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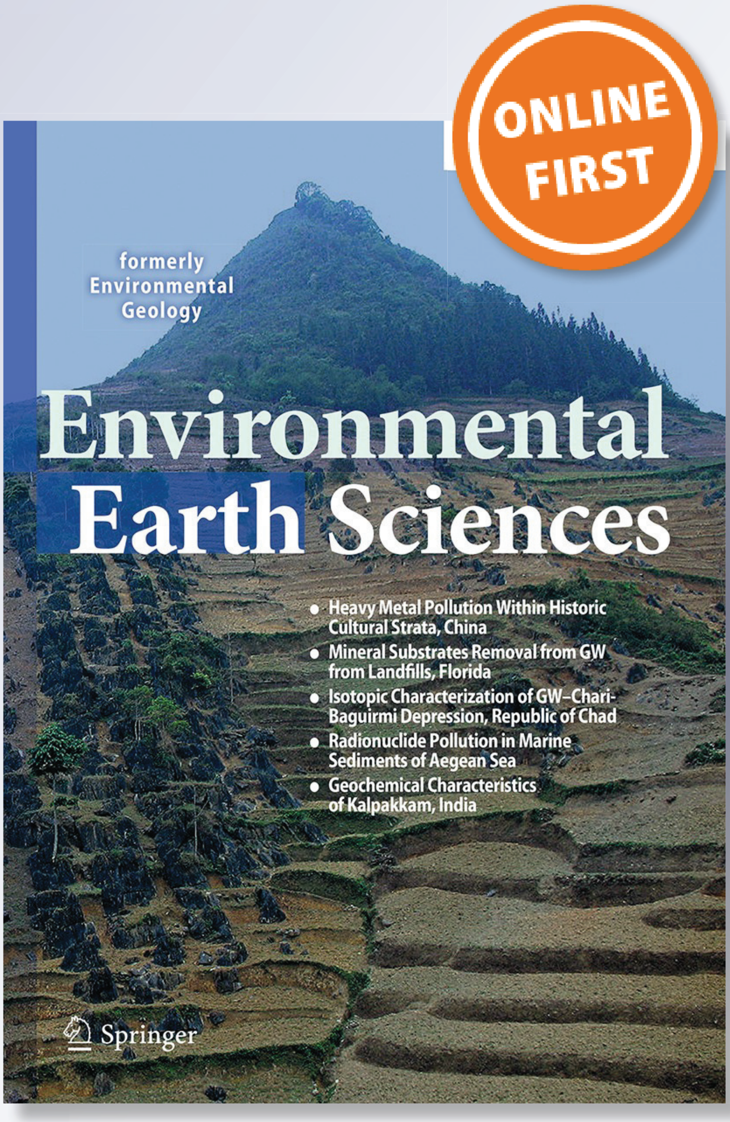

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ORIGINAL ARTICLE

Carbon isotopes and geochemical processes in CO_2-rich cold mineral water, N-Portugal

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Abstract This paper summarizes a new outlook on the conceptual model of Melgaço–Messegães CO_2-rich cold (≈ 18 °C) mineral water systems, issuing in N of Portugal, based on their isotopic (^{2}H, ^{3}H, ^{13}C, ^{14}C and ^{18}O) and geochemical features. Stable isotopes indicate the meteoric origin of these CO_2-rich mineral waters. Based on the isotopic fractionation with the altitude, a recharge altitude between 513 up to 740 m a.s.l. was estimated, corroborating the tritium results. The lowest ^{3}H content (0 TU) is found in the groundwater samples with the highest mineralization. The mineral waters circulation are mainly related to a granitic and granodioritic environment inducing two different groundwater types (Ca/Na–HCO_3 and Na/Ca–HCO_3), indicating different underground flow paths. Calcium dissolution is controlled by hydrolysis of rock-matrix silicate minerals (e.g. Ca-plagioclases) and not associated to anthropogenic sources. The shallow dilute groundwaters exhibit signatures of anthropogenic origins (e.g. NO_3) and higher Na/Ca ratios. The stable isotopes together with the geochemistry provided no indication of mixing between the regional shallow cold dilute groundwater and mineral water systems. The heavy isotopic signatures identified in the δ^{13}C data ($\delta^{13}C = 4.7$ ‰, performed on the total dissolved inorganic carbon (TDIC) of CO_2-rich mineral waters) could be derived from a deep-seated (upper mantle) source or associated to methanogenesis (CH_4 source). The negligible ^{14}C content (≈ 2 pmC) determined in the TDIC of the mineral waters, corroborates the hypothesis of a mantle-derived carbon source to the mineral groundwater systems or dissolution of carbonate layers at depth.

Keywords CO_2-rich mineral waters · Environmental isotopes · Geochemistry · Conceptual model · Groundwater sustainability · N-Portugal

Introduction

In this study, the CO_2-rich mineral groundwater systems are located in the Iberian Massif at the NW part of Portuguese mainland inside of the Galicia–Trás-os-Montes Zone and, the geological environment comprised Variscan granites and granodiorites (Farías et al. 1987; Ribeiro et al. 1990) (Fig. 1).

Over the last few decades, local groundwater resources in this study area have become progressively more endangered, both in quality and quantity, by accelerated modification of their natural conditions by industry (mineral bottled waters) and agricultural activities (Nascimento 2000; Carreira et al. 2005a, b; Carreira et al. 2007). In order to update knowledge on Melgaço–Messegães CO_2-rich

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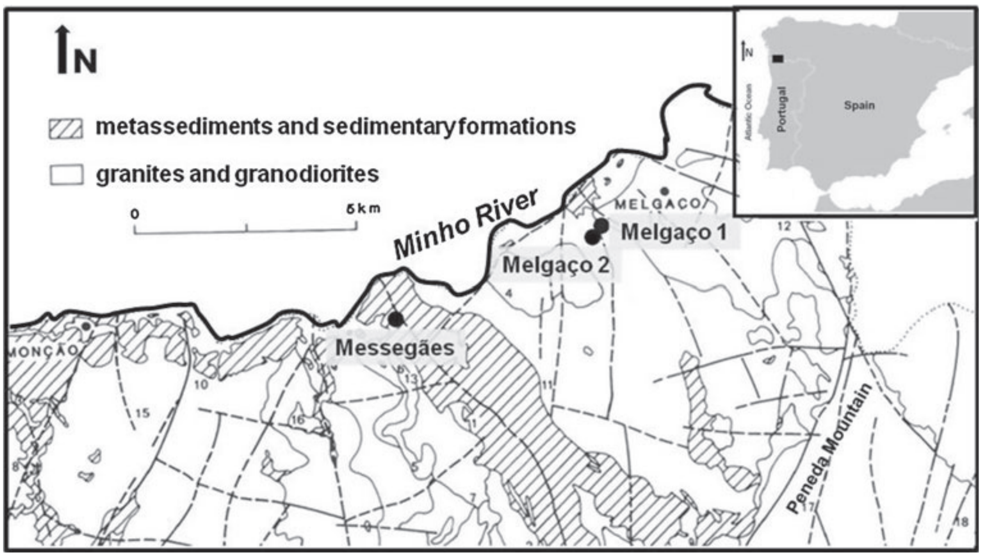


Fig. 1 Simplified geological map of the region. *Filled circle* the location of the mineral borehole waters. Adapted from Ribeiro and Moreira (1986)

mineral groundwater systems, emphasis was set on the definition of the recharge areas, underground flow paths and identification of possible mixing between shallow dilute waters and deep mineral water systems based on geochemical and isotope fingerprints. Moreover, radiocarbon and ^{13}C content analyses were performed to identify the origin of the CO_2 gas present in these systems.

Environmental isotope methodologies have been applied successfully in many regional and local investigations in order to understand the origin, flow paths, mean residence time and to identify water–rock mechanisms occurring within the aquifer systems. Sodium bicarbonate CO_2-rich mineral waters have been described from different regions of the globe in different geological environments in several continents from Europe—France, Germany, Czech Republic and Spain (Griesshaber et al. 1992; Pérez et al. 1996; Pauwels et al. 1997; Cerón et al. 1999; Rihs et al. 2000; Krásný 2001, 2007) to Australia, China and USA (Chapelle and Knobel 1985; Schofield and Jankowski 2004; Xumei et al. 2009). Within the different studies and the different geochemical approaches, the isotopic composition of CO_2 in mineral waters is an effective indicator of the carbon sources such as magmatic degassing, oxidation of organic matter and interaction of water with sedimentary carbonates and/or metamorphic devolatilisation (Cerón et al. 1998, 2000; Giggenbach 1992; Giggenbach and Corrales-Soto 1992; Griesshaber et al. 1992).

Several attempts have been made on these particular hydrogeological systems to use carbon-14 as a groundwater dating tool. The use of the total dissolved inorganic carbon (TDIC) present in the water samples is not easy, due to the incorporation of old carbon of different origins (Changkuon et al. 1989; Wang and Pang 1995; Horvatincic et al. 1996; Carreira et al. 2008; Jiráková et al. 2010). Small quantities of CO_2 in the recharge waters, derived from the atmosphere or the soil environment, exhibit high percentages of modern carbon (pmC), close to 100 pmC for ^{14}C (Clark and Fritz 1997). Under confined situations the radiocarbon signatures may be changed by CO_2 sources with 0 pmC, either from dissolution of the carbonate rock matrix, from thermal metamorphism or magma sources (Truesdell and Hulston 1980).

This paper presents a re-evaluation and discussion of the data obtained in different field work campaigns performed in Melgaço–Messegães mineral water systems (NW-Portugal) through the application of environmental radioisotopes (^{14}C and ^{3}H), not only as groundwater dating tools, but also to identify the origin of carbon, together with the oxygen-18, deuterium, carbon-13 and geochemical data, to foster knowledge and understanding on the hydrogeological conceptual circulation model of this type of groundwater resources, fundamental to their proper management and sustainability. Furthermore, in the studied region Spas and bottled water industry are an important issue of local and regional development. The present work aims not only on updating the geochemical evolution of CO_2-mineral waters but also on the use of environmental isotopic signatures as a hydrogeological tool in the evaluation of the groundwater resources of the region, increasing our knowledge on groundwater flow circulation paths. Characterization of these waters is important in the assessment of local/regional low-temperature geothermal resources, trying to determine whether the carbon dioxide waters should be considered (or not) surface manifestations of a large-scale deep-seated hydrothermal system.

Geological and geomorphological setting

Several authors have described in detail the geology of the region (e.g. Ribeiro and Moreira 1986; Moreira and Simões

1988). According to these authors, three types of granitic rocks can be distinguished locally, based on their structural relationships and internal deformation. Thus, this group of rocks can be divided into:

1. syn-tectonic granites with minute flakes of muscovite and biotite, usually presenting metamorphic minerals, and strongly correlated with migmatitic rocks;
2. late-tectonic granites (frequently associated with granodiorites), with abundant biotite and muscovite as a secondary mineral. The deformation indicates an origin associated with the last Hercynian deformation phase; and
3. post-tectonic granites: usually characterized by the presence of mega-crystals of K-feldspar and biotite. The absence of metamorphic minerals in these granites suggests an age younger than the last Hercynian deformation phase (Ferreira et al. 1987). The most recent formations in the region correspond to fluvial deposits, sandstones and conglomerates of Quaternary age, particularly found along the Minho River banks. The main fracture systems in the region are represented by structural lineaments (strike–slip faults), oriented ENE–WSW, WNW–ESE, NNE–SSW and NNW–SSE (Fig. 1), of late Hercynian age, and still active during the Meso-Cenozoic (Soares de Carvalho 1992).

The research region is part of the Iberian Plateau, or Central Plateau, composed by Precambrian and Palaeozoic formations affected by various stages of the Alpine tectonic (fracturing) activity. The regional morphology is marked by the contrast between the high plateaus at the top of individual remnant blocks and the carved valleys that follow a rigid pattern controlled by fractures. These geomorphologic features can be easily identified, ranging from 100 m a.s.l. by the Minho River to altitudes on the order of 800–900 m a.s.l. in the SE part of the region. The major topographic units in the region are directly associated with individual fractures (ENE–WSW to E–W; N–S and NW–SE). The geological studies carried out in the region have pointed out that the ENE–WSW fracture system (left strike–slip fault) is responsible for the morphology of the Minho River valley. Melgaço and Messegães mineral borehole waters issue along NNW–SSE fractures where the appropriate conditions are present.

Sampling collection and analysis

Three fieldwork campaigns were carried out during February 2002, and February/July 2006. Groundwater samples were collected from boreholes (mineral system) and from springs (located at different altitude sites within the surroundings of the research region) representative of the shallow dilute groundwater systems. Chemical analyses were performed at IST (CEPGIST), Portugal, for major dissolved species determination using the following methods: atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na and K; 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^- (Table 1).

Stable isotope composition was determined at ITN, Portugal. The δ^2H and $\delta^{18}O$ measurements (vs. V-SMOW) were performed by mass spectrometry (SIRA 10—VG ISOGAS) following the analytical methods of Friedman (1953) and Epstein and Mayeda (1953), with an accuracy of ±1 ‰ 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 liquid scintillation counting (standard deviation varies between ±0.6 and ±1.1 TU, depending on tritium content in the water sample. The $\delta^{13}C$ and ^{14}C determinations were performed at the Geochron Laboratories, USA, by AMS. The $\delta^{13}C$ values are reported in ‰ vs. V-PDB, with an accuracy of ±0.1 ‰. The ^{14}C content is given in pmC (percentage of modern carbon) and the error associated with these measurements is presented in Table 2 together with the other isotopic results.

Results and discussion

Groundwater geochemistry

The physical–chemical analytical data of mineral and dilute groundwater samples collected during the field work campaigns are displayed in Table 1. There is a correlation between the groundwater temperature and the time of the year, for shallow diluted waters and Messegães hydromineral system, that varies from 15.0 °C in February to 18.3 °C during the July 2006 campaign, reflecting the air temperature seasonal variation and indicating relatively shallow mineral systems. The temperature fluctuation is not evident at the Melgaço CO_2-rich mineral groundwater system, indicating deeper circulation, compared to the Messegães hydromineral system. Two groups of waters can be identified (Table 1), based on the electrical conductivity and dry residuum (DR). The high water mineralization measured in Melgaço–Messegães CO_2-rich mineral systems is associated with DR values ranging from 365 to 1,515 mg/L, while shallow dilute groundwaters exhibit DR values between 24 to 120 mg/L. Such a difference is also observed within the electrical conductivity data (Table 1). Also, both groundwater systems (mineral and shallow dilute) present dissimilar chemical facies Melgaço and

Messegães CO_2-rich mineral waters are Ca/Na–HCO_3 and Na/Ca–HCO_3-type waters, respectively, while the shallow dilute groundwater systems are Na–HCO_3-type waters (Fig. 2).

Na and Ca concentrations in natural waters are usually derived by feldspar hydrolysis in granitic environments, supported by the Na–HCO_3 nature of the waters. The high dissolved CO_2 in the mineral waters can act as a promoter of water–rock interaction processes, even more than the temperature at depth (Greber 1994). However, the Ca/Na–HCO_3 type of Melgaço and Messegães mineral waters, suggests different underground flow paths (fissure environments) and residence times, with different calcium availability in the aquifer matrix, probably associated with the hydrolysis of Ca-rich plagioclases occurring in granodioritic terrains (Ribeiro and Moreira 1986; Farías et al. 1987).

Many geologic and geochemical investigations, carried out in granitic regions, have demonstrated that the hydrolysis of rock-forming silicate minerals is an important process that controls the chemical composition of natural waters (Bowser and Jones 2002). This idea has long been the focus in relating the silicate mineral weathering by hydrolysis, to global geochemical cycling of elements and their response to natural and human-induced climate change, controls on the chemistry of groundwater, soil water, rivers and streams, and the fundamental chemical and physical mechanisms involved in silicate mineral dissolution and their rates under natural condition (Bowser and Jones 2002). In the Melgaço–Messegães system, considerable attention has been put on the consequences of rock weathering to the dynamics and the dissolved species within the mineral groundwater systems. The dilute shallow groundwaters have a relatively small residence time in the aquifer, as they represent local circulation groundwater systems, with strong seasonal variations.

The silicate alteration reactions, responsible for geochemical evolution trends in the groundwaters systems, are relatively slow. The CO_2-rich mineral waters exhibit systematic compositional trends ranging from low concentration acidic waters, rich in dissolved CO_2, to mineralized neutral bicarbonate waters that usually contain less dissolved CO_2 (May 2005). According to this author, the progressive evolution of water composition can be observed in regional water analyses. However, the rather small regional dimensions of this study make it difficult to clearly observe this trend in the groundwater geochemical evolution. May (2005) mentioned that: (1) the mass balances calculated for CO_2-rich waters give no evidence for non-conservative behaviour of solutes (e.g. Na) under a variety of weathering conditions in silicate terrains; and (2) that the Ca/Mg ratio in waters of crystalline watersheds depends on the Na/Ca ratios of plagioclase and the Fe/Mg and Ca/Mg

Table 1 Physico-chemical composition of mineral and dilute groundwaters from the Melgaço–Messegães region

Sampling campaign	Reference	"in situ" determinations				Concentrations in mg/L												
		Temp (°C)	pH	Cond (µS/cm)	Eh (mV)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al^{3+}	Fe_{total}	Li^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	SiO_2	DR
10/1999	B. Milagres[a,b]	16.0	6.13	162	260	6.7	3.5	17.8	1.8	n.a	n.d	n.d	12.2	9.7	1.7	23.8	24.4	119.6
	S. Caetano[a,b]	13.3	5.30	62	246	0.8	0.6	10.5	2.1	n.a	0.08	n.d	8.1	1.2	9.2	4.2	22.8	59.2
02/2002	Melgaço 2[c]	19.2	6.22	1440	−21	181.5	39.0	108.0	4.7	0.7	10.2	0.80	1272.0	7.9	10.8	0.6	54	939.2
	Melgaço 1[c]	17.0	6.13	582	−94	62.0	12.5	42.0	2.7	0.2	3.5	0.36	420.2	6.7	10.2	1.6	37.9	364.8
	Messegães[c]	15.3	6.25	2070	−36	188.0	27.0	214.0	9.9	0.4	7.0	1.10	1653.0	1.4	12.0	2.3	59.8	1260.4
	B. Milagres[a]	14.4	6.55	114	154	4.0	1.65	11.6	1.3	n.d	n.d	n.d	15.2	8.5	9.0	9.2	9.8	87.2
02/2003	S. Caetano[a]	11.7	5.12	80	285	1.4	0.85	9.2	1.0	0.1	n.a	0.02	15.8	1.4	10.4	3.4	9.4	54.8
	N.S. Bonfim[a]	13.1	4.48	39	262	1.0	0.3	3.8	0.2	0.1	n.a	0.02	14.2	0.3	5.1	1.3	2.9	24.2
	B. Milagres[a]	12.8	5.78	122.7	307	5.0	2.0	12.0	1.4	0.1	n.a	0.02	8.1	7.4	13.8	12.8	9.4	84.8
03/2006	Melgaço 2[c]	19.1	5.72	1360	73	166.9	41.9	92.3	4.2	0.6	2.2	1.51	1196.8	9.4	12.6	1.9	58.6	945.4
	Melgaço 1[c]	17.2	5.72	654	115	72.7	13.9	47.0	2.5	0.2	0.1	1.16	523.5	7.3	10.8	1.3	42.6	447.6
	Messegães[c]	15.0	6.22	1750	86	176.6	24.3	201.7	8.4	0.7	0.1	1.70	1579.8	1.3	16.3	0.2	64.2	1263.8
07/2006	Melgaço 2[c]	20.4	5.76	1523	56	160.2	32.1	61.6	4.1	n.a	n.a	2.1	1189.4	7.9	12.8	0.3	62.7	986.4
	Melgaço 1[c]	18.6	5.56	758	108	70.1	16.6	41.5	2.8	n.a	n.a	1.8	522.2	7.6	11.7	n.a	45.1	516.8
	Messegães[c]	18.3	6.28	1956	41	196.8	45.4	272.2	16.4	n.a	n.a	4.6	1531.9	1.6	21.9	n.a	69.3	1514.8

Cond electrical conductivity, *DR* dry residuum, *n.a* not analysed, *n.d* not detected (below detection limit)

[a] Dilute water springs, [b] data from Nascimento (2000), [c] mineral waters

Table 2 Isotopic composition of mineral and shallow dilute groundwaters from Melgaço–Messegães region

Reference	Sampling campaign	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	$^{3}H \pm \sigma$ (TU)	$^{14}C \pm \sigma$ (pmC)	$\delta^{13}C$ (‰)
B. Milagres[a,b]	10/1999	−5.10	−30.0	5.2 ± 1.0		
S. Caetano[a,b]		−5.01	−27.7	4.8 ± 1.1		
Melgaço 2[c]	02/2002	−5.69	−33.6	n.d		
Melgaço 1[c]		−5.37	−34.6	2.2 ± 0.6		
Messegães[c]		−5.70	−31.1	n.d		
B. Milagres[a]		−4.66	−27.3	3.2 ± 0.6		
S. Caetano[a]	02/2003	−5.19	−33.6	2.1 ± 0.6		
N.S. Bonfim[a]		−5.50	−36.8	2.4 ± 0.5		
B. Milagres[a]		−4.81	−26.5	2.6 ± 0.6		
Melgaço 2[c]	03/2006	−5.60	−32.2	1.0 ± 0.7	1.01 ± 0.04	4.7
Melgaço 1[c]		−5.23	−32.5	2.2 ± 0.7	2.33 ± 0.07	4.7
Messegães[c]		−5.68	−35.5	n.d		
Melgaço 2[c]	07/2006	−5.63	−36.8	0.8 ± 0.7		
Melgaço 1[c]		−5.56	−37.5	0.9 ± 0.7		
Messegães[c]		−5.94	−36.5	0.3 ± 0.7		

n.d not detected

[a] Shallow dilute groundwaters (spring waters)

[b] data from Nascimento (2000)

[c] mineral waters

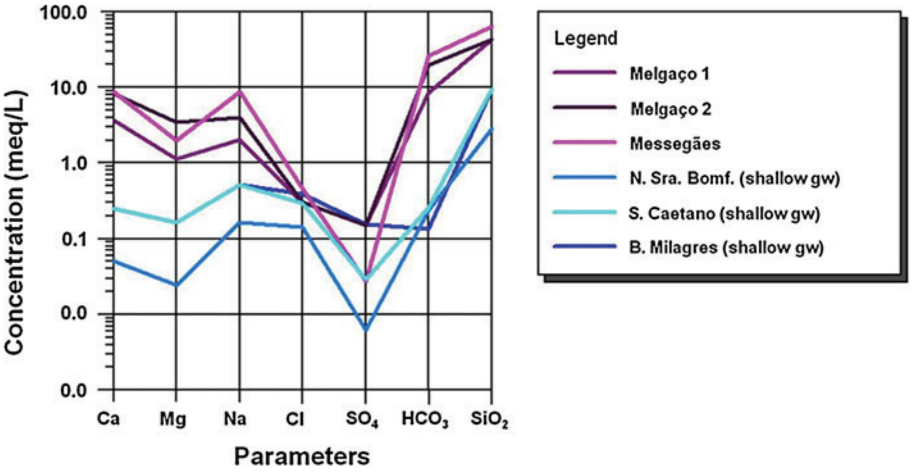


Fig. 2 Schoeller–Berkaloff diagram for Melgaço and Messegães CO_2-rich mineral waters and groundwater samples representative of the shallow dilute systems (mineral data from 03/2006 sampling campaign, and data from 02/2003 campaign for the shallow system)

ratios of weathered ferromagnesian silicates. Potassium, like Ca, has a silicate mineral source (feldspar), but can be heavily involved in vegetative biomass and may be have an anthropogenic source (e.g. fertilizers). In Melgaço–Messegães region, calcium dissolution seems to be controlled by hydrolysis of rock-matrix silicate minerals and is not associated with an anthropogenic source, since no "correlation" is found between the Ca content and the SO_4 or NO_3, "parameters" that are usually associated with agricultural practices. From the observation of Table 3, it can be seen that the Ca content is higher than Mg and Na in the mineral waters. However, an opposite trend is found in the shallow dilute groundwaters, which exhibit signatures of anthropogenic origins (e.g. NO_3) and higher Na/Ca ratios.

The geochemical signatures of the shallow dilute groundwater systems indicate dispersion (Table 1), ascribed to different spring locations downhill, frequently in areas of intensive agricultural activities, suggested by the increase in NO_3^-, Cl^- and SO_4^{2-} concentrations. In contrast the CO_2-rich mineral water compositional heterogeneity suggests water–rock reactions with different lithologies, with variable amount of available calcium, possibly related to different underground flow paths.

Oxygen-18 and deuterium signature

Variations in the stable isotopic composition of the rainfall in a given place will depend on many factors including seasonality, moisture source, rainfall amount and meteorological conditions during evaporation, condensation and precipitation. Match between the isotopic composition of precipitation and that of the groundwater is not perfect; ideally such a survey should be extended beyond the immediate study zone. The observation of the $\delta^{18}O$ and $\delta^{2}H$ diagram (Fig. 3) indicates that Melgaço and Messegães CO_2-rich mineral waters are derived from locally infiltrated meteoric waters. The dispersion of values can be ascribed mainly to: (1) the different time scale of the sampling, this relative isotopic dispersion, can be the reflection of the preservation of seasonal variations as they occur in local precipitation, similar situation have been described by Moser et al. (1989). Those authors mentioned a similar situation at Stripa for the δ^{18}O and δ^{2}H dispersion in shallow waters (<100 m). Similar dispersion of the isotopic data in precipitation have been reported in different works (Majumder et al. 2011; Liu et al. 2011). The Regional Meteoric Water Line (Regional-MWL) was calculated using the isotopic composition of the shallow dilute groundwater samples (spring waters). The isotopic relation obtained: $\delta^{2}H = 7.85\ \delta^{18}O + 9.42$. A difference in the oxygen-18 values of about 0.3 ‰ is found between Messegães–Melgaço 2 and Melgaço 1 waters during the winter campaigns (Table 2). However, this difference is not observed in the summer campaign, reflecting greater homogenization of Melgaço hydromineral system. An isotopic difference in the ^{18}O content was obtained between Melgaço and Messegães hydromineral systems (mean values) around 0.4 ‰ (Table 2).

Besides, comparing the isotopic composition of the mineral and the shallow dilute waters, two groups can be identified, indicating different recharge altitudes (Fig. 4). The "altitude effect" has been used successfully in the identification of the recharge areas and used to find interconnection of different water bodies. Data from the literature indicates isotopic gradient values from −0.15 to −0.50 ‰ δ^{18}O/100 m, with an average rate of depletion of about −0.26 ‰ (Yurtsever and Gat 1981; Araguás-Araguás et al. 2000; Gonfiantini et al. 2001).

Table 3 Ca/Mg and Na/Ca ratios calculated on the basis of geochemical data from mineral and shallow dilute groundwaters from Melgaço–Messegães region

Reference	Sampling campaign	Ca/Mg	Na/Ca
B. Milagres[a,b]	10/1999	1.161	2.315
S. Caetano[a,b]		0.809	11.436
Melgaço 2[c]	02/2002	2.823	0.518
Melgaço 1[c]		3.008	0.590
Messegães[c]		4.223	0.992
B. Milagres[a]		1.470	2.527
S. Caetano[a]	02/2003	0.999	5.726
N.S. Bonfim[a]		2.022	3.311
B. Milagres[a]		1.516	2.091
Melgaço 2[c]	03/2006	2.416	0.482
Melgaço 1[c]		3.172	0.563
Messegães[c]		4.408	0.995
Melgaço 2[c]	07/2006	3.027	0.335
Melgaço 1[c]		2.561	0.516
Messegães[c]		2.629	1.205

[a] Dilute spring water

[b] data from Nascimento (2000)

[c] mineral waters

The appraisal of the recharge area elevation was based on the δ^{18}O values of the shallow dilute groundwater samples. The results supported the relationship between δ^{18}O, the elevation of the sampling site, and the conservative behaviour of the oxygen isotopic composition of the groundwaters from recharge to discharge. At the Melgaço–Messegães research region the isotopic gradient obtained for δ^{18}O is −0.15 ‰ per 100 m of altitude (Fig. 4), which is in conformity with the above presented data, obtained using the discharge altitude of the spring waters.

Based on the isotopic gradient of the region (Fig. 4), the recharge altitude of the CO_2-rich mineral waters was estimated. The altitude values obtained range from 513 m a.s.l. (for Melgaço 1) up to 740 m a.s.l. (for Messegães). These elevation values suggest recharge areas located south of Minho River towards Peneda Mountain (see Fig. 1).

Radioactive isotopes: tritium and carbon-14

Groundwater samples were collected for ^{3}H determinations. In the shallow dilute groundwater systems, the ^{3}H content ranged from 5.2 ± 0.6 TU—October 1999 (Nascimento 2000) to 2.1 ± 0.6 TU—February 2003. The samples collected during October 1999 show higher tritium content, that decrease through time, similar to the pattern observed in the precipitation water samples from the Portuguese Network "Isotopes in Precipitation" (Carreira et al. 2005a, b). The mineral waters show the lowest ^{3}H concentrations varying from absence of tritium up to 2.2 TU (Table 2). There is a relation between the ^{3}H content and the water mineralization (here represented by the electrical conductivity values); the lowest ^{3}H contents are found in the water samples with the highest mineralization, suggesting a longer circulation path and/or more extensive water–rock interaction processes (Fig. 5). Further, when the tritium content is plotted as a function of the oxygen-18, a relation between these two environmental isotopes can also be recognized (Fig. 6). If the ^{18}O signatures of the water samples, among other parameters, are function of the recharge altitude, and since the boreholes are located more or less at the same altitude with similar depths, the water mineralization will reflect a longer circulation path with higher possibilities for water–rock reaction processes. Melgaço 1 CO_2-rich mineral waters have the highest tritium content within the hydromineral system and, simultaneously, the lowest recharge altitude and lower mineralization, indicating a relatively short circulation pathway. In contrast, Messegães has no ^{3}H and the highest recharge altitude, indicating a higher residence time suggesting greater water–rock interaction (Fig. 6).

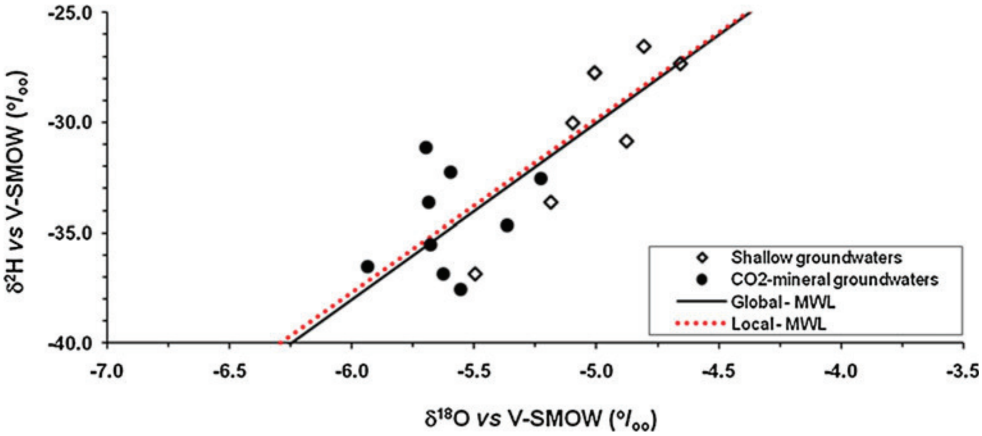


Fig. 3 $\delta^{18}O$ vs. $\delta^{2}H$ plot for CO_2-rich mineral and shallow dilute groundwaters from Melgaço–Messegães research area. The Global-MWL (after Craig 1961) and the Regional-MWL plotted as reference

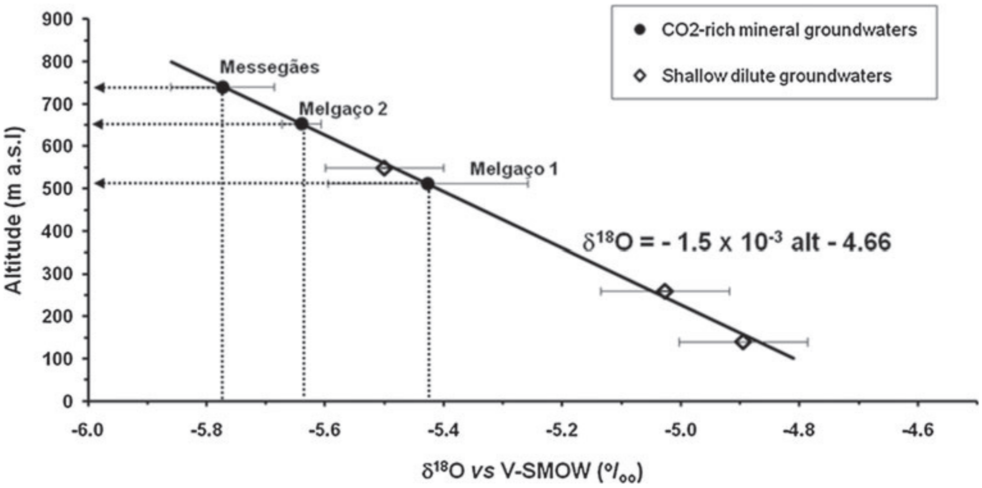


Fig. 4 Estimation of the recharge altitude of the CO_2-rich hydromineral systems based on the $\delta^{18}O$ values of the shallow dilute groundwater samples, as a function of the altitude of the sampling sites

The actual tritium input to the CO_2-rich mineral groundwater systems of Melgaço and Messegães is of the same order of magnitude as found in Porto Meteorological Station [4.5 TU—mean arithmetic weight value of monthly precipitation samples, Carreira et al. (2005a, b)]. Considering the range of ^{3}H data obtained in the CO_2-rich mineral borehole waters, a residence time that is at least >40 years is indicated.

Carbon-14 measurements were performed on the Total Dissolved Inorganic Carbon (TDIC) in two mineral water samples by AMS (Melgaço 1 and Melgaço 2). $\delta^{13}C$ determinations were carried out on the same mineral water samples. The results obtained were:

Melgaço 1: $^{14}C = 2.33 \pm 0.07$ pmC and $\delta^{13}C = 4.7$ ‰,
Melgaço 2: $^{14}C = 1.01 \pm 0.04$ pmC and $\delta^{13}C = 4.7$ ‰.

These results suggest that Melgaço mineral waters are “very old”. However, the radiometric age of the groundwater is that of the dissolved carbon and may not be that of the water. It is important to recall that most of the water samples from Melgaço hydromineral system have tritium (Table 2). Both carbon-14 content and the $\delta^{13}C$ values of groundwater are dependent upon many factors such as: (1) dissolution of carbonate minerals, that introduce relatively heavy carbon to the system; (2) oxidation of organic matter, with the addition of relatively light carbon; (3) transport of CO_2 in soil gas and addition of light carbon; and (4) methanogenesis (redox reactions involving methane) leading to a ^{13}C enrichment. In addition, the isotopic signature of the aquifer rock matrix within the research area, although the geological formations do not reveal carbonate minerals in their composition, may have an impact on the $\delta^{13}C$ values of groundwaters. Another source of carbon to the mineral water system can be CO_2 (gas) from upper mantle. Isotopic investigations of gases have been carried out in different parts of the world, and give $\delta^{13}C$ values ranging between −1.8 and −3.2 ‰, in the Bohemian Cretaceous Basin (Jiráková et al. 2010) and in the Czech Republic (Dupalova et al. 2012). The Geysers geothermal system, Clear Lake region, northern California, USA (Bergfeld et al. 2001; Truesdell and Hulston 1980) gives slightly more depleted ratios between −8 and −1 ‰. The

Fig. 5 Plot of ^{3}H content as a function of the electrical conductivity values, for the studied groundwaters sampled along several campaigns

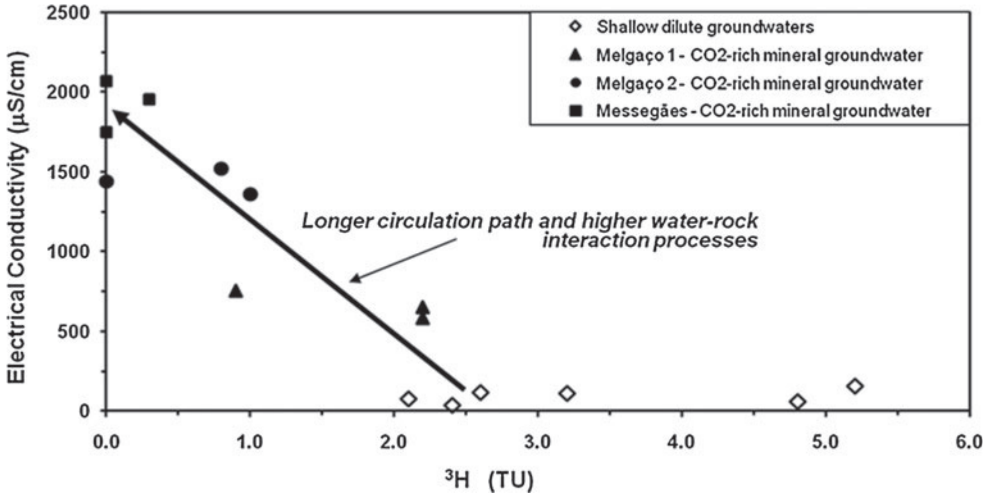
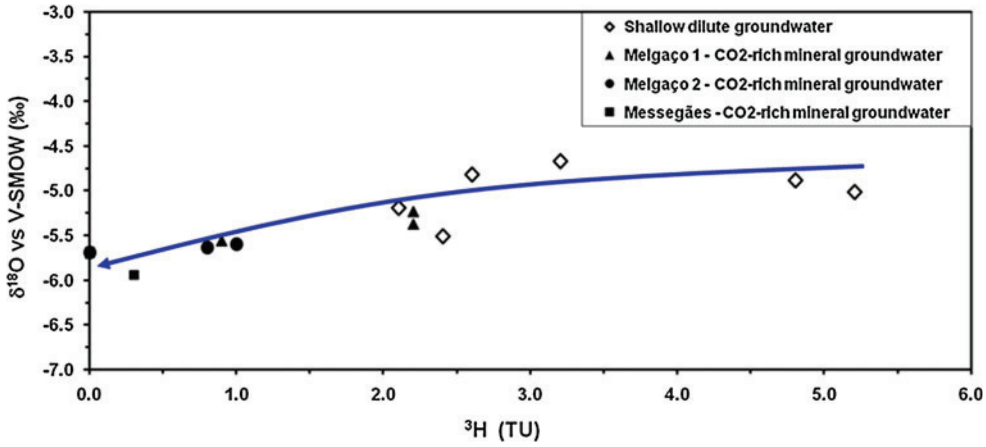


Fig. 6 ^{3}H vs. $\delta^{18}O$ plot, enhancing the isotopic evolution along the several campaigns



radiocarbon activity for geogenic $CO_2(g)$ is usually around 0 pmC, nevertheless Jiráková et al. (2010) mention a ^{14}C content of 2.4 pmC in the Cheb Basin.

Both ^{14}C and ^{13}C content in atmosphere are decreasing as the result of the industrial revolution because of the use of fossil C with depleted in ^{13}C (Clark and Fritz 1997). According to Mook (2000) the $\delta^{13}C$ mean value over the northern hemisphere is −7.85 ‰.

In temperate climate regions the soil, atmosphere and vegetation represent an important source of carbon to the groundwater systems usually characterized by 100 pmC of modern carbon (Clark and Fritz 1997). The $\delta^{13}C$ value of carbon dioxide in the soil zone is controlled to a large extent by the degree of fractionation passed on to atmospheric CO_2 as a result of photosynthetic uptake. According to the literature, for temperate climate ecosystems, like those of the study region, vegetation that follows the C3 photosynthetic cycle predominates, with $\delta^{13}C$ average values varying between −24 and −30 ‰ with a mean isotopic value of −27 ‰ (Mook 2000). The soil zone CO_2 associated with C3 vegetation presents $\delta^{13}C$ values typically around −23 ‰, as result of CO_2 out-gassing following decay of C3 organic matter (Clark and Fritz 1997). There is a small isotopic fractionation imparted during dissolution of soil zone CO_2 into recharging waters such that $CO_{2(aq)}$ has $\delta^{13}C$ value of around −24 ‰.

Melgaço CO_2-rich mineral waters present an enriched carbon-13 composition ($\delta^{13}C = 4.7$ ‰) that is almost impossible to explain in a granitic environment, without an important external source. Also, there is no relation between the $\delta^{13}C$ values with the HCO_3 content. The water samples present the same ^{13}C isotopic content that is completely independent of bicarbonate compositions (1,196.8 and 523.5 mg/L). Assuming that the only process controlling $\delta^{13}C$ in these waters is the relative contributions of soil zone and carbonate minerals (possible presence of carbonate layers at depth), a good correlation between the $\delta^{13}C$ and HCO_3 should be observed. In fact, some calcareous lenses have been reported by Brink (1960) in Vila Real area (south of our study region), with 30 m width and length of about 1.5 km, occurring in a zone of low-grade metamorphism, mainly comprising chlorite-sericite schists and phyllites. Schermerhorn (1956) correlates the limestones intercalated in the Beira schists (the so-called Ante-

Ordovician schisto-graywacke complex) of northern Portugal (Trás-os-Montes, Douro region) with those occurring in NW Spain (Galicia), a Spanish province located very close to our research region.

It is possible that the CO_2 in the mineral waters could be ascribed to degasification of deep-seated upper mantle gases, as was identified in the nearby region of Vidago–Pedras Salgadas (Carreira et al. 2010). Nevertheless, even considering a CO_2 source from the upper mantle, this external source of carbon is not sufficient to account for the measured composition, since ^{13}C associated with a mantle origin has values between −3 and −8 ‰ (Javoy et al. 1986; Marty and Zimmermann 1999). The δ^{13}C values of Melgaço mineral waters suggests the presence of CH_4, related with methane generated in depth due to inorganic reactions associated with mantle origin.

According to Barker and Fritz (1981), methane is a common trace constituent of groundwaters, sometimes reaching concentration values >20 % of the total carbon. Those authors stated that where methane-bearing groundwaters discharge into aerobic environments microbial methane oxidation could occur, leading to a progressive enrichment in ^{13}C in the residual methane. The fractionation between CO_2 and CH_4 is large, about 75 ‰, producing methane with depleted δ^{13}C values and CO_2 isotopically more enriched with δ^{13}C values between −20 and +10 ‰ (http://www2.fiu.edu/pricer/StableIsotopes_2010).

Studies in the NE part of the Portuguese mainland at Vidago–Pedras Salgadas CO_2-rich mineral water systems, also in a granitic environment, reported occurrences of methane in the groundwater systems, in the free gas phase, with a mean value of 583 ppm in CH_4, and ranging between 41 and 1,021 ppm (Carreira et al. 2010). Taking into account the results found within an area nearby our research region, the hypothesis that the heavy isotopic signatures ($\delta^{13}C = 4.7$ ‰), found in the Melgaço CO_2-rich mineral waters, could be ascribed to deep-seated (upper mantle) methanogenesis should not be excluded. Clark and Aravena (2007) mention that only during methanogenesis is there a substantial fractionation of ^{13}C, and consequently the DIC (dissolved inorganic carbon) produced is greatly enriched, pointing to a biogenic fractionation in the order of $\varepsilon^{13}C_{CO_2-CH_4} = 50$–$80$ ‰, by acetate fermentation.

Several authors (Hansen et al. 2001; Leybourne et al. 2006) referred to the fact that although the effects of methanogenesis in environments such as marine sediments, rice paddies and landfills have been deep investigated, less emphasis has been given to the production of methane in aquifer systems. Moreover, according to Hansen et al. (2001) approaches that were used to identify methanogenic conditions in aquifer systems comprise: (1) the presence of methane in groundwater systems; (2) the counting of methanogenic bacteria present in aquifer sediments; (3) measurement of the H_2 concentration in groundwater and (4) incubation of aquifer sediments. Methane production rate in aquifers has been determined from concentration gradients, groundwater transport rate, and from the release of methane gas from boreholes. Except for the last approach, all these calculations are indirect measures of the actual methane production in the aquifer sediments at a detailed scale and compared to other environments, methanogenesis in aquifers have been scarcely studied (Leybourne et al. 2006).

Although very few rocks do not contain calcite, or some other carbonate, as an alteration product, simple explanation for the ^{14}C and ^{13}C isotopic data by contamination with “old” carbon from minerals does not seem reasonable due to the lack of correlation between the isotopic and chemical composition of the groundwaters responsible for this isotopic shift. The negligible radiocarbon values in Melgaço 1 and Melgaço 2 borehole waters ($^{14}C \approx 2$ pmC) is possibly an indication of the existence of a mantle-derived carbon source into the CO_2-rich mineral water systems.

Several mathematical models, which have been summarized by Fontes and Garnier (1979) and by Gallagher et al. (2000), are available for dating groundwater systems to estimate the initial ^{14}C activity (A_o) of the total dissolved carbon. The initial ^{14}C activity (A_o) is derived from a combination of “two sources” and is defined as the ^{14}C content after all chemical and isotopic processes have taken place before any decay. Such models also attempt to account for the dilution of ^{14}C by less active carbon and for isotopic exchange reactions, which may take place between the different carbon-bearing chemical species. Among these models, the carbon-13 correction model can be an effective natural tracer of groundwater systems, due to the large variation in δ^{13}C values between the different carbon sources. For example, soil-derived dissolved inorganic carbon and carbonate minerals in the aquifer can provide a reliable measure of the ^{14}C dilution by carbonate dissolution (Petitta et al. 2011). An additional source is deep-seated (upper mantle) carbon. However, in the case of Melgaço CO_2-rich mineral water systems in addition to atmosphere and soil sources, deep-seated CO_2 may be an important source in changing the δ^{13}C values considerably, i.e. methanogenesis. The different sources of carbon do not allow the use of a simple model to estimate equilibrium isotope exchange between dissolved HCO_3^- and CO_2, important in this type of groundwater systems, since we are dealing with CO_2-rich mineral waters.

Considering the geological and tectonic environment of region, a potential origin for the CO_2 could be the upper mantle, by diffusion of CO_2 through the major fault systems in the region (see Fig. 1). Clark and Fritz (1997), in order to identify the deep-seated CO_2 dilution factor (q) to hydromineral systems proposed the following equation based on a $\delta^{13}C$ mixing model:

$$q_{\text{mantle}} = \left[\delta^{13}C_{\text{DICmeasured}} - \delta^{13}C_{\text{mantle}}\right] \Big/ \left[\delta^{13}C_{\text{recharge}} - \delta^{13}C_{\text{mantle}}\right] \qquad (1)$$

where $\delta^{13}C_{\text{DICmeasured}}$ represents the carbon-13 "content" measured in mineral water samples. According to Truesdell and Hulston (1980) $\delta^{13}C_{\text{mantle}}$ values range between −8 and −1 ‰. $\delta^{13}C_{\text{recharge}}$ stands for the carbon-13 "content" measured in the recharge waters, which near the studied region is represented by the values obtained in the shallow dilute spring waters ($\delta^{13}C = -22.9$ ‰, in Marques et al. 2000).

In this study, the value of $\delta^{13}C_{\text{mantle}} = -1$ ‰ was selected. The dilution factor obtained is 125 % indicating the occurrence of another process, beyond the upper mantle CO_2 contribution, responsible for the $\delta^{13}C$-enriched values, most probably methanogenesis. This input of carbon-14 to the CO_2-rich mineral water, depending on the amount, will immediately change groundwater radiocarbon ages. The corresponding carbon-14 contents (pmC) measured in Melgaço CO_2-rich mineral water samples were 2.33 ± 0.07 and 1.01 ± 0.04 pmC, indicating the presence of very old groundwater. The carbon isotopic signatures suggest that the carbon in the DIC is 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, only one sample (Melgaço 2, February 2002) presents 0 TU. All the remaining samples from the different campaigns are characterized by the systematic presence of ^{3}H (Table 2). In this case, the ^{3}H content found in the mineralised water systems are not in agreement with the ^{14}C values, similar isotopic data has been described by Hamed et al. (2011) at Southwestern Tunisia. The systematic presence of tritium could be related to:

1. Mixture with the upper aquifer system (shallow cold dilute groundwaters). However, this hypothesis seems not reliable. In this case the ^{14}C content in the mineral waters would be rather higher. Mook (2000) presented radiocarbon content in shallow aquifers close to 80 pmC.
2. Production of ^{3}H 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 boron, results in ^{3}H activity levels up to 0.5 TU. Moser et al. (1989), proposed a tritium source associated with underground production in granite at Stripa (Sweden). The authors showed isotopic homogeneity (during 5 years) of tritium data in water samples collected at 850 m depth. In the cold CO_2-rich Portuguese mineral waters, the ^{3}H content reveals no isotopic homogeneity (e.g. Marques et al. 2000; Carreira et al. 2008), indicating negligible tritium production at depth in the groundwater systems.
3. The tritium values found in regional precipitation are in the order of 5 TU (arithmetic mean of the weight annual mean at Porto = 4.5 TU and Vila Real = 6.4 TU, (Carreira et al. 2005a, b), both meteorological stations from the Portuguese Network Isotopes in Precipitation initiated in 1988). Based on this regional precipitation content and considering the (1) half-life of the ^{3}H (12.32 years in Lucas and Unterweger 2000); (2) ^{3}H content measured in Melgaço CO_2-rich mineral waters (Table 2) and (3) tritium input (regional precipitation data), one can classify these mineral waters as modern waters.

Final considerations and outlook

This study has demonstrated the usefulness of coupled geochemical and isotopic studies on a suite of CO_2-rich mineral waters issuing in the Northwest part of the Portuguese mainland. The results obtained on the processes and reactions involved in the mineral water pathways allow us to conclude that the: (1) Melgaço and Messegães mineral waters, belonging to the Ca/Na–HCO_3- and Na/Ca–HCO_3-type waters, respectively, result from different underground flow paths (fissure environments), with different calcium availability in the aquifer matrix, and are associated with hydrolysis of Ca-rich plagioclases in the granodioritic rocks of the region; (2) high CO_2 gas content observed in the mineral waters is responsible for the increase of water–rock interaction processes. Ca and Na in natural waters are usually derived from feldspars (plagioclase) hydrolysis in granitic environments, easily supported by the Ca–HCO_3 and Na–HCO_3 nature of Melgaço and Messegães CO_2-rich mineral waters, respectively; (3) regional geomorphology of the region seems to favour a conceptual circulation model being the recharge area of the CO_2-rich mineral water systems at south of Melgaço uphill between 513 and 740 m a.s.l. based on the isotopic composition ($\delta^{18}O$ values); (4) underground flow paths are strongly controlled by the NNW–SSE fault systems, issuing these waters when appropriate conditions are present; (5) recharge altitudes are in agreement with a longer circulation path for Messegães CO_2-rich mineral waters (recharge altitude 740 m a.s.l. and $^{3}H \approx 0$ TU) and a shorter circulation path for Melgaço 1 CO_2-rich mineral water (recharge altitude 513 m a.s.l. and ^{3}H from 1 to 2 TU); (6) the geological and tectonic environment indicate that the most probable origin of the CO_2 in the mineral water systems is an upper mantle contribution through significant fault systems. Carbon-14 content measured in Melgaço CO_2-rich mineral water samples indicates the presence of very old groundwater. However, this carbon content is 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; (7) $\delta^{13}C$ determinations carried out on DIC of Melgaço CO_2-rich mineral waters strongly imply methanogenesis within the system, leading to ^{13}C enrichment and a decrease to negligible values in the radiocarbon content derived from the upper mantle.

According to Sherwood Lollar et al. (1997), CO_2 is a reactive species, subject to loss and to a potential crustal sinks, mixing and dilution with varied sources of crustal-derived carbon. Furthermore, the authors call our attention to the fact that carbon isotopic values do not provide an unequivocal mean to distinguish between these various carbon sources. The exception is provided by the ratio $C/^3He$, regarding the origin of carbon within continental systems, based on the values obtained in mid-ocean ridge basalts (MORB). In the studies carried out in the NE part of the Portuguese mainland, near Melgaço, the $CO_2/^3He$ ratio vs. $\delta^{13}C$ of the gas phase of the CO_2-rich mineral waters, fall very close to the field of the gas typical of a mantle origin (Carreira et al. 2010).

The releasing of deep-seated fluids having a mantle-derived component in a region without recent volcanic activity leads to think that extensive neo-tectonic structures originated during the Alpine Orogeny seems to be still active. Decompression during diapiric rise of mantle material will result in deep partial melting. Geo-pressured mantle volatiles, such as CO_2 and methane, released during partial melting, may be absorbed through weak zones in the ductile lower crust, that are associated with the roots of the fault system. The release of volatiles can be limited to transmission or exsolution amounts of fluid along faults, from a magmatic source depth at the base of the crust. Some authors argue that CO_2 and He mantle can be entered and stored in the geosphere for millions of years, as a result of orogenic movements (Humphreys et al. 2003).

Future investigations of the CO_2-rich mineral waters located in the N of Portuguese mainland, will emphasize the $\delta^{13}C$ determinations of CH_4, and the importance of noble gases dissolved in the groundwaters, in order to enhance the identification of the processes responsible for the enriched $\delta^{13}C$ values found in Melgaço CO_2-rich mineral waters. In fact, increasing knowledge on the processes involved in groundwater circulation and interaction with the surrounding rocks is an important issue to ensure the economic use of the studied CO_2-rich mineral waters in terms of drinkable mineral waters as well as in terms of preventing potential future overexploitation.

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