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ABSTRACT

Geochemical and geophysical studies have been adopted to improve knowledge on the nature, circulation paths and water-rock interaction processes associated with hot (76ºC) and cold (17ºC) CO₂-rich mineral waters emerging at the northern part of Portuguese mainland. The studied CO₂-rich mineral waters derive from local meteoric water sources. Some differences detected in water mineralization and isotopic (δ²H, δ¹⁸O and ³H) signatures are the result of different recharge altitudes and groundwater circulation paths varying in depth, length and residence time. The lack of an ¹⁸O-shift reflects no water-rock interaction at elevated temperatures. δ¹³C values of total dissolved inorganic carbon indicate a deep-seated (upper-mantle) source for the CO₂. Geophysical methods, mainly resistivity and scalar audio-magnetotelluric, used to investigate the shallow and deep structures of the Chaves graben, show that conductive zones are concentrated in the central part of the graben as a result of high temperatures combined with the high salinity of the hot waters in fractured rock formations. Deep fractures trending NW-SE, ENE-WSW and N70E, shown in geophysical results, would provide an effective conduit system for fluid ascending towards the reservoir in the deep part of the graben.

Introduction

In the northern part of Portuguese mainland, the most important geothermal focus is situated along one of the major NNE-trending faults (the megalineament of Verin-Chaves-Régua-Penacova). There, hot (Chaves – 76ºC) and cold (Vilarelho da Raia, Vidago and Pedras Salgadas – 17ºC) CO₂-rich mineral waters are present in an area of approximately 800 km² (Figure 1). The aim of this paper is to review the geochemical and geophysical investigations performed at Vilarelho da Raia - Pedras Salgadas region, in order to demonstrate how a multi-technique approach is important to answer the most common addressed questions associated with these complex hydrogeologic systems.

Geological Background

The study area is located in the tectonic unit of Middle Galicia / Trás-os-Montes sub-zone of the Central-Iberian Zone of the Hesperic Massif. The main geological formations are: i) Hercynian granites (sin-tectonic - 310 My and post-tectonic - 290 My) and ii) Silurian metasediments of the Upper, Intermediate and Lower Peritransmontano Group, that consists on a sequence of quartzites, phyllites and carbonaceous slates (Sousa Oliveira and Portugal Ferreira 1996). The most recent formations are Miocene-Pleistocene graben filling sediments with variable thickness, showing their maximum development...
along the central axis of Chaves graben. The thermomineral waters flow from natural springs and drilled wells located either in granitic outcrops or in the perithallic boundaries parallel to the main NNE-SSW fault trend. Chaves hot CO₂-rich thermomineral waters emerge within a wide graben, whereas the cold mineral waters (e.g. Vidago / Pedras Salgadas) are found in areas where the NNE-SSW megalineament does not exhibit such an important morphological structure. The 200 km long NNE-SSW megalineament reaches a depth of about 30 km in the study area (Baptista et al., 1993).

Results and Discussion

The Geochemical and Isotopic Approaches

In the studied region, several hot (Chaves – 76°C) and cold (Vilarelho da Raia, Vidago, and Pedras Salgadas – 17°C) CO₂-rich mineral waters are present. These mineral waters have high carbon content (up to 5000 mg/L of free CO₂ and 5500 mg/L of HCO₃), reflecting the abundant presence of CO₂ in the system. Electrical conductivity values range from 1600 to 6500 µS/cm and pH values vary from 6 to 7. All mineralized waters belong to the HCO₃-Na-CO₂-rich type. Major element composition of the thermomineral waters indicates that subsurface circulation seems to be mainly ascribed to the granitic rocks. The associated gas phase issued from the CO₂-rich springs at Chaves is practically pure CO₂ (~99.5 % volume (O₂ = 0.05%, Ar = 0.02%, N₂ = 0.28%, CH₄ = 0.009%, C₂H₆ = 0.005%, H₂ = 0.005% and He = 0.01% in: Almeida, 1982).

The reason why some of the most mineralized waters in the area are cold waters (see diagram of Figure 2) is related with the fact that in CO₂-rich thermomineral systems carbon dioxide (more than temperature) is one of the most important species which influences the chemical characteristics of the fluids (Greber, 1994). In these type of hydrogeological systems, water-rock interaction is enhanced by low temperatures since the solubility of CO₂ in water increases with decreasing temperature. The mineralization of the cold mineral waters is favored by a water-gas-rock interaction in a low-temperature (shallow) environment.

The fact that water-rock interaction is mainly governed by CO₂ rather than by high temperatures is indicated by the good correlation between Cl (a tracer of water-rock interaction) and Na (the dominant cation). As stated by Stumm and Morgan (1981) the solubility of albite increases considerably with rising partial pressure of CO₂.

Concerning the studied CO₂-rich mineral waters, the simultaneous evaluation of the results of the SiO₂ and K²/Mg geothermometers have been performed by Aires-Barros et al. (1998). The cluster of data from Chaves CO₂-rich mineral waters (the most representative of the deep fluids in this area) indicate equilibrium temperatures between 100 and 120°C, which is in agreement with the issue temperatures of Chaves mineral waters. Considering the mean geothermal gradient 30°C/km (Duque et al., 1998), we can estimate a maximum depth of about 3.5 km reached by the water system.

The δ¹⁸O and δD values of the hot and cold CO₂-rich mineral waters lie on or close to the global meteoric water line (GMWL: δD = 8 δ¹⁸O + 10) indicating that they are meteoric waters which have not been subjected to water/rock interaction at very high temperatures (Figure 3), consistent with the results of chemical geothermometry.

The altitude dependence of the isotopic composition of the CO₂-rich mineral waters was recently re-estimated by Andrade (2003) based on δ¹⁸O signatures of shallow cold dilute groundwaters (collected from springs in the thermomineral waters area and its bordering mountains) showing δH concentrations up to 8.5 TU indicating local recharge. The isotopic gradient obtained for ¹⁸O was -0.23‰ per 100 m of altitude (Figure 4). Based on the altitude gradient obtained we have estimated the mean recharge elevations for the studied CO₂-rich thermomineral waters: 1000 m a.s.l. for Chaves and Vilarelho da Raia; 500 – 700 m a.s.l. for Vidago and 800 – 1200 m a.s.l. for Pedras Salgadas. The recharge areas seems to occur preferentially on the E side of the Chaves, Vidago and Pedras Salgadas grabens (along Padrela Mountain oriented NNE-SSW).

The δ¹³C determinations carried out on total dissolved inorganic carbon (TDIC) of the CO₂-rich mineral waters gave values lying in the range of -6‰ to -1‰ vs V-PDB (Marques et al., 2003).
et al., 2000) indicating a deep-seated (upper mantle) origin for the CO₂. The studied region is dominantly vegetated by C3 plants, explaining the δ¹³C values (TDIC) of local shallow cold dilute groundwaters (-23.4 < δ¹³C < -22.39‰ vs PDB). The δ¹³C values measured on two carbonaceous slates of the study area (-26.9 and -27.2‰ vs PDB) indicate that the hypothesis that carbon could be derived from oxidation of local carbonaceous slates by groundwater should be considered very limited (Marques et al., 2000).

The Geophysical Approach

Various geophysical methods, mainly resistivity, scalar audio-magnetotelluric (AMT) and magnetotelluric (MT), have been used to investigate the shallow and deep structures of the Chaves graben, since 1990. In this section the contribution of the resistivity and scalar-AMT surveys to the hydrothermal study will be presented. Both resistivity and AMT surveys were designed to provide information about the shallow (depth <1 km) geoelectrical structure of the graben and to detect and define the geometry of the shallow water circulation zones.

The Resistivity Survey

The resistivity survey comprised 29 Schlumberger vertical electrical soundings (VES), dipole-dipole lines, pole-dipole-lines and rectangle surveys (Monteiro Santos et al., 1996, 1997). The VES were carried out with current electrodes expanding in the NNE-SSW direction and with a maximum spacing ranging from 1200 to 2000 m (Figure 5). The VES can be divided into two main classes, corresponding to different electrical and geological sections. The first group of soundings comprising of curves of type QQH and HQH, were acquired in the eastern and central part of the graben, where the sedimentary sequences are thick. The second group of VES comprises curves of type QH obtained in areas where the bedrock is shallow, i.e. mainly in the western part of the graben. The VES data were inverted assuming layered models, the main features are: a) the sedimentary upper layers (Pleistocene) with a total thickness ranging from 100 to 300 m have resistivities in the 100-750 ohm-m range; b) the intermediate conductive layer (11–25 ohm-m), which has been associated with the geothermal reservoir, has a thickness ranging from 200 to 500 m; c) the bedrock, from 400 m to a greater depth is heterogeneous with the resistivity varying between 120 and 770 ohm-m in accordance with the geological nature of the geological formations (schistose or granitic).
The inversion results of the VES were combined to obtain a map of the low resistivity layer associated with the geothermal reservoir (Figure 5). Two resistivity cross sections along N-S and E-W directions were also obtained from the combination of the VES inversion results (Figure 6). These figures show that conductive zones are concentrated in the central part of the graben as a result of high temperatures combined with the high salinity of the hot waters in fractured and permeable rock formations.

**AMT Survey**

The AMT survey comprised more than 100 soundings, in the frequency range from 2300 to 4.1 Hz (Monteiro Santos et al., 1996). The agreement between AMT and Schlumberger apparent resistivity curves is excellent showing that AMT data were not affected by static-shift distortions. The AMT soundings can be classified in three main groups: the first group consists of soundings carried out over granite (west and northeast parts); the second group includes the soundings acquired on the schistose complex and, the third group is represented by curves obtained on the graben. AMT data were interpreted using 1-D approach. Figure 7 shows the contour map of the conductance values in the conductive layer as derived from the 1-D inversion of the AMT data. The high values coincide approximately with the great depth of the bedrock as resolved from 1-D interpretation of the VES (Figure 6).

Hutton et al. (1989) noted, in a geothermal field survey, the approximately coincidence of the maximum temperature gradient and the maximum conductance values. Temperature measurements in boreholes (Duque et al., 1998) indicate a similar behavior in the Chaves graben. The high conductance zones are therefore correlated to shallow geothermal aquifer in the Chaves graben and may reveal the preferential zones for ascent of hot waters.

Geological studies evidenced the existence and orientation of the fractures, either inside or outside the graben. Deep fractures trending NW-SE, ENE-WSW and N70E were reported either in the graben or in the surrounding area. These directions are also shown in geophysical results, reflecting the pattern of the fluid circulation in the fault system (Figures 5, 6 and 7). Such faults, and mainly fault intersections, would provide an effective conduit system for fluid ascending towards the reservoir in the deep part of the graben.

**Concluding Remarks**

The geochemical and geophysical approaches have provided important information on circulation depth of the studied CO₂-rich thermomineral waters, based on an understanding of regional tectonics and geology. The studied CO₂-rich mineral waters represent locally meteoric waters recharged at different altitude sites. Isotopic signatures of C present in these waters systems indicate a deep-seated (upper-mantle) origin for the CO₂. The most feasible means by which the CO₂ could be transported from its deep mantle source to the surface would be by migration as a separate gas phase incorporated in infiltrated meteoric waters. This process would occur at considerable depth in the case of the Chaves hot CO₂-rich mineral waters and at shallow depth in the case of the Vilarelho da Raia, Vidago and Pedras Salgadas cold CO₂-rich mineral waters. In the case of Chaves low-temperature geothermal system, the deep fractures trending NW-SE, ENE-WSW and N70E shown in geophysical results, reflecting the pattern of the fluid circulation in the fault system, would provide an effective conduit system for fluid ascending towards the reservoir in the deep part of the graben. The results show that conductive zones are concentrated in the central part of the graben as a result of high temperatures combined with the high salinity of the hot waters in fractured rock formations. A clear vertical separation between the low resistivities from higher ones defines the top of the reservoir. From the geophysical data, the minimum thickness of the reservoir zone is about 200 m (for a resistivity of 12 ohm-m and conductance of 16 S) and the maximum thickness is of 500 m (for a resistivity of 25 ohm-m and a conductance of 20 S).

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