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## **A peculiar case of coastal springs and geogenic saline groundwater**

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### **ABSTRACT**

The coastal carbonate Apulian aquifers, located in southern Italy, feed numerous coastal cold springs and constitute the main local source of high quality water. The group of Santa Cesarea Terme springs constitutes the unique occurrence of thermal groundwater outflow, observed in partially submerged coastal caves. The spring water is rich of hydrogen sulfide and the water temperature ranges from 22 to 33 °C.

Geological and hydrogeological surveys including chemical and isotopic analyses of both groundwater and seawater have been carried out. Stable isotopes  $\delta^{18}\text{O}$ ,  $\delta\text{D}$  were used to define the origin of the thermal waters and the recharge mechanism of the geothermal systems while the unstable isotope  $^3\text{H}$  was determined for estimating the age of the thermal waters and to define the conceptual model of this low temperature geothermal resource.

It was demonstrated that the spring groundwater of Santa Cesarea, which has been used for spa from several decades, is due to mixing of three components: a thermal saline fluid rich in sulphur, saline water due to seawater intrusion and fresh water that derives from meteoric infiltration in the carbonate outcrops.

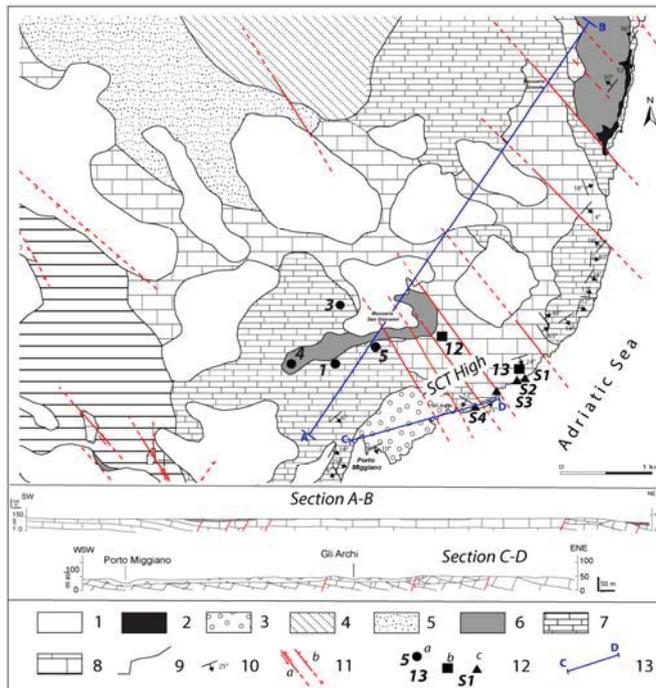
### **INTRODUCTION**

These springs are known from ancient times (Aristotele in III century BC) and the physical-chemical features of their thermal waters resulted to be partly influenced by the sea level variations. Some hypotheses about the origin of these warm waters have been proposed up to now by some researchers (Zezza, 1980, Calò et al., 1991, Maggiore and Pagliarulo, 2004) but some uncertainties existed. For this reason, the area was selected in order to define the conceptual model of the geothermal resources related to the thermal springs and, as a consequence, the origin of the thermal springs (pilot site of the Vigor Project).

### **GEOLOGICAL AND HYDROGEOLOGICAL SETTING**

The Santa Cesarea Terme area is located along the south-eastern coast of the Salento peninsula, a carbonate plateau defined by a wide, WNW–ESE trending, antiformal structure, dissected by a series of extensional and strike-slip faults (Tozzi, 1993). Starting from the Early Triassic, the area was part of the Apulia platform palaeo-domain, characterized by shallow-water carbonate sedimentation (Mostardini and Merlini, 1986). Since Cretaceous times, the Salento peninsula experienced a series of alternating transgression and regression phases, giving rise to a succession characterized by lacunae and unconformities. In particular, during the Middle Pleistocene, the area underwent a severe regional uplift (Doglioni et al., 1994). As shown in the geological map of Figure 1, the Altamura Limestone (Upper Cretaceous) represents the calcareous bedrock at Santa Cesarea Terme, consisting in well-bedded, peritidal dolomitic limestone. This Cretaceous formation is overlaid, through a marked angular unconformity, by coral reef limestone belonging to the Castro Limestone (Late Eocene–Early Oligocene; Bosellini et al., 1999; Bossio et al., 2005).

Locally, both Altamura Limestone and Castro Limestone are unconformably overlain by the bentonic foraminifer-bearing Oligocene calcarenite (Porto Badisco Calcarenites) and by the Messinian poorly bedded white calcarenite (Andrano Calcarenites). The younger formations cropping out at Santa Cesarea Terme are the Uggiano La Chiesa Formation (Middle Pliocene-Lower Pleistocene) and the Salento Calcarenites (Pleistocene). The first is mainly made of yellow calcarenites while the latter consists of massive to poorly bedded, weakly cemented calcarenites, related to a slope environment, as testified by the presence of slumpings and submarine slides. The offshore equivalent of the Salento Calcarenites are well imaged in the seismic lines and form a series of prograding units settled during a forced regression (Aiello and Budillon, 2004).



**Figure 1: Simplified geological map of the studied area. Legend: 1) red clays, 2) talus deposits, 3) Salento Calcarenites, 4) Uggiano La Chiesa Formation, 5) Andrano Calcarenites, 6) Porto Badisco Calcarenites, 7) Castro Limestone, 8) Altamura Limestone, 9) stratigraphic contact, 10) strata attitude, 11) fault (a-transensional, b-normal, dashed when inferred), 12) water sampling sites (a-cold well, b-thermal well, c-thermal spring), 13) trace of the geological sections.**

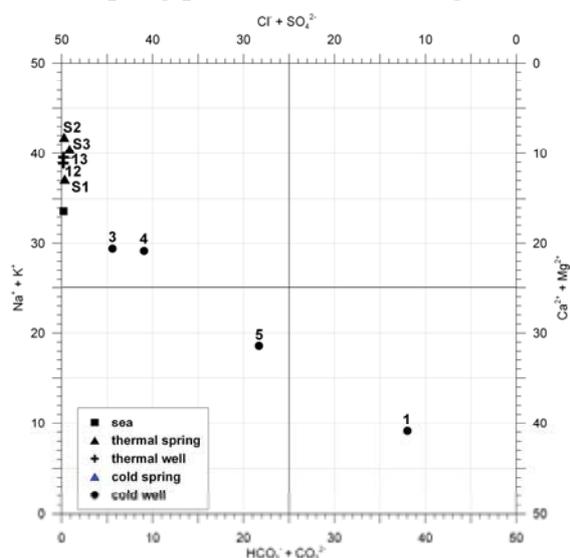
limited extension, are located within the Neogene deposits. Usually they occur in topographically depressed areas, where Quaternary sands and calcarenites overlie impermeable clay formations.

Belonging to a coastal area, the deep groundwater, which top is located almost at the sea level, is involved in saltwater intrusion, with the salt-fresh water interface at some meters below the sea level moving inland. Therefore the deep fresh groundwater has been intercepted only some meters above the sea level. Locally, where the thermal wells are, the piezometric level has been measured at some meters above the ground level.

## CHEMICAL ANALYSES OF WATERS

Temperature, electrical conductivity, dissolved oxygen, redox potential, pH, alkalinity of waters have been determined in the field. Cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ) and anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) were analyzed by means of ion chromatography (IC) methods.

Minor and trace elements were determined by inductively coupled plasma mass spectrometry. Values for  $\delta^{18}\text{O}$ ,  $\delta\text{D}$  and  $^3\text{H}$  were obtained by mass spectrometry. Location of the sampling points is shown in Figure 1.



**Figure 2: Langelier-Ludwig diagram of some of the analyzed groundwater samples.**

chloride ion. High contents of alkali earth metal ions ( $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$ ) have been found for the fresh groundwater (sample 1), which displays the typical composition of the groundwater flowing within the deep aquifer within the Salento peninsula (Fidelibus and Tulipano, 1986). The other cold-water samples (5, 3, 4) are a mixture of fresh groundwater and seawater.

As concerns the secondary constituents, the thermal waters are marked by higher concentration of  $\text{Li}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{F}^-$  and  $\text{Br}^-$  respect to those measured for the cold-water samples. Lithium is considered as a reliable indicator for the residence time of groundwater in the aquifer (Edmunds and Smedley, 2000). Most of the trace element concentrations are related to the redox environment of thermal waters. As a matter of fact, the measured redox potential values range from negative to slightly positive (-300 mV to 30 mV).

The D/H isotopic ratios suggest that the cold water samples (1, 5, 4, 3) have a meteoric origin. The thermal waters sampled at both wells (12, 13, 14) and springs (S1, S2, S3, S4) have an enrichment in oxygen  $\delta^{18}\text{O}$ . This enrichment could be interpreted as due to evaporation of deep fluids (Panichi, 1982). The thermal waters sampled at the wells (12 and 13) record a low tritium content while higher contents, up to almost 5 TU, occur for the cold water samples. These results suggest that the thermal waters should be recharged by groundwater characterized by a relatively long residence time (greater than 55 years), connected to a deep groundwater circulation system. In addition, the data for the cold-water samples provide evidence of recent recharge.

## CONCLUSION

The thermal system of Santa Cesarea, which has been used for spa from several decades, seems essentially due to three water types or components: 1) pure fresh groundwater from meteoric infiltration in the carbonate rocks, 2) saline water due to seawater intrusion, 3) a thermal saline fluid rich in sulphur. The resulting mixture is undersaturated with respect to calcite, thus aggressive enough to enhance the karst processes in the area.

In this narrow area, the source of geogenic salinization of spring groundwater was referred to ascending very deep groundwater, more saline than current sea water.

The highest temperatures (22°-33° C) of the waters have been measured in some wells (thermal wells in Figure 1) located in a narrow area not far from the coastal sector where the thermal springs develop. Some meters from these thermal wells, the groundwater temperature decreases reaching the typical values of the deep Salento aquifer, that is about 18-19°. The thermal groundwater has higher total dissolved solids (e.g. 58000 mg/L) with respect to the fresh groundwater (generally up to 500 mg/L).

The major constituents are plotted in the Langelier-Ludwig diagram shown in Figure 2. The thermal waters are characterised by high values of alkaline ions ( $\text{Na}^+$ - $\text{K}^+$ ), higher than those measured for the seawater.

Moreover, they show high content of

The geochemical composition and the physical features of the sampled waters suggest that thermal waters should be moving from ancient seawaters subjected to intense evaporation processes, infiltrated at great depth within the seabed substratum. Afterwards, these thermal fluids should flow up through the almost vertical structures, related to the transtensional structures, identified within a narrow sector of the studied territory. Thermal waters are five times older than the deep aquifer (Santaloia et al. in print).

#### ACKNOWLEDGEMENTS

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