

## Ischia Island (Italy) Geothermal System

Alessandro. Sbrana (1), Paolo Fulignati (1), Italo Giulivo (2), Lucilla Monti (2) and Geoffrey Giudetti (1)

(1) Dipartimento di Scienze della Terra, Universita' degli Studi di Pisa, via Santa Maria, 53 56126 Pisa, Italy

E-mail address, sbrana@dst.unipi.it, fulignati@dst.unipi.it

(2) Assessorato Ambiente e Difesa Suolo, Settore Difesa Suolo e Geotermia, Regione Campania, Via De Gasperi 21 Napoli, Italy  
carg.campania@regione.campania.it

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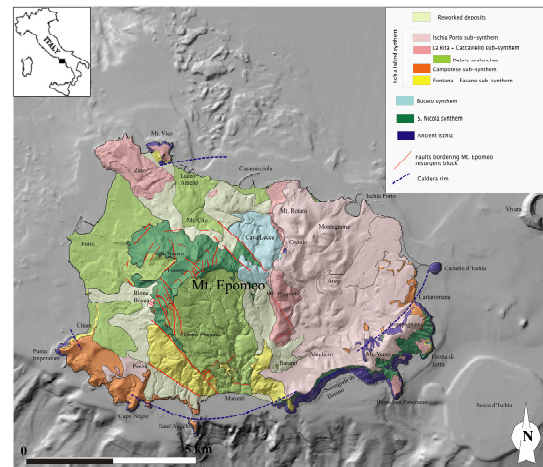
### ABSTRACT

Ischia Island is located in the north-western part of the Gulf of Naples and is part of the Phlegrean Fields Volcanic District. Ischia is marked to be an example of resurgent caldera and is characterized by high heat flux comprised between 200 and 400 mW/m<sup>2</sup>. Hydrothermal activity is well known on the island since Roman Age and more than 200 hotels and SPA resources, located all over the island, use thermal waters (T ranges from 30°C to 99°C) for balneo-therapeutic medical cures. The deep wells, drilled in 1950's and subsequent investigations also revealed the occurrence of high temperature fluids in the subsoil of the island, hosted within a possible geothermal reservoir. The aim of this work is to characterize the main geochemical processes that explain the water geochemistry of the thermal fluids of Ischia Island, to classify the water composition data into genetic groups and to delineate a conceptual model to explain the composition of the discharges. The chemical composition of water sample allows distinguishing six chemical groups that reflect complex processes of water/rock interaction and admixtures in different proportions with surficial fluids and deep geothermal fluids. Geothermometric calculations (based either on solute geothermometers and Saturation Index of minerals vs temperature) suggest the existence of two different deep reservoirs in the subsoil of the Island, in which fluids attain equilibrium with host rock at about 160-180°C and 220-240°C. These results are in agreement with data from Ischia3 deep well (1053m depth) drilled in early 1950' where it was found T = 224°C and a ~180°C convective zone at shallower depths (between 400 and 890m depth). All these data allow proposing a conceptual model of the Ischia Island hydrothermal system.

### 1. INTRODUCTION

Ischia Island is formed by volcanic and epiclastic rocks. The volcanic activity started more than 147 ky ago with the emplacement of lava flows and domes, which form a huge volcanic field, and has lasted up to 1302 A.D. with the Arso eruption (Fig. 1).

The central part of the island is characterized by Mt. Epomeo (787 m a.s.l.), a volcano-tectonic resurgent complex structure, bounded by a polygonal system of near vertical faults. Recent data of Sbrana (2009) fixed the main resurgence of Mt. Epomeo in the time interval 56-33 kyr, further resurgent steps go on up to ~5 kyr.



**Figure 1: Schematic geological map of Ischia (Sbrana et al, 2009 modified).**

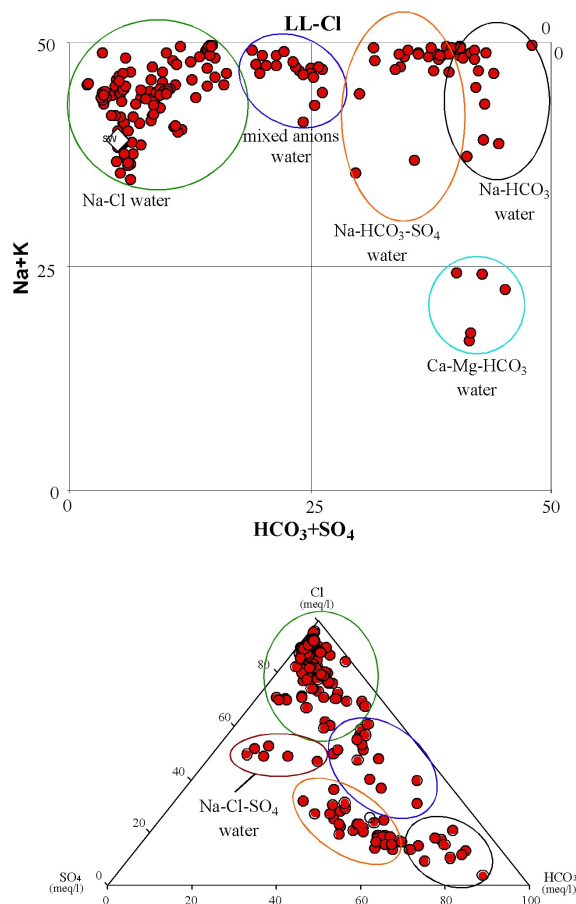
The geological and volcano-tectonic complexity of Ischia is evidenced by its hydrogeological shape. On the island, thermal waters are hosted within aquifers mainly located in tuffs, lavas and incoherent material (sands and debris flow deposits). Geological units with very different permeability can be found close one to another; by the hydrogeological point of view, in a rough shape, two main areas can be distinguished on the island: the eastern sector in which the main aquifer is hosted within lavas and underlying sands; the western sector in which tuffs represent the main aquifer. Clearly, the permeability of lavas in the eastern sector is higher than tuffs in the west. This is reflected by lower temperature and higher salinity of fluids from this sector, suggesting significant fresh seawater recharge. Measuring hydraulic heads, Celico et al. (1999) found that piezometric levels seem to define a unique water table, with a radial shape that follows the island morphology. Despite the existence of a continuous water body is questionable, because of the differences in water geochemistry, perched aquifers exist in the La Rita-Bagni area, near Citara zone (in the north and west Mount Epomeo flank debris flows and avalanche deposits, respectively) and in the Vateliero zone (in the younger volcanic and reworked deposits). The presence of these water bodies is very important to investigate the origin of some of the geochemical water groups found on the island. Regarding the water balance of the island, Celico et al (1999), on a pluviometric, infiltration potential and outflow basis only, thus not considering wells pumping nor reinjection, estimated a negative value. The authors assumed that seawater intrusion as well as deep geothermal fluids inflow must compensate to obtain equilibrium.

## 2. ANALYTICAL METHODS AND DATA PRESENTATION

Water from springs and wells were sampled and analyzed in the period May 2000 to May 2006. A total of 185 water samples were collected at different times according to the methodology proposed by Giggenbach and Gougel (1989). Water samples were filtered (0.45  $\mu$ m cellulose membrane filter) upon collection and kept in double capped pre-cleaned HDPE bottles. Samples for analysis of cations and trace elements were acidified (pH <2) by adding concentrated  $\text{HNO}_3$ . Samples for analysis of anions were kept unacidified. Temperature, pH, conductivity and  $\text{HCO}_3^-$  were determined directly in the field.  $\text{HCO}_3^-$  concentration was determined by titration with  $\text{HCl}$  0.1 N. Major and trace elements were analyzed at the Dipartimento di Scienze della Terra di Pisa.  $\text{SiO}_2$  and B were determined by using a visible spectrophotometer (HACH DR 2000). Major and minor species ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) were determined by ion chromatography (Dionex DX 120). Electrical balances are excellent with all waters showing less than 10% difference between cations and anions.

### 2.1 Hydrogeochemical outline

The chemical composition of water samples of Ischia Island are investigated in terms of  $\text{HCO}_3^-$ - $\text{Cl}^-$ - $\text{SO}_4^{2-}$  and Langelier-Ludwig diagrams (Fig. 2) and allow distinguishing six chemical groups: (1) a Na-Cl group; (2) a Na- $\text{HCO}_3$ - $\text{SO}_4$  group; (3) a Na- $\text{HCO}_3$  group; (4) a Na-Cl- $\text{SO}_4$  group; (5) an



**Figure 2: Langelier-Ludwig and  $\text{HCO}_3^-$ - $\text{Cl}^-$ - $\text{SO}_4^{2-}$  diagrams of Ischia thermal waters. SW = sea water**

Ca-Mg-Na- $\text{HCO}_3$  group; (6) mixed anions group. The Na-Cl waters (1) are generally found in the wells and springs

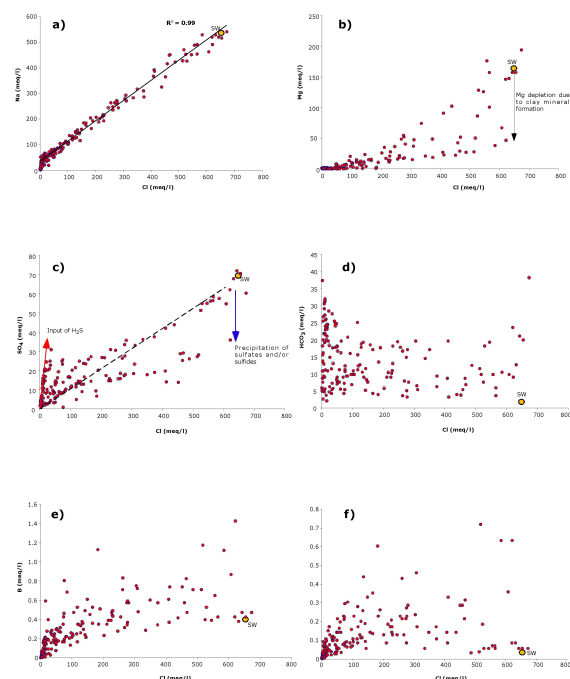
located near the coast. They are characterized by high TDS, high Na, Cl, B and Li contents and a wide range of temperature (30°-99°C). Na- $\text{HCO}_3$ - $\text{SO}_4$  waters (2) are found in La Rita-Bagni area. They are characterized by high temperature (50°-80°C), low TDS, and high  $\text{Na}^+$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  contents. Na- $\text{HCO}_3$  waters (3), mostly found in the inner part of the island, come from shallow wells. Generally high temperatures, up to 90°C, and low salinity characterize this group of waters. Na-Cl- $\text{SO}_4$  waters (4) are only found in the Monte Nuovo and Succivo areas (Fig. 2) and are characterized by medium-low salinity and high temperatures (64 – 82°C). The Ca-Mg- $\text{HCO}_3$  group (5) is representative of shallow ground waters whose temperatures range from 19 to 23°C and TDS is generally low. The sixth group of waters is defined as mixed anions group. Although these waters probably do not represent a co-genetic facies, and are likely to be the result of mixing between the previously mentioned types (in particular 1, 2 and 3 groups) in different proportions, they will be considered in the following discussion as a single group. They show a wide range of temperatures (24 - 75°C) and TDS.

### 3. DISCUSSION

In Fig. 3 a, b, c, d, e, f the concentrations of Na, Mg, B, Li,  $\text{HCO}_3$  and  $\text{SO}_4$ , for thermal waters of Ischia Island are plotted against Cl. In the Na vs Cl diagram (Fig. 3a) the high positive correlation ( $R=0.99$ ) between Cl and Na indicates that high Na and Cl concentrations of thermal waters mainly arise from the contribution of seawater. Nevertheless, most of the samples with low Na and Cl concentrations (up to about 100 meq/l) lie slightly above a conservative mixing line between meteoric water and seawater and therefore the relative enrichment in Na could be considered indicative of water-rock interaction processes that leach Na from volcanic rocks and glasses. A similar trend is also observed in K vs Cl plot. The Mg depletion seen in some samples (Fig. 8b) could be instead ascribed to the incorporation of Mg in secondary clay minerals in the aquifer, as commonly reported in geothermal fluids (Giggenbach, 1988).

In  $\text{SO}_4$  vs Cl diagram (Fig. 8c), together with a simple mixing trend between cold low salinity water and seawater, we observe two other trends displaying respectively  $\text{SO}_4$  enrichment and  $\text{SO}_4$  depletion with respect to seawater mixing trend. These latter trends should reflect input of  $\text{H}_2\text{S}$  from depth and precipitation of sulfides and/or sulfates respectively (Fig. 3c). Trends recognizable in the  $\text{HCO}_3$  vs Cl plot (Fig. 3d) support the occurrence of both (1) a mixing between Na-Cl waters and low salinity waters and (2) the formation of low salinity  $\text{HCO}_3$  rich waters through conversion of  $\text{CO}_2$  to  $\text{HCO}_3$ . However, all the samples present  $\text{HCO}_3$  contents clearly above typical seawater composition (Fig. 8d) suggesting diffuse  $\text{CO}_2$  degassing at Ischia as suggested by Pecoraino et al. (2005). In order to calculate how much  $\text{HCO}_3$  is due to seawater mixing or to geothermal and/or volcanic-derived processes that may introduce  $\text{CO}_2$ , the fraction of seawater in these samples was estimated considering chloride as a conservative, and is in the range of about 10% to 100%. The recalculated  $\text{HCO}_3$  content in waters reveals that bicarbonate enrichment occurs compared to the expected values, according simply to a conservative mixing model. This suggests that geothermal and/or magmatic volatiles input significantly influence the composition of Ischia thermal waters. On the other hand, Pecoraino et al. (2005) found high  $\text{CO}_2$  flux (average value 15 Kg/s) affecting the entire island. In this view, Na- $\text{HCO}_3$ - $\text{SO}_4$  and Na- $\text{HCO}_3$  waters would originate through either absorption of  $\text{CO}_2$ -( $\text{H}_2\text{S}$ ) bearing gases

and/or condensation of  $\text{CO}_2$ -( $\text{H}_2\text{S}$ )-rich geothermal steam in low salinity waters. This kind of fluids is commonly found in the "condensation zone" of vapor-dominated geothermal systems and in the marginal parts of liquid-dominated geothermal systems (Giggenbach, 1988).



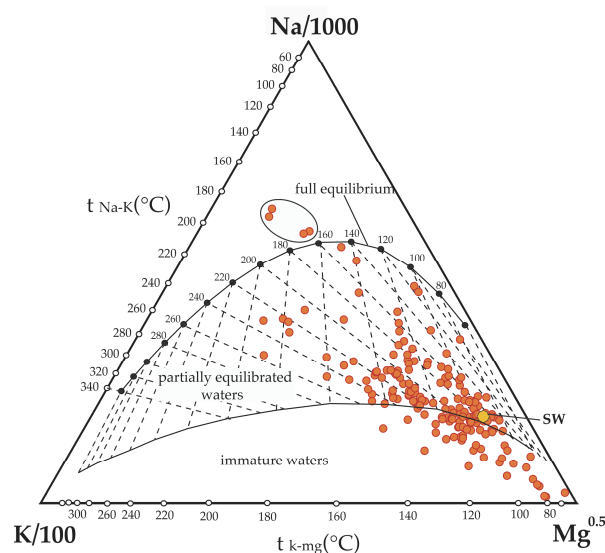
**Figure 3: Plots of Cl vs. Na, Mg,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , B and Li. SW = sea water**

B and Li are considered as conservative elements and commonly used to display mixing processes between geothermal fluids, which are enriched in these elements, and surficial waters (Giggenbach and Corrales Soto, 1992; Marini et al., 1998). B-Cl and Li-Cl diagrams (Fig. 3 e,f) show similar patterns characterized by a significant scattering of the data points, suggesting that these waters are not the result of a simple mixing process between a "geothermal" end-member and a cold meteoric or seawater component. Additional processes such as surficial water-rock interactions and leaching of volcanic glasses in the shallow aquifers are needed to explain the observed scattered patterns.

### 3.1 estimated subsurface temperatures

The Na/1000–K/100–Mg0.5 diagram (Fig. 4) proposed by Giggenbach (1988) is often used to assess reservoir temperatures and to recognize waters, which have attained equilibrium with the host lithology. The composition of most of the waters belonging to the Na-Cl- $\text{SO}_4$  group, if plotted in the ternary diagram of Giggenbach (1988), falls very close to the thermal-chemical equilibrium line; while some samples plot slightly above the equilibrium line (see circle in Fig. 4). This suggests that these latter waters were affected by boiling processes (Fournier, 1990). The distribution of sample data points in the ternary diagram (Fig. 4) shows that many waters fall within the field of partial equilibrium with rocks and are aligned with those in full equilibrium with two different temperatures of about 160–180°C and 220–240°C respectively. The cold waters and a few of alkali-chloride thermal waters fall in the immature water field indicating that none of these waters attained equilibrium with their associated host rock. The application of Na-K, Na-K-Ca and  $\text{SiO}_2$  geothermometers to the partial and full equilibrated thermal waters gave

temperatures comparable to those observed in ternary diagram of Fig. 4. Most of the sodium chloride waters show an apparent geothermometric estimated temperature of about 150°C, which is the value of the Na-K temperature for seawater. Obviously, this does not reflect equilibrium conditions between water solution and alkali feldspars, but this readily testifies the seawater intrusion in the shallow aquifer near the coast.



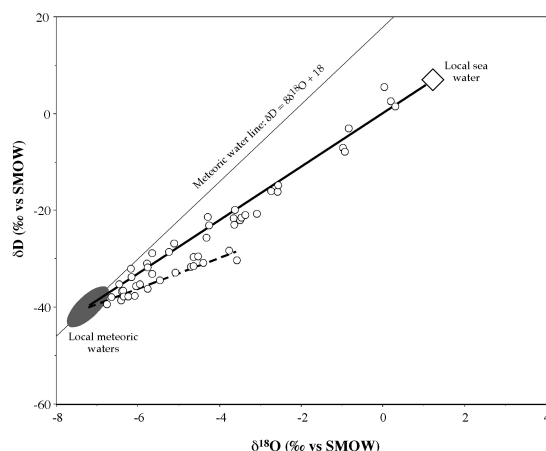
**Figure 4: Na-K-Mg ternary diagram (Giggenbach, 1988) showing the composition of Ischia thermal waters. The diagram shows the fields for the different equilibrium states (immature-partial equilibrium-full equilibrium), and isotherms.  $t_{\text{K-Mg}}(^{\circ}\text{C})$  and  $t_{\text{Na-K}}(^{\circ}\text{C})$  are the temperatures calculated with K-Mg and Na-K geothermometers of Giggenbach (1988). SW = seawater.**

These results suggest the existence of two different deep reservoirs in the subsoil of Ischia Island, in which fluids attain equilibrium with host rock at about 160–180°C and 220–240°C as already hypothesized by Panichi et al. (1992). Data coming from SAFEN deep wells, confirms the temperature framework depicted above: the higher temperature measured in Ischia3 deep well (1053m depth), in the Rione Bocca Region, was 224°C and a ~180°C convective zone seems to be present at shallower depths (between 400 and 890m depth). Fluid sampled at 890m depth shows a salinity of about 4.5 g/l NaCl (Penta F. & Conforto B., 1951). The strong dilution observed in the thermal fluids near the coast seems to be compatible with mixing between a low salinity geothermal fluid and seawater. The occurrence of geothermal reservoirs at 160–180°C and 220–240°C in the first ~ 1000m depth does not necessary exclude the existence of a deeper high-T geothermal reservoir in accordance with the temperature estimated on chemistry of fumarolic fluids by Chiodini et al. (2004).

### 3.2 Stable isotopes

The  $\delta^{18}\text{O}$  vs.  $\delta\text{D}$  diagram (Fig. 5) shows that the majority of the thermal waters plot close to a mixing line (full line) that joins seawater and local meteoric water end-members. The deviation from the mixing line towards higher  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values, shown by some samples (dashed line), suggests that these waters are interested by evaporation processes,

undergoing non-equilibrium fractionation at the surface (Giggenbach and Stewart, 1982). An oxygen isotopic shift, typical of water/rock interaction processes in hydrothermal systems, is not evident. This may be due to high water/rock ratio or a limited resident time of the fluid in the reservoir that prevents an efficient isotopic exchange between water and rock.

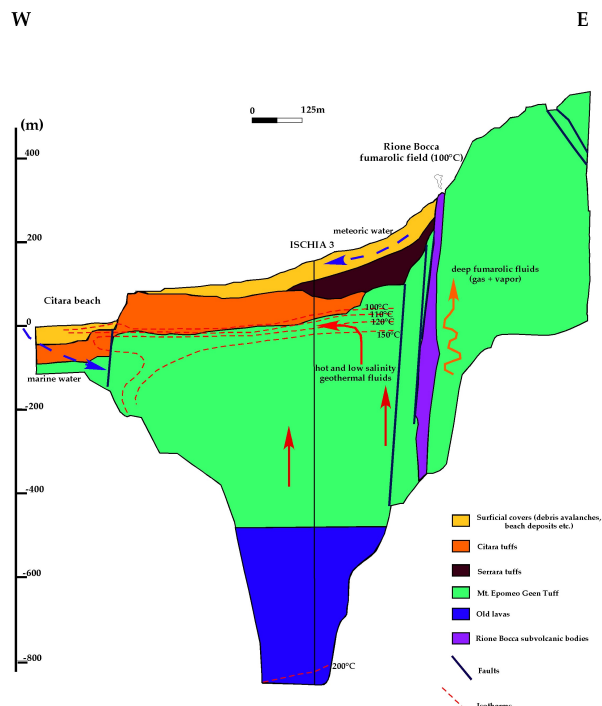


**Figure 5: Oxygen and hydrogen isotopic composition of Ischia thermal waters. Full line = mixing line between local meteoric waters and seawater; dashed line = waters interested by evaporation. Local meteoric line and the isotopic composition of local seawater and local meteoric waters are also shown as comparison (Panichi et al., 1992).**

#### 4. HYDROGEOCHEMICAL CONCEPTUAL MODEL

A hydrogeochemical conceptual model of Ischia Island hydrothermal system is proposed in this work. In particular, we analyzed two different sectors of the island schematically shown in Fig. 6 and 7: the Northern sector and the Western sector.

**Western sector:** the section, shown in Fig. 6, represents the western sector of the island. The main features may be summarized as follow: seawater plays a major role as constituent of the thermal waters of Ischia island in this area. Shallow recharge is supposed to be effective as seawater intrusion, which becomes strongly modified by water-rock interaction processes that lead to various degree of enrichment or depletion in chemical elements. Solute geothermometry suggests the existence of two different deep reservoirs in the subsoil of this area of Ischia Island, in which fluids attain equilibrium with host rock at about 160-180°C and 220-240°C. Chemical composition of hydrothermal fluids present in wells near the coast is in agreement with a thermal modification of seawater by water/rock interaction, boiling and admixtures in different proportions with surficial fluids (water group 1). CO<sub>2</sub> rising from deep reservoir interacts with shallow groundwaters, hosted in the uppermost deposits, originating sodium-bicarbonate waters (water group 3). Along the coast a major zone exists (water group 6) where mixing between the components described above takes places, thus leading to the formation of mixed waters with various chemical characteristic, depending on the prevailing component.

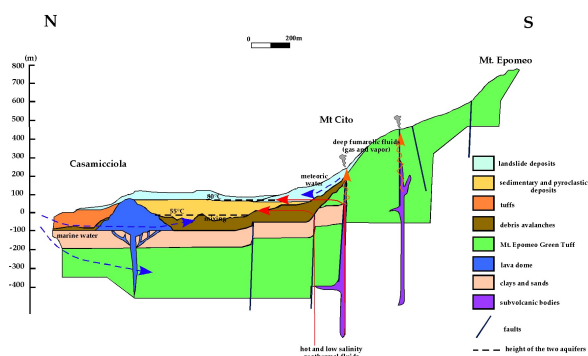


**Figure 6: Schematic section of the western sector of Ischia Island.**

**Northern sector:** The section in Fig. 7, is situated in the north cost of the island. Here the aquifer exploited by the thermal wells is mostly located in Holocene deposits, constituted of pyroclastic and sedimentary deposits (sandy silts, clays and heavily fractured marls) and the underlying debris avalanche deposits. In this zone, at least two main aquifer exist. The first, located at 60m a.s.l., has high temperatures up to 80°C and Na-HCO<sub>3</sub>-SO<sub>4</sub> composition (group 2) originated by the absorption of CO<sub>2</sub> and H<sub>2</sub>S, raised from a deep reservoir, in shallow low salinity Ca-Mg-HCO<sub>3</sub> groundwaters of meteoric origin (group 5 waters); the second aquifer is next to seawater level and is being exploited either by wells near the coast and deeper wells in the internal part of the island. The temperature of this aquifer is about 50-55°C and the composition is Na-Cl (group 1) and mixed anions waters (group 6), with the salinity increasing towards the coast. This indicates that, as depicted above for the Western sector, seawater results an important component also in Northern sector. The occurrence of fractured and buried lava dome (Fundera dome) at shallow depth in this area could further favor seawater intrusion.

We infer that the geological structures strongly condition the circulation of hydrothermal fluids in the subsoil of the island determining the complex hydrogeochemical features in a multilayer fractured hydrothermal system. The thermal fluids tend to rise in correspondence of the main direct master faults, bordering Mt. Epomeo horst and are often associated with a CO<sub>2</sub>-(H<sub>2</sub>S)-rich phase rising from deep geothermal reservoir(s).





**Figure 7: Schematic section of the northern sector of Ischia Island.**

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