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# Preliminary geochemical and isotopic results in thermal and cold waters of Graciosa volcanic Island (Azores)

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**Abstract**

Graciosa Island is located in the Azores Archipelago, along the so-called Terceira Rift, NE boundary of the Azores Plateau. From the hydrochemical point of view, two types of Na-Cl groundwater systems were identified: a cold aquifer system emerging at springs and exploited through boreholes for public water supply with different degrees of mineralization, and a hydrothermal system with issuing temperatures around 45 ºC. Geothermometers applied to the thermal waters point to deep temperature around 167 ºC and to immature waters, not reaching complete equilibrium with the reservoir rock. The isotopic composition and geochemistry of the thermal waters indicate mixture groundwater - seawater in different percentages and ion-exchange mechanisms that will be able to: i) increase groundwater salinity, ii) strongly change the isotopic composition to more enriched values, with different degrees of mixing.



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*Keywords:* Thermal waters; volcanic island, seawater-groundwater mixture; Azores (Portugal)

## 1. Introduction

In volcanic islands, the vulnerability of the aquifers is high and the chemical and environmental isotope composition of the groundwater is affected by several processes such as incorporation of marine salts due to

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proximity of the sea or seawater intrusion, input of species of volcanic and/or hydrothermal origin and anthropogenic contamination. In these cases, modifying processes affecting the groundwater composition, such as mineral dissolution / precipitation, ionic exchanges and redox reactions can occur, and also from the isotopic point of view can have a strong effect within the groundwater composition.

Aquifers in the Azores archipelago are supporting an increase of pressure for social, industrial and agriculture development, as already recognized in several studies[1]. Groundwater contamination by salinization, due to overexploitation, agricultural activities, lack of appropriate waste water drainage and treatment systems and also due to rock–water interaction in acidic environment have been reported in the majority of the nine islands of Azores archipelago as the main cause for groundwater quality degradation, that may lead to a failure to fulfill the EU and national water quality regulations[1].

The research area is located at Graciosa Island, one of the nine islands of the Azores archipelago on the North Atlantic Ocean, about 1,800 km west of Portugal mainland. The Azores archipelago is located at the Triple junction where the Eurasian, the North American and Nubian plates meet, in the mid-Atlantic Ridge (Fig. 1). Graciosa Island is located along the so-called Terceira Rift, a major tectonic structure that makes the NE boundary of the Azores Plateau.In Graciosa Island, groundwater is represented by cold to thermal waters with low and high mineralization. Waters are of sodium chloride type with strong deviation in the environmental isotopic composition, in both oxygen-18 and deuterium, to more enriched values (thermal waters). For proper management and protection of water resources on the island, it is important to identify the salts sources present in water and to understand the groundwater flows.

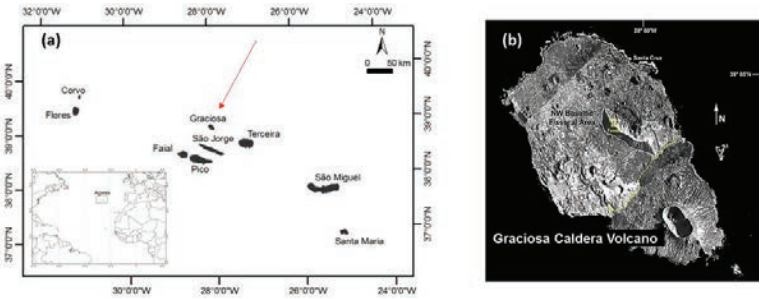


Fig. 1- (a) Geographic setting of the Azores archipelago, location of Graciosa Island; (b) Graciosa Island. Adapted from[2]

## 2. Methods

Three sampling campaigns were carried out in Graciosa Island from 2008 to 2009. 14 Groundwater samples were collected from boreholes, springs and 1 lake. Temperature (ºC), electrical conductivity (μS/cm) and pH were measured in situ; environmental isotopes determinations were performed at C2TN/IST – Sacavém, the $\delta^2H$ and $\delta^{18}O$ content were obtained using SIRA 10 – VGISOGAS mass spectrometer and the results are reported in δ notation reported to V-SMOW in ‰; the tritium content of the groundwater samples was obtained using a tritium enrichment unit and after measured in PACKARD Tri-Carb 2000 CA/LL, liquid scintillation counter, the values are reported in TU. Major and minor ions were measured in all water samples; these analyses were performed at ActLabs, Canada.

## 3. Hydrogeological Settings

Hydrogeological setting at Graciosa Island is directly connected to the main tectonic structures and also associated to the volcanic activity occurred or happening today, varying from a steady outpouring of lava to explosive events and resulting in several types of volcanic deposits outcropping[1,2].Thus, in general terms, the geology of the island includes: i) a polygenetic siliceous volcano with a summit collapse caldera, on the SE (e.g. the Graciosa Caldera Volcano - Fig.1) and, ii) the so-called "NW Plateau", of basaltic *s.l.* nature and including 56 monogenetic volcanoes, almost all as scoria cones and associated aa or pahoehoe lava flows[2]. In spite of its small size (about 61 sq. km), Graciosa Island has an important diversity of landscapes and volcanic products (Fig. 1).

The groundwater systems occur in two major aquifer configurations namely: i) the basal aquifer system which corresponds to freshwater lenses, floating on underlying saltwater, characterized by a low hydraulic gradient, and ii) the altitude aquifer systems, corresponding to perched-water bodies discharging at springs, distributed along the major volcanoes slopes and where the morphological conditions favor the discharge. Exploitation of the basal aquifer systems occurs mainly through boreholes, reinforcing the plan that the water supply, and groundwater abstraction relies almost exclusively on the basal aquifer[1].

The main hydrothermal manifestations in Graciosa Island are associated to the Caldera Volcano, particularly inside the huge (150m wide, 80 m high) Furna do Enxofre lava cave, that includes a cold water lake at its bottom, a bubbling mud pool and, some fumaroles of steaming grounds type, that release steam and gases, leading sometimes to the accumulation of deadly $CO_2$ concentrations. Steaming grounds fumaroles with temperatures up to 98 ºC are also present in the NW Plateau. The most important thermal springs are those located near the sea level, at the Homiziados Bay and Carapacho. The latter is used for balneotherapy since 1750 A.D. and is presently exploited through boreholes for Thermal SPA proposes, while Homiziados spring represents itself as a small spring at the base of coastal cliffs, visible during low tide periods.

### *3.1. Hydrogeochemistry*

In Graciosa Island two types of Na-Cl groundwater systems were identified: a cold one emerging at springs and exploited by wells for public water supply with pH higher than 7 and different degree of mineralization related to the proximity to the sea; and a hydrothermal system of low enthalpy, with temperatures around 45 ºC, pH varying between 6.20 and 6.94 and total dissolved solids (TDS) reaching 35000 mg/L, indicating the possibility of seawater input (Fig. 2). The thermal waters also show a mean $SiO_2$ content of 166 mg/L, and a significant concentration of metals, such as Mn, Fe, Co, Ni, Cu and Zn. The thermal water mineralization varies strongly, showing EC from 8.87 mS/cm (shallow aquifer) to 47.4 mS/cm (deep aquifer). The highest mineralized water is rich in $CO_2$(g), with 2130 mg/L of total dissolved $CO_2$. Waters from the lake located inside of the Furna do Enxofre lava cave have intermediate characteristics between cold groundwater (low mineralization) and thermal waters (relatively high $CO_2$(g) content, 396 mg/L), likely indicating that their mineralization is mainly due to the dissolution of magmatic/hydrothermal $CO_2$ and that water-rock interaction processes are quite limited. Geothermometers were used to calculate the aquifer temperature at depth. The inferred temperature values at depth are around 167ºC and immature or mixed waters, indicating the lack of complete equilibrium with reservoir rock[3]. The geochemistry of the thermal waters indicates the occurrence of seawater/host rock interaction processes at high temperature and slightly acid conditions, favored by $CO_{2(g)}$ input, and a different degrees of mixing with cold and shallow groundwater.

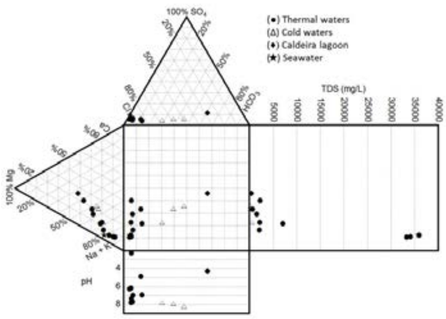


Fig. 2 – Durov diagram. The symbols stand for: (●) thermal water; (Δ) cold groundwater; (♦) Caldera Volcano lake and (★) seawater.

### *3.2. Isotopic signatures*

The groundwater samples from Graciosa Island were plotted in the $\delta^{18}$O vs. $\delta^{2}$H diagram (Fig. 3a) where two clusters of groundwater samples can be recognized. Although some thermal waters lie along the groundwater-seawater mixing line, three thermal water samples show an isotopic composition more enriched than seawater. The splitting of the samples is also visible when the O-18 content is plotted as a function of the total dissolved solids or even as a function of the groundwater electrical conductivity, besides the differences in temperature (Fig. 3).

The isotopic shift towards more enriched values probably indicate not a simple mixture between two end-members, seawater – fresh water, but also the presence of other processes responsible for modifying the isotopic and chemical signatures of the thermal waters in Graciosa Island, as found in S. Miguel Island[1]. Like in Graciosa, at S. Miguel island, the isotopic enrichment and the high mineralization found in the basal aquifer systems, were attributed to a mixture groundwater - seawater and ion-exchange mechanisms.

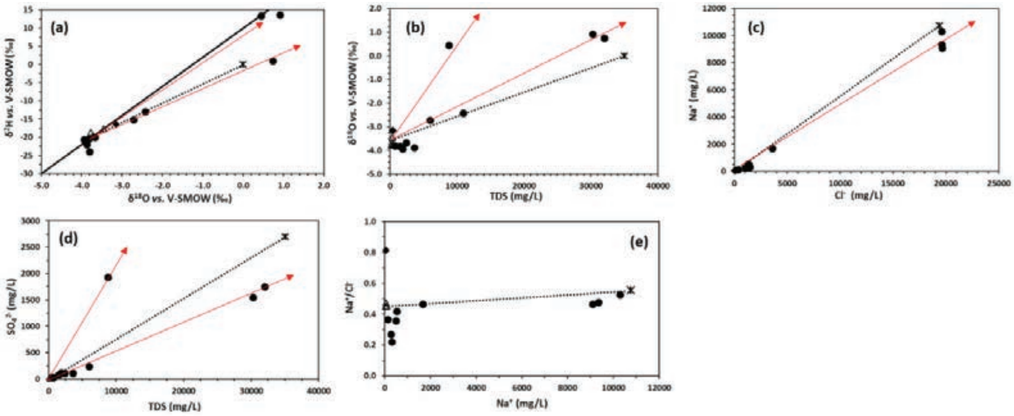


Fig. 3 – (**a**) $\delta^2H$ *vs.*$\delta^{18}O$; (**b**) $\delta^{18}O$ *vs.*TDS; (**c**) $Na^+$*vs.*$Cl^-$; (**d**) $SO_4^{2-}$*vs.* TDS; (e) Ratio $Na^+/Cl^-$*vs.* $Na^+$ for groundwater samples from Graciosa Island. The symbols stand for: (●) thermal water; (Δ) cold groundwater; (♦) Caldera Volcano lake; (✱) seawater; (·····) groundwater – seawater mixing line; (→) stands for the different evolution trend.

No tritium was found in thermal waters while the cold water showed $^3H$ concentration around 1.3 ±0.8 TU, indicating an active recharge of the system.

## 4. Final Remarks

The geochemistry of the thermal occurrences at Graciosa Island indicates: i) the presence of seawater in different percentages of mixing; ii) water - host rocks interaction processes in several degrees at high temperature (≈167ºC), and, iii) the presence of water – rock interaction processes in the shallow aquifer systems. The isotopic and chemical composition observed in the thermal waters (i.e. Carapacho and Homiziados springs) may result from a mixture of meteoric waters with seawater and ion exchange processes, explaining by this way the groundwater composition (isotopic enrichment and sodium-chloride type) and sodium depletion.

Additional data on trace elements, dissolved gases and carbon isotopes of the dissolved $CO_2$ will help to discriminate the origin of the fluids and processes of interaction with the hydrothermal systems in Graciosa Island.

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