Nature and role of CO_2 in some hot and cold HCO_3/Na/CO_2-rich Portuguese mineral waters: a review and reinterpretation

José M. Marques · Paula M.M. Carreira · Luís Aires-Barros · Rui C. Graça

Abstract At the northern part of the Portuguese mainland, the upflow zone of several hot and cold HCO_3/Na/CO_2-rich mineral waters is mainly associated with important NNE–SSW faults. Several geochemical studies have been carried out on thermal and non-thermal hydromineral manifestations that occur along or near these long tectonic alignments. The slight chemical differences that exist between these meteoric hot and cold HCO_3/Na/CO_2-rich mineral waters seem to be mainly caused by CO_2. $\delta^{13}C_{(TIDC)}$ values observed in these groundwaters range between -6.00 and -1.00‰ versus V-PDB (V denotes Vienna, the site of the International Atomic Energy Agency; PDB originates from the $CaCO_3$ of the rostrum of a Cretaceous belemnite, *Belemnitella americana*, collected in the Peedee formation of South Carolina, USA) indicating a deep-seated (mantle) origin for most of the CO_2. Nevertheless, in the case of the heavier $\delta^{13}C_{(TIDC)}$ values, the contribution of metamorphic CO_2 or the dissolution of carbonate rock levels at depth cannot be excluded. Concerning the hot waters, the lack of a positive ^{18}O-shift should be attributed to water-rock interaction in a low temperature environment, rather than to the isotopic influence of CO_2 on the $\delta^{18}O$-value of the waters.

Keywords $\delta^{13}C$ values · Northern Portugal · Origin of CO_2 . Stable isotopes · Thermal and cold mineral waters

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Introduction

During the last decades, we have witnessed an increasing worldwide interest on the exploitation of low temperature geothermal resources. Because low temperature geothermal systems and cold carbon dioxide waters are linked in many parts of the world (e.g. Iceland, the Geyser in California and French Massif Central), special emphasis has been given to the study of hot and cold CO_2-rich mineral water discharge in many parts of the world (Panichi and Tongiorgi 1975; Barnes and Irwin 1980; Arnórsson and Barnes 1983; Fouillac 1983; Wexteen and others 1988; Duchi and others 1991; Verma and others 1992; Arnórsson and Gíslason 1994).

On the Portuguese mainland, most hot (Chaves) and cold (Vilarelho da Raia, Vidago and Pedras Salgadas) HCO_3/Na/CO_2-rich mineral waters flow from natural springs and drilled wells that are located either in granitic outcrops or in the peribatholitic boundaries concordant to the main NNE–SSW fault trend (Fig. 1), which attains 30 km depth in the study area (Baptista and others 1993). Chaves thermal waters have been well known since Roman times and today they are mainly used for heating swimming pools and hydrotherapy. These thermal waters are also currently being utilised to heat an experimental greenhouse.

Special emphasis has been given to the geohydrological characterisation of the Vilarelho da Raia-Pedras Salgadas region to allow a more complete knowledge of groundwater circulation paths and to determine correlations that exist between the hot and cold CO_2-rich mineral waters that discharge in the northern part of the Portuguese mainland (Aires-Barros and others 1991, 1994, 1995; Marques 1993; Marques and others 1995, 1996, 1998). Geochemical and isotopic studies have enabled the formation of a conceptual geohydrological model of the low-temperature geothermal system of Chaves (Aires-Barros and others 1995). Isotope techniques (^{18}O, ^{2}H and ^{3}H) have been used to identify groundwater origin, altitude of recharge and underground flow paths. Recently, new research on isotope techniques in investigations on the nature of hot and cold mineral waters was initiated. Special attention has been given to the identification of the origin of carbon dioxide in these hot and cold CO_2-rich mineral waters. Because of its peculiar geochemistry, the

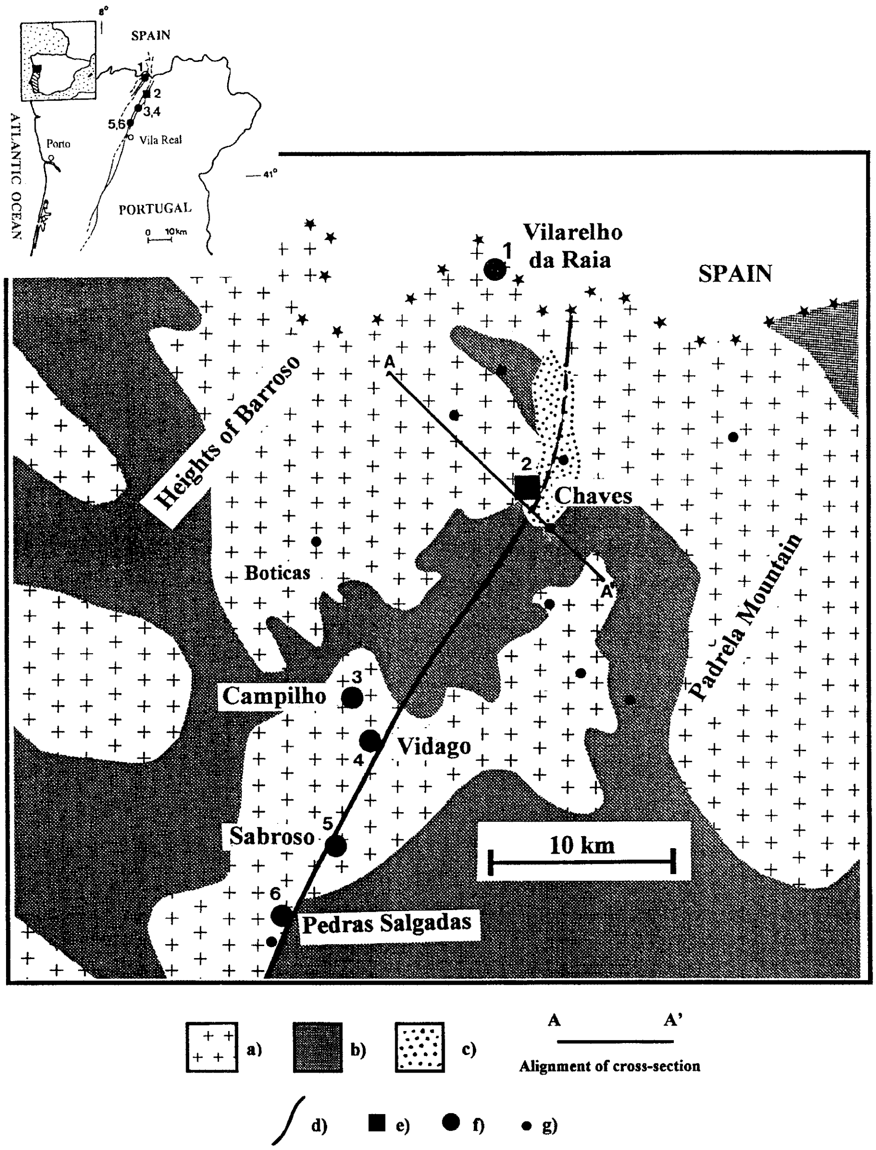


Fig. 1
Geological sketch map of the region, showing the position of main water samples. *a* Hercynian granites and granodiorites; *b* Silurian phyllites, quartzites, carbonaceous slates and migmatites; *c* Cenozoic cover sediments; *d* major faults; *e* hot saline waters; *f* cold saline waters; *g* dilute cold superficial waters (recharge waters). *1* Vilarelho da Raia (Facha, ACP1 and ACP2) area; *2* Chaves (AC2 and VI) area; *3* Campilho area; *4* Vidago (AC16 and AC18) area; *5* Sabroso area; *6* Pedras Salgadas (AC17) area

role of carbonaceous slates, which are well displayed in the study area, as a hydrochemical signature of the groundwaters, has been considered. The understanding of the origin of these waters is directly related to the origin of carbon dioxide.

Field and laboratory methods

Hot and cold CO_2-rich mineral waters and cold superficial low mineralised waters (spring waters) were sampled and chemically and isotopically analysed. Physicochemical characteristics of the groundwater samples studied between 1990 and 1992 are shown in Table 1. Table 2 includes the most relevant physicochemical and isotopic variables analysed in the water samples taken during 1996 fieldwork campaigns. Some data from the literature have been used for the Chaves hot waters (Almeida 1982). The Nuclear and Technological Institute (ITN) in Portugal carried out the determinations of $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$ values in waters by mass spectrometry. $\delta^{13}C$ analyses were performed on total inorganic dissolved carbon (TIDC) precipitated in situ as $BaCO_3$ at pH>9.0. The gas used in $^{13}C/^{12}C$ measurements was CO_2. Carbonates were reacted with 100% phosphoric acid to liberate CO_2. ^{3}H analyses were also performed at the ITN. $\delta^{18}O$ and $\delta^{2}H$ were measured following the analytical methods of Epstein and Mayeda (1953) and Friedman (1953) respectively. Analytical precision is $\pm 0.10‰$ for $\delta^{18}O$ and $\delta^{13}C$, and $\pm 1.0‰$ for $\delta^{2}H$. Tritium determinations were performed using electrolytic enrichment and subsequent measurement of counting rates by liquid scintillation. For ^{3}H analyses, the standard deviation varied between ± 0.7 and ± 1.2 depending on tritium content. $\delta^{13}C$ values in rocks (carbonaceous slates) have been measured by mass spectrometry at Delta Isotopes Laboratory/The Netherlands. The standard δ notation per mil is used through-

Table 1
Hydrogeochemical data of the water samples collected at different times (during 1990, 1991, and 1992) in drilled wells and spring. *SD* Standard deviation. Number of samples: $n=6$. *Temp* Issue temperature of sampled water; *Cond* conductivity at the issue temperature. pH values are from field measurements

	Vidago AC16[a]		Pedras Salgadas AC17[a]		Vidago AC18[a]		Chaves AC2[a]		V. Raia Facha[b]	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Temp. (°C)	18.3	0.5	17.0	0.4	17.8	0.3	75.1	1.5	16.3	1.5
pH	6.16	0.1	6.42	0.2	6.79	0.1	7.15	0.2	6.61	0.4
Cond. (μS/cm)	1618	100	2623	202	5648	337	2822	339	2543	489
Na (mg/l)	365	54	521	136	1246	255	574	66	724	126
K (mg/l)	32	5	28	2	105	3	65	6	28	11
Ca (mg/l)	62	13	182	13	203	12	22	2	33	5
Mg (mg/l)	10	3	28	5	37	4	5	1	5	2
Fe_{total} (mg/l)	3	1	4	2	2	2	0.2	0.1	0.9	0.5
Li (mg/l)	2	0.5	2	0.5	6	0.3	3	0.5	2	2
HCO_3 (mg/l)	1262	88	2135	123	4716	169	1724	58	2059	311
SO_4 (mg/l)	9	4	12	3	3	2	26	11	3	3
Cl (mg/l)	22	5	38	8	76	13	47	15	30	13
SiO_2 (mg/l)	52	4	72	2	52	2	74	1	54	9

[a] Drilled wells
[b] Spring

Table 2
Chemical and isotopic analyses of water samples taken during 1996 fieldwork campaigns at Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas areas. Concentrations are in mg/l. *DR* Dry residue. $\delta^{18}O$ and $\delta^{2}H$ are in ‰ vs V-SMOW. ^{3}H is in tritium units. $\delta^{13}C$ is in ‰ vs V-PDB. Temp stands for the issue temperature of sampled water (°C). pH values are from field measurements. *Cond* Conductivity (μS/cm) at the issue temperature; *n.d.* not detected (concentrations below detection limit). P_{CO_2} is in atm

	Vilarelho da Raia ACP1[a]	Vilarelho da Raia ACP2[a]	Chaves No. VI[b,c]	Chaves AC2[a]	Vidago AC16[a]	Vidago AC18[a]	Pedras Salgadas AC17[a]	Boticas[b,d]	Pedras Salgadas[b,d]
Temp.	17.7	17.1	75.0	76.0	17.5	17.2	16.3	11.1	11.0
pH	5.78	–	6.80	7.30	6.10	6.75	6.25	5.26	5.26
Cond.	2100	3050	–	2890	1708	6060	2870	28	270
Na	706	832	610	551	379	1576	585	3	4
K	28	41	63	64	34	104	27	0.7	0.2
Ca	32	34	21	24	66	207	171	0.8	0.7
Mg	7	9	6	6	12	39	35	0.8	0.2
Li	1.35	2.10	–	2.95	1.95	6.50	2.00	n.d.	0.00
Fe_{total}	0.90	1.35	–	0.30	3.25	0.20	4.80	0.10	0.10
HCO_3	1869	2174	1640	1686	1234	4474	1931	12	10
SO_4	2	2	31	18	9	2	10	1	1
Cl	24	30	46	63	16	58	36	4	9
F	19.75	19.5	7.2	–	10.8	13.45	8.35	n.d.	1.75
Rb	0.35	0.55	–	0.47	0.30	1.00	0.30	n.d.	n.d.
Cs	0.15	0.30	–	0.50	0.25	0.75	0.10	n.d.	n.d.
SiO_2	52.6	54.2	80.0	73.6	57.6	54.8	74.2	9.9	10.1
D.R.	1828	2157	–	1714	1136	4396	1850	26	26
Free CO_2	916	1100	–	350	2250	3220	4670	–	–
P_{CO_2}	2.53	–	0.22	0.18	0.82	0.59	0.85	–	–
log SI (calcite)	−1.21	–	0.64	–	−0.70	0.74	−0.05	–	–
log SI (aragonite)	−1.36	–	0.53	–	−0.85	0.59	−0.20	–	–
$\delta^{18}O$	−7.98	–	−8.04	−8.15	−6.54	−6.74	−7.04	−6.58	−6.29
$\delta^{2}H$	−54.7	–	−55.9	−56.6	−50.9	−58.2	−41.2	−49.0	−44.2
^{3}H	0.00	–	–	0.30	1.37	0.67	2.12	4.39	3.25
$\delta^{13}C$(TIDC)	−6.0	–	−2.4	–	−5.2	−1.1	−3.8	−23.4	−22.4

[a] Drilled well water
[b] Spring water
[c] Data from Almeida (1982), where the $\delta^{13}C$ value was measured on the $SrCO_3$
[d] Cold superficial low mineralised water (recharge water)

out the paper and is relative to values found in references V-SMOW (Vienna standard mean ocean water) for $\delta^{18}O$ and $\delta^{2}H$, and V-PDB for $\delta^{13}C$. ^{3}H is in TU (tritium units).

Temperature (°C), pH and electrical conductivity (µS/cm) were determined in the field at the time of sampling. Total alkalinity was measured a few hours after sampling. The following methods were used in chemical analyses performed at the Laboratory of Mineralogy and Petrology of Instituto Superior Técnico (LAMPIST): atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na, Li, Rb and Cs; colorimetric methods for Fe_{total}, F and SiO_2; ion chromatography for SO_4 and Cl; potentiometry for alkalinity, here referred to as HCO_3. The data on free CO_2 content relative to the Vilarelho da Raia, Chaves and Vidago/Pedras Salgadas waters were kindly supplied by the Águas de Carvalhelhos Company, the Municipality of Chaves and Vidago-Melgaço & Pedras Salgadas Company respectively.

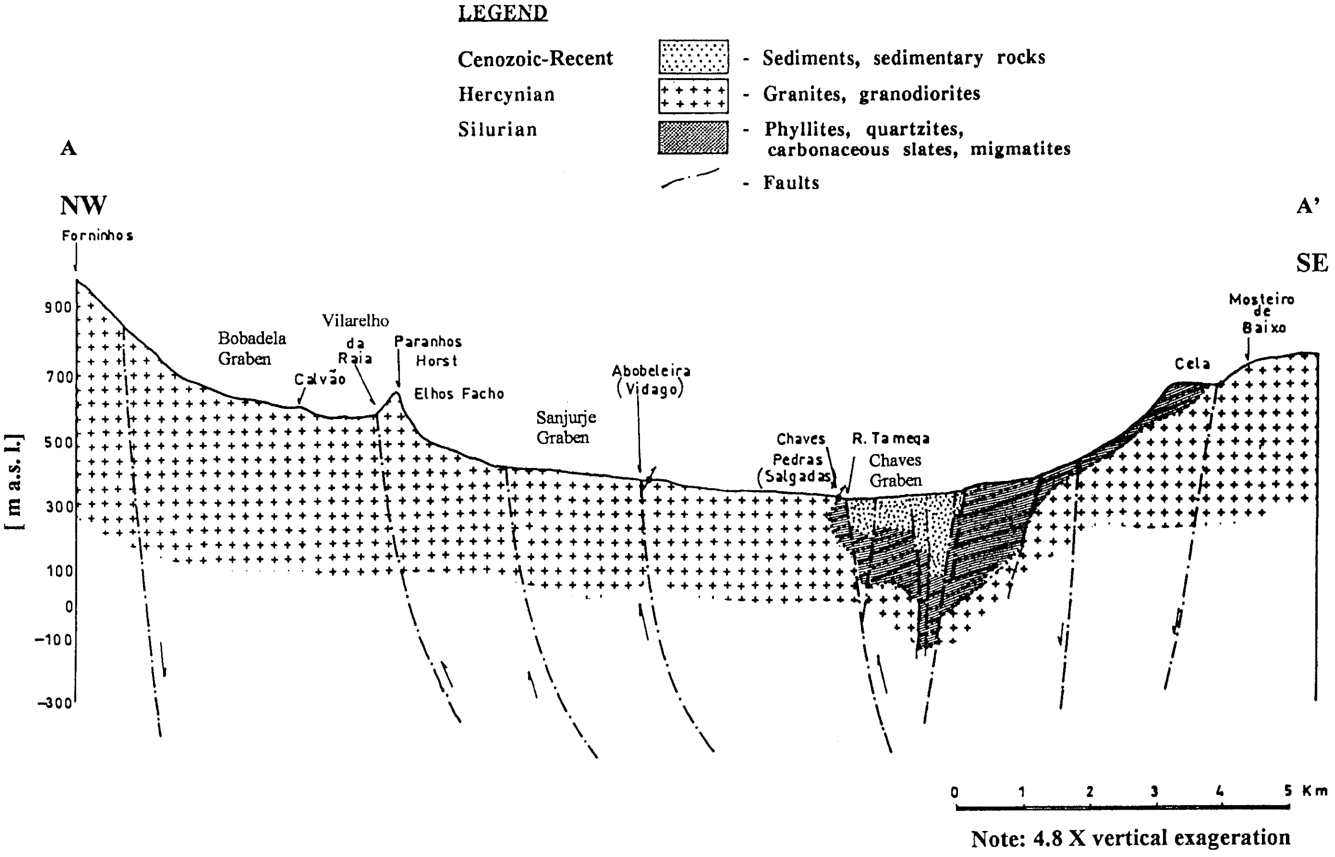
Study area

Geological background

The geology of Vilarelho da Raia-Chaves-Vidago and Pedras Salgadas areas has been described by Portugal Ferreira and others (1992), Baptista and others (1993) and Sousa Oliveira and Portugal Ferreira (1995). In Fig. 2 a schematic cross section of the overall composite graben of Chaves is presented. The geomorphology is determined by the 'Chaves Depression', a graben structure whose axis is oriented NNE–SSW. It is bounded on the east by the edge of the Padrela Mountain escarpment (Mosteiro de Baixo) with a 400-m throw. The western block is formed by several horsts and grabens coming from the Heights of Barroso (Forninhos) towards the 'Chaves Depression'. In Fig. 2 a schematic cross section of the overall composite graben of Chaves is presented. In the cross section, several examples of the main NNE fault trend (Fig. 1) are shown. The emergence of Vilarelho da Raia mineral water is controlled by the fault that makes the boundary between the graben of Bobadela and the horst of Elhos-Facho. The springs of Vidago are associated with the fault that bounds on the east the graben of Sanjurge. The spas of Chaves and Pedras Salgadas are seated on the western limit of the graben of Chaves, and are controlled by the most important area of the NNE fault trend (Portugal Ferreira and others 1992).

The region under research is situated in the Ante-Mesozoic Hesperic Massif, which consists mainly of Hercynian

Fig. 2
Schematic cross-section, of the overall composite graben of Chaves, oriented NW–SE and crossing the Chaves spas. Taken from Portugal Ferreira and others (1992)



granites and Palaeozoic metasediments. The oldest formations correspond to an ante-Ordovician schisto-graywacke complex. In Ordovician and Silurian times quartzites and schists were formed, and metamorphosed at the end of Palaeozoic by Hercynian granitic intrusions. Inserted between the schistoid complex there are bands of carbonaceous slates. The carbonaceous slates are well displayed at 1.5 km SSW of the Chaves spa, mostly along the railway track. They are mostly composed of quartz with significant amounts of graphite and minute flakes of biotite and muscovite. The most recent formations are from the Miocene-Pleistocene sedimentary series (lacustrine, alluvial, detritic etc.) and have variable thickness; they have their maximum development along the central axis of Chaves graben. The Alpine orogeny has caused extensive tectonic features that are responsible for the formation of several hydrothermal circuits. In the Chaves area, the thermal water ascent is likely to occur along narrow, steep conduits such as those along the intersections of near-vertical faults. In the Chaves area, the geothermal system is mainly governed by the NNE–SSW megalineament (which is hydrothermally active along a belt extending 150 km within the Portuguese mainland) and by the E–W fault system that crosses the area in the neighbourhood of Chaves (Marques and others 1996).
The Vidago/Pedras Salgadas area is also mainly composed of Hercynian granites with some outcrops of metamorphic rocks of Silurian age covered by Cenozoic deposits. Geological studies in the area have shown that the mineral waters emerge in places where the following subvertical 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).

Geophysical setting

Resistivity surveys have been performed mainly to detect low resistivity zones that are predictably connected to the geothermal circulation in the Chaves area (Andrade Afonso and others 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 and that the tectonic setting could play an important role in CO_2 extraction and migration from the mantle to the surface (Monteiro Santos 1994). An analysis of the regional geoelectrical structure of the Chaves region has been made using the magnetotelluric method (Monteiro Santos and others 1995). Related to the deep faults, two distinct directions have been found: a NNE–SSW direction in the upper part, and a N–S direction at the deep sectors (Monteiro Santos and others 1995). A conductive layer that exists at a depth of 7–12 km was also detected. Reconnaissance of geothermal anomalies in the Chaves area was carried out using the scalar audiomagnetotelluric method (Monteiro Santos and others 1996). These authors have shown that, in the Chaves graben, the geohydrological system has two main circuits: (1) a shallow circuit, made up of cold groundwaters flowing through the metamorphic/sedimentary sequences, controlled by local permeability, and (2) a deeper circuit, characterised by hot mineral water circulation, linked to deep structures. These results strongly support the circulation conceptual model associated with the Chaves thermal waters, proposed by Aires-Barros and others (1995), based on isotopic composition of local superficial (recharge) waters (see following section). Recently, Duque and others (1998) presented thermal models for the Chaves basin and for the region using a structure obtained by geoelectrical methods and a mean heat flow value of 95 mW m^{-2} derived from borehole measurements. They concluded that heat transfer in the region takes place mainly by conduction, except near faults, where convective flow is important.

Geochemistry of the waters

The studied hot and cold $HCO_3/Na/CO_2$-rich mineral waters emerge from boreholes and springs and exhibit outgassing phenomena. Chaves hot (76 °C) mineral waters and Vilarelho da Raia cold (17 °C) mineral waters are characterised by high mineralisation ($1700 < \text{dry residue} < 2200$ mg/l) and free CO_2 of ~350 and 1100 mg/l respectively. The Vidago and Pedras Salgadas cold (17 °C) mineral waters are also characterised by high mineralisation ($1100 < \text{dry residue} < 4400$ mg/l), higher concentrations of Mg^{2+} and Ca^{2+} and higher free CO_2 contents (up to 4670 mg/l). Almeida (1982) presented the analytical results of the gas phase associated with the Chaves thermal waters. The following gases are present in varying concentrations (vol%): $CO_2 = 99.5$, $O_2 = 0.05$, $Ar = 0.02$, $N_2 = 0.28$, $CH_4 = 0.009$, $C_2H_6 = 0.005$, $H_2 = 0.005$ and $He = 0.01$. The low H_2 concentrations suggest low equilibration temperatures for the gas phase at shallow depths, as referred to by Duchi and others (1995).
The $\delta^{18}O$ and $\delta^{2}H$ values of the hot and cold CO_2-rich mineral waters are presented in Fig. 3b. The difference in the isotopic composition of Vilarelho da Raia/Chaves group and Vidago/Pedras Salgadas group has been interpreted as the result of different recharge altitudes (Aires-Barros and others 1998). Some years before, the altitude dependence of the isotopic composition of Chaves thermal waters was determined by $\delta^{18}O$ values of superficial waters (dilute cold spring waters) issuing in the geothermal area and its bordering mountains (Aires-Barros and others 1994). Those authors estimated an isotopic gradient of $-0.26‰$ for ^{18}O per 100 m of altitude. Stable isotopic composition of dilute cold spring waters of the region (Fig. 4) indicated that the more depleted waters were those from sampling sites located at higher altitudes (Padrela Mountain), and show $\delta^{18}O$ values close to those of Chaves thermal waters. These meteoric waters percolate at great depth and then emerge, as thermal waters in a discharge area at lower altitude (Chaves plain). The cold groundwaters found in the sedimentary sequences of Chaves graben are representative of precipitation falling at midhillside locations (Aires-Barros and others 1995). Vilarelho da Raia cold mineral waters have an isotopic

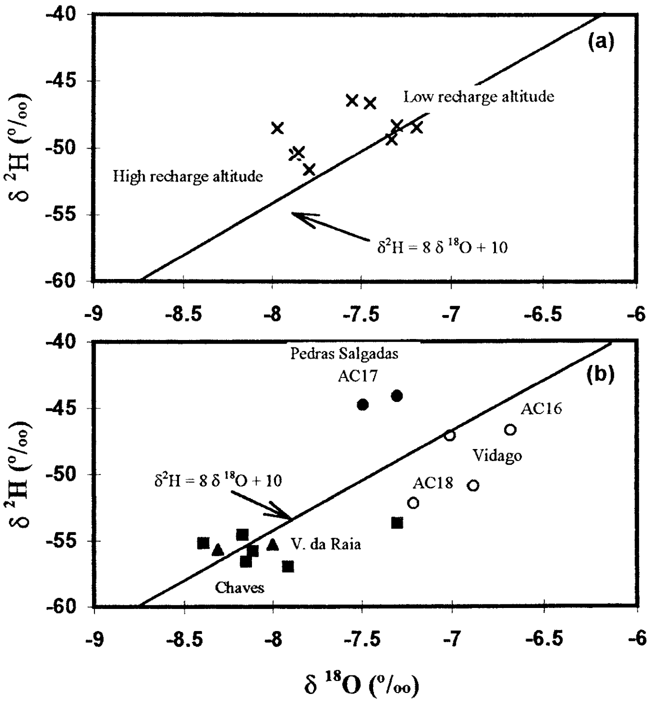


Fig. 3

$\delta^{18}O$ vs $\delta^{2}H$ (‰ vs V-SMOW) relationship in **a** cold superficial dilute waters and **b** hot and cold CO_2-rich mineral waters of Vilarelho da Raia/Chaves and Vidago/Pedras Salgadas areas. Taken from Aires-Barros and others (1998). × Cold superficial low mineralised waters; ▲ Vilarelho da Raia; ■ Chaves; ○ Vidago; ● Pedras Salgadas CO_2-rich mineral waters

($\delta^{18}O$ and $\delta^{2}H$) composition similar to Chaves hot waters, suggesting a common origin for these waters.

Results and discussion

Carbon isotope geochemistry

The origin of CO_2-rich waters is very controversial and many questions may arise in the appraisal of underground circulation of hot and cold CO_2-rich mineral waters of a given area (Fouillac 1983). The present paper summarises the available geochemical data on the origin of CO_2 in some Portuguese hot and cold CO_2-rich mineral waters. Using the $\delta^{13}C$ values in mineral waters and in other carbon components, such as carbonaceous slates, the authors have tried to increase their knowledge of groundwater circulation paths and to determine correlations between the thermal and cold CO_2-rich mineral waters that discharge in the northern part of the country.

Carbon dioxide (or total carbon) is present in mineral water in various forms: CO_2 (g), CO_2 (aq), HCO_3^- and CO_3^{2-}. The proportion of these species is related to the pH and the temperature of the fluid. The carbon dioxide undergoes hydration and ionisation (Hem 1970). The hydration of CO_2 forms H_2CO_3, and the ionisation of H_2CO_3 produces HCO_3^- and CO_3^{2-}.

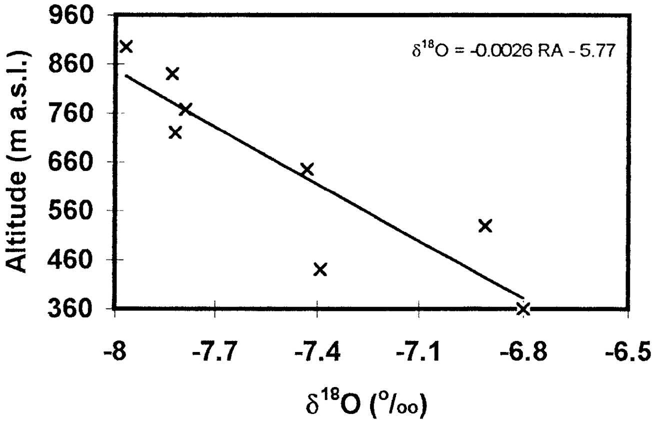


Fig. 4

Relation of $\delta^{18}O$ to altitude of sampling sites. Taken from Aires-Barros and others 1994. *Symbols* as in Fig. 3. *RA* Recharge altitude

The carbon dioxide present in thermo-mineral waters can be attributed to two main origins: organic and inorganic (Panichi and Tongiorgi 1975). Concerning the organic source, CO_2 can be produced from decay of organic matter with mean $\delta^{13}C$ values of ~ -26 and -22‰. Among the inorganic sources, carbon in hydromineral systems may originate from: (1) deep-seated (upper mantle) carbon showing $\delta^{13}C$ values ranging between -8 and -1‰, (2) dissolution of limestones that have mean $\delta^{13}C$ values close to 0‰, or (3) metamorphism of carbonates producing CO_2 with slightly positive $\delta^{13}C$ values (Truesdell and Hulston 1980). Gerlach and Taylor (1990) consider a $\delta^{13}C$ value of -3.4‰ ± 0.05 to be the best estimate of the mean for the total summit gas emission of Kilawea/Hawaii, the volcano where gases have been collected and analysed for the longest time (Hoefs 1997). Similar $\delta^{13}C$ values have been observed for CO_2 released from MORB gases (-3.7‰, Javoy and Pineau 1991) and for CO_2 from the Iceland plume (-3.8‰, Poreda and others 1992).

Almeida (1982) concluded from his $\delta^{13}C$ value measured on a CO_2 gas sample ($\delta^{13}C_{(CO2)} = -5.72$‰ versus PDB) that most of the ^{13}C in the free CO_2 related to the Chaves hot mineral waters was of upper mantle origin. It should be noted that the use of measurements on free CO_2 may lead to incorrect conclusions if the carbon remaining in water is not considered (R. Kreulen 1996, personnel communication).

Aires-Barros and others (1998) presented $\delta^{13}C$ values (performed at the Utrecht University/The Netherlands) associated with the thermo-mineral waters of Chaves, Vilarelho da Raia, Campilho, Sabroso and Pedras Salgadas. They stated that, because the values obtained range from 1 to 3‰ versus V-PDB, a simple interpretation of the data obtained could suggest a mixing of magmatic CO_2 and CO_2 derived from limestones. However, during the fieldwork performed by experts from Utrecht University, no groundwater samples were collected by LAMPIST for chemical (major elements) analysis. Therefore, the specia-

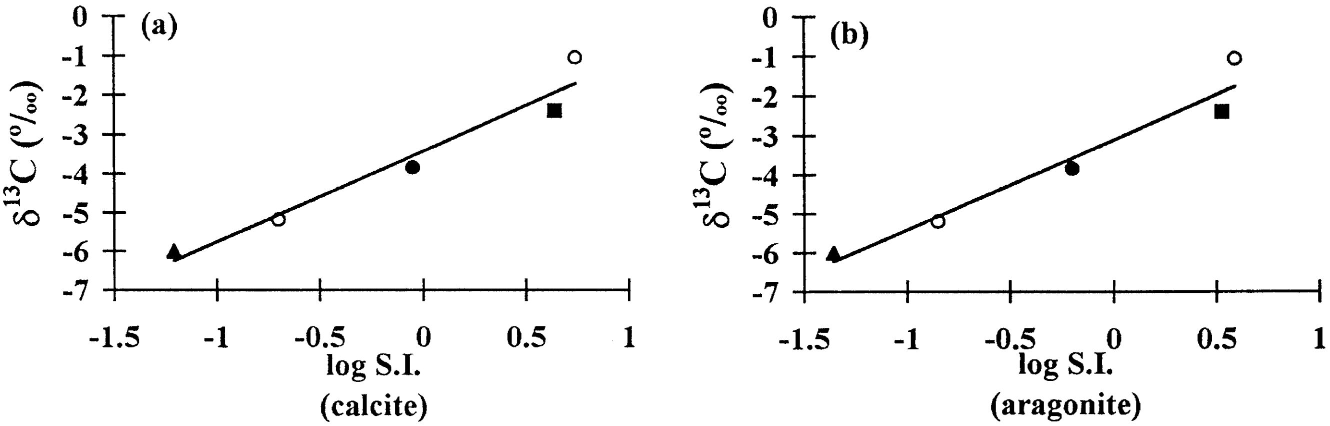


Fig. 5
Log S.I.-$\delta^{13}C$ diagram for the samples investigated. Chaves $\delta^{13}C$ value is the $\delta^{13}C_{(SrCO_3)}$ value from Almeida, 1982. *Symbols* as in Fig. 3

tion and saturation index estimation could not be carried out on those samples, and interpretation could not be more conclusive.

In order to clarify the origin of CO_2 in the CO_2-rich mineral waters of Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas, $\delta^{13}C$ determinations were carried out on total inorganic dissolved carbon (TIDC) of four drilled well waters associated with the deeper hydromineral circuits (highly mineralised waters), and two spring waters associated with the shallow groundwater circuits (low mineralised waters). Chemical analyses were also performed on the same water samples.

The results obtained (Table 2) allowed the identification of two distinct origins for the CO_2. $\delta^{13}C$ values associated with the CO_2-rich highly mineralised waters: they lay in the range of −6–1‰ and could be ascribed to either (1) a deep-seated (mantle) origin (Vilarelho da Raia, Pedras Salgadas AC17 and Vidago AC16), or (2) to a mixing process of mantle and limestone CO_2 (Chaves and Vidago AC18). Concerning the second hypothesis, one has to look for the existence of carbonate rocks at depth in the stratigraphic section crossed by the circulating waters because this type of geological formations is not exposed in the study area. In order to achieve this objective, deep in situ exploration should be considered in future drilling strategies in the area. Nevertheless, some calcareous lenses have been reported by Brink (1960) in Vila Real area (at the south of our study area). They have a width of ~30 m and a length of ~1.5 km, and occur in a zone of low-grade metamorphism that are mainly comprised of chlorite-sericite schists and phyllites. Much larger limestone intercalations cross the Douro river several kilometres to the south of our study area. A limestone zone traversing the Douro river could be traced for more than 13 km (Medeiros and Faria 1953). 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 that occur in NW Spain (Galicia). This author states that 'in view of the fact that in the adjacent area of NW Spain thick limestones occur only at the Georgian-Acadian boundary, it seems not unlikely that the limestones of northern Portugal represent this level, while thinning and disappearing towards the south-west' (Schermerhorn 1956). An alternative interpretation is that the heavier $\delta^{13}C$ values could be explained by metamorphic decarbonation reactions of country rocks that mix with magmatic CO_2.

When the $\delta^{13}C$ data from the mineral waters analysis is plotted against the logarithm of the saturation indexes (log SI) with respect to (1) calcite and (2) aragonite remarkable regularities emerge for all the data points (Fig. 5). The saturation indexes have been calculated using the computer program HIDSPEC (Carvalho and Almeida 1989), which is a hydrogeochemical model that calculates the speciation of natural waters. Using physical and chemical analyses of water, it estimates the activity of 68 aqueous species and the saturation indexes of 55 minerals. The SI for a given mineral is defined (at any temperature) as the ratio between the activity product of the species involved in the hydrolysis reaction and the equilibrium constant. The less negative $\delta^{13}C$ values are associated with those waters that present the highest SI values (Chaves and Vidago AC-18 waters). The high mineralisation and low tritium activity found in Vidago AC-18 cold mineral waters (see data from Table 2) could be viewed as signatures of a long residence time at depth because of regional circulation (as indicated by the lighter $\delta^{2}H$ values) and because they are fed at a recharge area located on the highest topography in the Padrela Mountain. These elevations are realised in the surrounding areas of Chaves. If we assume that Vidago AC18 waters are regional waters, we may presume that they display the highest probability of interacting with carbonate rocks levels at depth along the regional flow path. The authors believe that the linear correlations observed in Fig. 5 indicate that the presence of carbonate rock levels at depth as a possible carbon contributor should not be excluded. However, as previously stated by Aires-Barros and others (1998), an alternative interpretation is that the $\delta^{13}C$ values of the CO_2 (of magmatic origin) could be shifted to less negative values as a result of fractionation at low temperature. Fractionation could take place during the release of dissolved CO_2.

The $\delta^{13}C$ values measured on two carbonaceous slates in the study area (−26.9 and −27.2‰ versus V-PDB) indicate that the role of these rocks as a hydrochemical signature of the mineralised waters should be considered to be very limited. Only the cold spring waters low in mineralisation sampled close to Boticas and Pedras Salgadas display $\delta^{13}C$ values (−23.4 and −22.4‰ versus V-PDB, respectively) that could be attributed to the decay of organic matter. Comparison with the thermo-mineral waters shows that these very low mineralised waters belong to a shallow circuit and present distinct geochemical signatures (Table 2).

CO_2 versus water mineralisation

In CO_2-rich hydromineral systems, carbon dioxide is one of the most important species that influences the chemical and physical characteristics. Water-rock interaction is enhanced by low temperatures because the solubility of CO_2 in water increases with decreasing temperature (Criaud and Fouillac 1986; Greber 1994). Otherwise, during the ascent of CO_2-rich water from the reservoir to the surface, pH of the deep fluid could decrease as a result of cooling and/or mixing with shallow waters, the acidity of the water would increase and water-rock interactions would become more active leading to metal dissolution. Aires-Barros and others (1998) have plotted the HCO_3, Na, K and Li contents in waters against a conservative element such as Cl (Fig. 6). They stated that the alignment of the regression line seems to indicate that the presence of these ionic species in water could be associated with water-rock interactions that are related to the same geological environment (granitic rocks). However, the behaviour of Ca and Mg is different (Fig. 7). The scatter of the data presented in Fig. 7 could be ascribed to (1) the fact that the solubility of Ca and Mg increases with decreasing temperature or (2) the dissolution of a different rock type at depth (carbonate rock levels). In Figs. 6 and 7, the points representing Chaves hot waters form a cluster, which indicates the existence of a common reservoir for these waters. The waters from Vilarelho da Raia, Vidago and Pedras Salgadas have different chemical tracer contents indicating that each of these cold mineral waters had different flow-paths and different degrees of water-rock interaction. Higher salinities (Vidago AC18) should correspond to larger residence times, which would be probably associated with deeper circulations.

In the logarithmic Ca^{2+}-HCO_3^- diagram (Fig. 8), the hot and cold CO_2-rich mineral waters do not plot on the line $2[Ca^{2+}]=[HCO_3^-]$. This trend indicates that most HCO_3^- should be related to the dissolution of deep-seated CO_2 in water. However, the presence of carbonate rocks levels percolated by Vidago AC16 and Pedras Salgadas AC17 mineral waters (those showing high Ca^{2+} concentrations) could be postulated. In this case, the presence of Ca^{2+} in waters could be related to the following reaction:

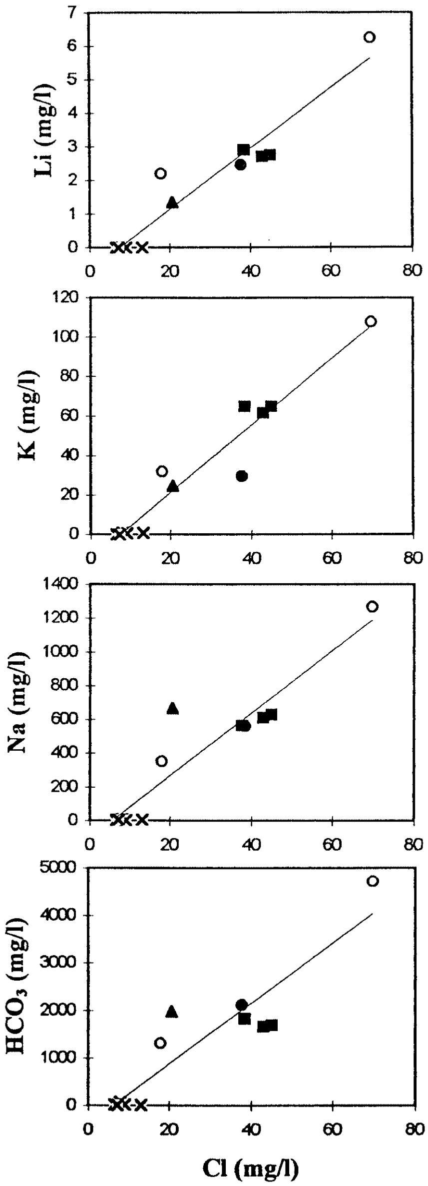


Fig. 6
HCO_3, Na, K and Li ionic species plotted as a function of Cl contents in water samples. Taken from Aires-Barros and others (1998). *Symbols* as in Fig. 3

$$H_2O + CO_{2(g)} + CaCO_{3(s)} = 2\,HCO_3^- + Ca^{2+}$$

The calculated P_{CO_2} values (Table 2), using the computer program HIDSPEC, strongly suggest a deep source for the CO_2. The P_{CO_2} values were calculated using the following equation:

$$\log P_{CO_2} = \log a_{HCO_3^-} - pH - \log K_0 - \log K_1$$

where $K_0 = \frac{a_{H_2CO_3}}{P_{CO_2}}$, $K_1 = \frac{a_{HCO_3^-} \cdot a_{H^+}}{a_{H_2CO_3}}$ and a_i = activity of the i species

The calculated P_{CO_2} values (Table 2) also indicate that it is unlikely that mixing between deep waters and more re-

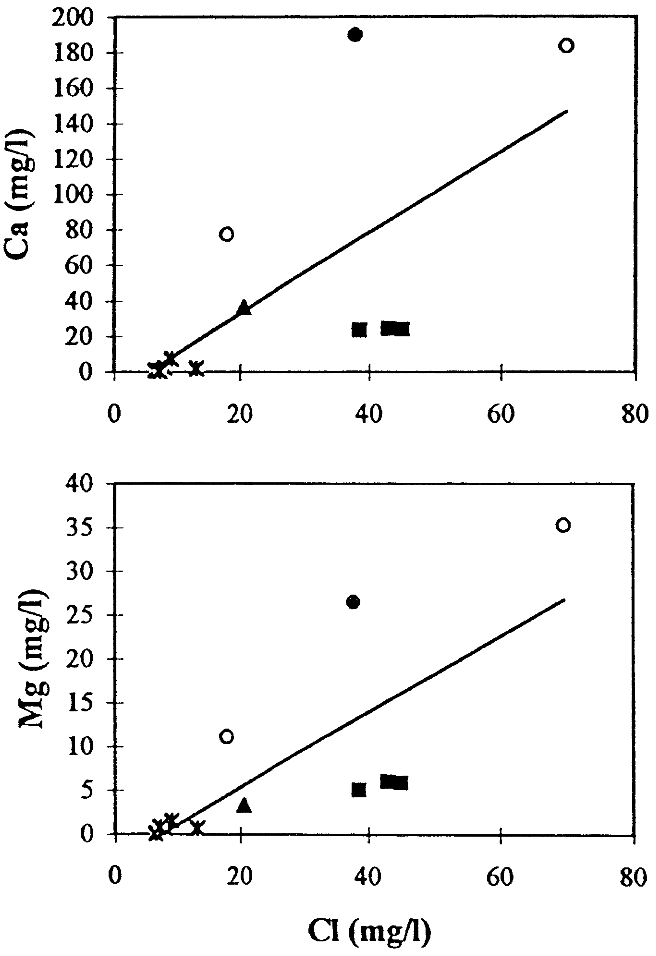


Fig. 7
Ca and Mg ionic species plotted as a function of Cl contents in water samples. Data from Aires-Barros and others (1998). *Symbols* as in Fig. 3

cent meteoric waters satisfactorily explains the higher tritium activity found in Vidago (AC16) and Pedras Salgadas (AC17) non-thermal waters. It could be mainly related to shallow underground flow paths because the water mineralisation is strongly controlled by CO_2 content. The high CO_2 content of Vidago/Pedras Salgadas mineral waters could be associated by the fact that Chaves hot (76 °C) waters emerge from a deep (high temperature) environment, whereas the Vidago/Pedras Salgadas cold (17 °C) mineral waters are the result of shallow (low temperature) underground flow paths. The hypothesis of the existence of a significant CO_2 source in the south, which is not present in Chaves area, should not be ruled out. However, because the Vilarelho da Raia cold (17 °C) mineral waters show much higher CO_2 values than the Chaves hot waters, the first hypothesis seems to be the most reliable.

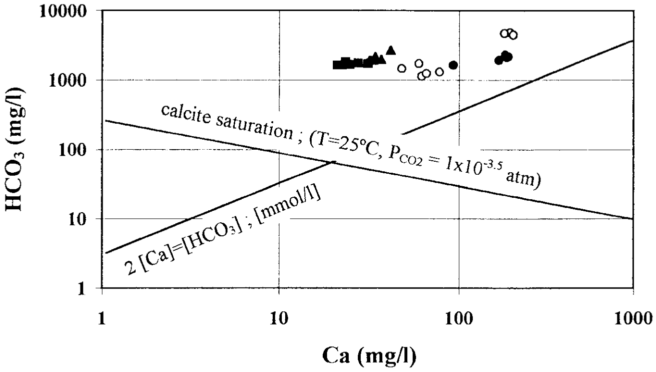


Fig. 8
Logarithmic Ca^{2+}–HCO_3^- diagram for Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas waters, including data from Aires-Barros and others (1998) and new data presented in Table 2. *Symbols* as in Fig. 3

Isotopic water-CO_2 equilibrium

In many cases, deep groundwaters related to the geothermal systems display a positive oxygen-18 shift as a consequence of isotopic water-rock interaction with the rocks that constitute the reservoir. The deuterium content is usually identical to that of local meteoric recharging waters. This situation is the most characteristic for high temperature geothermal systems (Ellis and Mahon 1977). Chaves hot mineral waters show that a lack of oxygen-18 shift could represent either an old geothermal system in which the isotopic composition of the rock is adjusted to equilibrium with the recharge waters, or a deep reservoir recharged by local meteoric waters with relatively short circulation time and small isotope exchange with rocks. This second hypothesis seems to be the most likely because the issue temperature of Chaves thermal waters is not as high, and the results of chemical geothermometers indicate reservoir temperature of ~120 °C (Aires-Barros and others 1995). However, a lack of an ^{18}O-shift could also be explained by oxygen isotope exchange between $H_2O_{(l)}$ and $CO_{2(g)}$ (D'Amore and Panichi 1987). Almeida (1982) presented $\delta^{18}O$ values of water and CO_2 related to Chaves hot waters. $\delta^{18}O$ value of $H_2O_{(l)}$ was −8.04‰ versus V-SMOW (similar to the isotopic composition of present-day Chaves thermal waters), and the corresponding value in $CO_{2(g)}$ was +25.62‰ versus V-SMOW. Using this data, we have calculated the additive fractionation factor (CO_2–H_2O). The value obtained (+33.93‰) indicates that the equilibrium temperature (Friedman and O' Neil 1977) is close to the measured temperature of 75 °C at sampling. Concerning oxygen isotopes, it seems that $H_2O_{(l)}$ and $CO_{2(g)}$ are in equilibrium.

Concluding remarks

The low temperature and the systematic presence of tritium in Vidago AC16 and Pedras Salgadas AC17 cold mineral waters seems to indicate that, in contrast to Chaves hot waters, the chemistry of these cold CO_2-rich mineral waters is mainly related to water-rock interaction favoured by the presence of CO_2 in a low temperature (shallow) environment. Recent $\delta^{13}C$ data ($-6.0 < \delta^{13}C < -1.0‰$ versus V-PDB) seems to indicate that the lightest $\delta^{13}C$ values could be assumed to be derived mainly from a deep-seated (mantle) source, whereas a more complex origin could be proposed for the heavy $\delta^{13}C$ values: mixing of mantle CO_2 with carbonate CO_2 (derived from thermal decarbonation or rock dissolution). The most probable explanation by which the carbon dioxide could be transported from its deep source (mantle) to the surface involves migration as a separate gas phase and incorporation in the infiltrated meteoric waters (at considerable depth in the case of the hot CO_2-rich waters and at shallow levels in the case of cold CO_2-rich waters). This hypothesis is supported by the fact that the $\delta^{18}O$ and $\delta^{2}H$ data related to the studied hot and cold CO_2-rich mineral waters do not show any evidence of mixing with magmatic waters. The fact that most of the studied CO_2-rich hot and cold springs are located near faults indicates that those tectonic features must have access to deep levels in the study area (to explain the formation of the carbon dioxide waters) because, along the NNE–SSW megalineament, we can encounter Carvalhal (43 °C) and S. Pedro do Sul (69 °C) hot mineral waters that are characterised by lower mineralisation (dry residue values of ~340 mg/l) and total absence of CO_2 (gas). We believe that, besides its peculiar geochemistry, the role of the carbonaceous slates that are displayed in Chaves, Vidago and Pedras Salgadas areas do not influence the hydrochemical signature of the mineralised groundwaters. Spring and shallow drilled well waters can be considered external manifestations of the hydrothermal processes that occur at depth in the studied region, but their origin are not completely known because there has been no deep in situ exploration and very little is known about the basement.

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