 2001) and calculations (e.g. Symonds et al. 1987; 1992; Symonds and Reed 1993; Churakov et al. 2000) predict the transport of these elements as Cl-compounds in the gas phase over a wide range of temperatures (Table 4). Some typical chalcophile elements like Sb, As, Pb and Hg are instead mainly transported as S-volatile-species and occur in comparable (or lower) amounts in 2002-2003 than in the ‘80s, although the 2002-2003 emissions are characterized by higher S_{tot} contents. This could in part be a sampling artifact due to partial loss of highly volatile sulfur-metal compounds due to the high temperatures reached during sampling.

Temperature		Cl-compounds	S-compounds	Mono-atomic metals	Oxo-anion compounds
F9	800-700°C	Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Al, Ag, Tl	As, Sb, Sn, Au, Pb, Bi	Zn, Se, Cd, Hg, Bi	Mg, V, Cr, Fe, Mo, W
F7	600°C	Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Ga, Ag, Tl, Pb, Bi	As, Sb, Sn, Au, Pb, Bi	Se, Cd, Hg	Mg, V, Cr, Fe, Mo, W
F15	500-400°C	Li, Na, K, Rb, Cs, Ca, Sr, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Ga, Mo, Ag, Sn, W, Au, Tl, Pb, Bi,	As, Sn, Au, Pb, Bi	Se, Cd, Hg	Mg, V, Cr, Fe, Mo, W

Table 4. Estimated most common transport form of trace elements at 1bar and at the temperatures of the fumaroles (CRC 2001, Krauskopf 1957; Symonds et al. 1987; 1992; Symonds and Reed 1993; Churakov et al. 2000)

The concentrations of Mo, W and Se in the volatile phase are independent of both Cl and S availability, since these elements tend to form gaseous oxides (Symonds et al. 1987; 1992; Symonds and Reed 1993; Churakov et al. 2000). In the 2002-2003 fumarolic gases Mo and W behave identically and vary with emission temperature and are together with Tl among the most enriched metalloids in the Momotombo fumarolic emissions.

We conclude that the lower Cl contents and temperatures of the 2002-2003 gases with respect to the ‘80s could be partly responsible for the general lower metal contents in the present-day fumarolic emissions. However the availability of ligands in the 2002-2003 gases should not represent a particular limitation for the transport of trace elements in the volatile phase (i.e. Cl^- is 10^2-10^3 higher then the total amounts of trace elements). The final concentration of trace elements in fumarolic condensates prevalently depends on the tendency of trace elements to be mobilized. Therefore changes in the redox state of the magma, temperature and pressure of crystallization, due to new magmatic input in 2000 and 2003 (Chapter 3) could play much more important roles in determining the tendency of the elements to migrate in the gas phase separating from the magma (Hedenquist and Lowerstern 1994).

4.5.2 Volcanic metal emissions

In order to assess the importance of quiescent magmatic degassing as a pollutant emitter we have to constrain emission rates. The above considerations illustrate the significant short-term, long-term, and inter-fumarole variations in volcanic gas chemistry at Momotombo. Any flux calculations can therefore only give a rough estimate of emission rates. We have anyhow calculated averaged emission rates of some highly volatile and potentially harmful trace metals during magma degassing at Momotombo volcano in 2002-2003 ("metal" is defined deliberately broadly in this context and may include elements, such as As or Se, which are not metallic).

As we cannot measure emission rates of trace metals directly and as the only available flux measurement is for SO_2 in the volcanic plume, we have to rely on an indirect approach. This approach is based on the comparison between species measured within different types of samples/emissions. We assume that trace metal condensation is complete and that the measured concentrations are therefore representative for the total metal discharge into the atmosphere at Momotombo. Furthermore, we assume that the mean SO_2 flux of 44 Mg/d (0.52 kg/s, 251 Mmol/y) measured at the bottom of Momotombo by the mini-DOAS technique (Galle et al. 2002) in November 2002 is a good approximation of the magmatic SO_2 flux in 2002-2003.

In order to calculate emission rates we first normalize the trace element concentrations in the condensate to Cl^-. Chlorine is chosen because it is less volatile than the sulfur species and partitions readily into water at temperatures < 350°C (Fischer et al. 1998). Therefore, only minor amounts of chlorine are lost during the condensation of the gases, allowing for a quantitative comparison. Second, to obtain the original trace metal fraction in the fumarolic gases we multiply the obtained trace metal/Cl^- ratios with the molar concentrations of HCl in the sampled gases. We then determine the trace metal/SO_2 molar ratios and can then, since we know the SO_2 flux, derive the flux (Φxi) of the trace metal (x_i) in g/d:

$$\Phi x_i = k\,(x_i/SO_2)\,\Phi SO_2$$

Here x_i/SO_2 is the average mole ratio, k is the ratio of the molecular weights of x_i to SO_2, and ΦSO_2 is the mass emission rate of SO_2 (g/d).

The calculated mean emission rates from some common and very toxic elements discharged at Momotombo are 150 g/d for As, 70 g/d for Mo and Ni, 50 g/d for Pb and Zn, 30 g/d for Se, 20 g/d for Cu, 15-10 g/d for W, Sn and Tl, 7.0 g/d for Hg, 6.0 g/d for Sb, 2.5 g/d for Cd and 2.5 g/d for Bi. These metals emission fluxes are very low compared to the emission rates determined at other (degassing) Nicaraguan and worldwide volcanoes (Table 5).

There are several explanations for the relatively small estimated fluxes of trace metals from Momotombo volcano. One reason is that the measured SO_2 flux from Momotombo is also relatively small which inevitably results in lower trace metals emissions rates. But even if we account for this lower SO_2 flux our estimates of trace metal emissions rates are still several orders of magnitude lower than the reference values given in Table 5. This could indicate that at Momotombo many metals are not readily mobilized and tend to remain at depth (remain dissolved in the magma, partition into saline brine or being deposited below the surface). Additionally we have to consider that trace metal fluxes are usually determined on gas plumes at open vent volcanoes. In such scenario, magma can emerge in the conduit and degas directly into

Volcano	As	Se	Cd	Hg	Pb	SO_2	Ref.
Momotombo	150	30	2.5	7.0	48	$44*10^6$	This study
Masaya	$1500*10^3$			$80*10^3$		$950*10^6$	Wardell et al. 2004
Mt. Erebus	$30*10^3$	$4.6*10^3$	$10*10^3$			$43*10^6$	Zreda-Gostynska et al. 1997
Stromboli	$62*10^3$	$9.6*10^3$	$1.9*10^3$		$140*10^3$	$340*10^6$	Allard et al. 2000
Mt. Etna	$300*10^3$		$190*10^3$		$600*10^3$	$3600*10^6$	Delmelle 2004

Table 5. Emissions rates of some trace metals at Momotombo (g/d). Data from other volcanoes are shown for comparison

the atmosphere, strongly promoting the efficiency of the degassing process. This is not the case of Momotombo, which has a sealed conduit.

Furthermore, some of our 'working assumptions' may also influence our flux estimates. In particular the SO_2 flux measured in the gas plume at distance from the emission source may not equal the total SO_2 flux from the fumaroles. The amount of SO_2 emitted at the fumaroles is higher then that measured in the gas plume at distance from the emission source. In fact, upon reaching the atmosphere the emitted volcanic gases become affected by physical and chemical process, which lead to rapid or slow deposition. Air dilution and SO_2 oxidation to SO_4^{2-} in the atmosphere with production of aerosols lower the SO_2 concentration in the gas plume (e.g. Horrocks et al 2003; McGonigle et al. 2004). SO_2 and metals have contrasting atmospheric properties. Metals show longer atmospheric residence time then SO_2, and can be transported in the atmospheric media for long distances (Hinkley 1991, Matsumoto and Hinkley 2001). We would therefore expect to measure higher metal/SO_2 ratios in the gas plume than at the emissions source. This might imply that element ratios in the fumaroles are different than in the gas plume. It thus appears likely to us that the suspiciously low emission values we determined for the release of metals during magmatic degassing of Momotombo volcano likely result from the 'inconsistent' comparison between different types of samples and emissions. The same is true for the comparison of our metal fluxes with those estimated for other volcanoes on the basis of passive and active filter sampling analysis of the volcanic gas plumes (e.g. Delmelle 2004 and reference therein). Filter sampling yields estimates that are probably more representative for the gas plume than for fumarolic gases (e.g. Aiuppa et al. 2004).

In conclusion it is probably safe to say that the “true” flux of trace metals from the magma at Momotombo is likely higher than what we have estimated due to the above reasons. Additional data is needed in order to better assess if element ratios in the gas plume are similar to the ones determined at the fumaroles. Furthermore, a direct measurement of SO_2 or total gas flux (gas discharge rate) at the individual fumaroles could help to better estimate the release of main and trace elements/species from magma degassing into the atmosphere.

4.6 Conclusions

The detailed analysis of fumarolic gases from 2002 and 2003 has shown that major changes occur in degassing behavior of Momotombo - both on a seasonal time scale and on a decadal time scale. In the present study we have focused on trace metal degassing, and conclude that:

1. Trace metal concentrations are sensitive to seasonal variations in precipitation. Repeated analysis of fumarolic gases emitted at F9 and F7 show that meteoric dilution is the principle factor controlling the trace metal concentration between March 2002 and March 2003.
2. Degassing of a deeper-seated and fresh magma batch though fractures opened during tectonic events May-June 2003 (INETER 2003a; 2003b) led to the venting of pristine and relatively dry and CO_2 rich gases in July 2003 (Chapter 3). This change in main gas chemistry resulted in significantly lower trace metal concentrations at F9 and F7 in July 2003.
3. Detailed comparison of trace metal concentrations in the gases venting from F7, F9, and F15 reveals significant inter-fumarolic differences. This illustrates the complex dependence of gas chemistry on emission temperatures, dilution processes, host-rock chemistry, and chemical and physical processes during gas ascent.

4. Calculation and analysis of Enrichment Factors show that the trace elements Tl, Bi, As, Se, Mo, Sb, Hg, Au, W, Pb, Cd, Sn in the fumarolic gases are most likely of magmatic origin.
5. Comparison of fumarolic gases from the 1980s and 2002-2003 shows that change in the volcano-magma-system (degassed magma batch richer in HCl and H_2O and dry-out of the hydrothermal system) are reflected in trace element distribution. Trace metal concentrations are higher in the 1980s than they were in 2002-2003.
6. Flux estimates of some highly volatile and potentially harmful trace metals of magmatic origin show that Momotombo is only a minor source of pollutants in the atmosphere. The suspiciously low values in comparison to other Nicaraguan and worldwide volcanoes call, however, for additional data acquisition on element ratios in the Momotombo gas plume. This could reveal eventual discrepancies in element ratios between the gas plume and the fumarolic gases.

We conclude that fumarolic gas analysis is a powerful tool for understanding how changes in the volcano-magma-system affect quiescent degassing of Momotombo volcano. The presented variations in fumarole chemistry illustrate the importance of detailed multi-element and isotopic studies of degassing volcanoes in order to better understand element transport within the volcano-magma-system and into the atmosphere.

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References

Aiuppa A, Burton M, Murè F, Inguaggiato S (2004) Intercomparison of volcanic gas monitoring methodologies performed on Vulcano Island, Italy. Geophys Res Lett 31: L02610, DOI:10.1029/2003GL018651

Allard P, Aiuppa A, Dongarra G (2000) Acid Gas and Metal Emission Rates during Long-lived Basalt Degassing at Stromboli Volcano. Geophys Res Lett 27: 1207-1210

Anders E, Ebihara M (1982) Solar-System Abundances of the Elements. Geochimica et Cosmochimica Acta 46: 2363-2380. doi: 10.1016/0016-7037(82)90208-3

Churakov SV, Tkachenko SI, Korzhinskii MA, Bocharnikov RE, Shmulovich KI (2000) Evolution of Composition of High-Temperature Fumarolic Gases from Kudryavy Volcano, Iturup, Kuril Islands: the Thermodynamic Modeling. Geochem Intern 38: 436-451

CRC (2001) Handbook of chemistry and physics. 82nd, Lide DR (eds), CRC press, Boca Raton, Florida, USA

Delmelle P (2003) Impact of Throposferic volcanic plumes. In: Oppenheimer C, Pyle DM, Barkley J (eds) Volcanic Degassing. Geol Soc, London, Spec

Delmelle P, Stix J, Baxter P, Garcia-Alvarez J, Barquero J (2002) Atmospheric dispersion, environmental effects and potential health hazard associated with the low-altitude gas plume of Masaya volcano, Nicaragua. Bull Volcanol 64: 423 - 434

Frische M, Garofalo K, Hansteen TH, Borchers R. (2006) Fluxes and origin of halogenated trace gases from Momotombo volcano (Nicaragua). Geochem Geophys Geosys in press

Fulignati P, Gioncada A, Sbrana A (1999) Rare-earth element REE behaviour in the alteration facies of the active magmatic–hydrothermal system of Vulcano Aeolian Islands, Italy. J Volcanol Geotherm Res 88: 325–342

Fischer TP, Shuttleworth S, O'Day PA (1998) Determination of trace and platinum-group elements in high ionic-strength volcanic fluids by sector-field inductively coupled plasma mass spectrometry (ICP-MS). Fresen J Anal Chem 362: 457-464

Galle B, Hansteen TH, Frische M, Garofalo K, and Strauch W (2003) An estimate of the SO2 emissions from four volcanoes in Nicaragua, made using mini-DOAS spectroscopy. IAVCEI 8th Field Workshop Volc Gas, abs vol

Garbe-Schömberg CD (1993) Simultaneous determination of thirty-seven trace elements in twenty-eight international rock standards by ICP-MS. Geostand Newslett 17: 81-97

Gautier P-J, Le Cloarec, M-F (1998) Variability of alkali and heavy metal fluxes released by Mt. Etna volcano, Sicily, between 1991 and 1995. J Volcanol Geotherm Res. 81: 311–326

Gemmell JB (1987) Geochemistry of metallic trace elements in fumarolic condensates from Nicaraguan and Costa Rican volcanoes. J Volcanol Geotherm Res 33: 161-181

Hedenquist JW, Lowenstern JB (1994) The role of magmas in the formation of hydrothermal ore deposits. Nature 370: 519-527

Hinkley TK (1991) Distribution of metals between particulate and gaseous forms in volcanic plume. Bull Volcanol 53: 395-400

Hinkley TK, Lamothe PJ, Wilson SA, Finnegan DL and Gerlach TM (1999) Metal emissions from Kilauea, and a suggested revision of the estimated worldwide metal output by quiescent degassing of volcanoes. Earth Planet Sci Lett 170: 315-325

Horrocks LA, Oppenheimer C, Burton MR, Duffell HJ (2003) Compositional variation in tropospheric volcanic gas plumes: Evidence from ground-based remote sensing. In Oppenheimer C, Pyle DM, Barclay J, Volcanic Degassing Geol. Soc Spec Publ 213: 349-369

Hradecky P, Mayorga E, Mrazova S, Novák Zd, Havlicek P, Opletal M, Sebesta J, Sevcik J (2001) Estudio Geológico y Reconocimiento de las Amenazas Geológicas en el Volcán Momotombo, Nicaragua. Informe del Servicio Geológico Checo y Instituto Nicaraguense de Estudios Territoriales, Praga-Managua

Imai N, Terashima S, Itoh S, Ando A (1995) Compilation of analitical data for minor and trace elements in seventeen GSJ geochemical reference samples, "igneous rock series". Geostand Newslett 19: 135-213

INETER (2003a) Actividad Sísmica Tectónica: Volcan Momotombo. Sismos y Volcanes de Nicaragua, Boletín Mensual Mayo 2003. http://www.ineter.gob.ni/geofisica/boletin/2003/05/volcan-momotombo0305.htm

INETER (2003b) Lista de sismos registrados en 2003. Sismos y Volcanes de Nicaragua, Boletín Anual 2003. http://www.ineter.gob.ni/geofisica/boletin/2003/anual/lista-sismos2003.htm

Matsumoto A, Hinkley TK (2001) Trace metal suites in Antarctic pre-industrial ice are consistent with emissions from quiescent degassing of volcanoes worldwide. Earth Planet Sci Lett 186: 33-43

McGonigle AJS, Delmelle P Oppenheimer C, Tsanev VI, Delfosse T, Williams-Jones G, Horton K, Mather TA (2004) SO2 depletion in tropospheric volcanic plumes. Geophys Res Lett 31: L13201, DOI:10.1029/2004GL019990

Menyailov IA, Nikitina LP, Shapar VN, Pilipenko VP (1986) Temperature increase and chemical change of fumarolic gases at Momotombo Volcano, Nicaragua, in 1982-1985: Are these indicators of possible eruption? J Geophys Res 91: 12,199-12,214

Nho EY, Le Cloarec MF, Ardouin B, Tjetjep WS (1996) Source strength assessment of volcanic trace elements emitted from the Indonesian arc. J Volcanol Geotherm Res 74: 121-129

Nriagu JO (1989) A global assessment of natural sources of atmospheric trace metals. Nature 338: 47–49

Patino LC, Carr MJ, Feigenson MD (2000) Local and regional variations in Central American arc lavas controlled by variations in subducted sediment input. Contrib Mineral Petrol 138: 265-283

Pokrovski GB, Roux J, Harrichoury JC (2005) Liquid density control on vapor-liquid partitioning of metals in hydrothermal systems. Geology 33: 657-600

Parnell RA, Burke KJ (1990) Impacts of acid emissions from nevado del Ruiz volcano, Colombia, on selected terrestrial and aquatic ecosystems. J Volcanol Geotherm Res 42:69-88

Quisefit JP, Toutain JP, Bergametti G, Javoy M, Cheynet B and Person A (1989) Evolution versus cooling of gaseous volcanic emissions from Momotombo Volcano, Nicaragua: Thermochemical model and observations. Geochim Cosmochim Acta 53: 2591-2608

Ruaya JR, Seward TM (1987) The ion-pair constant and other thermodynamic properties of HCl up to 350°C. Rollinson H (1993) Using Geochemical Data: Evaluation, Presentation, Interpretation: Longman Scientific & Technical Ltd, Harlow, UK, pp 1-352

Shinohara H (1994) Exsolution of immiscible vapor and fluid phases from a crystallizing silicate melt: Implications for chlorine and metal transport. Geochim Cosmochim Acta 58: 4215–5221

Shmulovich KI, Churakov SV (1998) Natural fluid phases at high temperatures and low pressures. J Geochem Expl 62: 183–191

Shock EL, Koretsky CM (1995) Metal-organic complexes in geochemical processes: Estimation of standard partial molal thermodynamic properties of aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. Geochim Cosmochim Acta 59: 1497-1532

Symonds RB, WI Rose, MH Reed, FE Lichte, DL Finnegan (1987) Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia. Geochim Cosmochim Acta 51: 2083-2101

Symonds RB, Reed MH, WI Rose (1992) Origin, speciation, and fluxes of trace-element gases at Augustine Volcano, Alaska: Insights into magma degassing and fumarolic processes. Geochim Cosmochim Acta 56: 633-657

Symonds RB, Reed MH (1993) Calculation of multicomponent chemical equilibria in gas–solid–liquid system: calculation methods, thermochemical data, and application to studies of high-temperature volcanic gases with examples from Mount St. Helens. Am J Sci 293: 758–864

Taran Y, Hedenquist JW, Korzhinsky MA, Tkachenko SI, Shmulovic KI (1995) Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands. Geochim Cosmochim Acta 59: 1749-1761

Zreda-Gostynska G, Kyle PR, Finnegan D, Meeker Prestbo K (1997) Volcanic gas emissions from Mount Erebus and their impact on the Antartic environment. J Geophys Res 102:15039-15055

Wardell LJ, Peterson A, Stix J, McGonigle A (2004) Trace Element Flux Values from the Gas Plume of Masaya Volcano, Nicaragua. AGU Montreal conf abs

Williams-Jones AE, Migdisov AA, Archibald SM, Xiao Z (2002) Vapor-transport of ore metals. In: Hellmann R, Wood SA (eds) Water-Rock Interactions, Ore Deposits, and Environmental Geochemistry: a Tribute to David A. Crerar. Geochem Soc Spec Publ 7

Wilson M (1989) Igneous Petrogenesis, Kluwer, Dordrecht, 450 pp

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