Salt ground waters in the Salento karstic coastal aquifer (Apulia, Southern Italy)

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Abstract The chemical and isotopic features of salt ground waters in the Salento coastal karstic aquifer (Apulia, Southern Italy) reveal that they are very different from modern seawater. Chemical data allow identifying the role of water-rock interaction (Ca^{2+}-Mg^{2+} exchange due to dolomitization, Na^+-Ca^{2+} or Mg^{2+} base-exchange, SO_4^{2-} reduction, solution of evaporite salts) in the modification of the chemical characteristics of original seawater. $^{87}Sr/^{86}Sr$ isotope ratios and Sr indicate that salt waters are very ancient and, given the structural features of this aquifer and the paleogeography of the region, they probably date back to the Flandrian transgression. New findings in a thermal area overlooking the Adriatic Sea suggest new scenarios for the role of Ca-Cl_2 brines, until now unknown.

1 Introduction

In coastal aquifers, groundwater salinization can originate from salt sources different from modern seawater (Kapelj et al. 2003; Richter and Kreitler 1993). Among potential salt sources, slow-moving saline fluids, some even thousands of years old, are frequently recognized (Darling et al. 1997; Han et al. 2011). In the coastal aquifers of the Mediterranean area, saline fluids can derive from seawater intruded into aquifers during the sea level rise occurred about 10-15 ka ago, ensuing the last glacial period (Cotecchia et al. 1974; Yechieli et al. 2009); after intrusion, seawater underwent geochemical diagenesis due to water-rock interaction.

Saline fluids show chemical and isotopic features different from those of modern seawater, as do the wider range of saline fluids and brines found in sedimentary basins (Hanor 1983; Land and Prezbindowsky 1985). Generally, in relation to increasing residence time, saline fluids and brines show significant alteration of major and minor (Sr, Li, Br) ion concentrations (Hanor 1983). Moreover, they differ from seawater for stable (D, ^{18}O, ^{13}C, ^{11}B) and radioactive (^{14}C, ^{36}Cl) isotope concentrations, and $^{87}Sr/^{86}Sr$ isotope ratio. Particularly saline fluids in carbonate aquifers, due to dolomitization and sulphate bacterial reduction, show decreasing

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Mg/Ca and SO_4/Cl ratios as residence time increases (Ng and Jones 1995; Oetting et al. 1996). The characteristics of saline fluids can be inferred through the extrapolation of saline end-members from the chemical composition of brackish waters (Barbecot et al. 2000). Fidelibus and Tulipano (1996) derived the characteristics of a saline fluid with high Sr and Li concentrations and a very low Mg/Ca ratio from those of the brackish coastal spring of Apulia's karstic coastal aquifers (Southern Italy). In these aquifers, samples of saline fluids were taken at the observation-wells of a net set up in the 1960s for the control of seawater intrusion (Cotecchia et al. 1974; Fidelibus and Tulipano 1991, 1996; Tulipano and Fidelibus 1984). Their Mg/Ca ratios and Sr concentrations respectively range from 6 (modern seawater) to 2 and from 6.8 to 18 mg/L; Li is enriched up to 300 µg/L, with sulphates significantly varying around the seawater value and a very low ^{14}C (pcm), giving apparent ages of 15 to 17 Ka. Later, Barbieri et al. (1999) inferred the existence of very old saline fluids within Apulia's karstic aquifers through their observation of $^{87}Sr/^{86}Sr$ ratios and Sr concentrations.

No further information was until recently available on this area due to lack of perforations that reached salt waters. New findings only came in over the last few years from sampling of salt waters performed in municipal and private wells, drilled in the Salento karstic coastal aquifer (Apulia, Southern Italy). They allow further views regarding the origin and digenesis of saline fluids in the Apulian Region.

2 Geological and hydrogeological framework

The Salento Peninsula (Fig. 1) is one of the three coastal karstic aquifers in the Apulian Region. To the NE, the structural setting features a series of reliefs and tectonic depressions, with faults having mainly NNW-SSE direction. To the SW, the fault system determines rhomboidal basins and ridges: major and minor folds respectively show NNW-SSE to NW-SE, and ENE to NE trending axes; faults (of normal sub-vertical, strike-slip and oblique-slip types) follow directions from NNW-SSE to NW-SE. In some areas, the Mesozoic carbonate basement, about 6,000 meters thick, is covered by Eocene to Quaternary transgressive sediments of variable thickness and sequence, depending on the structural features of the same basement. Throughout the Tertiary and the Quaternary, at regional scale, Salento was subject to the combined effects of isostatic and tectonic uplift, and of sea level cyclical fluctuations. The most depressed areas, varying from time to time, acquired the characteristics of subsident sedimentary basins, interested by various and diverse depositional cycles. This gave rise to many sedimentary successions, whose litho-stratigraphic and sequential characteristics vary depending on the bathymetry and degree of evolution of each basin. The Cretaceous formation constitutes the regional coastal karstic aquifer. Karst drains, mostly sub-horizontal, highly karstified, and connected by fissures, give a homogeneous and high degree of permeability. Freshwater floats on salt water of marine origin; discharge occurs through brackish focused/diffuse coastal springs. The recharge is around 880 Mm^3/y. Hydraulic heads reach 4 m AMSL in the NW and SE areas, with a maximum thickness of the freshwater lens of about 120 m; the mean hydraulic gradient is 0.02 ‰. Groundwater exploitation, starting from the 1950s, has been causing progressive groundwater salinization.

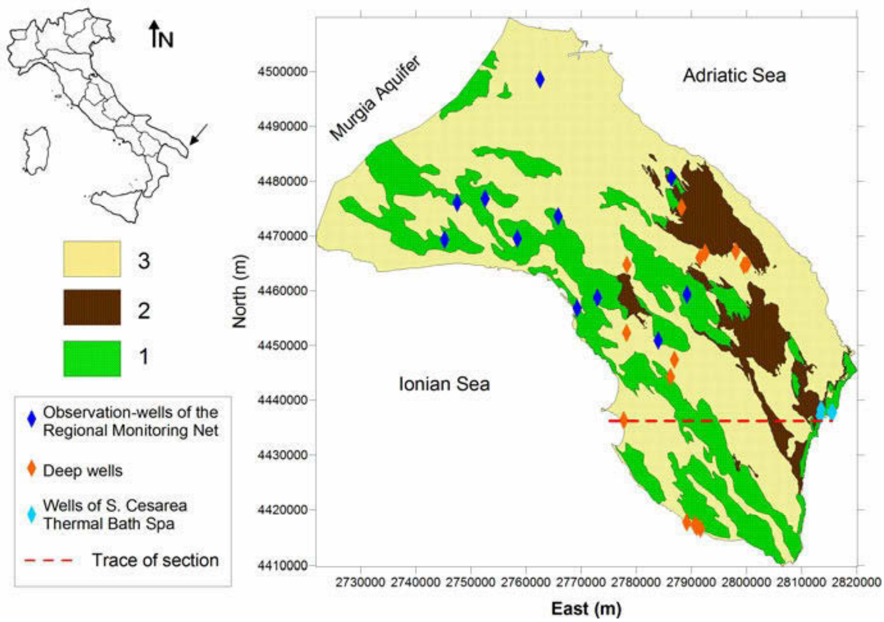

Fig. 1. Geological scheme of the Salento Peninsula (Apulia, Southern Italy) and location of wells (Italian Local Reference System, Gauss Boaga, Rome40). 1: Limestones and dolomitic limestones (Cretaceous); 2: Calcarenites and marly calcarenites (Miocene); 3: Calcarenites, sands and clays (Pliocene-Quaternary). Trace of geological section.

3 Methodology and results

This study is based on chemical and isotope data related to saline/salt ground waters and modern seawater sampled in the Salento aquifer over the last 40 years. Historical data derive from 13 observation-wells (OW) used for the control of seawater intrusion (Fig. 1). New data come from 26 deep wells (DW) aimed at draining storm water and supplying salt water to touristic settlements and fish farms; other new data come from 4 wells drilled to serve the Thermal Health Spa of S. Cesarea (SCW). DWs and SCWs reach salt ground waters underneath the transition zone; before their equipment, such wells were available to carry out temperature and conductivity logs, and take samples of saline/salt fluids.

Chemical analyses of major ions, and sometime of Li and Sr, are available for all samples. Analyses of ^{14}C, δD and $\delta^{18}O$ are available for a total of 12 historical and new samples. The following considerations are largely based on the evaluation of major and minor ions, and $^{87}Sr/^{86}Sr$ ratios related to 15 water samples from DWs, SCWs, and Adriatic and Ionian Seas.

The main application of the $^{87}Sr/^{86}Sr$ ratio methodology in the context of seawater intrusion relates to the identification of saline end-members of mixing (Jørgensen and Banoeng-Yakubo 2001).

Such method is founded on the fact that strontium enters the lattice of aragonite, calcite, fluorite, gypsum, anhydrite and barite: if minerals form in equilibrium with seawater, their $^{87}Sr/^{86}Sr$ ratio is the same as that of coeval seawater. Variations in the $^{87}Sr/^{86}Sr$ ratio of seawater are known to have occurred through the whole Phanerozoic. Sr isotopes show no detectable fractionation by any natural process involving water-rock interaction or mixing and ground waters acquire their $^{87}Sr/^{86}Sr$ ratio from the aquifer rock: the longer the residence time of ground waters, the nearest their chemical equilibrium with the rocks. In coeval ground waters, Sr enrichment is determined by rock mineralogy, while the $^{87}Sr/^{86}Sr$ ratio depends on the rock age: the $^{87}Sr/^{86}Sr$ ratio of salt waters may be influenced by base-exchange, re-crystallization and dolomitization of carbonate rocks.

Chemical compositions of saline/salt ground waters sampled in the DWs and SCWs of the Salento aquifer show differences from modern seawater similar to those shown by salt ground waters from OWs (Fidelibus and Tulipano 1996). TDS (Total Dissolved Solids) ranges from 26 to 44 g/L, reaching 48 g/L in SCWs; average seawater TDS is 40.2 g/L. The correlation between Mg and Ca (Fig. 2A) shows that for all samples except one, even when TDS is lower than seawater TDS, Ca is enriched up to 64 meq/L (SCW) compared to the average seawater value (17.2 meq/L). Mg is mainly depleted (up to a minimum of 70 meq/L); however, some DWs intercept salt waters having Mg concentrations up to 210 meq/L. These variations result in Mg/Ca equivalent ratios different from 7 (average seawater). Other significant variations refer to sulphates (Fig. 2B), which show both enrichment and depletion with highest values of about 94 meq/L (SO_4/Cl equivalent ratio = 0.173) and 44 meq/L respectively, and SO_4/Cl ratios as low as 0.075 accompanying the lowest Mg/Ca ratios. Fig. 2C shows the relationship between Na/Cl and Ca/Cl equivalent ratios: all waters differ from modern seawater for higher Ca/Cl ratios. As to the Na/Cl ratio, salt waters show values either higher or lower than seawater. Minor constituents (Li and Sr) are mostly enriched with respect to present sea water. Sr increases to about 20 mg/L in SCW salt waters (Fig. 2D). Lithium reaches 420 μg/L in the salt water with the highest TDS (48 g/L).

Fig. 3 shows a series of $^{87}Sr/^{86}Sr$ ratio - Sr mixing curves (Barbieri et al.1999) estimated according to Banner et al. (1994) on the basis of the $^{87}Sr/^{86}Sr$ ratios measured on freshwater (9 samples), seawater, and brackish coastal spring waters (19 samples) belonging to the karstic aquifers of the Apulian Region. The freshwater end-member is identified by the average values of fresh waters (Sr = 0.2 mg/L and $^{87}Sr/^{86}Sr$ ratio = 0.70788). Modern seawater is the salt end-member for the uppermost mixing curve ($^{87}Sr/^{86}Sr = 0.709198 \pm 0.000020$, De Paolo and Ingram 1985; Sr = 9.2 mg/L); the intermediate mixing curves intercept the values measured for coastal springs ($^{87}Sr/^{86}Sr$ from 0.70761 to 0.70889, Sr from 1 to 5 mg/L).The lowest mixing curve is driven by the lowest value of $^{87}Sr/^{86}Sr$ (0.70760) and by Sr of about 4 mg/L (Tara spring). The hyperbola connecting the mixing curves at their right ends led Barbieri et al (1999) to assume the existence in Apulia of aged salt waters featuring, with respect to seawater, progressively lower strontium isotope ratios, and higher Sr concentrations. The $^{87}Sr/^{86}Sr$ ratio and Sr concentration of the most evolved salt end-member were respectively 0.70760 and 50 mg/L.

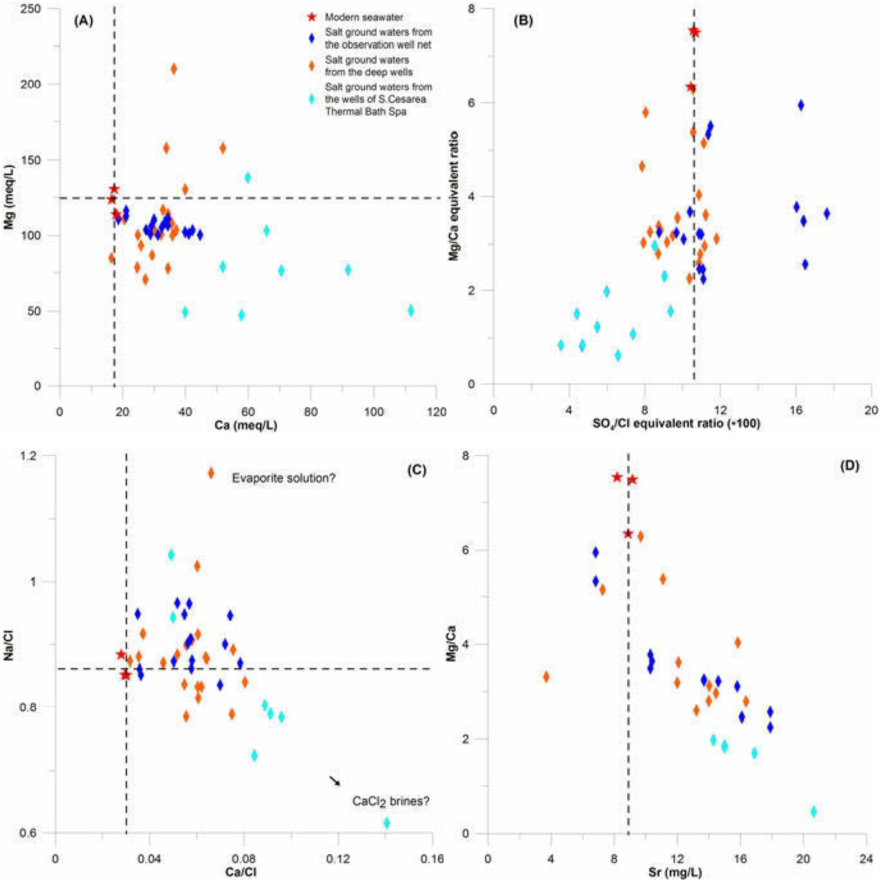

Fig. 2. Salt ground waters in the Salento aquifer: (A) Mg vs. Ca relationship; (B) Mg/Ca equivalent ratio vs. SO_4/Cl equivalent ratio; (C) Na/Cl equivalent ratio vs. Ca/Cl equivalent ratio; (D) Mg/Ca equivalent ratio vs. Sr concentration. Dashed lines mark modern seawater ratios/concentrations.

The $^{87}Sr/^{86}Sr$ ratio of salt ground waters sampled in the DWs and SCWs ranges from 0.70911 to 0.70825. Data almost perfectly adjust along the assumed hyperbola: the matching of real measured data to those hypothesized by extrapolation validates the approach maintained by Barbieri et al. (1999). If salt ground waters were in equilibrium with rocks, their $^{87}Sr/^{86}Sr$ ratio would vary between 0.70720 (lowest limit of Lower Cretaceous) and 0.70780 (highest limit of Upper Cretaceous). However, neither salt waters nor the (assumedly) most evolved salt end-member reach such low values. In fact Tara spring, which drives the lowest mixing curve, does not discharge from the Salento aquifer: its related end-member may be in the Murgia aquifer, in the basement sunk under the Plio-Pleistocene clay covers of Bradanic Trough. Yet data unequivocally indicate that salt waters are very ancient, as do the few historical and new data available on ^{14}C (as low as 2.2 pmc).

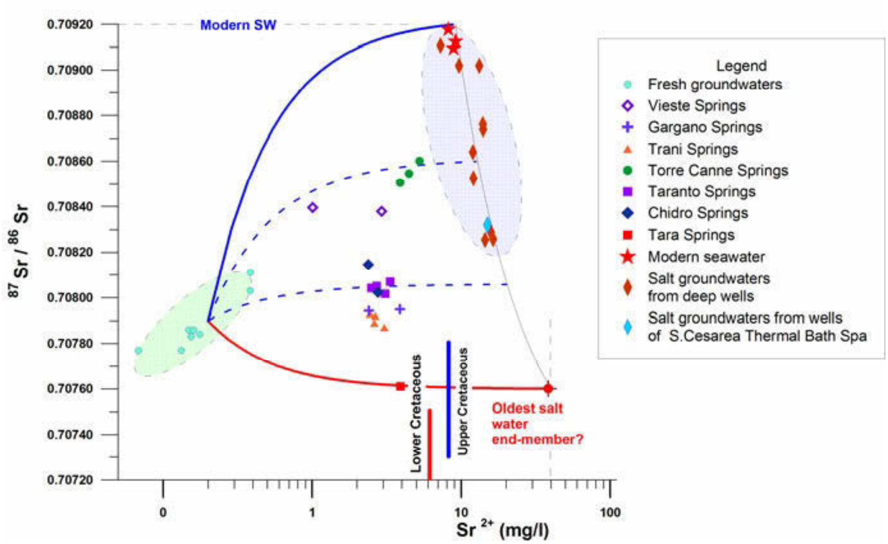

Fig. 3. $^{87}Sr/^{86}Sr$ ratio vs. Sr concentration for seawater (Salento), salt waters (Salento aquifer) and coastal brackish springs (Murgia and Gargano aquifers). The dotted areas respectively gather fresh waters and salt waters (from Barbieri et al. 1999, modified).

4 Discussion and conclusions

Major reactions that could explain all the examined variations are: Ca^{2+}-Mg^{2+} exchange due to dolomitization, Na^{+}-Ca^{2+} or Mg^{2+} base-exchange, SO_4^{2-} reduction, solution of evaporite salts, and mixing with high TDS Ca-Cl_2 brines.

The concurrent Ca enrichments and Mg depletions found in the salt waters of Apulia's karstic coastal aquifers (Fidelibus and Tulipano 1991; Tulipano and Fidelibus 1984) were previously explained as due to dolomitization, dissolution and precipitation of carbonate rocks. The low SO_4/Cl ratios, in a few cases similar to those found in subsurface waters of ancient basins, indicate sulfate reduction, which can also occur due to thermo-chemical reduction at high temperatures. This could explain the very low SO_4/Cl ratios found in the salt thermal waters of SCWs. Reduction processes produce CO_2 and H_2S: thermal salt waters of SCWs, as well as some salt waters from DWs, show bicarbonate contents up to 5.3 meq/L (higher than seawater) and sulfides up to 14.8 mg/L in connection with temperatures of about 30°C. The reduction process produces either high or lower pH: a reductive environment and a pH decrease favor the dissolution of carbonate minerals: this way sulfate reduction can contribute to Mg/Ca ratio variations. The feasibility of Na^+-Ca^{2+} or Na^+-Mg^{2+} base exchange in coastal carbonate aquifers has been demonstrated by Pascual and Custodio (1990) and Nadler et al. (1980). In the study area, the appreciable depletion of Na (low Na/Cl ratios) in some salt waters could be ascribed to the presence of *terra rossa* or, locally, to the influence of clay formations lying on the basement top (Fig. 4). A Na/Cl ratio exceeding seawater value points to the solution of evaporite salts of marine origin. On the other hand, Ca/Cl ratios highly exceeding the seawater value in SCW waters point to the influence of very old brines deeply modified. Sr is abundant in almost all salt waters, and Sr/Cl ratio is higher than that of modern seawater: carbonate rock-water interaction is the main source of Sr. Li, generally enriched in Salento salt waters, shows very high contents in SCW thermal waters: this occurrence confirms that Li is a useful pathfinder for hydrothermal systems (Brondi et al. 1973).

Figure 4 shows a geological section, outlined between a deep well along the Ionian coast and S. Cesarea thermal area: it can be representative of the general structural features of Southern Salento. If we consider its averagely low topographic elevations, it is easy to imagine how the last glaciation and the following Flandrian transgression may have changed the position and thickness of fresh-, brackish- and salt-waters within the rock mass (Calò et al. 2005). To the E (left of section) the covers have acted as a barrier for further exchange with the open sea, blocking seawater entered during transgression: such setting has the chance to favor reductive conditions, whose effects have been recognized in some salt water samples. To the W (right of section) the structural reconstruction indicates the presence of an important fault that could be the entryway for thermal brines present in the bottom sediments of the Adriatic Sea.

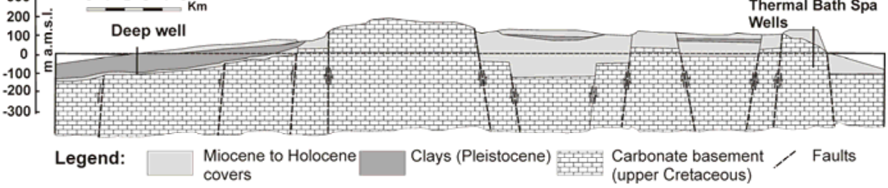

Fig. 4. Schematic geological section (trace in Fig. 1) of Southern Salento.

In conclusion, the chemical and isotope variations shown by salt ground waters can be mainly interpreted as caused by water-rock interactions acting during a progressive aging of original seawater. The new data on S. Cesarea thermal waters (Adriatic coast) reveal the presence of a new salt end-member ($CaCl_2$ brine?), whose genesis is surely different from that of other end-members. This occurrence opens new scenarios for the interpretation of the features of salt waters located near the Adriatic border that can only be explored with further purposed surveys.

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