MULTIDISCIPLINARY INVESTIGATIONS ON THE MASS AND ENERGY BUDGETS IN THE ITALIAN ACTIVE VOLCANOES

SCIENTIFIC COORDINATOR OF THE PROJECT : **Prof. Mariano Valenza**

Dipartimento di Chimica e Fisica della Terra (CFTA)
Via Archirafi # 36- 90123 Palermo Italy,
tel: (+39) 091-6175400/6161574,
fax: (+39) 091-6168376,
E-Mail: valenza@pa.ingv.it.

ACTIVITY REPORT – 2nd YEAR

LIST OF PARTECIPANTS

RU	AFFILATION	RESPONSIBLE
1	Dip. CFTA UNIPA	Valenza Mariano
2	IGGI C.N.R. Pisa	Cioni Roberto
3	CNRS LSCE, CEA-CNRS	Allard Patrick
4	INGV-Ct	Caltabiano Tommaso
5	Dip. Geomineralogico UNIBA	Vurro Filippo
6	INGV-Pa	Gurrieri Sergio
7	Dip. CFTA UNIPA	Parello Francesco
8	INGV-Pa	Favara Rocco
9	INGV-Pa	D'Alessandro Walter

GENERAL OBJECTIVES

The final objective of the present project is **defining the budgets of mass and energy of Etna by means of a multidisciplinary approach**. According to the modalities of mass and energy transfer toward the surface, this project will be articulated through the following three lines:

1. direct and remote measures in the plume;
2. measurements of the diffuse soil gas emissions;
3. measurements of the concentrations of major, minor and trace constituents in ground waters, discrimination of the volcanic component, estimates of ground water discharge.

The research activities of the second year were essentially those reported in the original project except for some changes in the program derived from:

- the suggestions of the Evaluation Committee on the First Year of Activity.
- the still on going eruption on Mt Etna. In particular, during the second half of 2002 the volcanic activity increased and in October a new eruption started. In this context the remote measurements of the SO_2 output and S/Cl ratio in the

plume and the soil degassing surveys at the Zafferana and Paternò areas have been intensified.

1. Plume investigations.

The objectives of RU **1, 3, 4, 5** focussed on the quantification of the budget of volatiles released from the volcanic plume of Mt. Etna, by the use of different and complementary methodologies (COSPE, FTIR, DIRECT SAMPLING). The research units involved performed the following activities:

- In situ active and passive techniques of sampling and analysis of plume volatiles (**RU 1**). The method used included: (a) common filtration techniques ("filter packs"), allowing for the determination of acidic gases and airborne particles in the plume; (b) passive samplers, which diffusely collect acidic gases in air and provide mean concentrations of SO_2, HCl and HF during their exposure time; (c) continuous spectro-fotometric determination of CO_2, SO_2 and H_2S in the plume atmosphere. Among the main results, the measure of elemental/sulphur dioxide ratios allowed the computation of elemental fluxes by coupling with COSPEC measurements, providing a new and accurate reference point for the assessment of volatile atmospheric emission rates from Etna and for a careful evaluation of the impact of volcanic emissions on the regional environmental. Secondly, the analysis SO_2/HCl and HCl/HF ratios allowed to define the features of a degassing model, which provided insights helpful in tracking the progressive exhausting trend of volatiles during the 2001 eruption. The forecasting capabilities of the model are actually under testing during the eruptive phase which started at Etna on October 2002 and is still taking place. Results acquired up to now highlighted fluctuating SO_2/HCl (from low to high, and the to low again), indicative of a discontinuous but persistent replenishment of the magma batch involved in the eruption.

- Several remote sensing measurements of the volcanic plume composition using an open-path Fourier Transform Infrared (FTIR) spectrometer. Simultaneously the concentration ratios of three volcanic gas components in the plume - SO_2, HCl e HF – and their variations along with volcanic activity have been determined (**UR3**). Measurements relatively close to the lateral vent have been performed in order to determine CO2, CO and H2O in the gases of high temperature. These measurements combined with COSPEC data for the SO_2 flux (UR 4) and with the data acquired by UR1 , provide an accurate estimates of the fluxes of the acidic gases as well as the other volatiles. Furthermore , about two hundred of melt inclusions trapped in olivine crystals were analyzed in the erupted lavas to confirm the simultaneous extrusion of two different magmas during the 2001 eruption and to reinforce the interpretation of FTIR data.

- Period campaigns of SO2 flux measurements from Etna's Summit Craters were carried out, which frequency was intensified (up to two-three measurements per week) due to the renewal of volcanic activity at Etna since the second half of 2001. In the study period, SO2 flux emission averaged 5200 t/d (metric tons per day), and showed the following time features: a minimum value (1100 t/d, 9 May 2001), marking the start of a significant increasing trend which ended with the onset of the 2001 eruptive event; ii) high values associated with the July-August 2001 eruption, with a maximum value of about 20500 t/d (July, 20th); low SO2 values recorded since the end of the 2001 eruption (**UR4**). The acquired data provide a baseline for the computation of the fluxes of other elements. Also, the correlation between plume SO2 fluxes and soil CO2 output was investigated.

- The second year activities of (**UR 5),** focusing on the mineralogical characterization of sub-volcanic sublimates on Etna and Vulcano Island, were just funded for the handling and interpretation of data acquired during the first year of activities.

2. CO_2 Output from the ground.

The objectives for the second year included soil gas investigations in new unexplored areas and a drilling of explorative borehole to study degassing processes at different depths (**UR6**).
All the second year objectives of this task were totally reached with exception of the delay in the drilling of the borehole. This was due to volcanic emergency and the consequent need of extending the soil gas surveys to the top of the volcanic edifice. The borehole is planned to be drilled in January 2003.

- The new investigated area for soil degassing surveys (Pernicana Fault, Sapienza and Citelli huts, Ragalna faults and Piano del Lago) were characterized by low CO2 fluxes.
- NE-SW trending soil degassing anomaly was detected at the Piano del Lago, the area interested by the recent 2001 and 2002 eruptions.
- Electronics and sensors to investigate degassing inside the borehole were developed and successfully tested at ground level by two remote stations.

3. Ground water investigations.

The main objective of this line of research was the definition of the input of deep volcanic fluids in the aquifers of Etna volcano.

- 16 Rainwater samples and 14 rainwater samples were collected each month and analysed in order to determine O and H isotopic composition. Furthermore, in the upper part of Etna two devices to collect the liquid equivalent of solid

precipitation were installed. These last samples gave the first results on the amount and on isotopic composition of solid precipitation on Mt. Etna (**RU 8**).

- Groundwater samples were periodically collected in the Etnean area at thirty sampling sites, and analysed for their major, minor and trace composition, as long as O and H isotope composition. Data have been critically evaluated in order to assess the mean discharge rate of chemical in the Etnean aquifer (**RU 9**).

- The experimental study on the dissolution of Etna rocks and minerals has been continued for the investigation of some trace elements behaviour during the watering process (**RU 7**). The experimental results have been compared to the results of the (**RU 9**) and a first simple model for the main aquifer has been performed.

- Rainwater samples were periodically collected at 16 rain gauges, and analysed for major ion content. These data will be used in the third year project in order to get a quantification of the magnitude of wet deposition processes in the Etnean area (**RU 9**).

- The multi parametric probe prototype to measure T, piezometric level, pH and conductivity in natural waters has been realized. A very interesting result is that the probe accurately works in the range 50 -120 °C **(RU 2)**.

MAJOR AND TRACE ELEMENTS IN THE GASES AND PARTICULATE OF THE PLUME.

RU 1 Responsible**:** Prof. **Mariano Valenza –** Full Professor
Dipartimento di Chimica e Fisica della Terra ed Applicazioni, Università di Palermo.

ACTIVITY REPORT - 2° YEAR

RU Partecipants:

Name – Position	Affiliation	Months/man
Prof. Mariano Valenza Full Professor	Dip Chimica e Fisica della Terra ed Applicazioni UNIPA	4
Prof. Gaetano Dongarra' Full Professor	Dip Chimica e Fisica della Terra ed Applicazioni UNIPA	3
Dr. Benedetto Badalamenti Researcher	Istituto Geochimica dei Fluidi CNR di Palermo	2
Dr. Alessandro Aiuppa Researcher	Dip Chimica e Fisica della Terra ed Applicazioni UNIPA	1

2nd YEAR OBJECTIVES

The main objective of UR1 Research Unit for the second year was to contribute, in collaboration with units UR 3, 4 e 5, to the quantification of the budget of volatiles released from the volcanic plume of Mt. Etna. The targets of the research project included: (a) major compounds (SO_2, inorganic acids), which relative abundances in volcanic plumes are known to be precious indicators of volcanic activity; (b) trace species, such as heavy metals, with the aim of getting new data useful in increasing our understanding of volcanic particulate airborne matter.
In the second year, the main aim of the research was to use the field data acquired during the first year in order to draw up a coherent geochemical interpretative model concerning: (i) the dynamics of degassing processes at Etna, and the chemical fractionations taking place during melt-vapor separation processes; (ii) the relationships between plume chemistry and volcanic activity; iii) the estimate of volatile output rates from Etna, including volcanic activity states ranging from quite steady-degassing to eruptive. Furthermore, it was planned for the second year project the development of new methodologies for the "passive" air sampling of volcanogenic volatiles. The techniques to be developed were devoted to the measurements of acidic gases in the atmosphere of rural sites from the upper and lower slopes of Etna, with the aim of quantifying the possible effects of volcanic emissions on the local environment and the chemical evolution of some species during atmospheric dispersion.

2ndYEAR RESULTS

Data acquisition and analysis: Basing on the samples collected with active techniques in spring-summer 2001, both on the summit crater plume and on the plume of the eruptive fracture opened during the 2001 eruption, it has been possible to get original data useful for (i) a better assessment of magmatic degassing processes at Etna; (ii) a new evaluation of the budget of atmospheric volatiles at Etna.

The analysis of data concerning the abundance of acidic gases in the plume (Aiuppa et al., 2002a) allowed to define the features of a degassing model concerning SO_2, HCl and HF. According to the model, a plume gas phase with volatile ratios S/Cl ~2.5 and Cl/F ~5 is released during steady-state non-eruptive degassing at Etna. These characteristic ratios are interpretable as resulting from significant (S, ~ 50%; Cl, ~20%; F, ~ 5%) open-system degassing of Etnean

hawaiites, with solubility ratios among volatiles (given by Henry's constant ratios) being H_S/H_{Cl} ~ 0.33 e H_S/H_F ~ 0.18, respectively. The model also allows interpreting the chemistry of plume volatiles emitted by the eruptive fracture opened on the southern flank of Etna at an altitude of 2100m, having elemental ratios S/Cl ~ 0.1-0.3 and Cl/F ~ 1. According to the model, this composition is representative of degassing from a residual magma, which suffered extensive open-system Raleigh-type degassing upon emplacement. During the 2001 eruption, the model provided insights helpful in tracking the progressive exhausting trend of volatiles from the small batch of magma involved in the eruption. Also, the forecasting bents of such a model are actually under testing, thanks to the analysis of gas samples collected on the eruptive fracture opened at 2750m altitude on the southern flank of Etna volcano during the eruptive phase which started on October 2002 and is still taking place.

Data collected during the first two years of the present project allowed a new and accurate estimate of volatile emission rates from Etna plume. The plume fluxes of Cl, F and trace metals, provided in the table, were computed based on SO_2 fluxes measured by COSPEC during May-June 2001 by Caltabiano et al. 2001 (pers. comm.). Data listed in the table constitute a reference point for a more precise estimate of volatile atmospheric emission rates from Etna and for a careful evaluation of the impact of volcanic emissions on the regional environmental. They also demonstrate further the huge contribution of Etna to the global volcanic flux of volatiles (about 10% of total volcanic emissions).

$S0_2$*	**HCl**	**HF**	**Ag**	**Al**	**As**	**A u**	**Ba**	**Bi**	**Br**	**Ca**	**Cd**	**Ce**
3450	1130	154	0.002	106	0.07	0.0003	0.15	0.02	1.3	22.4	0.04	0.04
Co	**Cr**	**Cs**	**Cu**	**Dy**	**Er**	**Eu**	**Fe**	**Ga**	**Gd**	**Ge**	**Hf**	**Hg**
0.06	0.04	0.01	1.1	0.0014	0.0007	0.0009	11.2	0.015	0.003	0.001	0.001	0.002
Ho	**I**	**In**	**K**	**La**	**Li**	**Lu**	**Mg**	**Mn**	**Mo**	**Na**	**Nb**	**Nd**
0.0002	0.027	0.006	28.6	0.02	0.01	0.00009	7.7	0.9	0.01	22.5	0.01	0.02
Ni	**Pb**	**Pr**	**Pt**	**Rb**	**Re**	**Sb**	**Sc**	**Se**	**Si**	**Sm**	**Sn**	**Sr**
0.02	0.15	0.004	0.00002	0.14	0.0008	0.94	0.01	0.17	13.2	0.0034	0.0008	0.30
Tb	**Te**	**Th**	**Ti**	**Tl**	**Tm**	**U**	**V**	**W**	**Y**	**Yb**	**Zn**	**Zr**
0.0003	0.0130	0.0027	4.5	0.11	0.0001	0.002	0.13	0.0006	0.008	0.0006	0.25	0.04

Table 1 – Element emission rates from Etna (T/day) – May-June 2001.
* Data from Caltabiano et al. 2001 (Pers. Comm.)

The significant emission rates from Etna are responsible for important effects on the regional atmospheric environments. In order to better evidence this important topic, which has been the object of several investigations in the past, a network of 20 passive samplers was installed on Etna during the second year of the project. The samplers are able to diffusely collect acidic gases in air, and to provide a mean concentrations of SO_2, HCl and HF during the exposure time (one month). Data collected on a first preliminary survey highlight that the whole Etnean area is affected by a generalized deposition of volcanogenic volatiles, with concentrations of volatiles far above the background concentrations. A systematic trend of increasing SO_2, HCl and HF concentrations, from low (2, 0.1 e <0.1 $\mu g/m^3$) in distal location, up to very high (370, 74 e 3 $\mu g/m^3$) close to the summit craters is observed.

RESEARCH PRODUCTS
n° 4 articles published on international journals
n° 1 automatic station for the continuous monitoring of CO_2, H_2S, $SO2_2$

PUBLICATION LISTS

AIUPPA A., FEDERICO C., PAONITA A., PECORAINO G., VALENZA M. (2002) S, Cl and F degassing as an indicator of volcanic activity: the 2001 eruption of Mount Etna. Geophys Res. Lett., Vol. 26, July 2002.

AIUPPA A., FEDERICO C., PAONITA A., PECORAINO G., VALENZA M. (2002) Degassing of trace volatile elements during the 2001 eruption of Mount Etna. AGU Geophysical monographies, Volcanism and the Earth atmosphere (submitted).

BADALAMENTI B., LIOTTA M., VALENZA M. (2001) An automatic system for continuous monitoring of CO_2, H_2S and SO_2 and meteorological parameters in the atmosphere of volcanic areas. Geochem. Trans 5.

AIUPPA A., BONFANTI P., BRUSCA L., D'ALESSANDRO W., FEDERICO C., PARELLO F. (2001) Evaluation of the environmental impact of volcanic emission from the chemistry of rainwater: Mount Etna area (Sicily). Appl. Geochem. 16, 985-1000.

AIUPPA A., P. ALLARD, W. D'ALESSANDRO, S. GIAMMANCO, F. PARELLO & M. VALENZA, Magmatic Gas Leakage at Mount Etna (Sicily, Italy): Relationships with the Volcano-Tectonic Structures, the Hydrological Pattern and the Eruptive Activity. AGU Monography on Mt. Etna (submitted, 2002).

DESIGN AND MANUFACTURE OF A PROTOTIPE MULTIPARAMETRIC PROBE FOR THE MEASUREMENT OF T, PIEZOMETRIC LEVEL, pH, AND ELECTRIC CONDUCTIVITY IN WELLS WITH TEMPERATURES BETWEEN 50 AND 120 °C.

RU 2 Responsible **:Roberto Cioni** Senior Researcher IGGI - CNR ,Pisa

ACTIVITY REPORT –2nd YEAR

RU PARTICIPANTS

Name – position	affilation	months/man
Roberto cioni - Senior Researcher	IGGI - CNR	3
Scozzari Andrea - Researcher	IGGI - CNR	3
Raco Brunella – Researcher	IGGI - CNR	3

- 2nd YEAR OBJECTIVES

  Laboratory test, revision of the project, tests on the field (Vulcano Island)

- 2nd YEAR RESULTS

Laboratory tests indicated that the fundamental stated at the beginning of the project for the device under development are almost completely confirmed; also the architectural aspetct of the design has kept the same as in thge previous document.
In the following table there are the specifications for the working prototype which has been built in the successive phase of this project; some specifications are calculated but not tested, others have been tested on the bench. In general, the reported specifications have shown to be exceeeded in the tests performed.

Parameter	**Range**	**Initial error**	**+(drift+repeatability+…)**
pH	-500 ÷ 500 mV	±2 mV	±15 µV/°C**RTI [1]**
ORP	-1 ÷ 1 V	±2 mV	±15 µV/°C**RTI [1]**
T	0 ÷ 203°C	±2°C	±0.5°C over 0 ÷120°C
Level	0 ÷ 75m	Res. unbalance	±80mm
Conductivity	345µS ÷ 415mS	± 1% of reading	**TBD [2]**
Operating temperature range (specified)	0…110°C		
Operating temperature range (absolute maximum)	0…120°C		

[1] RTI = Referred To the Input

[2] TBD = To Be Defined

Sensors used

Most of the sensors are custom built for this application. A brief description of each sensor is as follows:

- 3 wire PT100 for temperature measurement.
- Reference electrode in Tallium with KCl container (liquid electrolyte) and solid electrolyte in the cane.
- ORP electrode in Platinum
- PH electrode in Tallium
- Conductivity cell (2 plates glass-Platinum)
- Absolute pressure gauge (strain-gauge)

In addition, all the wetted parts are made of AISI316 stailess steel, glass, and PVDF. All the sensors are sealed by double O-rings in Viton.

Activities

A list of the activities made up to now follows, in nearly chronological order.

- Design of the first schematic for the preliminary tests with a wire-wrap board
- Building of the wire-wrap prototype
- Testing of it
- Final design entry in a CAD system
- PCB layout, routing and manufacturing
- Mounting the board and the mecanical assembly
- Bench tests on the PCB prototype

The bench tests have been performed interfacing the sonde with a data acquisition board based on a 16 bits ADC, interfaced via a sinchronous serial bus to an SBC board.
The software running on he microcontroller board implements a TCP-IP stack and an http server, so to be able to access to the real-time data measured by the sonde in the form of a web page.

- RESEARCH PRODUCTS OF THE PROJECT
  - Other

The tests made up to now have shown that the method used for the electric conductivity measurement seems to be suitable for the project purposes, so we are evaluating the possibility to file a patent application.

CHEMICAL SPECTRUM AND MASS OUTPUT OF MAJOR AND MINOR VOLATILE ELEMENTS IN CRATER PLUME EMISSIONS FROM MOUNT ETNA.

RU 3 Scientific Responsible **: Dr. Patrick Allard** Dirigente di ricerca presso il CNRS

Laboratoire Pierre Süe, CNRS-CEA
CE-Saclay, 91191 Gif sur Yvette France
Phone:0033-169089067, Fax: 0033-16908776923; E-mail: allard@drecam.cea.fr

ACTIVITY REPORT –2nd YEAR

RU PARTICIPANTS

Name-Position	Affiliation	man/month
P. Allard, Dir. Ricerca/Dir. Res.	CNRS, France	3
M. Burton, Ricercatore/Researcher	INGV, Catania	1
F. Murè, Tecnico/Technician	INGV, Catania	1
N. Métrich, Dir. Ricerca/Dir. Res.	CNRS, Francia	2
E. Mignot, Stag. Univ./Univ. Cont.	UNIV., Francia	1

2nd YEAR OBJECTIVES

During this second year we had two main objectives: a) to develop and continue the remote measurements of the chemical composition of gas plume emissions from Mount Etna using the open-path Fourier Transform infrared spectrometry (FTIR) initiated in 2000 and to evaluate the variations in gas chemistry with the volcanic activity. The mass output of gas components retrieved in sistematic way (SO2, HCl e HF) could determined from routine COSPEC sensing performed simultaneously by INGV-CT (Caltabiano et al.); and b) to better assess the magma degassing process at Etna by studying the content and evolution of volatiles dissolved in the magma (olivine melt inclusions).

2nd YEAR RESULTS

2.1 FTIR remote sensing

The FTIR spectrometer operated since 2000 (Bruker OPAG-22) was used regularly for remote analysis of the volcanic plume vulcanico of Etna. The measurements were performed at variable distance (2 to 15 km) from the summit craters and at different sites, according to the wind direction, using infrared absorption of the solar radiation across the plume. In those conditions we determined in systematic way and simultaneously the concentrations of SO2, HCl and HF, the three main acid gas components in Etna plume. Because these have a contrasted solubility behaviour in the magma along with pressure (SO2 starting to exsolve earlier and at greater depth than HCl and HF), the chemical ratios of these gas components provide constraints upon the evolution of the depth and the dynamics of magma degassing processes (Métrich et al., 1993; Burton et al., BSGL 2002; see below). Using the infrared radiation from hot lavas, we were also able to measure the composition of high temperature gases emitted from new eruptive vents during the July-August 2001 flank eruption.

The results obtained have revealed a relative steadiness of the SO2/HCl, SO2/HF and HCl/HF ratios in the plume of Etna during the first half of 2001, indicating relatively steady-state conditions of magma degassing through the central volcano conduits in this period. Then, 4 days before the onset of the July 2001 eruption and in straight coincidence with precursory geophysical signals, a spike increase of SO2/HCl and SO2/HF ratios was observed, suggesting the fast uprise of SO2-rich gas bubbles coming from greater depth. During the 23 days of the eruption itself we could measure the composition of both the summit crater plume and the hot gases from the new vents opened on the southern and eastern flanks of Etna. Figure 1 shows the variations of the SO2/HCl ratio at different sites, a well as the evolution of the total SO2 output measured with COSPEC, before, during and after the eruption. The data have allowed us: i) to distinguish the separate intrusion and eruption of a finite batch of rather evolved magma through the new vents opened at 2100 e 2550 m elevation on the south flank, whereas degassing at the upper vents (2700, 2900 m e Valle del Leone) was fed by magma residing in the central conduits; ii) to put in evidence a strong separation of gas and magma at the 2550 and 2100 m vents, respectively; and iii) to anticipate by about 9 days the end of the eruption on basis of a trend of gradual decrease of SO2/HCl e SO2/HF ratios at the 2100 m vent, which indicated a progressive depletion (distillation) of sulfur in the erupting magma (Figure 2). In addition to SO2, HCl and HF, our FTIR measurements at short distance from the new eruptive vents allowed us to determine the concentrationd of H2O, CO2 and CO, and their evolution with the volcanic activity. These results were presented at the annual meeting of the GNV (Roma, Oct. 2001) eand in other international meetings. It is actually the first time that the evolution of magma degassing processes during a basaltic flank eruption have been closely monitored with combined FTIR and COSPEC remote sensing techniques (Science, 3 Agosto 2001). After the eruption and in the following months, SO2/HCl, SO2/HF and HCl/HF ratios in the summit plume recovered their background values, typical of open-conduit bulk magma degassing, while the SO2 flux collapsed immediately down to a mean level of 1000 t/d that persisted until the new eruption in 2002.

2.2 Analysis of volatiles dissolved in the magma

In order to deepen our interpretation of the FTIR data, we sampled and analyzed the new products of the 2001 flank eruption with the objective to determine the original content and the exsolution behaviour of volatiles in the magma during ascent and degassing. About two hundred of melt inclusions trapped in olivine crystals were thus analyzed in the erupted lavas, using different techniques (microscopy and thermometry, electron microprobe, FTIR spectroscopy, and nuclear microprobe).The results, presented at the EGS-2002 and in submission to EPSL, allowed us i) to gather the most detailed data base yet obtained on volatiles in Etna magma, ii) to confirm the simultaneous extrusion of two different magmas during the 2001 eruption, and iii) to reinforce our interpretation of FTIR data (Figure 3) with a modelling of magma degassing as a function of pressure and the conditions of opening of the system (Figure 4). This model, validated with experimental data of high quality, could serve of reference for future studies of the dynamics of magmatic processes at Etna.

RESEARCH PRODUCTS

Pubblications:

SCIENCE, Vol. 293, 3 August 2001, Etna eruption puts volcano monitoring to the test, News by R. Stone, 774-775.

Research staff of INGV Catania, Multidisciplinary approach yields insight into Mt. Etna eruption, EOS, Trans. Am. Geophys. Union, 82, 52, December 2001.

BURTON M., ALLARD P., MURE F. and OPPENHEIMER C.: FTIR remote sensing of fractional magma degassing on Mt. Etna volcano, Sicily. Bull. Geol. Soc. London (in press, 2002).

T. CALTABIANO, M. BURTON, S. GIAMMANCO, P. ALLARD, N. BRUNO, F. MURE & R. ROMANO, Volcanic gas Emissions From the Summit Craters and Flanks of Mt. Etna, 1987-2000. AGU Monography on Mt. Etna (submitted, 2002).
AIUPPA A., P. ALLARD, W. D'ALESSANDRO, S. GIAMMANCO, F. PARELLO & M. VALENZA, Magmatic Gas Leakage at Mount Etna (Sicily, Italy): Relationships with the Volcano-Tectonic Structures, the Hydrological Pattern and the Eruptive Activity. AGU Monography on Mt. Etna (submitted, 2002).
METRICH N., ALLARD P., ANDRONICO A., BURTON M. & MIGNOT E., Source mechanism of the 2001 flank eruption of Mt. Etna tracked from olivine melt inclusions and dissolved volatiles. Earth Plan. Science Letters (in submission, 2002).

Communications:

ALLARD P., BRUNO N., BURTON M., CALTABIANO T., LONGO E., AIUPPA A., FEDERICO C., BELLOMO S., Evolution of magma degassing during the July-August 2001 eruption of Mount Etna tracked by COSPEC-FTIR remote sensing and filter pack sampling. GNV Assembly, Roma, 8-11 October 2001.

ALLARD P. and METRICH N., Magma degassing processes at Etna and Stromboli: constraints from melt inclusions and volatile emissions. Workshop of the Geological Society of London, "Origins, Emissions and Impact of Volcanic Gases", Londres, 25-27 October 2001 (invited talk).

BURTON M., ALLARD P., AND MURÈ F., FTIR detection of chemical changes in volcanic gas emissions before and during the 2001 flank eruption of Mt. Etna, Peter Francis Memorial Meeting, Geological Society , 25-26 October 2001, London UK.

ALLARD P., ALPARONE S., ANDRONICO D., BURTON M., LODATO L., MURÈ F. AND SGROI T.,Dynamics and source mechanisms of periodical lava fountaining at southeast crater of Etna in January-June 2000: evidence from a multidisciplinary study of the July 14, 2000 paroxysm, Peter Francis Memorial Meeting, Geological Society , 25-26 October 2001, London UK.

ALLARD P., BRUNO N., BURTON M., CALTABIANO T., LONGO E., MURE F., Geochemistry of Volcanic Plume Emissions during the July-August 2001 Flank Eruption of Mount Etna. XVII Assemb. European Geophysical Society, Nice, 22-25 avril 2002 (invited talk).

MÉTRICH N., ALLARD P. and ANDRONICO D., Preliminary Constraints On Volatile Abundances In Basalts Erupted During The 2001 Flank Eruption Of Mount Etna. XVII Assemb. European Geophysical Society, Nice, 22-25 avril 2002.

ALLARD P., BURTON M. and MURE F., FTIR Remote Sensing of Volcanic Gas Emissions: a new tool for Volcano Monitoring and Eruption Forecasting. Etna and Stromboli cases. International Worshop for the Centennary of the Mount Pelée eruption, Martinique, 11-17 mai 2002.

PLUME SO2 MEASUREMENTS

RU 4 Scientific Coordinator**: Dr. Caltabiano Tommaso** – Primo Tecnologo
Istituto Nazionale di Geofisica e Vulcanologia – Sezione di Catania

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RU PARTICIPANTS

Name - position	Affilation	Months/man
Bruno Nicola - CTER	INGV	3
Caltabiano Tommaso – Primo Tecnologo	INGV	6
Longo Vincenza - CTER	INGV	3

- 2nd YEAR OBJECTIVES
  - continuation of SO_2 flux data analysis acquired with periodic measurements in "*Surveillance*" research program
  - continuation of the study about earth tide and meteorological influences on SO_2 emission and historic behavior;
  - cooperation with other research groups for the SO_2 analysis, image analysis and other conjunct measurements;
  - correlations with other volcanological, geophysical and geochemical data;
  - cooperation with other research group, in order to carried out conjunct routine measurements with FTIR equipment on Mt. Etna volcano.

- 2nd YEAR RESULTS

- Methodology

The measurements of sulfur dioxide (SO_2) flux emitted from Mt. Etna using COSPEC instrument, started in 1987, have been continued in year 2001 allowing us to improve the Mt. Etna gas emission model for a better understanding of the magma behavior in the main feeder system of the volcano. Conjunct measurements have been carried out with FTIR research group to estimate HCl, HF flux from Mt. Etna's summit craters especially during the 2001 Etna's eruption. Other conjunct measurements were done with foreign colleagues to study the use of a new type of UV spectrometer for SO_2 flux estimation; the first measurements showed very good comparisons in the results.

- Data acquisition

During the second year of this project (July 2000- July 2001), 136 campaigns of SO_2 flux measurements from Etna's Summit Craters have been carried out (adopting the sampling rate of two-three measurements per week) using a car mounted correlation spectrometer (COSPEC). The mean value of SO_2 flux emission in the considered

period was about 5200 t/d (metric tons per day). The SO_2 measurements have pointed out: i) a minimum value of about 1100 t/d (May, 9th) related with the start of a significant increasing trend which ended with the start of the eruptive event of July-August 2001; ii) a maximum value of about 20500 t/d (July, 20th), associated with July-August 2001 eruptive period; this flux value was also the maximum value recorded during this eruption.
The increasing trend started on May 9th indicates a new magma up-rise in the main feeder system of the volcano which started (on July) the July-August 2001 eruptive activity.

- Processing and interpretation

The extension of the study of crater SO_2 fluxes together with soil CO_2 emissions from Mt. Etna during the period November 1997 to September 2000 with an high frequency of data acquisition with both methods, allowed to analyze in detail the time variations of both parameters. Anomalous values of soil CO_2 dynamic concentration always preceded periods of increased flux of crater SO_2, and these in turn were recorded before the occurrence of important summit eruptions in 1999 and 2000. The variations were modeled in terms of gas efflux increase due to magma ascent to shallow depth and its consequent depressurization and degassing. The rates of increase both of soil CO_2 dynamic concentration and of crater SO_2 flux seem positively correlated both to the velocity of magma ascent within the volcano and to lava effusion rate once magma is erupted at the surface. Furthermore, the time interval between the peaks of CO_2 and SO_2 in a single sequence of gas anomalies is likely to be controlled by magma ascent velocity.

- Other

We contributed to INGV reports on Etna's activity, giving information about SO_2 flux variations, in conjunction with other Sections of INGV. Some reports about SO_2 degassing have been presented, especially after intense measurements campaigns carried out in order to monitoring Etna volcano and during the eruptive activity of July-August 2001. Actually we are cooperating, with a paper, to the Etna's book edited by our Institute, analyzing SO_2 frequency behavior and a new paper in collaboration with IGF, about Etna's SO_2 e CO_2 degassing presented for the publication on Bulletin of Volcanology. Another paper was about some intense SO_2 flux campaigns which have been carried out on Mt. Etna in conjunction with researchers of the Open University (UK) and of Chalmers University (Sweden) to compare COSPEC data with new remote sensing UV spectrometer.

• RESEARCH PRODUCTS OF THE PROJECT

- n° 3 submitted international publication
- n° 1 abstract accepted for a monography on Mt. Etna (AGU Etnabook)
- n° 5 technical report and for surveillance
- n° 1 oral presentation in GNV congress
- n° 2 poster presentation in GNV congress
- update of SO_2 flux data base

PUBLICATIONS LIST

BRUNO N., CALTABIANO T., GIAMMANCO S., ROMANO R., 2001. Degassing of SO_2 and CO_2 at Mount Etna (Sicily) as indicator of pre-eruptive ascent and shallow emplacement of magma. *J. Volcanol. Geotherm. Res.*, 110, 137-153.

CALTABIANO T., BRUNO N., ROMANO R., GIAMMANCO S., ALLARD P. & BURTON M.. Summit Craters and flank gas emissions at Mt. Etna (1987-2000). Accepted Abstract for AGU Etnabook.

WEIBRING P., SWARTLING J., EDNER H., SVANBERG S., CALTABIANO T., CONDARELLI D., CECCHI G., PANTANI L., 2002. "Optical monitoring of volcanic sulphur dioxide emissions - comparison between four different remote-sensing spectroscopic techniques". *Optical and Lasers in Engineering, 37, 267-284*.

BADALAMENTI B., BRUNO N., CALTABIANO T., DI GANGI F., GIAMMANCO S.. Continuous soil CO_2 and discrete plume SO_2 measurements at Mt. Etna (Italy) during 1997-2000: a contribution to volcano monitoring. *Bull. Volc*. Presentato 2001 e accettato con minori correzioni.

McGONIGLE A.J.S., OPPENHEIMER C., HAYES A.R., GALLE B., EDMONDS M., CALTABIANO T., SALERNO G., BURTON M.. Volcanic sulphur dioxide fluxes from Etna, Vulcano and Stromboli measured with an automated scanning ultraviolet spectrometer. Submitted to *Geoph. Res. Letter.*

SUBLIMATES, FUMAROLIC DEPOSITS AND GEOCHEMICAL SURVEILLANCE

RU 6 Responsible **Prof. Filippo Vurro** – Associated professor
Dipartimento Geomineralogico Università degli Studi di Bari

ACTIVITY REPORT – 2nd YEAR

RU PARTECIPANTS

Name - Position	Affiliation	man/month
Vurro Filippo - Associate Professor	Geomineralogical Dept.- Bari University	2
Garavelli Anna - Researcher	Geomineralogical Dept.- Bari University	2
Laviano Rocco - Associate Professor	Geomineralogical Dept.- Bari University	1
Vittoria Aldo - Technical	Geomineralogical Dept.- Bari University	1
Grasso Maria Felicia – Ph.D.	External researcher	1
Di Muccio Lucantonio- Ph.D. student	External researcher	1
Pinto Daniela	External researcher	1

- 2nd YEAR OBJECTIVES

According to the suggestions given by the Commission the objective of this RU were concluded in the first year of activity.

- 2nd YEAR RESULTS

The elaboration of aquired data is still in progress.

- RESEARCH PRODUCTS

No. 2 Pubblications on international magazines.

- PUBLICTIONS LIST

CHEYNET, B., DALL'AGLIO, M., GARAVELLI, A., GRASSO M. F. & VURRO, F. (2000): Trace elements from fumaroles at Vulcano Island (Italy): rates of transport and a thermochemical model. J. Volcanol. Geotherm. Res., 95, 273-283.

BORODAEV, Y. S., GARAVELLI, A., GARBARINO, C., GRILLO, S. M., MOZGOVA, N.N., ORGANOVA, N. I., TRUBKIN, N. V.& VURRO, F. (2000): Rare sulfosalts from Vulcano, Aeolian Islands, Italy. III: Wittite and cannizzarite.Can. Mineral., 38, 23-34.

STUDIES ON DIFFUSE SOIL DEGASSING AND TECTONICS

RU 6 Responsible**: Dr. Sergio Gurrieri ,** Senior Researcher
Istituto Nazionale di Geofisica e Vulcanologia**.**

ACTIVITY REPORT–2nd YEAR

RU PARTICIPANTS

Name - Position	Affiliation	Months/man
Dr. Sergio Gurrieri – Senior Researcher	INGV-Pa	4
Dr. Salvatore Giammanco – Researcher	INGV-Pa	3
Sig. Giuseppe Riccobono – Technical Collab.	INGV-Pa	1
Sig. Fabio Di Gangi – Technical Collab.	INGV-Pa	2
Sig. Lorenzo Calderone - Technical Collab.	INGV-Pa	2

- 2nd YEAR OBJECTIVES

- Continuation of the spatial investigations on the diffuse CO_2 emissions in the etnean edifice.
- Study of the effects of atmospheric variations on emitted gases in a borehole specifically drilled.

- 2nd YEAR RESULTS

During the second year, the spatial investigations on soil degassing were extended to the areas interested by the Pernicana Fault, the Sapienza and Citelli huts, the Ragalna faults and Piano del Lago. In general, low flux values were measured. Very interesting data were carried out at Piano del Lago area, where soil degassing anomalies were aligned along a NE-SW tectonic direction (the same structures interested by the 2002 eruptions).

As regards the borehole, all government permits were obtained and the ground where to drill the borehole was rented. This area is located close to S.Venerina village, in corrispondence with a gas sampling point used since 1988 for volcanic surveillance (P78). According to the drill company, next January the borehole should be drilled. With respect to the original project details, a significative variation was produced. In fact, due to the increase of the drill costs, the borehole size was reduced to 20 cm in diameter and the measuring equipment was reassembled in order to fit this dimension. During this year, several tests on the electronic equipments were also performed to investigate on the borehole geochemistry and the atmospheric effects on the gas component. Two remote stations located near Paterno' area (P39) and at the same place selected for the borehole, were used to test soil CO_2 sensor and electronics at ground level. Good results were obtained therefore the same assemblage of sensors and electronics will be used in the borehole investigations.

- RESEARCH PRODUCTS
  - n° 1 article published on international journals
  - n° 1 presentation at international meetings
  - n° 1 Computation code for automatic acquisition of geochemical parameter inside the borehole.
  - Equipment developed to measure geochemical parameters inside borehole.

PUBLICATIONS LIST

- AIUPPA A., FEDERICO C., GURRIERI S., VALENZA M. LINE FINDER - A computer code to find the most probable tectonic direction from soil gas distribution. Proceedings of the IAMG 2002 Conference, Berlin, Germany, 15-20 September 2002.

- M. CAMARDA, S. GURRIERI, M. VALENZA - Measurements of In Situ soil permeability a new method based on induced spherical gas sources. Submitted to Pure and Applied Geophysics.

DEVELOPMENT OF WATER-ROCK INTERACTION MODELS IN ACTIVE VOLCANIC AREAS

RU 7 Responsible **Prof. Francesco Parello**
Name-Position Prof. Associato
Affiliation Dip. CFTA Università di Palermo

ACTIVITY REPORT-2nd YEAR

RU7 PARTICIPANTS

Name-position	Affilation	Months/men
Parello Francesco Professor .	Dip.CFTA Uni Pa	6
Parisi Bianca Researcher	Dip. CFTA Uni Pa	6

_ 2nd YEAR OBJECTIVES

In the framework of volcanic activity surveillance of mount etna, a model will be developed, in order to evaluate aquifer residence times on the basis of either water major ions chemical composition or experimental elements dissolution kinetics .
Different operating conditions will be selected to carry on the experiments, with the aim to quantify the role of chemico-physical parameters on dissolution as temperature, partial pressure of co2 and rock grains size**.**

_ 2nd YEAR RESULTS

Six dissolution experiments were performed on fresh and undisturbed basaltic rock samples (hawaiite), that were collected from two quarries of Mount Etna area. They can be attributed to the well studied historical 1669 lava flow.
The molal release of chemical elements from the solid to the interacting solution was normalized to specific surface area of grains and to the reaction time, in order to get the gradient of chemical elements concentration changes with respect to time. In longer reaction times, only Na and silica appear to reach a steady state where concentration changes linearly with time. Na and silica dissolution constants were determined in this linear regime stage.
Then, they were applied to natural ground waters from wells and springs of Mount Etna. If no sources or sinks other than weathering process are involved, residence time can be considered the time elapsed since when water was separated from the atmosphere to when it emerged to the surface.
Therefore, residence time is calculated on a) element concentration in sampled water in a given time, b) on initial element concentration in local rain waters, and c) on the geometric parameter evaluating water-rock contact effective surface area (like the mean open fractures width in the rock).
Experimental results indicate that higher PCO2 increase dissolution constants up to two orders of magnitudes, causing an apparent decrease of residence times. Nevertheless, calculations show that longer residence times can be registered in higher dissolved salts contents (TDS) groundwaters. Generally, these are the waters that can be considered in equilibrium with a gaseous phase that is rich in magmatic origin CO2.
As a consequence, all these factors allow to evaluate, for the analysed waters of eastern and north-eastern sectors of the volcano, residence times from few years to some decades. They are approximatively coherent with the ages calculated on the basis of the ^{3}H content.

PUBLICATIONS LIST

EGS (2002) An experimental study of rock dissolution kinetics and implications on weathering rates in an active volcanic area: the case study of mount etna, italy .Bianca Parisi, Francesco Parello, Mariano Valenza *Dipartimento C.F.T.A), Università di Palermo, Italy*

GES 6 (2002) An experimental study of rock dissolution kinetics and implications on weathering rates in an active volcanic area: the case study of mount etna, italy .Bianca Parisi, Francesco Parello, Mariano Valenza *Dipartimento C.F.T.A), Università di Palermo, Italy*

ISOTOPIC CHARACTERISATION OF METEORIC PRECIPITATIONS FOR MODELING OF AQUIFERS IN VOLCANIC SYSTEMS

RU8 Responsible **Rocco Favara** - researcher
Istituto Nazionale di Geofisica e Vulcanologia – Sezione di Palermo

ACTIVITY REPORT–2nd YEAR

RU PARTICIPANTS

Name-Position	Affiliation	man/month
Dr. Rocco Favara - researcher	INGV-PA	3
Dr. Walter D'Alessandro - researcher	INGV-PA	4
Dr Giovannella Pecoraino - researcher	INGV-PA	3
Dr Giammanco Salvatore- researcher	INGV-PA	2
Sergio Bellomo – PhD student	Uni-PA	1
Fabio Di Gangi – Technical Supporter	INGV	1
Vincenzo Francofonte– Technical Supporter		1

- 2nd YEAR OBJECTIVES

The main objective of this research unit for the 2nd year was to continue the periodic sampling surveys on Mt. Etna. In particular 16 rainwater samples and 14 groundwater samples were collected each month.
The test of a new type of snow gauge collecting the liquid equivalent of solid precipitations was continued. A second device was installed on the northern flank of the volcano at Piano Provenzana (1800 m a.s.l.). Both devices collected successfully samples monthly during the winter season 2001/2002.

- 2nd YEAR RESULTS

All samples were analysed for their oxygen isotopic composition.
Preliminary data treatment allowed defining the geographical distribution of rainwater recharge and its isotopic characterisation. This is the first step to better constrain the amount of annual meteoric recharge.
Furthermore, the variation of isotopic composition of the rain with altitude helps to estimate recharge altitudes of groundwaters and consequently the length of subsurface circulation. In particular isotopic gradient on Mt. Etna displays a great difference between lower and higher altitudes (below or above 1000 a.s.l.). The value of the former (0.27 ‰/100m) falls in the world-wide measured normal range, while the latter (0.06 ‰/100m) probably reflects the important influence from the vapour emission of the Etnean summit craters.
Groundwater data evidence the great differences in mean recharge altitudes between the eastern

sector of the volcanic edifice (about 500 m) and the other sectors (about 1000 m).
Time series highlight the low annual variability of groundwaters in contrast to highly variable isotopic values of rainwaters evidencing a well-mixed groundwater reservoir, although a comparison with previous data reveals some small but significant long term variations.

RESEARCH PRODUCTS

- 1 presentation at international meetings
- Technical Supporter

PUBLICATIONS LIST (inclusive of papers in print and accepted)

W. D'ALESSANDRO AND R. FAVARA - "Geochemical and hydrologic modelling of the aquifer of Mt. Etna to constrain the evolution of volcanic activity" – Poster presented at the International Conference on Calibration and reliability in groundwater modelling (ModelCARE 2002), Praga, Cech Rep., 17-20 June 2002.

GEOCHEMICAL AND HYDROLOGIC MODELLING OF THE ETNEAN VOLCANIC AQUIFER

RU 9 Responsible **Walter D'Alessandro** - Researcher
Istituto Nazionale di Geofisica e Vulcanologia – Sezione di Palermo

ACTIVITY REPORT–2nd YEAR

RU PARTICIPANTS

Name-Position	Affiliation	man/month
Dr. Walter D'Alessandro - researcher	INGV-PA	4
Sergio Bellomo – PhD student	Uni-PA	2
Dr. Alessandro Aiuppa – researcher	Uni-PA	2
Fabio Di Gangi – Technical Supporter	INGV-PA	2

- 2nd YEAR OBJECTIVES

The main objective of this research unit for the 2nd year was to complete the periodic sampling surveys on Mt. Etna. In particular 28 groundwater samples were collected in each survey (July and October 2001, January, April and July 2002). Additionally 16 rainwater samples were collected montly for chemical analysis in collaboration with UR8.

- 2nd YEAR RESULTS

Groundwater samples were analysed for their chemical composition (major and some minor constituents). The samples of the October survey were also analysed for their trace element content. Oxygen isotopic composition was determined in all groundwater samples, while hydrogen isotopic composition only for the July 2002 survey.
Rainwater samples were analysed for major ions content.
Preliminary graphic and statistic analysis of the gathered data was made.

- RESEARCH PRODUCTS

  - 1 article published on international journals
  - 2 presentations at international meetings

PUBLICATIONS LIST (inclusive of papers in prints and accepted)

S. BELLOMO, W. D'ALESSANDRO, M. LONGO - "Volcanogenic fluorine in rainwater around active degassing volcanoes: Mt. Etna and Stromboli island, Italy", The Science of the Total Environment 2002, 301(1-3), 175-185

W. D'ALESSANDRO, A. AIUPPA, S. BELLOMO, S. HAUSER, B. PALUMBO - "Sources and sinks of fluorine in the atmosphere and hydrosphere of the active volcanic area of Mt. Etna (Italy)" – Poster presented at the 6th International Symposium on the Geochemistry of the Earth's Surface GES-6, Honolulu, Hawaii, 20-24 maggio 2002.

W. D'ALESSANDRO E R. FAVARA - "Geochemical and hydrologic modelling of the aquifer of Mt. Etna to constrain the evolution of volcanic activity"– Poster presented at the International Conference on Calibration and reliability in groundwater modelling (ModelCARE 2002), Praga, Rep. Ceca, 17-20 giugno 2002.