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SANTA CESAREA COASTAL THERMAL SPRINGS (SOUTHERN ITALY)

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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 springs constitutes the unique occurrence of thermal groundwater outflow, observed in partially submerged coastal caves. The spring water is rich of hydrogen sulfide; temperature ranges from 25 to 33 C°. For their properties, spring waters are used for spa activities from several decades. Hydrogeological spring conceptualisations proposed up now were not able to justify water geochemical peculiarities or were not completely confirmed up now. To reduce these uncertainties, a complex hydrogeological survey has been defined. Geological and structural surveys, chemical and isotopic groundwater analyses, spring and well discharge measurements, well loggings, multi-parameters spring automatized measurements, and cave explorations are ongoing. All available data have been used to improve the knowledge of groundwater flow system, including the valuable deep aquifer, the origin of the thermal waters, and to investigate the possibility of using low-enthalpy geothermal fluids to fulfil the thermal needs of the town of Santa Cesarea Terme.*

Keywords **Carbonate aquifer; sulphur groundwater; thermal springs, coastal aquifer, Apulia, Italy**

1. INTRODUCTION

The Santa Cesarea spring group is located in the town of Santa Cesarea Terme (*terme* is the Italian translation of spa), a touristic villages of Salento, the south-easternmost portion of the Apulia region (Southern Italy; Figure 1). These springs are characterized by sulphureous and warm waters (Zezza, 1980). Their special groundwater characteristics were discovered in ancient times and were described by historians, such as Aristotele (III century BC), Strabone, Claudiano, Leto (I, III, and XV century respectively), as well as by recent authors. Spring water characteristics are almost variable as consequence of tides (Visintin 1944; Zezza 1988). In particular, the ion chloride content increases with tides, while the hydrogen sulphide content and temperature decrease. The paper presents some preliminary results of an ongoing research project of the (Italian) National Research Council, aimed at the assessment of the geothermal potential of regions located in southern Italy (VIGOR Project).

2. GEOLOGICAL AND HYDROGEOLOGICAL SETTINGS

The Santa Cesarea group is represented by four main springs, located in Salento Peninsula, along about 500 of the Adriatic coast, where the outcropping limestone of the Apulian carbonate platform is dissected by a series of NO-SE faults dipping towards East and West.

Figure 1. Location of study area.

Offshore, the carbonate sequence underlies a thick succession of Quaternary sediments, which forms the foredeep in-fill of Dinaric chain (Figure 1). Salento peninsula is part of the Apulia carbonate platform, part of the African passive margin. The main geological units outcropping in the study area, extended along the coast between Porto Badisco and Castro, are represented by (i) a carbonate sequence constituted by Cretaceous and Oligocene limestones, intensely fissured and karstified; (ii) a Miocene calcarenite; (iii) Pliocene weakly clayey sand and (iv) Pleistocene calcarenite (Figure 2).

The main aquifer, called “deep aquifer”, is constituted by the Mesozoic limestone of Apulian platform (Oligocene limestone is not relevant at the aquifer scale). The maximum piezometric head is less than 4 m asl in the whole Salento. Where limestone does not outcrop, calcarenite and sands can constitute a shallow narrow aquifer. The aquifer’s base level corresponds to the sea level; fresh groundwater, flowing over saline water of sea origin, outflow trough several coastal springs.

As concerns the origin of the sulfide in the spring waters, according to Zezza (1980), it should be due to the reduction of sulphate contained in the seawaters which occurs when these waters come into contact with the organic matter included in the Miocene calcarenite layers. This reduction would occurs by means of an exothermic chemical reaction warming locally the flowing groundwater. The origin proposed by Zezza (1980) was also substantiated by Calò (1991). On the other side, according to Maggiore and Pagliarulo (2004), warm deep fluids, flowing below the Adriatic Sea, rise through the pre-pliocenic carbonate substratum, explaining the spring water peculiarity. The flow of these connate water should be due to the tectonic “pressure” of the Dinaric-Hellenic thrust-sheets convergence toward the Apulian foreland.

3. FIELD AND LABORATORY DATA

Temperature, electrical conductivity, dissolved oxygen, redox potential, pH, alkalinity (titration with HCl) and SiO_2 (determined using a portable colorimeter) have been determined in the field. Cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (Cl^{-}, SO_4^{2-}, NO_3^{-}) were analyzed by means of ion chromatography (IC) methods. The overall precision of the analyses based on major ions is within 5%. Data processing was carried out using the PHREEQC software. The location of sampling points is shown in Figure 2. Ion chromatography results and the water classification are shown in Figure 3.

The diagram show that the sample 3, fresh groundwater, lies in the (Ca+Mg)–(HCO_3) field, and represents the typical groundwater of Salento peninsula. The samples 4 and 5 are a mixture of fresh groundwater and sea water. The thermal groundwater has higher total

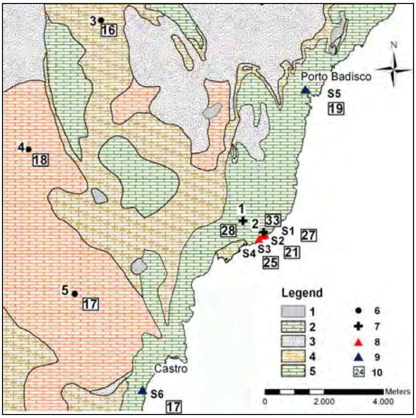

Figure 2. Hydrogeological schematic map: 1) continental deposits (Quaternary); 2) calcarenite (Pleistocene); 3) weakly clayey sand (Pliocene); 4) calcarenite (Miocene); 5) limestone (Cretaceous-Oligocene); 6) well; thermal 7) well and 8) spring; 9) fresh spring; (10) groundwater temperature.

dissolved solids (58000 mg/L, sample 2) with respect to fresh groundwater (generally up to 500 mg/L). The temperature of thermal groundwater varies from 25 °C to 33 °C.

Some thermal groundwater samples (1, 2, S1, S6) are located close to the point which represents the composition of seawater, with a enrichment in Ca^{2+} and Mg^{2+}, relative to Na^{+} and K^{+} ions.

Minor and trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS). Thermal waters are chemically characterized by high concentration of Li^{+}, Sr^{2+}, F^{-} and Br^{2+}. Most of the trace element concentrations are related to the redox environment of thermal waters. The redox potential values range, for some of the samples, from negative to slightly positive (-300 mV to 30 mV), corresponding to reducing environments.

The D/H isotopic ratios have been plotted in a δ18O–δD diagram (Craig, 1961) shown in Figure 4 where the Global Meteoric Water (GMWL) and the Mediterranean Meteoric Water Lines (Gatt and Carmi, 1970) are also reported. The sample of cold water (3) falls between the Global Meteoric Water Line and the Mediterranean Meteoric Water Lines, suggesting so a meteoric origin of this sample. Samples 1, 2 and S2 plot to the right side of the GMWL and the MMWL lines, indicating so an enrichment in oxygen ^{18}O. It could be simply justified considering the interaction of ions in solution and water molecules in a fluid system at high salinity, even at low temperature (Gonfiantini, 1986). Moreover, since the salinity of these samples seem to be high, a certain contribution of isotopically heavy connate waters could occur.

The studied water samples are undersaturated with respect to calcite and dolomite as resulted from the calculations of equilibrium of waters with these carbonates.

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 that derives from meteoric infiltration in the carbonate outcrops, 2) saline water due to seawater intrusion, 3) a thermal saline fluid rich in sulphur. The resulting mixture is undersaturated with respect to calcite and thus aggressive. Bögli (1964) considered "mixing corrosion" the key process for karstification. Previous conceptualizations of Santa Cesarea springs do not seem to be fully coherent with available preliminary results. Very high salinity and high

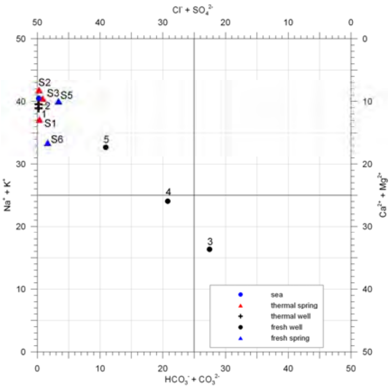

Figure 3. Langelier-Ludwig diagram of analyzed groundwater samples

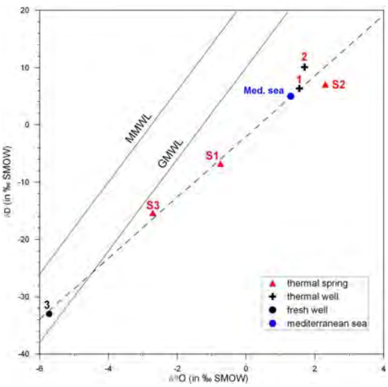

Figure 4. Binary δ_D - δ_{18O} diagram for some of the samples investigated.

temperature of the third water type seem due to the interaction water-carbonate rocks, defining an almost steady fluid system at high salinity, even at not particularly high temperature.

The completion of surveys, which will be enlarged thanks to deep geophysical campaigns, should be sufficient to clarify the source of third-type water, the source of pressure forced out these waters, justifying the steady characteristics of their outflows.

REFERENCES

Bogli, A., 1964. Mischungskorrosion ein Beitrag zum Verkastungsproblem. *Erkunde* 18, 83-92.

Calò, G., & Tinelli, R., 1995. Systematic hydrogeological study of a hypothermal spring (S. Cesarea Terme, Apulia), Italy. *Journal of Hydrology*, vol 165, pp 185 – 205.

Calò, G., Spizzico, M., Tinelli, R., & Zezza, F., 1983. Hydrogeological investigations on the area sourroundig santa Cesarea Terme Springs (Southern Apulia), *Geologia Applicata e Idrogeologia*, vol XVIII, pp 129 – 144.

Craig, H., 1963. Isotopic variations in meteoric waters. *Science* 123, 1702–1703.

Gatt, J.R., & Carmi, I. 1970. Evolution of the isotopic composition of atmospheric waters in the Mediterranean Sea area. *J. Geophys. Res*. 75, 3032 – 3048.

Gonfiantini, R., 1986. Environmental isotopes in lake studies. In: Fritz, P., Fontes, J.Ch. (Eds.). *Handbook of Environmental Isotope Geochemistry, Elsevier*. pp. 113–168.

Maggiore, M., & Pagliarulo, P., 2004. Circolazione idrica ed equilibri idrogeologici negli acquiferi della Puglia. Geologi e territorio, n. 1/2004. pp. 13-35

Visintin, B., 1944. Studio dell'acqua della grotta Gattulla delle Terme demaniali di S. Cesare. *Rendiconto Istituto Superiore Sanità*, vol. VII, p. II.

Zezza, F., 1980. Le sorgenti ipotermali solfuree di Santa Cesarea Terme. Azienda di cura e soggiorno e turismo Santa Cesarea Terme. *Estratto dalla rivista quadrimestrale di cultura e civiltà salentina "Salentum"* - Anno III nn. 1–2 – edita dall'E.p.t. di Lecce.