Geofluids (2006) **6**, 273–287 doi: 10.1111/j.1468-8123.2006.00144.x

Chemical and isotopic signatures of $Na/HCO_3/CO_2$-rich geofluids, North Portugal

J. M. MARQUES[1], M. ANDRADE[1], P. M. CARREIRA[2], H. G. M. EGGENKAMP[3], R. C. GRAÇA[1], L. AIRES-BARROS[1] AND M. ANTUNES DA SILVA[4]

[1]Instituto Superior Técnico, Centro de Petrologia e Geoquímica, Lisboa, Portugal; [2]Instituto Tecnológico e Nuclear, Estrada Nacional N°10, Sacavém, Portugal; [3]Rijsenborch 111, 4132 HL Vianen (Ut.), The Netherlands; [4]Unicer Águas, S.A., Matosinhos, S. Mamede de Infesta, Portugal

ABSTRACT

Geochemical and isotopic studies have been undertaken to assess the origin of CO_2-rich waters issuing in the northern part of Portugal. These solutions are hot (76°C) to cold (17°C) Na–HCO_3 mineral waters. The δ^2H and δ^{18}O signatures of the mineral waters reflect the influence of altitude on meteoric recharge. The lack of an ^{18}O-shift indicates there has been no high temperature water–rock interaction at depth, corroborating the results of several chemical geothermometers (reservoir temperature of about 120°C). The low ^{14}C activity (up to 9.9 pmC) measured in some of the cold CO_2-rich mineral waters (total dissolved inorganic carbon) is incompatible with the presence of ^{3}H (from 1.7 to 4.1 TU) in those waters, which indicates relatively short subsurface circulation times. The δ^{13}C values of CO_2 gas and dissolved inorganic carbon range between −6‰ and −1‰ versus Vienna-Peedee Belemnite, indicating that the total carbon in the recharge waters is being diluted by larger quantities of CO_2 (^{14}C-free) introduced from deep-seated (upper mantle) sources, masking the ^{14}C-dating values. The differences in the $^{87}Sr/^{86}Sr$ ratios of the studied thermal and mineral waters seem to be caused by water–rock interaction with different granitic rocks. Chlorine isotope signatures ($-0.4‰ < \delta^{37}Cl < +0.4‰$ versus standard mean ocean chloride) indicate that Cl in these waters could be derived from mixing of a small amount of igneous Cl from leaching of granitic rocks.

Key words: CO_2-rich geofluids, earth degassing, geochemistry, isotopes, Portugal, thermal and mineral waters

Received 7 October 2005; accepted 10 March 2006

Corresponding author: José Manuel Marques, Instituto Superior Técnico, Centro de Petrologia e Geoquímica, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.
Email: jmmarques@mail.ist.utl.pt. Tel/fax: +351 218400806.

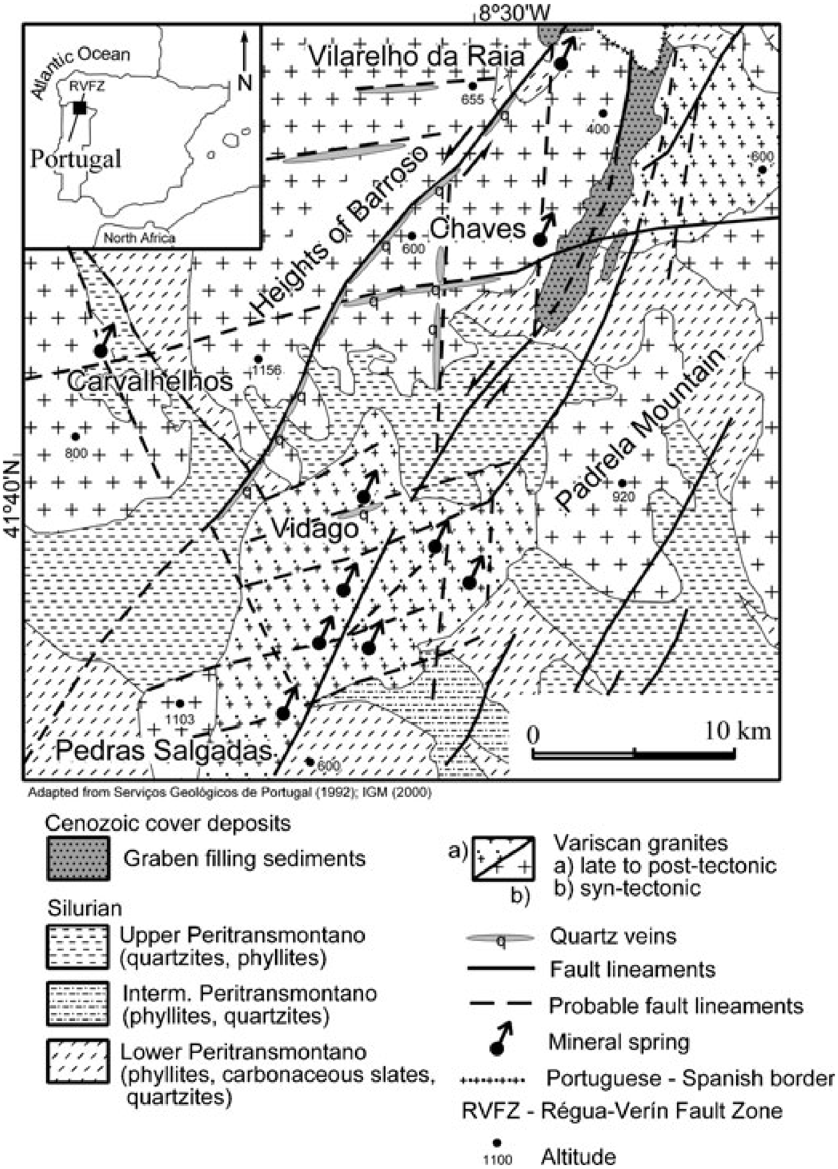
Geofluids (2006) **6**, 273–287

INTRODUCTION

In mainland Portugal about 50 natural low-temperature geothermal springs occur all throughout the country. Most of these thermal waters belong to the Na–HCO_3–sulphureous type and issue at temperatures between 20 and 69°C. Their geographical distribution is not uniform throughout the country. Most sites are located in the northern part of the Portuguese mainland and are associated with granitic rocks of Hercynian age.

However, thermal and mineral waters described in this paper do not belong to the above-mentioned hydrogeochemical *facies*. They are Na–HCO_3–CO_2-dominated thermal and mineral waters (unusual in the Portuguese mainland), and should be included in a very special water-type occurring at several places over the world, mainly related to local and/or regional fault systems. Most CO_2 discharges are associated with tectonic processes, being located along zones of increased seismicity (Barnes *et al.* 1978). A lot of data exist on the present-day CO_2 emissions from volcanoes, but this is not the case for nonvolcanic CO_2 degassing in areas where high CO_2 fluxes directly affect local/regional aquifers. Discussions about the origin of CO_2-dominated waters are still controversial, mainly dealing with the influence of the uprising CO_2 on the chemical properties of the circulating groundwaters and the isotopic interaction between CO_2 and water (e.g. Greber 1994; Chiodini *et al.* 2004; Siegel *et al.* 2004).

The geohydrology of the Vilarelho da Raia–Pedras Salgadas region (Fig. 1) has been the object of several studies



Adapted from Serviços Geológicos de Portugal (1992); IGM (2000)

Fig. 1. Schematic geological map of the Vilarelho da Raia–Pedras Salgadas region. After Sousa Oliveira (1995).

(e.g. Aires-Barros *et al.* 1995, 1998; Marques *et al.* 2001a,b; Andrade 2003) in order to understand the relations between the hot (Chaves, 76°C) and cold (Vilarelho da Raia, Vidago, Pedras Salgadas, 17°C) Portuguese CO_2-rich mineral waters. The aim of this paper is to summarize the geohydrological investigations performed at Vilarelho da Raia–Pedras Salgadas region, based on a geochemical and isotopic approach designed to answer the most common questions associated with these complex type of waters, namely: (i) what is the origin of the waters? (ii) what is the nature of CO_2? (iii) what are the main water–rock interactions occurring at depth?

Increasing knowledge on the local geohydrology is extremely important to achieve the sustainable use of this ‘invisible’ georesource, contributing to the preservation of valuable water resources and to the protection of recharge areas. It should be stated that most of the studied CO_2-rich thermal and mineral waters are being utilized for spa treatments since the Roman settlement in the Iberian Peninsula. At the moment they are used both as bottled waters and recreational resources (spa facilities, tourism, etc.) and at Chaves in a cascade concept for a swimming pool, and for heating a hotel and greenhouses.

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. Sousa Oliveira & Portugal Ferreira (1996) describe the main regional geological formations: (i) Hercynian granites (syn-tectonic, 310 Ma; post-tectonic, 290 Ma) and (ii) Silurian metasedimentary rocks of the Upper, Intermediate and Lower Peritransmontano Group, consisting of a sequence of quartzites, phyllites and carbonaceous slates.

The youngest rocks are Miocene to Pleistocene graben filling sediments that are thickest in the central axis of Chaves Depression. The axis of this graben is oriented NNE–SSW and is bounded on the east by the edge of Padrela Mountain escarpment with a 400 m throw. The western block boundary is formed by several grabens coming from the Heights of Barroso towards the Chaves Depression.

Thermal and mineral springs are located along a NNE–SSW active fault system (Fig. 1), the so-called Régua-Verín Fault Zone, which extends for 200 km and reaches 30 km depth in the study area. Some authors pointed out that the spring waters emerge in places where the NNE–SSW and ENE–WSW subvertical fracture systems intersect (e.g. Baptista *et al.* 1993; Sousa Oliveira & Portugal Ferreira 1996). The flow rate of these springs ranges from 0.25 to 20 m^3 day^{-1}. The exploitation flow rates of boreholes are between 20 and 400 m^3 day^{-1}.

In the study area, Baptista *et al.* (1993) and Sousa Oliveira & Portugal Ferreira (1996) stated that Chaves is the only site where the mineral waters issue at high discharge temperature (76°C) most probably because they emerge within a wide graben (3 km width by 7 km length) with a thickness of graben filling sediments greater than 250 m. On the other hand, Vidago and Pedras Salgadas cold (17°C) mineral waters issue in places where the local geologic structures (small grabens) do not exhibit such important features. According to those authors, deeper groundwater circulation is favoured at the Chaves area because of (i) high relief (tectonic throw), (ii) deep fracturing and (iii) thickness of graben filling sediments.

FIELD INVESTIGATIONS AND METHODS

Water samples for geochemical and isotopic analysis were collected from rain, shallow cold dilute groundwaters (spring waters) and from the Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas CO_2-rich thermal and mineral waters. Rock samples and mineral separates from local geologic outcrops were also analysed for Sr concentrations and $^{87}Sr/^{86}Sr$ ratios. Temperature (°C), pH, Eh (mV) and electrical conductivity ($\mu S\ cm^{-1}$) of the waters were determined '*in situ*'. Total alkalinity was measured a few hours after collection. The following methods were applied for chemical analyses performed at the Laboratório de Mineralogia e Petrologia of Instituto Superior Técnico (LAMPIST): atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na, K, Li, Rb and Cs; colorimetric methods for SiO_2, Fe_{total}, F and Al; ion chromatography for SO_4, NO_3 and Cl; potentiometry for alkalinity, here referred to as HCO_3. The data on free CO_2 content of the thermal and mineral waters were kindly supplied by the Águas de Carvalhelhos Company, the Municipality of Chaves and Vidago–Melgaço & Pedras Salgadas Company. The free CO_2 data were obtained through the carbonate alkalinity, determined by the back acid–base titration method. The free CO_2 of the samples was estimated by means of a graphical technique, taking into consideration the carbonate alkalinity, pH and ionic strength. A detailed description of this method is given by Ellis & Mahon (1977).

The δ^2H and $\delta^{18}O$ measurements [versus Vienna-standard mean ocean water (V-SMOW)] were performed by mass spectrometry (SIRA 10–VG ISOGAS) at the Instituto Tecnológico e Nuclear (ITN, Portugal) following the analytical methods of Epstein & Mayeda (1953) and Friedman (1953), with an accuracy of ±1.0‰ for δ^2H and ±0.1‰ for $\delta^{18}O$. The ^3H water content (reported in Tritium Units, TU) was also determined at ITN, using electrolytic enrichment followed by the liquid scintillation counting method (standard deviation varies between ±0.9 and ±1.3 TU, depending on tritium activity). The $^{37}Cl/^{35}Cl$ ratios [versus standard mean ocean chloride (SMOC)] were determined by mass spectrometry at the Geochemistry Department of Utrecht University as described by Eggenkamp (1994). Standard deviation mean value is 0.17‰. The $\delta^{13}C$ values were measured, at ITN, on the total dissolved inorganic carbon (TDIC) of groundwater, precipitated in the field as $BaCO_3$ at a pH environment higher than 9.0. The values are reported in ‰ to Vienna-Peedee Belemnite (V-PDB) standard, with an accuracy of ±0.1‰. The ^{14}C content was measured at the Physics Department of Utrecht University through accelerator mass spectrometry as described by Van der Borg *et al.* (1984, 1987). ^{14}C is given in percentage of modern Carbon (pmC). The Sr concentrations and Sr isotope ratios ($^{87}Sr/^{86}Sr$) were performed at Geochron Laboratories-USA. The Sr concentrations were determined by isotope mass dilution spectrometry and $^{87}Sr/^{86}Sr$ ratios have been performed by mass spectrometry. All Sr data were normalized to $^{87}Sr/^{86}Sr = 0.1194$ [long-term reproducibility of NBS-987 at MIT: 0.710247 ± 0.000014 (2σ SD)].

RESULTS AND DISCUSSION

The geochemical approach

The tectonic and geomorphologic features of Chaves, Vidago and Pedras Salgadas grabens and the geologic environment (dominated by granitic rocks) seem to be responsible for the occurrence of the studied hot and cold $Na/HCO_3/CO_2$-rich mineral waters (gas bubbles can be directly observed in the springs). Recent hydrogeochemical data (Andrade 2003) confirm the previous thermal and mineral water classification (Aires-Barros *et al.* 1998;

Marques *et al.* 1998) where two main groups of CO_2-rich mineral waters have been proposed.

Type A.

Chaves spring and borehole waters – presenting temperatures ranging from 48 to 76°C, dry residuum (DR) of about 1600–1850 mg l^{-1}, and free CO_2 between 350 and 1100 mg l^{-1}. The pH values are close to 7. The associated gas phase issued from the CO_2-rich springs is practically pure CO_2 (other minor components are $O_2 = 0.05\%$, $Ar = 0.02\%$, $N_2 = 0.28\%$, $CH_4 = 0.009\%$, $C_2H_6 = 0.005\%$, $H_2 = 0.005\%$ and $He = 0.01\%$ – data from Almeida 1982). In this group is also included the low temperature (approximately 17°C) Vilarelho da Raia cold spring and borehole waters, with similar chemical composition compared with Chaves hot waters (DR values are between 1790 and 2260 mg l^{-1} and free CO_2 is of about 790 mg l^{-1}).

Type B.

Vidago and Pedras Salgadas spring and borehole mineral waters – showing low temperature (approximately 17°C) and pH values (pH $\approx$ 6) and are distinguished from *Type A* thermal waters, by higher Ca, Mg and free CO_2 content (CO_2 up to 2500 mg l^{-1}). Within this group, Vidago (AC18) borehole waters present the highest mineralization (DR $\approx$ 4300 mg l^{-1}). Physico-chemical data of the waters from Vilarelho da Raia/Pedras Salgadas region are presented in Tables 1 and 2.

HCO_3, Na and Sr are plotted against a conservative element such as Cl (Fig. 2) to assess the extent of water–rock interaction. The mineral waters displaying the highest HCO_3 and Na concentrations are also those presenting the highest Cl values. The trend suggests that most Cl in the mineral waters could be derived from granitic rocks by leaching through acid hydrolysis of plagioclase and biotite (e.g. Edmunds *et al.* 1985).

The most mineralized waters in the area are cold waters (*Type B* waters; see Fig. 2), due to the fact that, in CO_2-rich thermal and mineral waters, carbon dioxide (more than temperature) is the most important specie which influences the chemical and physical characteristics of the fluids (Criaud & Fouillac 1986; Greber 1994). In these types of waters the process of water–rock interaction is improved by low temperatures as the solubility of CO_2 in aqueous systems increases with decreasing temperature, lowering the pH of the waters and consequently increasing water–rock interaction. Stumm & Morgan (1981) stated that the solubility of albite increases considerably with rising partial pressure of CO_2. The calculated values of P_{CO_2}, using the HIDSPEC hydrogeochemical model (Carvalho & Almeida 1989), are high, between 0.16 atm in Chaves and 1.20 atm in Vidago mineral waters (Aires-Barros *et al.* 1998).

In the diagrams of Fig. 2 the data from Chaves hot waters plot in a cluster, which is a good indication of the existence of a common reservoir for these waters. On the other hand, Vidago and Pedras Salgadas cold CO_2-rich mineral waters (*Type B* waters) seem to represent surface manifestations of distinct underground flow paths, because the different water mineralization ascribed to different CO_2 contents is responsible for pH decrease and diverse degrees of water–gas–rock interaction. The relatively low Sr (and HCO_3) found in the Chaves hot waters may be caused by boiling whereas the relatively high Sr and HCO_3 at Vidago and Pedras Salgadas cold mineral waters strongly demonstrate the increasing solubility of divalent ions (also for Ca and Mg, see Tables 1 and 2) with decreasing temperature (Marques *et al.* 2001a). As stated by Goff *et al.* (1991) the Sr concentration could decrease due to loss of CO_2 during flashing by the reaction:

$$Sr^{2+} + 2HCO_3^- \rightarrow SrCO_3 + CO_2 + H_2O$$

In the case of Chaves hot CO_2-rich mineral waters (*Type A*) the results of silica (quartz and chalcedony) and K^2/Mg geothermometers are in fair agreement indicating water–rock interaction at temperatures around 120°C (Marques *et al.* 1999). In the studied region, crustal geothermal gradients are estimated to be 30°C km^{-1} (Duque *et al.* 1998) indicating a circulation depth for the Chaves hot CO_2-rich geofluids of about 3.5 km. This is in agreement with the discharge temperatures (48–76°C) of Chaves CO_2-rich mineral waters.

The isotopic approach

Nature of the CO_2-rich mineral waters.

The $\delta^{18}O$ and δ^2H values of the hot and cold CO_2-rich mineral waters (Table 3; Fig. 3) lie on or close to the World Meteoric Water Line (WMWL: $\delta^2H = 8\ \delta^{18}O + 10$), defined by Craig (1961), excluding seawater and/or magmatic waters as a source of salinity in these mineral waters.

The local meteoric water line (LMWL: $\delta^2H = 7.01 \pm 0.74\ \ \delta^{18}O + 4.95 \pm 3.9$) was calculated (Fig. 4), based on $\delta^{18}O$ and δ^2H values of shallow cold dilute groundwater samples collected from springs located at different altitude sites in the Vilarelho da Raia–Pedras Salgadas region (Andrade 2003).

Data presented in Figs 3 and 4 indicate that both hot and cold mineral waters and shallow cold dilute groundwaters show a similar range in the isotopic composition (δ^2H and $\delta^{18}O$). The isotopic values indicate that both shallow cold dilute groundwaters and mineral waters have been recharged under similar climatic conditions, and that even the hot CO_2-rich mineral waters do not show evidences of a strong water–rock isotopic exchange at elevated temperatures (consistent with the results of the chemical geothermometry).

Table 1 Physico-chemical data of the waters from Vilarelho da Raia/Pedras Salgadas region collected during the first field work campaign – February 2000. Concentrations in mg l^{-1}.

Ref.	Local	*T* (°C)	pH	Conductivity (μS cm^{-1})	Na	K	Ca	Mg	Li	Fe	Al	HCO_3	SO_4	Cl	NO_3	F	SiO_2	D.R.	Rb	Cs
ACP1 (+)	Vilarelho da Raia	17.2	6.6	2350	600.0	22.8	26.3	5.25	1.20	0.80	0.32	1578.9	13.0	21.5	0.3	5.40	54.9	1522.8	0.28	0.16
CH1Ch. (*)	Chaves	n.a.	n.a.	n.a.	0.2	0.2	0.8	0.07	n.d.	n.d.	0.08	0.6	2.2	0.9	1.4	n.d.	n.d.	8.8	n.d.	n.d.
Assureiras (x)	Chaves	8.6	6.8	71	6.9	0.5	3.7	1.40	0.02	0.17	0.02	5.7	8.2	3.8	8.6	n.d.	16.8	57.4	n.d.	n.d.
Castelões (x)	Chaves	11.6	5.8	34	4.6	0.5	1.3	0.40	0.04	0.14	0.01	12.1	0.4	2.7	1.8	0.15	21.6	31.0	n.d.	n.d.
Campo de futebol (x)	Chaves	14.5	5.8	547	31.0	8.1	35.8	15.50	0.01	0.12	0.14	47.0	68.0	34.1	92.0	0.14	17.7	329.0	n.d.	n.d.
AC2 (+)	Chaves	77.0	6.9	2550	668.0	62.5	22.1	5.25	2.68	0.38	0.30	1706.9	18.3	35.3	n.d.	7.20	86.1	1702.4	0.54	0.46
Nas. (+)	Chaves	66.0	6.8	2430	633.0	63.0	23.4	5.75	2.56	0.17	0.34	1604.4	23.8	38.1	0.3	6.90	82.9	1633.6	0.50	0.44
CH1 V. (*)	Vidago	n.a.	n.a.	n.a.	1.9	0.3	0.1	0.22	n.d.	n.d.	n.d.	n.d.	1.3	3.6	0.2	n.d.	n.d.	7.3	n.d.	n.d.
Baldio (x)	Vidago	11.9	6.4	74	9.2	0.2	2.8	1.25	0.01	0.12	0.10	11.9	10.3	5.3	3.8	n.d.	26.5	76.4	n.d.	0.04
N3 (x)	Vidago	10.1	6.5	49	8.6	0.1	1.3	0.34	0.01	0.38	0.12	13.1	2.8	5.2	n.d.	n.d.	22.6	47.2	n.d.	n.d.
N6 (x)	Vidago	11.4	6.3	69	7.8	0.2	1.6	0.52	0.00	0.12	0.14	11.4	3.6	4.7	1.1	0.20	24.5	51.4	n.d.	0.04
N7 (x)	Vidago	9.7	6.8	70	10.0	0.6	2.3	0.72	0.02	0.26	0.00	24.4	2.0	5.1	0.3	n.d.	34.8	76.0	n.d.	n.d.
AC16 (+)	Vidago	17.6	6.1	1910	423.0	37.3	73.5	11.50	1.94	3.52	0.41	1285.3	7.9	17.3	n.d.	3.50	58.4	1217.0	0.30	0.22
AC18 (+)	Vidago	17.0	6.7	6230	1525.0	106.5	223.0	37.00	6.40	1.37	1.10	4689.5	1.9	66.0	1.6	3.40	59.8	4346.0	0.95	0.72
Areal 3 (+)	Vidago	12.3	6.9	6250	1585.0	96.5	132.0	28.00	9.44	0.43	0.77	5418.3	n.d.	54.0	n.d.	2.70	68.1	4205.0	0.90	0.24
CH1 P.S. (*)	Pedras Salgadas	n.a.	n.a.	n.a.	1.0	0.1	0.3	0.12	n.d.	n.d.	n.d.	n.d.	0.7	2.2	0.2	n.d.	n.d.	12.2	n.d.	n.d.
N1 (x)	Pedras Salgadas	10.1	5.6	39	6.4	0.1	1.3	0.36	0.00	0.12	0.12	9.2	1.1	2.8	n.d.	n.d.	22.1	42.2	n.d.	n.d.
N2 (x)	Pedras Salgadas	10.4	5.1	20	2.6	0.1	0.2	0.20	n.d.	0.01	0.20	n.d.	0.3	3.0	1.2	n.d.	4.3	14.4	n.d.	n.d.
N5 (x)	Pedras Salgadas	10.0	6.0	32	2.3	0.4	0.5	1.50	0.00	0.14	0.12	7.0	1.3	3.2	1.8	n.d.	8.3	23.8	n.d.	n.d.
AC17 (+)	Pedras Salgadas	16.1	6.3	2880	580.0	28.3	183.5	26.00	2.00	5.03	0.77	2010.2	10.3	32.0	n.d.	2.50	79.9	1886.0	0.32	0.12
AC25 (+)	Pedras Salgadas	17.9	6.4	4120	957.0	48.5	193.0	50.00	3.10	5.95	0.90	3057.4	2.3	32.6	n.d.	1.50	73.9	2781.0	0.36	0.12
AC22 (+)	Pedras Salgadas	14.8	6.5	5340	1285.0	37.0	227.0	41.00	1.00	2.25	1.28	4545.8	n.d.	51.0	n.d.	1.00	61.2	3663.2	0.16	0.14

T, water temperature; D.R., dry residuum; n.d., not detected; n.a., not analysed. (*) rain waters, (x) shallow (cold dilute) groundwaters, (+) thermal and mineral waters.

Table 2 Physico-chemical data of the waters from Vilarelho da Raia/Pedras Salgadas region collected during the second field work campaign – July 2000. Concentrations in mg l^{-1}.

Ref.	Local	T (°C)	pH	Conductivity (μS cm^{-1})	Na	K	Ca	Mg	Li	Fe	Al	HCO_3	SO_4	Cl	NO_3	F	SiO_2	D.R.	Rb	Cs
ACP1 (+)	Vilarelho da Raia	19.4	6.5	2120	728.0	26.3	26.4	5.0	1.16	0.83	0.32	1949.2	6.2	20.7	2.2	8.52	56.1	1550.2	0.30	0.16
Assureiras (x)	Chaves	20.8	6.1	64	7.3	0.3	3.4	1.4	n.d.	0.22	0.04	7.8	10.0	3.6	6.2	0.17	18.1	67.6	n.d.	n.d.
Castelões (+)	Chaves	13.7	5.4	22	3.9	0.4	0.9	0.3	n.d.	0.22	0.04	5.6	0.7	2.2	0.7	0.15	16.7	n.a.	n.d.	n.d.
Campo de futebol (X)	Chaves	20.6	7.7	496	31.0	9.1	36.8	15.0	n.d.	0.27	0.04	48.9	78.2	35.6	94.9	0.59	21.1	354.0	n.d.	n.d.
AC2 (+)	Chaves	77.0	6.8	2630	672.0	63.5	21.9	5.3	2.58	0.43	0.04	2027.4	20.1	37.1	0.6	10.31	87.3	1693.2	0.56	0.50
Nas. (+)	Chaves	68.0	6.8	2620	668.0	62.5	22.1	5.8	2.50	0.19	0.04	1948.8	25.9	39.2	2.2	9.99	85.8	1652.4	0.52	0.48
Tresmundes (x)	Tresmundes	17.5	5.7	70	8.1	1.6	3.7	1.9	n.d.	0.18	0.04	9.2	6.9	4.8	11.9	0.15	21.3	77.8	n.d.	n.d.
Baldio (x)	Vidago	13.9	6.5	61	9.1	0.4	4.4	1.3	n.d.	0.21	0.04	12.1	12.2	4.8	3.5	0.19	26.6	57.6	n.d.	n.d.
N6 (x)	Vidago	14.0	5.8	42	8.2	0.4	1.7	0.5	n.d.	0.12	0.04	11.9	4.1	4.2	0.7	0.29	25.4	51.6	n.d.	n.d.
AC16 (+)	Vidago	18.8	6.1	1646	464.0	36.3	67.0	11.0	1.90	3.36	0.07	1493.3	8.0	15.8	0.3	5.04	59.0	1187.4	0.30	0.24
AC18 (+)	Vidago	18.9	6.7	5580	1653.0	107.0	281.0	37.0	6.30	1.29	0.51	5756.3	2.3	70.4	2.8	10.53	61.0	4533.0	2.40	0.74
Areal 3 (+)	Vidago	19.8	6.5	4160	1266.0	74.5	79.0	18.0	6.98	0.30	0.41	4137.4	n.d.	42.2	0.6	8.90	68.3	3520.2	1.60	0.20
N1 (x)	Pedras Salgadas	16.5	5.6	38	6.8	0.2	1.3	0.4	n.d.	0.22	0.04	10.7	1.5	2.7	0.3	0.16	23.3	48.8	n.d.	n.d.
N2 (x)	Pedras Salgadas	11.9	5.1	15	2.0	0.2	0.2	0.2	n.d.	0.21	0.13	n.d.	0.8	2.4	1.0	0.15	4.7	16.0	n.d.	n.d.
N5 (x)	Pedras Salgadas	10.8	6.5	31	2.2	0.6	0.5	1.5	n.d.	0.24	0.04	8.3	1.7	2.9	1.1	0.15	9.2	11.6	n.d.	n.d.
AC17 (+)	Pedras Salgadas	18.4	6.3	2570	630.0	29.0	187.0	27.0	2.00	5.24	0.56	2552.0	10.0	31.5	1.3	5.29	81.9	1973.8	0.30	0.10
AC25 (+)	Pedras Salgadas	19.6	6.4	3540	983.0	47.5	126.5	40.0	2.78	5.24	0.25	3526.0	2.5	31.5	0.2	6.42	74.7	2670.0	0.34	0.10
AC22 (+)	Pedras Salgadas	16.0	6.4	4300	1348.0	38.0	233.0	41.0	4.24	2.25	1.03	5061.4	n.d.	56.5	3.8	7.91	31.1	3899.0	0.16	0.12

T, water temperature; D.R., dry residuum; n.d., not detected; n.a., not analysed. (*) rain waters, (x) shallow (cold dilute) groundwaters, (+) thermal and mineral waters.

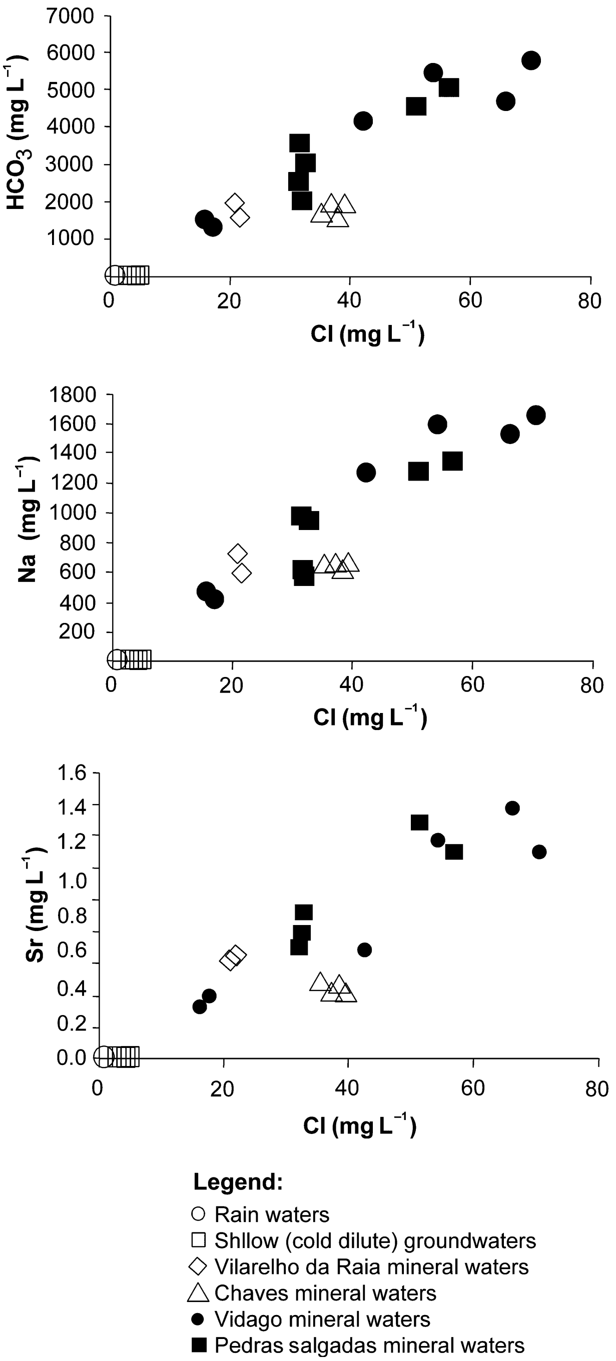


Fig. 2. Cl versus HCO_3, Cl versus Na and Cl versus Sr (mg l^{-1}) for the waters from Vilarelho da Raia–Pedras Salgadas region. (◇) and (△) stands for *Type A* waters; (●) and (■) stands for *Type B* waters. Modified from Andrade (2003).

Nevertheless, in the case of CO_2-rich fluids, the isotopic influence of CO_2 on the $\delta^{18}O$ value of the water should not be excluded. In fact, the lack of an ^{18}O-shift could be explained by oxygen isotope exchange between $H_2O(l)$ and $CO_2(g)$. Almeida (1982) presented $\delta^{18}O$ values of water and CO_2 related to Chaves thermal waters. The $\delta^{18}O$ value of $H_2O(l)$ was -8.04‰ versus SMOW and the corresponding value in $CO_2(g)$ was $+25.62$‰ versus SMOW. Using this data, Marques *et al.* (1999) have calculated the additive fractionation factor $\varepsilon_{CO_2}(g)-H_2O$ (l). The value obtained ($+33.66$‰) indicates that the equilibrium temperature (Friedman & O'Neil 1977) is close to the measured temperature of 76°C at sampling. Concerning oxygen isotopes, it seems that $H_2O(l)$ and $CO_2(g)$ are in equilibrium.

The isotopic composition of shallow groundwaters generally matches the mean isotopic composition of precipitation over a given recharge area (see IAEA 1981). Based on this criterion, locally derived shallow groundwaters (cold dilute spring waters) were collected to estimate the isotopic altitude effect in the region. The selected springs were located at different altitude sites, and show a ^3H content up to 8.5 TU indicating local circulation. Rain water samples from Chaves, Vidago and Pedras Salgadas areas (collected near the Spas) have been used as a local pattern. The results obtained indicate a decrease in $\delta^{18}O$ of -0.22‰ per 100 m rise in elevation (Fig. 5). According to Yurtsever & Gat (1981) the isotope gradients vary between 0.15 and 0.5‰ $\delta^{18}O/100$ m, pointing to an average rate of depletion of -0.26‰ (calculations based on the isotopic composition of precipitation water samples).

Based on this altitude gradient we can estimate the mean recharge elevations for the studied CO_2-rich thermal and mineral waters (see Fig. 6). Approximate recharge elevations can be determined by (i) using the equation of the local isotopic gradient ($\delta^{18}O = -0.0023$ Altitude $- 5.38$) obtained from the shallow cold diluted groundwater and precipitation, or (ii) extrapolating the isotopic composition of the CO_2-rich thermal waters to the regression line, and then dropping a perpendicular to the abscissa. The recharge elevations achieved from this methodology were: 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. According to the geomorphology of the region, the recharge of the Chaves, Vidago and Pedras Salgadas CO_2-rich thermal and mineral waters seems to occur preferentially on the Padrela Mountain (see Fig. 1). Concerning Vilarelho da Raia cold CO_2-rich mineral waters, the estimated recharge altitudes are only realized on Larouco Mountain, NW of Vilarelho da Raia springs.

The systematic presence of tritium (2–4.5 TU) measured (Aires-Barros *et al.* 1995, 1998; Marques *et al.* 1998; Andrade 2003) in some of the Vidago and Pedras Salgadas cold CO_2-rich mineral waters (AC16 and AC17 boreholes, respectively) should not be attributed to a mixing process with local shallow (cold dilute) groundwaters (^3H content between 3.6 and 8.2 TU). In a first approximation, the Cl concentration of Vidago AC16 CO_2-rich mineral waters could be explained as a mixing signature between AC18 or Areal 3 waters with local dilute waters (see Fig. 7), which

Table 3 Isotopic (^{18}O, ^{2}H and ^{3}H) data of the waters from Vilarelho da Raia/Pedras Salgadas region.

Reference	Local	Altitude (m a.s.l.)	δ^{18}O (‰)	δ^{2}H (‰)	^{3}H(TU ± σ)
First field work campaign (February 2000)					
ACP1 (+)	Vilarelho da Raia	370	−7.71	−53.2	1.7 ± 1.0
CH1Ch. (*)	Chaves	350	−5.83	−39.1	4.8 ± 1.0
Assureiras (x)	Chaves	690	−7.52	−50.7	6.4 ± 1.1
Castelões (x)	Chaves	980	−7.72	−50.1	8.2 ± 1.0
Campo de futebol (x)	Chaves	360	−5.76	−38.5	7.0 ± 1.0
AC2 (+)	Chaves	350	−8.03	−55.9	n.d.
Nascente (+)	Chaves	350	−7.96	−54.9	0.5 ± 0.9
CH1 V. (*)	Vidago	325	−6.00	−38.3	–
Baldio (x)	Vidago	510	−6.73	−42.9	4.3 ± 1.0
N3 (x)	Vidago	480	−6.20	−40.8	3.6 ± 1.4
N6 (x)	Vidago	420	−6.42	−41.6	4.7 ± 1.0
N7 (x)	Vidago	580	−6.73	−42.5	7.2 ± 1.3
AC16 (+)	Vidago	355	−6.63	−48.0	4.1 ± 1.0
AC18 (+)	Vidago	325	−6.81	−44.5	n.d.
Areal 3 (+)	Vidago	350	−7.12	−52.2	n.d.
CH1 P.S. (*)	Pedras Salgadas	560	−6.48	−43.2	3.7 ± 1.0
N1 (x)	Pedras Salgadas	660	−6.53	−40.1	4.2 ± 1.0
N2 (x)	Pedras Salgadas	1080	−6.79	−40.0	5.3 ± 1.1
N5 (x)	Pedras Salgadas	885	−7.20	−45.8	6.9 ± 1.0
AC17 (+)	Pedras Salgadas	580	−7.26	−47.3	2.2 ± 1.0
AC25 (+)	Pedras Salgadas	560	−7.70	−53.1	n.d.
AC22 (+)	Pedras Salgadas	570	−8.27	−53.5	n.d.
Second field work campaign (July, 2000)					
ACP1 (+)	Vilarelho da Raia	370	−7.78	−51.3	0.8 ± 1.0
Assureiras (x)	Chaves	690	−7.54	−47.5	5.7 ± 1.1
Castelões (x)	Chaves	980	−7.74	−46.5	5.4 ± 1.0
Campo de futebol (x)	Chaves	360	−5.80	−36.8	5.3 ± 1.0
AC2 (+)	Chaves	350	−8.03	−52.4	0.5 ± 1.0
Nascente (+)	Chaves	350	−7.99	−53.8	n.d.
Tresmundes (x)	Chaves	780	−7.75	−49.4	7.8 ± 1.0
Baldio (x)	Vidago	510	−6.67	−43.5	3.6 ± 1.1
N6 (x)	Vidago	420	−6.45	−41.6	5.1 ± 1.1
AC16 (+)	Vidago	355	−6.62	−45.0	4.0 ± 1.1
AC18 (+)	Vidago	325	−6.87	−42.1	1.5 ± 1.0
Areal 3 (+)	Vidago	350	−7.08	−43.4	0.1 ± 0.9
N1 (x)	Pedras Salgadas	660	−6.56	−40.9	5.8 ± 1.1
N2 (x)	Pedras Salgadas	1080	−6.86	−41.3	7.2 ± 1.1
N5 (x)	Pedras Salgadas	885	−7.19	−46.5	6.1 ± 1.0
AC17 (x)	Pedras Salgadas	580	−7.22	−46.5	4.1 ± 1.0
AC25 (x)	Pedras Salgadas	560	−7.64	−48.8	0.6 ± 1.1
AC22 (x)	Pedras Salgadas	570	−8.27	−54.2	0.3 ± 1.0

(*) Rain waters; (x) shallow (cold dilute) groundwaters; (+) thermal and mineral waters; n.d., not detected (below detection limit).

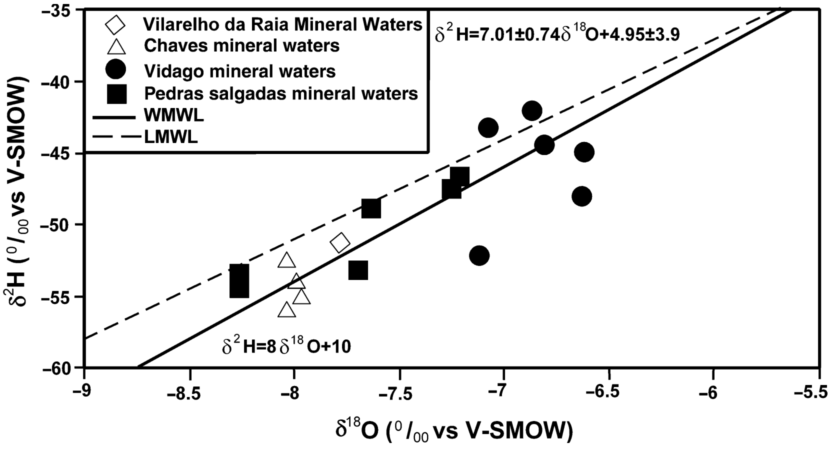


Fig. 3. Plot of δ^{18}O versus δ^{2}H (‰ versus V-SMOW) for the hot and cold CO_2-rich mineral waters. Modified from Andrade (2003).

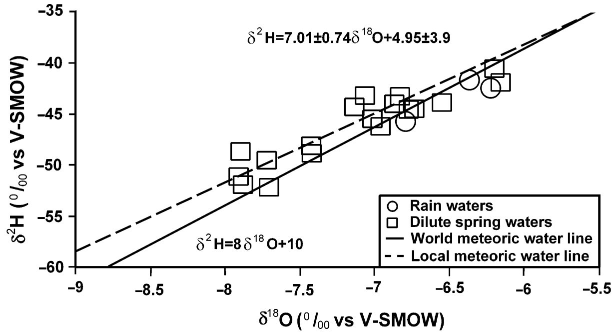


Fig. 4. Plot of $\delta^{18}O$ versus δ^2H (‰ versus V-SMOW) for the cold dilute spring and rain waters of the region. Modified from Andrade (2003).

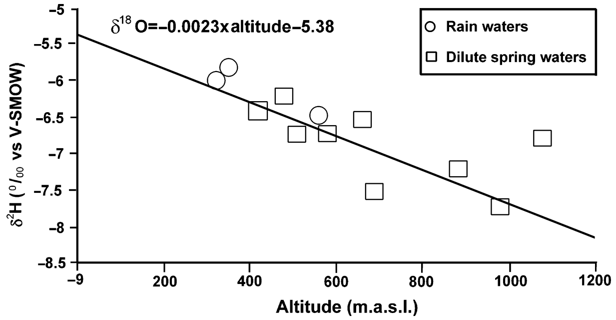


Fig. 5. Plot of altitude versus $\delta^{18}O$ (‰ versus V-SMOW) for the cold dilute spring and rain waters of the region. Modified from Andrade (2003). Data from the Winter (February 2000) campaign.

is not consistent with the calculated P_{CO_2} values (around 1.20 atm, *in*: Aires-Barros *et al.* 1998). On the other hand, Pedras Salgadas AC25 CO_2-rich mineral waters present similar Cl contents to the AC17 CO_2-rich mineral waters (see Fig. 7), but low ^3H content (Table 3). So, the ^3H concentrations determined in Vidago AC16 and Pedras Salgadas AC17 CO_2-rich mineral waters seems to be ascribed to shallow (and short) underground flow paths, being the water mineralization strongly controlled by the CO_2 content. Furthermore, the tritium concentrations in the regional precipitation (arithmetic mean of the weighted annual mean) are in the order of 5 TU (Porto = 4.5 TU; Vila Real = 6.36 TU, both meteorological stations from the Portuguese Network for Isotopes in Precipitation initiated in 1988, in collaboration with the International Atomic Energy Agency). Considering (i) the half-life of the ^3H (12.32 yr *in*: Lucas & Unterweger 2000), (ii) the ^3H content measured in the cold AC16 and AC17 CO_2-rich mineral waters and (iii) the tritium input (precipitation data) one can classify those cold CO_2-rich mineral waters as modern waters. The hot CO_2-rich mineral waters displaying the lowest ^3H content should be ascribed to oldest underground flowpaths.

Origin of carbon and ^{14}C dating.

Carbon dioxide in thermal and mineral waters can be derived from many sources, including oxidation of organic matter, interaction with sedimentary carbonates, metamorphic devolatilization, and magmatic degassing (Clark & Fritz 1997). The $\delta^{13}C$ determinations carried out on TDIC of the CO_2-rich mineral waters range from −6‰ to −1‰ (Marques *et al.* 1998). These results corroborate the $\delta^{13}C$ values measured on CO_2 gas samples ($\delta^{13}C_{CO_2} = -5.72‰$ versus PDB) for the Chaves hot mineral waters (Almeida 1982). The $\delta^{13}C$ values are suggestive of an inorganic source of CO_2, but mantle degassing and thermal decarbonation of limestone can produce CO_2 with $\delta^{13}C$ values in this range. On one hand, the 200 km long NNE–SSW mega lineament (the Régua-Verín Fault Zone, see Fig. 1), which reaches a depth of 30 km in the study area (Baptista *et al.* 1993), could act locally as a conduit for deep CO_2 to rise to the surface. On the other hand, some calcareous lenses (width of about 30 m and length of about 1.5 km) have been reported by Brink (1960) in Vila Real area (25 km to the south of our study area). Schermerhorn (1956) correlates these limestones of northern Portugal (Trás-os-Montes, Douro region) with those occurring in NW Spain (Galicia). However, the $^{87}Sr/^{86}Sr$

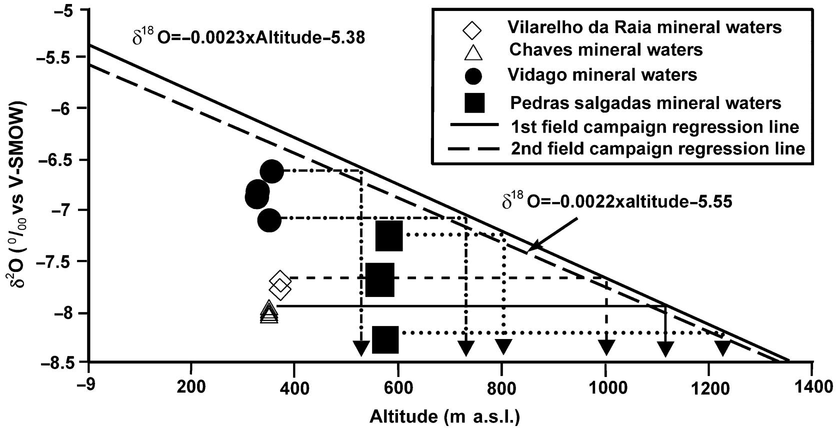


Fig. 6. Determination of recharge elevations of the hot and cold CO_2-rich mineral waters, from the relationship between $\delta^{18}O$ of the cold dilute spring and rain waters of the region and elevation. Modified from Andrade (2003).

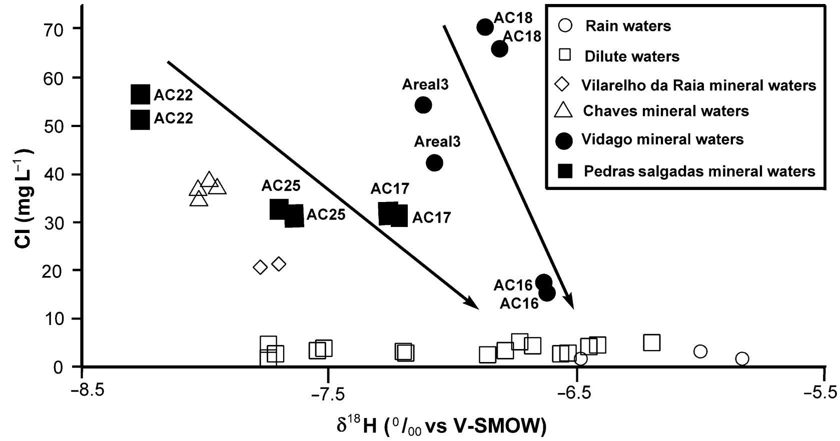


Fig. 7. Cl versus $\delta^{18}O$ for the waters from Vilarelho da Raia–Pedras Salgadas region. Adapted from Andrade (2003).

data (forward discussed) suggests that the presence of carbonate rock levels at depth as a possible carbon contributor for the mineral waters should be considered rather small. So, an alternative interpretation is that the $\delta^{13}C$ values of the CO_2 (of mantle origin) could be shifted to less negative values as the result of fractionation at low temperature. Fractionation could take place during the release of dissolved CO_2 (Aires-Barros *et al.* 1998).

In order to investigate the possible contribution of oxidation from local carbonaceous slates as a source of the CO_2 content in the thermal and mineral waters, $\delta^{13}C$ measurements were performed. The values obtained −26.9‰ and −27.2‰ versus V-PDB indicate a negligible contribution from these rocks as a possible carbon source (Marques *et al.* 1998).

Another hypothesis should consider the contribution of vegetation and soil CO_2 into the $\delta^{13}C$ signatures of the thermal and mineral waters during recharge and associated path through the soil zone. The CO_2 is formed in the soil by decay of plant remains and by root respiration. In this case, the $\delta^{13}C$ values should be centred around −25‰ in temperate climates where Calvin (C_3) plants dominate (Mook 2000), as in the regions in the surroundings of the studied thermal and mineral springs. Some $\delta^{13}C$ determinations performed on the local cold dilute groundwaters (Marques *et al.* 1998) range from −24‰ to −22‰ versus V-PDB. These values, attributed to the decay of organic matter, indicate that the cold dilute waters correspond to a shallow underground flow path.

Pérez *et al.* (1996) described the $^3He/^4He$ and $^4He/^{20}Ne$ isotope characteristics of terrestrial fluids in the Iberian Peninsula. According to them, the isotopic signature of helium in a fluid sample from Cabreiroa (Spain), obtained from the same NNE-trending fault as the CO_2-rich thermal and mineral waters, is significantly higher than typical crustal helium ($^3He/^4He$ value of 0.69). They estimated that, in the fluid sample from Cabreiroa, fractions of helium from mantle, crustal and atmospheric reservoirs were 8.35%, 91.62% and 0.02%, respectively. The relatively high $^3He/^4He$ found in Cabreiroa sample suggests the potential of a small percentage of mantle carbon. Further studies including the measurement of $CO_2/^3He$ ratios may be used to support the mantle origin for the CO_2 in these thermal and mineral waters. These ratios could be used to identify the migration direction from the source to the most distal field in the CO_2 system (Sherwood Lollar *et al.* 1997).

Among the radioactive isotopes with a half-life higher than 10^3 years, carbon-14 ($\tau = 5730$ years, *in:* Mook 2000) represents the most important tool in groundwater dating. In the last decades, some attempts have been carried out in hydrothermal systems, in order to use ^{14}C content as a dating tool (Wang & Pang 1995; Horvatincic *et al.* 1996). Groundwater dating with ^{14}C is complex due to the geochemical reactions that can occur within the aquifer. The radiometric age of the groundwater is that of the dissolved carbon, which may not be that of the water.

In these waters the radiocarbon values (7.9–9.9 pmC), presented by Aires-Barros *et al.* (1998), indicates that total carbon in the recharge waters is being masked by larger quantities of CO_2 (^{14}C-free) introduced from deep-seated (upper mantle) sources.

The carbon-14 age calculations were based upon the assumption that the initial activity of the dating material is 100% modern CO_2 activity (100 pmC); the $\delta^{13}C$ of the aquifer matrix is 1 ± 1‰; the $\delta^{13}C$ for the CO_2 in the soil zone is −25 ± 2‰; the fractionation factor ε_{HCO_3} is 8 ± 0.5‰, and the error associated with the measurements of the TDIC is 0.5‰. A closed system model was used (Salem *et al.* 1980) to calculate the apparent carbon-14 age of the hot and cold mineral waters. The mathematical model chosen includes mixture of soil CO_2 and carbonates dissolution in the soil with isotopic differences. The apparent groundwater ages of the CO_2-rich mineral waters obtained using this model were: Vilarelho da Raia 4.97 ± 3.07 ka BP; Pedras Salgadas 8.58 ± 4.33 ka BP and

Chaves 13.29 ± 2.65 ka BP (Carreira *et al.* 2001). The systematic presence of tritium in the cold (17°C) CO_2-rich mineral waters from Pedras Salgadas indicates local circulation systems with relatively short residence time. The apparent ^{14}C groundwater ages are close to 9 ka BP, which are not in agreement with ^{3}H content.

Water–rock interaction.

The scatter of the Sr data of local rain waters, shallow cold dilute groundwaters and thermal and mineral waters (Table 4), can be understood through the existence of three end-members [(a) Vilarelho da Raia/Chaves, (b) Vidago and (c) Pedras Salgadas] of a concentration trend, from the rain waters towards the thermal and mineral waters (Fig. 8; Marques *et al.* 2001a). Following the Vilarelho da Raia/Chaves–Vidago–Pedras Salgadas suite of fluids, one can observe a progressive depletion in radiogenic strontium. This trend shows that these three groups of thermal and mineral waters are ascribed to different underground components of flow.

The $^{87}Sr/^{86}Sr$ data of the different types of thermal and mineral waters can be compared with their inferred or known reservoir rocks. $^{87}Sr/^{86}Sr$ data are available from several rock suites from the Vilarelho da Raia–Chaves–Vidago and Pedras Salgadas region (Table 5). Samples of granites, slates and quartzites from local outcrops were collected at Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas areas. In addition, samples from gra-

Table 4 Sr data of the waters from Vilarelho da Raia/Pedras Salgadas region.

Ref.	Local	Sr (ppm)	$^{87}Sr/^{86}Sr$
First field work campaign (February 2000)			
ACP1(+)	Vilarelho da Raia	0.5827	0.728033
CH1Ch. (*)	Chaves	0.0010	0.710599
Assureiras (X)	Chaves	0.0242	0.729536
Castelões (X)	Chaves	0.0059	0.722967
Campo de futebol (X)	Chaves	0.2942	0.723488
AC2 (+)	Chaves	0.4349	0.727191
Nascente (+)	Chaves	0.4181	0.727154
CH1 V. (*)	Vidago	0.0015	0.710804
Baldio (X)	Vidago	0.0254	0.717003
N3 (X)	Vidago	0.0060	0.722858
N6 (X)	Vidago	0.0089	0.719087
N7 (X)	Vidago	0.0104	0.714352
AC16 (+)	Vidago	0.3424	0.723194
AC18 (+)	Vidago	1.3977	0.724280
Areal 3 (+)	Vidago	1.2130	0.720622
CH1 P.S. (*)	Pedras Salgadas	0.0013	0.711326
N1 (X)	Pedras Salgadas	0.0075	0.715094
N2 (X)	Pedras Salgadas	0.0018	0.730712
N5 (X)	Pedras Salgadas	0.0098	0.731135
AC17 (+)	Pedras Salgadas	0.7001	0.716969
AC25 (+)	Pedras Salgadas	0.8195	0.717572
AC22 (+)	Pedras Salgadas	1.3250	0.716754
Second field work campaign (July 2000)			
ACP1 (+)	Vilarelho da Raia	0.5470	0.728035
Assureiras (X)	Chaves	0.0200	0.729496
Castelões (X)	Chaves	0.0050	0.723071
Campo de futebol (X)	Chaves	0.2540	0.723485
AC2 (+)	Chaves	0.3760	0.727181
Nascente (+)	Chaves	0.3730	0.727171
Tresmundes (X)	Chaves	0.0360	0.726818
Baldio (X)	Vidago	0.0230	0.716821
N6 (X)	Vidago	0.0090	0.719034
AC16 (+)	Vidago	0.2920	0.723205
AC18 (+)	Vidago	1.1560	0.724243
Areal 3 (+)	Vidago	0.6050	0.720714
N1 (X)	Pedras Salgadas	0.0070	0.714902
N2 (X)	Pedras Salgadas	0.0020	0.731297
N5 (X)	Pedras Salgadas	0.0080	0.731496
AC17 (+)	Pedras Salgadas	0.6280	0.716936
AC25 (+)	Pedras Salgadas	0.6790	0.717566
AC22 (+)	Pedras Salgadas	1.1560	0.716713

(*) Rain waters; (x) shallow (cold dilute) groundwaters; (+) thermal and mineral waters.

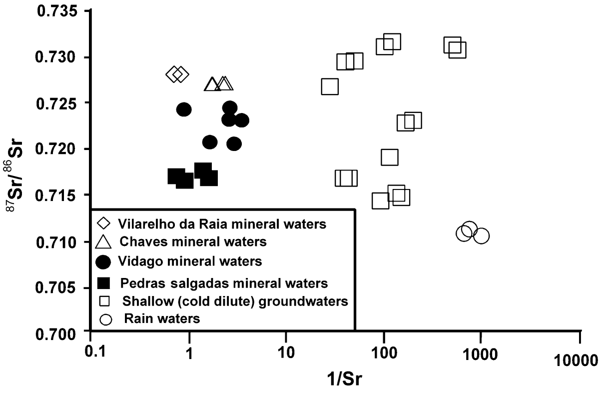


Fig. 8. 1/Sr versus $^{87}Sr/^{86}Sr$ for the waters from Vilarelho da Raia–Pedras Salgadas region. Sr in mg l^{-1}. Modified from Marques *et al.* (2001a)).

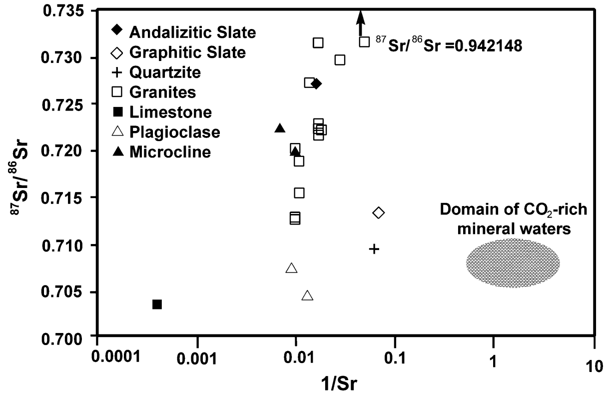


Fig. 9. Plot of 1/Sr versus $^{87}Sr/^{86}Sr$ for the rocks, minerals and hot and cold CO_2-rich mineral waters. Sr in mg l^{-1}. Modified from Andrade (2003).

nitic cores were collected at the Vilarelho da Raia AC2 drill hole.

A comparison of $^{87}Sr/^{86}Sr$ variations among the thermal and mineral waters and the rocks from Vilarelho da Raia–Pedras Salgadas area is shown in Fig. 9. The Sr isotopic signatures shows a clear-cut picture for each type of rock encountered (andalusitic slate, carbonaceous slate, quartzite, limestones and granites). Sr isotope ratios of granitic rock samples collected at Vilarelho da Raia, Chaves and Pedras Salgadas areas are far higher than the ratios of the thermal and mineral waters (Fig. 9), indicating that fluids and rocks are far from equilibrium with respect to Sr. Figure 9 shows that $^{87}Sr/^{86}Sr$ ratios in waters are dominated by the dissolution of plagioclases from granitic rocks. The low $^{87}Sr/^{86}Sr$ ratio in waters could be also interpreted as a

Table 5 Sr data of rocks (and mineral separates) from Vilarelho da Raia/Pedras Salgadas region.

Reference	Local	Lithology	Sr (ppm)	$^{87}Sr/^{86}Sr$
Samples from outcrops				
AM1*	Vilarelho da Raia	Granite	74.0	0.777260
AM60	Chaves	Andaluzitic slate	63.5	0.777421
AM1164	Chaves	Graphitic slate	14.4	0.737563
AM1163	Chaves	Quartzite	16.8	0.726642
AM1149	Chaves	Chaves Granite	87.6	0.753397
AM1150	Chaves	Outeiro Seco Granite	99.5	0.757173
AM1160	Chaves	Faiões Granite	93.1	0.743689
AM1161	Chaves	Faiões Granite	97.5	0.735697
AM2*	Vidago	Vila Pouca de Aguiar Granite	98.0	0.735900
Pflum7	Vila Real	Carbonates	2348	0.709485
Samples from drill cores				
VR13 (53.0 m)	Vilarelho da Raia	Granite	20.1	0.942148
VR18 (70.5 m)	Vilarelho da Raia	Granite	58.8	0.789683
VR70 (195.30 m)	Vilarelho da Raia	Granite	58.7	0.765128
AC21a (14.8 m)	Pedras Salgadas	Vila Pouca de Aguiar Granite	59.91	0.763068
AC21e (106.35 m)	Pedras Salgadas	Vila Pouca de Aguiar Granite	35.99	0.784371
AC26a (25.15 m)	Vidago	Vila Pouca de Aguiar Granite	54.67	0.762890
AC26b (34 m)	Vidago	Vila Pouca de Aguiar Granite	57.63	0.761298
		Mineral		
Minerals				
AM1*	Vilarelho da Raia	Microcline	152.0	0.76359
AM1*	Vilarelho da Raia	Plagioclase	108.0	0.72087
AM1*	Vilarelho da Raia	Muscovite	26.0	0.84459
AM1*	Vilarelho da Raia	Biotite	11.0	4.18370
AM2*	Vidago	Microcline	101.0	0.75644
AM2*	Vidago	Plagioclase	75.0	0.71261
AM2*	Vidago	Muscovite	12.0	2.43938
AM2*	Vidago	Biotite	108.0	0.70948

(*) Data from Aires-Barros *et al.* (1998).

result of the reduced contribution from K-feldspar, which contains Sr with relatively high $^{87}Sr/^{86}Sr$ ratios (see Table 5).

As indicated by Stettler & Allègre (1978), the $^{87}Sr/^{86}Sr$ ratio of the waters is usually constrained by the relative leaching stabilities of the different minerals (plagioclase provides most of dissolved ions, whereas K-feldspars are less soluble). This behaviour is consistent with the thermodynamic-kinetic modelling of granite–water interaction (Fritz *et al.* 1992).

The hypothesis of the existence of water–limestone interaction to explain the origin of CO_2 should be considered rather limited, because the composition of the Sr and the $^{87}Sr/^{86}Sr$ ratio of local limestones ($^{87}Sr/^{86}Sr = 0.709485$) is rather different from the thermal and mineral waters. This interpretation was also based on the fact that the CO_2-rich mineral waters displaying the less depleted $\delta^{13}C$ value (Vidago AC18: $-1.0‰$ versus V-PDB) show a rather high $^{87}Sr/^{86}Sr$ ratio ($^{87}Sr/^{86}Sr = 0.724280$).

The $\delta^{37}Cl$ values of Chaves, Vilarelho da Raia, Vidago and Pedras Salgadas thermal and mineral waters range between $-0.4‰$ and $+0.4‰$ versus SMOC (Table 6). This range of values is rather similar to the chlorine isotopic signatures of local rain waters and shallow cold dilute groundwaters (Fig. 10). This trend seems to indicate that chloride in these thermal and mineral waters could be derived from mixing of a small amount of igneous Cl from leaching of granitic rocks with meteoric water. A similar behaviour was reported by Coleman (2004), where the $\delta^{37}Cl$ data was used to define the hydrodynamic stability of the sub-surface waters associated with fractured granitic rocks at a potential radioactive waste site.

The hypothesis of water–rock interaction as the main source of Cl in these thermal and mineral waters is supported by the similar isotopic composition reported by Eggenkamp (1994) on the same waters (collected during 1985). This pattern points out that the $\delta^{37}Cl$ values do not change with time. In fact, although some of the studied mineral waters present slightly positive $\delta^{37}Cl$ values, which could be consistent with a deep-seated (mantle) source for chloride, the dissolved salts in these waters are believed to result from water–granite (mainly plagioclase) interaction.

Table 6 Cl isotopic data of the waters from Vilarelho da Raia/Pedras Salgadas region.

Reference	Local	$\delta^{37}Cl$ (‰)
First field work campaign (February 2000)		
ACP1 (+)	Vilarelho da Raia	−0.31
Assureiras (x)	Chaves	0.14
Castelões (x)	Chaves	0.43
Campo de futebol (x)	Chaves	−0.06
AC2 (+)	Chaves	0.09
Nascente (+)	Chaves	0.07
CH1 V. (*)	Vidago	0.07
Baldio (x)	Vidago	−0.27
N3 (x)	Vidago	0.13
N6 (x)	Vidago	0.11
N7 (x)	Vidago	0.18
AC16 (+)	Vidago	0.07
AC18 (+)	Vidago	0.00
Areal 3 (+)	Vidago	0.24
CH1 P.S (*)	Pedras Salgadas	0.94
N2 (x)	Pedras Salgadas	0.49
N5 (x)	Pedras Salgadas	0.15
AC17 (+)	Pedras Salgadas	0.21
AC25 (+)	Pedras Salgadas	0.15
AC22 (+)	Pedras Salgadas	0.19
Second field work campaign (July 2000)		
ACP1 (+)	Vilarelho da Raia	0.12
Assureiras (x)	Chaves	0.02
Castelões (x)	Chaves	0.12
Campo de futebol (x)	Chaves	−0.08
AC2 (+)	Chaves	−0.01
Nascente (+)	Chaves	−0.11
Tresmundes (x)	Chaves	−0.04
Baldio (x)	Vidago	−0.32
N6 (x)	Vidago	−0.16
AC16 (+)	Vidago	0.22
AC18 (+)	Vidago	−0.10
Areal 3 (+)	Vidago	0.04
N1 (x)	Pedras Salgadas	−0.23
N2 (x)	Pedras Salgadas	0.08
N5 (x)	Pedras Salgadas	0.37
AC17 (+)	Pedras Salgadas	0.15
AC25 (+)	Pedras Salgadas	0.31
AC22 (+)	Pedras Salgadas	0.19

(*) Rain waters; (x) shallow (cold dilute) groundwaters; (+) thermal and mineral waters.

CONCLUDING REMARKS

The combined geochemical and isotopic data suggests that the hot and cold CO_2-rich mineral waters of Vilarelho da Raia–Pedras Salgadas region derive from local meteoric waters. Deuterium and oxygen-18 isotopic signatures indicate recharge areas at different altitude sites. The $\delta^{13}C$ determinations of the CO_2-rich mineral waters range from $-6‰$ to $-1‰$, indicating an inorganic source of CO_2. Therefore, a deep-seated (upper-mantle) origin for the CO_2 seems to be the most plausible hypothesis. However, one has to consider the possibility of limestones dissolution (ascribed to the observed calcareous lenses) which could induce the shift of the $\delta^{13}C$ values in the mineral waters to more enriched ones (e.g. $\delta^{13}C = -1‰$). Nevertheless, Sr isotopic signatures of the mineral waters indicate that the hypothesis of the existence of water–limestone interaction to explain the origin of CO_2 should be considered rather limited. The relatively high $^{3}He/^{4}He$ found in Cabreiroa sample seems to support a mantle source for most of the carbon present in the northern Portuguese mineral waters. Calculation of $CO_2/^{3}He$ ratios may reveal similarities with other mantle sources. The systematic ^{3}H

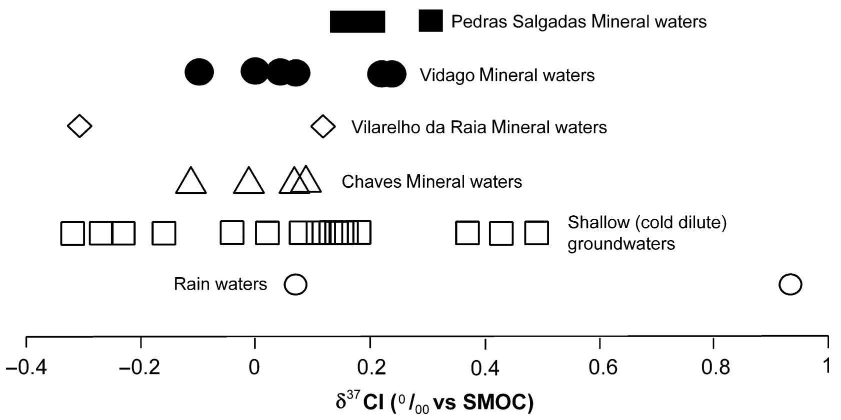


Fig. 10. Range of δ^{37}Cl values (‰ versus SMOC) in waters from Vilarelho da Raia–Pedras Salgadas region. Modified from Andrade (2003).

content of some of the cold CO_2-rich mineral waters, explained as a signature of a shallow (and short) underground circulation path, is incompatible with the ^{14}C age determinations. Probably the carbon is much older than the water. Solutes such as Na and HCO_3 originate from the hydrolysis of plagioclase in different granitic bodies, as indicated by the ^{87}Sr/^{86}Sr ratios, because these water–rock interaction processes are favoured by the higher CO_2 content of the circulating waters.

Recently, a new project was launched (with a special emphasis on the geochemistry of the gaseous phases associated with this group of thermomineral waters) to improve basic knowledge on the origin of northern Portuguese waters. To improve fundamental concepts on the origin of chloride (mantle versus water–rock interaction) in these waters, future studies on the δ^{37}Cl signatures of local granitic rocks are also foreseen.

ACKNOWLEDGEMENTS

We would like to thank the Águas de Carvalhelhos Enterprise, the Municipality of Chaves and the Vidago, Melgaço and Pedras Salgadas Enterprise for help during fieldwork campaigns. This work was funded by the PRAXIS Project 'FLUMIRE' under the Contract No. C/CTE/11004/98. An early draft of this manuscript was critically read by four anonymous reviewers and we gratefully acknowledge their contribution. Fraser Goff (University of New Mexico) is thanked for editing the English. The authors also would like to thank José Teixeira and Helder Chaminé for redrawing all the figures.

REFERENCES

Aires-Barros L, Marques JM, Graça RC (1995) Elemental and isotopic geochemistry in the hydrothermal area of Chaves/Vila Pouca de Aguiar (Northern Portugal). *Environmental Geology*, **25**(4), 232–8.

Aires-Barros L, Marques JM, Graça RC, Matias MJ, van der Weijden CH, Kreulen R, Eggenkamp HGM (1998) Hot and cold CO_2-rich mineral waters in Chaves geothermal area (northern Portugal). *Geothermics*, **27**(1), 89–107.

Almeida FM (1982) Novos dados geotermométricos sobre águas de Chaves e de S. Pedro do Sul. *Comunicações Serviços Geológicos Portugal*, **68**(2), 179–90.

Andrade MPL (2003) A geoquímica isotópica e as águas termominerais. Contribuição dos isótopos do Sr (^{87}Sr/^{86}Sr) e do Cl (^{37}Cl/^{35}Cl) na elaboração de modelos de circulação. O caso de algumas águas gasocarbónicas do N de Portugal. Unpublished MSc Thesis, Technical University of Lisbon, Lisbon, 104 pp.

Baptista J, Coke C, Dias R, Ribeiro A (1993) Tectónica e geomorfologia da região de Pedras Salgadas/Vidago e as nascentes minerais associadas. *Comunicações da XII Reunião de Geologia do Oeste Peninsular*, **I**, 125–39.

Barnes I, Irwing WP, White DE (1978) Global distribution of carbon dioxide discharges and major zones of seismicity. U.S. Geological Survey Water Resources Investigations 78-39, Open-File Report, 12 pp.

Brink AH (1960) Petrology and ore geology of the Vila Real - Sabrosa - Vila Pouca de Aguiar region, northern Portugal. *Comunicações dos Serviços Geológicos de Portugal*, **XLIII**, 143.

Carreira PMM, Marques JM, Aires-Barros L (2001) A problemática da datação por ^{14}C em águas gasocarbónicas. *Actas do VI Congresso de Geoquímica dos Países de Língua Portuguesa/XII Semana de Geoquímica*, pp. 698–702. Universidade do Algarve, Faro, Portugal.

Carvalho MR, Almeida C (1989) HIDSPEC, um programa de especiação e cálculo de equilíbrios água/rocha. *Revista da Universidade de Aveiro*, **4**(2), 1–22.

Chiodini G, Caliro S, Cardellini C (2004) Origin of the carbon dissolved in the groundwater and derivation of Earth diffuse emission of CO_2: the case of the Italian Peninsula. In: *Water–Rock Interaction*, Vol. 1 (eds Wanty RB, Seal RR II), pp. 21–9. A. A. Balkema, London, UK.

Clark ID, Fritz P (1997) *Environmental Isotopes in Hydrogeology*, 327 pp. Lewis Publishers, New York.

Coleman M (2004) Chlorine stable isotopes in sedimentary systems: does it matter? In: *Water–Rock Interaction*, Vol. 1 (eds Wanty RB, Seal RR II), pp. 31–7. A. A. Balkema, London, UK.

Craig H (1961) Isotopic variations in meteoric waters. *Science*, **133**, 1703.

Criaud A, Fouillac C (1986) Étude des eaux thermominérales carbogazeuses du Massif Central Français. II. Comportment de quelques métaux en trace, de l'arsenic, de l'antimoine et du germanium. *Geochimica et Cosmochimica Acta*, **50**, 1573–82.

Duque R, Monteiro Santos FA, Mendes-Victor LA (1998) Heat flow and deep temperatures in the Chaves Geothermal system, northern Portugal. *Geothermics*, **27**(1), 75–87.

Edmunds WM, Kay RLF, McCartney RA (1985) Origin of saline groundwaters in the Carnmenellis granite (Cornwall, England): natural processes and reaction during hot dry rock reservoir circulation. *Chemical Geology*, **49**, 287–301.

Eggenkamp HGM (1994) δ^{37}Cl – the geochemistry of chlorine isotopes. PhD Thesis, Utrecht. *Geologica Ultraiectina*, **116**, 150.

Ellis AJ, Mahon WAJ (1977) *Chemistry and Geothermal Systems. Energy Science and Engineering: Resources, Technology, Management. An International Series*, 392 pp. Academic Press, New York, USA.

Epstein S, Mayeda T (1953) Variation of ^{18}O content of waters from natural sources. *Geochimica et Cosmochimica Acta*, **4**, 213–24.

Friedman I (1953) Deuterium content of natural waters and other substances. *Geochimica et Cosmochimica Acta*, **4**, 89–103.

Friedman I, O'Neil JR (1977) *Compilation of Stable Isotope Fractionation of Geochemical Interest. Data of Geochemistry*, 6th edn. U.S. Geological Survey Professional Paper 440-KK. USGS, Menlo Park, USA.

Fritz B, Richard L, McNutt RH (1992) Geochemical modelling of Sr isotopic signatures in the interaction between granitic rocks and natural solutions. In: *Water–Rock Interaction, 2, Moderate and High Temperature Environments* (eds Kharaka YK, Maest AS), pp. 927–30. A.A. Balkema, Rotterdam.

Goff F, Wollenberg HA, Brookins DC, Kristler RW (1991) A Sr-isotopic comparison between thermal waters, rocks, and hydrothermal calcites, Long Valley caldera, California. *Journal of Volcanology and Geothermal Research*, **48**, 265–81.

Greber E (1994) Deep circulation of CO_2-rich palaeowaters in a seismically active zone (Kuzuluk/Adaparazi, northwestern Turkey). *Geothermics*, **23**(2), 151–74.

Horvatincic N, Srdoc D, KrajcarBronic I, Pezdic J, Kapelj S, Sliepcevic A (1996) A study of geothermal waters in northwest Croatia and east Slovenia. Isotopes. In: *Proceedings of the Symposium Water Resources Management* (ed. IAEA), pp. 470–4. IAEA, Vienna, Austria.

IAEA (1981) *Stable Isotopes Hydrology. Deuterium and Oxygen-18 in Water Cycle*, 339 pp. Technical Reports Series 210, International Atomic Energy Agency, Vienna.

IGM (2000) *Carta Geológica de Portugal, 1/200.000, folha 2 (Coordinator:. Pereira, E)*. Instituto Geológico e Mineiro, Lisboa.

Lucas LL, Unterweger MP (2000) Comprehensive review and critical evaluation of the half-life of tritium. *Journal of Research of the National Institute of Standards and Technology*, **105**(4), 541–9.

Marques JM, Carreira PM, Aires-Barros L, Graça RC (1998) About the origin of CO_2 in some HCO_3/Na/CO_2-rich Portuguese mineral waters. *Geothermal Resources Council Transactions*, **22**, 113–7.

Marques JM, Aires-Barros L, Graça RC (1999) Geochemical and isotopic features of hot and cold CO_2-rich mineral waters of northern Portugal: a review and reinterpretation. *Bulletin d'Hydrogéologie*, **17**, 175–83.

Marques JM, Andrade M, Aires-Barros L, Graça RC, Eggenkamp HGM, Antunes da Silva M (2001a) ^{87}Sr/^{86}Sr and ^{37}Cl/^{35}Cl signatures of CO_2-rich mineral waters (N-Portugal): preliminary results. In: *New Approaches Characterizing Groundwater Flow*, Vol. 2 (eds Seiler K-P, Wohnlich S), pp. 1025–9. A.A. Balkema, ?????.

Marques JM, Monteiro Santos FA, Graça RC, Castro R, Aires-Barros L, Mendes Victor LA (2001b) 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. *Hydrogeology Journal*, **9**, 584–96.

Mook WG (2000) *Environmental Isotopes in Hydrological Cycle. Principles and Applications*, 280 pp. IHP-V, Technical Documents in Hydrology, 39 (I). UNESCO & IAEA, Paris.

Pe´rez NM, Nakai S, Wakita H, Albert-Bertra´n JF, Redondo R (1996) Preliminary results on ^{3}He/^{4}He isotopic ratios in terrestrial fluids from Iberian peninsula: seismoctectonic and neotectonic implications. *Geogaceta*, **20**(4), 830–3.

Salem O, Visser JM, Deay M, Gonfiantini R (1980) Groundwater flow patterns in western Lybian Arab Jamahitiya evaluated from isotope data. In: *Arid Zone Hydrology: Investigations with Isotopes* (ed. IAEA), pp. 165–79. IAEA, Vienna, Austria.

Schermerhorn LJG (1956) The age of the Beira Schists (Portugal). *Boletim da Sociedade Geológica de Portugal*, **XII**(1/2), 77–100.

Serviços Geológicos de Portugal (1992) *Carta Geológica de Portugal, 1/500.000, (Coordinator: Carvalho, D)*, 5 editions. Serviços Geológicos de Portugal, Lisboa.

Sherwood Lollar B, Ballentine CJ, O'Nions RK (1997) The fate of mantle-derived carbon in a continental sedimentary basin; integration of C/He relationships and stable isotopic signatures. *Geochimica et Cosmochimica Acta*, **61**(11), 2295–307.

Siegel DI, Lesniak KA, Stute M, Frape S (2004) Isotopic geochemistry of the Saratoga Springs: implications for the origin of solutes and source of carbon dioxide. *Geology*, **32**(3), 257–60.

Sousa Oliveira A (1995) Hidrogeologia da Região de Pedras Salgadas. Unpublished MSc Thesis, University of Tra´s-os-Montes e Alto Douro, Vila Real, Portugal, 230 pp.

Sousa Oliveira A, Portugal Ferreira MR (1996) A estruturação do sistema graben – horst cruzado da região de Pedras Salgadas–Vidago (Norte de Portugal): enquadramento das emergências hidrominerais associadas. *Proceedings* 3° Congresso da Água/ VII SILUBESA (Lisboa, Portugal), **3**, 123–30.

Stettler A, Allègre CJ (1978) ^{87}Rb–^{87}Sr studies of waters in a geothermal area, the Cantal, France. *Earth and Planetary Science Letters*, **38**, 364–72.

Stumm W, Morgan JJ (1981) *Aquatic Chemistry – An Introduction Emphasizing Chemical Equilibria in Natural Waters*, 2nd edn. Wiley-Interscience, New-York.

Van der Borg K, Alderliesten C, Haitjema H, Hut G, Van Zwol NA (1984) The Utrecht accelerator facility for precision dating with radionuclides. *Nuclear Instruments and Methods in Physics Research*, **B5**, 150–4.

Van der Borg K, Alderliesten C, Houston CM, de Jong AFM, Van Zwol NA (1987) Accelerator mass spectrometry with ^{14}C and ^{10}Be in Utrecht. *Nuclear Instruments and Methods in Physics Research*, **B29**, 143–5.

Wang J-Y, Pang Z-H (1995) Application of isotope and geochemical techniques to geothermal exploitation in southeast – a review. In: *Proceedings of the Final ResearchCo-Ordination Meeting Isotope and Geochemical Techniques Applied to Geothermal Investigations* (ed. IAEA), *TECDOC*, **788**, 9–20.

Yurtsever Y, Gat JR (1981) Atmospheric waters. In: *Stable Isotope Hydrology. Deuterium and Oxygen-18 in the Water Cycle* (eds International Atomic Energy Agency), *Technical Reports Series*, **210**, 103–42.