

CONSIDERATIONS CONCERNING THE ORIGIN OF THE ESTORIL (PORTUGAL) THERMAL WATER

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ABSTRACT

In the urban area of Estoril, a Portuguese tourist village 20 km westward from Lisbon, hot mineral waters (thermal waters) spout out from natural springs which have been known since the 19th century. The thermal waters are of the sodium chloride type, with total dissolved solids and temperatures higher than the ones of the regional waters. Isotopic data are consistent with a meteoric origin for both the regional and thermal waters of the Estoril area: $\delta^{18}\text{O}$ (‰), -4.16 to -3.52 and $\delta^2\text{H}$ (‰), -25.5 to -18.7. The thermal water composition can be derived from the regional water composition assuming the dissolution of evaporite minerals, cation exchange and precipitation of calcite. The thermal water flow system has probably the recharge area somewhere in between Estoril and the Sintra mountain. The elevation difference between the recharge area and the sea provides the driving force for groundwater movement to the Estoril area where the upward movement of the mineralised and warm water is controlled by an impermeable barrier of dykes and open fractures in the pre-existing rocks.

Keywords: *Thermal water, mineral water, hydrochemistry, stable isotopes, Estoril, Portugal.*

RESUMEN

En la zona urbana de Estoril surgen aguas termales calientes de fuentes naturales conocidas desde el siglo XIX. Las aguas termales son del tipo cloruro sódico, y tienen una cantidad total de sólidos disueltos y una temperatura mayores que la habitual en las aguas regionales. Los datos isotópicos sugieren un origen meteórico tanto para las aguas regionales como para las termales, ya que los valores $\delta^{18}\text{O}$ están comprendidos entre -4.16 y -3.52 (‰) y los $\delta^2\text{H}$ entre -25.5 y -18.7 (‰). La composición de las aguas termales puede deducirse de la composición de las aguas regionales, teniendo en cuenta la disolución de minerales evaporíticos, el intercambio de cationes y la precipitación de calcita. La zona de recarga del sistema de flujo acuático se localiza probablemente entre Estoril y las montañas de Sintra. La diferencia de cota topográfica entre la zona de recarga y el mar es la causante del movimiento del agua subterránea hacia la zona de Estoril, donde el ascenso de aguas mineralizadas y calientes está controlado por una barrera impermeable de diques y fracturas abiertas en la roca pre-existente.

Palabras clave: *Agua termal, agua mineral, hidroquímica, isotopos estables, Estoril, Portugal.*

Introduction

In the urban area of Estoril, a Portuguese tourist village 20 km westward from Lisbon (fig. 1), there are two main mineral water springs which waters are of the sodium chloride type, with total dissolved solids (TDS) and temperatures higher 3 to 5 g/L and 10 to 15 °C than the ones of the regional waters, respectively. These thermal springs are known since

the 19th century and their water was used for therapeutic purposes in an old spa which building has already been demolished.

According to Portuguese law, mineral waters are State property and their exploitation must be authorized by government since it is a concession. In order to reduce the pollution potencial, to protect the quality and to improve the quantity of mineral water resources, the policy of the Por-

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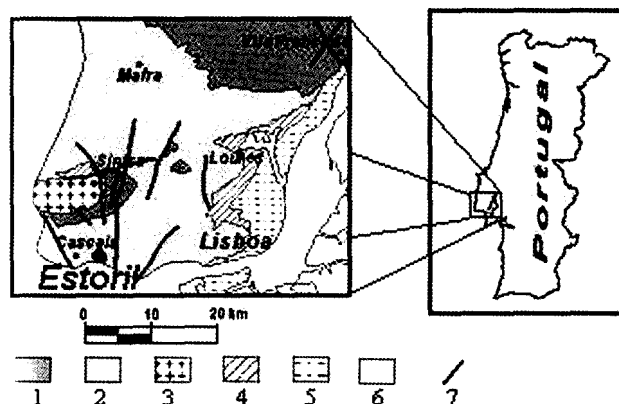


Fig. 1.—Location of the Estoril area and prominent geological features (1-Jurassic, 2-Cretaceous, 3-Sintra subvolcanic massif, 4 and 5-Tertiary, 6-Quaternary, 7-fault.)

tuguese authorities has encouraged the construction of the deep wells in exchange of the springs (Carvalho, 2002). According to these guidelines, at present the Estoril thermal springs are not exploited and in the Estoril concession there are two deep wells (TW1 and TW2) which thermal water will be exploited for a new spa. However, the plan has yet to be approved by the Portuguese administration. These wells were constructed in the late 1980's after an hydrogeologic study of the Estoril area. The main conclusions of this study were presented by Carvalho *et al.* (1982). They pointed out that the water is of meteoric origin, infiltrate somewhere in between Estoril and the Sintra mountain, percolate to great depth in the sedimentary basin, and ascend in the low-altitude Estoril area. In order to explain the high TDS they pointed out the mixing of seawater and hot fresh-water and the hypothesis of percolation trough the evaporites of the Dagorda formation (Hettangian stage).

The main objectives of this paper are to present new data about the chemistry and the isotope composition and to update the conceptual model of the origin and circulation of the Estoril thermal waters. In order to do that, the data on the chemistry of thermal water from the TW1 and TW2 wells will be considered. Also the chemical and isotopic composition of the thermal water will be compared with the ones of the regional waters of some wells located northward of the TW1 and TW2 wells.

Climate

The Estoril thermal springs are located in a region of great tourist activity which greatly bene-

fits from a pleasant climate with some mediterranean characteristics. The average rainfall in Monte Estoril is 636 mm/year and the mean annual air temperature is 17 °C. December and January are the coldest months (the mean temperature is about 10 °C) and July and August are the hottest ones (the mean temperature is about 22 °C). Rainfall contribution is 80% during the cold season (October-March) and 20% during the warm season (April-September). The rainy season has two rainfall peaks (January and March) and during July and August there is practically no rain. The annual rainfall steadily increases from the south to the north in direction of the Sintra mountain, located about 5 km northward of Estoril (the average rainfall in Sintra-Granja is 840 mm/year). On the other hand, the temperature decreases from the south to the north (the mean annual air temperature is 15 °C in Sintra-Granja).

Geology

The Estoril thermal springs field is located about 5 km southward of the Sintra subvolcanic massif. The intrusion formed a dome surrounded by a ring syncline (Alcabideche syncline) which northern limb dip increases from the south to the north in direction of the Sintra massif (fig. 2).

South of the Alcabideche syncline, a flat monocline structure with some second order folds was developed (Costa & Kullberg, 1981). The thermal springs are located at the E limb of a second order fold (Abuxarda-Bicesse anticline) which core is formed by lower Cretaceous terranes. In the thermal springs area the Cenomanian-Albian argillaceous limestones dip 5° to 8° to E. Dykes of basic rocks cut the sedimentary units with the N5°W general trend (fig. 3).

At the beginning of the 1980's two 250 m long boreholes were drilled in the area surrounding the Estoril Spring using diamond core bits to investigate the geological and structural conditions connected with the thermal water discharge. The results of the detailed study of the core samples were presented by Carvalho *et al.* (1982). They defined the following stratigraphic units beneath the Cenomanian-Albian argillaceous limestones outcrops:

— Lower Albian - Upper Aptian (Upper Almargem Sandstones): fine and coarse sandstones and clays.

— Lower aptian - Upper Barremian (Layers with *Orbitolina*): limestones and argillaceous limestones with some intercalated sandstones and clays.



Fig. 2.—Simplified geological map of the Estoril-Cascais-Sintra area (adapted from Ramalho *et al.*, 1981).

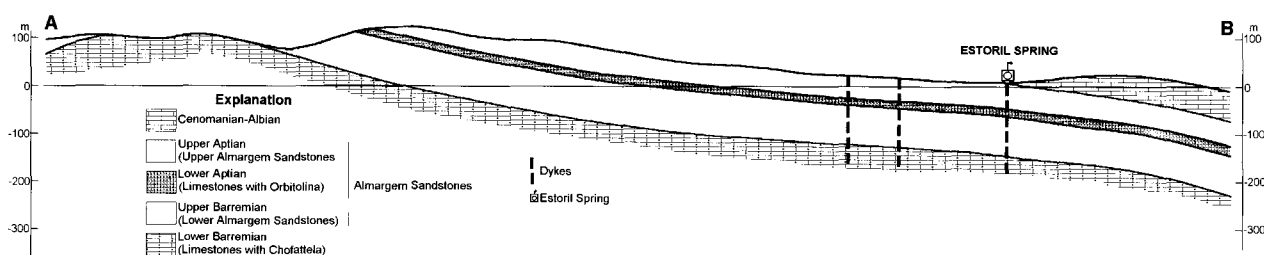


Fig. 3.—Geological section A-B. Line of section is shown in figure 2.

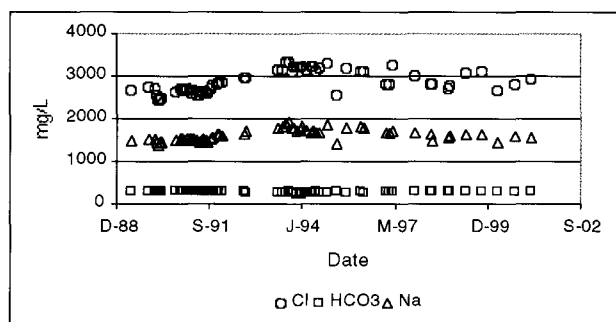


Fig. 4.—Seasonal variation of TW1 water chemical composition.

— Upper Barremian - Lower Barremian (Lower Almagem Sandstones): clays, marls and coarse sandstones.

— Lower Barremian (Limestones with *Chofatella* and *Dasicladaceae*): argillaceous limestones.

They also pointed out that these units are partially obliterated by dykes of basic rocks.

Sources of the Estoril thermal water

In the urban area of the Estoril village hot mineral waters (thermal waters) issue from natural springs as well as from drilled wells. A detailed inventory of springs and dug and drilled wells was presented by Carvalho et al (1982). The water of the most important spring (≈ 2 L/s), *Nascente do Estoril* (Estoril Spring), has TDS = 3.4 g/L and temperature = 30 °C. This spring is located at the end of a 44 m length gallery, about 350 m landward from the Atlantic coastline and 10 m a.s.l., in the contact zone of the Albian argillaceous limestones with the Upper Almagem Sandstones. The *Nascente da Poça* (Poça Spring), with a diminutive yield, discharges at the Albian argillaceous limestones of the S. João do Estoril beach, about 2 m a.s.l. The water has TDS = 3.1 g/L and temperature = 26 °C. Besides these sources, 3 hot

Table 1.—Characteristics of the selected drilled wells

Well	Altitude (m)	Depth of the intake zone (m)	Yield (L/s)	Static water level (m, a.s.l.)	Dinamic water level (m, a.s.l.)
TW1	15	135-267	12	14.7	2.6
TW2	15	152-248	1.6	15.4	8.8
RW13	80	132-183	10	20.0	13.2
RW17	85	71-190	22.5	18.7	15.5
RW19	80	139-160	5	34.0	23.3

water drilled wells located into the spring area are also reported by Carvalho *et al.* (1982).

The intake part of the Estoril concession wells (TW1 and TW2) was placed in the limestones of the lower Barremian (Limestones with *Chofatella* and *Dasicladaceae*). The data on the chemistry of groundwater from the TW1 and TW2 wells include about one hundred analyses from 1989 until now. The water pumped out of these wells has identical facies to the thermal water springs but the TDS and the temperature are higher. The maximum TDS and temperature values were measured for the TW1 water: 6 g/L and 35.5 °C, respectively. Although the groundwater level in the wells presents some seasonal and tidal fluctuations the chemical composition maintains a remarkable constancy (fig. 4) - the variation coefficient for the main chemical parameters is lower than 10% ($n = 60$ for the TW1 water).

Methodology

Representative chemical analysis of the major ions and isotopic data for ¹⁸O, ²H and ³H from the Estoril thermal waters (TW1 and TW2 deep wells) and from the assumed regional groundwater (RW13 and RW17 deep wells) were made from samples collected during July 1995. The RW13 and RW17 wells are located northward of the thermal area (fig. 2). The main characteristics of the wells are presented in Table 1.

The Nuclear and Technological Institute (ITN) in Portugal carried out the isotopic determinations. The ¹⁸O and ²H of water were measured with a mass spectrometer (SIRA 10 VG ISOGAS) using the methods of Epstein and Mayeda and Friedman, respectively (Gonfiantini, 1981). The results are

Table 2.—Chemical and isotopic composition of the Estoril thermal water (TW wells and Estoril Spring) and regional groundwater (RW wells). Well and spring locations are shown in figure 2

Sample	RW13	RW17	RW19	TW1	TW2	Estoril Spring
Date	7/1995	7/1995	9/1979	7/1995	7/1995	9/1979
t (°C)	21.0	24.0	21.0	35.5	30.5	30.0
pH	7.0	7.0	7.3	6.9	7.0	6.9
HCO ₃ ⁻ (mg/L)	344.0	392.4	385.5	272.0	299.6	309.9
Cl ⁻ (mg/L)	1,359.3	892.9	124.3	3,081.1	2,420.6	1,675.6
SO ₄ ⁻² (mg/L)	182.1	127.6	36.9	387.5	297.9	227.1
Na ⁺ (mg/L)	731.9	451.1	66.7	1,721.6	1,324.7	984.9
K ⁺ (mg/L)	21.0	8.3	—	51.8	41.3	—
Ca ²⁺ (mg/L)	211.3	181.0	121.6	312.7	260.4	196.8
Mg ²⁺ (mg/L)	50.6	68.8	20.4	95.8	88.2	55.4
δ ¹⁸ O (‰)	-3.88	-4.16	—	-3.52	-3.75	—
δ ² H (‰)	-25.5	-22.3	—	-22.3	-18.7	—
³ H (T.U.)	—	—	—	0.78 ± 0.70	—	—

expressed in delta notation relative to the Vienna-Standard Mean Ocean Water (V-SMOW). The standard deviation is 0.10‰ for δ¹⁸O and 1.0‰ for δ²H (Paquete, 1998).

Analyses for ³H were made using electrolytic enrichment and subsequent measurement of counting rates by liquid scintillation (IAEA, 1976). The ³H are in TU (tritium units) and the standard deviation of the measurements is 0.7 TU (Paquete, 1998).

The Laboratory of Analyses of the Department of Geology of the Coimbra University carried out the chemical analysis. Alkalinity and pH of these water samples were not measured in the field, so it is possible that are some minor errors in these parameters. Nevertheless, the alkalinity and pH values are about the same as the ones measured in the field at other time.

The physico-chemical and isotopic characteristics of the sampled water are presented in Table 2. The physico-chemical characteristics of Estoril Spring thermal water and of the water in the meantime abandoned well (RW19), sampled during September 1979 as reported by Carvalho *et al.* 1982, are also presented.

Chemical composition and the origin of solutes

Figure 5 shows the major solute concentrations plotted on a Piper trilinear diagram. Two geochemical groupings are defined: (1) Na-Cl-type waters with TDS values between 2,1 and 5,9 mg/L and (2) Ca-HCO₃-type water with TDS value of 0.75 g/L which is consistent with what is expected from the water-rock interaction in carbonated terranes. The Na-Cl-water group includes the Estoril hot mineral waters (T >25 °C) and colder waters (21 and 24 °C) from the RW13 and RW17 wells, respectively.

A t test for the significance of sample correlations, r, is performed (Davis, 1986)

$$t = r \frac{\sqrt{n-2}}{\sqrt{1-r^2}}$$

which has n-2 degrees of freedom.

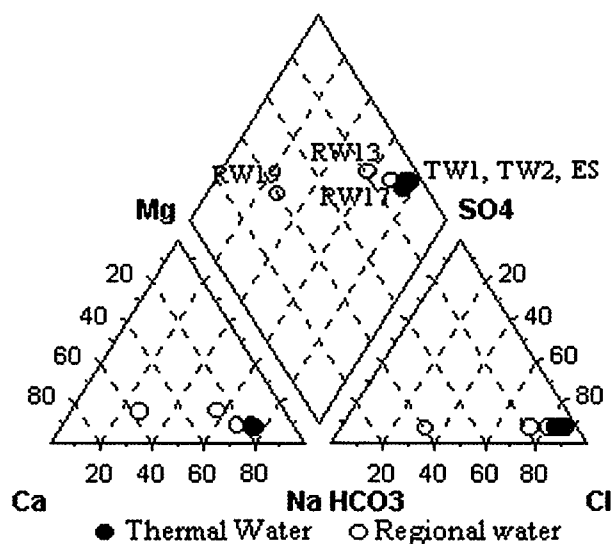


Fig. 5.—Piper diagram showing the ionic composition of Estoril thermal water (TW wells and Estoril Spring) and regional groundwater (RW wells).

Table 3.—Correlation matrix (the correlation values with statistical significance at 5% level are in bold)

	K ⁺	Mg ²⁺	Ca ²⁺	Na ⁺	Cl ⁻	SO ₄ ⁻²	HCO ₃ ⁻	T	pH
K ⁺	1.0	0.80	0.99	0.99	0.99	0.99	-0.99	0.89	-0.72
Mg ²⁺		1.0	0.92	0.88	0.90	0.89	-0.71	0.81	-0.35
Ca ²⁺			1.0	0.97	0.98	0.98	-0.87	0.83	-0.48
Na ⁺				1.0	0.99	0.99	-0.96	0.91	-0.61
Cl ⁻					1.0	0.99	-0.94	0.90	-0.58
SO ₄ ⁻²						1.0	-0.95	0.91	-0.61
HCO ₃ ⁻							1.0	-0.88	0.69
T								1.0	-0.75
pH									1.0

The critical values for t with 4 and 2 degrees of freedom and a 5% level of significance are t = 2.776 and t = 4.303.

Most of the species in solution are positively correlated (Table 3); the only exception is the negative correlation of HCO₃⁻ with the other major ions. The correlation of the temperature with the ionic species is also positive with the bicarbonate exception. This suggests the precipitation of carbonates while in meantime the TDS increases and the water percolates deeper. The correlations with pH have not statistical significance.

The saturation indexes of calcite and dolomite, shown in Table 4, reflect supersaturation conditions and suggest precipitation. On the contrary, the negative saturation indexes of the evaporite minerals, like halite and gypsum, reflect subsaturation and

Table 4.—Saturation indexes calculated by the WATEQX program*

Sample	RW13	RW17	RW19	TW1	TW2	Estoril Spring
SI _{calcite}	0.09	0.16	-0.02	0.13	0.17	0.01
SI _{dolomite}	-0.21	0.17	-0.58	0.08	0.18	-0.23
SI _{aragonite}	-0.06	0.02	-0.17	0.02	0.04	-0.12
SI _{gypsum}	-1.05	-1.23	-1.70	-0.80	-0.91	-1.05
SI _{anhydrite}	-1.30	-1.44	-1.95	-0.91	-1.07	-1.21
SI _{halite}	-4.66	-5.05	-6.67	-4.02	-4.21	-4.48

* Version 1987 by PFM Van Gaans, Thermodynamic Centre, Institute for Earth Sciences, Ryksuniversiteit, Utrecht, The Netherlands.

dissolution is expected. These facts also support the above hypothesis of mineral dissolution with increasing carbonate precipitation.

The value of $\text{Na}^+ + \text{K}^+ / \text{Cl}^-$ (Table 5) for all the water samples is lower than the expected 1:1 stoichiometric relation of halite+sylvite dissolution, indicating that a fraction of about 15 to 20% chloride is associated with cations different from the sodium and potassium. On the contrary, the value $\text{Ca}^{2+} / \text{SO}_4^{2-}$ is greater than the stoichiometry of gypsum dissolution and the increasing of Ca^{2+} with TDS is greater than the one of SO_4^{2-} . So, a supplementary origin for the Ca^{2+} is necessary once the reduction of the SO_4^{2-} is unexpected in this geochemistry environment. The exchange of Ca^{2+} for Na^+ is a possible hypothesis.

The dedolomitization is another geochemical process suggested by the ratios presented in Table 5. In fact, the dissolution of gypsum induces the transformation of dolomite to calcite in the rock and produces waters with increased Mg^{2+} , Ca^{2+} , and SO_4^{2-} concentrations, and decreases alkalinity as observed in the studied waters. When equilibrium with calcite and dolomite is maintained, the ratio of $\text{Mg}^{2+} / \text{Ca}^{2+}$ must remain around 0.8 and ideal stoichiometric relations for the reaction are $\text{Ca}^{2+} : \text{SO}_4^{2-} = 1:1.8$ and $\text{Mg}^{2+} : \text{SO}_4^{2-} = 0.8:1.8$. (Appelo & Postma, 1996). These ideal values deeply differ from the ratios presented in table Table 5. So, the dedolomitization does not seem to be a relevant geochemical process in the Estoril aquifer and the responsible for Mg^{2+} and Ca^{2+} dissolution.

According to our interpretation of the data, the excess of solutes of the thermal waters over the ones of the "normal" water is originated from the dissolution of evaporite sediments. These ones can occur dispersed in some Cretaceous and Jurassic carbonated rocks or like evaporite deposits on the base of the Mesozoic sediments ("Dagorda" formation of the Hettangian stage). These evaporite deposits can also occur at upper levels as a result of the upward intrusion of the salt through faults. Although there

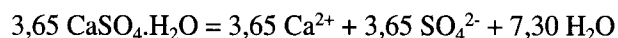
Table 5.—Ionic ratios of the selected groundwater samples

Sample	RW13	RW17	RW19	TW1	TW2	Estoril Spring
Na+K/Cl (molar)	0.84	0.79	0.83	0.88	0.86	0.91
Mg/Ca (molar)	0.39	0.63	0.28	0.51	0.56	0.46
Mg/SO ₄ (molar)	1.10	2.13	2.18	0.98	1.17	0.96
Ca/SO ₄ (molar)	2.78	3.40	7.90	1.93	2.10	2.08
Ca/HCO ₃ (molar)	0.93	0.70	0.48	1.75	1.32	0.97
Mg/HCO ₃ (molar)	0.37	0.44	0.13	0.88	0.74	0.45

is no outcrop of the Dagorda formation in the Estoril area its deep occurrence it is admitted as in other areas of the Lusitanian Basin.

For example, TW1 water composition can be schematically derived from the RW19 water composition assuming the mass balance approach and the following reactions:

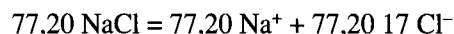
Dissolution of gypsum according to



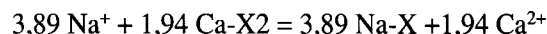
Dissolution of Mg-chlorides, for example bischofite



Dissolution of halite and some sylvite, in terms of halite

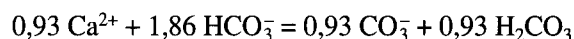


The exchange of Ca^{2+} for Na^+



where X indicates the exchanging solid surface

The precipitation of calcite



The temperature is another peculiar feature of the Estoril thermal water. Assuming a geothermal gradient of 3 °C per 100 m of depth and the mean annual air temperature of 16 °C, a minimum depth of 700 m would be required to obtain the temperature of 35.5 °C (temperature of the TW1 well water). In fact the depth and temperature reservoir must be higher because in the upward movement the water loses temperature in contact with the upper rocks - according to temperature measurements in the TW1 and TW2 wells the loss estimate is 1 to 1.5 °C per 100 m. So a reservoir depth up 1,500 m seems possible.

Isotopic composition

In the classical plot of $\delta^2\text{H}$ as a function of $\delta^{18}\text{O}$ the samples of the thermal and regional water are

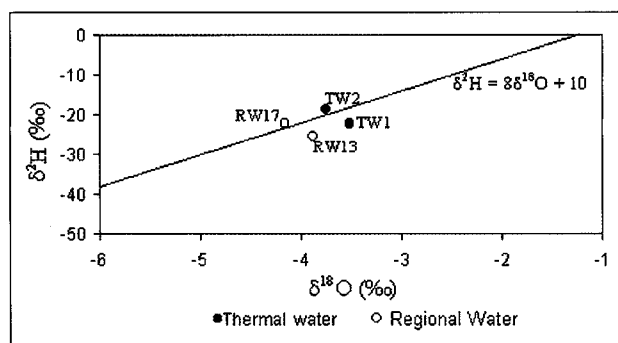


Fig. 6.—Relationship between stable isotopes ($\delta^2\text{H}$; $\delta^{18}\text{O}$) of groundwater in the Estoril area.

grouped close to the meteoric water line (fig. 6). So the groundwater is assumed to have originated from the precipitation falling in the recharge area.

The ^3H concentration of the TW1 thermal water is 0.78 ± 0.70 (TU) which means that this groundwater can be dated prior to 1952 in a qualitative manner.

Conclusions

The Estoril thermal water is a mineral water of the sodium chloride type, with TDS and temperature higher than the ones of the regional waters. The maximum TDS and temperature values were measured for the TW1 water: 6 g/L and 35.5 °C, respectively.

The thermal water is assumed to have originated from the precipitation falling in the recharge area and the dissolution of evaporite minerals, such as halite, sylvite, magnesium chlorides and gypsum results in an excess of solutes of the thermal waters over the ones of the “normal” water. Gypsum dissolution is mainly responsible for SO_4^- and Ca^{2+} . The cation exchange also contributes to the content of Ca^{2+} . The released calcium precipitates as calcite when the water reaches a critical supersaturation condition. Bicarbonate originated by the CO_2 absorbed from the atmosphere and decomposition of organic matter in the recharge area decreases with the increasing water TDS values.

The thermal water flow system has the recharge area somewhere in between Estoril and the Sintra

mountain (≈ 5 km northward of Estoril) probably in the limestone outcrops (upper Jurassic) at the base of this mountain. The elevation difference between the recharge area and the sea provides the driving forces for groundwater movement to the Estoril area. During the deep circulation the groundwater mineralization and temperature increase. The flow system has the discharge in the Estoril area, where the upward movement of the mineralised and warm water is controlled by an impermeable barrier of dykes and open fractures in the pre-existing rocks.

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Recibido el 18 de marzo de 2004
Aceptado el 29 de diciembre de 2004