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: δ¹⁸O (‰) = −4.16 to −3.52 and δ²H (‰) = −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.

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 potential, to protect the quality and to improve the quantity of mineral water resources, the policy of the Por-

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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 freshwater 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.
THE ORIGIN OF THE ESTORIL (PORTUGAL) THERMAL WATER

Explanation

- Cenomanian-Albian
- Aptian-Upper Barremian (Almargem Sandstones)
- Lower Barremian and Neocomian
- Portlandian-Upper Kimmeridgian (Ramalhao Slates)
- Upper Oxfordian (S. Pedro Limestones)
- Portlandian-Upper Kimmeridgian
- Middle Kimmeridgian (Ramalhao Slates)
- Upper Oxfordian (S. Pedro Limestones)
- Dykes
- Spring
- Fault
- Strike and dip of stratification
- Drilled well
- Line of geological section shown in Fig. 2

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.

— Lower Barremian (Limestones with *Choaffatella* 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 Almargem 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 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 *Choaffatella* 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>
<thead>
<tr>
<th>Well</th>
<th>Altitude (m)</th>
<th>Depth of the intake zone (m)</th>
<th>Yield (L/s)</th>
<th>Static water level (m, a.s.l.)</th>
<th>Dynamic water level (m, a.s.l.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TW1</td>
<td>15</td>
<td>135-267</td>
<td>12</td>
<td>14.7</td>
<td>2.6</td>
</tr>
<tr>
<td>TW2</td>
<td>15</td>
<td>152-248</td>
<td>1.6</td>
<td>15.4</td>
<td>8.8</td>
</tr>
<tr>
<td>RW13</td>
<td>80</td>
<td>132-183</td>
<td>10</td>
<td>20.0</td>
<td>13.2</td>
</tr>
<tr>
<td>RW17</td>
<td>85</td>
<td>71-190</td>
<td>22.5</td>
<td>18.7</td>
<td>15.5</td>
</tr>
<tr>
<td>RW19</td>
<td>80</td>
<td>139-160</td>
<td>5</td>
<td>34.0</td>
<td>23.3</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RW13</th>
<th>RW17</th>
<th>RW19</th>
<th>TW1</th>
<th>TW2</th>
<th>Estoril Spring</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (°C)</td>
<td>21.0</td>
<td>24.0</td>
<td>21.0</td>
<td>35.5</td>
<td>30.5</td>
<td>30.0</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
<td>7.0</td>
<td>7.3</td>
<td>6.9</td>
<td>7.0</td>
<td>6.9</td>
</tr>
<tr>
<td>HCO₃ (mg/L)</td>
<td>344.0</td>
<td>392.4</td>
<td>385.5</td>
<td>272.0</td>
<td>299.6</td>
<td>309.9</td>
</tr>
<tr>
<td>Cl (mg/L)</td>
<td>1,359.3</td>
<td>892.9</td>
<td>124.3</td>
<td>3,081.1</td>
<td>2,420.6</td>
<td>1,675.6</td>
</tr>
<tr>
<td>SO₄ (mg/L)</td>
<td>182.1</td>
<td>127.6</td>
<td>36.9</td>
<td>387.5</td>
<td>297.9</td>
<td>227.1</td>
</tr>
<tr>
<td>Na⁺ (mg/L)</td>
<td>731.9</td>
<td>451.1</td>
<td>66.7</td>
<td>1,721.6</td>
<td>1,324.7</td>
<td>984.9</td>
</tr>
<tr>
<td>K⁺ (mg/L)</td>
<td>21.0</td>
<td>8.3</td>
<td>51.8</td>
<td>41.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>211.3</td>
<td>181.0</td>
<td>121.6</td>
<td>312.7</td>
<td>260.4</td>
<td>196.8</td>
</tr>
<tr>
<td>Mg²⁺ (mg/L)</td>
<td>50.6</td>
<td>68.8</td>
<td>20.4</td>
<td>95.8</td>
<td>88.2</td>
<td>55.4</td>
</tr>
</tbody>
</table>

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

The value of Na⁺+K⁺/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 Ca²⁺/SO₄²⁻ is greater than the stoichiometry of gypsum dissolution and the increasing of Ca²⁺ with TDS is greater than the one of SO₄²⁻. So, a supplementary origin for the Ca²⁺ is necessary once the reduction of the SO₄²⁻ is unexpected in this geochemistry environment. The exchange of Ca²⁺ 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 Mg²⁺, Ca²⁺, and SO₄²⁻ concentrations, and decreases alkalinity as observed in the studied waters. When equilibrium with calcite and dolomite is maintained, the ratio of Mg²⁺/Ca²⁺ must remain around 0.8 and ideal stoichiometric relations for the reaction are Ca²⁺: SO₄²⁻ = 1:1.8 and Mg²⁺: SO₄²⁻ = 0.8:1.8. (Appelo & Postma, 1996). These ideal values deeply differ from the ratios presented in Table 5. So, the dedolomitization does not seem to be a relevant geochemical process in the Estoril aquifer and the responsible for Mg²⁺ and Ca²⁺ 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 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

\[
3.65 \text{CaSO}_4 \cdot \text{H}_2\text{O} = 3.65 \text{Ca}^{2+} + 3.65 \text{SO}_4^{2-} + 7.30 \text{H}_2\text{O}
\]

Dissolution of Mg-chlorides, for example bischofite

\[
3.10 \text{MgCl}_2 \cdot 6\text{H}_2\text{O} = 3.10 \text{Mg}^{2+} + 6.20 \text{Cl}^- + 18.60 \text{H}_2\text{O}
\]

Dissolution of halite and some sylvite, in terms of halite

\[
77.20 \text{NaCl} = 77.20 \text{Na}^+ + 77.20 \text{Cl}^- + 77.20 17 \text{Cl}^-
\]

The exchange of Ca²⁺ for Na⁺

\[
3.89 \text{Na}^+ + 1.94 \text{Ca}-\text{X} = 3.89 \text{Na}-\text{X} + 1.94 \text{Ca}^{2+}
\]

where X indicates the exchanging solid surface

The precipitation of calcite

\[
0.93 \text{Ca}^{2+} + 1.86 \text{HCO}_3^- = 0.93 \text{CO}_3^{2-} + 0.93 \text{H}_2\text{CO}_3
\]

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 δ²H as a function of δ¹⁸O the samples of the thermal and regional water are...
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.

Fig. 6.—Relationship between stable isotopes (δ2H; δ18O) 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 SO4²⁻ and Ca²⁺. The cation exchange also contributes to the content of Ca²⁺. The released calcium precipitates as calcite when the water reaches a critical supersaturation condition. Bicarbonate originated by the CO2 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

References


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