Halogenated trace compounds in fumarolic gases of the Nicaraguan subduction zone volcanoes: variation patterns, budgets and impact on the Earth's atmosphere

Dissertation
zur Erlangung des Doktorgrades der
Mathematisch-Naturwissenschaftlichen Fakultät
der Christian-Albrechts-Universität zu Kiel

vorgelegt von

Matthias Frische

Kiel

2005

Referent: PD Dr. Thor H. Hansteen
Korreferent: Prof. Dr. Anton Eisenhauer
Tag der mündlichen Prüfung: ....
Zum Druck genehmigt: Kiel, den ....

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.

Matthias Frische

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, description of sampling and analytical methods, data presentation, discussion, conclusion, and reference list.

The three papers are:

1. Variations of alkylhalide emissions from fumaroles in Nicaragua: Dynamics of quiescently degassing volcanoes; by M. Frische, K. Garofalo, T.H. Hansteen and R. Borchers; prepared for submission to Journal of Volcanology and Geothermal Research

2. Fluxes and origin of halogenated trace gases from Momotombo volcano (Nicaragua); by M. Frische, K. Garofalo, T.H. Hansteen and R. Borchers; prepared for submission to Geochemistry Geophysics Geosystems

3. A volcanic contribution of stable halogenated compounds?; by M. Frische, K. Garofalo, T.H. Hansteen, R. Borchers and J. Harnisch; prepared for submission to Environmental Science and Pollution Research

For these publications I carried out comprehensive field work in Nicaragua during five campaigns of durations between three and five weeks, including extensive sampling; I conducted measurement campaigns for GC/MS analyses; processed and interpreted the data; and prepared the manuscripts. This thesis is focussed on halogenated organic trace compounds in fumarolic gases.

In addition to the work presented in this thesis, I contributed to the following submitted papers, publications in preparation and conference abstracts:

1. Garofalo K., F. Tassi, O. Vaselli, D. Tedesco, A. Delgado-Huertas, M. Frische, T.H. Hansteen and W. Strauch, The fumarolic gas discharges at Mombacho Volcano (Nicaragua): presence of magmatic gas species and implication for a volcanic surveillance, to be submitted to Rose, W.I. (ed.): Volcanic Hazards in Central America, Geologic Society of America Special Paper

2. Garofalo K., F. Tassi, M. Frische, T.H. Hansteen, O. Vaselli, A. Delgado Huertas, D. Tedesco and W. Strauch, “The collapsing volcano” Mombacho (Nicaragua): is it experiencing a renew phase of volcanic activity?, 19th LAK Colloquium on Latin American Geosciences, Potsdam, Germany, Abs. Vol., 2005

3. Garofalo K., T.H. Hansteen, M. Frische, F. Tassi, O. Vaselli and W. Strauch, Geochemical and isotopic study of fumarolic emissions from three Nicaraguan Volcanoes, IAVCEI General Assembly Pucon, Chile, Abs. Vol., 2004

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

5. Galle B, T.H. Hansteen, M. Frische, K. Garofalo and W. Strauch, 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., 2003

6. Garofalo K., F. Tassi, O. Vaselli, A. Delgado-Huertas, M. Frische and T.H. Hansteen, Geochemical and isotopic study of fumarolic gases discharged at Momotombo volcano (Nicaragua), in prep.

7. Garofalo K., F. Tassi, O. Vaselli, A. Delgado-Huertas, M. Frische and T.H. Hansteen, Volcanic degassing and release of trace metals in the environment: a case study for Nicaraguan volcanoes, in prep.

8. Galle B., T.H. Hansteen, M. Frische and K. Garofalo, Time-averaged SO_2 fluxes from Nicaraguan volcanoes, in prep.

Abstract

Quiescently degassing volcanoes continuously release large amounts of organic and inorganic compounds. Several of these substances influence already in trace concentrations the properties of the Earth's atmosphere. Some halogenated compounds are involved in the greenhouse effect or in the degradation of stratospheric ozone. In order to study halogenated trace compounds in volcanic gases I took during four field campaigns (July 2001- July 2003) gas samples from fumaroles of the Nicaraguan volcanoes Momotombo, Cerro Negro and Mombacho.

The most abundant halogenated hydrocarbons in these samples were CH_3Cl, CH_3Br, CH_3I, CH_2Cl_2, $CHCl_3$, CCl_4, C_2H_5Cl, C_2H_5Br, C_2H_5I and C_2H_3Cl. Mean time-dependent variations (1σ) in concentration of these halohydrocarbons amount to ±73%, ±60% and ±47% for long-term (months-years), medium-term (hours-days) and short-term variations (minutes), respectively. An increase in trace gas concentrations up to a factor 50 were recorded for Momotombo volcano between March and November 2002. Observed variations in concentration do not agree with the timescale of typical periodic fluctuations like ocean or earth-tides and precipitation rates.

Using a simultaneous record of trace- and main-compounds in fumarolic gases from high temperature fumaroles (472-776°C) at Momotombo as well as SO_2-fluxes of the gas plume, fluxes of volcanic halohydrocarbons like methyl halides (CH_3Cl, CH_3Br and CH_3I), ethyl halide (C_2H_5Cl, C_2H_5Br and C_2H_5I) and higher chlorinated methanes (CH_2Cl_2, $CHCl_3$ and CCl_4) were quantified to assess the contribution of quiescently degassing volcanoes to the global halocarbon inventory. Estimated mean halohydrocarbon fluxes from Momotombo were in the range of 390-3,300 g/yr for methyl halides, 28-200 g/yr for ethyl halides and 2.1-19 g/yr for higher chlorinated methanes. When the results for Momotombo are scaled up to the total SO_2 fluxes estimated for the active Quaternary Nicaraguan volcanoes (San Cristóbal, Telica, Cerro Negro, Momotombo, and Masaya), fluxes of 1.1×10^5 g/yr of CH_3Cl and 69 g/yr of CCl_4 are attained for Nicaragua. Scaled up to the estimated global SO_2 flux, this translates to global fluxes of 3.7×10^6 g/yr CH_3Cl and 2.3×10^3 g/yr CCl_4. These

volcanic fluxes are negligible compared to global anthropogenic and natural emissions of about 3 x 10^{12} g/yr CH_3Cl and 2 x 10^{10} g/yr CCl_4.

Mean molar ratios of bromine and iodine relative to chlorine of the methyl halides CH_3Cl, CH_3Br, CH_3I were 10 : 1.0 : 1.1 and 11 : 1.0 : 1.9 for the ethyl halides C_2H_5Cl, C_2H_5Br, C_2H_5I, and thus much higher compared to bulk analyses of the gases and to melt inclusions and volcanic glasses from Nicaraguan volcanic rocks. The strong enrichment of bromine and iodine vs. chlorine in Nicaraguan fumarolic trace gas samples and the high variability of halohydrocarbon concentrations, even at a local scale, points to important processes at mantle and crustal depths leading to the generation of volcanic halohydrocarbons: a) subduction and recycling of large volumes of marine sediments, and b.) shallow-level crustal processes like interactions between the magmatic system and marine deposits present at depth in the Nicaraguan Depression, and probably rapid cyclic variations within the porous volcanic edifices involving disequilibrium reactions in the fluid-rock or fluid-fluid systems.

Further I investigated the controversially discussed existence and relevance of a volcanic contribution of chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), halons (bromine containing halo(hydro)carbons), and fully fluorinated compounds (e.g. CF_4 and SF_6) to the atmospheric budget. In most fumarolic samples from Momotombo, Cerro Negro and Mombacho certain species of CFCs, HFCs, HCFCs, halons, and the fully fluorinated compounds CF_4 and SF_6 were present above detection limits. However, these compounds occur in the fumarole gases in relative proportions characteristic for ambient air. This atmospheric fingerprint can be explained by variable amounts of air entering the porous volcanic edifices and successively being incorporated into the fumarolic gas stream. I used the typical fingerprint both in fumarolic and ambient air samples to determine the air dilution factor for the fumarolic gas samples and to calculate the geogenic portion. The results clearly show that the investigated volcanoes do not constitute a significant natural source for CFCs, HFCs, HCFCs, halons, CF_4, SF_6 and NF_3.

Zusammenfassung

Still entgasende Vulkane emittieren kontinuierlich große Mengen an organischen und anorganischen Substanzen. Bei einigen dieser Substanzen handelt es sich um Halogenverbindungen, die als atmosphärische Spurengase am Treibhauseffekt oder am Abbau des stratosphärischen Ozons beteiligt sind. Um halogenierte Spurenstoffe in vulkanischen Gasen zu untersuchen, habe ich während vier Geländekampagnen (Juli 2001- Juli 2003) Fumarolen der nicaraguanischen Vulkane Momotombo, Cerro Negro und Mombacho beprobt. Die halogenierten Kohlenwasserstoffe (*HKW*) CH_3Cl, CH_3Br, CH_3I, CH_2Cl_2, $CHCl_3$, CCl_4, C_2H_5Cl, C_2H_5Br, C_2H_5I und C_2H_3Cl waren die am häufigsten vorkommenden Spurengase in diesen Proben. Mittlere Variationen der Konzentration dieser Substanzen als Funktion der Zeit beliefen sich auf ±73%, ±60% und ±47% für Langzeit- (Monate bis Jahre), mediale- (Stunden bis Tage) und Kurzzeit-Variationen (Minuten). Zwischen März und November 2002 konnte am Momotombo ein bis zu 50-facher Anstieg der Spurengaskonzentrationen verzeichnet werden. Die beobachteten Konzentrations-Variationen stimmten nicht mit den Zeitskalen typischer saisonaler Fluktuationen wie Ozean- und Erd-Tiden oder Niederschlagsmengen überein. Um den Beitrag still entgasender Vulkane zur globalen *HKW*-Bilanz zu berechnen, wurden für den Momotombo die Stoffflüsse der Methylhalide (CH_3Cl, CH_3Br, CH_3I), der Ethylhalide (C_2H_5Cl, C_2H_5Br, C_2H_5I) und der höher chlorierten C_1-Verbindungen (CH_2Cl_2, $CHCl_3$, CCl_4) durch eine simultane Erfassung von Spuren- und Hauptkomponenten in Gasen der Hochtemperaturfumarolen (472-776°C) sowie des SO_2-Flusses in der Gaswolke des Vulkans ermittelt. Die so geschätzten mittleren *HKW*-Flüsse des Momotombo beliefen sich auf 390-3300 g/a Methylhalide, 28-200 g/a Ethylhalide und 2,1-19 g/a der höher chlorierten C_1-Verbindungen. Wenn die Ergebnisse für den Momotombo auf den gesamten SO_2-Fluss der quartären nicaraguanischen Vulkane (San Cristóbal, Telica, Cerro Negro, Momotombo, Masaya) hochgerechnet werden, erhält man für Nicaragua einen Stofffluss von $1,1 \times 10^5$ g/a CH_3Cl und 69 g/a CCl_4. Hochgerechnet mit geschätzten globalen SO_2-Flüssen ergeben sich Emissionen von $3,7 \times 10^6$ g/a CH_3Cl und $2,3 \times 10^3$ g/a CCl_4 aller Vulkane

weltweit. Verglichen mit den weltweiten anthropogenen und natürlichen Emissionen von etwa 3×10^{12} g/a CH_3Cl und 2×10^{10} g/a CCl_4 sind die vulkanischen Flüsse demgegenüber vernachlässigbar.

Die mittleren molaren Verhältnisse von Brom und Jod zu Chlor sind bei den Methylhaliden (CH_3Cl, CH_3Br, CH_3I) 10 : 1.0 : 1.1 und bei den Ethylhaliden (C_2H_5Cl, C_2H_5Br, C_2H_5I) 11 : 1.0 : 1.9 und damit deutlich höher als in den Gesamt-Gasproben oder in Schmelzeinschlüssen und vulkanischen Gläsern nicaraguanischer Vulkanite. Die starke Anreicherung der schweren Halogene in Spurengasproben von nicaraguanischen Fumarolen und die hohe, auch auf lokaler Ebene zu beobachtende Variabilität der *HKW*-Konzentrationen deuten auf wichtige Prozesse in Mantel- und Krusten-Tiefe, die an der Bildung der *HKW* beteiligt sind: a.) die Subduktion und Wiederverwertung großer Volumina mariner Sedimente und b.) oberflächennahe krustale Prozesse wie die Interaktion zwischen dem magmatischen System und marinen Sedimentablagerungen des Nicaraguanischen Beckens und möglicherweise Ungleichgewichtsreaktionen in der Fluid-Fluid- und Fluid-Gestein-Wechselwirkung durch rasche zyklische Veränderungen im porösen Vulkangebäude.

Außerdem habe ich die kontrovers diskutierte Existenz und Relevanz eines vulkanischen Beitrags von FCKWs, Halonen (bromierte *HKW*) und vollfluorierten Verbindungen (z.B. CF_4 und SF_6) zum atmosphärischen Haushalt untersucht. In den meisten Fumarolenproben des Momotombo, Cerro Negro und Mombacho lagen die Konzentrationen einiger FCKWs, Halone und vollfluorierter Verbindungen wie CF_4 und SF_6 über der Nachweisgrenze. Diese Verbindungen traten allerdings immer in den für die Umgebungsluft charakteristischen Mengenverhältnissen auf. Dieser „atmosphärische Fingerabdruck“ kann durch die unterschiedlichen Mengen an Luft, die in das poröse Vulkangebäude eingedrungen ist und die Fumarolengase verdünnt, erklärt werden. Ich habe diesen typischen Fingerabdruck benutzt, um den Luft-Verdünnungsfaktor zu ermitteln und damit den geogenen Anteil in den Proben zu errechnen. Die Resultate zeigen deutlich, dass die untersuchten Vulkane keine bedeutsame Quellen für FCKWs, Halone oder vollfluorierte Verbindungen darstellen.

Contents

Chapter 1

1 Introduction

Halogenated compounds are important constituents of the Earth's atmosphere despite of their occurrence in trace concentrations, because they may have strong influence on its physical and chemical properties (Seinfeld & Pandis 1998). This thesis addresses reactive (short-lived) halohydrocarbons as well as more stable (long-lived) halocarbons and fully-fluorinated compounds released from volcanoes. Halohydrocarbons are organic compounds containing one or more halogens and hydrogen (e.g. CH_3Br or methyl bromide). Halocarbons containing halogens and carbon only (e.g. CCl_4 or carbon tetrachloride). In fully fluorinated compounds, all bonds are occupied by fluorine (e.g. SF_6 or sulphur hexafluoride).

1.1 Halogenated compounds in the Earth's atmosphere

Halohydrocarbons have large natural sources like oceans, soils, and the biosphere (WMO 2003). Human activity has merely led to an increase in the abundances of halohydrocarbons (Trudinger *et al.,* 2004), while some halocarbons and fully-fluorinated compounds seems to have exclusively anthropogenic sources (Butler *et al.,* 1999; WMO 2003). The reactivities of halogenated compounds and their resulting atmospheric lifetimes vary over a large time range from seconds to thousands of years (WMO 2003). Depending on emission rates and reactivities, several substances have shown a rapid increase in atmospheric concentrations during the last couple of decades (Thompson *et al.,* 2004). Since negative effects of halogenated compounds on the stratospheric ozone layer (Molina & Rowland 1974; Stolarski & Cicerone 1974) and their influence on the Earth's radiative balance due to the greenhouse effect (IPCC 2001) and aerosol-formation (Andreae & Crutzen 1997) have been recognized, many scientists and politicians have turned their attention to these substances. International agreements (e.g. the Montreal Protocol (UNEP 2003) and the Kyoto Protocol (UNFCCC 1998)) have been adopted in order to control and reduce the anthropogenic contribution to the atmospheric load of halogenated compounds. For a further understanding of the processes concerning halogenated compounds in the atmosphere, and to guide policy decisions, detailed knowledge of the source strength of the different emitters are of extraordinary importance.

1.2 Degassing of the Earth

The early atmosphere was generated due to degassing processes of the young Earth (Press & Siever 1994). Degassing processes have continued until these days and are mainly focussed along active plate boundaries i.e. subduction zones and mid-ocean ridges. At subduction zones, oceanic lithosphere together with oceanic sediments and seawater, return back into the Earth's mantle (Stern 2002). The sinking of the subducted slab is intimately connected with spreading at the mid-ocean ridges to produce new seafloor. Subduction zones are the largest recycling system on Earth, which introduces large amounts of volatiles from the downgoing slab to the overriding plate. Interaction between these water-dominated volatiles and the overlying mantle wedge leads to partial melting of mantle material. The melts may ascend through the lithosphere due to their lower density compared to the surrounding material, and can reach the surface to erupt at arc volcanoes. During eruptions volcanoes releases huge amounts of volatiles. Degassing processes continue at many volcanoes also between eruptions, in phases of quiescent degassing occurring through open vents, at fumaroles, solfatares, or diffusively.

The composition of gases released from subduction zone volcanoes depends on the source material of the magma, on physical subduction parameters such as crustal thickness, angle of dip, sediment underplating, faulting style and subduction erosion, and on magma generation processes in the mantel, followed by ascent and magma differentiation (Stern 2002). Deep processes like vapour-melt separation and crustal assimilation, as well as shallow level interaction with meteoric water and fluids of the hydrothermal system, may influence the composition of volcanic gases (Carroll & Holloway 1994; Scarpa & Tilling 1996).

1.3 Location and geologic setting:

The Quaternary Nicaraguan volcanoes are part of the Central American volcanic arc (CAVA), which results from subduction of the Cocos Plate underneath the Caribbean Plate along the Middle American trench. The CAVA extends from the border of Mexico, across Guatemala, El Salvador and Nicaragua to central Costa Rica. The ocean floor which is subducted underneath Nicaragua at convergence rates of c. 8 cm/yr (DeMets 2001) was produced at the East Pacific Rise, is 5.5 km thick and overlain by ~225 m of carbonate, which is in turn overlain by ~200 m of hemipelagic sediments (Auboudin *et al.,* 1982; Kimura *et al.,* 1997; Walther *et al.,* 2000). Lavas from the volcanic front in western Nicaragua show the highest input of carbonate and hemipelagic sediments along the CAVA (Patino *et al.,* 2000). The slab signal reflected by e.g. high Ba/La values in Nicaraguan volcanic rocks is the strongest along the CAVA (Carr *et al.,* 2003), and the dip of the subducting plate at Nicaragua is the steepest (65–75°) (Patino *et al.,* 2000). Intensive bend-faulting to mantle depth of the downgoing slab offshore Nicaragua facilitate a deep penetration of seawater into the subduction zone (Ranero *et al.,* 2003). The recent volcanic chain is aligned along the Cordillera de los Marrabios that rises from the Nicaraguan Depression, a large NW-SE trending graben crossing the central part of the country. The Depression is characterized by a mafic igneous basement of oceanic lithosphere (Walther *et al.,* 2000), overlain by Cretaceous to Miocene marine sediments (tuffaceous shale, siltstone, greywacke, sandstone and limestone), and is buried by the Quaternary ignimbrite deposits of Malpaisillo and La Sierra Group (McBirney & Williams 1965; Elming *et al.,* 2001).

We choose the volcanoes Momotombo, Cerro Negro and Mombacho for detailed investigations, because they exhibit fumaroles of a wide range in temperature and gas composition. Magmatically dominated high-temperature fumaroles are accessible at Momotombo, more diffusive degassing ones in a medium-temperature range occurs at

Cerro Negro, and Mombacho's low temperature discharges are groundwater dominated and mixed with juvenile magmatic compounds (Garofalo *et al.,* 2005a).

1.4 Outline and research objectives of the thesis

The overall objective of this thesis is to enhance our knowledge about halogenated trace compounds in fumarolic gases. Their occurrence, their variability and especially their fluxes are unknown in detail. In Chapter 2, the most abundant halogenated hydrocarbons in fumarolic gases from Momotombo, Cerro Negro and Mombacho, and their variability in concentrations at different time-scales, ranging from minutes to years, are presented. Chapter 3 is a detailed study of trace gas fluxes at Momotombo, to assess the contribution of a quiescently degassing volcano to the global halocarbon inventory. This is the first study in which a flux estimation is based solely on original main and trace gas compound data. In Chapter 4, the question of a volcanic contribution of stable halogenated compounds to the atmospheric budget is answered and a new sampling setup for fumarolic gases is presented in detail. Chapters 2-4 have been written as scientific papers, which are prepared for submission.

Bibliography

Andreae, M.O. and P.J. Crutzen, Atmospheric Aerosols: Biogeochemical Sources and Role in Atmospheric Chemistry, Science, 276, 1052-1058, 1997.

Auboudin, J., J. Azema, J.-Ch. Carfantan, A. Demant, C. Rangin, M. Tardy and J. Tournon, The Middle America trench in the framework of Central America. In Init Repts DSDP, 67:747- 755 College Station, TX (Ocean Drilling Program), 1982.

Butler, J.H., M. Battle, M.L. Bender, S.A. Montzka, A.D. Clarke, E.S. Saltzman, C.M. Sucher, J.P. Severinghaus and J.W. Elkins, A record of atmospheric halocarbons during the twentieth century from polar firn air, Nature, 399, 749-755, 1999.

Carr, M.J., M.D. Feigenson, L. Patino and J.A. Walker, Volcanism and Geochemistry in Central America: Progress and Problems, Inside the Subduction Factory, Geophysical Monograph 138, American Geophysical Union, 153-174, 2003.

Carroll, M.R. and J.R. Holloway, Volatiles in Magmas, Rev. Min., v.30, 509pp., 1994.

DeMets, C., A new estimate for present-day Cocos-Caribbean plate motion: Implications for slip along the Central American volcanic arc, Geophys. Res. Lett., 28(21), 4043-4046, 2001.

Elming, S.A., P. Layer and K. Ubieta, A paleomagnetic study and age determinations of Tertiary rocks in Nicaragua, Central America, Geophys. J. Internat., 147(2): 294-309, 2001.

Garofalo, K., F. Tassi, O. Vaselli, A. Delgado-Huertas, M. Frische and T.H. Hansteen, unpubl. data in prep..

IPCC (Intergovernmental Panel on Climate Change), Climate Change 2001: The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, edited by J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, and C.A. Johnson, 881 pp., Cambridge University Press, UK and New York, 2001.

Kimura, G, Silver E, Blum P et al., Proc ODP Init Repts, 170: College Station, TX (Ocean Drilling Program), 1997.

Molina, M.J. and F.S. Rowland, Stratospheric sink for chlorofluoromethanes: chlorine atom-catalyzed destruction of ozone, Nature, 249, 810-812, 1974.

McBirney, A.R., and Williams, H., Volcanic history of Nicaragua, Univ. Calif. Pub. Geo. Sci., 55, 1-65, 1965.

Patino, L.C., M.J. Carr and M.D. Feigenson, Local and regional variations in Central American arc lavas controlled by variations in subducted sediment input, Contrib. Min. Petrol., 138, 265-283, 2000.

Press, F. and R. Siever, Understanding Earth, W.H. Freeman and Co., 593pp., 1994.

Ranero, C.R., Morgan, J.P., McIntosh, K., and Reichert, C., Bending-related faulting and mantle serpentinization at the Middle American trench, Nature, 425, 367-373, 2003.

Scarpa, R. and R.I. Tilling, Monitoring and Mitigation of Volcanic Hazards, Berlin & Heidelberg, Springer, 841pp., 1996.

Seinfeld, J.H., S.N. Pandis; Atmospheric chemistry and physics, John Wiley & Sons Inc., New York, 1998.

Stern, R.J., Subduction zones, Rev. Geophys., 40(4), 38pp., 2002.

Stolarski, R.S. and R.J. Cicerone; Stratospheric chlorine: a possible sink for ozone, J. Can. Chem., 52, 1610-1615, 1974.

Thompson, T.M., J. H. Butler, B. C. Daube, G. S. Dutton, J. W. Elkins, B. D. Hall, D. F. Hurst, D. B. King, E. S. Kline, B. G. Lafleur, J. Lind, S. Lovitz, D. J. Mondeel, S. A. Montzka, F. L. Moore, J. D. Nance, J. L. Neu, P. A. Romashkin, A. Scheffer, and W. J. Snible, 5. Halocarbons and other Atmospheric Trace Species, in Climate Monitoring and Diagnostics Laboratory, Summary Report No. 27, 2002-2003, pp. 115-133, edited by R. C. Schnell, A.-M. Buggle, and R. M. Rosson, NOAA CMDL, Boulder, CO, 2004.

Trudinger, C.M., D.M. Etheridge, G.A. Sturrock, P.J. Fraser, P.B. Krummel and A. McCulloch, Atmospheric histories of halocarbons from analysis of Antarctic firn air: Methyl bromide, methyl chloride, chloroform and dichloromethane, J. Geophys. Res., 109, D22310, doi:10.1029/2004JD004932, 2004.

UNEP (United Nations Environment Programme), Handbook for the International Treaties for the Protection of the Ozone Layer- 6th edition, 2003, (http://www.unep.org/ozone/pdfs/Handbook-2003.pdf)

UNFCCC (United Nations Framework Convention on Climate Change), Kyoto Protocol to the United Nations Framework Convention on Climate Change, UNEP/INC/98/2, Information Unit for Conventions, UNEP, Geneva, 1998, (http://unfccc.int/resource/docs/convkp/kpeng.pdf).

Walther, C.H.E., E.R. Flueh, C.R. Ranero, R. von Huene, and W. Strauch, Crustal structure across the pacific margin of Nicaragua: Evidence for ophiolitic basement and a shallow mantle sliver, Geophys. J. Int., 141, 759-777, 2000.

WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2002, Rep. Global Ozone Res. and Monitor. Proj., Vol. No. 47, 498 pp., World Meteorol. Organ., Geneva, Switzerland, 2003.

Chapter 2

Variations of alkylhalide emissions from fumaroles in Nicaragua: Dynamics of quiescently degassing volcanoes

Matthias Frische[a,b,c,*], Kristin Garofalo[a], Thor H. Hansteen[a,b], Reinhard Borchers[c]

[a] *SFB 574, Christian-Albrechts-Universitaet, D-24148 Kiel, Germany*
[b] *IFM-GEOMAR Leibniz-Institut fuer Meereswissenschaften, D-24148 Kiel, Germany*
[c] *Max-Planck-Institut fuer Sonnensystemforschung, D-37191 Katlenburg/Lindau, Germany*

**Corresponding author: mfrische@ifm-geomar.de*

Abstract

During two years we have studied the temporal variations of halogenated organic compounds emitted from fumaroles of the Nicaraguan volcanoes Momotombo, Cerro Negro and Mombacho, based on periodic time series gas sampling campaigns. The mean time-dependent variations (1σ) in concentration for the most abundant halogenated hydrocarbons: CH_3Cl, CH_3Br, CH_3I, CH_2Cl_2, $CHCl_3$, CCl_4, C_2H_5Cl, C_2H_5Br, C_2H_5I and C_2H_3Cl were less than two orders of magnitude and amount to ±73%, ±60% and ±47% for long-term (months-years), medium-term (hours-days), and short-term variations (minutes), respectively. An increase in concentrations of these species up to a factor 50 could be recorded at Momotombo volcano between March and November 2002. Trace gas concentrations exhibited a weak negative relation with fumarole temperature, which points to an important role of the hydrothermal system in the generation of halohydrocarbons. The observed variations in concentrations do neither correspond to the timescale of typical seasonal fluctuations, nor to ocean or Earth-tide cycles. High variability in the concentrations of halohydrocarbons, also on a local scale, point also to the importance of shallow level processes for their synthesis. Jumps in absolute concentrations may be caused by spontaneous modifications to fluid pathways and thus to temperatures and to the availability of reactants within the volcanic edifice. Repeated fluctuations during minutes to days rather indicate cyclic variations in disequilibrium fluid-rock or fluid-fluid systems, which, however, remain to be quantified. Our results demonstrate that only long-term investigations can yield robust flux data, even for relatively steadily degassing volcanoes.

Keywords: *halocarbons, subduction zones, fumaroles, Momotombo, Cerro Negro, Mombacho.*

2.1 Introduction

About 300 subaerial volcanoes worldwide are active trough quiescent degassing. Both long- and short-term variations in major element compositions and minor hydrocarbon compounds from fumaroles have been previously reported (e.g. Symonds *et al.*, 1996; Shevenell & Goff 2000; Capaccioni & Mangani 2001; Saito *et al.*, 2002). However, detailed studies on the variability of halogenated organic compounds are rare (Jordan *et al.*, 2000; Jordan 2003). Many of these substances have influence on the physical and chemical properties of the Earth's atmosphere, already in trace concentrations (Seinfeld & Pandis 1998). Some of the substances are greenhouse gases (UNFCCC 1998; Reilly *et al.*, 1999), others are involved in the degradation of stratospheric ozone (WMO 2003), and most of them have toxic effects on life (WHO). Earlier investigations on volcanic halogenated organic compounds have been carried out either with single sample (e.g. from fumaroles, solfatares, and plumes), or with samples collected within relatively short time scales of minutes to days (Stoiber *et al.*, 1971; Rasmussen *et al.*, 1980; Inn *et al.*, 1981; Isidorov *et al.*, 1990; Jordan *et al.*, 2000; Schwandner *et al.*, 2004). Since Jordan (2003) reported short-term variations in concentration of halogenated hydrocarbons up to two orders of magnitude already within minutes at the same fumarole in the South East crater of Mt. Etna, the importance of long-term investigations became obvious.

In order to study temporal variations of halogenated organic compounds, we periodically took gas samples from the same fumaroles of the Nicaraguan volcanoes Momotombo, Cerro Negro and Mombacho, during four field campaigns (17 July- 21

August 2001, 22 February- 21 March 2002, 13 November- 13 December 2002, 09 July-23 July 2003). This time-series sampling was performed on three time intervals, comprising short-term series (minutes), medium-term series (hours to days) and long-term series (month to years). We thus compared long-, medium- and short-term variations in order to constrain the mechanisms of fluctuations in fumarolic trace gas emissions. Our investigation was focused on halomethanes and -ethanes because this type of C_1 and C_2 compounds exhibit much higher atmospheric lifetimes (WMO 2003) than longer-chain compounds, showing negligible water solubility (CRC 1993) which prevents quantitative tropospheric washout and permits subsequent transfer to the stratosphere (Symonds *et al.*, 1988; Seinfeld & Pandis 1998; Textor *et al.*, 2004).

2.2 Geological and volcanological background

The Quaternary Nicaraguan volcanoes Momotombo, Cerro Negro and Mombacho are part of the Central American volcanic arc (CAVA), which results from the subduction of the Cocos Plate underneath the Caribbean Plate along the Middle American trench. The CAVA extends from the border of Mexico, across Guatemala, El Salvador and Nicaragua to central Costa Rica. The ocean floor which is subducted underneath Nicaragua with convergence rates of c. 8 cm/yr (DeMets 2001) was produced at the East Pacific Rise, is 5.5 km thick and being overlain by ~225 m of carbonates, which is in turn overlain by ~200 m of hemipelagic sediments (Auboudin *et al.*, 1982; Kimura *et al.*, 1997; Walther *et al.*, 2000). Lavas from the volcanic front in western Nicaragua shows the highest input of carbonate and hemipelagic sediments along the CAVA (Patino *et al.*, 2000). The slab signal reflected by high Ba/La values in Nicaraguan volcanic rocks is the strongest (Carr *et al.*, 2003) and the dip of the subducting plate at Nicaragua is the steepest (65–75°) along the CAVA (Patino *et al.*, 2000). Intensive bend-faulting of the downgoing slab offshore Nicaragua to mantle depth facilitate a deep penetration of seawater into the subduction zone (Ranero *et al.*, 2003). The recent volcanic chain is aligned along the Cordillera de los Marrabios that rises from the Nicaraguan Depression, a large NW-SE trending graben crossing the central part of the country. The Depression is characterized by a mafic igneous basement of oceanic lithosphere (Walther *et al.*, 2000), overlain by Cretaceous to Miocene marine sediments (tuffaceous shale, siltstone, greywacke, sandstone and limestone), buried by the Quaternary ignimbrite deposits of Malpaisillo and La Sierra Group (McBirney & Williams 1965; Elming *et al.*, 2001).

For our investigations we selected the volcanoes Momotombo, Cerro Negro and Mombacho (Fig. 2.1), because they exhibit fumaroles covering a wide range in temperatures and gas compositions. Magmatic dominated high-temperature fumaroles are accessible at Momotombo, more diffusive degassing in a medium-temperature range occurs at Cerro Negro and Mombacho's low temperature discharges are groundwater dominated and mixed with juvenile magmatic compounds (Garofalo *et al.*, in prep.).

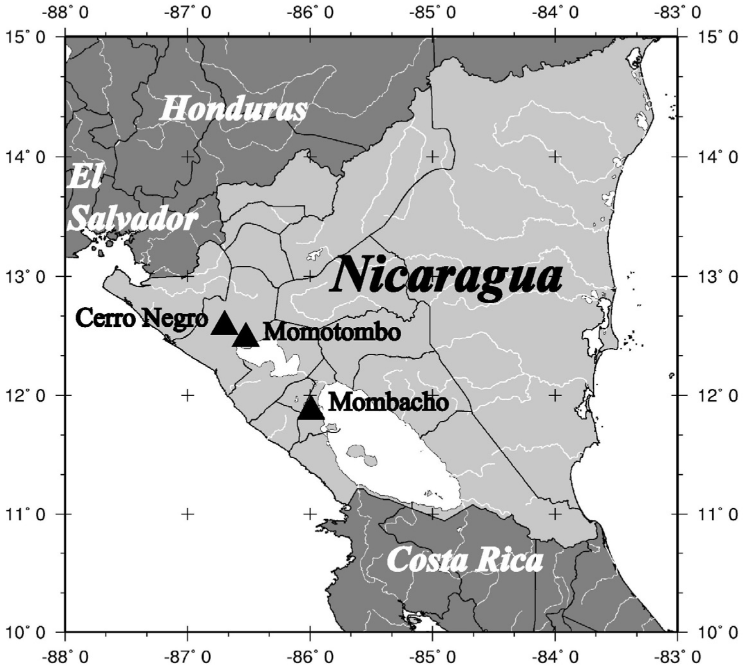

Figure 2.1 *Locality map of sampled Nicaraguan volcanoes.*

Momotombo volcano (1297 m, 12.25°N, 86.32°W) is situated on the north shore of Lake Managua. The stratovolcano erupted basaltic material last in 1905 and since that time has been in a persistent state of high-temperature fumarolic activity (Menyailov *et al.*, 1986).

The fumarolic activity occurs at the base of the inner walls of the summit area (Fig. 2.2), where gases were emitted over a wide range of temperatures, up to 776°C (fumarole F1) at the time of the survey (for individual temperatures of fumarolic gas samples used in this study see Table 2.2-2.3).

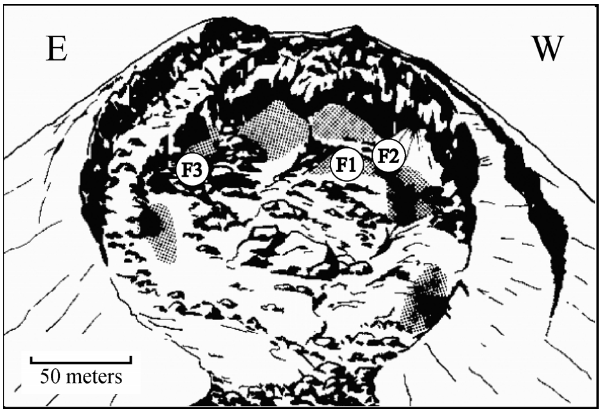

Figure 2.2 *Schematic map of the summit crater of Momotombo and locations of sampled fumaroles (courtesy of INETER). Common "official" fumarole numbers are F9, F7, and F16, respectively, instead of F1, F2 and F3.*

Cerro Negro (728 m, 12.30°N, 86.42°W), one of Central America's youngest volcanoes, is a basaltic cinder cone situated between the Volcán Rota and the Volcanic Complex of Las Pilas- El Hoyo. It has produced at least 22 eruptions since its formation in 1850 (Hill *et al.*, 1999), and the last eruption occurred in 1999.

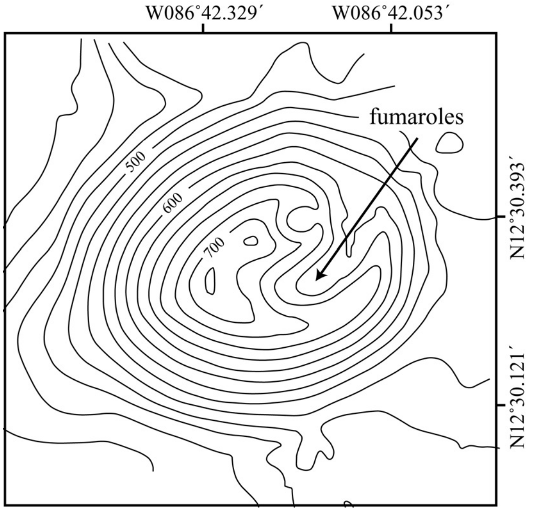

Figure 2.3 *Location of the main fumarolic field in the centre of Cerro Negro (after La Femina et al., 2004)*

During the period of the survey Cerro Negro has shown phases of both increasing and decreasing temperatures. Fumarolic gas samples for this study originate from the centre of the main cone (Fig. 2.3) and had outlet temperatures of 260–369°C.

Mombacho volcano (1344 m, 11.49°N, 85.58°W) towers above the northern shore of Lake Nicaragua. The volcano (basaltic-andesitic) is highly dissected and presents morphologic evidence of at least two different flank failures (Van Wyk de Vries & Francis 1997). On the upper north flank of the southern collapse structure (Fig. 2.4) H_2O-rich gases are ejected at a fairly constant temperature of about 120°C. Mombacho has not been active in historical time.

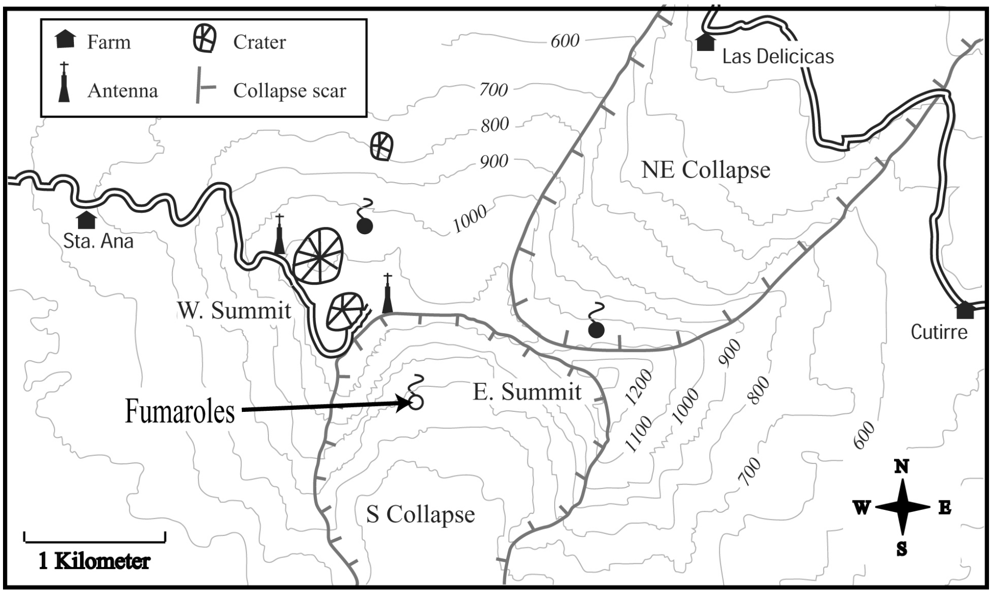

Figure 2.4 *Location of the sampled fumarole in the southern collapse of Mombacho (modified from Vallance et al., 2001)*

2.3 Methods

2.3.1 Sample Collection

Trace gas sampling in this study is performed by pushing a titanium tube into the fumarole and inserting a silica tube with slightly smaller diameter (Fig. 2.5).

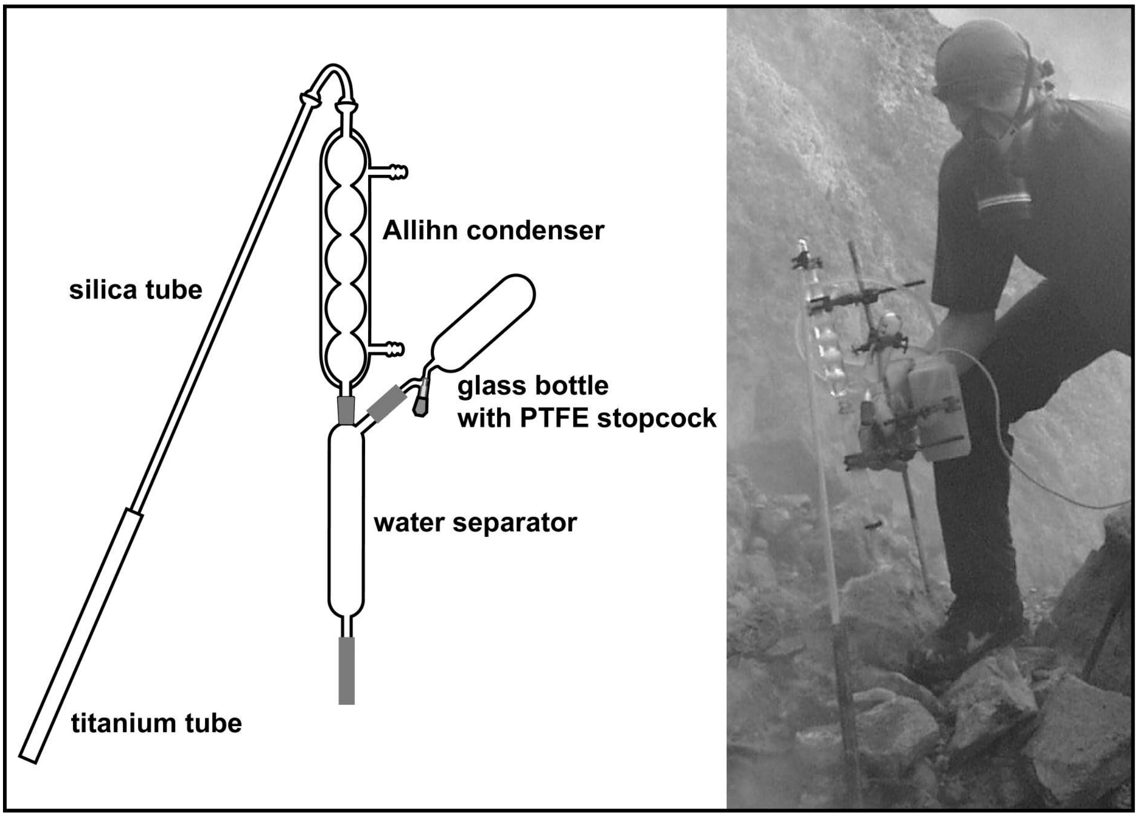

Figure 2.5 *Schematic diagram and picture of the setup for trace gas sampling.*

A water-cooled condenser, a water separator and an evacuated (10^{-5} mbar) 125 ml glass bottle which is sealed with a PTFE stopcock is utilized in the sampling train. After flushing the system with volcanic gas, the sample is sucked into the evacuated glass bottle (Details in Frische *et al.*, 2005b). The outlet temperature of gas samples was measured on the base of the titanium tube using a K-type thermocouple.

2.3.2 Analytical Methods

After absorption of acidic compounds with sodium hydroxide solution and dilution with blank-tested helium the gas sample was analyzed with gas chromatography/ion trap mass spectrometry (GC/ion trap-MS) over a mass scan range of 48 to 200 amu (Frische *et al.*, 2005b). Calibration was carried out by repeated injections of a working standard gas mixture during sample analysis. The working standard had been calibrated against calibration gases prepared in a three-step static dilution technique (except for C_2H_5Cl and C_2H_5Br), resulting in an absolute error of ±10 %. For an approximative quantification of C_2H_5Cl and C_2H_5Br, it was assumed the same instrumental response of C_2H_3Cl and CH_3Br, respectively. Detection limits for GC/ion trap-MS are 0.2 pptv (parts per trillion by volume) for calibrations standard (using volumes of 150 mL) and 0.7 pptv for ambient air samples (using volumes of 50 mL). The detection limits for fumarolic gas samples varied because of their different content of headspace[1] gas and amount to 1.8, 10, and 20 pptv, respectively for samples from Cerro Negro, Mombacho and Momotombo. Replicate analysis of individual samples gave values within ±10 % (see *Appendix* for details on blank and stability tests).

2.3.3 Calculation of the geogenic portion

Fumarolic gas samples commonly are mixtures of magmatic, hydrothermal and atmospheric components. Because volcanic edifices are comparatively porous and crosscut by faults and fractures, air can invade the gas feeding system and dilute the geogenic components (Ohsawa *et al.*, 2000; Saito *et al.*, 2002; CCVG 2004; Symonds *et al.*, 1996). The same effect can be caused by air-saturated meteoric waters feeding the volcanic hydrothermal system or ground waters circulating in the volcanic edifice and interacting in various proportion with the rising magmatic gases (Giggenbach 1996). Modern atmospheric air contains a multitude of natural and man-made organic compounds, many halogenated among them. Because most of these predominately

---

[1] Headspace gas is the portion of fumarolic gas which is not dissolved in the caustic solution and consist of N_2, O_2, Ar ,H_2, He, CO as well as hydrocarbons and halo(hydro)carbons.

anthropogenic originated substances show a high environmental stability, their characteristic ratios in mixtures with other volatiles remain unchanged and can be used as fingerprint for air detection e.g. in fumarolic gas samples. Using the characteristic ratios between certain purely anthropogenic (WMO 2003; Butler *et al.*, 1999) chlorofluorocarbons (CFCs) occurring in modern atmospheric air, the amount of air contamination in fumarolic gases can be calculated. From the routinely measured CFCs we used the species CCl_2F_2 (CFC-12), $C_2Cl_3F_3$ (CFC-113) and $C_2Cl_2F_4$ (CFC-114) to differentiate between the airborne and the geogenic fraction of trace components in fumarolic gas samples. After subtracting the atmospheric fraction from the mixture, we obtained the geogenic portion. This procedure has been discussed in detail by Frische *et al.* (2005b), and is presented in a compact form in the *Appendix* below. The range of air contents in headspace gas of our samples varied from 1.1 mol% in samples from Momotombo and Mombacho and reached a maximum of 38 mol% in some samples from Cerro Negro. The mean air values of Momotombo and Mombacho are comparable (3.7 and 2.8 mol%), but clearly different to the 33 mol% detected at Cerro Negro (Tab. 2.1).

Volcano	Range air content (headspace gas) [mol%]	Range air content (full sample) [mol%]	Mean air content (headspace gas) [mol%]	Mean air content (full sample) [mol%]
Momotombo	1.1 – 7.9	0.0045 - 0.033	3.7	0.016
Cerro Negro	28 - 38	-*	33	-*
Mombacho	1.1 – 9.4	0.0032 - 0.028	2.8	0.0083

Table 2.1 *Air content of fumarolic gas samples. The headspace portion in fumarolic gas samples amount to 0.42 mol% and 0.30 mol% at Momotombo and Mombacho, respectively (Garofalo et al., in prep.). *Main component data for Cerro Negro aren't available yet.*

The data presented in this study are corrected for atmospheric air in order to obtain values exclusively for the geogenic compounds present in the fumarolic gases.

2.4 Results

In fumarolic gases of Nicaraguan subduction zone volcanoes high but variable concentrations of halocarbons such as the methyl halides CH_3Cl, CH_3Br, and CH_3I, and at lower concentrations ethyl halides and higher chlorinated methanes (Tab. 2.2-2.5) were found. However, carbon tetrachloride was in many samples near or below detection limits. Vinyl chloride shows intermediate values. The highest concentrations with e.g. 19 ppmv CH_3Cl were detected in samples from the lower temperature fumarole F3 at Momotombo. Halo(hydro)carbon concentrations at the other fumaroles from Momotombo decrease with rising temperatures. Mombacho's low temperature discharges show the lowest concentrations, many C_2-compounds were below detection limits.

	Momotombo fumarole F1									
	Long-term				Medium-term			Short-term		
Date/time	August 2001	March 2002	November 2002	July 2003	17.11.02 11:00	18.11.02 15:00	19.11.02 7:30	12.07.03 12:45	12.07.03 12:50	12.07.03 12:55
Temp.[°C]	751	776	770-761	739	760	760	761	739	739	739
CH_3Cl	4.8	3.9	92	96	77	69	150	100	150	32
CH_3Br	0.64	0.34	11	30	7.6	5.3	24	13	75	3.8
CH_3I	0.50	0.24	12	16	8.4	8.5	24	18	23	7.2
CH_2Cl_2	0.27	0.10	0.88	0.10	1.1	0.67	0.70	0.059	0.10	0.13
$CHCl_3$	0.10	0.031	0.42	0.092	0.36	0.28	0.69	0.068	0.14	0.072
CCl_4	b.d.l.	0.11	0.12	n.c.	0.17	0.044	0.11	b.d.l.	b.d.l.	0.031
C_2H_5Cl	b.d.l.	0.21	3.3	1.0	3.2	1.2	5.5	1.5	1.4	0.24
C_2H_5Br	n.q.	n.q.	0.28	0.27	0.078	0.048	0.72	n.q.	0.48	b.d.l.
C_2H_5I	b.d.l.	b.d.l.	0.40	0.20	0.12	0.18	1.2	0.21	0.30	0.075
C_2H_3Cl	0.18	0.13	0.63	0.40	0.55	0.29	1.1	0.24	0.87	0.10

Table 2.2 *Trace gas concentrations [ppbv] in the headspace gas portion of fumarolic gas samples from fumarole F1 of Momotombo (b.d.l.: below detection limit, n.q. not quantified, n.c. not calculable because more than the half of relevant samples were b.d.l. or n.q.) at different time horizons. Outlet temperatures of fumarolic gas given in [°C].*

	Momotombo fumarole F2							Momotombo fumarole F3			
	Medium-term				Short-term			Medium-term			
Date/time	17.11.02 16:00	18.11.02 9:45	18.11.02 15:15	19.11.02 7:55	12.07.03 13:30	12.07.03 13:35	12.07.03 13:40	17.11.02 17:30	18.11.02 8:00	18.11.02 16:40	19.11.02 7:00
Temp. [°C]	615	615	615	616	600	600	600	472	475	475	478
CH_3Cl	83	38	160	49	8.0	21	17	9600	20000	7100	1100
CH_3Br	19	12	42	19	1.8	2.6	3.4	460	760	850	130
CH_3I	10	15	33	8.4	3.9	4.5	4.7	380	1400	1500	140
CH_2Cl_2	1.5	0.71	0.63	1.6	0.20	0.17	b.d.l.	23	54	16	1.1
$CHCl_3$	0.55	0.41	0.22	0.69	0.18	0.028	0.053	34	26	10	0.68
CCl_4	0.17	0.075	0.16	0.36	b.d.l.	b.d.l.	b.d.l.	0.30	0.43	n.c.	0.20
C_2H_5Cl	12	2.4	3.9	5.0	0.47	1.5	1.0	550	780	320	52
C_2H_5Br	2.1	0.31	0.54	0.30	0.071	0.25	0.17	20	70	48	11
C_2H_5I	1.0	0.49	0.76	0.31	0.21	0.55	0.46	16	110	97	12
C_2H_3Cl	1.6	n.q.	0.52	1.6	0.28	0.23	0.17	4.5	10	4.8	2.4

Table 2.3 *Trace gas concentrations [ppbv] in the headspace gas portion of fumarolic gas samples from fumarole F2 and F3 of Momotombo (b.d.l.: below detection limit, n.q. not quantified, n.c. not calculable because more than the half of relevant samples were b.d.l. or n.q.) at different time horizons. Outlet temperatures of fumarolic gas given in [°C]. Long-term data for fumarole F2 and F3 of Momotombo are not available due to the lack of data.*

	Cerro Negro								
	Long-term			Medium-term			Short-term		
Date/time	Jul./Aug. 2001	Nov./Dez. 2002	July 2003	24.11.02 10:00	25.11.02 11:30	05.12.02 12:45-48	5.12.02 12:45	5.12.02 12:47	5.12.02 12:48
Temp. [°C]	340	260-293	290-369	260	293	282	282	282	282
CH_3Cl	2.3	12	5.7	5.1	28	9	15	6.9	3.7
CH_3Br	0.27	1.4	0.28	0.70	4.4	0.58	1.0	0.45	0.27
CH_3I	0.24	1.1	0.86	0.23	1.0	1.4	2.6	1.0	0.73
CH_2Cl_2	0.087	0.22	0.12	0.12	b.d.l.	0.26	0.28	0.45	0.049
$CHCl_3$	0.11	2.6	0.44	1.9	0.26	3.6	5.2	4.5	1.2
CCl_4	b.d.l.	b.d.l	b.d.l	0.12	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
C_2H_5Cl	n.q.	0.35	b.d.l	0.18	b.d.l.	0.40	n.q.	0.23	0.09
C_2H_5Br	n.q.	b.d.l	b.d.l	0.016	b.d.l.	b.d.l.	n.q.	b.d.l.	b.d.l.
C_2H_5I	0.0044	0.018	0.0041	0.012	0.0048	0.025	0.008	0.035	0.031
C_2H_3Cl	0.071	0.19	0.064	0.14	0.083	0.25	0.44	0.20	0.10

Table 2.4 *Trace gas concentrations [ppbv] in the headspace gas portion of fumarolic gas samples from Cerro Negro (b.d.l.: below detection limit, n.q. not quantified, n.c. not calculable because more than the half of relevant samples were b.d.l. or n.q.) at different time horizons. Outlet temperatures of fumarolic gas given in [°C].*

	Mombacho						
	Long-term				Short-term		
Date/time	July 2001	March 2002	November 2002	July 2003	18.07.03 12:30	18.07.03 12:35	18.07.03 13:00
Temp. [°C]	120	121	119-120	119	119	119	119
CH_3Cl	0.66	0.34	1.5	1.4	1.4	1.0	1.8
CH_3Br	0.067	0.051	0.035	0.024	0.036	0.018	0.017
CH_3I	0.022	0.026	0.036	0.096	0.18	0.037	0.068
CH_2Cl_2	0.46	0.073	0.10	0.064	0.11	0.027	0.053
$CHCl_3$	0.33	b.d.l.	n.c.	0.15	0.14	0.18	0.14
CCl_4	b.d.l.	b.d.l.	0.067	n.c.	n.q.	b.d.l.	b.d.l.
C_2H_5Cl	n.q.	b.d.l.	0.094	n.c.	b.d.l.	b.d.l.	b.d.l.
C_2H_5Br	n.q.	b.d.l.	b.d.l	b.d.l.	b.d.l.	b.d.l.	b.d.l.
C_2H_5I	b.d.l.	b.d.l.	b.d.l.	n.c.	0.030	b.d.l.	b.d.l.
C_2H_3Cl	b.d.l.	0.020	0.052	n.c.	0.099	b.d.l.	b.d.l.

Table 2.5 *Trace gas concentrations [ppbv] in the headspace gas portion of fumarolic gas samples from Mombacho (b.d.l.: below detection limit, n.q. not quantified, n.c. not calculable because more than the half of relevant samples were b.d.l. or n.q.) at different time horizons. Outlet temperatures of fumarolic gas given in [°C]. Medium-term data for Mombacho are not available due to the lack of data.*

Strong variations in concentrations of respective gases at short-, medium-, and long-term scales could be observed. Variations in samples from Momotombo and Cerro Negro show similar trends (Fig. 2.6). The most obvious variations were in concentrations, less evident in the relative halogen ratios. Long-term variations of methyl- and ethyl halides exhibit a weak negative correlation with the outlet temperature of the relevant fumarole. In contrast samples from Mombacho show no clear trends in the halohydrocarbon patterns and the fumarole temperature was fairly constant.

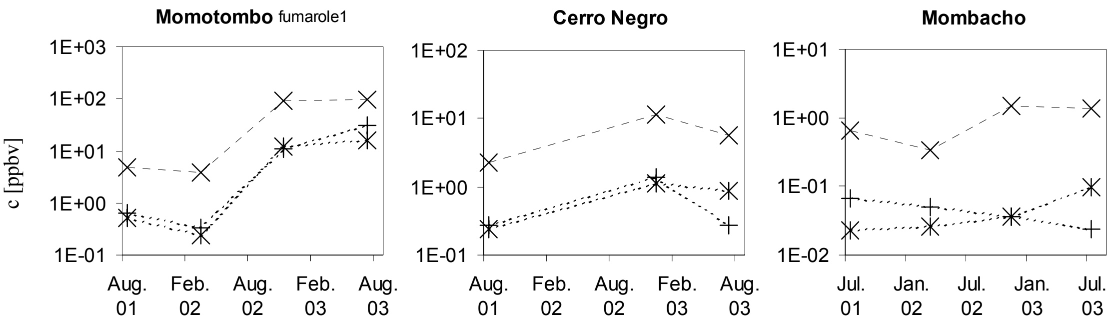

Figure 2.6 *Long-term trends of methyl halides (X: CH_3Cl, +: CH_3Br, ∗: CH_3I) in fumarolic gas samples from Momotombo, Cerro Negro and Mombacho. Note the logarithmic y-axis.*

The strongest long-term variations were observed at the highest temperature fumarole of Momotombo (F1), where concentrations e.g. of CH_3Cl, CH_3Br and CH_3I increased by a factor of 20, 30, and 50, respectively, from March to November 2002. A similar but less intense concentration increase was recorded at the neighbouring volcano Cerro Negro during the same time interval. The rate of increase in methyl halides and ethyl bromide contents at Momotombo slowed down from November 2002 on, but continued until the end of our campaigns in July 2003, while the concentrations of all other compounds decreased after November 2002. Cerro Negro reached the maximum concentrations in November/December 2002, then concentrations for all compounds dropped but remained slightly higher than during our first field campaign in July/August 2001. Data from Mombacho show less clear trends but most compounds also increased between March and November 2002.

To summarize the results of trace gas analysis, coefficients of variation (CV) for concentrations of samples from each time interval were calculated (E2.1) using the arithmetic mean ($\overline{X}$) and the standard derivation (σ).

$$CV(\%) = \frac{100\ \sigma}{\overline{X}} \qquad \text{(E2.1)}$$

Long-term variations in concentration of studied compounds were only a few percent higher than their short-term variations (Tab. 2.6). Three different samples taken from the same fumarole within a few minutes (short-term) show an average relative variation (CV) of ±47%. Medium-term variations were ±60% and long-term variations ±73%.

	CH_3Cl	CH_3Br	CH_3I	CH_2Cl_2	$CHCl_3$	CCl_4	C_2H_5Cl	C_2H_5Br	C_2H_5I	C_2H_3Cl	Mean all
long-term											
Momotombo F1	91	115	97	96	94	n.c.	86	n.c.	n.c.	59	91
Cerro Negro	59	82	50	40	106	n.c.	n.c.	n.c.	74	54	66
Mombacho	51	37	66	95	37	n.c.	n.c.	n.c.	n.c.	n.c.	57
mean	67	78	71	77	79	n.c.	86	n.c.	74	57	73
medium-term											
Momotombo F1	35	67	55	23	41	47	53	110	99	54	58
Momotombo F2	59	50	58	40	37	53	64	93	42	41	54
Momotombo F3	72	51	70	82	74	31	63	63	76	53	63
Cerro Negro	72	94	56	n.c.	72	n.c.	n.c.	n.c.	60	44	66
mean	59	65	60	48	56	44	60	89	69	48	60
short-term											
Momotombo F1	51	104	41	30	34	n.c.	54	n.c.	48	82	56
Momotombo F2	35	26	8	n.c.	77	n.c.	43	45	35	20	36
Cerro Negro	56	57	57	63	48	n.c.	n.c.	n.c.	47	59	55
Mombacho	24	37	65	55	11	n.c.	n.c.	n.c.	n.c.	n.c.	38
mean	41	56	43	50	43	n.c.	49	45	43	53	47

Table 2.6 *Coefficients of variation [%] for various time intervals (n.c.: not calculable because of less than 3 data values). Long-term data for fumarole F2 and F3 of Momotombo, medium-term data for Mombacho and short-term data for fumarole F3 of Momotombo are not available due to the lack of data.*

2.5 Discussion

2.5.1 Formation of halohydrocarbons

Momotombo and Cerro Negro are underlain by voluminous deep and shallow-water sediment deposits of the Sandino Basin (Snyder & Fehn 2002; Ranero *et al.*, 2000; Walther *et al.*, 2000), which are supposedly bromine and iodine rich. High Br and I contents in the local upper crust were also indirectly inferred from anomalously high heavy halogen contents in melt inclusions and volcanic glasses from the Fontana Tephra in Nicaragua (Wehrmann & Freundt 2005a, Wehrmann *et al.,* 2005b). Shallow level processes such as hydrothermal mobilization of bromine and iodine in these marine sediment deposits and the subduction of large volumes of marine sediments in combination with the formation of thermogenic methane (Botz *et al.*, 2002; Taran & Giggenbach 2003; Capaccioni *et al.*, 2004) would deliver the required reactants (hydrocarbons and halogens) for halohydrocarbon synthesis. Investigations of ^{129}I/I in geothermal gases and fluids from Nicaragua confirms the presence of two different end-members: One magmatic component (c. 25 Ma old) associated with presently subducting sediments, and a much older crustal component of c. 65 Ma (Snyder & Fehn 2002; Snyder *et al.*, 2003).

2.5.2 Correlations with external periodic events

Several publications deal with periodic events influencing magmatic systems. Mason *et al.* (2004) analyzed volcanic activity during the last 300 years and shows a statistically significant degree of correlation between volcanic eruptions and the annual surrounding fluctuations associated with the deformation of the Earth in response to the hydrological cycle, including decreases of the sea level, millimeter-scale motion of the Earth's crust, and drops of atmospheric pressure. Tolstoy *et al.* (2002) presented that fortnightly ocean tidal forces can influence seismicity on the seafloor. Mauk and Johnston (1973) and Emter (1997) described that volcanic eruptions can be triggered by the diurnal and fortnightly tidal forces in the Earth's crust (Earth-tide). But more recent publications indicate that Earth-tide induced stresses may have too short lifetimes and too high strain rates to significantly effect a viscous response in partially molten regions of the Earth's subsurface (Rydelek *et al.*, 1992; Neuberg 2000; Mason *et al.*, 2004). Correlations between seismic or eruptive activity and local scale meteorological parameters like storms (Mastin 1994), barometric pressure fluctuations (Neuberg 2000), or rainfall (Matthews *et al.*, 2002) have also been reported. Nicaragua has strong seasonal variations of meteoric water input (dry and rainy season). Strong rainfall during the rainy season has the potential to enhance the concentration of halogens at shallow levels of the hydrothermal zone due to the dissolution of water soluble metal halides on the surface area of the crater, or to mobilization of halogen-rich brines at shallow depths. But no correlation between halogenated trace gas concentrations and precipitation data (Fig. 2.7) can be observed. In addition, the described periodical cycles have higher frequencies than the observed periodicity of trace gas compounds and therefore none of this cycles alone appears to have significant influence on trace gas emissions.

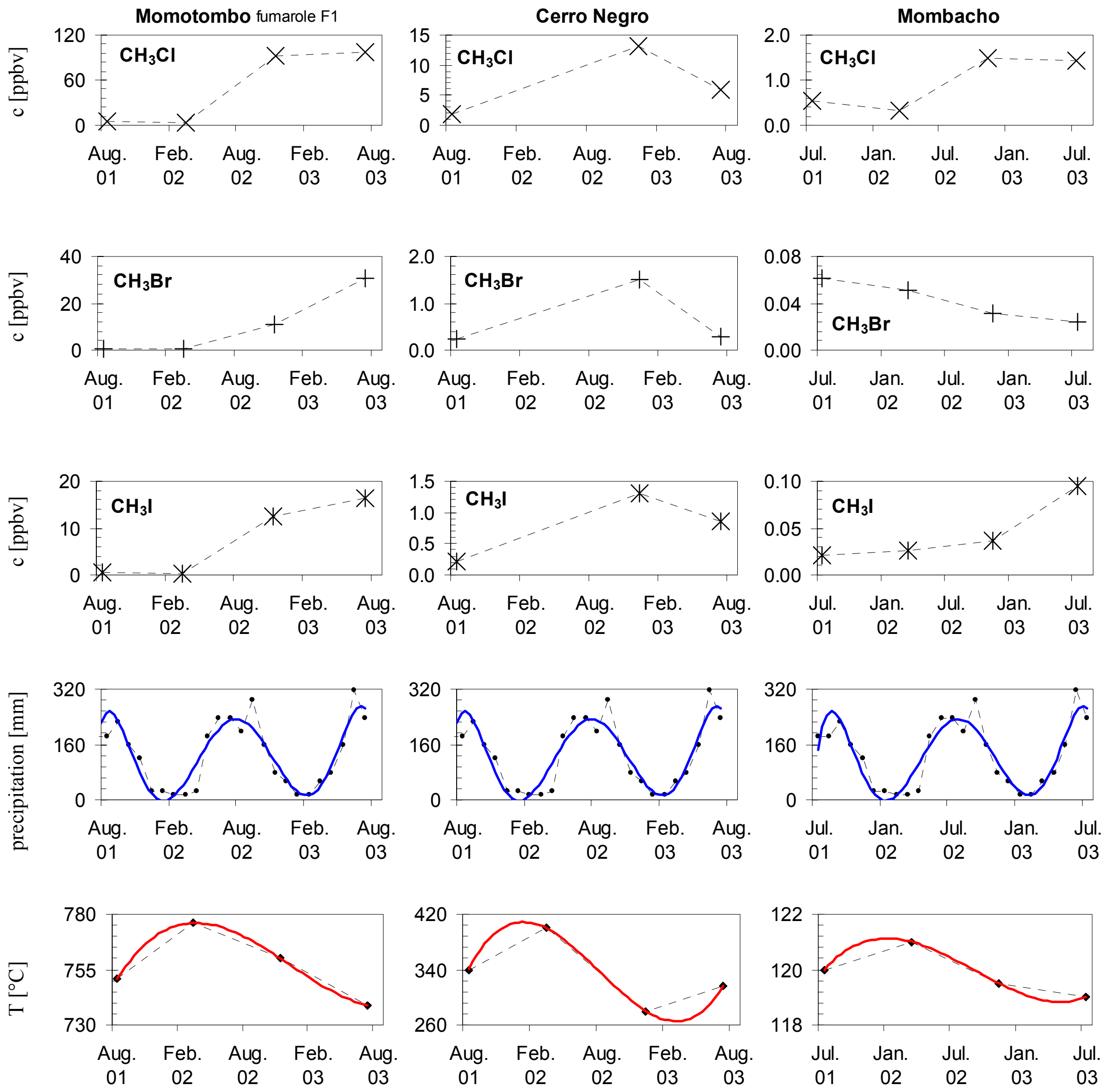

Figure 2.7 *Methyl halide concentrations at Momotombo, Cerro Negro and Mombacho vs. precipitation (NOAA-CIRES) and temperatures of fumaroles during two years of the sampling campaigns.*

2.5.3 Causes for periodic variations

The rapid increase in halogenated trace gas concentrations during 2002 (Tab. 2.2-2.5 and Fig. 2.6-2.7) could point to an increased volatile flux from the respective magma systems. However, increases in degassing rates of orders in magnitude are more likely expected to accompany significant magma movements before or during volcanic eruptions, and such events have not been registered either from seismic signals or from visual observations at INETER (Instituto Nicaragüense de Estudios Territoriales).

The negatively temperature-correlated long-term trends of methyl and ethyl halides observed at Momotombo and Cerro Negro (Fig. 2.7) point rather to an important role of the hydrothermal system in the synthesis of halohydrocarbons, since dropping fumarole temperatures have been interpreted as increasing influence of a hydrothermal system (Fischer *et al.*, 1996).

The comparison of halohydrocarbon concentration patterns in medium-term time-scales at the same volcano but from different fumaroles (Fig. 2.8) furthermore shows that the volcanic synthesis of halogenated trace gases take place on a very local scale. The three fumaroles from which the data origin from, are in the same crater within 100 meters distance and exhibit entirely different trends in variation. Thus small-scale fluctuations in reaction condition and possibly in the availability of reactants seem to strongly influence the output of halohydrocarbons. Combined with the observed negative relation between halohydrocarbon concentrations and temperature, we infer a strong shallow-level control on their formation. We speculate that concentration jumps may be caused by spontaneous modifications to fluid pathways and thus to the availability and temperatures of reactive surfaces within the volcanic edifice. Repeated fluctuations during minutes to days rather indicate variations within the porous volcanic edifices involving disequilibrium reactions in the fluid-rock or fluid-fluid systems, which, however, remain to be identified.

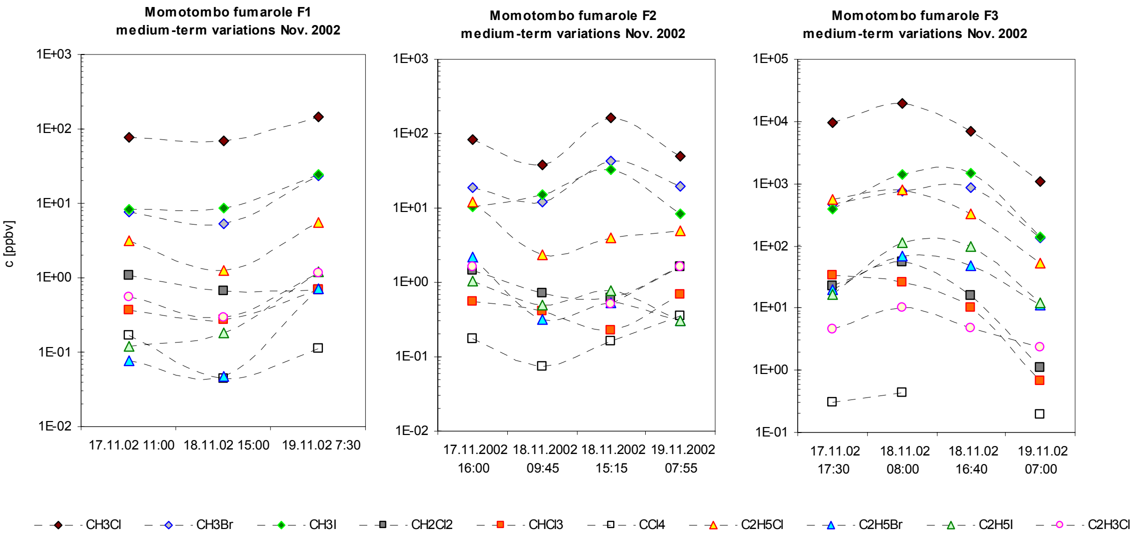

Figure 2.8 *Medium-term variations at three different fumaroles within the same time horizon of almost two days (Note that the x-axis are not chronological and that there are no data for fumarole F1 from the morning of 18.11.2002).*

The special case of Mombacho, showing other variation trends than the Momotombo and Cerro Negro fumaroles, could be related to a possible reactivation of Mombacho volcano (Garofalo *et al.*, 2005a), inferred from the occurrence of juvenile magmatic compounds in gas samples from this volcano.

This would result in rapid changes in formation conditions of the fluids at Mombacho and prevent the adjustment of relatively stable patterns of halogen ratios in halohydrocarbons, like observed at Momotombo and Cerro Negro on longer term time-scales (Fig. 2.6-2.7).

2.6 Conclusions

Periodic sampling within a two year study on fumaroles of the Nicaraguan subduction zone volcanoes Momotombo, Cerro Negro and Mombacho provided information about their variability in trace gas compounds. The magnitude of short-term fluctuations within minutes was comparable to that observed within days and within several months. Trends of variations in average values within several months are inversely related to the temperatures of the fumaroles. A rapid shift in trace gas concentrations of up to 50 times at Momotombo and Cerro Negro in the course of 2002 points to enhanced influence of the hydrothermal system, associated with the preferential incorporation of highly volatile compounds from marine sediment deposits of the Sandino Basin.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft as part of the Sonderforschungsbereich (SFB) 574 “Volatiles and Fluids in Subduction Zones: Climate Feedback and Trigger Mechanisms for Natural Disasters”, by the Volkswagen Stiftung (I/76 590), and by the Max-Planck-Society (Munich). This paper is SFB 574-contribution #xx. Special thanks go to Wilfried Strauch, Pedro Perez, and the Instituto Nicaragüense de Estudios Territoriales (INETER) for providing laboratory space and assistance during the field work. Jochen Harnisch and Armin Jordan made helpful comments on an earlier draft of this manuscript.

Appendix

Preparation and blank tests of sampling bottles

Sample bottles and PTFE-stopcocks were cleaned prior to usage by washing with aqueous Mucasol® solution, rinsing with purified water, drying and degassing in a vacuum oven at 80°C for 8 hours. In blank tests with sampling bottles, filled up with purified helium or in addition with degassed (Ohsawa *et al.*, 2000) sodium hydroxide solution (50% in water) all relevant compounds were below detection limit. For transport to Nicaragua the bottles were filled up with synthetic air. A few hours before sampling, they were evacuated to 10^{-5} mbar. Samples were stored under dark and cold conditions. The duration between sampling and analysis took around 1.5 month. Samples taken one after the other at the same location and analyzed in one month duration showed no systematic drift in concentration.

Stability of analytes

Some halohydrocarbons seem to be not stable under alkaline conditions. The short duration between injection of sodium hydroxide solution into the sample and analysis of around 10 minutes ensured no significant degradation of analytes. All relevant compounds showed during tests in alkaline milieu mean degradation rates of 0.4 % per hour with a range between 0.0 %/h for CCl_4 and 2.2 %/h for chloroform..

Calculation procedures for the amount of air contamination in a fumarolic sample using CFC "fingerprinting". The complete procedure has been presented by Frische et al. (2005b).

We calculated the air dilution factor $f_{(dil)}$ for the fumarolic gas samples (equation (E2.2)) by comparing concentrations of solely man-made (WMO 2003; Butler *et al.*, 1999) CFC-114, CFC-113 and CFC-12 both in fumarolic and in air samples. In equation (E2.1), *PA* is the peak area, and *V* the volume of individual CFC $_{(CFC\text{-}i)}$ in Nicaraguan air $_{(air)}$ and in the analyzed mixture $_{(mix)}$ of the fumarolic gas sample after adsorption of the acidic compounds and dilution with helium.

$$f_{(dil)} = \frac{1}{3}\sum_{i=1}^{3}\left(\frac{PA_{(mix)}V_{(air)}}{V_{(mix)}PA_{(air)}}\right)_{CFC\text{-}i} \qquad (\textit{CFC-i}\text{: CFC-12; CFC-113; CFC-114}) \qquad \text{(E2.2)}$$

By subtracting the atmospheric fraction from the mixture (E2.3) – (E2.5), we obtained volume $V_{(geo)}$ and peak area $PA_{(geo)}$ of the geogenic portion. Equation (E2.3) calculates the air-corrected volume for the diluted fumarolic sample $V_{(He+geo)}$. (E2.4) takes the dilution of the sample with helium during the sample preparation into account, where $p_{(fum)}$ is the pressure of headspace gas (geogenic and air compounds) in the sample bottle after injection of the caustic solution and $p_{(mix)}$ is the pressure after dilution with helium (details in Frische *et al.*, 2005b). (E2.5) is used to calculate the peak area of individual species in the geogenic portion of fumarolic samples $PA_{(geo)i}$.

$$V_{(He+geo)} = V_{(mix)}(1 - f_{(dil)}) \qquad \text{(E2.3)}$$

$$V_{(geo)} = \frac{V_{(He+geo)} p_{(fum)}}{p_{(mix)}} \qquad \text{(E2.4)}$$

$$PA_{(geo)_i} = \left(\frac{PA_{(mix)_i}}{V_{(mix)}} - \left(\frac{PA_{(air)_i} f_{(air)}}{V_{(air)}} \right) \right) V_{(mix)} \qquad (i\text{: species}) \qquad \text{(E2.5)}$$

Quantification of individual species in the geogenic portion of fumarolic gas samples $c_{(geo)i}$ was carried out by direct comparison of the corrected sample values for peak area $PA_{(geo)i}$ and volume $V_{(geo)}$ with peak area $PA_{(stda)i}$, volume $V_{(stda)}$ and concentration $c_{(stda)}$ of the gas standard (E2.6).

$$c_{(geo)_i} = \frac{\left(\frac{PA_{(geo)_i}}{V_{(geo)}} \right) c_{(stda)_i}}{\left(\frac{PA_{(stda)_i}}{V_{(stda)}} \right)} \qquad \text{(E2.6)}$$

References

Auboudin, J., J. Azema, J.-Ch. Carfantan, A. Demant, C. Rangin, M. Tardy and J. Tournon, The Middle America trench in the framework of Central America. In Init Repts DSDP, 67:747- 755 College Station, TX (Ocean Drilling Program), 1982.

Botz, R., H. Wehner, M. Schmitt, T.J. Worthington, M. Schmidt and P. Stoffers, Thermogenic hydrocarbons from the offshore Calypso hydrothermal field, Bay of Plenty, New Zealand, Chem. Geol., 186, 235-248, 2002.

Butler, J.H., M. Battle, M.L. Bender, S.A. Montzka, A.D. Clarke, E.S. Saltzman, C.M. Sucher, J.P. Severinghaus and J.W. Elkins, A record of atmospheric halocarbons during the twentieth century from polar firn air, Nature, 399, 749-755, 1999.

Capaccioni, B. and F. Mangani, 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, 2001

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

Carr, M.J., M.D. Feigenson, L. Patino and J.A. Walker, Volcanism and Geochemistry in Central America: Progress and Problems, Inside the Subduction Factory, Geophysical Monograph 138, American Geophysical Union, 153-174, 2003.

CCVG (Commission on the Chemistry of Volcanic Gases), 2004 (http://volcgas.unm.edu/2004newsletter.pdf).

CRC, Handbook of Chemistry and Physics; CRC Press, 74th Edition, 1993.

DeMets, C., A new estimate for present-day Cocos-Caribbean plate motion: Implications for slip along the Central American volcanic arc: Geophys. Res. Lett., 28(21), 4043-4046, 2001.

Elming, S.-A., P. Layer and K. Ubieta, A paleomagnetic study and age determinations of Tertiary rocks in Nicaragua, Central America, Geophys. J. Internat., 147(2): 294-309, 2001.

Emter, D., Tidal triggering of earthquakes and volcanic events, in Tidal Phenomena, Lect. Notes Earth Sci., vol. 66, edited by H. Wilhelm et al., 293- 309, Springer, New York, 1997.

Fischer, T.P., G.B. Arehart, N.C. Sturchio and S.N. Williams, The relationship between fumarole gas composition and eruptive activity at Galeras Volcano, Colombia, Geol., 24(6), 531-534, 1996.

Frische, M., K. Garofalo, T.H. Hansteen, R. Borchers and J. Harnisch, A volcanic contribution of stable halogenated compounds?, 2005b in prep..

Garofalo, K., F. Tassi, O. Vaselli, D. Tedesco, A. Delgado-Huertas, M. Frische, T.H. Hansteen and W. Strauch, Reactivation of Mombacho, 2005a, in prep..

Garofalo, K., F. Tassi, O. Vaselli, A. Delgado-Huertas, M. Frische and T.H. Hansteen, unpubl. data in prep..

Giggenbach, W.F., Chemical composition of volcanic gases, in Scarpa, M. and R.J. Tilling, eds., Monitoring and mitigation of Volcanic Hazards: Berlin Heidelberg, Springer-Verlag, 221-256, 1996.

Hill, B.E., P.C. La Femina, C.B. Connor, W. Strauch, G. Davoli, G. Guevera and A. Saballos, August 1999 eruption of Cerro Negro volcano, Nicaragua, successfully forecast using time-volume relationship, EOS, Trans. Am. Geophys. Union 80(46): F1111, 1999.

INETER (Instituto Nicaragüense de Estudios Territoriales), http://www.ineter.gob.ni.

Inn, E.C.Y., J.F. Vedder and E.P. Condon, Gaseous constituents in the plume from eruptions of Mount St. Helens, Science, 211, 821-823, 1981.

Isidorov, V.A., I.G. Zenkevich and B.V. Ioffe, Volatile Organic Compounds in Solfataric Gases, J. Atmos. Chem., 10, 329-340, 1990.

Jordan, A., J. Harnisch, R. Borchers, F. Le Guern, H. and Shinohara, Volcanogenic Halocarbons, Environm. Sci. Technol., 34(6), 1122-1124, 2000.

Jordan, A., Volcanic Formation of Halogenated Organic Compounds. The Handbook of Environmental Chemistry. Berlin Heidelberg, Springer-Verlag. 3, Part P, 121-139, 2003.

Kimura, G, Silver E, Blum P et al., Proc ODP Init Repts, 170: College Station, TX (Ocean Drilling Program), 1997.

La Femina, P.C., C.B. Connor, B.E. Hill, W. Strauch and J.A. Saballos, Magma-tectonic interactions in Nicaragua: the 1999 seismic swarm and eruption of Cerro Negro volcano, J. Volcanol. Geotherm. Res., 137, 187-199, 2004.

Mason, B.G., D.M. Pyle, W.B. Dade and T. Jupp, Seasonality of volcanic eruptions, J. Geophys. Res, 109, B04206, doi:10.1029/2002JB002293, 2004.

Mastin, L.G., Explosive tephra emissions at Mount St Helens, 1989 - 1991: The violent escape of magmatic gas following storms?, Geol. Soc. Am. Bull., 106, 175-185, 1994.

Matthews, A.J., J. Barclay, S. Carn, G. Thompson and J. Alexander, Rainfall-induced volcanic activity on Montserrat, Geophys. Res. Lett., 29(13), 1644, doi:10.1029/2002GL014863, 2002.

Mauk, F.J. and M.J.S. Johnston, On the triggering of volcanic eruptions by Earth tides, J. Geophys. Res., 78, 3356- 3362, 1973.

McBirney, A.R. and H. Williams, Volcanic history of Nicaragua, Univ. Calif. Pub. Geo. Sci., 55, 1-65, 1965.

Menyailov, I.A., L.P. Nikitina, V.N. Shapar and V.P. Pilipenko, Temperature increase and chemical change of fumarolic gases at Momotombo volcano, Nicaragua, in 1982-1985: Are these indicators of a possible eruption?, J. Geophys. Res., 91(B12), 12199-12214, 1986.

Neuberg, J., External modulation of volcanic activity, Geophys. J. Int., 142, 232- 240, 2000.

NOAA-CIRES (National Oceanic and Atmospheric Administration- Cooperative Institute for Research in Environmental Science)- Climate Diagnostics Center (http://www.cdc.noaa.gov/cgi-bin/DataMenus.pl?dataset=NCEP).

Ohsawa, S., Y. Yusa, K. Oue and K. Amita, Entrainment of atmospheric air into the volcanic system during the 1995 phreatic eruption of Kuju Volcano, Japan, J. Volcanol. Geotherm. Res., 96, 33-43, 2000.

Patino, L.C., M.J. Carr and M.D. Feigenson, Local and regional variations in Central American arc lavas controlled by variations in subducted sediment input, Contrib. Min. Petrol., 138, 265-283, 2000.

Ranero, C.R., J.P. Morgan, K. McIntosh and C. Reichert, Bending-related faulting and mantle serpentinization at the Middle American trench, Nature, 425, 367-373, 2003.

Rasmussen, R.A., L.E. Rasmussen, M.A.K. Khalil and R.W. Dalluge, Concentration distribution of methylchloride in the atmosphere, J. Geophys. Res., 85, 7350-7356, 1980.

Reilly, J., R. Prinn, J. Harnisch, J. Fitzmaurice, H. Jacoby, D. Kicklighter, J. Melillo, P. Stone, A. Sokolov and C. Wang, Multi-gas assessment of the Kyoto Protocol, Nature, 401, 549-555, 1999.

Rydelek, P.A., I.S. Sacks and R. Scarpa, On tidal triggering of earthquakes at Campi Flegrei, Italy, Geophys. J. Int., 109, 125-137, 1992.

Saito, G., H. Shinohara and K. Kazahaya, Successive sampling of fumarolic gases at Satsuma-Iwojima and Kuju volcanoes, southwest Japan: Evaluation of short-term variations and precision of the gas sampling and analytical techniques, Geochem. J., 36 (1), 1-20, 2002.

Schwandner, F.M., T.M. Seward, A.P. Gize, P.A. Hall and V.J. Dietrich, Diffuse emission of organic trace gases from the flank and crater of a quiescent active volcano (Vulcano, Aeolian Islands, Italy) J. Geophys. Res. 109, D04301, doi:10.1029/2003JD003890, 2004.

Seinfeld, J.H. and S.N. Pandis, Atmospheric chemistry and physics, John Wiley & Sons Inc., New York, 1998.

Shevenell, L. and F. Goff, 2000, Temporal geochemical variations in volatile emissions from Mount St. Helens, 1980-1994, Journal of Volcanology and Geothermal Research, 99, 123-138, 2000.

Snyder, G. T. and U. Fehn, The origin of iodine in volcanic fluids: 129I results from the Central American Volcanic Arc, Geochim. Cosmochim. Acta, 66, 3827-3838, 2002.

Snyder, G., R. Poreda, U. Fehn and A. Hunt, Sources of nitrogen and methane in Central American geothermal settings: Noble gas and 129I evidence for crustal and magmatic volatile components, Geochem. Geophys. Geosys., 4(1), 1-28, 2003.

Stoiber, R.E., D.C. Leggett, T.F. Jenkins, R.P. Murrmann and W.I. Rose, Organic compounds in volcanic gas from Santiaguito volcano, Guatemala, Geol. Soc. Am. Bull., 82, 2299-2302, 1971.

Symonds, R.B., Y. Mizutani and P.H. Briggs, Long-term geochemical surveillance of fumaroles at Showa-Shinzan dome, Usu volcano, Japan, J. Volcanol. Geotherm. Res., 73, 177-211, 1996.

Symonds, R.B., W.I. Rose and M.H. Reed, Contribution of Cl- and F-bearing gases to the atmosphere by volcanoes, Nature, 334, 415-418, 1988.

Taran, Y.A. and W.F. Giggenbach, Geochemistry of Light Hydrocarbons in Subduction-Related Volcanic and Hydrothermal fluids, Soc. Econom. Geol., Spec. Publ., 10, 61-74, 2003.

Textor, C., H.-F. Graf, C. Timmreck and A. Robock, Emissions from volcanoes, Chapter 7 of Emissions of Atmospheric Trace Compounds, C. Granier, P. Artaxo and C. Reeves, Eds., Kluwer, Dordrecht, 269-303, 2004.

Tolstoy, M., F.L. Vernon, J.A. Orcutt and F.K. Wyatt, Breathing of the seafloor: Tidal correlations of seismicity at Axial volcano, Geology, 30, 503-506, 2002.

UNFCCC (United Nations Framework Convention on Climate Change), Kyoto Protocol to the United Nations Framework Convention on Climate Change, UNEP/INC/98/2, Information Unit for Conventions, UNEP, Geneva, 1998 (http://unfccc.int/resource/docs/convkp/kpeng.pdf).

Vallance, J.W., S.P. Schilling and G. Devoli, Lahar Hazards at Mombacho Volcano, Nicaragua, USGS Open-File Report 01-455, 2001.

van Wyk de Vries, B. and P.W. Francis, Catastrophic collapse at stratovolcanoes induced by gradual volcano spreading, Nature, 387, 387-390, 1997.

Walther, C.H.E., E.R. Flueh, C.R. Ranero, R. von Huene and W. Strauch, Crustal structure across the pacific margin of Nicaragua: Evidence for ophiolitic basement and a shallow mantle sliver, Geophys. J. Int., 141, 759-777, 2000.

Wehrmann, H. & A. Freundt, Bromine and iodine in volcanic glasses determined by Synchrotrone-XRF: origin and partitioning in basaltic-andesitic and rhyolitic arc magma systems, 2005a subm.

Wehrmann, H., Freundt, A., Kutterolf, S., Wiedenbeck, M. and Schmincke H.U., Water, halogen, and sulphur degassing of the basaltic-andesitic Fontana Tephra, Nicaragua, 2005b subm.

WHO (World Health Organization), http://www.who.int/en/

WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project - Report No. 47, 498pp, Geneva, 2003.

Chapter 3

Fluxes and origin of halogenated trace gases from Momotombo volcano (Nicaragua)

Matthias Frische[a,b,c,*], Kristin Garofalo[a], Thor H. Hansteen[a,b], Reinhard Borchers[c]

[a] *SFB 574, Christian-Albrechts-Universitaet, D-24148 Kiel, Germany*
[b] *IFM-GEOMAR Leibniz-Institut fuer Meereswissenschaften, D-24148 Kiel, Germany*
[c] *Max-Planck-Institut fuer Sonnensystemforschung, D-37191 Katlenburg/Lindau, Germany*

**Corresponding author: mfrische@ifm-geomar.de*

Abstract

To assess the contribution of quiescent degassing volcanoes to the global halocarbon inventory, we quantified the fluxes of volcanic halohydrocarbons like methyl halides (CH_3Cl, CH_3Br and CH_3I), ethyl halides (C_2H_5Cl, C_2H_5Br and C_2H_5I) and higher chlorinated methanes (CH_2Cl_2, $CHCl_3$ and CCl_4). Within two years (July 2001-July 2003), about every eight months, gas samples were collected and analysed from high temperature fumaroles (472-776°C) at the Nicaraguan subduction zone volcano Momotombo. Using a simultaneous record of trace- and main-compounds in fumarolic gases as well as SO_2-fluxes of the plume, we were able to calculate trace gas fluxes for Momotombo and extrapolate our results to estimate trace gas fluxes for the whole Quaternary Nicaraguan volcanic arc, and for all global volcanoes. The most abundant halogenated hydrocarbon was CH_3Cl with concentrations up to 19 ppmv. Further major halohydrocarbons were CH_3Br, CH_3I, CH_2Cl_2, $CHCl_3$, CCl_4, C_2H_5Br, C_2H_5I, C_2H_5Cl and C_2H_3Cl with an average concentration of 0.20 to 720 ppbv. Estimated mean halohydrocarbon fluxes from Momotombo were in the range of 390-3,300 g/yr for methyl halides, 28 to 200 g/yr for ethyl halides and 2.1 to 19 g/yr for higher chlorinated methanes. When the results for Momotombo are scaled up to SO_2 fluxes of the Nicaraguan volcanic transect, fluxes of 1.1×10^5 g/yr CH_3Cl and 69 g/yr CCl_4 are attained for Nicaragua. Scaled up to the estimated global SO_2 flux, this translates to global fluxes of 3.7 x 10^6 g/yr CH_3Cl and 2.3 x 10^3 g/yr CCl_4. These volcanic fluxes are negligible compared to global anthropogenic and natural emissions of about 3 x 10^{12} g/yr CH_3Cl and 2 x 10^{10} g/yr CCl_4. Halogenated trace gases in fumarolic gas samples show relatively higher molar ratios of bromine and iodine vs. chlorine-bearing compounds than volcanic rocks or fumarolic main compounds. Mean molar ratios of the methyl halides CH_3Cl, CH_3Br, CH_3I were 10:1.0:1.1 and 11:1.0:1.9 for the ethyl halides C_2H_5Cl, C_2H_5Br, C_2H_5I. Sediment recycling in the Nicaraguan sector of the subduction zone, in combination with the interaction between the magmatic system and marine deposits present at depth in the Nicaraguan Depression are responsible of the relatively high bromine and iodine vs. chlorine ratios of the halogenated trace gases.

Keywords: *trace gases, halohydrocarbons, halides, subduction zones, fumaroles, Momotombo, fluxes.*

3.1 Introduction

More than 300 active subaerial volcanoes continuously emit large amounts of organic and inorganic substances into the Earth's atmosphere (Graf *et al.*, 1997; Andres & Kasgnoc 1998; Halmer *et al.*, 2002). Numerous data sets exist on the major elements composition of volcanic gases (e.g. Carroll & Holloway 1994; Scarpa & Tilling 1996) and on the occurrence of minor components (including hydrocarbons) in fumarolic gases (e.g. Capaccioni *et al.*, 1995; Capaccioni *et al.*, 2001; Taran & Giggenbach 2003), but only few studies have been carried out on halogenated organic trace compounds (e.g. Jordan *et al.*, 2000; Jordan 2003). Thus the occurrence, composition, variation and fluxes of halogenated organic trace gases are unknown for most volcanic systems. It has to be pointed out that already in trace concentrations a couple of natural and anthropogenic halogenated organic components influence negatively the physical and chemical properties of the earth atmosphere (Seinfeld & Pandis 1998). In fact, some of these substances (e.g. CCl_4) are involved in the greenhouse effect (IPCC 2001), others (e.g. CH_3Br) in the degradation of the stratospheric ozone (WMO 2003), and most of them have toxic effects on life (cp. WHO). Since Molina & Rowland (1974) and contemporaneously Stolarski & Cicerone (1974) discovered the degradation effect of chlorine radicals, originating from photolysed man made chlorofluoromethanes, on the stratospheric ozone layer, many scientists focussed their attention on further possible sources of ozone depleting compounds. Wofsy *et al.* (1975) showed that bromine has the same destructive effects on ozone as chlorine and Solomon *et al.* (1994) also confirmed such an effect for iodine. The first measurements of halogenated organic compounds in volcanic gases are from Stoiber *et al.* (1971). They detected CH_3Cl and C_2HCl_3 in fumarole gas samples (95 % air content) from Santiaguito volcano in Guatemala. Rasmussen *et al.* (1980) reported elevated levels of CH_3Cl in ambient air samples collected in the vicinity of the Kilauea and Mauna Loa volcanoes (Hawaii). Furthermore Inn *et al.* (1981) measured high concentrations of CH_3Cl in the gaseous constituents of the eruption plume of Mount St. Helens. Considerable amounts of methyl halides (CH_3Cl, CH_3Br and CH_3I) were also released during thermodesorption experiments of ash emitted during the Mount St. Helens eruption of 18th May 1980 (Rasmussen *et al.*, 1982). In gas samples from 10 volcanoes of the Kurile Islands, Kamchatka, and Nicaragua Isidorov *et al.* (1996) detected e.g. chlorinated methanes. Jordan *et al.* (2000) described more than 100 halogenated compounds (5 fluorinated, 100 chlorinated, 25 brominated and 4 iodated) measured in volcanic gases from Kuju and Satsuma Iwojima volcanoes (Japan) and Etna and Vulcano (Italy), among methyl halides (CH_3Cl, CH_3Br, and CH_3I), ethyl halides (C_2H_5Cl, C_2H_5Br and C_2H_5I) and higher chlorinated methanes (CH_2Cl_2, $CHCl_3$ and CCl_4). Schwandner *et al.* (2004) measured in fumarolic and diffuse gas samples from Vulcano (Italy) the same methyl halides and higher chlorinated methanes as well as ethyl bromide (C_2H_5Br).

During four field campaigns (17/07-21/08/2001, 22/02/-21/03/2002, 13/11-13/12/2002, 09/07-23/07/2003) we performed a time series sampling of fumarole gases at the Nicaraguan subduction zone volcano Momotombo. In order to calculate trace gas fluxes we quantified in addition within three days (17- 19 November 2002) the SO_2-flux of the plume with Mini-DOAS (Miniaturized Differential Optical Absorption Spectrometer) (Galle *et al.*, 2003). Our investigation was focused on halomethanes and -ethanes, since such C_1 and C_2 compounds exhibit much higher atmospheric lifetimes (WMO 2003) than longer-chain compounds, showing negligible water solubility (CRC 1993) which prevents quantitative tropospheric washout. This allows them to reach the stratosphere (Seinfeld & Pandis 1998), especially through explosive volcanism(Inn *et al.*, 1981; Textor *et al.*, 2003; Textor *et al.*, 2004). In the stratosphere, degradation releases chlorine, bromine and iodine radicals which act as catalysts for reactions that cause ozone destruction (Seinfeld & Pandis 1998). To design ozone protection policies, the relevance of various sources contributing relevant halogenated substances to the atmosphere needs to be clearified. The calculated atmospheric budgets of methyl halides are largely out of balance, because identified sinks by far overweigh identified sources (Butler 2000; WMO 2003; Harper & Hamilton 2003). These unbalanced atmospheric budgets suggest additional unknown natural sources, and volcanoes could potentially be considered as an important source.

3.2 Geological and volcanological background

The Quaternary Nicaragua volcano Momotombo is part of the Central American volcanic arc (CAVA), which results from the subduction of the Cocos Plate underneath the Caribbean Plate along the Middle American trench and extends from the border of Mexico, across Guatemala, El Salvador and Nicaragua to central Costa Rica.

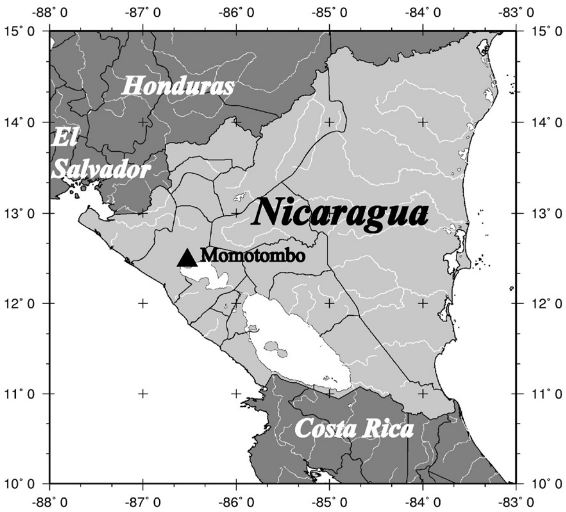

Figure 3.1 *Locality map for Momotombo volcano.*

The present volcanism in Nicaragua is focussed along the volcanic chain known as the Cordillera de los Marrabios, that rises from the Nicaraguan Depression, a large NW-SE trending graben crossing the central part of the country.

The Depression is characterized by a mafic igneous basement of oceanic lithosphere (Walther *et al.*, 2000), which is overlain by Cretaceous to Miocene marine sediments (tuffaceous shale, siltstone, greywacke, sandstone and limestone), and buried by the Quaternary ignimbrite deposits of Malpaisillo and La Sierra Group (McBirney & Williams 1965; Elming *et al.*, 2001).

The ocean floor underneath Nicaragua is subducted with convergence rates of c. 8 cm/yr (DeMets 2001), and was produced at the East Pacific Rise, is 5.5 km thick and overlain by ~225 m of carbonate, which is in turn overlain by ~200 m of hemipelagic sediments (Auboudin *et al.*, 1982; Kimura *et al.*, 1997; Walther *et al.*, 2000).

Momotombo volcano (1297 m, 12.25°N, 86.32°W) is situated on the north shore of Lake Managua (Fig. 3.1) and presents a stratovolcano near the centre of the volcanic arc that passes through western Nicaragua. The last eruption of basaltic material was in 1905, since that time Momotombo has been in a persistent state of high-temperature fumarolic activity (Menyailov *et al.*, 1986).

Fumaroles are localized at the base of the inner walls of the summit area (Fig. 3.2), where gases are emitted at a wide range of temperatures, from 472-478°C at fumarole F3, 600-616°C at fumarole F2, and 739-776°C at fumarole F1, respectively, at the time of the survey.

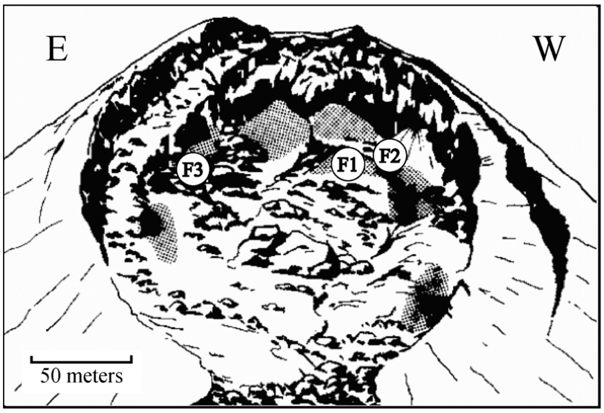

Figure 3.2 *Schematic map of the summit crater of Momotombo and sampled fumaroles (courtesy of INETER). Common "official" fumarole numbers are F9, F7, and F16, respectively, instead of F1, F2 and F3.*

Volatiles at Momotombo

The magmatic component of volatiles present in fumaroles of the Nicaraguan volcanic arc derived from subducted marine carbonate and hemipelagic sediments (Patino *et al.*, 2000), altered oceanic crust and the wedge of depleted upper mantle, which is between the subducting Cocos Plate and the overriding Caribbean Plate (Snyder *et al.*, 2001). Intensive bend-faulting of the downgoing slab offshore Nicaragua to mantle depth facilitate a deep penetration of seawater into the subduction zone (Ranero *et al.*, 2003). Momotombo's fluid system in addition is associated with large deep and shallow-water sediment deposits of the Sandino Basin (Snyder & Fehn 2002; Ranero *et al.*, 2000; Walther *et al.*, 2000). These circumstances make Momotombo a preferred object of investigation. The above presented potential sources of volatiles are rich in halogens (Tab. 3.6), and water as transport medium for fluid mobile ($D^{f/m}$>1) elements is available to a great extent and the high fumarole temperatures suggest high contents of magmatic compounds and comparatively limited interaction with meteoric water or the hydrothermal system.

3.3 Methods

3.3.1 Sampling

For sampling we used 125 mL glass bottles with PTFE-stopcocks. Sample bottles and stopcocks were cleaned prior to usage by washing with aqueous Mucasol® solution, rinsing with purified water, drying and degassing in a vacuum oven at 80°C for 8 hours. In blank tests with sampling bottles, filled up with purified helium all relevant compounds were below detection limit. For transport to Nicaragua the bottles were filled up with synthetic air. A few hours before sampling, they were evacuated to 10^{-5} mbar. Sampling is performed by pushing a titanium tube into the fumarole and inserting a silica tube with slightly smaller diameter. A water-cooled condenser, a water separator and an evacuated (10^{-5} mbar) 125 mL glass bottle which is sealed with a PTFE stopcock is utilized in the sampling train (Fig. 3.3). After flushing the system with volcanic gas, the sample is sucked into the evacuated glass bottle (Details in Frische *et al.*, 2005b). The application of our sampling method and device for collection of fumarolic gases addressed to halogenated trace compounds is comparatively simple (no collection of different aliquots, no use of hazardous chemicals) and fast (reduced time exposure at direct fumarolic fumes, self-protection!).

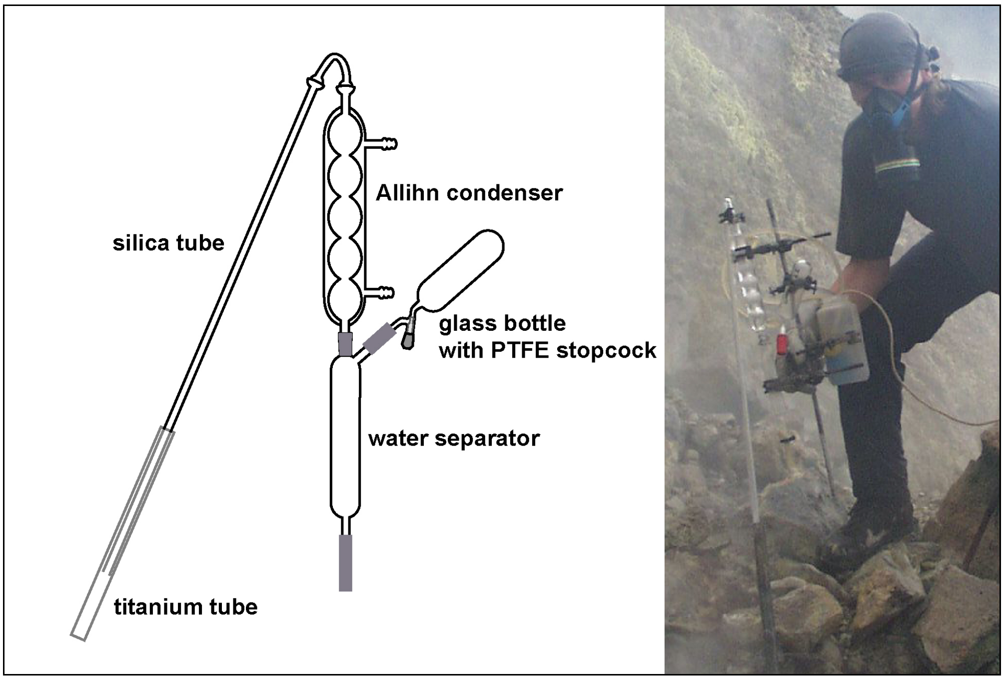

Figure 3.3 *Schematic diagram and picture of the setup for trace gas sampling.*

Samples for main component analysis were taken at the same locations using Giggenbach-type (Giggenbach & Goguel 1989; Montegrossi *et al.*, 2001; Garofalo *et al.*, in prep.) gas sampling. Outlet temperatures of gas samples were measured on the base of the titanium tube using a K-type thermocouple.

In order to estimate possible variations in the trace gas emissions induced by physical-chemical parameters governing the fumarolic discharges we chose emission points of a wide range of outlet temperatures and the highest gas emission rates. High temperature gas emissions e.g. of 739-776°C at fumarole F1 (Fig. 3.2) and 600-616°C at fumarole F2 suggest that a high portion of volatiles came directly from the magma, lower temperature gases like at fumarole F3 (472-478°C) pointed to a more extensive interaction with hydrothermal or meteoric fluids (Fischer *et al.*, 1996).

3.3.2 Analytical Methods

After absorption of acidic compounds with 2 mL of degassed (Ohsawa *et al.*, 2000) sodium hydroxide solution (50% in water) and dilution with blank-tested helium the gas sample was analysed with gas chromatography/ion trap mass spectrometry (GC/ion trap-MS) within a mass scan range of 48 to 200 amu (*Frische et al., 2005b*). Since some halohydrocarbons seem to be not stable under alkaline conditions, we injected the sodium hydroxide solution into the sample shortly before the analysis (less than 10 minutes) to prevent significant degradation of the analytes. All relevant compounds showed during tests in alkaline medium mean degradation rates of 0.4% per hour with a range between 0.0%/h for CCl_4 and 2.2%/h for chloroform. Calibration of the GC/ion trap-MS was carried out by several injections per day of a working standard gas mixture. The working standard had been calibrated against calibration gases prepared in a three-step static dilution technique (except for C_2H_5Cl and C_2H_5Br), resulting in an absolute uncertainty of ±10 %. For an approximative quantification of C_2H_5Cl and C_2H_5Br, the same instrumental response as for C_2H_3Cl (vinyl chloride) and CH_3Br, respectively, was assumed. Detection limits for GC/ion trap-MS are 0.2 pptv (parts per trillion by volume = pmol/mol) for calibrations standard (using volumes of 150 mL), 0.7 pptv for ambient air samples (using volumes of 50 mL), and 20 pptv for fumarolic gas samples from Momotombo (using volumes of 50 mL)). Replicate analysis of individual samples gave values within ±10 %. The analyses were performed around 1.5 months after the collection of the samples. Tests with samples taken one after the other at the same location showed no systematic drift in the concentrations of relevant compounds when analysed with one month interval.

The main headspace[2] compounds and the acid soluble gases dissolved in a NaOH-$Cd(OH)_2$ solution were determined with Giggenbach-type methods (Giggenbach & Goguel 1989; Montegrossi *et al.*, 2001; Garofalo *et al.*, in prep.). Measurements of SO_2-Fluxes using the Mini-DOAS technique were performed as described in Galle *et al.* (2003).

---

[2] Headspace gas is the portion of fumarolic gas which is not dissolved in the caustic solution and consist of N_2, O_2, Ar ,H_2, He, CO as well as hydrocarbons and halo(hydro)carbons.

3.4 Results

At three locations in the crater of Momotombo we took during two years 22 gas samples from fumaroles discharging in a temperature range of 472-776°C. The variety of detected halogenated compounds with concentrations up to several orders of magnitude greater than ambient air includes short-chain halohydrocarbons, halogenated aromatics and heterocycles. Our results are comparable to those of Jordan *et al.* (2000) in gas samples from volcanoes in Italy and Japan. The most abundant halohydrocarbon was CH_3Cl with concentrations up to 19 ppmv (parts per million by volume = µmol/mol) in the headspace gas of fumarole F3. Further major halohydrocarbons were (in order of their mean relative abundance) CH_3I, CH_3Br, C_2H_5Cl, C_2H_5I, C_2H_5Br, CH_2Cl_2, $CHCl_3$, C_2H_3Cl as well as CCl_4. Average and maximum concentrations of the ten most abundant halogenated trace compounds are listed for each fumarole in Table 3.1.

Fumarole	F1		F2		F3	
Temperature [°C]	739 - 776		600 - 616		472 - 478	
Sample no.	10		7		5	
Sampling horizon	2001 - 2003		2002 - 2003		2002	
	mean	max.	mean	max.	mean	max.
CH_3Cl	51	140	54	160	9,000	19,000
CH_3Br	13	67	14	41	510	790
CH_3I	9.5	24	11	32	720	1,400
C_2H_5Cl	1.6	5.4	3.6	12	430	760
C_2H_5Br	0.26	0.70	0.52	2.1	31	68
C_2H_5I	0.35	1.2	0.52	1.0	48	110
CH_2Cl_2	0.50	1.4	0.76	1.7	22	52
$CHCl_3$	0.24	0.69	0.33	0.72	20	48
CCl_4	0.19	0.34	0.30	0.62	0.45	0.60
C_2H_3Cl	0.41	1.1	0.47	1.6	5.1	9.9

Table 3.1 *Mean and maximum concentrations in ppbv (parts per billion by volume = nmol/mol) in headspace gas from fumarole F1, F2 and F2, respectively, of Momotombo.*

Methyl halides were the predominant species in our samples. Methyl and ethyl halide concentrations correlate well with each other (Fig. 3.4-3.6), the coefficient of determination R^2 were obtained from linear regression and range between 0.95 for the positive correlation of CH_3Br with CH_3I, and 0.83 for CH_3Br with C_2H_5Br. As depicted in Figure 3.4 methyl halides show very good positive correlations with each other, presenting R^2 values of 0.95 for CH_3I vs. CH_3Br, 0.93 for CH_3I vs. CH_3Cl, and 0.92 for CH_3Br vs. CH_3Cl.

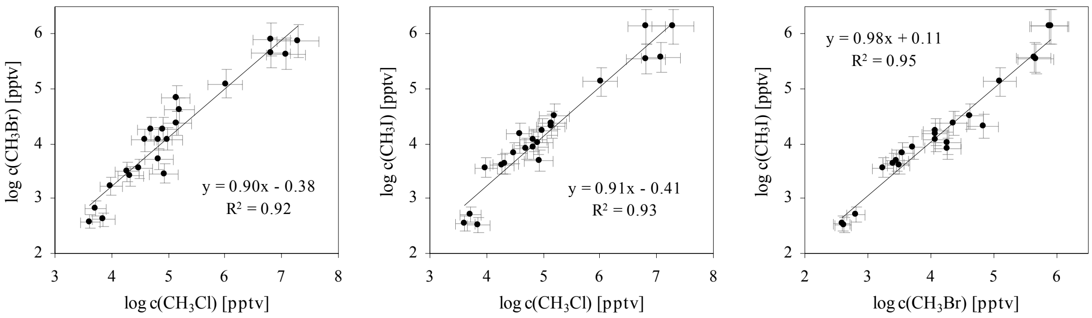

Figure 3.4 *Correlation in concentration between methyl halides (CH_3Cl, CH_3Br, and CH_3I) in headspace gas from fumarole F1, F2, and F3, respectively, of Momotombo.*

A comparably good positive correlation exist for ethyl halides (Fig. 3.5) with R^2-values of 0.94 for C_2H_5I vs. C_2H_5Br, 0.93 for C_2H_5Br vs. C_2H_5Cl, and 0.88 for C_2H_5I vs. C_2H_5Cl.

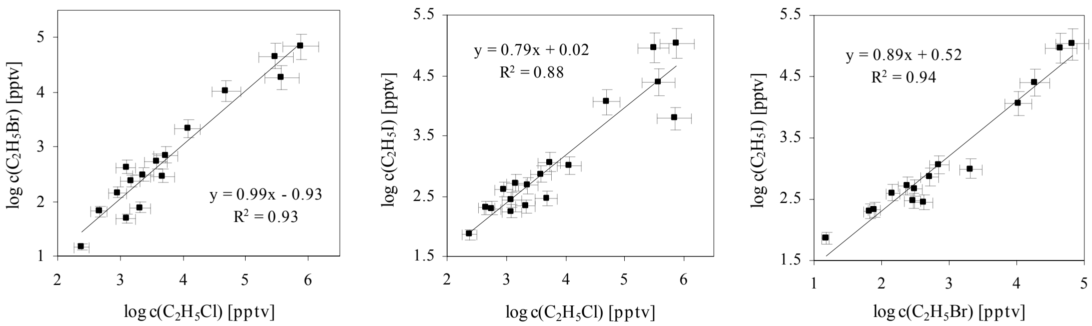

Figure 3.5 *Correlation in concentration between ethyl halides (CH_3Cl, CH_3Br, and CH_3I) in headspace gas from fumarole F1, F2, and F3, respectively, of Momotombo.*

As shown in Figure 3.6, also methyl halides and ethyl halides with the same type of halogen in the molecule correlates positively with R^2 values of 0.90 for C_2H_5Cl vs. CH_3Cl, 0.87 for C_2H_5I vs. CH_3I, and 0.83 for C_2H_5Br vs. CH_3Br.

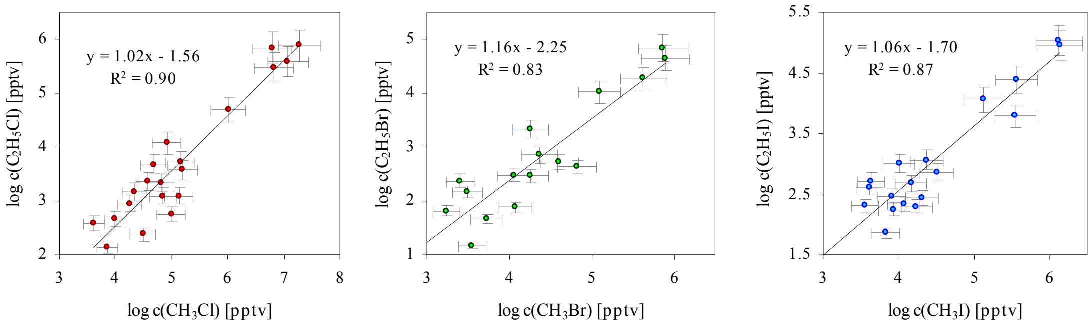

Figure 3.6 *Correlation in concentration between methyl halides (CH_3Cl, CH_3Br, and CH_3I) and ethyl halides (C_2H_5Cl, C_2H_5Br, and C_2H_5I) in headspace gas from fumarole F1, F2, and F3, respectively, of Momotombo.*

Also a positive correlation between methane (Garofalo *et al.*, in prep.) and methyl halides, and a positive relation between ethane (Garofalo *et al.*, in prep.) and ethyl halides, could be observed (Fig. 3.7 and 3.8). The coefficient of determination for the linear regression of methyl halide vs. methane concentrations (Fig. 3.7) range from 0.86 for CH_3Cl and CH_3I to 0.77 for CH_3Br.

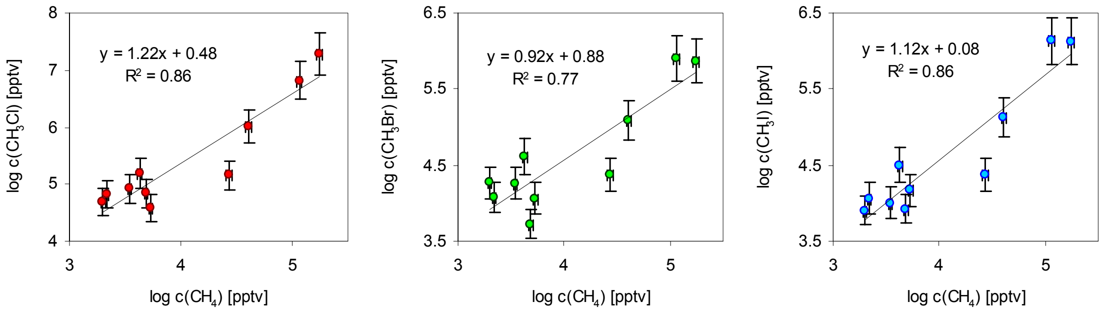

Figure 3.7 *Correlation between methane and methyl halide concentrations in headspace gas from fumarole F1, F2, and F3, respectively, of Momotombo.*

Ethyl halides vs. ethane concentrations show relatively clear positive relations among each other with R^2 of 0.79 for C_2H_5I, 0.74 for C_2H_5Cl, and 0.67 C_2H_5Br (Fig. 3.8).

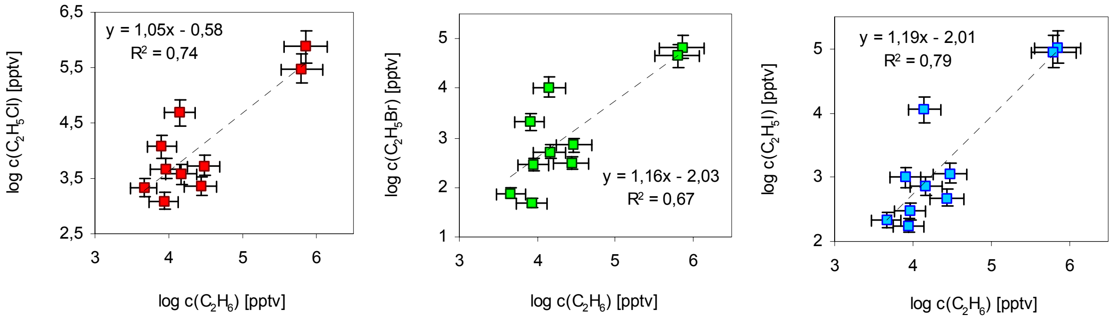

Figure 3.8 *Relation between ethane and ethyl halide concentrations in headspace gas from fumarole F1, F2, and F3, respectively, of Momotombo.*

A weak negative relation exists between temperature vs. methyl and ethyl halides (Fig. 3.9). Fumarole F1 and F2 show generally comparable abundances of halogenated trace compounds (Tab. 3.1), with the exception of CH_3I and C_2H_5Cl that occur in higher concentration in the gas samples from fumarole F2.

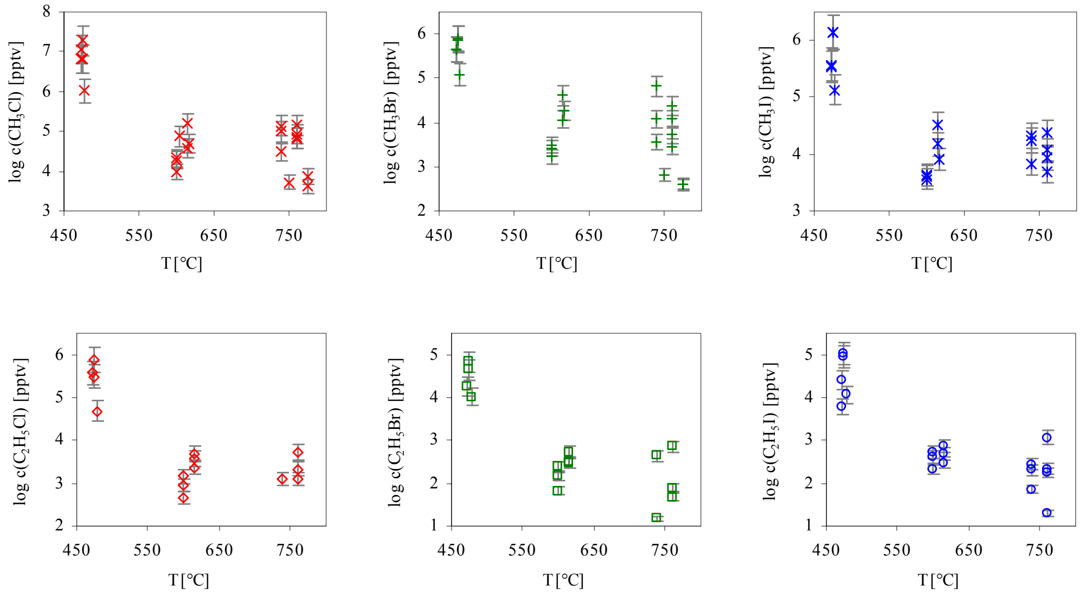

Figure 3.9 *Temperature dependence of methyl halide (CH_3Cl, CH_3Br, and CH_3I) and ethyl halide (C_2H_5Cl, C_2H_5Br, and C_2H_5I) concentration in headspace gas of fumarole F1, F2 and F3, respectively, of Momotombo.*

In order to calculate trace gas fluxes $flux_{(trace\ gas)}$ [mol/yr] (equation (E3.1)) we scale sulphur data from wet chemistry main component analysis (Giggenbach *et al.*, 1989; Garofalo *et al.*, in prep.) $c_{(SO2+H2S)}$ [mol/mol] with the flux estimations of Mini-DOAS $flux_{(SO2)}$ [mol/yr] (Galle *et al.*, in prep.) and the headspace gas content of the wet chemistry solution $c_{(headspace)}$ [mol/mol] (which is equivalent to the headspace gas fraction used for the trace gas measurements).

$$flux_{(trace\ gas)} = \frac{c_{(headspace)}flux_{(SO_2)}}{c_{(SO_2+H_2S)}} \qquad \text{(E3.1)}$$

Fluxes of individual compounds $flux_{(i)}$ [mol/yr] are calculated on the base of their concentration in headspace gas $c_{(i)}$ [mol/mol].

$$flux_{(i)} = flux_{(trace\ gas)}c_{(i)} \qquad (i\text{: compound}) \qquad \text{(E3.2)}$$

Mobile traverses with the zenith sky mini-DOAS were made at the bottom of Momotombo and SO_2 fluxes varied from of 0.53 ± 0.10 kg/s on 18 November to 0.49 ± 0.12 kg/s on 19 November (Galle *et al.*, in prep.). SO_2 gas plume measurements of the five permanently degassing Nicaraguan volcanoes San Cristóbal, Telica, Cerro Negro, Momotombo and Masaya were repeatedly carried out during 2002 and 2003. The total SO_2 flux for Nicaragua sums up to 1.5 Mg/day (Mg= 10^6g), or 0.54 Tg/yr (Tg= 10^{12}g), respectively (Galle *et al.*, in prep.).

To give an overview about the influence of main and trace gas composition on fluxes (Tab. 3.2), we scale data from individual fumarole with SO_2-fluxes of Momotombo. The mean values of main and trace compounds from fumarole F1, F2 and F3 are used to estimate the total flux of Momotombo.

	Momotombo flux [g/yr]					
	Fumarole F1	Fumarole F2	Fumarole F3	Mean F1-F3	Nicaragua	Global*
CH_3Cl	540	120	9,200	3,300	110,000	3,700,000
CH_3Br	120	64	980	390	13,000	440,000
CH_3I	200	70	2,100	790	27,000	880,000
C_2H_5Cl	24	11	570	200	6,900	230,000
C_2H_5Br	3.6	2.7	78	28	970	32,000
C_2H_5I	7.2	3.0	150	53	1,800	61,000
CH_2Cl_2	9.1	3.0	39	17	570	19,000
$CHCl_3$	6.0	1.8	48	19	630	21,000
CCl_4	3.2	1.6	1.4	2.1	69	2,300
C_2H_3Cl	4.6	2.3	6.4	4.4	150	5,000

Table 3.2 *Trace gas fluxes in g/yr of fumarole F1, F2, and F3, respectively, at Momotombo, their mean values and the resulting global fluxes *(based on a global volcanic SO_2-flux of 18 Tg/yr (Halmer et al., 2002))*

The highest fluxes for all the quantified compounds, with the exception of CCl_4, could be observed at fumarole F3. Fumarole F1 shows intermediate fluxes while fumarole F2 always showed the lowest ones. Calculated annual trace gases fluxes at individual fumaroles range between a maximum of 9.2 kg for CH_3Cl and minimum of 1.4 g for CCl_4 at fumarole F3. The arithmetic mean in trace gas composition of fumarole F1, F2 and F3 results in annual fluxes of 3.3 kg CH_3Cl, 390 g CH_3Br, 790 g CH_3I, over 28 g C_2H_5Br to 2.1 g CCl_4 at Momotombo. Based on estimated global volcanic SO_2-fluxes of 18 Tg/yr (Halmer *et al.*, 2002), our calculations result in annual volcanic halo(hydro)carbon fluxes of 3.7 metric tonnes for CH_3Cl, 440 kg for CH_3Br, 880 kg of CH_3I over 32 kg of C_2H_5Br to 2.3 kg of CCl_4.

3.5 Discussion

During subduction the slab releases large volumes of water from oceanic sediments, altered basalts and serpentinite. At the depths of mineral breakdown fluids are released into the mantle wedge causing melting. When fluid is exsolved from the ascending magma, chlorine, bromine, and iodine, are almost entirely partitioned into the fluid phase (Kravchuk & Keppler 1994; Keppler 1999; Bureau *et al.*, 2000), because of their large ionic radii (Cl= 181 pm= 181 x 10^{-12}m, Br= 196 pm and I= 220 pm) (Mortimer 1987) that prevent sufficient incorporation into most minerals (Mason & Moore 1982). The relative abundance of iodine, chlorine, and bromine in high temperature magmatic fluids is a function of their concentration in the melt, as well as their fluid/melt partition coefficients ($D^{f/m}$). Experimentally determined $D^{f/m}$ for albitic melts are 8.1, 17.5 and 104 for chlorine, bromine, and iodine, respectively (Bureau *et al.*, 2000). This implies that iodine, bromine and chlorine entering the magmatic system should be released almost quantitatively into the atmosphere during shallow-level magma degassing (Webster *et al.*, 1999). The strong halogen enrichment in the fluid phase greatly facilitates halocarbon formation at shallow depths. Because of the environmental impact of halogenated organic compounds, detailed information about their emission rates through quiescent degassing is important for the discussion of a possible volcanic importance in atmospheric halogenated organic load since the high number of volcanoes in quiescent degassing state all over the world. Our estimation of global methyl halide fluxes are comparatively low like the data extrapolated from various other subduction zone volcanoes (Kuju, Satsuma Iwojima, Mt. Etna, Vulcano) (Tab. 3.3), even though different sampling and calculating methods were used: Jordan *et al* (2000) took samples with evacuated, empty glass-bottles and used for trace gas flux estimations literature data for typical fumarolic gas compositions and global SO_2-fluxes. Schwandner *et al* (2004) used adsorption tubes for sampling and estimated fluxes through comparison of own CO_2-data with literature data for global CO_2-fluxes.

	This work	Jordan *et al.*, (2000)	This work	Schwandner *et al.*, (2004)	All other known emission sources
	value range	value range	mean value	mean value	value range [a,b]
CH_3Cl	$1.4x10^5$-$2.2x10^7$	$6.2x10^4$-$1.2x10^7$	$3.7x10^6$	$7.4x10^7$	$1.9x10^{12}$ – $1.2x10^{13}$
CH_3Br	$7.2x10^4$-$1.7x10^6$	$1.9x10^3$-$8.2x10^5$	$4.4x10^5$	$7.8x10^5$	$7.7x10^9$ – $2.9x10^{11}$
CH_3I	$7.8x10^4$-$4.4x10^6$	$5.7x10^3$-$2.5x10^6$	$8.8x10^5$	$1.3x10^6$	$2.5x10^{11}$ – $1.6x10^{12}$

Table 3.3 *Comparison of global methyl halide flux estimations [g/yr] for fumarolic emissions and for all other known sources. Ref.:* [a]*(WMO 2003),* [b]*(Harper & Hamilton 2003).*

In our samples the most abundant methyl and ethyl halides were followed in concentration by higher chlorinated methanes. This characteristic distribution sequence suggest that thermally and catalytically activated radical reactions occurring in the gas phase (Jordan *et al.*, 2000) are important for the origin of the halogenated trace gases. In fact, the synthesis of halogenated trace gases is possible as light alkanes like CH_4 and C_2H_6 are produced at shallow depth in the volcanic and hydrothermal systems by thermal decomposition of organic matter (Taran & Giggenbach 2003). In simple gas-phase catalytic reaction cycles, these hydrocarbons can react with reactive radicals e.g. Cl• and Br• generated in ppb – ppm levels by shallow magma degassing (Bobrowski *et al.*, 2003; Gerlach 2004) (equation (E3.3)-(E3.5)).

$$X\bullet + CH_4 \rightleftharpoons \bullet CH_3 + HX \qquad (X: Cl, Br, I) \qquad (E3.3)$$

$$\bullet CH_3 + X_2 \rightleftharpoons CH_3X + X\bullet \qquad (E3.4)$$

$$\bullet CH_3 + X\bullet \rightleftharpoons CH_3X \qquad (E3.5)$$

The total equation of (E3.3)-(E3.5) is:

$$CH_4 + X_2 \rightleftharpoons CH_3X + HX \qquad (E3.6)$$

Higher hydrocarbons would react in an analogous way.

$$C_2H_6 + X_2 \rightleftharpoons C_2H_5X + HX \qquad (E3.7)$$

Also higher halogenated halocarbons can be synthesized in this way ((E3.8)-(E3.10)).

$$CH_3X + X_2 \rightleftharpoons CH_2X_2 + HX \qquad (E3.8)$$

$$CH_2X_2 + X_2 \rightleftharpoons CHX_3 + HX \qquad (E3.9)$$

$$CHX_3 + X_2 \rightleftharpoons CX_4 + HX \qquad (E3.10)$$

Another possible mechanism leading to the generation of these compounds could be the thermal cracking of larger hydrocarbons, which produce smaller hydrocarbons with free radicals (E3.11). Reactions of short chain hydrocarbons with halogen radicals could generate e.g. methyl and ethyl halides((E3.12)-(E3.13)).

$$C_3H_8 \rightleftharpoons C_2H_5\bullet + CH_3\bullet \qquad (E3.11)$$

$$CH_3\bullet + X\bullet \rightleftharpoons CH_3X \qquad (E3.12)$$

$$C_2H_5\bullet + X\bullet \rightleftharpoons C_2H_5X \qquad (E3.13)$$

Furthermore electrophilic addition reactions, through catalytic cracking of alkanes on zeolites or silica-alumina (catalysts commonly present in volcanic-hydrothermal environment), could produce unsaturated hydrocarbons (e.g. C_nH_{2n}) and addition of magmatic hydrogen halides could produce halohydrocarbons (E3.14).

$$C_nH_{2n} + HX \rightleftharpoons C_nH_{2n+1}X \qquad (E3.14)$$

In the specific case of Momotombo the mean molar halogen ratio of the methyl halides CH_3Cl, CH_3Br, CH_3I is 10:1.0:1.1 and 11:1.0:1.8 for the ethyl halides C_2H_5Cl, C_2H_5Br, C_2H_5I (Tab. 3.4). Fumarole F2 shows the lowest values for chlorinated compounds. Bromine and iodine values from methyl bromide and methyl iodide are comparable at all fumaroles, the ethyl halides show higher values for iodine than for bromine.

	Fumarole F1	Fumarole F2	Fumarole F3	Mean all
CH_3Cl	9.6 ± 5.7	4.8 ± 0.9	17 ± 8.5	10 ± 5.0
CH_3Br	1.0 ± 0.5	1.0 ± 0.4	1.0 ± 0.1	1.0 ± 0.0
CH_3I	1.0 ± 0.3	1.0 ± 0.3	1.2 ± 0.3	1.1 ± 0.1
C_2H_5Cl	15 ± 8.4	7.7 ± 3.2	11 ± 5.9	11 ± 2.9
C_2H_5Br	1.0 ± 0.2	1.0 ± 0.3	1.0 ± 0.0	1.0 ± 0.0
C_2H_5I	2.5 ± 1.3	1.6 ± 0.7	1.5 ± 0.3	1.9 ± 0.5

Table 3.4 *Mean relative molar ratios of methyl and ethyl halides concentrations in headspace gas from fumarole F1, F2, and F3, respectively, of Momotombo.*

The relatively high ratios in bromine and iodine vs. chlorine in fumarolic gases from Momotombo point to a driving role of marine sediments in the generation of halogenated trace gases. As can be seen in Table 3.5, the global iodine distribution is dominated by the marine system. Nearly 70% of iodine in the earth's crust (including seawater) is calculated to exist in ocean sediments (Muramatsu & Wedepohl 1998). Iodine is associated with organic material (e.g. 1,020 mg/kg in marine organisms), which results in a relatively low abundance of this element in seawater (0.06 mg/kg) and a relative enrichment in marine deep-see sediments (e.g. 28 mg/kg in oceanic pelagic clay). Bromine instead exhibits moderate affinity to organic material (e.g. 440 mg/kg in marine organisms) which results in slightly higher concentrations in marine deep-sea sediments (e.g. 70 mg/kg in oceanic pelagic clay) than in seawater (67 mg/kg). Chlorine is the most conservative of the three halogens, it is enriched in seawater (18,800 mg/kg) and shows no particular affinity for organic material.

	Relative molar ratios			Concentration		
	Chlorine	Bromine	Iodine	Chlorine	Bromine	Iodine
Methyl halides Momotombo F1	5.8-29	1.0–3.2	1.0–1.9	4.2-143 nmol/mol	0.39-67 nmol/mol	0.33-24 nmol/mol
Ethyl halides Momotombo F1	4.5-28	1.0–1.5	1.0–4.9	0.24-5.4 nmol/mol	0.015-0.70 nmol/mol	0.072-1.2 nmol/mol
Condensates Momotombo F1 [a]	1,320	1.1	1.0	781 µmol/mol	0.64 µmol/mol	0.59 µmol/mol
Volcanic glasses Apoyeque [b,c]	1,830	23	1.0	3,900 mg/kg	112 mg/kg	7,6 mg/kg
Volc. melt inclusions Apoyeque [b,c]	700	10	1.0	3,900 mg/kg	125 mg/kg	20 mg/kg
Volcanic glasses Fontana [b,c,d]	1,160	19	1.0	1,100 mg/kg	40 mg/kg	3,4 mg/kg
Volc. melt inclusions Fontana [b,c,d]	120	1.0	1.0	1,300 mg/kg	24 mg/kg	40 mg/kg
Oceanic pelagic clay [e,f]	2,680	4.0	1.0	21,000 mg/kg	70 mg/kg	28 mg/kg
Marine organisms [g]	24	1.0	1.5	4,700 mg/kg	440 mg/kg	1020 mg/kg
Seawater [e]	1,120,000	1770	1.0	18,800 mg/kg	67 mg/kg	0.06 mg/kg
Meteoric water [e]	3,990	4.5	1.0	7.8 mg/kg	0.020 mg/kg	0.007 mg/kg
Primitive mantle [h]	1,700	5.0	1.0	17 mg/kg	0.050 mg/kg	0.010 mg/kg
Continental crust [i]	590	1.25	1.0	472 mg/kg	1 mg/kg	0.8 mg/kg

Table 3.5 *Mean relative molar ratios and concentrations of halogens in different reservoirs. [a](Garofalo et al., unpubl. data in prep.), [b](Wehrmann & Freundt 2005a) [c](Wehrmann pers. commun., 2005), [d](Wehrmann et al., 2005b), [e](Li 1982), [f](Li 1991), [g](Bowen 1979), [h](McDonough & Sun 1995), [i](Wedepohl 1995).*

Momotombo is underlain by voluminous deep and shallow-water sediment deposits of the Sandino Basin (Snyder & Fehn 2002; Ranero *et al.*, 2000, Walther *et al.*, 2000), which are supposedly bromine and iodine rich. High Br and I contents in the local upper crust were also indirectly inferred from anomalously high heavy halogen contents in melt inclusions and volcanic glasses from the Fontana Tephra in Nicaragua (Tab. 3.5) (Wehrmann & Freundt 2005a; Wehrmann *et al.*, 2005b). Subduction of large volumes of also bromine and iodine rich marine sediments in combination with shallow level processes such as hydrothermal mobilization of bromine and iodine in the local marine sediment deposits (Snyder *et al.*, 2003) followed by the formation of thermogenic methane (Snyder *et al.*, 2003) would deliver the required reactants (hydrocarbons and halogens) for halohydrocarbon synthesis. Investigations of ^{129}I/I in geothermal gases and fluids from Nicaragua confirm the presence of two different end-members: One magmatic component (c. 25 Ma old) associated with presently subducting sediments, and a much older crustal component of c. 65 Ma (Snyder & Fehn 2002; Snyder *et al.*, 2003). These results prove the involvement of a crustal source in the generation of Nicaraguan volcanic volatiles.

3.6 Conclusions

The similar abundances of halogenated trace gas compounds in fumarolic gas samples from different subduction zone volcanoes suggest common processes responsible for their formation. Mono halogenated C_1 and C_2 compounds predominate in the fumarolic gas samples from Momotombo while higher chlorinated C_1 compounds are less abundant at somewhat lower concentrations. This pattern is the likely result from thermally and catalytically activated radical reactions occurring in the gas phase and involving magmatic hydrogen halides and hydrocarbons deriving from thermal decomposition of organic material. Sediment recycling in the Nicaraguan sector of the subduction zone, in combination with the interaction between the magmatic system and marine deposits present at depth in the Nicaraguan Depression are likely to be responsible of the relatively high bromine and iodine vs. chlorine ratios of the halogenated trace gases. Scaling our data to the estimated global volcanic SO_2 flux of 18 Tg/yr (Halmer *et al.*, 2002) yields an average global volcanic source strength of 3.7×10^{-6} Tg/yr for methyl chloride, 4.4×10^{-7} Tg/yr for methyl bromide, 8.8×10^{-7} Tg/yr for methyl iodide, 1.9×10^{-8} Tg/yr for dichloromethane, 2.1×10^{-8} Tg/yr for trichloromethane, and 2.3×10^{-9} Tg/yr for carbon tetrachloride. The estimated mean global fluxes of the total known non-volcanic sources for the same compounds sum up to 3.0 Tg/yr methyl chloride (WMO 2003), 0.16 Tg/yr methyl bromide (WMO 2003), 0.30 Tg/yr methyl iodide (Bell *et al.*, 2002), 0.84 Tg/yr dichloromethane (Keene *et al.*, 1999), 0.65 Tg/yr trichloromethane (Keene *et al.*, 1999), and 0.022 Tg/yr carbon tetrachloride (Khalil 1999). This indicates that subduction zone degassing has no significant impact on the global atmospheric budgets of halocarbons.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft as part of the Sonderforschungsbereich (SFB) 574 “Volatiles and Fluids in Subduction Zones: Climate Feedback and Trigger Mechanisms for Natural Disasters”, by the Max-Planck-Society (Munich), and by the Volkswagen Stiftung (I/76 590). This is SFB 574-contribution #xx. Special thanks go to Wilfried Strauch, Pedro Perez, and the Instituto Nicaragüense de Estudios Territoriales (INETER) for providing laboratory space and their assistance during the field work. Jochen Harnisch and Armin Jordan made helpful comments on an earlier draft of this manuscript.

References

Anders, E. and N. Grevesse, Abundances of the elements: meteoric and solar. Geochim. Cosmochim. Acta, 53, 197-214, 1989.

Andres, R.J. and A.D. Kasgnoc, A time-averaged inventory of subaerial volcanic sulfur emissions, J. Geophys. Res., 103(D19), 25251-25261, 1998.

Auboudin J, J. Azema, J-Ch. Carfantan, A. Demant, C. Rangin, M. Tardy and J. Tournon, The Middle America trench in the framework of Central America. In Init Repts DSDP, 67,747- 755 College Station, TX (Ocean Drilling Program), 1982.

Bell, N., L. Hsu, D. J. Jacob, M. G. Schultz, D. R. Blake, J. Butler and E. Maier-Reimer, Global budgets of oceanic and atmospheric methyl iodide: Development of methyl iodide as a tracer for marine convection in atmospheric models, J. Geophys. Res., 107(D17), 2002

Bobrowski, N., G. Hönninger, B. Galle and U. Platt, Detection of bromine monoxide in a volcanic plume, Nature, 423, 273- 276, 2003.

Bowen, H.J.M., Environmental Chemistry of the Elements. Academic Press, London. 333, 1979.

Bureau H, H. Keppler and N. Métrich, Volcanic degassing of bromine and iodine: experimental data and applications to stratospheric chemistry, Earth. Planet. Sci. Lett., 183, 51-60, 2000.

Butler, J.H., Better budgets for methyl halides? Nature, 403, 260-261, 2000.

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

Capaccioni, B., F. Tassi and O. Vaselli, Organic and inorganic geochemistry of low temperature gas discharges at the Baia di Levante beach, Vulcano Island, Italy, J. Volcanol. Geotherm. Res., 108, 173-185, 2001.

Carroll, M.R. and J.R. Holloway, Volatiles in Magmas, Rev. Min., v.30, 509pp., 1994.

DeMets, C., A new estimate for present-day Cocos-Caribbean plate motion: Implications for slip along the Central American volcanic arc, Geophys. Res. Lett., 28(21), 4043-4046, 2001.

Elming, S.-A., P. Layer and K. Ubieta, A paleomagnetic study and age determinations of Tertiary rocks in Nicaragua, Central America, Geophys. J. Internat., 147(2), 294-309, 2001.

Fischer, T.P., G.B. Arehart, N.C. Sturchio and S.N. Williams, The relationship between fumarole gas composition and eruptive activity at Galeras Volcano, Colombia, Geol., 24(6), 531-534, 1996.

Frische M., K. Garofalo, T.H. Hansteen, R. Borchers and J. Harnisch, A volcanic contribution of stable halogenated compounds?, 2005b in prep.

Galle B., T.H. Hansteen, M. Frische, K. Garofalo and W. Strauch, An estimate of the SO_2 emissions from four volcanoes in Nicaragua, made using mini-DOAS spectroscopy, IAVCEI 8th Field Workshop Volc. Gases, Abstr. Vol., 2003.

Galle B, T.H. Hansteen, M. Frische, K. Garofalo et al., Time-averaged SO_2 fluxes from Nicaraguan volcanoes, in prep..

Galle, B., C. Oppenheimer, A. Geyer, A.J.S. McGonigle, M. Edmonds and L.A. Horrocks, A miniaturised ultraviolet spectrometer for remote sensing of SO_2 fluxes: a new tool for volcano surveillance, J. Volcanol. Geotherm. Res., 119, 241-254, 2003.

Garofalo K., F. Tassi, O. Vaselli, D. Tedesco, A. Delgado-Huertas, M. Frische, T.H. Hansteen and W. Strauch, Reactivation of Mombacho, 2005a, in prep..

Garofalo K., F. Tassi, O. Vaselli, A. Delgado-Huertas, M. Frische and T.H. Hansteen, unpubl. data in prep..

Gerlach T.M., Volcanic sources of tropospheric ozone-depleting trace gases, Geochem., Geophys., Geosys., 5, Q09007, doi:10.1029/2004GC000747, 2004.

Giggenbach, W.F. and R.L. Goguel, Method for the collection and analysis of geothermal and volcanic water and gas samples, NZ-DSIR Report, CD 2387, 53, 1989.

Graf, H.-F., J. Feichter and B. Langmann, Volcanic sulfur emissions: Estimates of source strength and its contribution to the global sulfate distribution, J. Geophys. Res., 102(D9), 10727-10738, 1997.

Halmer, M., H.-U. Schmincke and H.-F. Graf, The annual volcanic gas input into the atmosphere, in particular into the stratosphere: a global data set for the past 100 years., J. Volcanol. Geotherm. Res., 115, 511-528, 2002.

Harper, D. B. and J. T. G. Hamilton, The global cycles of the naturally-occurring halomethanes, p. 17-41. In G. W. Gribble (ed.), The handbook of environmental chemistry, Springer-Verlag, Berlin, Germany, 2003.

Inn E.C.Y., J.F. Vedder and E.P. Condon, Gaseous constituents in the plume from eruptions of Mount St. Helens, Science, 211, 821-823, 1981.

IPCC, Climate Change 2001: The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, edited by J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell and C.A. Johnson, 881 pp., Cambridge University Press, UK and New York, 2001.

Isidorov, V., V. Povarov and E.B. Prilepsky, Geological sources of radiative and photochemically active components of the atmosphere, EUROTRAC Symposium '96, 79-85, 1996.

Jordan, A., Volcanic Formation of Halogenated Organic Compounds. The Handbook of Environmental Chemistry. Berlin Heidelberg, Springer-Verlag. 3, Part P, 121-139, 2003.

Jordan, A., J. Harnisch, R. Borchers, F. Le Guern and H. Shinohara, Volcanogenic Halocarbons, Environm. Sci. Technol., 34(6), 1122-1124, 2000.

Keene W.C., M.A.K. Khalil, D.J. Erickson, A. McCulloch, T.E. Graedel, J.M. Lobert, M.L. Aucott, S.L. Gong, D.B. Harper, G. Kleiman, P. Midgley, R.M. Moore, C. Seuzaret, W.T. Sturges, C.M. Benkovitz, V. Koropalov, L.A. Barrie and Y.F. Li , Composite global emissions of reactive chlorine from anthropogenic and natural sources: Reactive Chlorine Emissions Inventory, J. Geophys. Res., 104, 8429-8440, 1999.

Keppler H., Experimental evidence for the source of excess sulfur in explosive volcanic eruptions, Science, 284, 1652-1654, 1999.

Khalil, M. A. K., Reactive Chlorine Compounds in the Atmosphere, Chapter 2 in Reactive Halogen Compounds in the Atmosphere, Volume 4, Part E, of The Handbook of Environmental Chemistry, Edited by P. Fabian and O.N. Singh. Springer-Verlag, 45-79, 1999.

Kimura G, Silver E, Blum P et al., Proc ODP Init Repts, 170: College Station, TX (Ocean Drilling Program), 1997.

Kravchuk F. and H. Keppler, Distribution of chloride between aqueous fluids and felsic melts at 2 kbars and 800°C, Europ. J. Mineral., 6, 913-923, 1994.

Li, Y.H., A brief discussion on the mean oceanic residence time of elements, Geochim. Cosmochim. Acta, 46, 2671-2675, doi: 10.1016/0016-7037(82)90386-6, 1982.

Li, Y.H., Distribution Patterns of the Elements in the Ocean - a Synthesis, Geochim. Cosmochim. Acta, 55(11), 3223-3240, 1991.

Mason, B. and C.B. Moore, Principles of geochemistry, 4th ed., John Wiley and Sons Inc., New York, 344pp., 1982.

McBirney, A.R. and H. Williams, Volcanic history of Nicaragua, Univ. Calif. Pub. Geo. Sci., 55, 1-65, 1965.

McDonough, W.F. and S.-S. Sun, Composition of the Earth, Chem. Geol., 120, 223-253, 1995.

Menyailov, I.A., L.P. Nikitina, V.N. Shapar and V.P. Pilipenko, Temperature increase and chemical change of fumarolic gases at Momotombo volcano, Nicaragua, in 1982-1985: Are these indicators of a possible eruption?, J. Geophys. Res., 91(B12), 12199-12214, 1986.

Molina M.J. and F.S. Rowland, Stratospheric sink for chlorofluoromethanes: chlorine atom-catalyzed destruction of ozone, Nature, 249, 810-812, 1974.

Montegrossi, G., F. Tassi, O. Vaselli, A. Buccianti and K. Garofalo, Sulfur species in volcanic gases, Anal. Chem., 73(15), 3709-3715, 2001.

Mortimer, C.E., Chemie, 5. Auflage, Georg Thieme Verlag, Stuttgart, 1987.

Muramatsu Y. and K.H. Wedepohl, The distribution of iodine in the Earth's crust, Chem. Geol., 147, 201-216. 1998.

Ohsawa, S., Y. Yusa, K. Oue and K. Amita, Entrainment of atmospheric air into the volcanic system during the 1995 phreatic eruption of Kuju Volcano, Japan, J. Volcanol. Geotherm. Res., 96, 33-43, 2000.

Patino, L.C., M.J. Carr and M.D. Feigenson, Local and regional variations in Central American arc lavas controlled by variations in subducted sediment input, Contrib. Mineral. Petrol., 138, 265-283, 2000.

Ranero, C.R., R. von Huene, E. Flueh, M. Duarte, D. Baca and K.D. McIntosh, A cross section of the convergent Pacific margin of Nicaragua, Tectonics, 19, 335-357, 2000.

Ranero, C.R., J.P. Morgan, K. McIntosh and C. Reichert, Bending-related faulting and mantle serpentinization at the Middle American trench, Nature, 425, 367-373, 2003.

Rasmussen, R.A., L.E. Rasmussen, M.A.K. Khalil and R.W. Dalluge, Concentration distribution of methylchloride in the atmosphere, J. Geophys. Res., 85, 7350-7356, 1980.

Rasmussen, R.A., M.A.K. Khalil, R.W. Dalluge, S.A. Penkett and B. Jones, Carbonyl sulfide and carbon disulfide from the eruptions of Mount St. Helens, Science, 215(4533), 665-667, 1982.

Scarpa, R. and R.I. Tilling, Monitoring and Mitigation of Volcanic Hazards, Berlin & Heidelberg, Springer, 841pp., 1996.

Schwandner F.M., T.M. Seward, A.P. Gize, P.A. Hall and V.J. Dietrich, Diffuse emission of organic trace gases from the flank and crater of a quiescent active volcano (Vulcano, Aeolian Islands, Italy), J. Geophys. Res., 109, D04301, doi:10.1029/2003JD003890, 2004.

Seinfeld, J.H. and S.N. Pandis; Atmospheric chemistry and physics, John Wiley & Sons Inc., New York, 1326pp., 1998.

Snyder, G.T. and U. Fehn, The origin of iodine in volcanic fluids: ^{129}I results from the Central American Volcanic Arc, Geochim. Cosmochim. Acta, 66, 3827-3838, 2002.

Snyder, G.T., R. Poreda, A. Hunt and U. Fehn, Regional variations in volatile composition: Isotopic evidence for carbonate recycling in the Central American volcanic arc, Geochem. Geophys. Geosys., 2, 2001GC000163, 2001.

Snyder, G., R. Poreda, U. Fehn and A. Hunt, Sources of nitrogen and methane in Central American geothermal settings: Noble gas and ^{129}I evidence for crustal and magmatic volatile components, Geochem. Geophys. Geosys., 4(1), 1-28, 2003.

Solomon, S., R.R. Garcia and A.R. Ravishankara; On the role of iodine in ozone depletion, J. Geophys. Res., 99, 20491-20499, 1994.

Stoiber, R.E., D.C. Leggett, T.F. Jenkins, R.P. Murrmann and W.I. Rose; Organic compounds in volcanic gas from Santiaguito volcano, Guatemala, Geol. Soc. Am. Bull., 82, 2299-2302, 1971.

Stolarski, R.S. and R.J. Cicerone; Stratospheric chlorine: a possible sink for ozone, J. Can. Chem., 52, 1610-1615, 1974.

Taran Y.A. and W.F. Giggenbach, Geochemistry of Light Hydrocarbons in Subduction-Related Volcanic and Hydrothermal fluids, Society of Econom. Geol., Spec. Pub., 10, 61-74, 2003.

Textor C., H.F. Graf, M. Herzog and J.M. Oberhuber, Injection of gases into the stratosphere by explosive volcanic eruptions J. Geophys. Res., 108(D19), 2003.

Textor, C., H.-F. Graf, C. Timmreck and A. Robock, Emissions from volcanoes, Chapter 7 of Emissions of Atmospheric Trace Compounds, C. Granier, P. Artaxo and C. Reeves, Eds., Kluwer, Dordrecht, 269-303, 2004.

CRC, Handbook of Chemistry and Physics; CRC Press, 74th Edition, 1993.

Walther, C. H. E., E. R. Flueh, C. R. Ranero, R. von Huene and W. Strauch, Crustal structure across the pacific margin of Nicaragua: Evidence for ophiolitic basement and a shallow mantle sliver, Geophys. J. Int., 141, 759-777, 2000.

Webster, J.D., R.J. Kinzler and E.A. Mathez, Chloride and water solubility in basalt and andesite melts and implications for magmatic degassing, Geochim. Cosmochim. Acta, 63(5), 729-738, 1999.

Wedepohl, K.H., The composition of the continental crust, Geochim. Cosmochim. Acta, 59, 1,217-1,239, 1995.

Wehrmann, H. and A. Freundt, Bromine and iodine in volcanic glasses determined by Synchrotrone-XRF: origin and partitioning in basaltic-andesitic and rhyolitic arc magma systems, 2005a subm..

Wehrmann, H., A. Freundt, S. Kutterolf, M. Wiedenbeck and H.U. Schmincke, Water, halogen, and sulphur degassing of the basaltic-andesitic Fontana Tephra, Nicaragua, 2005b subm..

Wofsy, S.C., M.B. McElroy and Y.L. Yung, The chemistry of atmospheric bromine, Geophys. Res. Lett., 2, 215-218, 1975.

WHO (World Health Organization) http://www.who.int/en/

WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project - Report No. 47, 498pp., Geneva, 2003.

Chapter 4

A volcanic contribution of stable halogenated compounds?

Matthias Frische[a,b,c,*], Kristin Garofalo[a], Thor H. Hansteen[a,b], Reinhard Borchers[c], Jochen Harnisch[d]

[a] *SFB 574, Christian-Albrechts-Universitaet, D-24148 Kiel, Germany*
[b] *IFM-GEOMAR Leibniz-Institut fuer Meereswissenschaften, D-24148 Kiel, Germany*
[c] *Max-Planck-Institut fuer Sonnensystemforschung, D-37191 Katlenburg/Lindau, Germany*
[d] *Ecofys GmbH, D-90443 Nuernberg, Germany*

**Corresponding author: mfrische@ifm-geomar.de*

Abstract

Halogenated compounds in the atmosphere are of great environmental concern due to their demonstrated negative effect on atmospheric chemistry and climate. Detailed knowledge of the emission budgets of halogenated compounds are important to understand their specific impact on ozone chemistry and the climate and furthermore to guide policy decisions in connexion with the international agreements about protection of the ozone layer. In selected cases, the relevance of specific emission sources for certain compounds has remained unclear. We present in this study new and comprehensive evidence to find a conclusive answer regarding the existence and relevance of a volcanic contribution of chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), halons (bromine containing halo(hydro)-carbons), and fully fluorinated compounds (e.g. CF_4 and SF_6) to the atmospheric budget. In order to obtain new evidence of a volcanic incidence of these compounds, we collected repeatedly, during four field campaigns covering a period of two years, gases from fumaroles discharging in a wide range of temperatures at the Nicaraguan subduction zone volcanoes Momotombo, Cerro Negro and Mombacho. In most fumarolic samples certain CFCs, HFCs, HCFCs, halons, and the fully fluorinated compounds CF_4 and SF_6 were present above detection limits. However, these compounds occur in the fumarole gases in relative proportions characteristic for ambient air. This atmospheric fingerprint can be explained by variable amounts of air entering the porous volcanic edifices and successively being incorporated into the fumarolic gas discharge. Our results suggest that the investigated volcanoes do not constitute a significant natural source for CFCs, HFCs, HCFCs, halons, CF_4, SF_6 and NF_3.

Keywords: *CFCs, HFCs, HCFCs, fumaroles, subduction.*

4.1 Introduction

It is well established that active volcanoes continuously release significant quantities of inorganic halogen compounds into the atmosphere. Most of them are removed from the atmosphere within days through various dry and wet removal processes like degradation due to hydroxyl-radical reactions and washout by precipitation. Those halogenated compounds which persist in the atmosphere for years or decades exhibit significant, substance-specific contributions to global warming through greenhouse effect and ozone depletion. Their impact depends mainly on their atmospheric concentration, atmospheric lifetime, affectivity as greenhouse gas, and the amount of halogens in each molecule and its stability (Tab. 4.1). Stratospheric ozone depletion observed since 1970 has been caused primarily by increasing concentrations of reactive chlorine and bromine compounds that are released by degradation of anthropogenic ozone depleting substances (WMO 2003), predominantly chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and halons (bromine containing halo(hydro)carbons). Their use is regulated under the Montreal Protocol (UNEP 2003). Anthropogenic HFCs and fully fluorinated compounds are meanwhile covered by the Kyoto Protocols (UNFCCC 1998) due to their contribution to global warming (IPCC 2001).

However, the occurrence of CFCs in volcanic gases is controversially discussed. The first data on volcanogenic CFC-11 (CCl_3F) in fumarolic gas samples (with a 95 vol% air content) were reported by Stoiber *et al.* (1971) at Santiaguito volcano in western Guatemala, where concentration “well above unpolluted atmospheric levels” were described. Rasmussen *et al.* (1979) rejected a volcanic formation of CFCs in fumarolic gases from Mauna Loa, Hawaii. CFC-11 and CFC-12 (CCl_2F_2) have been used for the determination of air contents in plume gas samples and ash particles from Mount St. Helens (Rasmussen *et al.*, 1982). Stratospheric measurements of the 1980 eruptive plume of Mount St. Helens show no enrichment in CFC-11 and CFC-12 (Inn *et al.*, 1981). Symonds *et al.* (1988) furthermore exclude the formation of CFCs in gas phase under volcanic conditions on the base of thermodynamic model calculations. Isidorov *et al.* (1990) published solfataric gas data from Mendeleev and Golovnin volcano on Kunashir Island (Kurile Island) with concentrations of up to 80 ppbv (parts per billion by volume= nmol/mol) CFC-11 and 160 ppbv CFC-12. Jordan *et al.* (2000) detected more than 300 organic substances, including numerous halogenated organic compounds, in fumarolic and lava gas from Japanese (Kuju and Satsuma Iwojima) and Italian (Mt. Etna and Vulcano) volcanoes. With the exception of CFC-11 found in concentration up to 1 ppbv in some samples, CFCs were generally present at concentrations equal to or below ambient air levels (Jordan 2003). Schwandner *et al.* (2004) reported 3,700 pptv (parts per trillion by volume = pmol/mol) of CFC-11 in dry fumarolic gas from Vulcano (Aeolian Islands, Italy). Using a H_2O concentration of 95 vol% for typical fumarolic gases, this value translates into 185 pptv of CFC-11, which is less than the reported ambient air level of 268 pptv, but nevertheless this does not explain the relative enrichment of CFC-11 in the dry gas found by Schwandner *et al.* (2004). Analyses of fumarolic and lava gas samples from Kuju and Satsuma Iwojima (Japan) as well as Mt. Etna and Vulcano (Italy) confirm that these volcanoes do not contribute to the atmospheric load of CF_4 and SF_6 (Harnisch & Eisenhauer 1998).

To detect a possible volcanic source for halogenated organic compounds we took gas samples from fumaroles at the Nicaraguan subduction zone volcanoes Momotombo, Cerro Negro and Mombacho during four field campaigns (July 2001 to July 2003). Deploying very sensitive GC/MS systems (gas chromatographs coupled with mass spectrometers), we analysed fumarolic gas samples for halogen-containing, relatively short chain organic compounds. The species we measured routinely include CFCs, HFCs, HCFCs, halons, and the fully fluorinated compounds CF_4, NF_3 and SF_6.

(Physical properties of several halogenated compounds are presented in Tab. 4.1). The three quiescent degassing volcanoes Momotombo, Cerro Negro and Mombacho (Fig. 4.1) were selected for this study because they emit gases from fumarolic vents in a wide temperature range of around 120°C at Mombacho, over 260-465°C at Cerro Negro, to 368-776°C at Momotombo.

Figure 4.1 Locality map of sampled Nicaraguan volcanoes.

4.2 Geological and volcanological background

The Quaternary Nicaraguan volcanic front results from subduction of the Cocos Plate underneath the Caribbean Plate along the Middle American trench and comprises of 18 major volcanic centres. The recent volcanic chain is aligned along the Cordillera de los Marrabios that rises from the Nicaraguan Depression, a large NW-SE trending graben crossing the central part of the country. The Depression is characterized by a mafic igneous basement of oceanic lithosphere (Walther *et al.*, 2000), overlain by Cretaceous to Miocene marine sediments (tuffaceous shale, siltstone, greywacke, sandstone and limestone) buried by the Quaternary ignimbrite deposits of Malpaisillo and La Sierra Group (McBirney & Williams 1965; Elming *et al.*, 2001).

Momotombo volcano (1297 m, 12.25°N, 86.32°W), situated at the northern shore of Lake Managua is a stratovolcano near the centre of the Nicaraguan volcanic chain. It erupted basaltic material most recently in 1905 (Menyailov *et al.*, 1986). The fumarolic activity occurs at the base of the inner walls of the summit area (Fig. 4.2), where gases are emitted in a wide range of temperatures at the time of the survey, from 368-537°C at fumarole F4, over 426-478°C and 600-616°C at fumarole F3 and F2, respectively, to 739-776°C at fumarole F1.

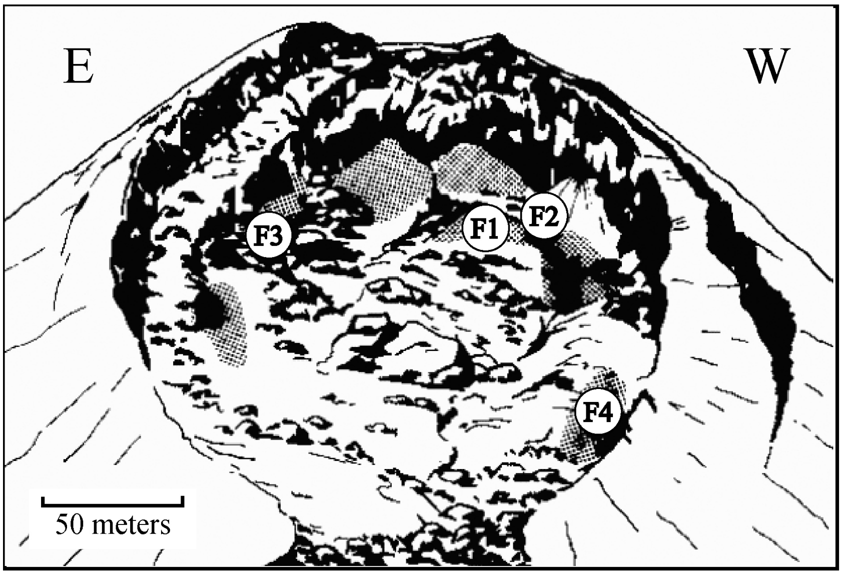

Figure 4.2 *Schematic map of the summit crater of Momotombo and the sampled fumaroles (courtesy of INETER).*

Cerro Negro (728 m, 12.30°N, 86.42°W), one of Central America's youngest volcanoes is a basaltic cinder cone situated between the Volcán Rota and the Volcanic Complex of Las Pilas- El Hoyo. It has produced at least 22 eruptions since its formation in 1850 (Hill *et al.*, 1999). The last eruption occurred in 1999. During the period of the survey, Cerro Negro has shown phases of both increasing and decreasing temperatures, releasing gases at temperatures from 194°C up to 465°C at a fissure located inside the 1995 crater (Fig. 4.3). Gases from the fumarolic field in the centre of the main cone have outlet temperatures of 260–369°C.

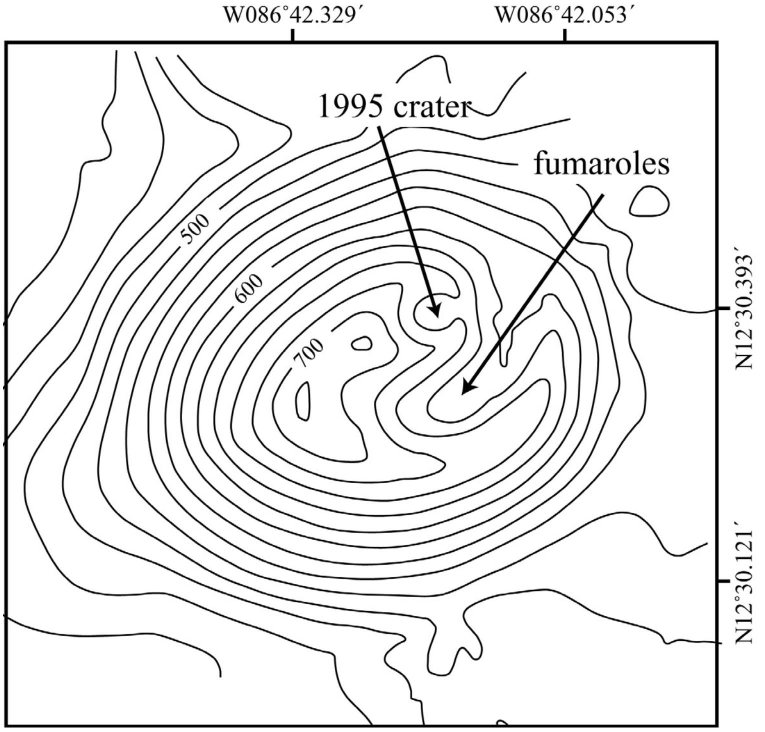

Figure 4.3 *Location of the 1995 crater and the main fumarolic field in the centre of Cerro Negro (after La Femina et al., 2004).*

Mombacho volcano (1344 m, 11.49°N, 85.58°W) towers above the northern shore of Lake Nicaragua and consists of basaltic-andesitic material. The volcano is highly dissected and presents morphologic evidence of at least two different flank failures (van Wyk de Vries & Francis 1997). On the upper north flank of the southern collapse structure (Fig. 4.4) H_2O-rich gases were ejected at a temperature of about 120°C. Mombacho has not been active in historical times.

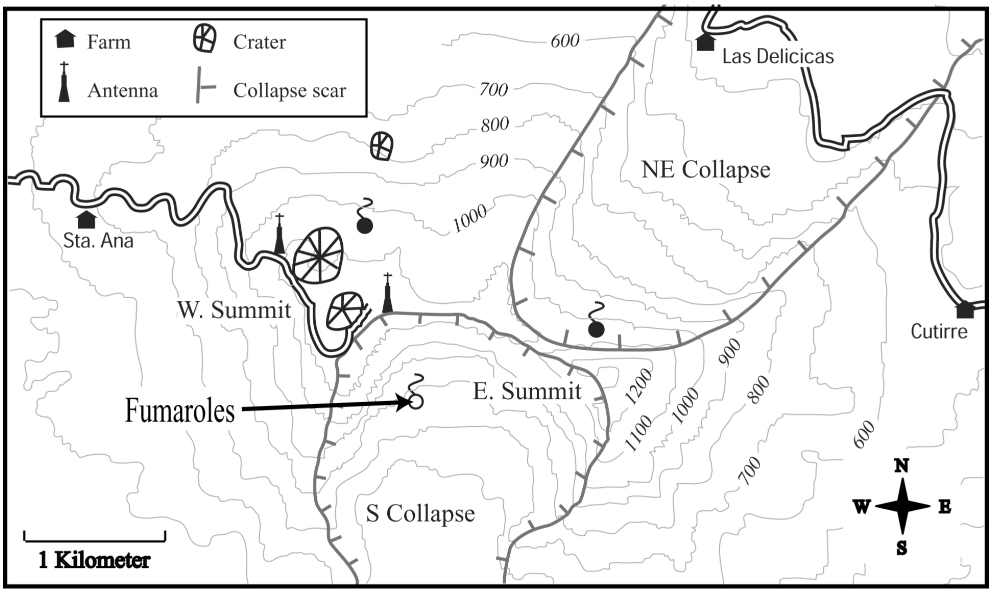

Figure 4.4 *Topographic map of Mombacho volcano (modified from Vallance et al., 2001)*

4.3 Methods

4.3.1 Sample Collection

A 30-60 cm-long titanium tube was inserted into the fumarole vent and a silica tube with a slightly smaller diameter was successively guided inside it. Sampling was performed using a silica sampling assemblage consisting of a water-cooled condenser and a water separator, connected with each other and with the silica tube that has been inserted into the fumarole orifice (Fig. 4.5).

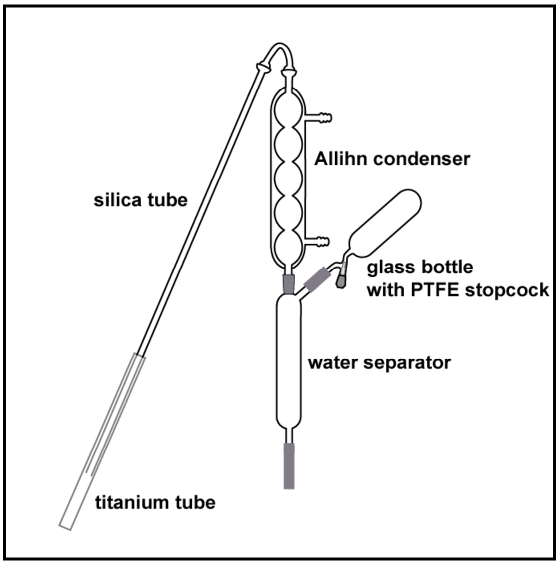

Figure 4.5 *Schematic diagram of the sampling assemblage used for collection of trace gases at fumaroles*

After the system has been sufficiently flushed by the passing fumarolic gas, an evacuated (10^{-5} mbar) 125 mL glass bottle sealed with a polytetrafluoroethylene (PTFE) stopcock was connected via silicon tube. To reduce the dead volume of the connection, the capillary tube of the sampling bottle was filled with glass wool.

After a second phase of sufficient passive flushing of the system, the sampling device was isolated from the surrounding atmosphere by closing the silicon outlet tube at the bottom of the water separator using a tube squeezer. A fraction of water soluble acid gases (that constitute a potential damage for the GC/MS) is already removed as condensate during sampling by cooling down the temperature of the fumarole gas (making water circulating continuously in the condenser via an electric pump) while the sample for the specific trace gas analysis is collected into the evacuated glass bottle after opening the PTFE-stopcock.

Once the sampling device is assembled, it can be disconnected from the silica tube and transported as one piece (dimensions are around 100 x 30 cm, weight of 1 kg, mostly cooling water) to the next sampling location, giving the possibility to optimise the time in the field and to collect higher numbers of samples around the fumarolic field. The application of our sampling method and device for collection of fumarolic gases addressed to trace compounds is comparatively simple (no collection of different aliquots, no use of hazardous chemicals) and fast (reduced time exposure at direct fumarolic fumes, self-protection!). Furthermore, our technique avoids the problems of fumarolic gas sampling with adsorption tubes (Schwandner *et al.*, 2004) where very volatile compounds are not quantitatively trapped (Isidorov *et al.*, 1990; Wahrenberger 1997) and the adsorbed substances could be modified on the trap e.g. by halogen exchange reactions (Jordan *et al.*, 2000).

The gas outlet temperature was measured immediately before and after the sampling, inserting a K-type thermocouple deeply into the titanium tube.

4.3.2 Analytical Methods

Immediately before proceeding to the analysis of the samples we injected 2 mL of degassed (Ohsawa *et al.*, 2000) sodium hydroxide solution (50% in water) into the sample-bottle to absorb the acidic compounds not removed as condensate phase in the field. After measuring the pressure of the remaining headspace[3] gas, the bottle was filled up to 2 bar with blank-tested helium.

For gas chromatography/ion trap mass spectrometry (GC/ion trap-MS) analysis sample volumes of 50-60 mL are sucked through a trap filled with an alkaline absorber (Ascarite®) and a desiccant ($Mg(ClO_4)_2$) and passed through a stainless steel pre-concentration loop filled with glass beads at liquid nitrogen temperature (-196°C). After pumping away the permanent gases the sample loop was heated to 90°C and its content was transferred to a small diameter unpacked focusing loop at -196°C. The sample was then injected into the GC/ion trap-MS by rapidly heating the second loop up to 90°C. Gas chromatographic separation was carried out on a ZB1 column (60 m x 0.32 mm, 1 µm phase) using the following temperature program: from -65° to 175°C at a rate of 8°C min^{-1}, then 5 min isothermal. Mass spectrometric detection was performed over a scan range of 48 to 200 amu (atomic mass unit). Quantification was made using one to three of the most abundant fragment ions. GC/ion trap-MS was used for compounds with boiling points of higher than –50°C (e.g. $CHClF_2$ (HCFC-22): T_{boil}= -41°C and CFC-12: T_{boil}= -30°C).

---

[3] Headspace gas is the portion of fumarolic gas which is not dissolved in the caustic solution and consist of N_2, O_2, Ar ,H_2, He, CO as well as hydrocarbons and halo(hydro)carbons.

For gas chromatography mass spectrometry (GC/MS) analysis of CF_4, NF_3, $CBrF_3$ (H-1301), CH_2F_2 (HFC-32) and CH_3F (HFC-41), sample volumes of 50 mL are pumped through a trap filled with an alkaline absorber (Ascarite®) and a desiccant ($Mg(ClO_4)_2$). For quantitative adsorption of low boiling substances such as NF_3 (T_{boil}= -129°C) or CF_4 (T_{boil}= -128°C) the sample is passed through a concentration loop filled with Spherosil® XOB adsorbent cooled to liquid nitrogen temperature (-196°C). Permanent gases were partly removed by a vacuum pump. The trapped gases were desorbed by rapidly heating the loop to 90°C and injected into the GC/MS. A GASPRO capillary column (30 m x 0.32 mm) was used for separation. The column oven of the GC was heated up from -70°C to 175°C at a rate of 10°C min^{-1}. Detection was carried out in single ion detection mode of the quadrupole MS on respective characteristic masses (e.g. 69 amu for CF_3^+). To identify substances, retention times were used as inferred from analyses of mixtures of pure compounds in blank-tested synthetic air.

Calibration of both systems was carried out by several injections of a working standard gas mixture per day. The working standard had been calibrated against calibration gases prepared in a three-step static dilution technique, resulting in an absolute uncertainty of ±10%. Detection limits for GC/ion trap-MS are 0.2 pptv for calibrations standard (using volumes of 150 mL) and 0.7 pptv for ambient air samples (using sample volumes of 50 mL). The detection limits for fumarolic gas samples varied because of their different content of headspace gas and amount to and 1.8, 20, and 10 pptv, respectively, for fumarolic gas samples from Cerro Negro, Momotombo and Mombacho (using sample volumes of 50 mL). Detection limits for GC/MS are about two-thirds better and amounting to 0.1 pptv for calibration standards (using volumes of 150 mL), 0.2 pptv for ambient air samples (using sample volumes of 50 mL) and 0.6, 7, and 4 pptv, respectively, for fumarolic gas samples from Cerro Negro, Momotombo and Mombacho. Replicate analysis of individual samples gave values within ±10%. The detector signals from individual compounds (peaks) at both systems were integrated to peak area.

Sample bottles and PTFE-stopcocks were cleaned prior to usage by washing with aqueous Mucasol® solution, rinsing with purified water, drying and degassing in a vacuum oven at 80°C for 8 hours. In blank tests with sampling bottles, filled up with purified helium or in addition with degassed sodium hydroxide solution (50% in water) all relevant compounds were below detection limit. For transport to Nicaragua the bottles were filled up with synthetic air. A few hours before sampling, they were evacuated to 10^{-5} mbar. Typical products of thermolysis of fluoropolymers (e.g. C_2F_4, C_3F_6, C_4F_8) (Ellis *et al.*, 2001), which would argue against the use of PTFE-stopcocks in the sample train, were not detectable.

4.3.3 Calculation of the geogenic portion

Fumarolic gases are typically mixtures of magmatic, hydrothermal and atmospheric components. Because volcanic edifices are comparatively porous and crosscut by faults and fractures, air can invade the gas feeding system and dilute the geogenic components (Symonds *et al.*, 1996; Ohsawa *et al.*, 2000; Saito *et al.*, 2002; CCVG 2004). The same effect can be caused by air-saturated meteoric waters feeding the volcanic hydrothermal system or ground waters circulating in the volcanic edifice and interacting in various proportions with the rising magmatic gases. Modern atmospheric air contains a multitude of organic compounds, with many halogenated ones among them. Because most of these predominately anthropogenic originated substances show extraordinary environmental stability, their characteristic ratios in mixtures with other volatiles remain unchanged and can be used as fingerprint for air detection (e.g. in volcanic gas samples). The concentrations of several halogenated compounds measured in Nicaraguan air during the sampling campaigns are listed with some of their physical and environmental properties in Table 4.1.

	Conc. air Nica [pptv]	Atmospheric lifetime [yr]^{a}	GWP (100 yr)^{b}	ODP (rel. CFC-11)^{a}
Tetrafluoromethane (CF_4)	80	50,000	5,820	-
Sulfur hexafluoride (SF_6)	5.5	3,200	22,450	-
CFC-114 ($C_2Cl_2F_4$)	17	300	9,880	0.94
CFC-113 ($C_2Cl_3F_3$)	85	85	6,030	1.0
CFC-12 (CCl_2F_2)	503	100	10,720	1.0
CFC-11 (CCl_3F)	274	45	4,680	1.0
HCFC-22 ($CHClF_2$)	129	12	1,780	0.05
Halon-1301 ($CBrF_3$)	3.9	65	7,030	12
Halon-1211 ($CBrClF_2$)	4.0	16	1,860	6.0

Table 4.1 *Mean concentrations of several halogenated compounds in Nicaraguan air samples and some of their physical or environmental properties (GWP: direct global warming potential based on an 100 year horizon, ODP: ozone depleting potential relative to CFC-11). Ref.: ^{a}(WMO 2003), ^{b}(IPCC 2001).*

Jordan *et al.* (2000 and pers. commun.) used CFC-114, CFC-113, CFC-11, and CFC-12 for the identification of an atmospheric air component in fumarolic an lava gas samples. In analogy and with regard to possible CFC-11 sources, we calculated the air dilution factor $f_{(dil)}$ for the fumarolic gas samples (equation (E4.1)) by comparing concentrations of solely man-made (WMO 2003; Butler *et al.*, 1999) CFC-114, CFC-113 and CFC-12 both in fumarolic and air samples. In equation (E4.1), *PA* is the peak area, and *V* the volume of individual CFC $_{(CFC\text{-}i)}$ in Nicaraguan air $_{(air)}$ and in the analyzed mixture $_{(mix)}$ of the fumarolic gas sample after adsorption of the acidic compounds and dilution with helium.

$$f_{(dil)} = \frac{1}{3}\sum_{i=1}^{3}\left(\frac{PA_{(mix)}V_{(air)}}{V_{(mix)}PA_{(air)}}\right)_{CFC\text{-}i} \quad (CFC\text{-}i\text{: CFC-12; CFC-113; CFC-114}) \qquad \text{(E4.1)}$$

By subtracting the atmospheric fraction from the mixture (E4.2) – (E4.4), we obtained volume $V_{(geo)}$ and peak area $PA_{(geo)}$ of the geogenic portion of the gas. Equation (E4.2) calculates the air-corrected volume for the diluted fumarolic sample $V_{(He+geo)}$. (E4.3) takes into account the dilution of the gas with helium during the sample preparation, where $p_{(fum)}$ is the pressure of the headspace gases (geogenic and air compounds) in the sample bottle after injection of the caustic solution and $p_{(mix)}$ is the pressure after dilution with helium (details in *Analytical Methods*). (E4.4) is used to calculate the peak area of individual species in the geogenic portion of fumarolic samples $PA_{(geo)i}$.

$$V_{(He+geo)} = V_{(mix)}(1 - f_{(dil)}) \tag{E4.2}$$

$$V_{(geo)} = \frac{V_{(He+geo)}p_{(fum)}}{p_{(mix)}} \tag{E4.3}$$

$$PA_{(geo)_i} = \left(\frac{PA_{(mix)_i}}{V_{(mix)}} - \left(\frac{PA_{(air)_i} f_{(air)}}{V_{(air)}} \right) \right) V_{(mix)} \qquad (i\text{: species}) \tag{E4.4}$$

Quantification of individual species in the geogenic portion of fumarolic gas samples $c_{(geo)i}$ was carried out by direct comparison of the corrected sample values for peak area $PA_{(geo)i}$ and volume $V_{(geo)}$ with peak area $PA_{(stda)i}$, volume $V_{(stda)}$ and concentration $c_{(stda)}$ of the gas standard (E4.5).

$$c_{(geo)_i} = \frac{\left(\frac{PA_{(geo)_i}}{V_{(geo)}} \right) c_{(stda)_i}}{\left(\frac{PA_{(stda)_i}}{V_{(stda)}} \right)} \tag{E4.5}$$

4.4 Results

The calculated air contents of our samples are shown in Table 4.2. Typical air contents in the headspace gas range between 1 and 9 mol% for Mombacho and Momotombo whereas some samples from Cerro Negro reach 38 mol%. This is in qualitative accordance (Garofalo *et al.*, in prep.) with Giggenbach-type gas sampling (Giggenbach & Goguel 1989; Montegrossi *et al.*, 2001;), which proved to be nearly impossible at Cerro Negro due to the high contents of air in the fumarolic gas stream.

Volcano	Range air content (headspace gas) [mol%]	Range air content (full sample) [mol%]	Mean air content (headspace gas) [mol%]	Mean air content (full sample) [mol%]
Momotombo	1.1 – 7.9	0.0045 - 0.033	3.7	0.016
Cerro Negro	2.6 - 38	-*	23	-*
Mombacho	1.1 – 9.4	0.0032 - 0.028	2.8	0.0083

Table 4.2 *Calculated air content of volcanic gas samples. The headspace gas portion in fumarolic gas samples averages 0.42 mol% and 0.30 mol% at Momotombo and Mombacho, respectively (Garofalo et al., in prep.). *Main components not available.*

The mean air content in samples from Momotombo was 3.7 mol%, 2.8 mol% in those from Mombacho and 23 mol% at Cerro Negro. At Momotombo and Mombacho the proportions of air at different fumaroles are relatively comparable, while at Cerro Negro the air contents are strongly dependent upon the sampling location. In fact, at Cerro Negro samples from a fissure in the 1995 crater show relatively low air contents (12 mol%) compared to samples from the bottom of the main crater, which contain 33 mol% air.

Our analyses show that CFCs (CFC-11, CFC-112 ($C_2Cl_4F_2$), and CFC-112a ($C_2Cl_4F_2$)) HFCs (HFC-32, HFC-41, and HFC-152a (CH_3CHF_2)), HCFCs (HCFC-22, HCFC-141b ($C_2H_3Cl_2F$), HCFC-142b ($C_2H_3ClF_2$), HCFC-123 (CF_3CHCl_2), HCFC-124 (C_2HClF_4), and HCFC-124a (C_2HClF_4)), halons (H-1301, H-1211, and H-2402 ($C_2Br_2F_4$)) and the fully fluorinated compounds CF_4, NF_3, and SF_6 are not concentrated in the geogenic portion of fumarolic gases from the investigated Nicaraguan volcanoes. Most of these substances either occurred in concentrations below detection limits (see *Analytical Methods*) or could clearly be ascribed to the atmospheric fraction in the gas samples. Table 4.3 shows typical, selected examples of results obtained from a total of more than 60 analysed fumarolic gas samples together with the uncorrected (*raw*) data for trace gas compounds. It is obvious that an “excess” air content in gas samples would cause overestimations or misinterpretations of fumarolic trace gas analysis. It is also worth noting that air contamination before, during, or after sample collection (Giggenbach *et al.*, 2001) would lead to additional errors in data interpretation.

	Mo_4_19 F3 475°C (18.11.02_16:40)							**CN_4_9_F5 194°C (25.11.02_10:35)**							**Momba_4_3_F1 119°C (28.11.02_13:40)**						
GC/i-MS	PA$_{(stda)}$	PA$_{(mix)}$	PA$_{(air)}$	PA$_{(geo)}$	c$_{(stda)}$	c$_{(geo)}$	c$_{(raw)}$	PA$_{(stda)}$	PA$_{(mix)}$	PA$_{(air)}$	PA$_{(geo)}$	c$_{(stda)}$	c$_{(geo)}$	c$_{(raw)}$	PA$_{(stda)}$	PA$_{(mix)}$	PA$_{(air)}$	PA$_{(geo)}$	c$_{(stda)}$	c$_{(geo)}$	c$_{(raw)}$
CFC-12	27491	1798	27593	b.d.l.	490	b.d.l.	490	24690	8475	24782	b.d.l.	490	b.d.l.	365	24701	181	24793	b.d.l.	490	b.d.l.	47
CFC-113	11632	767	8364	b.d.l.	86	b.d.l.	121	7622	2610	7710	b.d.l.	86	b.d.l.	64	7369	129	7454	37	86	b.d.l.	19
CFC-114	20	b.d.l.	2001	b.d.l.	15	b.d.l.	b.d.l.	1420	601	1653	26	15	b.d.l.	14	1412	b.d.l.	1644	b.d.l.	15	b.d.l.	b.d.l.
CFC-11	1719	1770	22756	b.d.l.	258	b.d.l.	310	20453	7056	20677	b.d.l.	258	b.d.l.	193	21403	309	21637	43	258	b.d.l.	48
H-1211	251	b.d.l.	333	b.d.l.	4	b.d.l.	b.d.l.	245	124	302	19	3.5	b.d.l.	3.9	235	b.d.l.	289	b.d.l.	3.5	b.d.l.	b.d.l.
SF_6	270	65	744	b.d.l.	10	b.d.l.	b.d.l.	1054	177	636	b.d.l.	10	b.d.l.	4	1100	42	663	b.d.l.	10	b.d.l.	b.d.l.
HCFC-22	1254	186	6405	b.d.l.	159	b.d.l.	62	6586	1973	5818	b.d.l.	159	b.d.l.	103	6630	103	5899	30	159	b.d.l.	32
	V$_{(air)}$:	100							V$_{(air)}$:	100						V$_{(air)}$:	100				
	V$_{(mix)}$:	120							V$_{(mix)}$:	120						V$_{(mix)}$:	120				
	V$_{(stda)}$:	100			V$_{(geo)}$:	6			V$_{(stda)}$:	100		V$_{(geo)}$:	33			V$_{(stda)}$:	100		V$_{(geo)}$:	8	
	p$_{(fum)}$:	105			f$_{(dil)}$:	0.07			p$_{(fum)}$:	740		f$_{(dil)}$:	0.29			p$_{(fum)}$:	125		f$_{(dil)}$:	0.01	
	p$_{(mix)}$:	1925							p$_{(mix)}$:	1928						p$_{(mix)}$:	1944				

GC/MS	PA$_{(stda)}$	PA$_{(mix)}$	PA$_{(air)}$	PA$_{(geo)}$	c$_{(stda)}$	c$_{(geo)}$	c$_{(raw)}$	PA$_{(stda)}$	PA$_{(mix)}$	PA$_{(air)}$	PA$_{(geo)}$	c$_{(stda)}$	c$_{(geo)}$	c$_{(raw)}$	PA$_{(stda)}$	PA$_{(mix)}$	PA$_{(air)}$	PA$_{(geo)}$	c$_{(stda)}$	c$_{(geo)}$	c$_{(raw)}$
CF_4	36606	702	40843	b.d.l.	66	b.d.l.	105	44632	14531	49798	b.d.l.	66	b.d.l.	56	46528	84	51914	b.d.l.	66	b.d.l.	b.d.l.
H-1301	3996	b.d.l.	4294	b.d.l.	4	b.d.l.	b.d.l.	4917	1570	5284	37	4	b.d.l.	3	4654	b.d.l.	5001	b.d.l.	4	b.d.l.	b.d.l.
		V$_{(air)}$:	100						V$_{(air)}$:	100						V$_{(air)}$:	100				
		V$_{(mix)}$:	100						V$_{(mix)}$:	100						V$_{(mix)}$:	100				
		V$_{(stda)}$:	100						V$_{(stda)}$:	100						V$_{(stda)}$:	100				
		V$_{(geo)}$:	5.1						V$_{(geo)}$:	27						V$_{(geo)}$:	6.4				

Table 4.3 *Selection of typical analytical results for each volcano (Mo: Momotombo, CN: Cerro Negro, Momba: Mombacho, b.d.l.: below detection limit,* c$_{(raw)}$*: uncorrected concentration).*

The analysis without air correction of e.g. 100 ml ($V_{(mix)}$) sample *Mo_4_19 F3 475°C (18.11.02_16:40)* from Momotombo would result in CFC-11 (via GC/ion trap-MS) and CF_4 (via GC/MS) concentrations ($c_{(craw)}$) of 310 and 105 pptv, respectively. These apparently relatively high calculated CFC-11 contents in the fumarolic gas are artefacts caused by admixture of air ($f_{(dil)}$) in combination with the removal of reactive compounds ($p_{(fum)}$) and the dilution with helium ($p_{(mix)}$) during sample preparation. The geogenic portion of the sample ($PA_{(geo)}$) is calculated using equation (E4.4) and the typical CFC-12, CFC-113, and CFC-114 content of ambient air ($PA_{(air)}$). The solution of (E4.4) gives concentration values ($c_{(geo)}$) below detection limit. In analogy, the use of uncorrected data for sample *CN_4_9_F5 194°C (25.11.02_10:35)* or *Momba_4_3_F1 119°C (28.11.02_13:40)* would result in 193 and 48 pptv of CFC-11, respectively, and in 56 pptv of CF_4 for the Cerro Negro sample, even though neither CFC-11 and CF_4 nor the further halo(hydro)carbons listed above are in the geogenic portion of the samples.

4.5 Discussion

The relatively high concentrations of CFC-11 in fumarolic gas from Santiaguito (Guatemala) (Stoiber *et al.*, 1971) and in samples from Volcano (Italy) (Jordan *et al.*, 2000; Schwandner *et al.*, 2004) are not mirrored by Nicaraguan fumarolic gases. The absence of continental crust underneath the Quaternary active Nicaraguan volcanic front may be a plausible explanation of the low CFCs contents in the fumarole gases. It is possible that magma evolving in chambers located at the base or within the continental crust would eventually experience various degrees of crustal contamination by felsic material derived from the reservoir wall rocks, delivering a typical spectrum of halogenated organic species such as CFC-11, CFC-12, CF_4 and SF_6 (Harnisch & Eisenhauer 1998; Harnisch *et al.*, 2000). Rocks from the Quaternary Nicaraguan volcanoes show isotopic compositions indicative for absence of crustal assimilation during magma storage and evolution, in contrast to the supposedly CFC-11 emitting volcanoes Santiaguito, whose ejecta show evidence for slight contamination with continental crust (Carr *et al.*, 2003; Feigenson *et al.*, 2004), and also from Vulcano, where continental crust occurs beneath the volcanic edifice (Tedesco & Nagao 1996).

If felsic continental crust in the volcanic environment leads to fluorinated compounds such as CFCs in the fumarolic gases, the significance of this contribution to the global inventory can be clarified with two recent publications on fumarolic and diffuse fluxes of CFC-11 at Vulcano (Italy): Jordan *et al.* (2000) calculated on the base of their fumarolic trace gas data, combined with literature data for typical SO_2-contents in fumarolic gases and global SO_2 fluxes, a global source strength for CFC-11 of less than 300 kg/yr and a resulting atmospheric background concentration of less than 1 ppqv (parts per quadrillion by volume = fmol/mol). Schwandner *et al.* (2004) calculated CFC-11 fluxes of 8.56±4.7 metric tons per year due to diffuse and fumarolic emissions by scaling their own data with literature data for global volcanic CO_2-fluxes. Documented global man-made emissions of CFC-11 in 2000 amounted to 75 Gg (Gg= 10^9g) with a peak value of 350 Gg in 1988 (McCulloch *et al.*, 2001), resulting in a tropospheric CFC-11 concentration of around 255 pptv in 2004 and a maximum of almost 280 pptv in 1992 (Thompson *et al.*, 2004).

Our flux estimate (Frische *et al.*, 2005a) is based on simultaneous measurements of trace gases, main volatile components (Giggenbach-modified-bottles) (Montegrossi *et al.*, 2001; Garofalo *et al.*, in prep.) and SO_2-fluxes (mini-DOAS) (Galle *et al.*, 2003; Galle *et al.*, in prep.) at Nicaraguan volcanoes in addition to literature data of global SO_2-fluxes (Halmer *et al.*, 2002). If we use not-air-corrected data, we calculate a maximum global volcanic CFC-11 flux of 3.2 kg/yr.

Another possible reason for the absence of fluorinated compounds such as CFCs in fumarolic gases can be the relatively low fluorine concentrations in Nicaraguan fluids (Garofalo *et al.*, in prep.), which could prevent fluorination reactions. It is likely that in magmatic systems with higher concentrations of fluorine the synthesis of CFCs is facilitated. The most common reaction forming CFCs is the fluorination of CCl_4 with magmatic HF in catalytic gas phase reactions (E4.5) (Jordan 2003).

$$CCl_4 + HF \rightleftharpoons CCl_3F + HCl \qquad \text{(E4.5)}$$

Shallow magma degassing could provide reactive radicals (e.g. Cl•) in ppb – ppm levels (Bobrowski *et al.*, 2003; Gerlach 2004). At the same time production of methane and other hydrocarbons through conversion of organic material at high temperature in magmatic and hydrothermal systems (Taran & Giggenbach 2003) could lead to formation of e.g. chlorinated methanes. Catalytic gas-phase chlorination cycles under magmatic-hydrothermal conditions would proceed from ((E4.6) to (E4.8)) as follow:

$$Cl\bullet + CH_4 \rightleftharpoons \bullet CH_3 + HCl \qquad (E4.6)$$

$$\bullet CH_3 + Cl_2 \rightleftharpoons CH_3Cl + Cl\bullet \qquad (E4.7)$$

$$\bullet CH_3 + Cl\bullet \rightleftharpoons CH_3Cl \qquad (E4.8)$$

The final formula for the reaction above and for further halogenation reactions is shown in ((E4.9)-(E4.12)).

$$CH_4 + Cl_2 \rightleftharpoons CH_3Cl + HCl \qquad (E4.9)$$

$$CH_3Cl + Cl_2 \rightleftharpoons CH_2Cl_2 + HCl \qquad (E4.10)$$

$$CH_2Cl_2 + Cl_2 \rightleftharpoons CHCl_3 + HCl \qquad (E4.11)$$

$$CHCl_3 + Cl_2 \rightleftharpoons CCl_4 + HCl \qquad (E4.12)$$

The produced CCl_4 could react through a catalytic gas phase reaction with magmatic HF and form CFC-11 (E4.5). We detected all products of equation (E4.9) to (E4.12) in fumarolic gas from Nicaragua (Frische *et al.*, 2005a; Frische *et al.*, 2005c), but neither CFC-11 or higher fluorinated compounds like CF_4, nor HCFCs, HFCs and fully fluorinated compounds listed above were enriched in our samples.

Our results, however, are in line with reported analyses of trace gases trapped in polar firn (Reeves *et al.*, 2005; Butler *et al.*, 1999), where no natural background for the investigated substances could be found. A significant volcanic source of CFCs as reported by Isidorov *et al.* (1990) would require a significant background concentration in pre-industrial air. These findings are not widely accepted (Gaffney 1995; Jordan 2003; Harnisch & Eisenhauer 1998) and should be used with caution.

4.6 Conclusions

Fumarolic gas samples are very commonly gas mixtures containing variable amounts of ambient air. The characteristic concentration ratios of halogenated organic compounds in the atmosphere is a potent tool for calculating the atmospheric contribution to volcanic gas samples. After subtraction of the atmospheric portion from the gas mixture, a potential geogenic fraction can be determined. This method prevents an over-estimation of atmospherically derived compounds, especially in gas samples from relatively air-enriched fumaroles like that ones at Cerro Negro. Our investigations on CFCs, HFCs, HCFCs, halons and fully fluorinated compounds in fumarolic gases demonstrate that the investigated Nicaraguan subduction zone volcanoes are not significant natural sources for such compounds. This, together with other recent analyses, suggests that many studies reporting significant emissions of fully halogenated compounds from volcanoes have not properly considered the effect of atmospheric contamination of volcanic gases.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft as part of the Sonderforschungsbereich (SFB) 574 “Volatiles and Fluids in Subduction Zones: Climate Feedback and Trigger Mechanisms for Natural Disasters” and by the Max-Planck-Society (Munich). This paper is SFB 574-contribution #xx. Special thanks go to Wilfried Strauch, Pedro Perez, and the Instituto Nicaragüense de Estudios Territoriales (INETER) for providing laboratory space and assistance during the field campaigns. Heidi Wehrmann and Armin Jordan made helpful comments on an earlier draft of this manuscript.

References

Bobrowski, N., G. Hönninger, B. Galle and U. Platt, Detection of bromine monoxide in a volcanic plume, Nature, 423, 273-276, 2003.

Butler, J.H., M. Battle, M.L. Bender, S.A. Montzka, A.D. Clarke, E.S. Saltzman, C.M. Sucher, J.P. Severinghaus and J.W. Elkins, A record of atmospheric halocarbons during the twentieth century from polar firn air, Nature, 399, 749-755, 1999.

Carr, M.J., M.D. Feigenson, L. Patino and J.A. Walker, Volcanism and Geochemistry in Central America: Progress and Problems, Inside the Subduction Factory, Geophysical Monograph 138, American Geophysical Union, 153-174, 2003.

CCVG (Commission on the Chemistry of Volcanic Gases), 2004 (http://volcgas.unm.edu/2004newsletter.pdf).

Ellis, D.A., S.A. Mabury, J.W. Martin and D.C.G Muir, Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment, Nature, 412, 321-324, 2001.

Elming, S.-A., P. Layer and K. Ubieta, A paleomagnetic study and age determinations of Tertiary rocks in Nicaragua, Central America, Geophys. J. Internat., 147(2), 294-309, 2001.

Feigenson, M.D., M.J. Carr, S.V. Maharaj, S. Juliano and L.L. Bolge, Lead isotope composition of Central American volcanoes: Influence of the Galapagos plume, Geochem. Geophys. Geosys., 4(6), 2004.

Frische, M., K. Garofalo, T.H. Hansteen and R. Borchers, Fluxes and origin of halogenated trace gases from Momotombo volcano (Nicaragua), 2005a in prep.

Frische, M., K. Garofalo, T.H. Hansteen and R. Borchers, Variations of Alkylhalide Emissions from Fumaroles in Nicaragua: Dynamics of Quiescently Degassing Volcanoes, 2005c in prep..

Gaffney, J. S., Volcanic CFCs, Environ. Sci. Technol., 29(1), A8, 1995.

Galle, B., T.H. Hansteen, M. Frische, K. Garofalo and W. Strauch, An estimate of the SO_2 emissions from four volcanoes in Nicaragua, made using mini-DOAS spectroscopy, IAVCEI 8th Field Workshop Volc. Gases, Abstr Vol., 2003.

Galle, B., Hansteen T.H., Frische M., Garofalo K. et al., Time-averaged SO_2 fluxes from Nicaraguan volcanoes, in prep..

Garofalo, K., F. Tassi, O. Vaselli, D. Tedesco, A. Delgado-Huertas, M. Frische, T.H. Hansteen and W. Strauch, Reactivation of Mombacho, 2005a, in prep..

Garofalo, K., F. Tassi, O. Vaselli, A. Delgado-Huertas, M. Frische and T.H. Hansteen, unpubl. data in prep..

Gerlach, T.M., Volcanic sources of tropospheric ozone-depleting trace gases, Geochem., Geophys., Geosys., 5, Q09007, 2004.

Giggenbach, W.F. & R.L. Goguel, Method for the collection and analysis of geothermal and volcanic water and gas samples: NZ-DSIR Report, CD 2387, 53, 1989.

Giggenbach, W.F., Chemical composition of volcanic gases, in Scarpa, M. and R.J. Tilling, eds., Monitoring and mitigation of Volcanic Hazards, Berlin Heidelberg, Springer, 221-256, 1996.

Giggenbach, W.F., D. Tedesco, Y. Sulistiyo, A. Caprai, R. Cioni, R. Favara, T.P. Fischer, J.-I. Hirabayashi, M. Korzhinsky, M. Martini, I. Menyailov and H. Shinohara, Evaluation of results from the fourth and fifth IAVCEI field workshops on volcanic gases, Vulcano island, Italy and Java, Indonesia, J. Volcanol Geotherm. Res., 108 (1-4), 157-172, 2001.

Halmer, M., H.-U. Schmincke and H.-F. Graf, The annual volcanic gas input into the atmosphere, in particular into the stratosphere: a global data set for the past 100 years, J. Volcanol. Geotherm. Res., 115, 511-528, 2002.

Harnisch, J. and A. Eisenhauer, Natural CF_4 and SF_6 on Earth, Geophys. Res. Let., 25(13), 2401-2404, 1998.

Harnisch, J., M. Frische, R. Borchers, A. Eisenhauer and A. Jordan, Natural fluorinated organics in fluorite and rocks, Geophys. Res. Let., 27, 1883-1886, 2000.

Hill, B.E., P.C. La Femina, C.B. Connor, W. Strauch, G. Davoli, G. Guevera and A. Saballos, August 1999 eruption of Cerro Negro volcano, Nicaragua, successfully forecast using time-volume relationship, EOS, Trans. Am. Geophys. Union, 80(46), F1111, 1999.

Inn, E.C.Y., J.F. Vedder and E.P. Condon, Gaseous Constituents in the Plume from Eruptions of Mount St. Helens, Science, 211, 821-823, 1981.

IPCC (Intergovernmental Panel on Climate Change), Climate Change 2001: The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, edited by J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell and C.A. Johnson, 881 pp., Cambridge University Press, Cambridge, U.K., 2001.

Isidorov, V.A., I.G. Zenkevich and B.V. Ioffe, Volatile Organic Compounds in Solfataric Gases, J. Atmos. Chem., 10, 329-340, 1990.

Jordan, A., J. Harnisch, R. Borchers, F. Le Guern and H. Shinohara, Volcanogenic Halocarbons, Environm. Sci. Technol., 34(6), 1122-1124, 2000.

Jordan, A., Volcanic Formation of Halogenated Organic Compounds. The Handbook of Environmental Chemistry. Berlin Heidelberg, Springer-Verlag. 3, Part P, 121-139, 2003.

La Femina, P.C., C.B. Connor, B.E. Hill, W. Strauch, J.A. Saballos, Magma-tectonic interactions in Nicaragua: the 1999 seismic swarm and eruption of Cerro Negro volcano, J. Volcanol. Geotherm. Res., 137, 187-199, 2004.

McBirney, A.R. and H. Williams, Volcanic history of Nicaragua, Univ. Calif. Pub. Geo. Sci., 55, 1-65, 1965.

McCulloch, A., P. Ashford and P.M. Midgley, Historic Emissions of Fluorotrichloromethane (CFC-11) Based on a Market Survey Atmos. Environ., 35(26), 4387-4397, 2001.

Menyailov, I.A., L.P. Nikitina, V.N. Shapar and V.P. Pilipenko, Temperature increase and chemical change of fumarolic gases at Momotombo volcano, Nicaragua, in 1982-1985: Are these indicators of a possible eruption?, J. Geophys. Res. 91(B12), 12199-12214, 1986.

Montegrossi, G., F. Tassi, O. Vaselli, A. Buccianti and K. Garofalo, Sulfur species in volcanic gases, Anal. Chem., 73(15), 3709-3715, 2001.

Ohsawa, S., Y. Yusa, K. Oue and K. Amita, Entrainment of atmospheric air into the volcanic system during the 1995 phreatic eruption of Kuju Volcano, Japan, J. Volcanol. Geotherm. Res., 96, 33-43, 2000.

Rasmussen, R.A., M.A.K. Khalil, R.W. Dalluge, S.A. Penkett and B. Jones, Carbonyl sulfide and carbon disulfide from the eruptions of Mount St. Helens. Science, 215(4533), 665-667, 1982.

Rasmussen, R.A., S.A. Penkett and N. Prosser, Measurement of carbon tetrafluoride in the atmosphere, Nature, 277, 549-551, 1979.

Reeves, C.E., W.T. Sturges, G.A. Sturrock, K. Preston, D.E. Oram, J. Schwander, R. Mulvaney, J.M. Barmola and J. Chappellez, Atmospheric trends of the halon gases from polar firn air, Atmos. Chem. Phys. Diskuss., 5, 937-960, 2005.

Saito, G., H. Shinohara and K. Kazahaya, Successive sampling of fumarolic gases at Satsuma-Iwojima and Kuju volcanoes, southwest Japan: Evaluation of short-term variations and precision of the gas sampling and analytical techniques, Geochem. J., 36(1), 1-20, 2002.

Schwandner, F.M., T.M. Seward, A.P. Gize, P.A. Hall and V.J. Dietrich, Diffuse emission of organic trace gases from the flank and crater of a quiescent active volcano (Vulcano, Aeolian Islands, Italy), J. Geophys. Res., 109, D04301, doi:10.1029/2003JD003890, 2004.

Stoiber, R.E., D.C. Leggett, T.F. Jenkins, R.P. Murrmann and W.I. Rose, Organic compounds in volcanic gas from Santiaguito volcano, Guatemala, Geol. Soc. Am. Bull., 82, 2299-2302, 1971.

Symonds, R.B., Y. Mizutani and P.H. Briggs, Long-term geochemical surveillance of fumaroles at Showa-Shinzan dome, Usu volcano, Japan, J. Volcanol. Geotherm. Res., 73, 177-211, 1996.

Symonds, R.B., W.I. Rose and M.H. Reed, Contribution of Cl- and F-bearing gases to the atmosphere by volcanoes, Nature, 334, 415-418, 1988.

Taran, Y.A. and W.F. Giggenbach, Geochemistry of Light Hydrocarbons in Subduction-Related Volcanic and Hydrothermal fluids, Society of Econom. Geol., Spec. Publication, 10, 61-74, 2003.

Tedesco, D. and K. Nagao, Radiogenic ^{4}He, ^{21}Ne and ^{40}Ar in fumarolic gases on Vulcano: implication for the presence of continental crust beneath the island, Earth Planet. Sci. Lett., 144, 517-528, 1996.

Thompson, T.M., J. H. Butler, B.C. Daube, G.S. Dutton, J.W. Elkins, B.D. Hall, D.F. Hurst, D.B. King, E.S. Kline, B.G. Lafleur, J. Lind, S. Lovitz, D.J. Mondeel, S.A. Montzka, F.L. Moore, J.D. Nance, J.L. Neu, P.A. Romashkin, A. Scheffer and W.J. Snible, 5. Halocarbons and other Atmospheric Trace Species, in Climate Monitoring and Diagnostics Laboratory, Summary Report No. 27, 2002-2003, 115-133, edited by R. C. Schnell, A.-M. Buggle and R. M. Rosson, NOAA CMDL, Boulder, CO, 2004.

UNEP (United Nations Environment Programme), Handbook for the International Treaties for the Protection of the Ozone Layer– 6th edition, 2003, (http://www.unep.org/ozone/pdfs/Handbook-2003.pdf)

UNFCCC (United Nations Framework Convention on Climate Change), Kyoto Protocol to the United Nations Framework Convention on Climate Change, UNEP/INC/98/2, Information Unit for Conventions, UNEP, Geneva, 1998, (http://unfccc.int/resource/docs/convkp/kpeng.pdf).

Vallance, J.W., S.P. Schilling and G. Devoli, Lahar Hazards at Mombacho Volcano, Nicaragua, USGS Open-File Report 01-455, 2001.

van Wyk de Vries, B. and P. W. Francis, Catastrophic collapse at stratovolcanoes induced by gradual volcano spreading, Nature, 387, 387-390, 1997.

Wahrenberger, C.M., Some Aspects of the chemistry of volcanic gases, Diss. ETH Zuerich, 1997.

Walther, C.H.E., E.R. Flueh, C.R. Ranero, R. von Huene and W. Strauch, Crustal structure across the pacific margin of Nicaragua: Evidence for ophiolitic basement and a shallow mantle sliver, Geophys. J. Int., 141, 759-777, 2000.

WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project - Report No. 47, 498pp., Geneva, 2003.

Appendix

Trace gas data Chapter 2 and 4

Sample	Mo_2_28_F1	Mo_3_48_F1	Mo_3_49_F1	Mo_4_2_F1	Mo_4_3_F1	Mo_4_15_F1	Mo_4_23_F1	Mo_5_1_F1	Mo_5_2_F1	Mo_5_3_F1
Temperature	751°C	776°C	776°C	760°C	760°C	760°C	761°C	739°C	739°C	739°C
Date	11.08.01	8.03.02	8.03.02	17.11.02	17.11.02	18.11.02	19.11.02	12.07.03	12.07.03	12.07.03
Time	13:45	13:05	13:15	11:00	11:05	15:00	7:30	12:45	12:50	12:55
CH_3Cl	4,844	2,846	5,018	85,198	68,430	69,012	145,798	103,888	150,781	31,999
CH_3Br	641	336	345	3,066	12,178	5,339	23,850	12,619	74,546	3,829
CH_3I	501	235	243	4,989	11,795	8,518	24,374	18,334	23,259	7,238
CH_2Cl_2	273	95	98	1,360	811	668	699	59	98	129
$CHCl_3$	104	b.d.l.	31	346	375	275	692	68	136	72
CCl_4	b.d.l.	148	62	175	161	44	113	b.d.l.	b.d.l.	31
C_2H_5Cl	b.d.l.	314	111	4,149	2,154	1,244	5,491	1,513	1,365	244
C_2H_5Br	n.q.	n.q.	n.q.	n.q.	78	48	721	70	477	b.d.l.
C_2H_5I	b.d.l.	b.d.l.	b.d.l.	20	218	178	1,183	210	305	75
C_2H_3Cl	184	123	141	780	318	289	1,144	243	867	104

Table A *Concentrations of halohydrocarbons in headspace gas from fumarole F1 of Momotombo in [pptv] (b.d.l.: below detection limit, n.q.: not quantified).*

Sample	Mo_4_5_F2	Mo_4_12_F2	Mo_4_16_F2	Mo_4_24a_F2	Mo_5_8_F2	Mo_5_9_F2	Mo_5_10_F2
Temperature	615°C	615°C	615°C	616°C	600°C	600°C	600°C
Date	17.11.02	18.11.02	18.11.02	19.11.02	12.07.03	12.07.03	12.07.03
Time	16:00	9:45	15:15	7:55	13:30	13:35	13:40
CH_3Cl	83,491	38,274	162,666	48,658	8,026	20,949	17,030
CH_3Br	18,710	11,875	42,104	19,261	1,769	2,636	3,440
CH_3I	10,389	15,232	32,768	8,411	3,896	4,490	4,705
CH_2Cl_2	1,464	711	627	1,619	197	166	b.d.l.
$CHCl_3$	549	412	222	690	183	28	53
CCl_4	175	75	164	359	b.d.l.	b.d.l.	b.d.l.
C_2H_5Cl	12,099	2,367	3,905	4,960	467	1,509	975
C_2H_5Br	2,150	311	540	303	71	249	168
C_2H_5I	1,021	492	759	308	213	546	456
C_2H_3Cl	1,612	n.q.	520	1,592	280	232	169

Table B *Concentrations of halohydrocarbons in headspace gas from fumarole F2 of Momotombo in [pptv] (b.d.l.: below detection limit, n.q.: not quantified).*

Sample	Mo_4_6_F3	Mo_4_7_F3	Mo_4_10_F3	Mo_4_19_F3
Temperature	472°C	472°C	475°C	475°C
Date	17.11.02	17.11.02	18.11.02	18.11.02
Time	17:25	17:30	8:00	16:40
CH_3Cl	6,483,819	12,663,939	19,633,504	7,073,056
CH_3Br	465,443	460,376	763,646	846,323
CH_3I	358,572	401,265	1,394,834	1,466,499
CH_2Cl_2	30,179	14,928	53,795	15,982
$CHCl_3$	17,105	50,930	25,910	10,157
CCl_4	n.q.	303	430	n.q.
C_2H_5Cl	701,457	398,647	784,930	324,975
C_2H_5Br	n.q.	19,790	69,614	47,971
C_2H_5I	6,246	26,680	110,216	96,749
C_2H_3Cl	2,822	6,266	10,206	4,799

Table C *Concentrations of halohydrocarbons in headspace gas from fumarole F3 of Momotombo in [pptv] (b.d.l.: below detection limit, n.q.: not quantified).*

Sample	CN_2_19_F0	CN_2_25_F0	CN_4_2_F1	CN_4_10_F1	CN_4_17_F1	CN_4_18_F1	CN_4_19_F1
Temperature	340°C	340°C	260°C	293°C	282°C	282°C	282°C
Date	30.07.01	2.08.01	24.11.02	25.11.02	5.12.02	5.12.02	5.12.02
Time	12:20	13:05	10:00	11:30	12:45	12:47	12:48
CH_3Cl	2,374	2,163	5,059	27,674	15,035	6,910	3,740
CH_3Br	186	348	705	4,442	1,040	445	266
CH_3I	307	168	233	978	2,567	995	733
CH_2Cl_2	52	122	117	b.d.l.	280	452	49
$CHCl_3$	34	180	1,883	259	5,213	4,516	1,211
CCl_4	b.d.l.	b.d.l.	123	b.d.l.	b.d.l.	b.d.l.	b.d.l.
C_2H_5Cl	b.d.l.	b.d.l.	177	b.d.l.	887	229	90
C_2H_5Br	n.q.	n.q.	16	b.d.l.	n.q.	b.d.l.	b.d.l.
C_2H_5I	4	b.d.l.	12	5	8	35	31
C_2H_3Cl	115	26	139	83	444	204	96

Table D *Concentrations of halohydrocarbons in headspace gas from fumaroles of the main crater of Cerro Negro in [pptv] (b.d.l.: below detection limit, n.q.: not quantified).*

Sample	CN_5_1_F1a	CN_5_2_F1a	CN_5_3_F1b	CN_5_4_F1b	CN_5_5_F0
Temperature	315°C	315°C	290°C	290°C	369°C
Date	21.07.03	21.07.03	21.07.03	21.07.03	21.07.03
Time	9:55	10:00	10:45	10:50	11:20
CH_3Cl	9,955	7,050	2,727	2,733	6,241
CH_3Br	616	372	80	77	236
CH_3I	675	1,239	563	539	1,277
CH_2Cl_2	309	95	29	12	164
$CHCl_3$	375	124	38	124	1,534
CCl_4	b.d.l.	b.d.l.	b.d.l.	b.d.l.	83
C_2H_5Cl	b.d.l.	b.d.l.	4	b.d.l.	b.d.l.
C_2H_5Br	6	b.d.l.	b.d.l.	b.d.l.	b.d.l.
C_2H_5I	3	6	b.d.l.	b.d.l.	3
C_2H_3Cl	94	16	27	35	148

Table E *Concentrations of halohydrocarbons in headspace gas from fumaroles of the main crater of Cerro Negro in [pptv] (b.d.l.: below detection limit, n.q.: not quantified).*

Sample	Momba_2_23_F1	Momba_3_57_F1	Momba_3_59_F1	Momba_4_2_F1	Momba_4_3_F1	Momba_4_7_F1	Momba_4_8_F1
Temperature	120°C	121°C	121°C	119°C	119°C	120°C	120°C
Date	28.07.01	12.03.02	12.03.02	28.11.02	28.11.02	30.11.02	30.11.02
Time	13:30	13:00	13:10	13:35	13:40	12:11	12:13
CH_3Cl	663	478	195	1,412	1,816	1,233	1,615
CH_3Br	67	59	43	27	13	b.d.l.	66
CH_3I	22	26	25	37	43	28	n.q.
CH_2Cl_2	459	67	80	147	81	85	82
$CHCl_3$	329	b.d.l.	b.d.l.	b.d.l.	b.d.l.	56	b.d.l.
CCl_4	b.d.l.	b.d.l.	b.d.l.	104	b.d.l.	61	35
C_2H_5Cl	b.d.l.	b.d.l.	b.d.l.	80	144	60	92
C_2H_5Br	n.q.	n.q.	n.q.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
C_2H_5I	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	29
C_2H_3Cl	b.d.l.	24	15	65	19	38	86

Table F *Concentrations of halohydrocarbons in headspace gas from fumarole F1 of Mombacho in [pptv] (b.d.l.: below detection limit, n.q.: not quantified).*

Sample	Momba_5_1_F1	Momba_5_2_F1	Momba_5_3_F1
Temperature	119°C	119°C	119°C
Date	18.07.03	18.07.03	18.07.03
Time	12:30	12:35	13:00
CH_3Cl	1,386	999	1,820
CH_3Br	36	18	17
CH_3I	182	37	68
CH_2Cl_2	111	27	53
$CHCl_3$	141	177	140
CCl_4	n.q.	b.d.l.	b.d.l.
C_2H_5Cl	b.d.l.	b.d.l.	b.d.l.
C_2H_5Br	b.d.l.	b.d.l.	b.d.l.
C_2H_5I	30	b.d.l.	b.d.l.
C_2H_3Cl	99	b.d.l.	b.d.l.

Table G *Concentrations of halohydrocarbons in headspace gas from fumarole F1 of Mombacho in [pptv] (b.d.l.: below detection limit, n.q.: not quantified).*

Trace gas data Chapter 3

Sample	Mo_2_28	Mo_3_48	Mo_3_49	Mo_4_2	Mo_4_3	Mo_4_15	Mo_4_23	Mo_5_1	Mo_5_2	Mo_5_3
Fumarole	F1	F1	F1	F1	F1	F1	F1	F1	F1	F1
Temperature	751°C	776°C	776°C	760°C	760°C	760°C	761°C	739°C	739°C	739°C
Date	11.08.01	8.03.02	8.03.02	17.11.02	17.11.02	18.11.02	19.11.02	12.07.03	12.07.03	12.07.03
Time	13:45	13:05	13:15	11:00	11:05	15:00	7:30	12:45	12:50	12:55
CH_3Cl	5,258	4,170	7,140	84,177	67,635	68,449	142,901	98,432	136,010	30,632
CH_3Br	656	385	411	2,876	11,992	5,288	23,326	11,877	66,547	3,571
CH_3I	504	352	328	4,919	11,605	8,428	23,825	17,229	20,768	6,691
C_2H_5Cl	b.d.l.	380	135	3,857	2,119	1,230	5,367	571	1,235	239
C_2H_5Br	n.q.	n.q.	n.q.	n.q.	77	47	704	66	425	15
C_2H_5I	b.d.l.	b.d.l.	n.q.	19	214	176	1,157	199	276	72
CH_2Cl_2	315	281	360	1,373	838	684	734	79	137	150
$CHCl_3$	115	b.d.l.	77	352	382	280	693	75	138	79
CCl_4	79	325	339	221	218	78	186	74	174	232
C_2H_3Cl	185	127	150	769	313	286	1,119	230	777	99

Table H *Concentrations of halohydrocarbons in headspace gas from fumarole F1 of Momotombo in [pptv] (b.d.l.: below detection limit, n.q.: not quantified).*

Sample	Mo_4_5	Mo_4_12	Mo_4_16	Mo_4_24a	Mo_5_8	Mo_5_9	Mo_5_10	Mo_4_6	Mo_4_7	Mo_4_10	Mo_4_19	Mo_4_22
Fumarole	F2	F2	F2	F2	F2	F2	F2	F3	F3	F3	F3	F3
Temperature	615°C	615°C	615°C	616°C	600°C	600°C	600°C	472°C	472°C	475°C	475°C	478°C
Date	17.11.02	18.11.02	18.11.02	19.11.02	12.07.03	12.07.03	12.07.03	17.11.02	17.11.02	18.11.02	18.11.02	19.11.02
Time	16:00	9:45	15:15	7:55	13:30	13:35	13:40	17:25	17:30	8:00	16:40	7:00
CH_3Cl	82,131	38,046	158,381	47,893	9,786	21,489	18,444	6,338,287	11,839,612	19,078,648	6,612,732	1,028,259
CH_3Br	18,248	11,633	40,871	18,436	1,709	2,562	3,114	454,991	430,409	742,064	791,186	123,914
CH_3I	10,119	14,895	31,796	8,034	3,608	4,292	4,144	350,517	375,126	1,355,352	1,370,918	135,054
C_2H_5Cl	11,781	2,314	3,789	4,734	459	1,454	891	685,699	372,675	762,709	303,794	48,844
C_2H_5Br	2,093	304	524	289	65	236	146	n.q.	18,500	67,644	44,845	10,362
C_2H_5I	994	481	737	294	203	524	407	6,105	24,942	107,096	90,443	11,449
CH_2Cl_2	1,533	776	680	1,733	247	209	115	29,518	14,051	52,395	15,029	1,161
$CHCl_3$	570	430	239	720	197	44	87	16,726	47,643	25,217	9,525	677
CCl_4	330	193	265	619	281	173	217	n.q.	425	599	n.q.	340
C_2H_3Cl	1,570	n.q.	504	1,519	262	224	155	2,759	5,857	9,918	4,487	2,269

Table I *Concentrations of halohydrocarbons in headspace gas from fumarole F2 and F3 of Momotombo in [pptv] (n.q.: not quantified).*

Lebenslauf

Matthias Frische

Geb. am 17.12.1966
in Göttingen
Staatsangehörigkeit: deutsch

Jun. 1994	Abitur in Göttingen
Okt. 1994 - Feb. 2000	Studium der Mineralogie (Diplom) mit Schwerpunkt Petrologie, Geochemie und Lagerstättenkunde an der Universität Göttingen (11 Semester) Abschluss: Diplom-Mineraloge
Jul. 2001 - März 2005	Wissenschaftlicher Angestellter (Doktorand) am SFB 574 der Universität Kiel
Sep. 2003 - Sep. 2004	Studium der Mineralogie (Promotion) an der Universität Kiel (2 Semester)