

	<b>Research Networking Programmes</b>

**Short Visit Grant  or Exchange Visit Grant**

### Scientific Report

**Proposal Title:** Selection and characterization of sampling sites for S. Miguel Island fumaroles. Development of laboratory facilities to improve preparedness in emergency situations.

**Application Reference N°:** 5623

#### 1) Purpose of the visit

The visit is aimed to reinforce the collaboration between researchers of INGV-Osservatorio Vesuviano (Italy), Dr. Stefano Caliro and colleagues and the researchers in fluids geochemistry in the Centro de Vulcanologia e Avaliação de Riscos Geológicos (CVARG, Azores Portugal) (namely Dr. Fátima Viveiros), for a better understanding and modelling of the S. Miguel Island (Azores) hydrothermal systems. Previous cooperative work allowed a preliminary analysis of the gas and isotopic compositions of few fumarolic fluids of S. Miguel Island. This preliminary work resulted also from a MemoVolc Exchange Visit attributed last year to Fátima Viveiros to visit INGV-OV. Nevertheless, these preliminary results are very interesting from a geochemical point of view, at same time highlight the necessity to collect gas samples with more accurate procedures and to perform a field survey in order to select the most representative sampling sites in the fumarolic fields. The transfer of knowledge between both institutions has been guaranteed by the development and improvement of some methodologies used in the CVARG both in what concerns laboratory activities (i.e. improvement of analytical procedure, development of specific gas-chromatographic techniques) and field gas sampling procedure. At same time this travel grant gave us the opportunity to study a not well known hydrothermal system and to test here geochemical methods applied in the geochemical surveillance of the Italian volcanoes, allowing the exchange of experience and knowledge that is one of the main objectives of the MeMoVolc network.

## 2) Description of the work carried out during the visit

Before the beginning of the visit the stuff needed for fumarolic gas sampling, consisting of a gas line and bottles to be used in the field to collect gas samples, were sent to the CVARG laboratory. The work carried out during the visiting period mainly consisted in laboratory and field activities.

### 2.1 Laboratorial activities

Due to the severe rules to safely transport dangerous goods by aircraft, the preparation of the Giggenbach bottles ("soda" sample) have been carried out in the CVARG laboratories, namely in what concerns the preparation and filling of the bottles with soda solution. About 50 ml of a 4N NaOH solution are fed into the bottles, which are putted in a thermostatic bath at about 60 °C and then evacuated by means of a rotary oil pump (nominal vacuum  $1 \times 10^{-2}$  mb). Bottles are weighted before to be used in the field. The vacuum inside the bottle is indicated by the characteristic clicking sound upon shaking. Then the stuff has been packed and organized to be safety used in the field.

One of the main goals of this application is the development and the refining of some analytical techniques in the CVARG laboratories mainly in what concerns gas chromatography techniques. The purpose is to transfer the know-how about gas analytical techniques in order to allow CVARG researchers to perform complete chemical analyses of fumarolic fluids. The gas-chromatograph (GC) in charge in the CVARG laboratory is a Perkin Elmer XL AutoSystem equipped with one channel: six port injection valve, TCD (thermoconductivity detector) and a Molecular Sieve (MS) 5Å 1/8' x 50' packed column, He as gas carrier. The first operation has been to provide the instrument of an injection line made up of a vacuum valve, a pressure transducer and a variable volume (Fig. 1). In all connections high tightness gaschromatogaphy fittings have been used. The line has been connected to two-stage rotary pump (nominal vacuum  $1 \times 10^{-2}$  mb) to ensure a good vacuum avoiding possibly air contamination of the sample during the injection in the GC. Pressure transducer allow a control of the injection pressure both for samples and calibration standards avoiding potential analytical bias. This injection line at same time allow a multi points instrument calibration injecting the same standard gas mixture at different pressures. The variable volume is used to measure the volume of gas used for the analysis that must be considered in the computation of the final analysis. Exhaustive tests have been executed to ensure linearity and reproducibility of the instruments setup. Using helium as gas carrier the instrument allow determination of Argon+Oxygen (unfortunately the column available does not allow separation of Ar and O<sub>2</sub> without cooling down at about -50°C the GC oven), Nitrogen (N<sub>2</sub>) and Methane (CH<sub>4</sub>). In order to obtain almost complete chemical analyses a second injection of the sample is necessary. To measure Helium (He) and Hydrogen (H<sub>2</sub>) concentrations the instrument setup has been changed using Ar as gas carrier. Also with this setup, exhaustive tests have been executed in order to find the best instrumental parameters (gas flux, reference gas flux, oven temperature) to ensure the best "Efficiency" of the system. This GC setup allows to analyze chemical compositions of the non-absorbed gases, present in the headspace over the alkaline solutions ("soda" sample), for what concerns Ar+O<sub>2</sub>, N<sub>2</sub>,

CH<sub>4</sub>, He and H<sub>2</sub>, while H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub>S are analyzed by ponderal and titration techniques.



Fig. 1 a) original setup of GC where the vacuum was done by means of a manual pump b) Implementation of the GC with a vacuum gas line and a control of the injection pressure.

In order to make a complete analysis with a single sample injection an upgrade of the GC has been suggested, i.e. the implementation of the GC with a second channel characterized by split injector for capillary columns, six port injection valve and TCD detector.

## 2.2 Field activities

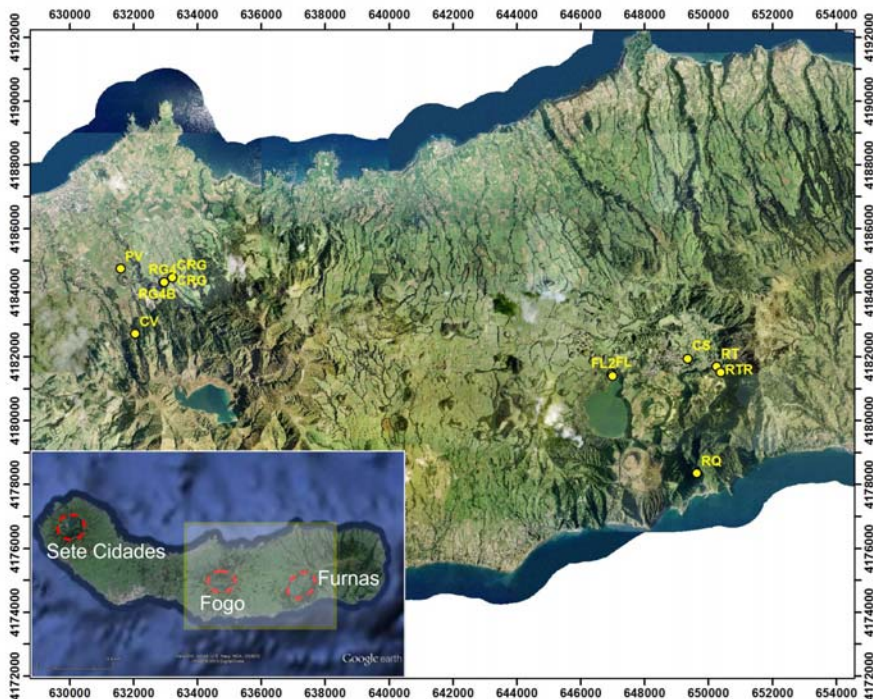


Fig. 2 Location of the fumaroles collected during field activity. In the inset S. Miguel Island with indication of the three collapsed strato-volcanoes of Sete Cidades, Fogo and Furnas.

The area investigated, S. Miguel island, is the largest of the Azores archipelago located 400 km east of the Mid-Atlantic-Ridge. It has three active strato-volcanoes (Fig. 2,

Furnas, Fogo, and Sete Cidades) characterized by summit calderas partly filled by lakes, which have a long record of both effusive and explosive eruptions, with last eruption in Furnas caldera in 1630 AD (Guest *et al.*, 1999). Both Furnas and Fogo volcanoes show intense hydrothermal manifestations, whereas at Sete Cidades volcano the only hydrothermal activity is represented by submarine gas emissions in the western sector of the caldera.

Considering the existence of some differences in the sampling strategies between the two institutions and in view of the preliminary results obtained following the methodologies used by the CVARG (Ferreira and Oskarsson, 1999; Ferreira *et al.*, 2005), samples were collected following the standardized procedures used by INGV-OV teams and routinely applied in the geochemical surveillance of Italian volcanoes (e.g. Caliro *et al.*, 2007). The sampling procedure is depicted in Figure 3 and is here briefly reported. A glass or titanium probe or a glass funnel must be inserted into the vent and a dewar to avoid steam condensation is inserted into the probe; for the “soda” sample the discharge end of the apparatus is equipped with a short tygon tube, where after a certain time sufficient to heat the line and purge it from air, the bottle is connected. Fumarolic gas is allowed to enter the bottle by slowly opening the stopcock in order to have a high gas flow entering the bottle to minimize water loss due to condensation. The bottle must be cooled with water and held with the entrance down, in order to improve the interaction between the gas and the alkaline solution. Separate samples of “dry gas” are collected, downstream of a condenser-separator (Fig. 3), which is cooled with either boiling diethyl ether or ice + liquid water or just water. Use of ether or ice maintains condensation temperature constant at 38°C or 0°C, respectively, whereas if water is used, condensation temperature must be checked and kept constant by regulating the water flow. Use of this equipment allows also to collect samples of steam condensates (for the determination of the  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios). Dry gases can also be used for isotopic analyses of the  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios of  $\text{CO}_2$  and  $^3\text{He}/^4\text{He}$  ratios.

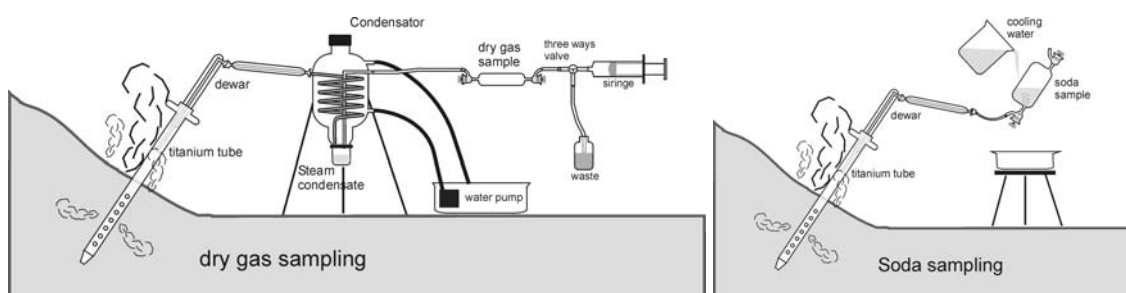


Fig. 3 Setup of sampling-line for “dry gas” and “soda” sampling.

Sampling sites have been selected based on the experience of the CVARG colleagues, field observations as well as on the use of an Infrared thermal camera (facility from CVARG). Samples were collected in four main fumarolic areas of Fogo Volcano and in five fumarolic areas of Furnas Volcano (Fig. 4). In total twelve sites have been investigated (Table 1, Fig. 2). For each site one soda sample, two dry gas samples and the fumarolic condensate have been collected. All the fumarolic fluids exhibit discharges temperatures close to the boiling temperature with a maximum of 99.8 °C.

Collected samples have been packed and sent to the INGV-OV laboratories for chemical and isotopic analyses. In particular “soda” samples are packed and delivered in accordance to the rules to safely transport dangerous goods by aircraft.



Fig. 4 Sampling of fumarolic fluids.

Table 1 – Fumarolic fluids collected during the field activities.

Sample	Label	Date (dd/mm/yyyy)	T (°C)
Caldeiras da Ribeira Gande	CRG	19/09/2013	97.8
RG4 geothermal well A	RG4	19/09/2013	99.3
Caldeira Velha	CV	19/09/2013	99.0
Pico Vermelho	PV	19/09/2013	96.9
Furnas Lagoa	FL	21/09/2013	96.7
Furnas Lagoa2	FL2	21/09/2013	99.8
Caldeira Seca	CS	21/09/2013	98.9
Ribeira dos Tambores	RT	21/09/2013	98.0
Ribeira Quente	RQ	23/09/2013	98.3
Ribeira Tambores River	RTR	23/09/2013	99.7
Caldeiras da Ribeira Grande	CRG	26/09/2013	96.4
RG4 geothermal well B	RG4B	26/09/2013	97.3

Chemical and isotopic analyses will be performed according with the methods reported in Cairo *et al.*, (2007; 2011) and Chiodini *et al.*, (2012).

### 3) Description of the main results obtained

First complete chemical and isotopic gas compositions on a larger number of samples will be obtained for the S. Miguel Island hydrothermal systems. The analyses that will be performed at INGV-OV laboratory will allow determination of the following components H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub>, H<sub>2</sub>, He, N<sub>2</sub>, CH<sub>4</sub>, CO, <sup>36</sup>Ar, <sup>40</sup>Ar, <sup>15</sup>N and <sup>3</sup>He/<sup>4</sup>He. The availability of more and accurate chemical and isotopic data of the fumaroles will allow the development of a more comprehensive geochemical picture of the hydrothermal

system, shedding light on the source of volcanic fluids in relation with the geodynamic setting of the region.

The transfer of knowledge, analytical and sampling protocols will help improving the methodologies used in the CVARG and reduce the scattering of data between different institutions. In addition, the development of gas chromatographic techniques and the improvement of the instrument setup, will allow CVARG Laboratory to perform more complete chemical analyses of fumarolic gases.

This visit aimed not only to collect new fumarolic samples and improving the strategies used in the CVARG institution, but also to compare/validate pre-existing datasets and better interpret some of the time series acquired in the last years. Analyses and discussion of the pre-existing data available for the Azores fumaroles highlighted also some gas ratio variations in the last 10 years. This is the particular case of the  $\text{CO}_2/\text{CH}_4$  that was already recognised as a good indicator of unrest phenomena (e.g. Chiodini, 2009). Integration of geochemical time series with other monitoring techniques (e.g. geophysical data) was also discussed. However, a reprocessing of chemical data is suggested in order to avoid eventual analytical bias.

#### **4) Future collaboration with the host institution**

Collaboration with the host institution will continue mainly in what concerns the study of chemical and isotopic composition of fumarolic fluids, aimed both to the development of a comprehensive geochemical model of the hydrothermal system and for geochemical monitoring purposes. The CVARG researchers will continue the geochemical monitoring sampling and analyzing fumarolic gases (using the methods above reported), and periodically they will send replicate samples to the INGV-OV, for comparison of chemical composition and for isotopic analyses (that cannot be carried out at CVARG).

A possibility to write a project proposal have been discussed together with the CVARG researchers, joining gas geochemistry data and petrological data to give new insights on the source of the fluids in relation with the geodynamic setting of the region.

#### **5) Projected publications/articles resulting or to result from your grant**

A paper characterizing the Azorean fumaroles is planned, however and as referred above, the analyses on the collected samples will be used to confirm and to strength some of the hypothesis already discussed with a preliminary analysis of the data both for what concerns thermodynamic gas equilibria (geothermo-barometric applications) and the implications on the source of volcanic fluids in relation with the geodynamic setting of the region. In future publications, the ESF will be duly acknowledged.

## **References**

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