A geochemical and geophysical approach to derive a conceptual circulation model of CO_2-rich mineral waters: A case study of Vilarelho da Raia, northern Portugal

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Abstract The Vilarelho da Raia-Chaves region, located in northern Portugal adjacent to the Spanish border, is characterized by both hot and cold CO_2-rich mineral waters issuing from springs and drilled wells. The present paper updates the conceptual circulation model of the Vilarelho da Raia cold CO_2-rich mineral waters. Vilarelho da Raia mineral waters, dominated by Na and HCO_3 ions, have formed mainly by interaction with CO_2 of deep-seated mantle origin. The $\delta^{18}O$, δ^2H and ^3H values indicate that these waters are the result of meteoric waters infiltrating into Larouco Mountain, NW of Vilarelho da Raia, circulating at shallow depths in granitic rocks and moving into Vilarelho da Raia area. The conceptual geochemical and geophysical circulation model indicates that the hot and cold CO_2-rich mineral waters of Chaves (76 °C) and Vilarelho da Raia (17 °C) should be considered manifestations of similar but not the same geohydrological systems.

Résumé La région de Vilarelho da Raia – Chaves, située au Portugal près de la frontière Espagnole, est caractérisée par des eaux carbogazeuses, chaudes et froides, émergeant à des sources et dans des puits. Ce travail constitue une mise au point du modèle conceptuel de circulation des eaux minérales carbogazeuses froides de Vilarelho da Raia. Les eaux minérales de Vilarelho da Raia, dans lesquelles les ions Na and HCO_3 sont dominants, résultent principalement d'interactions avec du CO_2 d'origine mantellique. Les $\delta^{18}O$, les δ^2H, et les te-
neurs en ^3H indiquent que ces eaux proviennent de l'infiltration d'eaux météoriques dans le Mont Larouco au NW de Vilarelho da Raia, circulant à faible profondeur dans les granites en direction de la région de Vilarelho da Raia. Le modèle de circulation géochimique et géophysique conduit à penser que les eaux minérales carbogazeuses chaudes et froides de Chaves (76 °C) et de Vilarelho da Raia (17 °C) doivent être considérées comme des manifestations de systèmes hydrogéologiques similaires, mais non identiques.

Resumen La región de Vilarelho-Chaves está situada en el Norte de Portugal, junto a la frontera con España. Se caracteriza por la existencia de aguas minerales calientes y frías enriquecidas en CO_2, que descargan mediante manantiales y pozos. El artículo tiene como objetivo la actualización del modelo conceptual de flujo de las aguas frías de Vilarelho de Raia, que son ricas en CO_2. Dichas aguas se han formado fundamentalmente por la interacción con el CO_2 procedente del manto profundo, y son del tipo bicarbonatado sódico. Los valores de $\delta^{18}O$, δ^2H y ^3H indican que proceden de la infiltración de agua meteórica en la Montaña Larouco –al Noroeste de Vilarelho de Raia–, que circulan a poca profundidad en un medio formado por de rocas graníticas y se mueven hacia el área de Vilarelho de Raia. El modelo conceptual de flujo, basado en datos geoquímicos y geofísicos, indica que las aguas minerales calientes de Chaves (76 °C) y las frías de Vilarelho de Raia (17 °C), ambas enriquecidas en CO_2, no deben ser consideradas como manifestaciones de un único sistema hidrogeológico, sino de dos similares.

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Introduction

In Portugal, the most important low-temperature geothermal field is the Caldas de Chaves situated in the northern part of the country, along the major NNE–SSW-trending fault system of Verin–Chaves–Penacova (Fig. 1). Along this fault system both hot (Chaves, 76 °C) and cold (Vidago, and Pedras Salgadas, 17 °C)
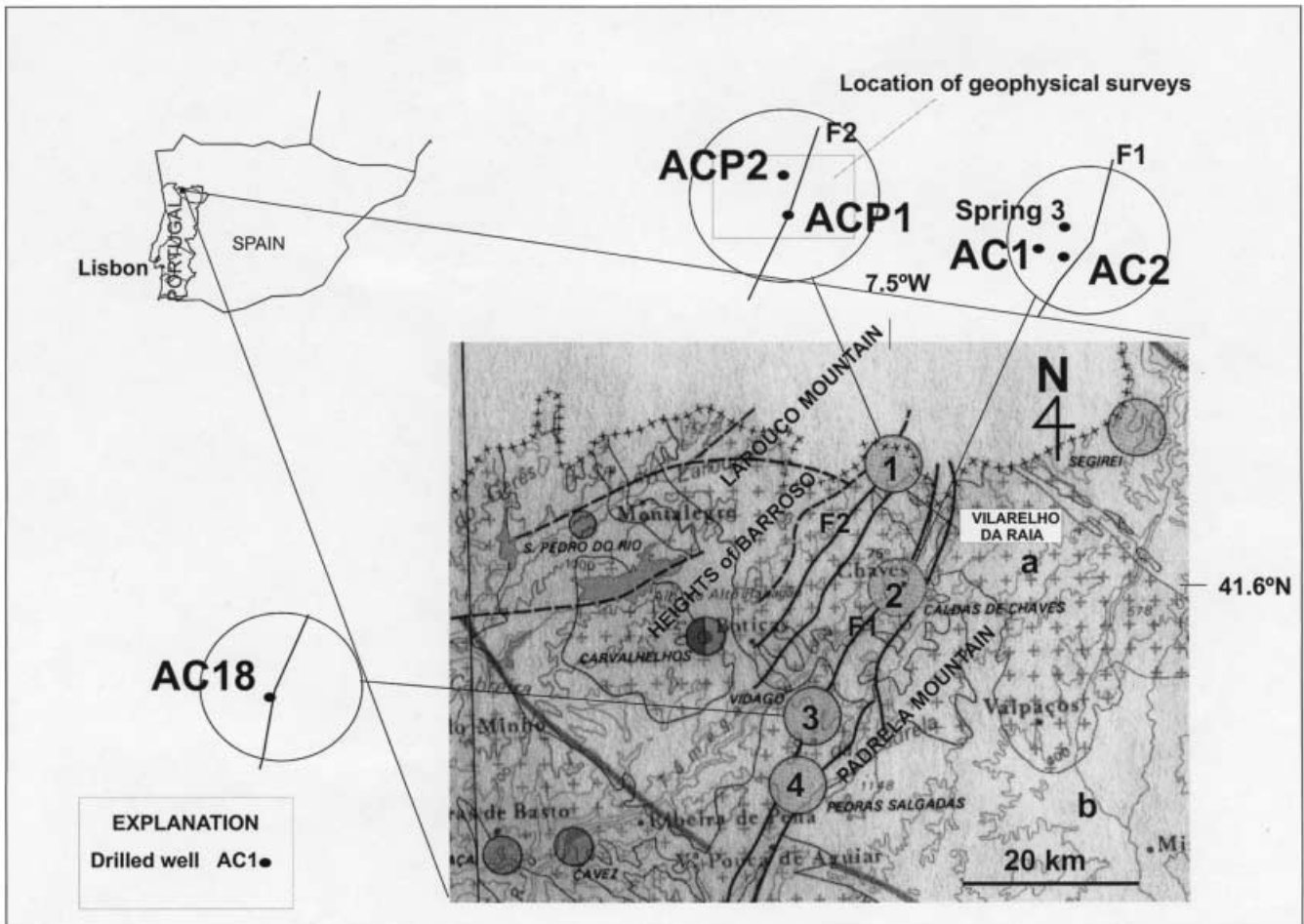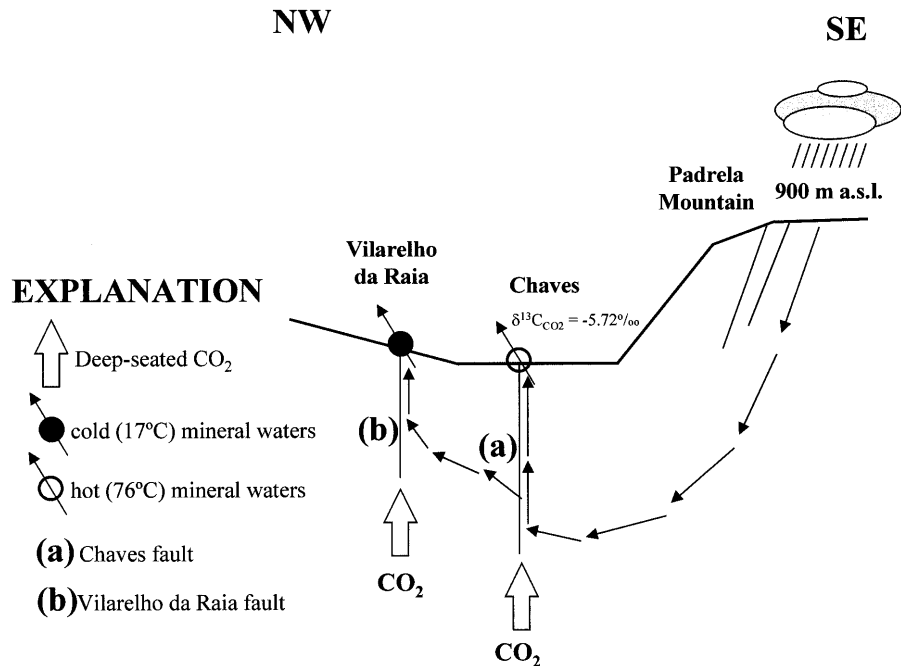
Fig. 1 Geological sketch map of the region, showing the location of the hot (*2* Chaves) and cold (*1* Vilarelho, *3* Vidago, *4* Pedras Salgadas) CO_2-rich mineral waters. Adapted from Carta de Nascentes Minerais/Atlas do Ambiente/Portugal. Instituto Hidrográfico (1991). **a** Hercynian granitic rocks; **b** Palaeozoic metasediments. *Dashed lines* are probable faults and *solid lines* are known faults. *F1* Chaves fault; *F2* VR fault. *Sketches in circles*, outside the map border, are not to scale

CO_2-rich mineral waters occur. The low-temperature (17 °C) CO_2-rich mineral waters of the Vilarelho da Raia (VR) area are associated with a separate but parallel NNE–SSW fault system (Fig. 1). These mineral waters issue from natural springs as well as drilled wells, most of which are used by local spas. During the past decade, particular emphasis has been given to the characterization of the Chaves low-temperature system (Aires-Barros et al. 1991, 1994, 1995, 1998; Monteiro Santos et al. 1995, 1996). A conceptual model of the Chaves low-temperature system was presented by Aires-Barros et al. (1995) and Monteiro Santos et al. (1996). As pointed out by Aires-Barros et al. (1995), the isotopic signatures of Chaves thermal waters indicate that they are of meteoric origin. They infiltrate mainly to the northeast of the Chaves graben on Padrela Mountain, at high altitude (900 m above sea level; a.s.l.), percolate to great depth in the deepest parts of the graben and then ascend in a low-

altitude area on the Chaves plain. Monteiro Santos et al. (1996) have shown that in the Chaves graben, the hydrogeological system involves two different circuits: (1) a shallow circuit, made up of cold dilute groundwater flowing through metamorphic and sedimentary rocks, and (2) a deeper circuit in which mineral water has circulated to considerable depth along faults. In the Chaves area, mixing of the hot deep waters with the cold shallow waters seems to be inhibited by the presence of sedimentary deposits of gravel, clay, sandstone, arkose, and argillite. As revealed by the logs of wells drilled in the Chaves plain for urban and irrigation purposes (Marques et al. 1996), the thickness of these sedimentary deposits exceeds 250 m.

The results of previous studies (Marques et al. 1996) indicate that the chemical and isotopic ($\delta^{18}O$ and δ^2H) composition of VR cold CO_2-rich mineral water is rather similar to that of Chaves hot CO_2-rich mineral waters. In a first approximation, the VR cold CO_2-rich mineral waters were postulated to be a ramification of the Chaves deep geothermal reservoir (Fig. 2). However, the lower temperature (17 °C) and flow rate (2.5 L/min) of the VR mineral springs, together with lower tritium activity, pointed to a longer circulation time from the groundwater reservoir to the surface. It was also noted that the VR fault system should play an important role in groundwa-

Fig. 2 Simplified NW–SE section of the conceptual circulation model proposed by Aires-Barros et al. (1995) for the Chaves and Vilarelho da Raia CO_2-rich mineral waters. $\delta^{13}C_{CO2}$ in ‰ vs PDB

NW

SE

Padrela Mountain

900 m a.s.l.

Vilarelho da Raia

Chaves

$\delta^{13}C_{CO2} = -5.72°/oo$

EXPLANATION

⬆ Deep-seated CO_2

● cold (17°C) mineral waters

○ hot (76°C) mineral waters

(a) Chaves fault

(b) Vilarelho da Raia fault

(b)

(a)

CO_2

CO_2

ter circulation (Fig. 2). The rather similar hydrogeochemistry, but different CO_2 content found in VR (CO_2, 1,100 mg/L) and Chaves (CO_2, 350 mg/L) mineral waters, could be interpreted to be the result of the role of the VR fault system in the migration of additional CO_2 from depth to the surface (Fig. 2). Almeida (1982) concluded from a $\delta^{13}C$ value measured in a CO_2 gas sample ($\delta^{13}C_{(CO2)}$, –5.72‰ vs PDB) that most of the ^{13}C in the CO_2 of the Chaves hot mineral water was of upper mantle origin. The so-called PDB reference standard is based on the $CaCO_3$ of the rostrum of a Cretaceous belemnite collected in the Peedee Formation of South Carolina, USA.

Recently, two lines of investigation have been used to evaluate the hot and cold mineral water resources of the region. These include an update of the conceptual model of the underground flow paths associated with the VR CO_2-rich mineral waters, and a determination whether or not the hot (Chaves) and cold (VR) CO_2-rich mineral waters can effectively be considered manifestations of the same geohydrological system. The Aquatransfer Project 'Heat and mass transfer induced in granitic rocks by hydrothermal fluids circulation' (funded by a national R&D Agency) was designed to increase knowledge of groundwater circulation paths, and the correlation between some of the most important hot and cold CO_2-rich mineral waters in the northern part of Portugal. Conjunctive geochemical, isotopic, and geophysical studies were used to distinguish source areas and flow-paths of these waters.

Geological and Geomorphological Setting

The Vilarelho da Raia-Chaves region, is part of a larger hydrogeological province in which the ascending thermomineral waters are structurally controlled by secondary faults of a larger NNE–SSW system. In this system, hydrothermal groundwater circulation is active along a belt of 150 km, extending from Verin in Spain to Penacova in central Portugal. The geology of the region is described in Portugal Ferreira et al. (1992), Baptista et al. (1993) and Sousa Oliveira and Portugal Ferreira (1995). The principal land form of the region is the 'Chaves Depression', which is a graben whose axis is oriented NNE–SSW. This graben is 3 km wide and 7 km long with an altitude of about 350 m a.s.l.. It is bounded on the east by the Padrela Mountain fault escarpment with a 400-m throw. In the west are several parallel horsts and grabens descending from the Heights of Barroso at 900 m a.s.l. toward the 'Chaves Depression'. To the NW of the Vilarelho da Raia area is Larouco Mountain at an altitude about 1,200 m a.s.l. and also oriented NNE–SSW. The region under study is situated in the pre-Mesozoic Iberian Massif, which consists mainly of Hercynian granites and Palaeozoic metasediments. The oldest formations belong to the pre-Ordovician Schisto-Greywacke Complex. Ordovician and Silurian quartzites and schists were further metamorphosed at the end of the Palaeozoic by intrusions of Hercynian granite. The Vilarelho da Raia and Chaves granites are grouped with the alkaline granites of the 3rd Hercynian phase (310 Ma). Silurian metamorphic rocks crop out both to the east and west of the Chaves graben. Intercalated in this schistose complex are bands of carbonaceous slates. It is possible that both the Silurian rocks and sulphide-bearing quartz veins, which are mainly present in the eastern part of the Chaves graben, could be responsible for minor differences in the hydrochemical signatures, which is the SO_4 content of the thermo-mineral groundwaters. The youngest rocks in the region are Miocene–

Table 1 Chemical and isotopic composition of mineral water samples taken during fieldwork in the Vilarelho da Raia area from April 1990 (4/90) to April 1999 (4/99). *Temp* Temperature of sampled water (°C); *Cond* electrical conductivity (µS/cm); *D.R.* dry residuum; *n.d.* not detected; Concentrations are in mg/L; $\delta^{18}O$ and δ^2H in ‰ vs V-SMOW, and ^3H in T.U.

	4/90[a]	7/90[a]	4/91[b]	7/91[a]	5/92[a]	3/96[c]	3/98[c]	7/98[c]	4/99[c]	Mean values[a] (meq/L)	Mean values[c] (meq/L)
Temp.	14.7	16.7	14.6	18.1	15.7	17.7	18.4	18.1	17.6		
pH	6.85	6.83	6.75	6.78	6.69	5.78	6.55	6.56	6.60		
Cond.	2,640	2,400	3,460	2,470	2,190	2,100	2,480	2,350	2,620		
Na	600.0	771.3	953.1	666.2	649.3	706.0	611.0	615.0	678.5	29.22	28.39
K	25.0	17.2	49.7	24.7	25.0	27.5	25.0	31.3	25.5	0.59	0.70
Ca	33.7	25.5	41.2	36.5	31.4	32.1	27.8	20.0	33.8	1.59	1.42
Mg	3.90	6.05	0.90	3.30	6.60	6.75	5.50	4.80	5.50	0.41	0.46
Li	1.30	n.d.	2.70	1.35	4.90	1.35	1.20	0.24	1.30	0.27	0.59
HCO$_3$	1,920.4	2,003.2	2,685.5	2,176.0	1,895.7	1,869.1	1,708.0	1,628.7	1,775.1	32.76	28.60
SO$_4$		7.60	0.48	1.70	1.70	2.0	6.8	5.7	2.7	0.02	0.09
Cl	29.8	32.5	54.7	20.6	20.1	24.1	17.1	28.9	22.38	0.73	0.65
F						19.75	8.6	5.6	5.85		0.52
SiO$_2$	72.1	46.9	53.1	48.2	49.8	52.6	59.6	50.4	56.9		
D.R.	1,790.6	1,822.4	2,261.6	1,878.0	1,750.2	1,827.6	1,624.4	1,557.6	1,740.6		
$\delta^{18}O$	−8.03	−8.11	−8.00	−8.31	−8.14	−7.98	−8.04	−7.66			
δ^2H	−51.0	−55.6	−55.3	−55.7	−54.8	−54.7	−53.6	−49.8			
^3H	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	n.d.		

[a] Facha Spring; [b] Filha da Facha Spring; [c] Well ACP1

Table 2 Chemical and isotopic composition of mineral water samples taken during fieldwork in the Chaves area from April 1990 (4/90) to April 1999 (4/99). *Temp.* Temperature of sampled water (°C); *Cond* electrical conductivity (µS/cm); *D.R.* dry residuum; Concentrations are in mg/L; $\delta^{18}O$ and δ^2H in ‰ vs V-SMOW, and ^3H in T.U.

	4/90[a]	7/90[a]	4/91[a]	7/91[a]	5/92[a]	3/96[b]	3/98[b]	7/98[a]	4/99[a]	Mean values[a] (meq/L)	Mean values[b] (meq/L)
Temp.	68.1	66.9	64.3	68.8	68.8	76.0	76.8	68.0	70.0		
pH	6.82	6.94	6.89	6.98	7.00	7.30	7.04	6.63	6.56		
Cond.	2,910	2,790	2,770	2,590	2,450	2,890	2,590	2,450	2,440		
Na	500.0	662.4	605.8	610.8	574.0	550.8	636.0	589.5	589.5	25.68	25.81
K	100.0	57.8	64.3	61.3	62.3	64.1	62.0	61.5	63.5	1.72	1.61
Ca	22.4	27.5	22.1	24.6	24.5	24.0	21.5	21.9	25.3	1.20	1.14
Mg	3.90	4.70	5.55	6.05	6.10	5.75	5.50	5.50	5.50	0.44	0.46
Li	2.60	1.50	2.75	2.70	2.95	2.95	2.70	0.46	2.61	0.32	0.41
HCO$_3$	1,643.8	1,712.2	1,640.8	1,655.1	1,662.4	1,685.7	1,714.1	1,661.6	1,567.7	27.03	27.86
SO$_4$		28.6	23.5	35.7	34.3	17.7	19.4	32.1	30.4	0.64	0.39
Cl	50.0	46.9	63.5	43.0	43.9	63.2	26.6	45.4	36.9	1.33	1.27
F							7.8	6.2	6.6		0.34
SiO$_2$	69.1	69.3	71.4	72.3	82.4	73.6	94.1	80.9	80.9		
D.R.	1,665.8	1,649.6	1,650.0	1,642.0	1,634.2	1,713.8	1,708.6	1,602.2	1,604.4		
$\delta^{18}O$	−8.18	−8.11	−8.11	−8.17	−8.23	−8.04	−8.32	−8.04			
δ^2H	−50.7	−57.8	−55.8	−54.6	−55.2	−55.9	−53.7	−55.7			
^3H	0.9	1.6	0.6	1.4	1.08	0.30	n.d.	1.2	1.0		

[a] Well AC1M; [b] Well AC2

Pleistocene formations of lacustrine and alluvial origin. These are thickest along the axis of the Chaves graben. Extensive faulting during the Alpine Orogeny provided the pathways for several hydrothermal circuits.

Methodology

Representative chemical analysis of the major ions and isotopic data for ^{18}O, ^2H and ^3H from the VR and Chaves CO_2-rich mineral waters were made from samples collected during 1990 and 1996. Also, during 1998 and 1999, several saline (VR and Chaves) and dilute (Cambedo, Castelões, S. Caetano, Ardaõs and Gamial) waters were sampled and analysed (Tables 1, 2, and 3). The applicability of isotopes as tracers of flow and their sensitivity to changes in temperature and physico-chemical processes, such as evaporation, dilution or mixing, make them excellent indicators of geochemical phenomena (IAEA 1981). Stable isotopes (^{18}O, ^2H) were used as natural tracers to ascertain the origin of waters and to identify recharge areas and underground flow paths. The radioactive isotope (^3H) was used to study the dynamics of the groundwater flow system. The physico-chemical

Table 3 Chemical and isotopic composition of cold dilute spring waters in the Vilarelho da Raia area, collected during March 1998 (*3/98*) and July 1998 (*7/98*).*T* Temperature of sampled water (°C); *Cond* electrical conductivity (µS/cm); *D.R.* dry residuum; *n.d.* not detected; Concentrations are in mg/L; $\delta^{18}O$ and δ^2H in ‰ vs V-SMOW, and ^3H in T.U.

Local	Date	T	pH	Cond.	Na	K	Ca	Mg	Li	HCO$_3$	SO$_4$	Cl	F	D.R.	SiO$_2$	$\delta^{18}O$	δ^2H	^3H
Cambedo	3/98	13.0	5.85	14.6	6.3	1.4	4.2	1.3	n.d.	18.3	4.6	3.4	n.d.	72.4	30.7	−7.65	−49.4	2.6
Castelões	3/98	11.8	5.80	28.7	4.3	0.5	1.1	0.3	n.d.	9.15	0.4	2.9	n.d.	32.8	18.8	−7.83	−51.5	3.8
S. Caetano	3/98	12.1	5.34	23.2	4.3	0.3	0.6	0.2	n.d.	3.05	0.3	2.8	n.d.	24.6	10.5	−8.03	−50.4	0.6
Ardãos	3/98	13.3	6.01	23.2	4.0	0.2	0.8	0.3	n.d.	6.1	0.5	2.4	n.d.	31.2	14.3	−7.91	−50.8	0.9
Gamial	7/98	18.0	6.84	60.2	8.9	0.7	2.3	0.6	n.d.	19.52	2.3	5.1	n.d.	64.2	27.8	−7.20	−48.9	5.4
Castelões	7/98	14.3	5.80	26.3	3.7	0.3	1.2	0.3	n.d.	10.37	0.4	2.4	n.d.	34.0	14.8	−7.90	−50.4	4.5
S. Caetano	7/98	15.0	6.06	25.2	3.5	0.2	1.0	0.2	n.d.	6.71	0.4	2.8	n.d.	34.6	11.9	−7.93	−48.5	4.9
Ardãos	7/98	17.7	6.15	29.2	4.4	0.2	1.0	0.3	n.d.	11.59	0.4	2.4	n.d.	38.0	17.3	−7.28	−47.4	5.7

and isotopic characteristics of the VR and Chaves CO$_2$-rich mineral waters are shown in Tables 1 and 2, respectively. Table 3 shows the most relevant physico-chemical and isotopic constituents in the dilute spring water samples of the VR area, collected during recent fieldwork.

The Nuclear and Technological Institute (ITN) in Portugal carried out the determinations of $\delta^{18}O$ and δ^2H by mass spectrometry (SIRA 10–VG ISOGAS). $\delta^{18}O$ and δ^2H were measured using the analytical methods of Epstein and Mayeda (1953) and Friedman (1953), respectively. The analytical precision is ± 0.10 ‰ for $\delta^{18}O$ and ±1.0 ‰ for δ^2H. Analyses for ^3H were also made, at the ITN, using electrolytic enrichment and subsequent measurement of counting rates by liquid scintillation. Analyses for $\delta^{13}C$ were made at ITN on total inorganic dissolved carbon (TIDC) precipitated in-situ as BaCO$_3$ at a pH higher than 9.0. The gas used in $^{13}C/^{12}C$ measurements was CO$_2$. Carbonates were reacted with 100% phosphoric acid to liberate CO$_2$. The standard δ notation in per mil used throughout this paper is relative to the reference V-SMOW. V signifies Vienna, Austria, the headquarters location of the International Atomic Energy Agency and SMOW is the standard universally adopted as the reference for oxygen and hydrogen stable-isotope variations in natural waters. It corresponds to a hypothetical water having both oxygen and hydrogen isotopic ratios equal to the mean isotopic ratios of ocean water for $\delta^{18}O$ and δ^2H. The V-PDB (defined in the Introduction) has been explained for $\delta^{13}C$. ^3H is in TU (tritium units) where TU corresponds to an isotopic ratio of $^3H/^1H=10^{-18}$.

Temperature (°C), pH and electrical conductivity (µS/cm) were measured at the sampling site. Total alkalinity was measured a few hours after sampling. Water samples for chemical analyses were stored in two polyethylene containers. Water in one of the containers was acidified upon collection by addition of concentrated HCl. Water in the second container was kept unacidified for Cl, SO$_4$ and total alkalinity determinations.

The following methods were applied for chemical analyses performed at the Laboratory of Mineralogy and Petrology of the Instituto Superior Técnico (LAMPIST): atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na, K and Li; colorimetric methods for F and SiO$_2$; ion chromatography for SO$_4$ and Cl; and potentiometry for alkalinity, here referred to as HCO$_3$. The data on the free CO$_2$ content of the VR and Chaves mineral waters were kindly provided by the Águas de Carvalhelhos Company and the Municipality of Chaves, respectively.

As pointed out by Albu et al. (1997), the investigation of mineral and thermal water systems takes place in progressive stages, which frequently overlap. Each stage of the investigation involves a number of operations to obtain, process and interpret field and laboratory data, with varying precision. No single method of study, be it geological, geochemical, or geophysical, can be expected to yield a unique and unambiguous result. The overall picture of a given hydrogeological system must be built up through a continuous process of coordinated data synthesis and cross checks. Therefore, several geophysical surveys (telluric, self-potential, electromagnetic and magnetotelluric) were carried out in the VR–Chaves region to determine shallow and deep electrical-resistivity distribution and its relation to faults and probable groundwater pathways. In this paper, however, only the electromagnetic (EM) and magnetotelluric (MT) data are presented and discussed. The chief objective is to give new insight into the structural model of the VR area where the main VR fault seems to control the upward flow of the mineral waters. The results of geophysical studies are used to improve the conceptual circulation model based on the geochemical and isotopic signatures of the waters. The main purpose of the geophysical studies was to investigate the presence of a hydraulic connection between the two main fault systems, which may control the deep water circulation in the region, i.e. the VR fault system and the Chaves fault system, and to identify probable flowpaths from recharge to discharge zones. The location of the sites of the electromagnetic and magnetotelluric surveys will be described in the section on Geophysical Surveys.

Hydrogeochemical Setting

Chaves hot (76 °C) CO$_2$-rich mineral waters emerge at an altitude of about 350 m a.s.l. in the Tâmega River alluvial plain, which is 7 km long and 3 km wide. VR CO$_2$-rich cold mineral waters discharge 10 km to the

north of the Chaves area near Vilarelho da Raia village, on the Portuguese–Spanish border. The therapeutic properties of the VR mineral waters have been well known for a long time. In the VR area, the main Facha Spring rises at an altitude of about 350 m a.s.l. and discharges about 2.5 L/min of water at 17 °C. This spring is characterized by bubbling of CO_2-rich gases. Another spring, Filha da Facha, rises about 50 m farther north. Recently, these springs ceased to flow after extraction of water began from wells ACP1 and ACP2, which are 200 m deep and close to these springs (Fig. 1). The main purpose of well installation, carried out by the Chaves Municipality and Águas de Carvalhelhos Enterprise, a local mineral-water enterprise, was to determine the technical and commercial feasibility of developing the VR mineral waters for bottled water. In the VR–Chaves region, several mineral waters emerge at different temperatures, but their chemical features are rather similar (Tables 1 and 2). These hot and cold CO_2-rich mineral waters have the following characteristics:

- pH values between 5.7 and 7.3.
- High mineralization (dry residuum values usually in the range of 1,600–2,300 mg/L).
- HCO_3^- is the dominant anion.
- Na^+ is the dominant cation.
- Considerable fluoride (F^-).
- High free CO_2 content of 350–1,100 mg/L.

Regardless of the chemical similarity of the waters, small differences permit the division of these waters into two groups. The VR group consists of the Facha and Filha da Facha Springs and water from drilled wells ACP1 and ACP2 (Fig. 1). The cold CO_2-rich mineral waters, with temperatures between 14 and 18 °C, have relatively low potassium concentrations (from 15–50 mg/L) and sulphate concentrations (from 0.5–8.0 mg/L). Waters from this group are also characterized by relatively high free CO_2 concentrations (between 900 and 1,100 mg/L). The Chaves group includes water from drilled wells AC1 and AC2 (Fig. 1) with hot CO_2-rich waters containing relatively high potassium concentrations (from 57–100 mg/L) and sulphate concentrations (from 17–36 mg/L). These hot waters are also characterized by relatively low free CO_2 concentrations (between 350 and 500 mg/L).

The results of laboratory analyses shown in a modified Schoeller–Berkaloff diagram (in Custódio and Llamas 1996) permit comparison of major-ion concentrations for samples from Vilarelho da Raia (Facha Spring and well ACP1) and Chaves (wells AC1 and AC2) mineral waters (Fig. 3). In this diagram one can clearly discern differences in the K and SO_4 content between the two above-mentioned groups. The higher sulphate concentration found in the Chaves thermal waters may be related to interaction with the Silurian rocks and sulphide-bearing quartz veins, which are mainly present in the eastern part of the Chaves graben. As pointed out by Aires-Barros et al. (1995), the eastern block of the Chaves graben forms the main recharge area of the Chaves groundwater system. It should also be noted that
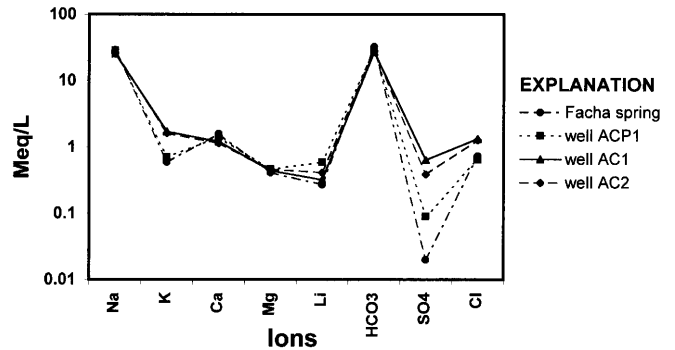

Fig. 3 Modified Schoeller–Berkaloff plot of major-ion concentrations of water from Vilarelho da Raia (Facha Spring and well ACP1) and Chaves (wells AC1 and AC2)

these Silurian rocks are scarcely represented in the VR area. In the case of VR waters, the lower K concentrations could be the result of lower water–K-feldspar interaction temperatures or the result of differences in the mineralogical composition of the granitic rocks through which they percolate. Effectively, the outlet temperatures of Vilarelho da Raia mineral waters are close to the average annual air temperature (14 °C) of the region, indicating that they are not likely to be the outflow of a thermal water system.

Waters from VR exhibit the highest relative dissolved HCO_3 content. This is most likely caused by the addition of CO_2-rich gas to the groundwaters in a low-temperature shallow environment, resulting in the conversion of dissolved CO_2 to HCO_3. A progressive neutralizing water–rock interaction at low temperature favours the formation of HCO_3, resulting in very high $rHCO_3/rCl$ ratios. This process would also favour the higher bicarbonate content seen in Vilarelho da Raia waters and the relatively high mineralization. Addition of external CO_2 to the bicarbonate waters makes the solution more aggressive in its interaction with the granitic rocks, enriching the solution in HCO_3 ions, whereas the pH remains relatively acid.

Aires-Barros et al. (1998) plotted the major ionic species (that is HCO_3, Na, K, and Li) of hot (Chaves) and cold (VR, Vidago, and Pedras Salgadas) CO_2-rich waters of the region against the conservative Cl ion. The resulting data from the Chaves hot mineral waters (wells AC1, AC2 and spring no. 3; see Fig. 1) form a cluster whose waters display similar HCO_3, Na, K, Li and Cl concentrations, indicating that these spring and well waters could be derived from a common geothermal reservoir. However, the VR cold mineral waters have chemical signatures different from those of the Chaves hot waters, indicating that VR waters have followed different underground flow-paths.

Isotopic Composition of Waters

In the evaluation of mineral water resources, isotope geochemistry is extremely important, together with
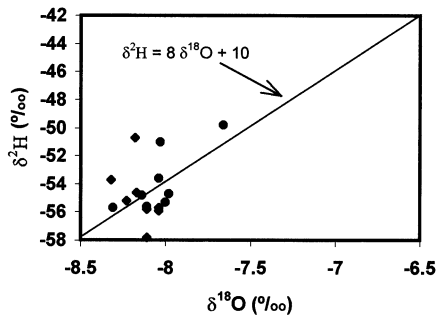
Fig. 4 Relationship between stable isotopes ($\delta^{18}O$; $\delta^{2}H$) of Vilarelho da Raia (*filled square*) and Chaves (*filled circle*) CO_2-rich mineral waters

Fig. 5 Relationship between stable isotopes ($\delta^{18}O$; $\delta^{2}H$) of cold dilute spring waters located in the Vilarelho da Raia mineral waters area and its bordering mountains

available information from other disciplines such as geophysics, to produce a conceptual hydrogeological model that is the basis for future drilling strategies and developmental plans. In this study, oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$ and ^{3}H) isotope data were used to determine recharge areas as well as local and regional circulation paths of VR cold CO_2-rich mineral waters.

In the classical $\delta^{2}H$ vs $\delta^{18}O$ diagram of Fig. 4, all the CO_2-rich mineral waters lie on or close to the world meteoric water line defined by Craig (1961), clearly suggesting that these waters are of meteoric origin. The total range from –9.8 to –57.8‰ and from –7.66 to –8.32‰ for $\delta^{2}H$ and $\delta^{18}O$, respectively, is the result of seasonal differences of rainfall in the region caused by local climatic factors and/or altitude effects. Some of the hot and cold CO_2-rich mineral waters show a shift towards higher $\delta^{2}H$ or lower $\delta^{18}O$ values. A negative shift in oxygen-18 was described by D'Amore and Panichi (1987) as the result of an oxygen-isotope exchange between $H_2O_{(l)}$ and $CO_{2(g)}$. However, in the case of the CO_2-rich thermal waters, Marques et al. (2000) concluded that oxygen isotopes in $H_2O_{(l)}$ and $CO_{2(g)}$ are in equilibrium. Using the $\delta^{18}O$ value for $H_2O_{(l)}$ (–8.04‰ vs V-SMOW) and the corresponding value in $CO_{2(g)}$ (+25.62‰ vs V-SMOW) they have calculated the additive fractionation factor $\varepsilon(CO_2–H_2O)$. The value obtained (+33.93‰) indicates that equilibrium temperature (Friedman and O'Neil 1977) is close to the measured temperature of 75 °C at sampling.

Because the isotopic composition of meteoric groundwater generally matches the mean isotopic composition of precipitation over the recharge area (IAEA 1983), local dilute spring waters were used in this study to characterize the isotopic content of meteoric waters in the VR area. Based on $\delta^{18}O$ and $\delta^{2}H$ values of dilute cold spring water samples collected at different altitudes in the VR area, the local meteoric water line was calculated. This method was based on the adjustment of the Craig (1961) relationship ($\delta^{2}H=8\ \delta^{18}O+10$) to the VR area. The local meteoric water line was obtained by means of the following equation proposed by Garcia (1986):

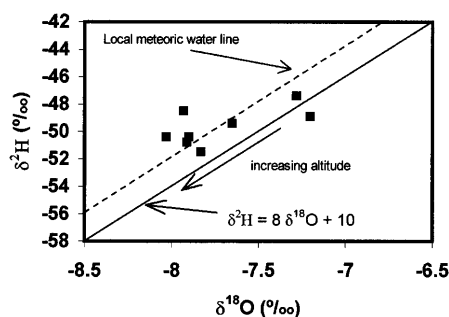$$Y = mX + \frac{\Sigma\delta^{2}H - m\Sigma\delta^{18}O}{N}$$

where: m is the slope of the line (fixed to 8), and N is the number of ($\delta^{2}H$, $\delta^{18}O$) data points.

In this case, the relation for the local meteoric water line is $\delta^{2}H=8\ \delta^{18}O+12$ (Fig. 5). This local meteoric water line is similar to the local meteoric water line reported by Aires-Barros et al. (1994) for the Chaves area ($\delta^{2}H=8\ \delta^{18}O+11$) using data from cold dilute spring water samples collected at different altitudes on the western and eastern blocks of Chaves graben. Both local meteoric water lines are in good agreement with the values found in the Mediterranean region (IAEA 1981). Therefore, the differences in $\delta^{2}H$ and $\delta^{18}O$ found in the saline CO_2-rich mineral waters (Fig. 4) may be related mostly to seasonal variations and/or differences in the altitude of infiltration of the recharge waters.

Geophysical Surveys

Electromagnetic (EM) Survey

The application of electromagnetic (EM) techniques to map the electrical-conductivity distribution in the subsurface is well established and this method has been used in many geothermal, hydrological and environmental studies. This type of study is based on the effect of water content on the electrical resistivity of a geological formation. In delineating shallow features EM34-3 equipment built by Geonics Limited is commonly used. The EM34-3 system consists of a transmitter coil, energized with an alternating current of a specific frequency, and a receiver coil located a short distance away from the transmitter. The transmitter creates a primary variable magnetic field that induces current in the subsurface. This current generates a secondary magnetic field that is detected together with the primary field by the receiver coil (see McNeill 1980). There are two basic modes of operation: the co-linear horizontal and the vertical dipole modes. In the first mode (HDM), both coils, the transmitter and receiver, are oriented vertically and, in the second mode (VDM), horizontally, on the surface. The data can be presented as apparent conductivity profiles or as maps.

The interpretation of the EM data is usually qualitative. In this paper, however, the data of three profiles

Fig. 6 Location of the EM survey (profiles L#3 and L#5) and of the MT soundings (marked *s*) carried out in the Vilarelho da Raia area around the main spring (Facha). *F2* VR fault
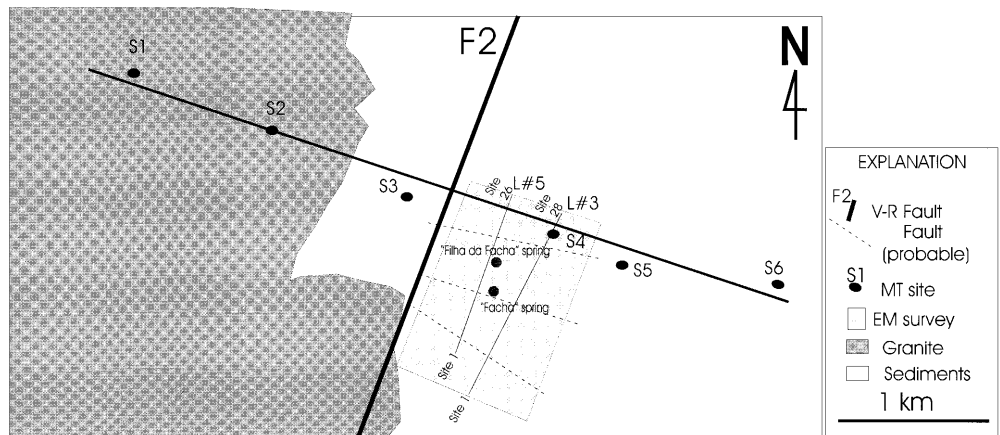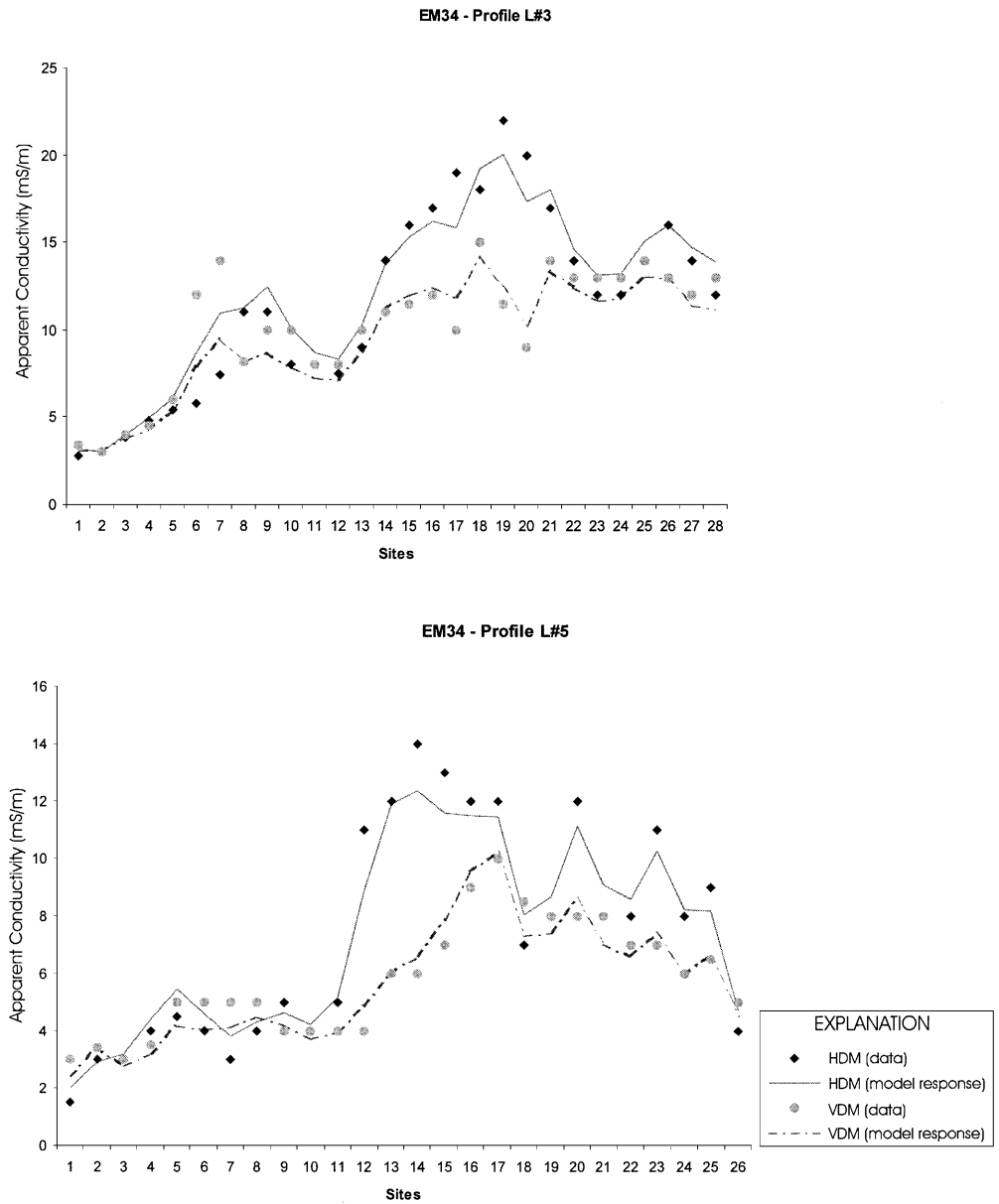

Fig. 7 L#3 and L#5 EM34 profiles. Field data represented by *symbols*, and calculated response of the quasi-two-dimensional models represented by *solid lines*. HDM Horizontal dipole mode; VDM vertical dipole mode. Distance between sites is 40 m
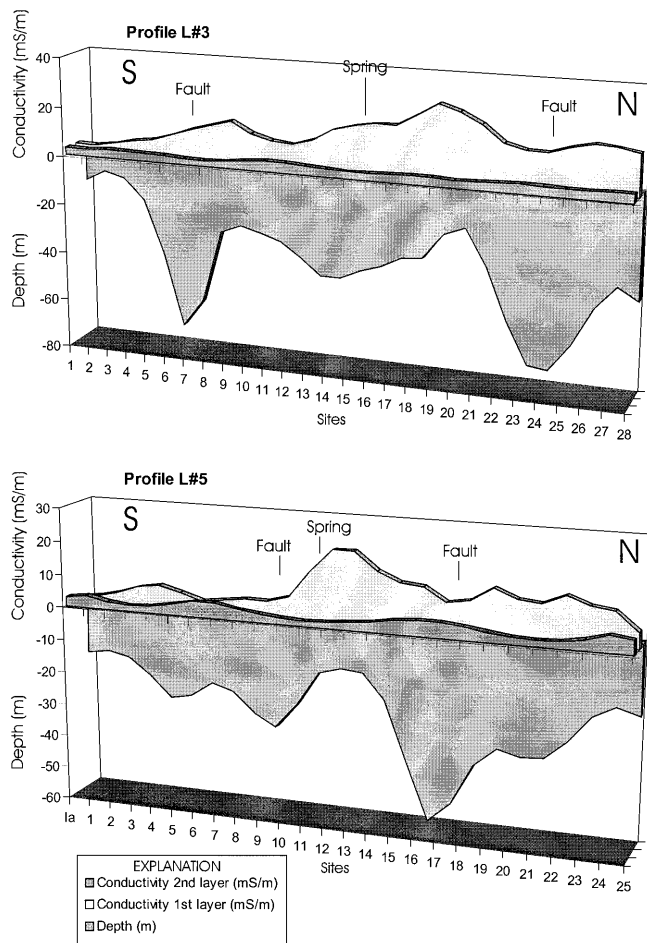
Fig. 8 Quasi-two-dimensional models obtained from L#3 and L#5 profiles, showing the location of the spring and probable faults

were inverted using a quasi-two-dimensional approach. All the measurements of a profile were inverted simultaneously using a layered-earth approach at each profile site. In order to construct a smooth conductivity model, spatial smoothness constraints were introduced during the inversion procedure. A non-linear smoothness-constrained inversion method, based on the algorithm of Sasaki (1989), was adopted. The final result obtained by applying such a method is not a true two-dimensional model but only a rough approximation. For this reason it is designated a quasi-two-dimensional model.

In the VR graben, the data were acquired along eight profiles in a quadrangle located around the Facha Spring (Fig. 6) with inter-coil spacing of 40 m. The distance between measurement points was also 40 m. The surveyed area is topographically flat at an altitude of 350 m a.s.l. The apparent conductivity of two profiles and for each dipole mode are plotted in Fig. 7.

According to the geological log for the ACP1 drilled well, the uppermost 200 m of the surveyed area is made up of sediments underlain by granitic rocks. Therefore, the data pertaining to the two profiles were inverted using a two-layer initial model in which: the conductivity of the uppermost layer was 10 mS/m for a thickness of

30 m; and the conductivity of the second layer was 3 mS/m. The final models are shown in Fig. 8 and its responses are shown in Fig. 7 (solid lines). As can be seen, the fit between data and model responses is very good. The final error, between field and calculated data is 1.2 and 0.72 for profiles L#3 and L#5, respectively.

These models reveal that the northeastern part of the surveyed area is the more conductive; conductivity ranges from 10–15 mS/m. This zone corresponds to sedimentary formations with high clay and water content (Fig. 8). The zone with conductivities ranging from 2–4 mS/m in the models corresponds to the bedrock, which is mainly altered granite. Some features of the models, such as relatively deep and narrow high-conductivity zones at sites 7 and 24 in L#3, and sites 4, 9, and 16 in L#5, are associated with faults in the granitic bedrock that were reactivated recently. These faults, which are mainly oriented WNW–SSE, are very important in controlling upward flow and local water circulation. From the models it can be noted that the mineral water springs, Facha and Filha da Facha, are located close to these faults.

Magnetotelluric (MT) survey

The magnetotelluric (MT) method is an attractive geophysical tool for delineating deep features, which has been used in several hydrogeological studies (Chouteau et al. 1994). In the present study, the MT method was used to delineate structures at depths greater than 500 m. In the MT method, simultaneously measured variations of the electric (E) and magnetic (B) fields are used to estimate the impedance tensor, which is the frequency-dependent complex transfer function between those electromagnetic field components. Apparent resistivity and phase curves are calculated from the off-diagonal impedance tensor elements, Z_{xy} and Z_{yx}. Excellent descriptions of the basic principles of the MT method are given in Vozoff (1972) or in Zhdanov and Keller (1994).

In the VR area, a preliminary profile (oriented approximately W–E) of six MT soundings were carried out to study the electrical behaviour of deep structures down to the middle of the crust. The MT data were collected in four frequency bands ranging from 180–0.01 Hz. The measured directions of the horizontal fields were N20°E and N110°E, in accord with the dominant strike of the regional structures. The MT time series were processed using the cascade decimation and the impedance tensors obtained by a least-square method (Vozoff 1972). Data quality was strongly affected by manmade noise and by small geomagnetic activity at the time of the survey. In the so-called 'MT dead-band' and for long periods the quality of the data was generally poor because of the weakness of the signal level. For this reason, only data from periods of 1–10 s is presented in this paper.

A preliminary analysis of the principal directions of the impedance tensors was made in order to determine the directions of maximum and minimum apparent resistivities. The results show that the main directions are
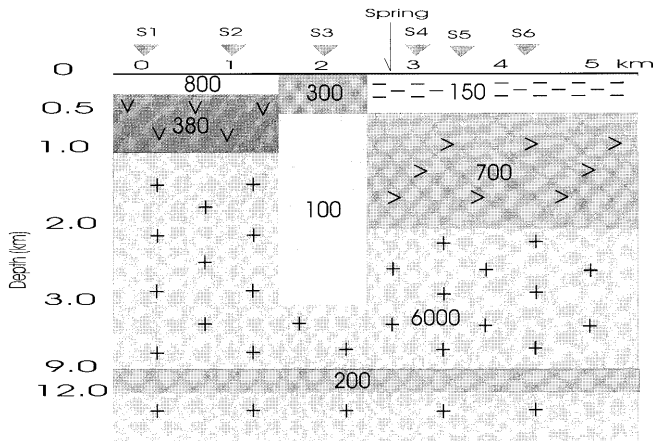
Fig. 9 Electrical-resistivity model obtained from MT data (TM mode). Note the change in the vertical scale at depth greater than 3 km. Values are in Ωm

N19°E and N109°E and are in good accord with the main geological structures (faults) present in the area. Therefore, the N19°E MT component represents the transverse electric mode (TE mode) and the N109°E component, the transverse magnetic mode (TM-mode). These designations are based on the component (electric or magnetic) that is parallel to the strike of a two-dimensional structure.

Wannamaker et al. (1984) showed that the TM mode is generally less affected by three-dimensional structures and can be modeled as two-dimensional structures. This modeling procedure was followed in this investigation. Therefore, TM-mode data was modelled using a forward program based on the finite-element algorithm proposed by Rijo (1977), in order to obtain the model of the electrical-resistivity distribution in the area of the profile. The main reason for the use of forward modelling and not inversion was the scarcity of data.

The final model is shown in Fig. 9. The main features of the model are as follows:

1. In the zone of the depression beneath sites S4, S5, and S6, the resistivity increases with depth. The 150-Ωm layer with a thickness of 500 m, corresponds to the sedimentary fill in the depression and the uppermost part of the bedrock made up of deeply weathered granite.
2. Underlying these layers the model shows a more resistive basement with resistivity of 700 Ωm corresponding mainly to altered and fractured granite.
3. At greater depth, the less altered fractured granite is associated with the deep (>1 km) structure having a resistivity of 6,000 Ωm.
4. The low-resistive zone of 100 Ωm beneath site S3 down to depths of 3 km is associated with the NNE–SSW fault system along the western boundary of the depression. Both the formation and the evolution of the VR depression were controlled by those faults. Moreover, the fault system in the western part of the depression is believed to play an important role

in the regional water circulation and CO_2 discharge, permitting fluid ascent toward the depression. Because the NNE–SSW faults are left-strike-slip faults (Portugal Ferreira et al. 1992) the preferential areas of upward fluid flow are located in the intersection of these structures with NW–SE faults, which were detected at shallow depths by the EM survey. It must be noted that because of the lack of spatial resolution of the survey it is difficult, if not impossible, to determine the exact width of this structure.

5. The conductive 200 Ωm layer at depths between 9 and 12 km is included in the model to match the features in apparent resistivity and phase curves around 1 s. This layer has a regional expression and was detected previously (Monteiro Santos et al. 1995). The significance of this layer is not clear yet. It could represent the old transition zone between ductile and brittle behaviour or it could be the expression of a detachment level in the median crust.
6. The zone that has a resistivity of 800 Ωm beneath sites S1 and S2 corresponds to the uppermost part of the weathered granite massif that outcrop in that area. Underlying this layer, the models shows a more conductive (380 Ωm) zone corresponding to a more weathered and wet zone of the massif.

The MT survey carried out in the Chaves graben and its surroundings indicated that the Chaves–Verin fault system reaches depths greater than those estimated in this study for the VR fault system (Monteiro Santos et al. 1995). Combining old and new results, it is not possible to discern the connection between these fault systems.

Recharge Areas and Circulation Paths

The application of the environmental isotope methods to define recharge areas is mainly based on the spatial variability of the isotope content of water expressed as the altitude effect (IAEA 1983). Groundwaters recharged from high-altitude precipitation can be distinguished from those originating from low-altitude precipitation because of a regular relationship between altitude and the condensation temperature of precipitation (IAEA 1981).

The altitude dependence of the isotopic composition of VR CO_2-rich mineral waters was determined by $\delta^{18}O$ and δ^2H values of dilute cold-spring waters rising in the mineral waters area and the bordering mountains. The studied area is rich in cold dilute spring waters, which discharge from the granitic rocks. Sampled cold dilute spring waters are located at altitudes ranging from 425–880 m. The mean outlet temperature of these waters, which range from 11–18 °C is close to the average annual air temperature, 14 °C, indicating that these waters come from shallow aquifers.

The altitude vs ^{18}O isotope composition of the cold dilute springs (Fig. 10a) reveals that these variations are closely interrelated. In the δ^2H values, such a close rela-

tionship with altitude as in the $\delta^{18}O$ values was not found (Fig. 10b). This could be attributed to the fact that analytical precisions were $\pm 0.10‰$ for $\delta^{18}O$ and $\pm 1.0‰$ for $\delta^2 H$. Nevertheless, on the basis of isotope composition it is possible to draw a line through the data points in order to obtain equations that can be used to calculate the minimum recharge altitude (RA) of the infiltration of local precipitation. This approach gives the following relationships:

$$\delta^{18}O = -0.0019\,RA - 6.41$$

$$H = -0.0049\,RA - 46.4$$

The altitude-stable isotope relationships estimated from these equations do not differ significantly from the altitude-stable isotope relationships given by Aires-Barros et al. (1995) for the adjacent areas of the Chaves graben. In the case of VR mineral waters, which show a mean isotopic composition of $-8.03‰$ for $\delta^{18}O$ and $-53.8‰$ for $\delta^2 H$, the above mentioned equations give an average infiltration altitude of 1,160 m. However, it must be emphasized that the isotope gradients obtained ($-0.19‰/100$ m for $\delta^{18}O$ and $-0.49‰/100$ m for $\delta^2 H$) are rather lower than those obtained by Aires-Barros et al. (1995) for the Chaves graben, indicating the possible influence of local climate on the altitude effect. The mean recharge altitude of 1,160 m is close to the mean altitude of Larouco Mountain, where infiltration occurs to the groundwater reservoir feeding the VR area (Fig. 11). These differences in the isotope gradients and the average infiltration altitudes seem to indicate that the VR and Chaves CO_2-rich mineral waters are not necessarily from the same recharge area. Effectively, the circulation system associated with VR CO_2-rich mineral waters could be mainly controlled by the east–west fault system that extends from Larouco Mountain across the VR study area (see Fig. 1). However, the NNE–SSW fault system in the VR area seems to provide the main conduit for groundwater rising to the surface. The absence of $^3 H$ in the VR CO_2-rich mineral waters supports the hypothesis of a relatively long circulation time. The
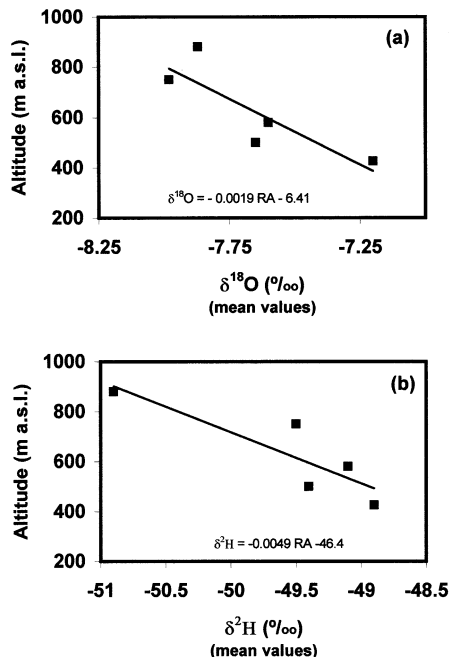

Fig. 10 Response of $\delta^{18}O$ and $\delta^2 H$ (mean values: data from Table 3) to altitude of sampling sites for cold dilute spring waters in the Vilarelho da Raia mineral-waters area and its bordering mountains

Fig. 11 Simplified NW–SE section of the conceptual circulation model for the Chaves and Vilarelho da Raia CO_2-rich mineral waters, derived from recent geochemical and geophysical studies presented in this paper. $\delta^{13}C_{TIDC}$ in ‰ vs V-PDB
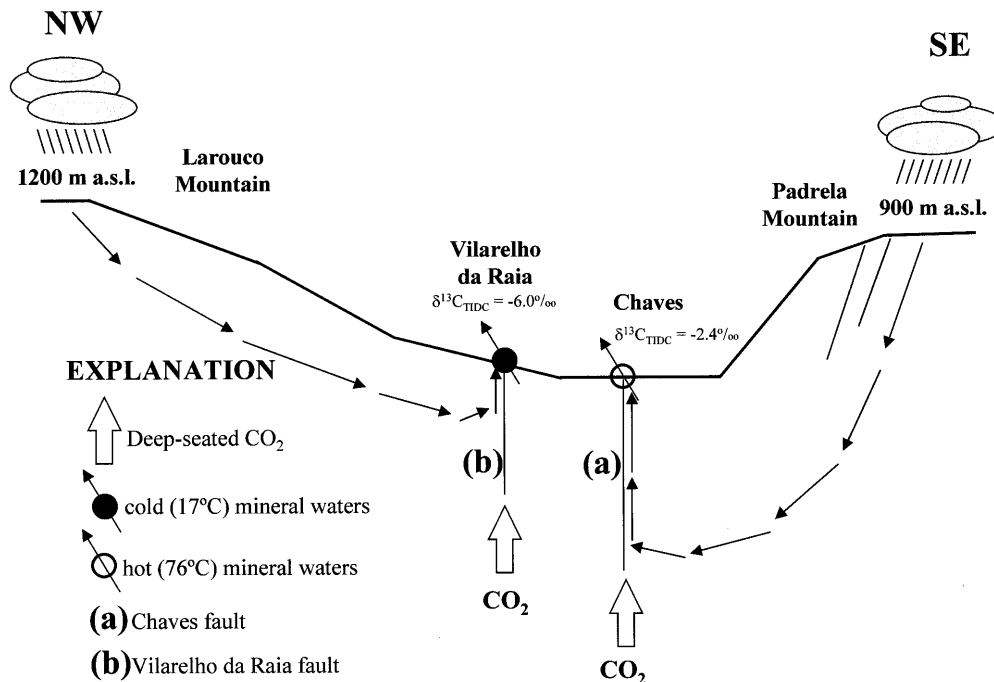
cold CO_2-rich mineral waters could, therefore, represent infiltrating waters that descend slowly, circulate at shallow depth and locally rise through the main NNE–SSW fault system. In the past, intensive alteration, which is kaolinization of the older granites in the western block of the NNE–SSW system, has probably caused self-sealing of the fractured zones to prevent rapid circulation through the subsurface rocks.

CO_2 Content vs Circulation Paths

The high CO_2 content of the VR mineral waters could be associated with (1) the fact that Chaves hot (76 °C) mineral waters emerge from a deep, high-temperature environment, whereas the Vilarelho da Raia cold (17 °C) mineral waters are the result of a shallow, low-temperature underground flow path and (2) the role of the VR NNE–SSW fault system in the migration of additional CO_2 from depth to the surface. This hypothesis is supported by the fact that, along the same Verin–Chaves–Penacova NNE–SSW fault system, the higher CO_2 values (up to 2,500 mg/L) are associated with the cold (17 °C) Vidago and Pedras Salgadas CO_2-rich mineral waters. As stated by Greber (1994), the solubility of CO_2 in water increases with decreasing temperature. According to Marques et al. (1998b), the $\delta^{13}C_{(TIDC)}$ (total inorganic dissolved carbon) values observed in the hot and cold CO_2-rich mineral waters of the region, range between –6.00 and –1.00‰ vs V-PDB, indicating a deep-seated mantle origin for most of the CO_2, which is carried to the surface, as a separate gas phase, through large regional faults. The addition of CO_2 from such an external source to the groundwaters locally leads to the formation of low pH waters and a water–rock interaction characterized by the leaching of Na from plagioclases of granitic rocks and partial attainment of mineral/fluid equilibrium (Marques et al. 1998a, 1999). In the case of water from the AC18 drilled well in the Vidago area (see Fig. 1), the $\delta^{13}C_{(TIDC)}$ value of –1.00‰ vs V-PDB indicates that the contribution of juvenile CO_2 or the dissolution of carbonate rock at depth cannot be excluded (Marques et al. 1998b). As stated by Marques et al. (1998b), VR and Chaves mineral waters show different $\delta^{13}C_{(TIDC)}$ values (–6.00 and –2.40‰ vs V-PDB, respectively). These differing $\delta^{13}C_{(TIDC)}$ values seem to indicate that the hypothesis for deep-seated CO_2 migrating from the Chaves fault system towards the VR fault system does not seem to be reliable. These data seem to confirm different origins for the Chaves and VR mineral waters. In the case of the Chaves thermal waters, the higher $\delta^{13}C_{(TIDC)}$ values could be explained by metamorphic decarbonation reaction of country rock that mixed with juvenile CO_2. An alternative explanation is that the $\delta^{13}C_{(TIDC)}$ values could be shifted to less negative values as a result of fractionation during the exsolution of dissolved CO_2.

Conceptual Model and Conclusions

Chemical, isotopic, and geophysical studies of hot (Chaves) and cold Vilarelho da Raia (VR) mineral waters make it possible to define groundwater movement from recharge to discharge zones, the most probable underground flow paths, the depths reached by groundwater circulation, the sources of CO_2 and the role of the Chaves and VR fault systems.

Two main groundwater systems were found in the region: (1) a deep hydrothermal reservoir related to the secondary permeability of the granitic rocks in Chaves area and (2) a shallow aquifer with regional movement towards the VR area. Both the Chaves and VR fault systems seem to play important roles in water ascent and CO_2 migration from the mantle to the surface. Lateral communication between these two NNE–SSW-trending fault systems, however, does not seem to be significant as indicated by the geophysical studies and the rather different $\delta^{13}C_{(TIDC)}$ values found in Chaves and VR mineral waters.

Figure 11 shows a new conceptual circulation model for the VR mineral waters based on the results presented in this paper. Figure 11 also shows the earlier conceptual circulation model of the Chaves thermal waters, proposed by Aires-Barros et al. (1995), including data on the $\delta^{13}C_{(TIDC)}$ values associated with the deep hot waters. This model has already been described in the Introduction of this paper (see Fig. 2).

The results of coupled geochemical and geophysical studies presented in this paper indicate that the hot Chaves and the cold VR CO_2-rich mineral waters should be considered as the surface discharges of two different hydrogeological systems. The VR mineral waters are of meteoric origin and infiltrated on Larouco Mountain NW of the Vilarelho da Raia area. A long residence time for water circulation exceeding 50 years is indicated by the low tritium levels (see Table 1). Circulation took place at shallow depth in the upper crust as is indicated by the low outflow temperature of these waters. The circulating waters were mineralized by water–gas–rock interactions in a low-temperature environment that favoured a high CO_2 content. The E–W fault system that extends from Larouco Mountain towards the VR area controls the regional circulation of these waters, whereas local structures create the conditions necessary for their ascent. The outflow of the VR mineral waters is closely related to the VR fault system being facilitated by the presence of CO_2 which reduces the density of the waters. The most feasible means by which the CO_2 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 CO_2-rich hot waters and at shallow depth in the case of the VR CO_2-rich cold waters. This hypothesis is supported by the fact that the $\delta^{18}O$ and δ^2H data related to the hot and cold CO_2-rich mineral waters do not show evidence of mixing with juvenile waters. Two main important conclusions can be drawn from this study of the VR and Chaves min-

eral waters: (1) conjunctive geochemical, isotopic, and geophysical methods are an effective means of obtaining fundamental information on any hydrogeological system; and (2) the Chaves hot waters have little or no influence on the discharge of the VR mineral waters.

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