Radiocarbon application in dating "complex" hot and cold CO_2-rich mineral water systems: A review of case studies ascribed to the northern Portugal

Paula M. Carreira [a,*], José M. Marques [b], Rui C. Graça [b], Luís Aires-Barros [b]

[a] *Instituto Tecnológico e Nuclear, Departamento de Química, Estrada Nacional N° 10, 2686-953 Sacavém, Portugal*
[b] *Instituto Superior Técnico, Laboratório de Mineralogia e Petrologia, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

ARTICLE INFO

ABSTRACT

The use of radioactive isotopes plays a very important role in dating groundwater, providing an apparent age of the systems in the framework of the aquifers conceptual modelling making available important features about the water fluxes, such as recharge, horizontal flow rates and discharge. In this paper, special emphasis has been put on isotopic constraints in the use of $\delta^{13}C$ and ^{14}C content as a dating tool in some hot (76 °C) and cold (17 °C) CO_2-rich mineral waters discharging in the Vilarelho da Raia–Pedras Salgadas region (N-Portugal). The radiocarbon content determined in these CO_2-rich mineral waters (^{14}C activity from 4.3 up to 9.9 pmc) is incompatible with the systematic presence of ^3H (from 1.7 to 7.9 TU). The $\delta^{13}C$ values of the studied CO_2-rich mineral waters indicate that the total C in the recharge waters is being masked by larger quantities of CO_2 (^{14}C-free) introduced from deep-seated (upper mantle) sources. This paper demonstrates that a good knowledge of mineral water systems is essential to allow hydrologists to make sound conclusions on the use of C isotopic data in each particular situation.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

The use of radioactive isotopes as a groundwater-dating tool plays an important role in assessing the dynamics of groundwater systems, essential for the characterization of water resources and planning its exploitation. In hydrogeological studies the application of radioisotopes with a short half-life (below 100 a) is limited in dating old groundwater. However, they can be extremely helpful in solving another type of question such as the identification of mixing between old and young groundwater systems.

Within the environmental radioisotopes, ^3H cannot be detected in waters more than approximately 50–60 a old due to the short half-life (τ) (^3H: τ = 12.32 a; Lucas and Unterweger, 2000). Among the radioactive isotopes with a half-life greater than 1 ka, ^{14}C (τ = 5730 a; Mook, 2000) represents the most important tool in groundwater dating.

This radioisotope is present in the atmosphere, soil, aquifer matrix, etc. In fact, radiocarbon dating of groundwater in the simplest form assumes that: the ^{14}C moves with the water molecules along the flowpath with a hydraulic gradient and the only mechanism enabling change of the ^{14}C content within the groundwater systems is radioactive decay [$A = A_0 e^{-\lambda t}$; where A stands for the measured activity of ^{14}C in the sample; A_0 initial ^{14}C activity; λ the decay constant for ^{14}C and t = time]. The time can be re-arranged to provide an estimation of the groundwater "age" [$t = -\lambda^{-1} \ln(A/A_0)$].

Following up these ideas, in order to apply the above equations, it is important to estimate the initial concentration of ^{14}C (A_0) at the time when the recharge occurred. In practice 100% of modern C (pre-industrial content) is at present a high value considering the atmospheric dilution as a consequence of the use of fossil fuel (industrial revolution). Usually the radiocarbon content of the atmosphere, is therefore, often thought to be lower then 100% mc. Problems can arise when the measurements are performed on

* Corresponding author. Fax: + 351 219946185.
E-mail address: carreira@itn.pt (P.M. Carreira).

total dissolved inorganic C (TDIC) as a consequence of the different sources of C in the water system since dissolved inorganic C in the surface is not conservative and potentially interacts with soil and the aquifer carbonate matrix and organic matter, leading to a dilution of the initial ^{14}C content, resulting in an overestimation of the groundwater age.

In the last decades, some attempts have been made to use ^{14}C content as a dating tool on hydrothermal systems (Changkuon et al., 1989; Wang and Pang, 1995; Horvatincic et al., 1996). Usually, the small quantity of CO_2 in the recharge waters derived from the atmosphere or from the soil environment has a high percentage of modern C.

However, under confined situations this signature may be diluted, particularly by zero-pmc CO_2 sources, i.e., it could be masked by larger quantities of radiocarbon-free CO_2 introduced in the groundwater system, either from dissolution of the carbonate rock matrix, or from thermal metamorphism and magma sources.

As a result of the different ^{14}C sources in the water system there is some scepticism about the validity or reliability of ^{14}C groundwater ages. Concerning this problem, this paper discusses the use/application of environmental radioisotopes (^{14}C and ^3H) as dating tools in CO_2-rich mineral waters located in the northern part of the Portuguese mainland, emphasizing the use of relative ages within the
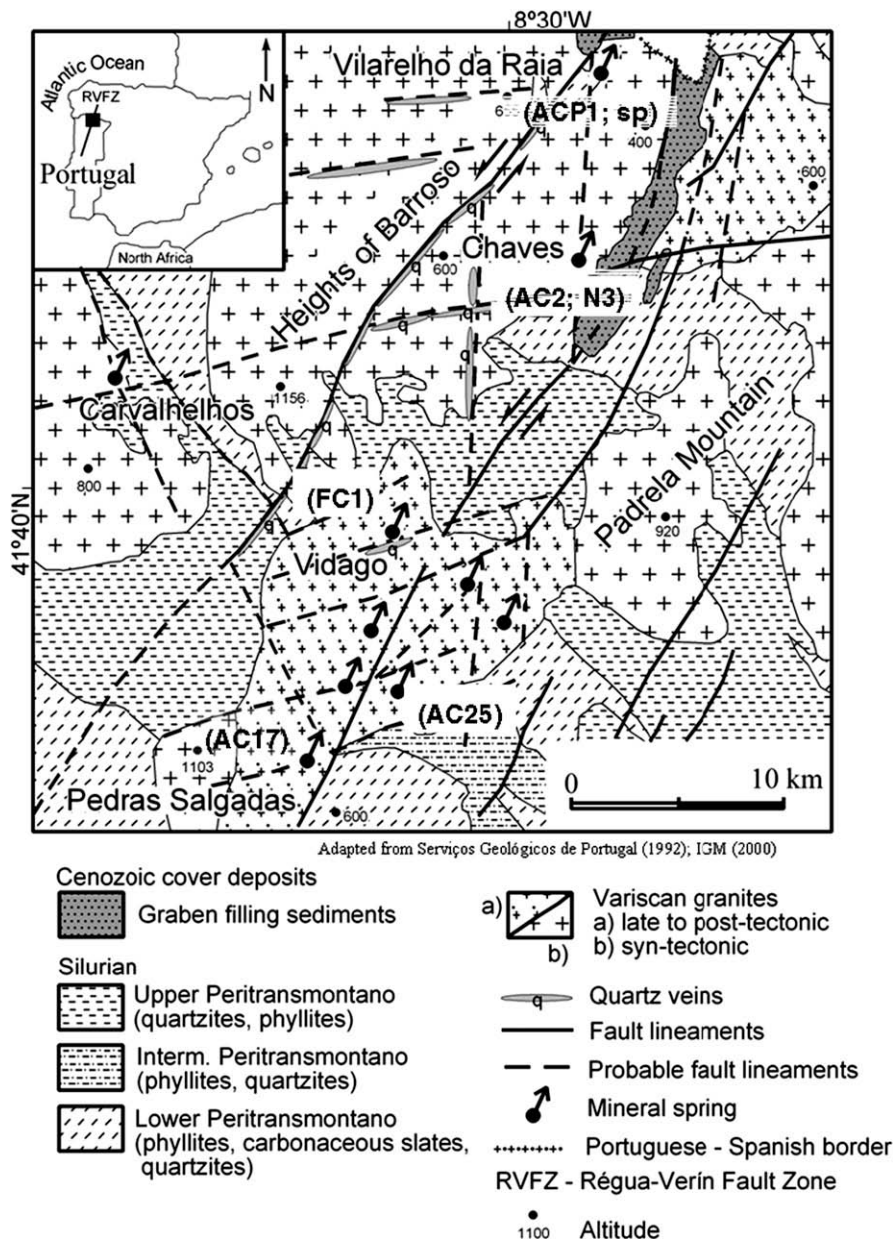

Fig. 1. Geological sketch of the region. Location of the main water sampling sites (adapted from SGP, 1992; Sousa Oliveira, 1995; IGM, 2000).

context of an appropriate hydrogeological conceptual model. The data discussed in this paper were obtained from previous work from research projects and theses coordinated by the authors (Aires-Barros et al., 1995, 1998; Marques et al., 2000; Andrade, 2003).

2. Geological and geophysical background

The region under study is located in the Ante-Mesozoic Hesperic Massif that consists mainly of Hercynian granites and Paleozoic metasediments (Fig. 1), and is dominated by the "Chaves Depression" characterized by a graben structure showing a NNE–SSW axis. These hydromineral systems are found either within the granitic outcrops or in the peribatholitic boundaries concordant to the main NNE–SSW fault trend shown in Fig. 1.

A geological characterization of the region (Fig. 1) has been performed by several authors (Portugal Ferreira et al., 1992; Baptista et al., 1993; Sousa Oliveira, 1995; Sousa Oliveira and Portugal Ferreira, 1995). The oldest formations are a pre-Ordovician schisto-graywacke complex. During Ordovician and Silurian times quartzites and schists were formed, being metamorphosed at the end of the Paleozoic by the Hercynian granitic intrusions. Inserted between the schistoid complex there are bands of carbonaceous slates. The carbonaceous slates are well-displayed 1.5 km SSW of the Chaves Spa. They are mostly made of quartz with large amounts of graphite and minute flakes of biotite and muscovite. The most recent formations are the Miocene-Pleistocene sedimentary series (lacustrine, alluvial, detritic, etc.) with variable thickness showing their maximum development along the central axis of Chaves graben. The Alpine Orogeny has caused extensive tectonic features responsible for the formation of several hydrothermal circuits.

At Chaves, the ascending hydrothermal circuits are structurally controlled by the NNE–SSW megafault, which is hydrothermally active along a belt extending 150 km in Portuguese mainland, and by the N70°–80°E faulted system, crossing the area in the neighbourhood of Chaves (Portugal Ferreira et al., 1992).

The Vidago/Pedras Salgadas area is mainly composed of Hercynian granites with some outcrops of metamorphic rocks of Silurian age covered by Cenozoic deposits. Geological studies in this area have shown that the mineral waters emerge in places where the sub-vertical fracture systems intersect: (1) N–S to NNE–SSW, (2) ENE–WSW, (3) NNW–SSE to NW–SE, and (4) WNW–ESE to W–E (Sousa Oliveira and Portugal Ferreira, 1995).

Resistivity surveys have been performed mainly to detect low resistivity zones predictably connected to the geothermal circulation at Chaves area (Andrade Afonso et al., 1994). Low resistivity zones detected southwards of the Chaves area are probably correlated with geothermal fluid circulation along the Chaves fault. The 2-D resistivity models from the soundings on Chaves graben, show low resistivity zones at great depth suggesting deep water circulation, indicating that the tectonic setting can play an important role in CO_2 extraction and migration from the mantle to the surface (Monteiro Santos, 1994). A conductive layer existing at a depth ranging from 7 to 12 km was also detected (Monteiro Santos, 1994).

The simultaneous evaluation of the results of the SiO_2 and K^2/Mg geothermometers has been performed by Aires-Barros et al. (1998). The data from Chaves CO_2-rich mineral waters (the most representative of the deep fluids in this area) indicate equilibrium temperatures around 120 °C, which are in agreement with the issue temperatures of Chaves thermal waters (76 °C). Considering the mean geothermal gradient of 30 °C/km (Duque et al., 1998), a maximum depth can be estimated of about 3.5 km for the Chaves mineral water system. This value was obtained considering that:

$$Depth = (T_r - T_a)/gg$$

where T_r is the reservoir temperature (120 °C), T_a the mean annual temperature (15 °C) and gg the geothermal gradient (30 °C/km).

The results obtained by Marques et al. (2001a) and Andrade (2003) based on the differences in the isotope gradients and the average infiltration altitudes, seem to indicate that the studied CO_2-rich mineral waters are not derived necessarily from the same recharge area. According to those authors, the circulation system associated with Vilarelho da Raia CO_2-rich mineral waters could be mainly controlled by the east–west fault system that extends from Larouco Mountain across the Vilarelho da Raia study area. On the other hand, Chaves, Vidago and Pedras Salgadas CO_2-rich mineral waters seem to be mainly ascribed to recharge areas located along the Padrela Mountain (the eastern block of the Chaves, Vidago and Pedras Salgadas grabens).

3. Hydrogeological aspects

Recently, the hydrogeology of the Vilarelho da Raia–Pedras Salgadas region (Fig. 1) has been studied in detail by several authors (e.g. Aires-Barros et al., 1995, 1998; Marques et al., 1998, 2000, 2001a,b; Andrade, 2003). The tectonic and geomorphologic features (Chaves, Vidago and Pedras Salgadas grabens), and the geological environment, dominated by granitic rocks, seem to be responsible for the occurrence of hot and cold $Na/HCO_3/CO_2$-rich mineral waters (gas bubbles can be directly observed in the springs). From the geochemical point of view, the waters from Vilarelho da Raia/Chaves and Vidago/Pedras Salgadas form two separate groups:

Group I: Chaves spring and borehole waters – are hot waters with temperatures ranging from 48 °C to 76 °C, dry residuum (DR) of about 1600–1850 mg/L, and free CO_2 between 350 mg/L and 1100 mg/L. 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 the low temperature (≈17 °C) Vilarelho da Raia cold spring and borehole waters are also included, with similar chemical composition comparatively to Chaves hot waters (DR values are between 1790 and 2260 mg/L and free CO_2 around 790 mg/L).

Group II: Vidago and Pedras Salgadas spring and borehole waters – have low temperature (≈17 °C) and pH values (pH ≈ 6) and are distinguished from Group I mineral

waters by higher Ca, Mg and free CO_2 content (CO_2 up to 2500 mg/L). Some of the Vidago borehole waters show considerably greater mineralization (DR $\approx$ 4300 mg/L).

According to (Aires-Barros et al., 1998) the fairly constant ratios of ionic species such as HCO_3, Na, and Sr against a conservative element such as Cl should be viewed as geochemical signatures of different degrees of water–rock interaction within a similar geological environment. This trend seems to indicate that most Cl in the mineral waters could be derived from granitic rocks by leaching. In fact, the mineral waters displaying the highest HCO_3 and Na concentrations are also those with the highest Cl values. Some samples show a rather wide variation in the Sr, Na and HCO_3 ions, and a relatively constant Cl content. This pattern seems to be ascribed to the fact that the recharge areas of this group of mineral waters is thought to be located within the contact between the phyllites and granitic rocks, where preferential leaching of phyllites can occur (Andrade, 2003).

4. Results and discussion

4.1. Methodology

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 geological outcrops were also analysed for Sr concentration and $^{87}Sr/^{86}Sr$ ratios. Temperature (°C), pH, Eh (mV) and electrical conductivity ($\mu S/cm$) 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 as HCO_3. The data on free CO_2 content of the thermal and mineral waters was 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 acid–base back 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 and Mahon (1977).

The δ^2H and $\delta^{18}O$ measurements (*vs.* V-SMOW, Vienna – Standard Mean Ocean Water) were performed by mass spectrometry using a SIRA 10-VG ISOGAS, at the Instituto Tecnológico e Nuclear (ITN – Portugal) following the analytical methods of Epstein and Mayeda (1953) and Friedman (1953). The results obtained have an accuracy of ±1.0‰ for δ^2H and ±0.1‰ for $\delta^{18}O$. The $\delta^{13}C$ data were obtained by mass spectrometry measurements, at ITN (SIRA 10-VG ISOGAS), on the TDIC of groundwater, precipitated in the field as $BaCO_3$ at pH environment higher than 9.0. The values are reported in ‰ *vs.* V-PDB (Vienna – Peedee Belemnite) standard, with an accuracy of ±0.1‰.

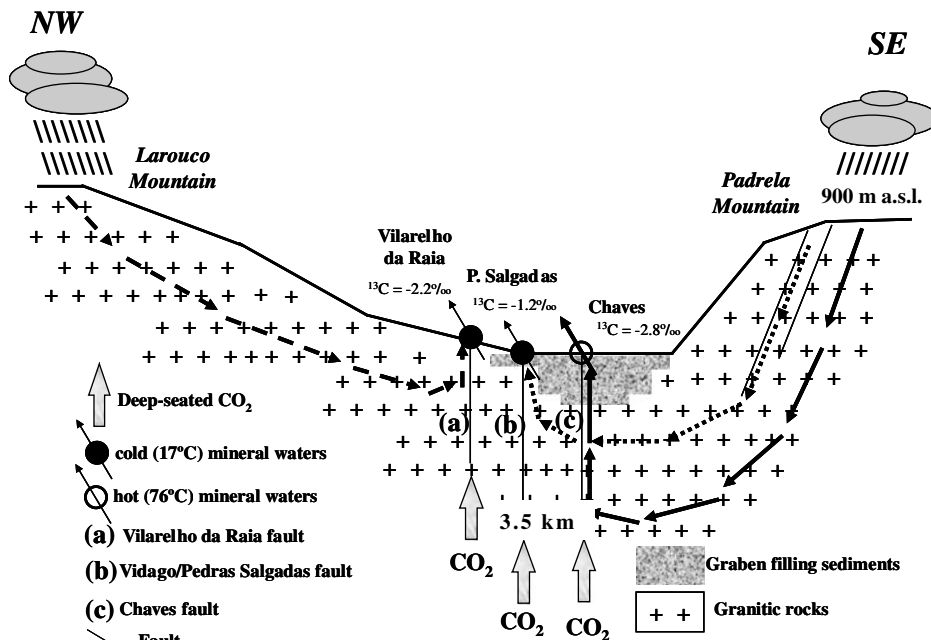The ^3H water content (reported in Tritium Units, TU) was also determined at ITN, using electrolytic enrichment

Fig. 2. Simplified NW–SE section of the conceptual circulation model for the Vilarelho da Raia, Chaves and Pedras Salgadas CO_2-rich mineral waters, derived from geochemical and geophysical studies presented by Marques et al. (2001a,b) and Andrade (2003). The $\delta^{13}C_{TIDC}$ values are expressed in ‰ *vs.* V-PDB, data from Table 2.

followed by a liquid scintillation counting method (PACK-ARD Tri-Carb 2000 CA/LL). The standard deviation associated varies between ±0.9 and ±1.3 TU, a function of the ^3H activity of the water sample.

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). Carbon-14 is given in pmc (percentage of modern C).

The Sr concentrations and Sr isotope ratios ($^{87}Sr/^{86}Sr$) were performed at the Geochron Laboratories-USA. The Sr concentrations were determined by isotope mass dilution spectrometry and $^{87}Sr/^{86}Sr$ ratios by mass spectrometry. All Sr data were normalised to $^{87}Sr/^{86}Sr = 0.1194$ (long term reproducibility of NBS-987 at MIT: $0.710247 ± 0.000014$ (2 sigma s.d.)).

4.2. Geochemical and isotopic aspects

The work presents and discusses a review of the research studies that have been performed by the authors in the region on the scope of previous research projects. The data presented (collected during the last decade) was gathered from existing publications. This geochemical and isotopic data enabled the authors to propose a conceptual hydrogeological circulation model (see Fig. 2) associated with the Chaves and Vilarelho da Raia mineral water

systems (Marques et al., 2001b). Isotopes (^{18}O, ^2H and ^3H) were used to identify groundwater origin, recharge areas and underground flow paths (Aires-Barros et al., 1995, 1998; Marques et al., 1996, 2001b). Special attention has been given to the identification of the origin of CO_2 in these hot and cold CO_2-rich mineral waters (Marques et al., 1998, 2000).

All mineral waters were plotted on a Piper Diagram (Fig. 3). This diagram enhances the two above mention groups of mineral waters. Representative physical, chemical and isotopic (^{18}O, ^2H and ^3H) characteristics of the studied CO_2-rich mineral waters are shown in Table 1.

The most probable explanation of why some of the most mineralised waters in the area are cold waters is linked with the fact that in CO_2-rich thermomineral systems, CO_2 (more than temperature) is one of the most important species which influences the chemical and physical characteristics of the fluids (Criaud and Fouillac, 1986; Greber, 1994). In addition, in these hydrogeological systems, water–rock interaction is enhanced by low temperatures, since the solubility of CO_2 in water increases with decreasing temperature, favouring the pH decrease.

The δ^2H and $\delta^{18}O$ values measured in these CO_2-rich mineral waters indicate meteoric waters, which have not been subjected to surface evaporation (Aires-Barros et al., 1995; Marques et al., 1996, 2001b). No evidence of
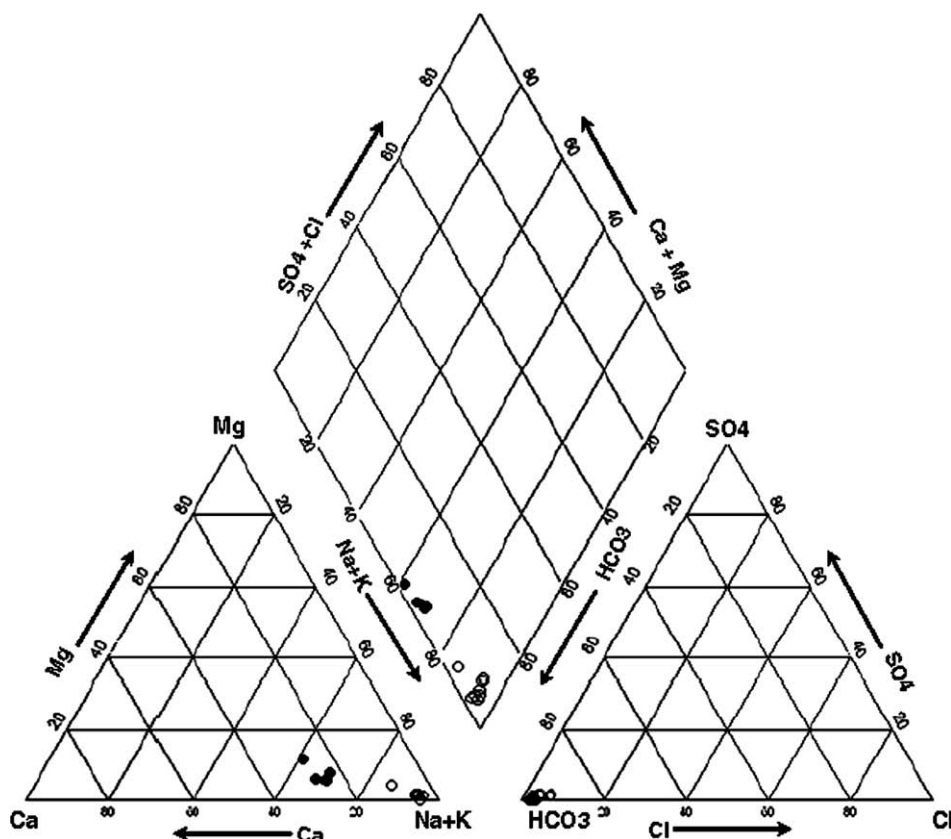

Fig. 3. Piper diagram for the studied CO_2-rich mineral waters: (●) stands for Sabroso and Pedras Salgadas water samples; (○) stands for Vilarelho da Raia, Campilho and Chaves water samples (data from Table 1).

Table 1
Representative physico-chemical and isotopic composition of the CO_2-rich mineral waters from Vilarelho da Raia/Pedras Salgadas region

Sample	Date	T	pH	Na	K	Ca	Mg	Li	Al	HCO_3	SO_4	Cl	SiO_2	$\delta^{18}O$	δ^2H	^3H
V. Raia (sp) ●	1991	14.6	6.75	953	49.7	41.2	0.9	2.7	0.05	2686	0.5	54.7	53.1	−8.00	−55.3	0.3
V. Raia ACP1 (bh) ♣	1996	17.7	5.78	706	28	32	7	1.35	n.d.	1869	2	24	52.6	−7.98	−54.7	0.1
V. Raia ACP1 (bh) ○	2000	17.2	6.6	600	22.8	26.3	5.3	1.2	0.32	1579	13	21.5	54.9	−7.71	−53.2	1.7
Chaves AC2 (bh) ●	1991	72.2	7.3	560	64.8	23.3	5.1	2.9	0.05	1826	24.2	38.6	73.9	−8.39	−55.2	0.8
Chaves AC2 (bh) ♣	1996	76	7.3	551	64	24	6	2.95	n.d.	1686	18	63.2	73.6	−8.15	−56.6	0.3
Chaves AC2 (bh) ○	2000	77	6.9	668	62.5	22.1	5.3	2.68	0.3	1707	18.3	35.3	86.1	−8.03	−55.9	.0.
Chaves N3 (sp) ▲	1991	48.6	6.87	626	66.2	30.9	5.1	2.95	n.d.	1727	22.4	67.8	73.8	−7.30	−53.7	0.3
Campilho FC1 (bh) ♦	1990	17.9	6.2	476	28.2	47.6	12.5	2.26	n.d.	1457	6.9	24.9	49.2	n.a.	n.a.	n.a.
Sabroso AC25 (bh) ○	2000	17.9	6.4	472	48.5	193	50	3.1	0.9	3057	2.3	32.6	73.9	−7.70	−53.1	0.0
P. Salg. AC17 (bh) ●	1991	17.5	6.43	535	27.6	193	25.8	2.3	0.2	2173	8.8	25	72.3	−7.30	−44.1	7.9
P. Salg. AC17 (bh) ♣	1996	16.3	6.25	585	27	171	35	2	n.d.	1931	10	36	74.2	−7.04	−41.2	2.1
P. Salg. AC17 (bh) ○	2000	16.1	6.3	580	28.3	183.5	26	2	0.77	2010	10.3	32	79.9	−7.26	−47.3	2.2

Notes: T is temperature of sampled water (°C); Concentrations are in mg/L. $\delta^{18}O$ and δ^2H are in ‰ (*vs.* V-SMOW) and ^3H content in TU (Tritium Units). (sp) spring waters; (bh) borehole waters. n.d. is not detected. n.a. is not analysed. (▲) data from Aires-Barros et al. (1995); (●) data from Aires-Barros et al. (1998); (♣) data from Marques et al. (2000); (○) data from Andrade (2003); (♦) data from the Portuguese Geologic and Mining Institute (IGM).

water/rock interaction at high temperatures (^{18}O shift) has been observed. These authors attribute the enrichment in ^{18}O (1‰) and in ^{2}H (10‰) in Pedras Salgadas mineral waters to a lower recharge altitude. Also, the $\delta^{18}O$ and δ^2H data related to the studied hot and cold CO_2-rich mineral waters does not show evidences of mixing with magmatic waters (Marques et al., 2000).

Based on temperature and ^{3}H content, Pedras Salgadas cold CO_2-rich mineral waters have been viewed as shallow groundwater systems, while the Chaves hot CO_2-rich mineral waters (without ^{3}H) are characterized by a deeper circulation (Aires-Barros et al., 1995; Marques et al., 1996, 2000).

On the other hand, the absence of ^{3}H in the Vilarelho da Raia cold CO_2-rich mineral waters has been attributed by Marques et al. (2001b) to a regional circulation associated

with meteoric water infiltration at Larouco Mountain (NW of the Vilarelho da Raia area). In this case, the mineral water circulation takes place at shallow depth in the upper crust as indicated by the low outflow temperature of these waters. The circulating waters were mineralised by water–gas–rock interactions in a low-temperature environment that favoured a high CO_2 content (Marques et al., 2001b).

The total dissolved C in mineral waters can be attributed to two main origins: organic and inorganic, that will be revealed in the $\delta^{13}C$ values (Fig. 4). Considering an organic source, CO_2 can be produced from decay of organic matter with mean $\delta^{13}C$ values around −26‰ to −22‰. Among the inorganic sources, C in hydromineral systems may originate from: (i) deep-seated (upper mantle) C showing $\delta^{13}C$ values ranging between −8‰ and −1‰, (ii) carbonate (marine origin) dissolution with $\delta^{13}C$ values
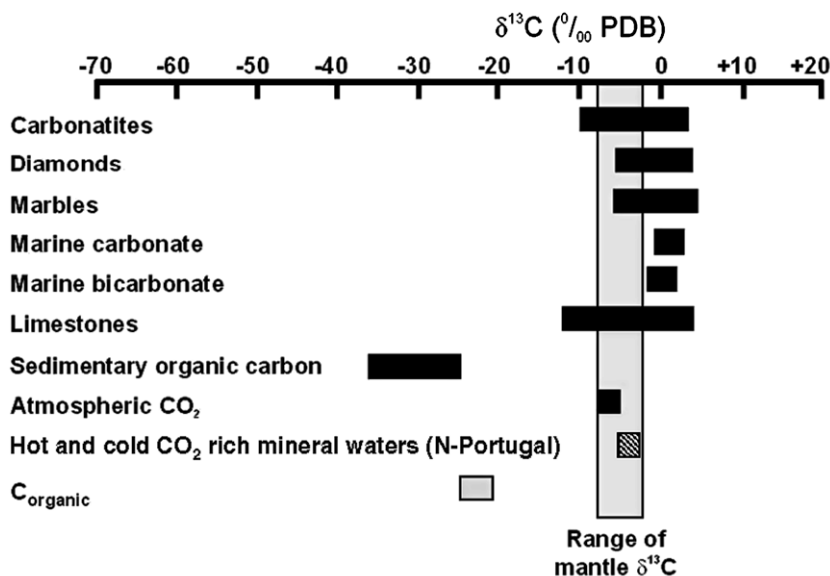

Fig. 4. The range of $\delta^{13}C$ values for different C-bearing substances as they compare to the $\delta^{13}C$ values of mantle C (vertical bar). Adapted from Bergfeld et al. (2001).

close to 0‰, or (iii) from the dissolution metamorphism of carbonates producing CO_2 with slightly positive $\delta^{13}C$ values (Bergfeld et al., 2001; Truesdell and Hulston, 1980).

The $\delta^{13}C$ determinations were carried out on TDIC in the studied CO_2-rich mineral waters, giving values in the range of $-6‰$ to $-1‰$ (Marques et al., 2000), indicating a deep-seated (upper mantle) origin for the CO_2. These results corroborate the $\delta^{13}C$ values measured on a CO_2 gas samples ($\delta^{13}C_{(CO2)} = -5.72‰$ vs. PDB) quoted by Almeida (1982), in the case of Chaves mineral waters.

Pérez et al. (1996) discussed the $^3He/^4He$ and $^4He/^{20}Ne$ ratios from terrestrial fluids measured in the Iberian Peninsula. According to these authors, the isotopic signature of He from crustal fluids is around 0.02 Ra (Ra = 1.4×10^{-6} = He isotope atmospheric ratio). The ^4He production in terrestrial fluids results from the decay series of U and Th. Higher He isotope ratios (from 9 to 30 Ra) are related to a mantle plume origin in regions such as Hawaii, Iceland, Yellowstone, Reunion and Canary Islands, indicating a He-degassing source in the upper mantle (^3He is an excellent tracer of a mantle component). In the case of fluids escaping from volcanic arc environments, the isotopic ratio $^3He/^4He$ ranges from 6 to 8 Ra reflecting a He magmatic source in the upper mantle (Pérez et al., 1996).

A sample from Cabreiroa mineral water, issuing in Spain on the same NNE-trending fault of the studied Portuguese CO_2-rich mineral waters, showed a $^3He/^4He$ value of 0.69, which is significantly higher than typical crustal helium (Pérez et al., 1996). Based on the equations suggested by Sano and Wakita (1985), quoted by Pérez et al. (1996), the authors estimated that in the fluid sample from Cabreiroa, the He fraction from mantle, crustal and atmospheric reservoirs were 8.35%, 91.62% and 0.02%, respectively. The relatively high $^3He/^4He$ found in the Cabreiroa sample corroborates an important mantle-degassing component.

4.3. ^{14}C groundwater dating

Groundwater dating with ^{14}C is complex due to the geochemical reactions that can occur within the aquifer. The radiocarbon is ubiquitous in the aqueous phase as a component of various dissolved C species (CO_2; HCO_3^-; CO_3^{2-} and in the form of dissolved organic C). The radiometric age of the groundwater is that of the dissolved C, when the atmosphere is the only source of gaseous CO_2, the TDIC is practically all in the form of HCO_3^-. This HCO_3^- has a ^{14}C content that reflects the atmospheric concentration. However, the radiocarbon age measured in the groundwater may not be "authentic" for that water, when different sources of C can be ascribed to the groundwater system, for instance: C from the leaching of solid carbonate will dilute the ^{14}C activity of bioorganic CO_2, since in general they are ^{14}C free.

Several mathematical models are available for the estimating the initial ^{14}C activity (A_0) of the total dissolved C, which have been summarised by Fontes and Garnier (1979) and by Gallagher et al. (2000). A_0 is derived from a combination of the two sources and is defined as the ^{14}C content after all chemical and isotopic processes have taken place before any decay. Models attempt to account for the dilution of ^{14}C by less active C and for isotopic ex-

change reactions, which may take place between the different C-bearing chemical species. In spite of the existence mathematical models to estimate groundwater ages, the results that will be presented for the radiocarbon age of the thermomineral groundwater were obtained using the formula

$$t = 8267 \ln(C_0/C) \tag{1}$$
$$C_0 = [100(\delta_{DIC} - \delta_R)(1 + 2.3\varepsilon_{13}/1000)]/(\delta_S - \delta_R + \varepsilon_{13}) \tag{2}$$

(Salem et al., 1980; Gonfiantini, 1988): where C is the measured ^{14}C activity and C_0 is the "initial" ^{14}C activity in the TDIC of the measured groundwater (expressed in pmc). It has been assumed that the ^{14}C activity of the soil CO_2 is equal to 100 pmc. δ_{DIC} is the measured ^{13}C content of carbonate species dissolved in the sample, δ_R is the ^{13}C content of $CaCO_3$ in the soil and in the rock matrix; δ_S represent the ^{13}C content of soil CO_2 whereas ε_{13} stands for the ^{13}C enrichment factor during dissolution of soil CO_2 in the infiltrating water.

The ^{13}C-correction model can be a good tracer for open and closed system evolution of dissolved inorganic carbon in groundwater systems. The large difference in $\delta^{13}C$ between the soil derived dissolve inorganic C and carbonate minerals in the aquifer can provide a reliable measure of the ^{14}C dilution by carbonate dissolution or, for instance the influx of deep-seated (upper mantle) C. The $\delta^{13}C$ mixing model allows for the incorporation of ^{14}C-active dissolved inorganic C during carbonate dissolution under open system conditions and subsequent ^{14}C dilution under closed system conditions.

Although the ^{13}C content of soil CO_2 may vary over a wide range depending on numerous parameters such as type of vegetation cover, temperature, water content and the depth of soil (Reardon et al., 1979; Hesterberg and Siegenthaler, 1991), the value of $\delta_S = 21 \pm 2‰$ was adopted for calculating the initial ^{14}C activity using Eq. (2). It should be noted that the soil CO_2 is enriched in ^{13}C with respect to the decomposing organic matter, as well as to CO_2 respired by roots of living plants by 4‰ due to kinetic fractionation associated with diffusion of this gas from the soil to the atmosphere (Dörr and Münnich, 1980, 1987). As representative for the soil and rock carbonates the value of $0 \pm 1‰$ was adopted for δ_R. To account for fractionation during dissolution of soil CO_2 in the infiltrating water $\varepsilon_{13} = 9.0 \pm 0.1‰$ was adopted. The ε_{13} value was estimated applying the relation $\varepsilon_b(g) = -9.483 \times 10^3/T + 23.89‰$ described by Mook et al. (1974), assuming a mean temperature in the area of 15°C (mean weight temperature for the 30 a record 1961–1991).

As mention previously, the main goal of this paper is to avoid the complexity of applying radiocarbon content in dating groundwater systems (especially in the case of the CO_2-rich mineral waters), and use a simple decay equation with the minimum corrections. The simple model chosen to estimate the thermomineral groundwater ages was that proposed by Salem et al. (1980) and Gonfiantini (1988). However simple, this model allows for complete equilibrium isotope exchange between dissolved HCO_3 and CO_2, which is important in this type of groundwater systems. From the atmospheric reservoir the CO_2 enters into the water cycle by two main mechanisms: (i) a pure chemical

process of dissolution controlled by solid carbonate saturation and (ii) by biochemical production of CO_2 and HCO_3. If the atmosphere is the only source of gaseous CO_2 in the water system, the TDIC is practically all in the form of HCO_3^- which ^{14}C content reflects the atmospheric concentration.

The biochemical production can be described as the assimilation of atmospheric CO_2 by plants accompanied by a release of this gas in the soil. In this case, two situations can be found: (i) all the dissolved C is organic and (ii) the total dissolved C is organic and from dissolution of solid carbonate. In the first case, the ^{14}C activity of the TDIC will exclusively reflect one CO_2 source. In the second case, the ^{14}C activity of organic CO_2 in the groundwater will be diluted by dissolution of solid carbonates (usually ^{14}C free). As a consequence, using the modern activity and following a simple decay calculation, one cannot evaluate groundwater age based on the ^{14}C content. This process is the predominant source of dissolved inorganic C in groundwater. However additional sources can play an important role in specific situations, such as in the case of the Portuguese CO_2-rich thermomineral water systems.

Table 2 lists the $\delta^{13}C$, ^{14}C and CO_2 content of the mineral waters from five different sampling sites. The $\delta^{13}C$ content of the CO_2-rich mineral water samples is rather uniform, varying between −3.5‰ and −1.2‰ with respect to the standard V-PDB (Table 2). The obtained range of these values (the apparent groundwater ages in Table 2 were achieved applying Eqs. (1) and (2)) requires an input of C to the mineral water systems other than from organic origin (the value of −21 ± 2‰ was adopted for ^{13}C composition for the soil CO_2). To account for fractionation during dissolution of soil CO_2 in the infiltrating water the value 9.02 ± 0.1‰ was adopted for ε_{13}. Among the inorganic sources, C in hydromineral systems from the studied region may originate from: (i) deep-seated (upper mantle) C showing $\delta^{13}C$ values ranging between −8‰ and −1‰, (ii) soil and rock carbonates, the value of 0 ± 1‰ is assumed, or (iii) metamorphism of carbonates producing CO_2 with slightly positive $\delta^{13}C$ values (Truesdell and Hulston, 1980).

It is relevant to mention the presence of important fault structures along which the sampled borehole and spring waters issue. The $\delta^{13}C$ determinations carried out on TDIC of the CO_2-rich mineral waters range from −3.5‰ to −1.2‰, indicating an inorganic source of CO_2. Therefore, a simple interpretation of the data obtained could suggest a possible mixing with mantle CO_2 (uprising through these fault structures) with CO_2 derived from carbonate dissolution (see Fig. 4). The possibility of limestone dissolution attributed to the described calcareous lenses in the region (Schermerhorn, 1956; Brink, 1960) could induce the shift of the $\delta^{13}C$ values in the mineral waters to more enriched ones (e.g. $\delta^{13}C$ = −1.2‰).

Considering the geochemical signatures of these waters it seems that the most probable origin of much of the CO_2 should be the upper mantle. To identify the deep-seated CO_2 dilution factor (q) to the hydromineral systems Clark and Fritz (1997) propose the following equation based on the $\delta^{13}C$ mixing model:

$$q_{mantle} = [\delta^{13}C_{DIC\ measured} - \delta^{13}C_{mantle}]/[\delta^{13}C_{recharge} - \delta^{13}C_{mantle}]$$

where $\delta^{13}C_{DIC\ measured}$ represents the ^{13}C content measured in the mineral groundwater samples; according to Truesdell and Hulston (1980) the $\delta^{13}C_{mantle}$ values range between −8‰ and −1‰; $\delta^{13}C_{recharge}$ represents the ^{13}C content measured in recharge waters, which in the studied region is represented by the values obtained in the shallow cold dilute spring waters ($\delta^{13}C$ = −22.9‰; Marques et al., 2000). Assuming the extreme value of $\delta^{13}C_{mantle}$ = −1‰ the dilution factor varies between 88‰ and 99% of a deep-seated CO_2 contribution in the TDIC in these mineral waters.

The influx of free ^{14}C to the studied mineral water systems must induce changes in the groundwater ages. The corresponding ^{14}C content (pmc) determined in these mineral water samples range from 4.3% up to 9.9%, pointing to the presence of very old groundwater systems (see Table 2).

Chaves hot mineral waters are characterized by the absence of ^3H (Table 1) and by a ^{14}C activity of 4.3 ± 0.4 pmc (Table 2). The issue temperature (76 °C) indicates the presence of a low-temperature geothermal system associated with a relatively deep circulation and consequently a long residence time (Aires-Barros et al., 1998). Nevertheless, admitting a residence time long enough to allow all ^3H decay, one would have to consider an influx of C, free of ^{14}C, to the water system. This assumption is based on the $\delta^{13}C$ signatures (−2.8 ± 0.1‰ *vs.* V-PDB) shown by Chaves hot CO_2-rich mineral waters and by the small concentrations of CO_2 in the recharge waters (derived from atmosphere

Table 2
^{14}C apparent groundwater age of Portuguese CO_2-rich mineral waters (data from Aires-Barros et al., 1998, referred to a fieldwork campaign carried out during 1987)

Local	$\delta^{13}C$ (TIDC) (‰ vs. PDB)	^{14}C (pmC)	CO_2 (mg/L)	Aparent age (ka ± σ)	$\delta^{18}O$ (‰ vs. V-SMOW)	δ^2H (‰ vs. V-SMOW)	^3H (TU)
Vilarelho da Raia (●)	−2.2	9.9 ± 0.4	900	5.24 ± 4.50	−8	−55.3	0.3
Chaves (○)	−2.8	4.3 ± 0.4	500	14.12 ± 3.73	−8.19	−55.9	0.3
Campilho (●)	−3.5	7.4 ± 0.6	1800	11.48 ± 3.14	n.a.	n.a.	n.a.
Sabroso (●)	−3	7.9 ± 0.5	2100	9.67 ± 3.50	−7.7	−53.1	0
Pedras Salgadas (●)	−1.2	4.4 ± 0.3	4300	6.93 ± 4.33	−7.15	−44.3	2.1

Notes: The age values were obtained using $\delta^{13}C$ content as a correction factor admitting a piston model for the system (Salem et al., 1980). (●) Cold CO_2 mineral water; (○) hot CO_2 mineral water; n.a. stands for not analysed.

or the geological environment). In fact, according to the C isotopic (^{14}C and δ^{13}C) signatures, one can state that the C in the TDIC should represent a mixture of different sources (e.g. deep-seated – upper mantle and/or carbonate dissolution), inducing lower ^{14}C values and consequently an older apparent groundwater age. In contrast, some of the cold (17 °C) mineral waters from Pedras Salgadas region, should be ascribed to local circulation systems (Aires-Barros et al., 1998; Marques et al., 2000; Andrade, 2003), characterized by the systematic presence of ^{3}H (Tables 1 and 2). In this case, the ^{3}H content found in the mineralised water systems are not in agreement with the ^{14}C values that were determined (see Table 2). The systematic presence of ^{3}H obtained in these systems could be related to:

(1) Mixture with the upper aquifer (shallow cold dilute groundwaters). However, this hypothesis seems unreliable. In fact, the ^{14}C content in the mineral waters would be rather higher. Mook (2000) gave the radiocarbon content in shallow aquifers as close to 80 pmc.
(2) The ^{3}H production at depth, derived from the rock matrix. According to Geyh (2000), in highly saline groundwaters, with high U, Th and Li content, underground ^{3}H production via B, results in ^{3}H activity levels up to 0.5 TU. On the other hand, Moser et al. (1989), during a study of Stripa groundwater (Sweden), considered a ^{3}H source associated to underground production in the granite. These authors showed an isotopic homogeneity (over 5 a) of ^{3}H data in water samples collected at 850 m depth. It is important to mention that in the studied cold CO_2-rich Portuguese mineral waters the ^{3}H content reveals no isotopic homogeneity (see Table 1), pointing to a negligible ^{3}H production at depth in these groundwater systems.
(3) On the other hand, the ^{3}H concentrations in the regional precipitation (arithmetic mean of the weight annual mean) are in the order of 5 TU (Porto = 4.5 TU; Vila Real = 6.4 TU; ITN database, both meteorological stations from the Portuguese Network Isotopes in Precipitation initiated in 1988, in collaboration with the International Atomic Energy Agency). Using these data and considering (i) the half-life of the ^{3}H (12.32 a; Lucas and Unterweger, 2000); (ii) the ^{3}H content measured in the CO_2-rich mineral waters (Table 1) and (iii) the
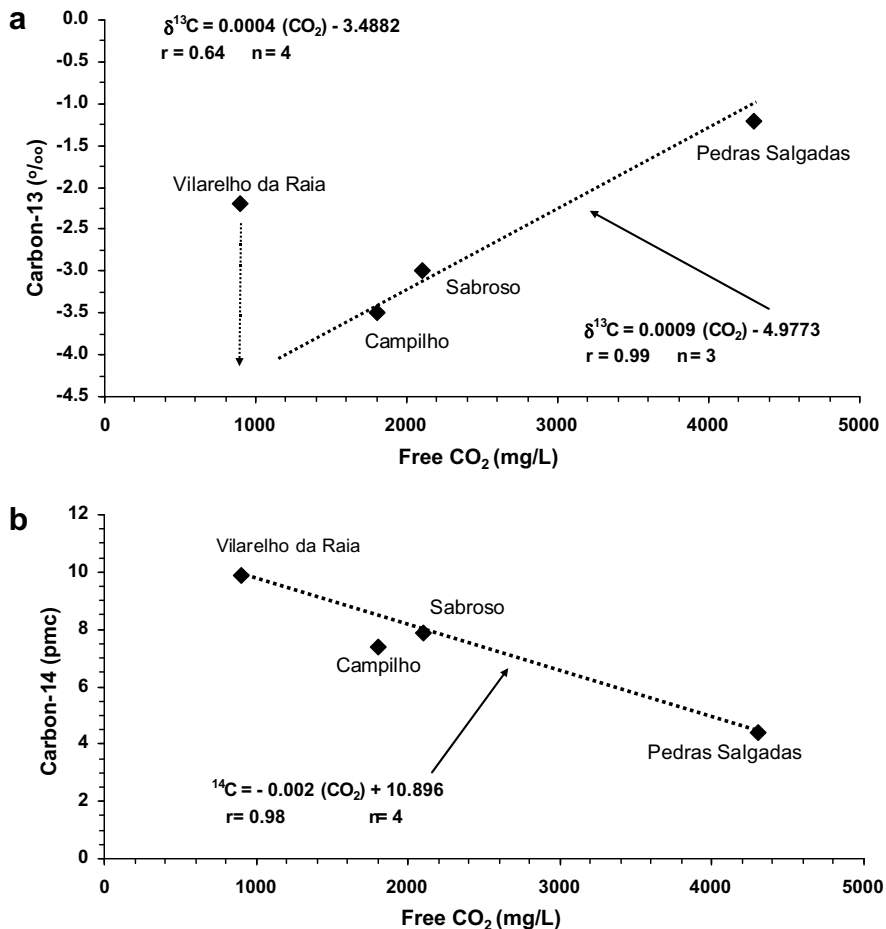

Fig. 5. (a) ^{13}C *vs.* free CO_2 and (b) ^{14}C *vs.* free CO_2 in the studied cold CO_2-rich mineral waters. Data from Aires-Barros et al. (1998).

[3]H input (precipitation data) one can classify those CO_2-rich mineral waters as modern waters. On the other hand, the hot CO_2-rich mineral waters displaying the lowest ^{3}H content should be viewed as the oldest groundwaters, ascribed to longer and deeper underground flowpaths.

In Fig. 5 the relationships (a) ^{13}C vs. free CO_2 content and (b) ^{14}C vs. free CO_2 content of the cold mineral waters is presented. The correlation coefficients obtained (r = 0.64 for ^{13}C vs. free CO_2; r = 0.98 for ^{14}C vs. free CO_2) seems to corroborate the hypothesis of a common CO_2 origin ascribed to a ^{14}C-free source. The obtained $\delta^{13}C$ values in the mineralised waters range from −3.5‰ to −1.2‰. This range fits between the values of magmatic CO_2 and C from marine limestones. A simple interpretation of the data could suggest mixing of magmatic CO_2 and CO_2 derived from limestones. An alternative interpretation is that the $\delta^{13}C$ values of the CO_2 (of magmatic origin) are shifted to less negative values (e.g. Vilarelho da Raia, see Fig. 5) due to fractionation at low temperature. Fractionation could take place during the exsolution of dissolved CO_2. Depending on temperature, chemistry of the waters and isotope exchange kinetics, the escaping CO_2 could be up to 8‰ heavier than the remaining C (e.g. HCO_3) (Faure, 1986). So, CO_2 exsolution should be considered as a very effective process in changing $\delta^{13}C$ values of the water. Carbon dioxide exsolution may occur at depth, but it is likely that most of it occurs at or close to the surface, not surprising in view of the travertine deposits found around some of the studied spring waters.

To investigate the possible contribution of carbonate-dissolution at depth (see Fig. 4) to the origin of CO_2 in the studied mineral waters, a fieldwork campaign was performed in order to collect carbonate rocks (from local outcrops in the south of the Pedras Salgadas area) and mineral water samples for Sr isotopic measurements (Marques et al., 2001a; Andrade, 2003). This approach was considered because Sr can replace Ca in carbonate minerals. Strontium isotopic signatures ([87]Sr/[86]Sr) can be used to identify the extent of water–rock interactions (Stettler, 1977; Stettler and Allègre, 1978; Goff et al., 1991; Dogramaci et al., 1998). The studied CO_2-rich hot and cold mineral waters show an [87]Sr/[86]Sr ratio evolution from 0.728033, in the northern part of the studied area, to a less radiogenic value of 0.716754 at the southern part of the area. These values are rather different from the [87]Sr/[86]Sr value of 0.709485 measured on the carbonate whole-rock samples (precision of 0.000014) indicating that the contribution of carbonate rock dissolution at depth to the C isotopic signatures of the CO_2-rich mineral waters should be considered rather limited or even non-existent (Marques et al., 2001a; Andrade, 2003)

Recently, under the scope of a new research project, the isotopic ratio of He and C ([3]He/[4]He, $\delta^{13}C$) and the geochemical composition of the gas phase of the CO_2-rich mineral waters were used to identify contributions of deep crustal and mantle volatile components associated with the "Chaves Depression" tectonics. The ratio [3]He/[4]He measured in the gas phase range from 0.89 in Chaves waters to 2.68 in Pedras Salgadas waters. The values obtained

are higher than those expected assuming an unique crustal source (∼0.02 Ra), pointing to the presence of a magmatic He component (Carvalho et al., 2006). It was concluded that the isotopic ratios indicate that 10–30% of the gases are from the upper mantle and CO_2/[3]He ratios of these mineral waters range between 5.1×10^8 and 7.5×10^9. The values obtained are typical of MORB fluids (1×10^9 and 7×10^9; Marty and Jambon, 1987).

5. Conclusions

As a result of the different ^{14}C influxes to the groundwater systems there is some scepticism about the validity or reliability of ^{14}C groundwater ages. In the present case of the Portuguese CO_2-rich mineral waters, ^{14}C age determinations have been used with caution since the results obtained pointed to the contribution of deep CO_2 (^{14}C-free). In Chaves hot (76 °C) CO_2-rich mineral waters the absence of ^{3}H and high issue temperature points to a deep and long circulation path through the subsurface rocks. In contrast, the systematic presence of ^{3}H in the cold (17 °C) CO_2-rich mineral waters from the Pedras Salgadas area indicates local circulation systems with relatively short residence times. The apparent ^{14}C groundwater ages are close to 9 ka BP, which are not in agreement with the ^{3}H content.

According to the $\delta^{13}C$ content of these CO_2-rich mineral waters, one can accept that most C in these mineral water systems could be ascribed to a deep-seated (upper mantle) source. The most probable explanation by which the CO_2 could be transported from its deep source to the surface involves migration as a separate gas phase being incorporated in the infiltrated meteoric waters (at considerable depth in the case of the hot CO_2-rich mineral waters and at shallow levels in the case of cold CO_2-rich mineral waters).

The suggested approach seems to indicate that radiocarbon application in dating old groundwaters, as an end itself, does provide a more a useful and meaningful framework for time scales in water fluxes, such as recharge, horizontal flow rates and discharge, extremely important in hydrological investigations. Nevertheless, the results obtained with ^{14}C-dating although having some uncertainties, could be usefull for groundwater management. A good knowledge of the mineral water systems, following-on from previous works, is a pre-requisite to make sound conclusions on the values and use of C isotope data in each particular situation.

Recently, a research and development project was launched and new approaches to the study of the nature of this group of CO_2-rich mineral waters will be applied, with special emphasis on the geochemistry of the gaseous phase associated with this group of mineral waters. The quantification of the chemical (CO_2, H_2S, H_2, CH_4, C_2H_6, NH_3, N_2, O_2, Ar, He) and isotopic (^{3}H/[3]He and [3]He/[4]He) composition of the gaseous phase will contribute to improve knowledgement on the origin of the studied mineral waters.

References

Aires-Barros, L., Marques, J.M., Graça, R.C., 1995. Elemental and isotopic geochemistry in the hydrothermal area of Chaves/Vila Pouca de Aguiar (Northern Portugal). Environ. Geol. 25, 232–238.

Aires-Barros, L., Marques, J.M., Graça, R.C., Matias, M.J., van der Weijden, C.H., Kreulen, R., Eggenkamp, H.G.M., 1998. Hot and cold CO_2-rich mineral waters in Chaves geothermal area (northern Portugal). Geothermics 27, 89–107.

Almeida, F.M., 1982. Novos dados geotermométricos sobre águas de Chaves e de S. Pedro do Sul. Comun. Serv. Geol. Portugal 68, 179–190.

Andrade, M.P.L., 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. MSc Thesis, Technical Univ. Lisbon, Instituto Superior Técnico.

Andrade Afonso, A.R., Monteiro Santos, F.A., Mendes-Victor, L.A., 1994. The resistivity method in the evaluation of geothermal resources. Application to Chaves geothermal field. In: Proc. Symp. Geothermics 94 in Europe (Eds. BRGM), 230, pp. 43–50.

Baptista, J., Coke, C., Dias, R., Ribeiro, A., 1993. Tectónica e geomorfologia da região de Pedras Salgadas/Vidago e as nascentes minerais associadas. Comun. XII Reun. Geol. Oeste Peninsular 1, 125–139.

Bergfeld, D., Goff, F., Janik, C.J., 2001. Carbon isotope systematics and CO_2 sources in the Geysers-Clear Lake region, northern California, USA. Geothermics 30, 303–331.

Brink, A.H., 1960. Petrology and ore geology of the Vila Real – Sabrosa – Vila Pouca de Aguiar region, northern Portugal. Comun. Serv. Geol. Portugal, XLIII.

Carvalho, M.R., Carreira, P.M., Marques, J.M., Capasso, G., Grassa, F., Antunes da Silva, A., Matias, M.J., 2006. Carbon and helium isotopes in gases of CO_2-rich hydromineral systems associated to Régua-Verin tectonic feature. In: VII Congresso Nacional de Geologia, Évora, Portugal, vol. II, pp. 533–536.

Changkume, I., Aranyossy, J.L., Oleas, M., Lopoukine, M., 1989. Determinacion del modelo geotermico del Valle de los Chillos (Ecuador), en base a isotopos ambientales. TECDOC – 502, Isotope Hydrology Investigations in Latin America. In: Proc. regional seminar for Latin America on the use of isotope techniques in Hydrology, organized by IAEA, pp. 291–303.

Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis Publishers, New York.

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. Geochim. Cosmochim. Acta 50, 1573–1582.

Dogramaci, S.S., Herczeg, A.L., Bone, Y., 1998. $^{87}Sr/^{86}Sr$ in groundwaters as indicators of carbonate dissolution. In: Arehart, G.B., Hulstron, J.R. (Eds.), Proc. 9th Internat. Symp. Water–Rock Interaction – WRI-9/Taupo, New Zealand. A.A. Balkema, Rotterdam, pp. 211–214.

Dörr, H., Münnich, K.O., 1980. Carbon-14 and carbon-13 in soil CO_2. Radiocarbon 22, 909–918.

Dörr, H., Münnich, K.O., 1987. Annual variations in soil respiration in selected areas of the temperate zone. Tellus 39B, 114–121.

Duque, R., Monteiro Santos, F.A., Mendes-Victor, L.A., 1998. Heat flow and deep temperatures in the Chaves Geothermal system, northern Portugal. Geothermics 27, 75–87.

Ellis, A.J., Mahon, W.A.J., 1977. Chemistry and Geothermal Systems. Energy Science and Engineering: Resources, Technology, Management. An International Series, Academic Press.

Epstein, S., Mayeda, T., 1953. Variation of ^{18}O content of waters from natural sources. Geochim. Cosmochim. Acta 4, 213–224.

Faure, G., 1986. Principles of Isotope Geology, second ed. John Wiley & Sons.

Fontes, J.Ch., Garnier, J.M., 1979. Determination of the initial activity of the total dissolved carbon. A review of existing models and a new approach. Water Resour. Res. 12, 399–413.

Friedman, I., 1953. Deuterium content of natural waters and other substances. Geochim. Cosmochim. Acta 4, 89–103.

Gallagher, D., McGee, E.J., Kalin, R.M., Mitchell, P.I., 2000. Performance of models for radiocarbon dating of groundwater: an appraisal using selected Irish aquifers. Radiocarbon 42, 235–248.

Geyh, M., 2000. Environmental isotopes in hydrological cycle. Principles and applications. IHP-V, Technical Documents in Hydrology, No. 39, vol. IV.

Goff, F., Wollenberg, H.A., Brookins, D.C., Kristler, R.W., 1991. A Sr-isotopic comparasion between thermal waters, rocks, and hydrothermal calcites, Long Valley caldera, California. J. Volc. Geotherm. Res. 48, 265–281.

Gonfiantini, R., 1988. Carbon isotope exchange in karst groundwater. In: 21st Congress on Karst Hydrology and Karst Environment Protection, vol. XXI. Part 2 (Ed. Association of Hydrological Sciences), Guilin, pp. 832–837.

Greber, E., 1994. Deep circulation of CO_2-rich palaeowaters in a seismically active zone (Kuzuluk/Adaparazi, northwestern Turkey). Geothermics 23, 151–174.

Hesterberg, R., Siegenthaler, U., 1991. Production and stable isotopic composition of CO_2 in a soil near Bern, Switzerland. Tellus 43B, 197–205.

Horvatincic, N., Srdoc, D., Krajcar Bronic, I., Pezdic, J., Kapelj, S., Sliepcevic, A., 1996. A study of geothermal waters in northwest Croatia and east Slovenia. Isotopes in Water Resources Management, vol. 2, IAEA, pp. 470–474.

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

Lucas, L.L., Unterweger, M.P., 2000. Comprehensive review and critical evaluation of the half-life of tritium. J. Res. Nat. Inst. Standards Technol. 105, 541–549.

Marques, J.M., Aires-Barros, L., Graça, R.C., 1996. The origin and relation among hot and cold CO_2-rich mineral waters in Vilarelho da Raia–Pedras Salgadas region, northern Portugal: a geochemical approach. Geotherm. Resour. Council Trans. 20, 363–369.

Marques, J.M., Andrade, M., Aires-Barros, L., Graça, R.C., Eggenkamp, H.G.M., 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: Seiler, K.P., Wohnlich, S. (Eds.), New Approaches Characterizing Groundwater Flow. A.A. Balkema, pp. 1025–1029.

Marques, J.M., Carreira, P.M., Aires-Barros, L., Graça, R.C., 1998. About the origin of CO_2 in some $HCO_3/Na/CO_2$-rich Portuguese mineral waters. Geotherm. Resour. Council Trans. 22, 113–117.

Marques, J.M., Carreira, P.M., Aires-Barros, L., Graça, R.C., 2000. Nature and role of CO_2 in some hot and cold $HCO_3/Na/CO_2$-rich Portuguese mineral waters: a review and interpretation. Environ. Geol. 40, 53–63.

Marques, J.M., Monteiro Santos, F.A., Graça, R.C., Castro, R., Aires-Barros, L., Mendes Victor, L.A., 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. Hydrogeol. J. 9, 584–596.

Marty, B., Jambon, A., 1987. $C/^3He$ in volatile fluxes from the solid Earth: implications for carbon geodynamics. Earth Planet. Sci. Lett. 83, 16–26.

Monteiro Santos, F.A., 1994. Interpretação integrada de dados de resistividade e magneto-telúrica: aplicação ao estudo de reservatórios geotérmicos de baixa entalpia. PhD Thesis, Univ. Lisboa.

Mook, W.G., 2000. Environmental isotopes in hydrological cycle. Principles and applications. IHP-V, Technical Documents in Hydrology (UNESCO/IAEA) No. 39, vol I.

Mook, W.G., Bommerson, J.C., Staverman, W.H., 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. Earth Planet. Sci. Lett. 22, 169–176.

Moser, H., Wolf, M., Fritz, P., Fontes, J-Ch., Florkowski, T., Payne, B., 1989. Deuterium, oxygen-18 and tritium in Stripa groundwater. Geochim. Cosmochim. Acta 5, 1757–1763.

Pérez, N.M., Nakai, S., Wakita, H., Albert-Bertrán, J.F., Redondo, R., 1996. Preliminary results on $^3He/^4He$ isotopic ratios in terrestrial fluids from Iberian Peninsula: seismoctectonic and neotectonic implications. Geogaceta 20, 830–833.

Portugal Ferreira, M., Sousa Oliveira, A., Trota, A.N., 1992. Chaves geothermal pole. Geological Survey, I and II. Joule I Program, DGXII, CEE. UTAD/Universidade de Trás-os-Montes e Alto Douro (internal report).

Reardon, E.J., Allison, G.B., Fritz, P., 1979. Seasonal chemical and isotopic variations of soil CO_2 at Trout Creek, Ontario. J. Hydrol. 43, 355–371.

Salem, O., Visser, J.M., Dray, M., Gonfiantini, R., 1980. Groundwater flow patterns in the western Libyan Arab Jamahiriya evaluated from isotopic data. In: IAEA (Eds.), Arid-Zone Hydrology: Investigation with Isotope Techniques, pp. 165–179.

Schermerhorn, L.J.G., 1956. The age of the Beira Schists (Portugal). Bol. Soc. Geol. Portugal XII (1/2), 77–100.

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

Sousa Oliveira, A., 1995. Hidrogeologia da Região de Pedras Salgadas. Provas de Aptidão Pedagógica e Capacidade Científica. Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal.

Sousa Oliveira, A., Portugal Ferreira, M.P., 1995. Controlo estrutural das emergências hidrominerais da região de Pedras Salgadas (Vila Pouca de Aguiar – Norte de Portugal). Universidade do Porto, Faculdade de Ciências Museu e Laboratório Mineralógico e Geológico. Memória 4, 485–489.

Stettler, A., 1977. ^{87}Rb–^{87}Sr systematics of a geothermal water–rock association in the Massif Central, France. Earth Planet. Sci. Lett. 34, 432–438.

Stettler, A., Allègre, C.J., 1978. ^{87}Rb-^{87}Sr studies of waters in a geothermal area, the Cantal, France. Earth Planet. Sci. Lett. 38, 364–372.

Truesdell, A.H., Hulston, J.R., 1980. Isotopic evidence on environments of geothermal systems. In: Fritz, P., Fontes, J.-Ch. (Eds.), Handbook of Environmental Isotope Geochemistry, vol. 1, The Terrestrial Environment, pp. 179–226.

Van der Borg, K., Alderliesten, C., Haitjema, H., Hut, G., Van Zwol, N.A., 1984. The Utrecht accelerator facility for precision dating with radionuclides. Nucl. Instrum. Meth. Phys. Res. B 5, 150–154.

Van der Borg, K., Alderliesten, C., Houston, C.M., De Jong, A.F.M., Van Zwol, N.A., 1987. Accelerator mass spectrometry with ^{14}C and ^{10}Be in Utrecht. Nucl. Instrum. Meth. Phys. Res. B 29, 143–145.

Wang, J.-Y., Pang, Z.-H., 1995. Application of isotope and geochemical techniques to geothermal exploitation in southeast – A review. IAEA – TECDOC – 788, Isotope and geochemical techniques applied to geothermal investigations, pp. 9–20.