

Water Rock Interaction [WRI 14]

A multi-isotope study of the Castrocaro mineral waters (northeastern Apennines, Italy)

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Abstract

An applied multi-isotope approach ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{11}\text{B}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$), coupled with chemical evidence, allowed us to constrain a conceptual hydrogeological model for the Castrocaro sulfurous groundwater system that is composed of fresh, brackish, and saline components. In this model, the meteoric recharge enters the turbidite sequence of the Marnoso-Arenacea Fm., undergoing chemical and isotopic modifications by interaction with fine grained pelite rocks, mixing with fossil seawater, and biochemical reactions. The groundwater then rises into a biocalcarenite unit, which acts just as a reservoir from which the resource is finally exploited by wells feeding the Castrocaro Terme spa.

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Keywords: saline sulfurous groundwater; H, O, B, C, N, S isotopes; hydrogeological model; Castrocaro Terme, Italy.

1. Introduction

According to Latines, the term “Salsubium” (*uber salsus*, site rich in salt waters) identified natural emergences of salt waters in the northeastern part of the Apennines. Castrocaro is located in this Apennine sector, where the local highly saline groundwater was exploited since the beginning of the nineteenth century for salt production and therapeutic applications [1]. The present-day Castrocaro spa concession extends nowadays over a surface of 24 km², a narrow area where groundwater displays large variations in salinity among the distinct exploited wells. The Castrocaro groundwater belongs to a much

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wider hydrogeological system, where highly saline fluids are often associated to methane and oil as well as to mud-volcanic activity [2]. The local hydrogeological and hydrogeochemical framework was poorly investigated in the past. In this contribution, new water analyses of major and minor elements, coupled with the isotopic data of oxygen (water and sulphate), boron, nitrogen (ammonium) and sulphur (sulphate and hydrogen sulphide) are discussed. Special attention was devoted to the dissolved sulphur species, since H₂S at Castrocaro spa is largely used for medical purposes.

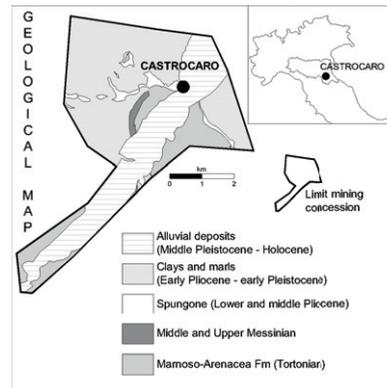


Fig.1. Sketched geological map of the study area

In the study area (Fig. 1), the most important geological unit is represented by the Marnoso-Arenacea Fm. (Langhian-Tortonian; 16-10 Ma), consisting of an arenaceous-pelitic turbidite sequence with a thickness averaging 3000 m. In some places, this formation is overlain by the evaporitic Gessoso-Solfifera Fm. (Upper Messinian), which is followed upwards mainly by pelitic deposits of Lower Pliocene to Lower Pleistocene age called "Argille Azzurre". A peculiar facies outcropping in the Castrocaro district, is the so called "Spungone", a Lower-Middle Pliocene biocalcarene, that hosts the investigated water. This lithological unit includes bioherma facies with biologically-built limestone and sandy-textured bioclastic horizons including abundant fossil remains. This formation outcrops with a spotty distribution over an area of about 1.5 km².

2. Analytical procedures

Groundwater was sampled on May and October 2011 from ten wells exploited by the Terme di Castrocaro spa. Temperature, pH, Eh, alkalinity and electrical conductivity were measured in the field. Water samples were analysed for major and minor elements using ion chromatography, and ICP-OES and ICP-MS techniques. Total sulphide in the waters was determined by iodometry, after NaOH/AlCl₃ treatment during sampling. For isotopic analyses (1) water $\delta^2\text{H}$ ($\pm 1\%$) and $\delta^{18}\text{O}$ ($\pm 0.2\%$) were determined by WS-CRDS; (2) $\delta^{11}\text{B}$ by TIMS after separation of boron by ionic exchange chromatography ($\pm 0.5\%$); (3) $\delta^{13}\text{C}$ on DIC by analyzing CO₂ obtained by acid extraction ($\pm 0.2\%$); (4) $\delta^{15}\text{N}$ ($\pm 0.2\%$) on ammonium as N₂, after conversion to and decomposition of ammonium sulfate; and (5) total sulphide in solution was recovered in the field as CdS, and sulphate was precipitated as BaSO₄ in the laboratory, after concentration of the water samples by evaporation at about 70°C. The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ analyses were carried out using the TC-CF-IRMS technique, with precision of $\pm 0.2\%$ for sulphur and $\pm 0.5\%$ for oxygen.

3. Results and discussion

Field parameters and chemical results indicate that the investigate samples are fresh, brackish, and saline waters. Na-Cl is the dominant chemical facies, only one sample being HCO₃-Cl-Na. Water temperature ranges from 13.2 to 17.7 °C, and pH is nearly neutral (6.8 to 7.4). Eh values range between -130 and +30 mV, thus testifying reducing conditions of the analyzed groundwater, in keeping with the presence of sulphide (1 to 118 mg/L) and ammonium (0.5 to 85.4 mg/L). Coherently, the sulphate content is extremely variable, ranging between 0.9 and 77 mg/L.

Huge variations are observed for the isotopic compositions ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{11}\text{B}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$). The water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values vary from -56 to -20 ‰, and from -9 to -2 ‰, respectively. For species in solution, the variations observed are: -21 to 3 ‰ for $\delta^{13}\text{C}_{\text{DIC}}$, 32 to 46 ‰ for $\delta^{11}\text{B}$, -1 to 3 ‰ for $\delta^{15}\text{N}_{\text{NH}_4}$, -36 to 23 ‰ for $\delta^{34}\text{S}_{\text{H}_2\text{S}}$, -2 to 50 ‰ for $\delta^{34}\text{S}_{\text{SO}_4}$, and 6 to 23 ‰ for $\delta^{18}\text{O}_{\text{SO}_4}$.

The Cl and Br concentrations and the $\delta^{18}\text{O}$ signatures in the water samples define positive correlations that clearly indicate that the Castrocaro hydrogeological system consists of mixing of meteoric and saline waters (Fig. 2). The latter should be fossil evaporated seawater, according to the $\delta^2\text{H}$ - $\delta^{18}\text{O}$ trend and the observed Na/Cl and Cl/Br ratios. In contrast, the deviations of non-conservative elements (Ca, Sr, Mg, K, and to some extent B) with respect to the meteoric-saline water mixing-line denote the significant role of rock interaction processes in modifying the original chemical composition of the water. The envisaged mixing model is also supported by the $\delta^{11}\text{B}$ values, that agree with a mixing between a fossil seawater enriched in ¹¹B, and a meteoric, slightly mineralized water, characterized by lower boron isotopic signature. The $\delta^{11}\text{B}$ of some saline samples is higher (up to 46‰) than the seawater value. This feature could point to boron removal due to adsorption by the solid matrix at low water/sediment ratio. This process seems to occur also for NH₄. The range of the $\delta^{15}\text{N}_{\text{NH}_4}$ values suggests the occurrence of decomposition of organic matter (3‰) followed by adsorption processes lowering the isotopic signature. The sulphate $\delta^{34}\text{S}$ signature is systematically higher than that of paired sulphide, this feature being expected as sulphide in low temperature aquifers generally derives from bacterial reduction of the parental sulphate in an anaerobic setting. The basic factor controlling this bacterial activity is the presence of organic matter, which undergoes oxidation providing carbonate species to the solution.

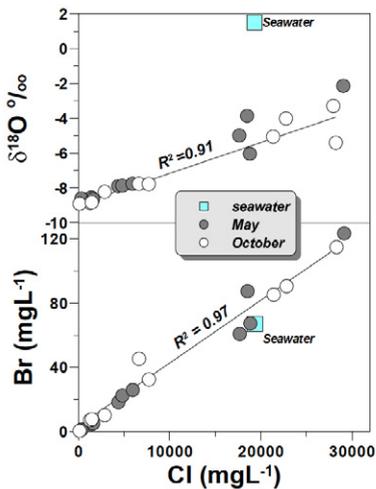


Fig.2. Cl vs. Br and $\delta^{18}\text{O}$ in the Castrocaro groundwater.

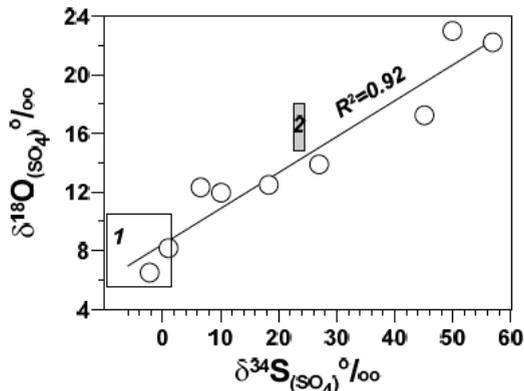


Fig. 3. $\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}$ values correlation of dissolved SO₄. In boxes the calculated $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ for initial SO₄ in group 1 waters (box 1) and group 2 waters (the two highest data points; box 2).

The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ -values of the $\text{SO}_4\text{-H}_2\text{S}$ system plotted against sulphate or sulphide concentrations identify two clearly separated groups (Fig. 3). The same behaviour is observed comparing the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulphate with the $\delta^{34}\text{S}$ of sulphide. These features point to different sources of sulphate in the two groups of wells. The initial $\delta^{34}\text{S}$ values of the analysed sulphates calculated by mass balance reveal that the involved sources can be oxidation of sulphides widespread in the rock matrix (group 1 waters; $\delta^{34}\text{S} = -5.9$ to 1.3‰) and evaporite dissolution (group 2 waters; $\delta^{34}\text{S} = 24$ to 25‰). Sulphate from both sources underwent microbial reduction under closed conditions, thus producing H_2S with the observed sulphur isotopic signature. Following the same approach, the initial $\delta^{18}\text{O}$ values were calculated for the initial sulphate in group 1 wells. They show a good correlation with the water $\delta^{18}\text{O}$ values ($R^2 = 0.74$), as expected for sulphate from oxidation of pyrite in low temperature environment [3]. Finally, the sulphate $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values show a remarkable correlation ($R^2 = 0.92$) defining a straight line with a slope of 0.25 (Fig. 3), as often observed in bacterial sulphate reduction experiments [4].

The $\delta^{13}\text{C}$ -TDIC values clearly show that oxidized carbon fractions from sulphate-reducing activity (low $\delta^{13}\text{C}$) and possibly from methanogenesis (high $\delta^{13}\text{C}$) co-exist in the studied groundwater.

4. Conclusions

The conceptual hydrogeological model delineated from the chemical and isotopic data can be formulated as follow: two types of water circulate within the Marnoso-Arenacea Fm. The first type is represented by slightly mineralized meteoric water with typical Ca-HCO_3 composition; the second type is represented by fossil evaporated seawater, further modified by interaction with the aquifer rocks. These two water types mix at depth in different proportions, then rise through a system of faults and fractures, finally entering the Spungone biocalcarene. The latter aquifer scarcely influences the redox reactions and/or adsorption/desorption processes recorded in the studied groundwater. Accordingly, the Spungone Fm. acts just as a reservoir (i.e. a “collecting pool”) from which the groundwater is finally exploited.

In our model, the abiological and biological processes controlling the geochemical composition of the Castrocaro waters should mostly occur in the Marnoso-Arenacea Fm., given its silicoclastic nature, characterized by sandy and clayed layers, which may provide organic matter, microbial flora and biogenic pyrite.

Acknowledgements

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A multi-isotope study of Castrocaro mineral water (North-Eastern Apennines, Italy)

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Spa activity

According to Latines, the term "Salsubium" (uber salsus, site rich in salt waters) identified natural emergences of salt waters in the North-Eastern part of the Apennines. Although the Castrocaro saline groundwater are exploited since the beginning of the nineteenth century for salt production and therapeutic applications, the local hydrogeological and hydrogeochemical framework was poorly characterized. The present-day Castrocaro spa concession extends nowadays over a surface of 24 km²

Aristide Conti, 1836-1927



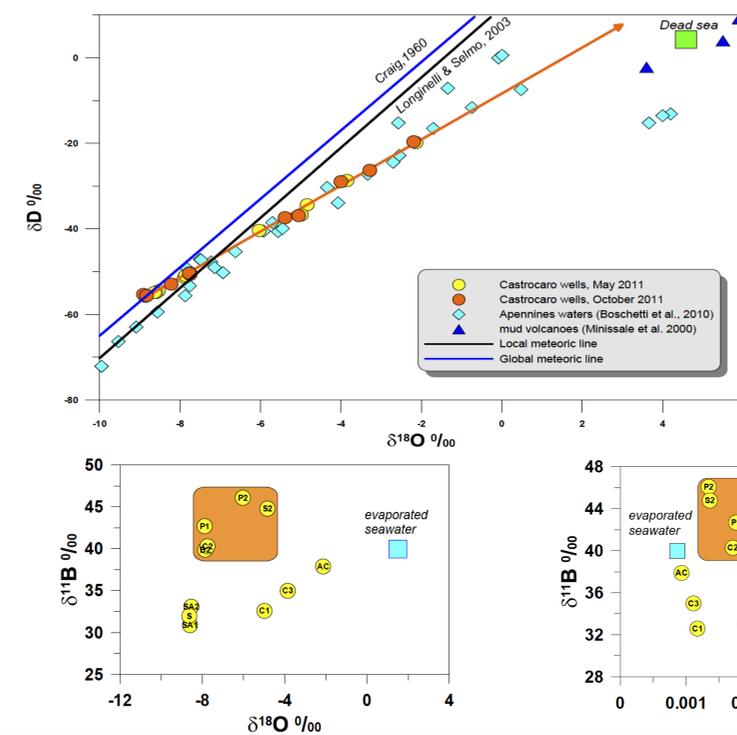
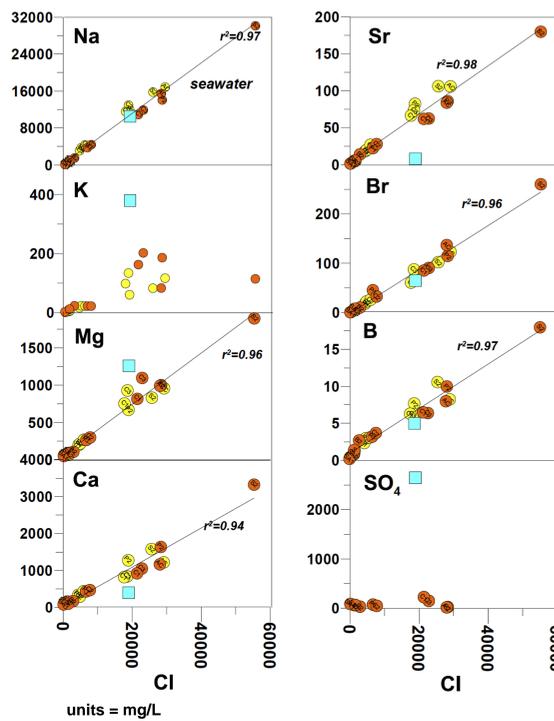
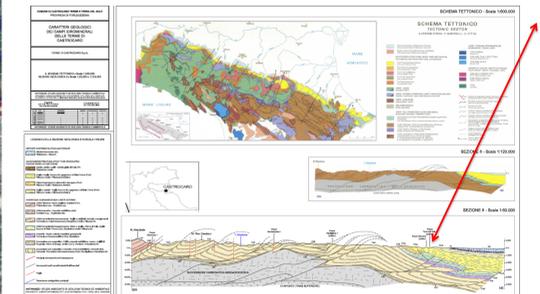
Research activity

The aim of this study was to investigate the origin of the mineral waters exploited at the Castrocaro spa. In this contribution new water analyses of major and minor elements, coupled with the isotopic data of oxygen (water and sulphate), boron, nitrogen (ammonium) and sulphur (sulphate and hydrogen sulphide) are discussed. Special attention was devoted to the dissolved sulphur species, since H₂S at Castrocaro spa is largely used for medical applications

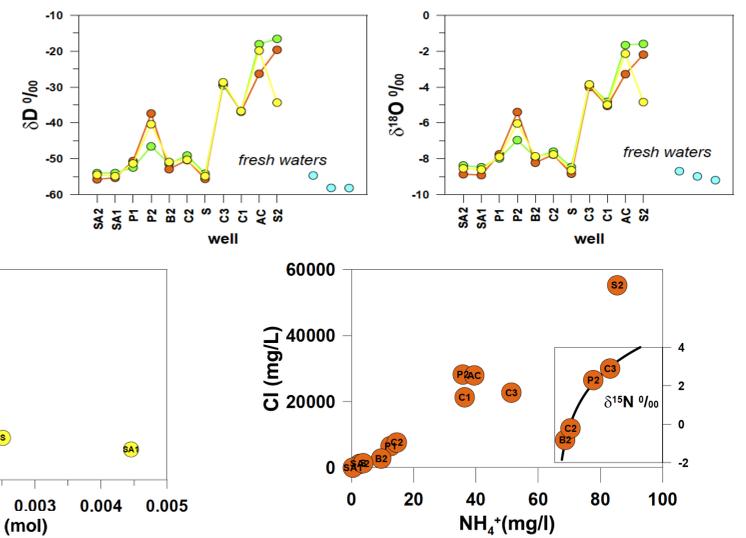


Geologic framework

In the study area the most important geological unit is represented by the Marnoso-Arenacea Fm. (Langhian-Tortonian; 16-10 Ma), an arenaceous-pelitic turbidite sequence with a thickness averaging 3000 m. In places this formation is overlaid by the evaporitic Gessoso-Solfifera Fm. (Upper Messinian), which is followed upwards mainly by pelitic deposits of Lower Pliocene to Lower Pleistocene age called "Argille Azzurre". A peculiar facies outcropping in the Castrocaro district is the so called "Spungone", a Lower-Middle Pliocene biocalcarene, that hosts the investigated water. This lithological unit includes bioherma facies with biologically-built limestone and sandy-textured bioclastic horizons including abundant fossils. This formation outcrops with a spotty distribution over about 1.5 km².

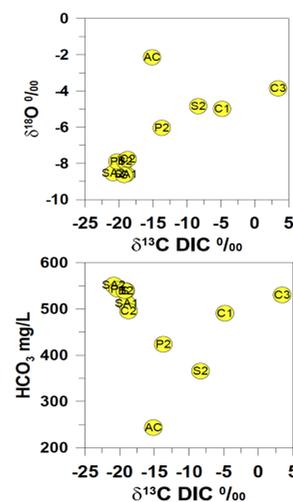
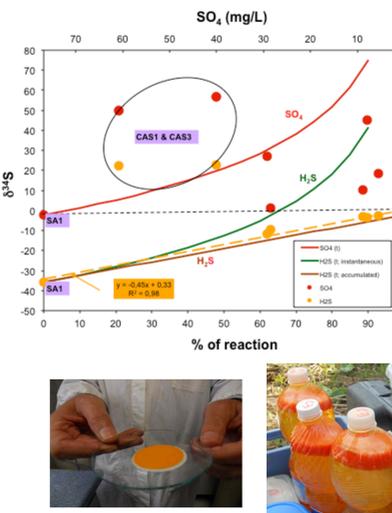
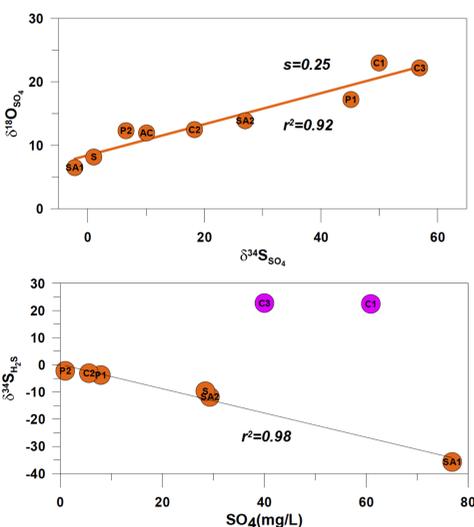


Field data and chemical results display large variations in spite of the limited extension of the study area. Waters are fresh, brackish, and saline. Na-Cl is the dominant chemical facies, only one sample being HCO₃-Cl-Na. Water temperature ranges from 13.2 to 17.7 °C, and pH is nearly neutral (6.8 to 7.4). Eh values range between -130 and +30 mV, thus testifying reducing conditions of the groundwater, in keeping with the presence of sulphide (1 to 118 mg/L) and ammonium (0.5 to 85.4 mg/L). Coherently, the sulphate content is extremely variable, ranging between 0.9 and 77 mg/L



Which origin for water salinity?

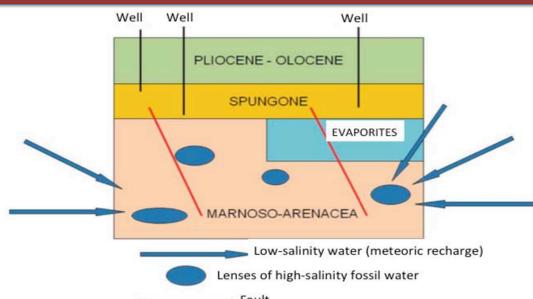
The Cl and Br concentrations and the δ¹⁸O signatures in the water samples define positive correlations that clearly indicate that the Castrocaro hydrogeological system consists of admixtures of meteoric and saline waters. The latter should be fossil evaporated seawater, according to the δ²H-δ¹⁸O trend and the observed Na/Cl and Cl/Br ratios. In contrast, the deviations of non-conservative elements (Ca, Sr, Mg, K, and to some extent B) with respect to the meteoric-saline water mixing-line denote the significant role of rock interaction processes in modifying the original chemical composition of the water. The δ¹¹B values agree with a mixing between a fossil seawater and a meteoric, slightly mineralized water, characterized by lower boron isotopic signature. The δ¹¹B of some saline samples is higher (up to 46‰) than the seawater value. This feature pinpoints adsorption by the solid matrix at low water/sediment ratio, as also suggested by first data on isotopic composition of nitrogen in ammonium. Finally, the Castrocaro system belongs to a much wider hydrogeological system, where highly saline fluids are often associated to methane and oil as well as to mud-volcanic activity



Which origin for sulphide and sulphate?

The sulphate δ³⁴S signature is systematically higher than that of paired sulphide, this feature being expected as sulphide in low temperature aquifers generally derives from bacterial reduction of sulphate in an anaerobic setting. The basic factor controlling this bacterial activity is the presence of organic matter, which undergoes oxidation providing carbonate species to the solution. The δ³⁴S and δ¹⁸O-values of the SO₄-H₂S system, when plotted against sulphate, identify two clearly separated groups. The same behaviour is observed comparing the δ³⁴S and δ¹⁸O of sulphate with the δ³⁴S of sulphide. These features point to different sources of sulphate in the two groups of wells. The initial δ³⁴S values of the analysed sulphates calculated by mass balance reveal that the involved sources can be oxidation of sulphide (pyrite) widespread in the rock matrix (group 1 waters; δ³⁴S = -5.9 to 1.3‰) and Messinian evaporite dissolution (group 2 waters; δ³⁴S = 24 to 25‰). Sulphate from both sources underwent microbial reduction under closed conditions, thus producing H₂S with the observed sulphur isotopic signature

The conceptual model



The multi-isotope approach (δ²H, δ¹⁸O, δ¹¹B, δ¹³C, δ¹⁵N, δ³⁴S), coupled with chemical evidence, allows to constrain a preliminary conceptual hydrogeological model for the Castrocaro sulfurous groundwater system made up of fresh, brackish and saline components. By this model, the meteoric recharge enters the turbidite sequence of the Marnoso-Arenacea Fm., undergoing chemical and isotopic modifications by interaction with fine-grained pelite rocks, mixing with fossil seawater, and biochemical reactions. The groundwater then rises into a biocalcarene unit, which acts just as a reservoir from which the resource is finally exploited by wells feeding the Castrocaro Terme spa

