Chemical composition of submarine degassing areas in São Miguel Island (Azores archipelago)

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ABSTRACT: Several secondary manifestations of volcanism are found in the Azores archipelago including subaerial and submarine hydrothermal fumaroles. This work shows the chemical composition of some submarine degassing vents located offshore of São Miguel Island, namely close to Porto Formoso, Ribeira Quente and Mosteiros villages. The samples were collected during the summers of 2013 and 2014 and spring of 2015. Analytical procedures included gas chromatography for the gases in the headspace of the Giggenbach bottles (CH_4, N_2, O_2, Ar, He and H_2) and titration for those dissolved in the alkaline solution (CO_2 and H_2S). The dry phase is dominated by CO_2 with more than 99 molar%. N_2, O_2 and Ar are also detected in minor amounts in all the samples, whereas H_2S and H_2 are present only in some of them. Characterization of these degassing emissions is important to identify and quantify the gases emitted and to identify future signals of volcanic activity.

I – GEOLOGICAL SETTING

São Miguel is the largest island of the Azores archipelago (Fig 1a). The island is formed by three quiescent central volcanoes: Sete Cidades at the western end of the island, Fogo, which lies in the central part of the island and, further to the east, Furnas Volcano (Fig. 1b). The submarine degassing vents discussed in this study are associated to these three volcanoes. Submarine degassing vents of Mosteiros are located in the NW flank of Sete Cidades Volcano; the submarine gas vents of Porto Formoso are located in the N flank of Fogo Volcano and submarine fumaroles of Ribeira Quente are located in the S flank of Furnas Volcano (Fig 1b).

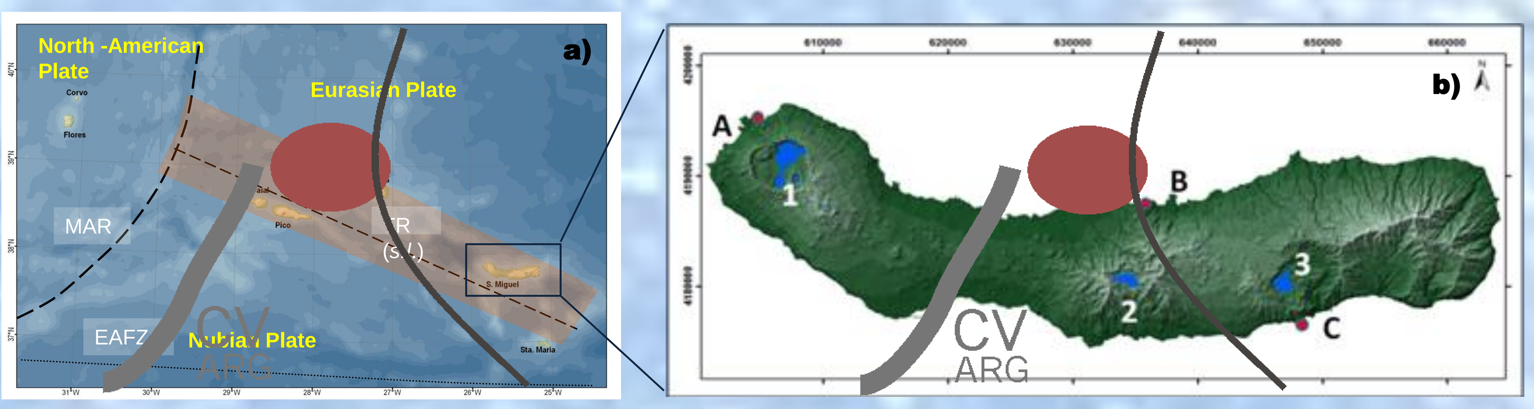

Fig. 1 – Location of the study site: a) Location of the Azores archipelago with the main tectonic structures (modified from Hipólito *et al.* 2010), b) DEM of São Miguel Island: 1- Sete Cidades, 2- Fogo, 3- Furnas volcanoes; A- Mosteiros, B- Porto Formoso, C- Ribeira Quente submarine gas vents.

II – SAMPLING METHODOLOGY

Gas samples were collected at the sea bottom by using pre-vacuum Giggenbach bottles filled with NaOH 4N.

The bottles were connected to an inverted funnel over the vent to catch and transfer the gas into the bottle (Giggenbach and Goguel, 1989) (Fig. 2).

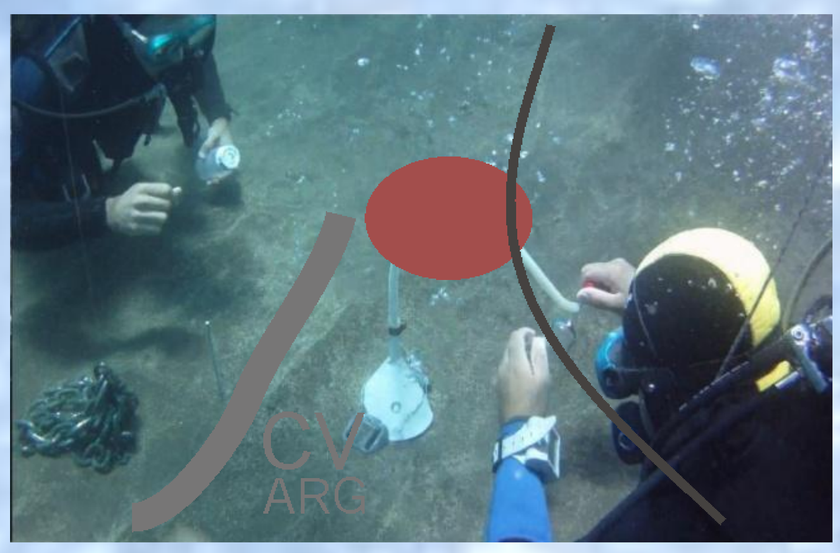

Fig. 2 – Collection of gases to the Giggenbach bottles during the surveys carried out at Ribeira Quente submarine fumaroles.

III – ANALYTICAL PROCEDURES

Gas samples were analyzed in the laboratory of gas geochemistry of the University of the Azores using:

- **Gas chromatography** — For the gases in the headspace of the bottle → **He, H_2, O_2, Ar, N_2** and **CH_4**
  Chromatograph Perkin Elmer Autosystem XL (Fig. 3a) equipped with a Thermal Conductivity Detector and MS packed column with He and/or Ar as carrier gases.
  Chromatograph Perkin Elmer Clarus 580 (Fig. 3b) equipped with two Thermal Conductivity Detectors and both a MS 5A plot column and a MS packed column, using He and Ar as carrier gases to quantify separately Ar and O_2.
- **Potentiometric titration** — For the gas dissolved in the alkaline suspension → **CO_2**
  Automatic titrator from Radiometer Copenhagen, model VIT90 Video Titrator (Fig. 3c).
- **Colorimetric titration** — For the gas dissolved in the alkaline suspension → **H_2S**
  Titration with mercury acetate using dithizone for end point detection (Fig. 3d).

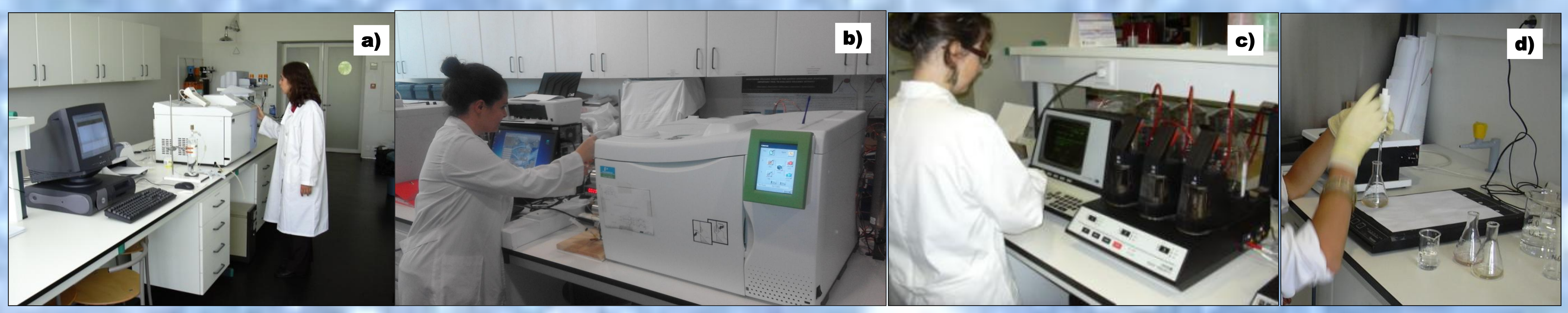

Fig. 3 – Equipment and material used to analyse the gas samples in the laboratory of gas geochemistry of the University of the Azores: a) GC Perkin Elmer Autosystem XL, b) GC Perkin Elmer Clarus 580, c) Automatic titrator Radiometer, d) Colorimetric titration with mercury acetate.

IV – RESULTS

Results are shown in Table I:

Table I – Gas composition of Porto Formoso, Ribeira Quente and Mosteiros representative samples. Legend: b.d.l.– below detection limit; a) – not detected due to technical limitations; b) – technical limitations did not allow separate detection of Ar and O_2.

Submarine Vent	Sampling date	CO_2 (molar%)	H_2S (molar%)	CH_4 (molar%)	H_2 (molar%)	He (molar%)	N_2 (molar%)	O_2+Ar (molar%)	O_2 (molar%)	Ar (molar%)	Gas chromatograph	Carrier Gas
Porto Formoso	08-07-2013	99.[illegible]7	b.d.l.	0.00004	b.d.l.	a)	0.0[illegible]	0.0043	b)	b)	Perkin Elmer Autosystem XL	He
Ribeira Quente	06-07-2014	9[illegible].59	0.095	0.01424	0.04	0.0011	0.21	0.0484	b)	b)	Perkin Elmer Autosystem XL	He and Ar
Mosteiros	21-04-2015	99.[illegible]5	b.d.l.	0.001[illegible]4	b.d.l.	0.0008	0.[illegible]	0.0597	0.0[illegible]46	0.0551	Perkin Elmer Clarus 580	He and Ar

- The most abundant dry gas in these submarine degassing vents is CO_2 with more than 99 molar%.
- N_2, O_2, Ar and CH_4 are also detected in minor amounts in all the samples.
- H_2S and H_2 were only detected in the Ribeira Quente submarine vents.

Differences between gas compositions are easier exposed using ratios that are very useful in seismovolcanic monitoring to evaluate the existence of equilibrium conditions on the reservoirs that feed these gas emissions and identify possible deviations that may indicate unrest periods. Table II shows the CO_2/CH_4 ratio, which was defined by Chiodini (2009) as an important indicator of deep-seated changes. Figure 4 shows the N_2/O_2 + Ar ratio that gives indication of the possible contamination of the samples with atmospheric air.

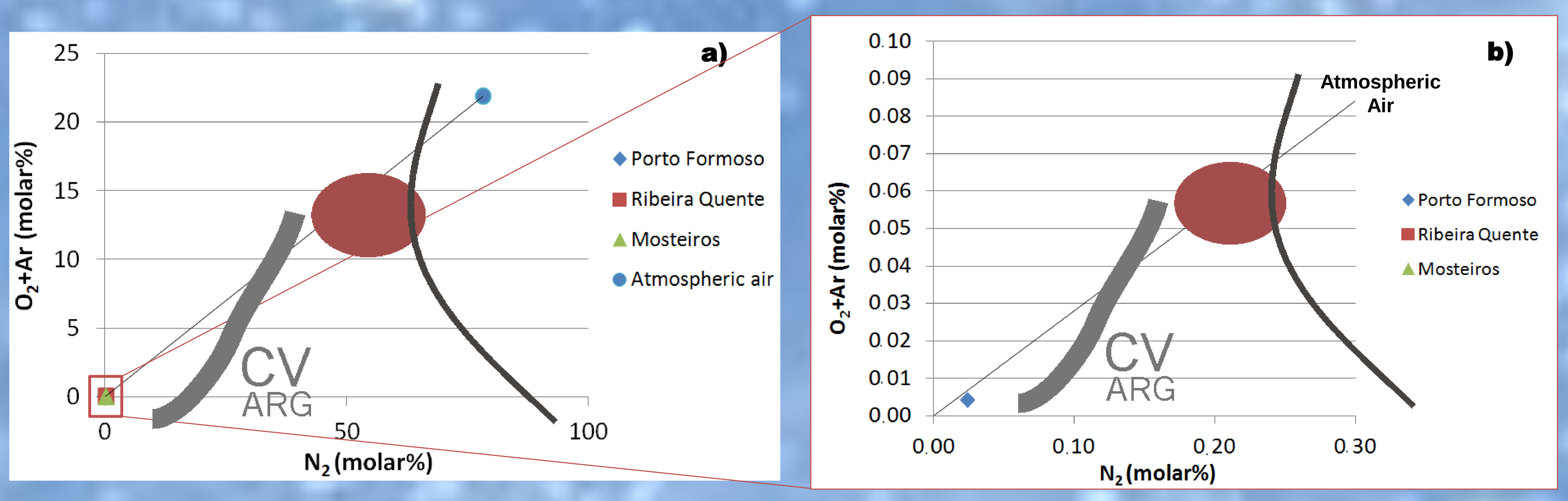

Fig. 4 – N_2/O_2+Ar ratios for the submarine gas vents and the atmospheric air composition; b) detail of the square area represented in 4a).

Table II – CO_2/CH_4 ratio for the different submarine gas vents.

Submarine Vent	CO_2/CH_4
Porto Formoso	2583204
Ribeira Quente	6993
Mosteiros	87546

V – DISCUSSION

- This work confirms that gas sampling methodologies applied inland seem to be appropriate to characterize these submarine vents.
- Ribeira Quente degassing area is dominated by CO_2 and shows a typical hydrothermal composition with the presence of H_2S, CH_4 and H_2.
- Emissions of Porto Formoso and Mosteiros are also dominated by the presence of CO_2, however H_2S and H_2 are absent, suggesting that these degassing vents may be the prolongation of the diffuse degassing areas identified inland, close to the sampled sites.
- Some gas ratios can be used to characterize the sampled submarine degassing sites:
  - CO_2/CH_4 → This ratio can be used to define the baseline during quiescent periods (Chiodini, 2009). Values presented in this work can be used as background level and future deviations may indicate eventual changes at depth.
  - N_2/O_2+Ar → This ratio is good indicator of air contamination as the typical ratio for atmospheric air is about 3.6. Porto Formoso is the sample closest to the atmospheric air ratio.

VI – CONCLUSIONS

- Additional gas sampling is necessary in order to confirm the stability of the presented gas ratio and evaluate the existence of potential variability.
- These results are also important for any seismovolcanic monitoring programme in order to recognize the baseline behaviour of the volcanic systems and eventually contribute to identify future signals of volcanic unrest.
- In that way more research in the offshore environments close to the islands should be carried out to try to discover also the existence of submarine degassing vents in other sites.

REFERENCES:

Chiodini, G. (2009). CO_2/CH_4 ratio in fumaroles a powerful tool to detect magma degassing episodes at quiescent volcanoes. *Geophysical Research Letters*, 36, L02302.

Giggenbach, W.F., Goguel, R.L. (1989). Collection and analysis of geothermal and volcanic water and gas samples. *DSIR New Zealand, Report No. CD 2387*, 53.

Hipólito, A., Madeira, J., Gaspar, J., Carmo, R. (2010). Structural Geology of Graciosa Island – a contribution for the geodynamics of the Azores triple junction. *Geophysical Research Abstracts,* 12, 9078.

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