



Project title: **Characterization and modelling of hydrothermal fumaroles. Sampling and analytical methodologies**

Reference number: 5187

Participant name: Fátima Viveiros

Period: 4th – 18th November 2012

1. Purpose of the visit

The project developed intended to establish a straight collaboration between Fátima Viveiros, post-doc researcher in the Centro de Vulcanologia e Avaliação de Riscos Geológicos (CVARG, Portugal) and the fluid geochemistry researchers of INGV-Osservatorio Vesuviano (Italy), Dott. Giovanni Chiodini and Dott. Stefano Caliro. The work carried out during the visit aimed to allow the post-doc researcher to acquire the know-how to improve sampling and analytical methodologies, as well as to establish long-term cooperation between both institutions that will allow a better understanding and modelling of the Azores hydrothermal fumaroles. Considering that in the CVARG laboratories the existing facilities do not allow to measure isotopic and some gas compositions, a complete set of analysis was obtained for the first time for some Azorean fumarolic emissions. These datasets can be compared with hydrothermal data from other geological settings (for instance Campi Flegrei fumaroles) and allow a preliminary characterization of the sampled fumaroles, as well as constitute a base level to program new analysis and cooperative work. The methodologies applied during this visit aimed not only improving the strategies used in the CVARG institution but also to compare/calibrate pre-existing datasets and better interpret some of the time series acquired in the last years.

2. Description of the work carried out during the visit

The project started some weeks before the travel with the selection of monitoring sites and sampling performed by the post-doc researcher in some fumarolic fields of São Miguel Island (Azores archipelago) (Photo 1a). Samples were collected in the three main fumarolic areas of Fogo Volcano and in the most representative fumarole of Furnas Volcano, Caldeira Grande. Considering the existence of some differences in the sampling strategies between the two institutions, samples were collected in evacuated Giggenbach flasks following the methodologies used by the CVARG (Ferreira and Oskarsson, 1999; Ferreira *et al.*, 2005) and the INGV-OV teams (e.g. Caliro *et al.*, 2007) in order to evaluate possible differences and to improve procedures. Sixteen samples in total were collected and sent to the INGV-OV

laboratories. Eight of the samples were collected in flasks filled with soda solutions and eight dry gas samples were collected for determination of CO concentrations. The packing of the samples was also programmed with some anticipation due to the rules to transport Gigenbach sampling flasks safely by aircraft (http://vulcanologia.uda.cl/index_archivos/IAVCEI-CCVG-Flasks-Aircraft_V3.pdf).

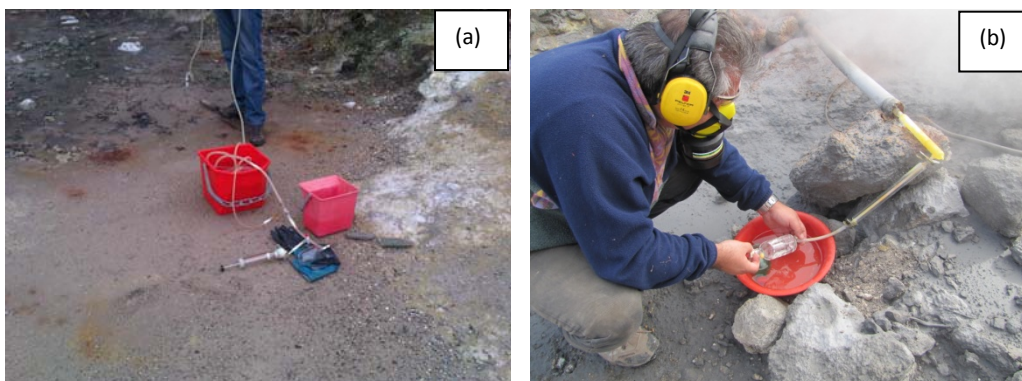


Photo 1. Collection of gas samples on the fumarolic emissions of Caldeiras da Ribeira Grande (Fogo Volcano, São Miguel Island) (a) and in Pisciarelli (Campi Flegrei system) (b).

During the time the researcher was received in the INGV-OV, several activities were carried out, as programmed in the initial proposal, and are referred below:

- In the first days the researcher was introduced to the laboratorial facilities of the INGV-OV in what concerns gas and ion chromatography and mass spectrometry equipments. The way of working and the specific needs of each instrument were also discussed as well as the way of preparing and introducing the samples in the instruments in order to avoid possible atmospheric contamination and/or gas fractionation. All these discussions were crucial and will contribute not only to interpret the final datasets but also to improve the analytical methodologies available in the CVARG laboratories.
- Observation and discussion of the pre-existing data for the Azores fumaroles was also done in order to discriminate limitations of the time series, highlight variations and select possible ratios that can be indicators of unrest phenomena and that can be used to compare with other monitoring techniques.
- A field survey was programmed during the first week and carried out in the Campi Flegrei main fumarolic fields (Solfatara and Pisciarelli fumaroles) (Photo 1b). This was a great opportunity to discuss some methodological differences in the sampling phase between both institutions and can explain some of the scatter observed.
- During the second week the various instruments were tested and calibrated and the samples collected in Campi Flegrei and in São Miguel fumaroles were prepared to perform the gas analyses. The gas and isotopic compositions were analysed in the INGV-OV laboratories using a wide range of methodologies, which include gas chromatography, mass spectrometry, titration and ion chromatography. The post-doc researcher was able to participate, together with the INGV-OV researchers, in all the analytical procedures and could acquire the know-how to apply some of the

methodologies in the CVARG laboratories. These works are methodical and long periods are required, since involve various phases, to prepare and analyse a complete set of data. The chemical compositions of the nonabsorbed gases, present in the headspace over the alkaline solutions were measured by gas chromatography, through a unique injection on two molecular-sieve columns (MS 5Å capillary, 30m×0.53mm×50µm; He and Ar were the carrier gases), using TCD detectors. The CO₂ and sulphur species absorbed in the alkaline solution were analyzed after oxidation via H₂O₂, and by acid-base titration and ion chromatography, respectively. CO was analyzed on dry gas samples by means of gas-chromatographic separation with a MS 5A ° 1/8' 50' column (He as carrier gas) coupled with a high-sensitivity reduced gas detector. The isotopic composition of N₂ and Ar were determined on the residual gases coupling the gas chromatograph with a mass spectrometer (MS). A post column switching device is used to split the column gas flow to the TCD detector and to the MS. In addition, this switching device allows one to invert the column flow after the species of interest (Ar, N₂ and CH₄) have reached the detector, preventing undesirable species (mainly CO and water) from reaching the MS (as detailed in the works of Caliro *et al.*, 2007; 2011; Chiodini *et al.*, 2012).

- Results obtained using the different techniques were integrated in order to obtain the final analyses, which were evaluated based on criteria of quality to distinguish the possible existence of atmospheric air contamination. This understanding is crucial for planning future works and may even imply changes in the areas selected to sample the fumarolic emission. In order to evaluate the existence of possible differences based on the methodologies used, the results obtained were also compared with the gas data previously measured using CVARG facilities (CO₂, H₂S, N₂, CH₄ and H₂). In addition, data were discussed in a preliminary way to identify differences with other hydrothermal areas and to prepare the elaboration of conceptual models, as well as to program future works and cooperation between the two institutions.

3. Description of the main results obtained

An inventory of procedures that should be taken into consideration before, during and after sampling hydrothermal fumaroles was performed and will help improving the methodologies and reduce the scattering of data between different institutions. In addition, analytical protocols were also discussed and a list of possible improvements to apply in the CVARG facilities was compiled, as well as a list of possible material to acquire.

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 CO₂/CH₄ that was already recognised as a good indicator of unrest phenomena (*e.g.* Chiodini, 2009). Integration of geochemical time series with other monitoring techniques (for example, geophysical data) was also discussed.

First complete gas composition and some isotopic data were obtained for the three fumarolic fields of Fogo Volcano and for the Caldeira Grande fumarole in Furnas Volcano (São Miguel Island). The analysed components were H₂O, CO₂, H₂S, O₂, H₂, He, N₂, CH₄, CO, ³⁶Ar, ⁴⁰Ar and

¹⁵N. The results obtained confirmed that the water vapour is the major component of all the sampled fumarolic emissions, followed by CO₂. The fumarolic gases have hydrothermal rather than magmatic characteristics as indicated by their CH₄ and CO contents, and by the absence of highly acid gases, such as SO₂, HCl, and HF. This is the first time that some of the gaseous species (He, CO, ³⁶Ar, ⁴⁰Ar and ¹⁵N) are investigated in the Azorean fumarolic fields and constitute a very promising dataset to apply geothermometers already defined for other hydrothermal areas. In fact, a very preliminary analysis of the data with application of the temperature geoindicators defined by Chiodini and Marini (1998) suggest initial temperatures around 250 °C.

4. Future collaboration with the host institution

The first datasets acquired during this Short Visit grant showed to be quite promising and a more extensive collection of gas comprising not only the fumaroles analysed during this visit, but also all the fumarolic fields of the Azores archipelago, is needed to have a complete “picture” of the fumarolic gas compositions in this particular geological setting. A complete survey carried out by researchers of both institutions is desired, but if not possible due to difficulty of funding for travels in the next months, the CVARG researcher will still sample the gases and send them to the INGV-OV, where the isotopic and gas compositions will be analysed. In addition, the INGV-OV researchers have provided to help in improving some methodologies existing in the CVARG laboratories if some future trips are planned.

5. Projected publications/articles resulting or to result from your grant

A paper characterizing the Azorean fumaroles is planned, however and as referred above, more data is needed to confirm and to strength some of the hypothesis already discussed with a preliminary analysis of the data. In future publications, the ESF will be duly acknowledged.

6. Other comments

Considering the wide range of methodologies used in the INGV-OV, and in order to better discuss the preliminary data obtained, the researcher realised that a longer period would have been very useful to allow also a better discussion and modelling of the data, as well as planning future works. However, the collaboration established between both institutions was reinforced and future analyses of data were already agreed.

The researcher flew from Ponta Delgada to Rome in the 2nd November due to the lower prices of the flight tickets; otherwise the price of the flight ticket would be higher than € 500. From Rome to Naples, the researcher went by car with a colleague that travels frequently between both cities. For this reason, no tickets are presented for the trips Rome – Naples – Rome in the 4th and in the 18th November.

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