Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

Geochemical Tools as a Contribution to Improve Geothermal Potential on the Azores Archipelago

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Keywords: Geochemical modelling, hydrothermal emissions, geothermometers, alteration minerals

ABSTRACT

Three high enthalpy geothermal power plants are currently managed by EDA Renováveis S.A. in the Azores archipelago (Portugal), two of them located at São Miguel Island and one at Terceira Island. The volcanic nature of the Azores islands, linked with a complex geodynamic context, converts the archipelago into a natural candidate not only for geothermal exploitation but also to develop research that can then be applied to other areas of the world.

Besides the application of traditional geophysical tools, geochemical data can also provide relevant information at different phases, from the exploration to the monitoring and reservoir management. One of the main objectives of the European project HEATSTORE (Geothermica Era-net) aims at constraining advanced numerical models that allow simulating the geothermal system under Fogo Volcano (São Miguel Island) through the use of geochemical data. To this end, chemical compositions of hydrothermal fumaroles, thermal and cold CO_2-rich springs have been used as geothermometers for the geothermal reservoir. In addition, thermal energy released in a target area and permeability zones (diffuse degassing structures) were identified by mapping diffuse degassing areas.

For the specific case of Ribeira Grande area (north flank of Fogo Volcano, São Miguel Island), equilibrium temperatures ranging between 231 and 258ºC were inferred for the reservoir feeding the fumaroles. Chemical composition of the springs highlighted disequilibrium conditions and oversaturation regarding silica solid phases making it challenging for the application of geothermometers. However, values in the range of 180 to 230ºC have been estimated. Despite some differences, these temperatures are quite similar to those measured in the geothermal wells, where maximum temperatures of 245ºC were detected. Radon (^{222}Rn) and carbon dioxide (CO_2) degassing maps carried out at Caldeiras da Ribeira Grande study site showed hidden diffuse degassing structures with general NW-SE direction, which are in agreement with the direction of the main tectonic structures identified in the area. A deep-derived CO_2 emission of approximately 63 t d^{-1} was estimated for an area with 0.218 km^2. Integration of this data with chemical composition of the fumaroles has allowed estimating a thermal energy of 7.7 MW for the study site.

Alteration minerals present in rock samples from a geothermal well also contributed to define temperatures at depth as well as permeable layers. Integration of all these geochemical parameters will feed and constrain a holistic geothermal reservoir model for the area and shows the potential of these relatively "low cost" tools to any geothermal exploitation area.

1. INTRODUCTION

High enthalpy geothermal power plants are currently running in the Azores in two of the nine volcanic islands that form the archipelago. The installed geothermal capacity is 23 and 3.5 MW at São Miguel and Terceira islands, respectively (Franco *et al*., 2017; 2019). The location of the Azores, in the triple junction of the Eurasian, North American and Nubian plates (Searle, 1980), together with the existence of a mantle geochemical anomaly (*e.g*., Métrich *et al*., 2014 and references therein), is responsible for the seismic and volcanic activity that characterizes the islands. Nowadays the volcanic activity is dominated by the occurrence of seismic swarms, in some cases associated with deformation episodes (Silva *et al*., 2012; Okada *et al*., 2015), as well as by the presence of secondary manifestations of volcanism. Currently the hydrothermal manifestations found out in the archipelago are the low temperature (< 100ºC) fumarolic fields, thermal and cold CO_2-rich springs, as well as several diffuse degassing areas (Cruz *et al*., 2010; Viveiros *et al*., 2010; 2020a; Caliro *et al*., 2015; Silva *et al*., 2015; Andrade *et al*., 2016).

The geodynamic context of the Azores archipelago associated with the quiescent volcanism converts the islands into natural laboratories for studying high enthalpy geothermal systems and developing tools that can be applied to other geothermal areas worldwide. Under the umbrella of the European project HEATSTORE (Geothermica Era-net), running from 2018 to 2021, the Portuguese subproject aims at applying innovative modelling tools in the Caldeiras da Ribeira Grande geothermal area (north flank of Fogo Volcano), based essentially on geochemical data. In fact, geophysical surveys are commonly chosen as the more adequate strategies to infer the subsurface conditions at a geothermal area. This study shows the relevance to integrate geochemical data to better discriminate percolation paths, infer thermodynamic conditions in the reservoir and identify the type of fluids.

2. CHARACTERIZATION OF THE STUDY SITE

Caldeiras da Ribeira Grande geothermal area is located in the north flank of Fogo Volcano (Fig. 1), a polygenetic volcano with a summit caldera that holds a lake with a surface of approximately 1.5 km^2. The volcano was formed more than 200 000 ago and has produced major trachytic explosive activity in the last 10 000 years, and included two Plinian scale events. The last eruption occurred in 1563 and corresponded to a sub-Plinian eruption inside the summit caldera, and four days later, it was followed by a Hawaiian event in the northwestern flank of the volcano. A phreatic explosion was reported in 1564, in the same site of the 1563 sub-Plinian eruption (Wallenstein *et al*., 2015 and references therein). The main hydrothermal manifestations found at Fogo Volcano are located in the north flank (Ferreira *et al*., 2005; Cruz *et al*.; 2010; Caliro *et al*., 2015; Viveiros *et al*., 2015a) and are controlled by the tectonic structures that cross the volcanic system, with particular relevance for the Ribeira Grande graben (Carmo *et al*., 2015). Recent studies (Andrade *et al*., 2020) highlighted the absence of volcanic degassing on the caldera lake.

Three main fumarolic fields are found at Fogo Volcano, which are Caldeira Velha, Caldeiras da Ribeira Grande and Pico Vermelho (Ferreira *et al*., 2005; Caliro *et al*., 2015). Thermal and cold CO_2-rich springs are also dispersed on the north flank of the volcano (Cruz *et al*., 2010) (Fig. 1). Despite the visible hydrothermal manifestations, several diffuse degassing areas were identified at Fogo Volcano, mainly associated with the NW-SE tectonic structures that traverse the volcanic system (Marcos, 2006; Viveiros *et al*., 2015a).

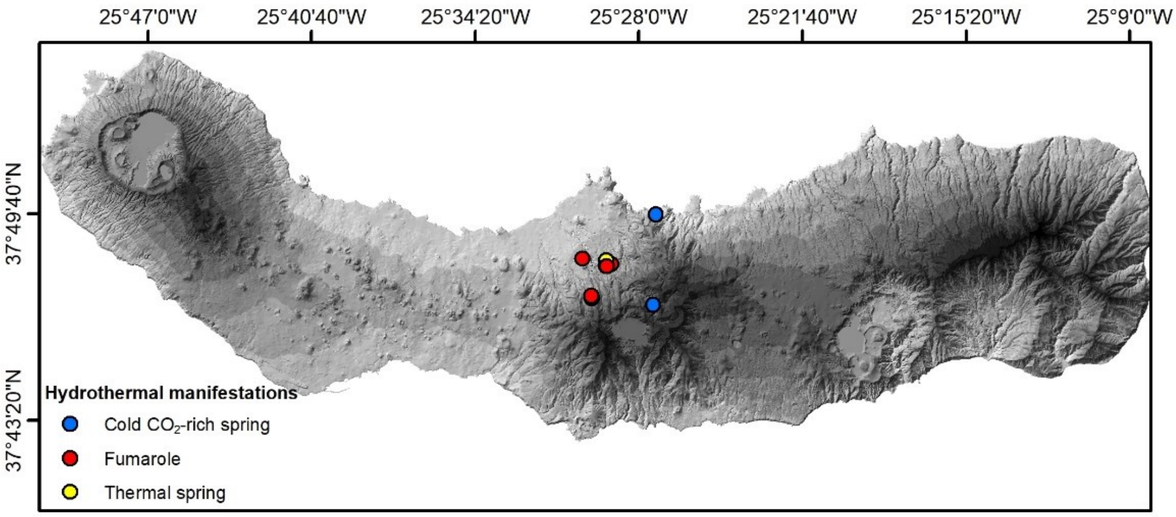

Figure 1: Location of the visible secondary manifestations of volcanism in the north flank of Fogo Volcano.

Two geothermal power plants are located in this volcanic system, in the so-called Ribeira Grande geothermal field. The Cachaço-Lombadas power plant is located at higher altitude, and the Pico Vermelho power plant is located in the northern area of the field, at lower altitude. The geothermal reservoir is liquid-dominated with maximum temperatures around 245 ºC (Franco *et al*., 2019 and references therein). Eight geothermal wells are currently in production, while new wells are being drilled nearby.

Since 2002, IVAR – Research Institute for Volcanology and Risk Assessment and CIVISA – Centre for Information and Seismovolcanic Monitoring of the Azores have established a permanent monitoring programme to detect eventual geophysical (seismic, deformation) and geochemical (gas composition) anomalies correlated with deep changes on the system. The geothermal company EDA Renováveis S.A. required its activity to be monitored through permanent gas, seismic and GPS stations, as well as through several regular surveys usually carried out every three months.

3. GEOCHEMICAL DATA

As previously mentioned, the current study aims at selecting geochemical data that can contribute for modelling a high enthalpy geothermal reservoir not only during the pre-drilling stage, but also during the exploitation and monitoring phases.

3.1 Hydrothermal fumaroles

As mentioned above, three main fumarolic fields are located in the north flank of Fogo Volcano. Gases collected on the Pico Vermelho emissions mostly consist of water vapour, with minor amounts of CO_2. High concentrations of nitrogen (N_2) and oxygen (O_2) indicate air contamination. For this reason, these fumaroles have been excluded from the current study. The gas compositions of the Caldeiras da Ribeira Grande and Caldeira Velha fumaroles are dominated by water vapour, followed by CO_2 as the main gas in the dry phase. The sulphur compound is the hydrogen sulphide (H_2S), as characteristic of hydrothermal environments. Methane (CH_4) amount at Caldeira Velha is higher than at Caldeiras da Ribeira Grande area. Minor concentrations of N_2, argon (Ar), O_2, helium (He), hydrogen (H_2) and carbon monoxide (CO) have been also detected (Ferreira *et al*., 2005; Caliro *et al*., 2015). Previous studies based essentially on the carbon and helium isotopic compositions also showed the mantellic origin of the gases released in the fumaroles (Caliro *et al*., 2015).

Very few studies applied geothermometers to the gases emitted at Fogo fumaroles (Truesdell *et al*., 1984; Caliro *et al*., 2015; Viveiros *et al*., 2020b), and ranges of temperatures between 209 and 240ºC were inferred by Truesdell *et al*. (1984) based on the D'Amore and

Panichi (1980) geothermometer. Caliro *et al*. (2015) suggested mostly temperatures from 259 to 278 ºC for the fumarolic emissions located at Caldeiras da Ribeira Grande area, based on the Chiodini and Marini (1998) geothermometer. More recently, Viveiros *et al.* (2020b) estimated equilibrium temperatures between 231 and 256 ºC for the Fogo fumarolic emissions. In this last study, the Arnórsson *et al*. (1998) geothermometer was applied to data collected during 2017.

Recently, several geothermometers (D'Amore and Panichi, 1980; Nehring and D'Amore, 1984; Giggenbach, 1991; Arnórsson *et al*., 1998) were applied to the gas compositions from Caldeiras da Ribeira Grande and Caldeira Velha fumaroles, for the period between 2015 and 2020. The H_2/Ar gas geothermometer from Arnórsson *et al.* (1998) showed to be the most adequate considering the gas composition of the fumaroles and the requested assumptions to apply this geothermometers. An average temperature of 258 ºC is estimated for the hydrothermal system reservoir feeding the Caldeiras da Ribeira Grande fumaroles, and an equilibrium temperature of 231 ºC is estimated for the Caldeira Velha fumaroles. The lower temperature inferred for the reservoir feeding Caldeira Velha fumarole is in agreement not only with the results obtained previously by Truesdell *et al.* (1984), but also with the temperatures measured in the geothermal wells located in the upper part of the volcanic system. These wells (CL1, CL5, CL6 and CL7), located closer to Caldeira Velha fumarole, show maximum temperatures ranging between 229 and 235 ºC (Franco, 2016; Franco *et al*., 2018) (Fig. 2).

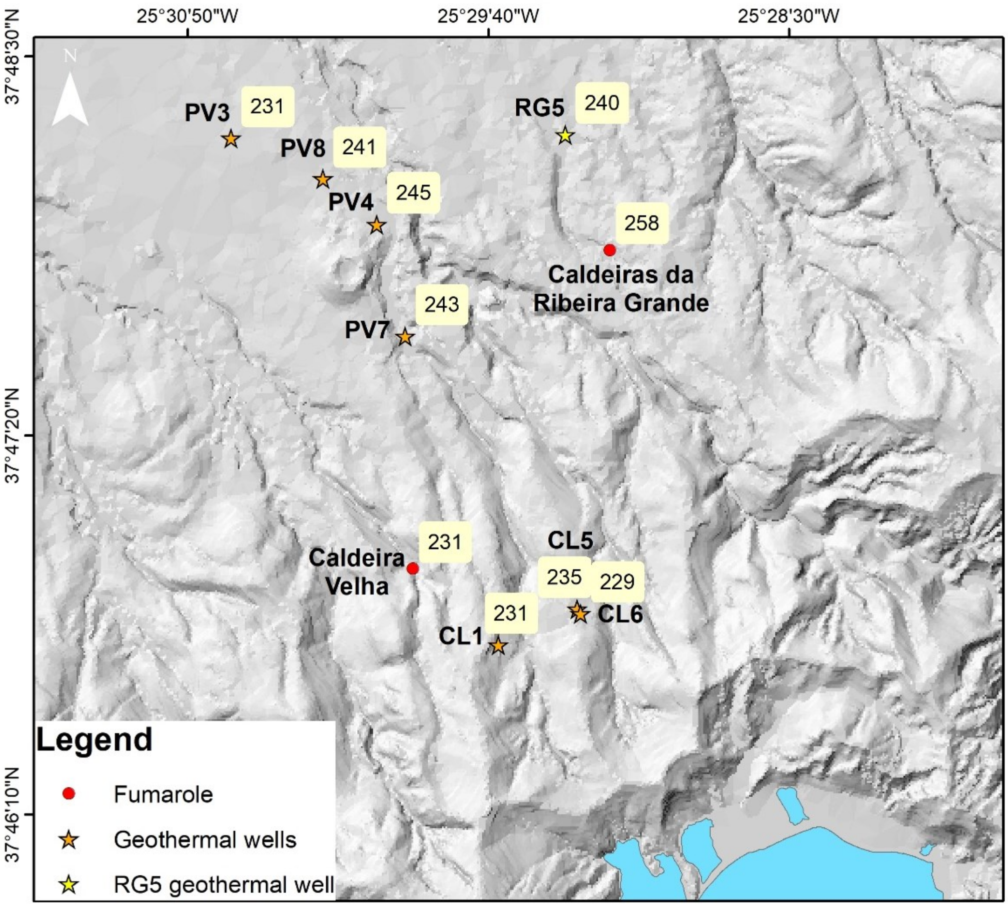

Figure 2: Maximum temperatures (yellow squares) measured in the geothermal wells and inferred reservoir temperatures based on the Arnórsson *et al.* (1998) geothermometer applied to the gas released from the fumaroles.

3.2 Thermal and cold CO_2-rich springs

Thermal springs located on the north flank of Fogo Volcano, namely associated with the Caldeiras da Ribeira Grande fumaroles, present Na-SO_4 dominated compositions and correspond to the more acidic springs measured in the Azores, with pH ranging between 2.02 and 2.27 (Cruz and França, 2006). The composition of the springs allows establishing the hydrogeochemistry processes dominating in the area, showing both water-rock interaction and the steam heating processes. Despite these subsurface controlled processes, sea salts dry deposition is also identified from the interpretation of the groundwater geochemistry (Cruz *et al*., 2010; Freire *et al*., 2015).

Stable isotopic composition of the springs confirms a meteoric origin for the water present in the system and a magmatic origin for the carbon and sulphur elements, in agreement with previous data for Furnas Volcano (Cruz *et al.,* 1999), and even with the isotopes measured in the gas fraction (Caliro *et al*., 2015).

Chemical composition of the springs highlighted immature composition of the waters and, consequently, the application of geothermometers to the data collected on the springs needs to be done carefully. Disequilibrium conditions and oversaturation regarding silica solid phases constitute major challenges and difficulties. Nevertheless, a set of geothermometers (*e.g*., Na-K-Ca, Na/Li, Mg/Li, Rb/Na, Sr/K^2, Serra and Sanjuan, 2004 and references therein) was applied and values ranging from 180 to 230 ºC were inferred.

3.3 Diffuse degassing areas

3.3.1 Degassing maps

Permanent and not visible gas emissions also characterize volcanic and geothermal areas. CO_2 and the radioactive gas ^{222}Rn are the main volatile species released in these areas, and are detected only using specific instruments. Previous surveys carried out at Fogo Volcano showed anomalous soil CO_2 concentrations mainly in the north flank of the volcano, essentially associated with the Pico Vermelho degassing area and the Ribeira Seca village (Marcos, 2006; Viveiros *et al*., 2015a).

Soil CO_2 flux surveys using the accumulation chamber method (Chiodini *et al*., 1998) were carried out at the Caldeiras da Ribeiras Grande area in 2012 and 2016. A total of 1093 measurements were carried out in an area with about 0.218 km^2 and gas fluxes varied between 0 and 20 780 g m^{-2} d^{-2}. Carbon isotopic composition of the soil CO_2 flux in the 2016 survey showed a mixture of volcanic and biogenic contribution for the released gas (Viveiros *et al*., 2020b). The total CO_2 emitted in the surveyed area was estimated to be 70 t d^{-1}, with 90 % of the gas showing a deep-derived origin.

^{222}Rn measurements, at about 50 cm depth in the soil, were carried out in the same area in July 2019 and values ranged between 17 and 298 500 Bq m^{-3}. The 133 measured sites showed anomalous gas concentrations spatially correlated with the soil CO_2 fluxes (Fig. 3). Soil temperature, at about 15 cm depth, was measured in all the surveys and values varied from 10.5 to 98.6 ºC. A positive correlation between soil temperature and the soil gases is also highlighted, showing that the main geochemical anomalies are located in thermal anomalous zones.

The degassing maps show lineaments of gas anomalies (for both CO_2 and ^{222}Rn) along general NW-SE trends, defining the so-called diffuse degassing structures (DDS) by Chiodini *et al*. (2001). Previous structural studies (Carmo *et al*., 2015) carried out in the area did not identify tectonic structures crossing Caldeiras da Ribeira Grande area, what can be explained by the existing vegetation together with the thick pumice deposits that hide eventual structures. However, the consistent lineament of gas anomalies for the different gas surveys point to a deep structural control and suggest the existence of tectonic structures in the study area. In addition, the integration of these maps with previous geological data, confirm similar trends for the gas lineaments and the identified faults (Carmo *et al*., 2015) (Fig. 3).

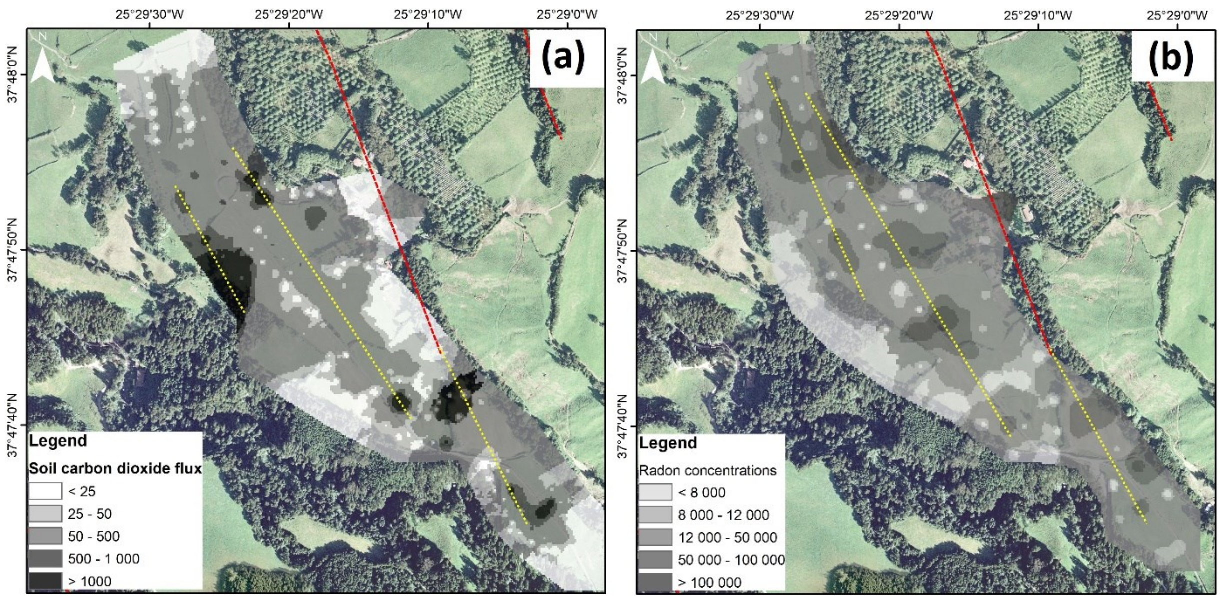

Figure 3: Soil CO_2 flux (a) and soil radon (b) anomaly maps for Caldeiras da Ribeira Grande area. Data were interpolated using the deterministic IDW method (6 neighbor points). The red line represents a tectonic lineament previously mapped by Carmo *et al*. (2015). The yellow lines represent degassing lineaments.

3.3.2 Permanent soil CO_2 flux stations

The first permanent soil CO_2 flux station was installed at Fogo Volcano in February 2002, at Pico Vermelho geothermal area. This station performs measurements based on the accumulation chamber method and has coupled several environmental sensors, to measure barometric pressure, soil and air temperature, soil water content, rainfall, wind speed and direction. This station, initially named GFOG1 (Viveiros *et al*., 2008), was later moved due to construction actions in the geothermal power plant. Since April 2008 the station is relocated inside the Pico Vermelho geothermal area and it is named GFOG3.1 (Viveiros *et al*., 2015b). In 2005 a second station was installed inside the Fogo caldera and until now only background biogenic values were measured, confirming the absence of volcanic gases inside the caldera. In June 2010 a third station was installed in the area surrounding Caldeiras da Ribeira Grande site (named GFOG4, Oliveira *et al*., 2018) to monitor the expansion of the gas anomaly associated with an incident that occurred in the RG4 geothermal well in 2010.

Considering the recognized interference that meteorological variations may have on the diffuse degassing (Viveiros *et al*., 2008; 2015b; Oliveira *et al*., 2018), all the permanent stations installed in the Azores archipelago have coupled several environmental sensors. Data recorded in the GFOG3.1 and GFOG4 sites show that the main controlling environmental factors on the CO_2 emission are soil water content, air and soil temperature, and wind speed (Viveiros *et al.,* 2015b, Oliveira *et al*., 2018). These stations perform measurements in an hourly basis and the data is automatically filtered through statistical methodologies (multivariate regression analysis) to evaluate the existence of potential anomalies that can represent unrest episodes on the volcanic system, and/or changes on the geothermal reservoir conditions.

3.3.3 Thermal energy released

Considering the positive correlation between soil CO_2 fluxes and soil temperature, the thermal energy released in the study area can be estimated following the method defined by Chiodini *et al*. (2005). Hydrothermal CO_2 emission (63 t d^{-1} as mentioned above) together with the mass ratio H_2O/CO_2 in the Caldeiras da Ribeira Grande fumaroles (4.07) allows to estimate a thermal energy of about 7.7 MW for the sampled area (0.218 km^2) (based in data from Viveiros *et al*., 2020b).

4. PETROGRAPHY AND MINERALOGY DATA

As well as geochemical data obtained from the secondary manifestations of volcanism existing in the study area, the mineralogy from the cuttings from the RG5 exploratory well was also studied. RG5 is located close to Caldeiras da Ribeira Grande area, at about 800 m from the main fumaroles. The mineral assemblages of drill cuttings from this well, down to a depth of 1343 m, were supplied by EDA Renováveis S.A. and were characterized firstly under stereo microscope (Nikon SMZ1000) and secondly with twenty X-ray diffraction (XRD) analysis. These last analytical procedures were done down to 644 m depth and carried out in an external laboratory (Activation Laboratories Ltd.).

The subsurface geology identified on the well corresponds to the Fogo Volcano erupted rocks. In the upper part of the well, trachyte lavas interbedded with pyroclastic deposits were identified, while in the reservoir sector the country rocks are mainly basalts (*sensu latu*) and separated by hematite-rich breccia. Towards the bottom of the well, a transition sequence was identified, with interbedded altered tuffs, basaltic lava, lava breccia and altered rock and grading to altered pyroclastic deposits. No submarine sequence has been identified up to the bottom of the well.

The main alteration minerals identified were clays, calcite, silica minerals (such as opal, chalcedony and quartz), chlorite, hematite, anatase, titanite, pyrite and adularia. Clay minerals, identified with XRD analysis, were kaolinite, smectite, illite, and interlayered illite-smectite. Smectites, coexisting with kaolinites, occur at shallow depths, while mixed-clay illite-smectite appears in impermeable tuffs indicating a diffuse flow of the fluid and a low permeability (Harvey and Browne, 1991; Utami and Browne, 1999; Pandarinath *et al.,* 2006). The smectite and kaolinite assemblage points out for temperatures lower than 160 °C. The presence of chlorite is constant throughout the entire well length and occurs for a wide range of temperatures. A peak of adularia suggests the existence of a boiling zone at the top of the reservoir, which is in line with previous studies at the Ribeira Grande reservoir (*e.g*., Henneberger and Nunes, 1990; Ponte *et al*., 2010; Rangel, 2014; Franco, 2016). The hydrothermal mineral assemblage of chlorite + quartz + calcite + hematite ± anatase ± titanite ± adularia indicates temperatures above 235 °C.

The existent clay minerals in the well contribute to establish the main alteration zones. An unaltered to slightly altered zone (with few argillization) is present from the surface until 123 m depth. At this depth, a smectite zone appears, since smectite, which coexists with kaolinite, and sometimes with illite and chlorite, is the predominant clay mineral. At a depth of 183 m, associated with a temperature of about 163 ºC, a chlorite zone is identified being this mineral abundant from this point on. However, in some zones (here identified as sub-zones) other clay minerals also appear as dominant, but in a discontinuous way. These two sub-zones were the chlorite + interlayered illite-smectite, and the chlorite + illite.

Besides the association with temperature ranges, alteration minerals together with the geology also contribute to understand the structure of the reservoir. An impermeable cap rock of silicified and impermeable tuffs should occur over the reservoir. The high abundance of adularia, as mentioned above, suggest a steam cap at the top of the reservoir. The country rocks of the geothermal reservoir are basalts (*sensu latu*), and are intruded by veins of quartz and calcite, sometimes associated with anatase and chlorite. These minerals seal the fractures and reduce the permeability. Furthermore, few losses in the circulation fluid during drilling were found for this well (Rangel, 2014).

5. CONCLUSIONS

This study evaluated the application of different data to contribute for a better understanding of the geothermal potential in an area, as well as to monitor eventual reservoir changes. In what concerns gas geochemistry data, despite the fact that the application of geothermometers can be quite challenging and need to fulfill specific conditions, equilibrium temperatures inferred for the feeding reservoirs based on the gas compositions seem to correlate well with the temperatures measured inside the geothermal wells. The H_2/Ar geothermometer defined by Árnorsson *et al.* (1998) showed to be adequate to apply to the Caldeiras da Ribeira Grande and Caldeira Velha fumarolic emissions. The application of geothermometers to the Fogo Volcano springs was challenging, as waters are not in equilibrium. Even though, chemical composition of the springs contributes to model the main processes occurring at depth (water-rock interaction, steam heating), to infer fluid composition as well as the origin of the gases released.

Soil diffuse degassing maps identify not only the gas geochemical anomalous zones, but also the existence of DDS that may represent permeability zones. In fact, several studies already showed the importance of mapping gas anomalies in areas as the Azores archipelago, where lush vegetation and/or thick pumice deposits may hide the tectonic structures. The DDS and lineaments suggested for the Caldeiras da Ribeira Grande area are in agreement with the direction of previously mapped tectonic structures in the north flank of Fogo Volcano.

In addition to the use of geochemical tools, the current study also highlights the importance of petrography and hydrothermal mineralogy to understand the structure of the reservoir, establish alteration zones, infer temperatures at depth and eventually define the permeability zones. The minerals assemblages in the RG5 geothermal well showed a former/original high-permeability, but now alteration minerals seal fractures, what is in agreement with the low permeability found during drilling operations. In addition, they also agree with the maximum temperatures measured in the well, which were 240 ºC (Fig. 2).

Gas geochemical tools may thus contribute to characterize the fluid composition, to discriminate the thermodynamic conditions in the reservoir and the main subsurface processes that control the gas and water compositions, to identify the origin of the volatiles released and even to recognize percolation paths. All this information is relevant not only during the pre-drilling phase, but also for monitoring and during reservoir management in order to identify possible changes on the deep feeding system. Data obtained using a set of different geochemical tools and geophysical techniques applied in a target area should be always integrated to better model the processes occurring at depth.

ACKNOWLEDGEMENTS

This study was funded by the project HEATSTORE – Geothermica Era net (European Project with Portuguese national funding from FRCT – Fundo Regional da Ciência e Tecnologia, Azores Government).

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