

## Mantle-derived carbon in Hercynian granites. Stable isotopes signatures and C/He associations in the thermomineral waters, N-Portugal

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### ARTICLE INFO

#### Article history:

Received 13 May 2009

Accepted 18 October 2009

Available online 29 October 2009

#### Keywords:

CO<sub>2</sub>-rich thermomineral waters

mantle volatiles

isotopes

Chaves geothermal system

N-Portugal

### ABSTRACT

Na–HCO<sub>3</sub>–CO<sub>2</sub>-rich thermomineral waters issue in the N of Portugal, within the Galicia-Trás-os-Montes region, linked to a major NNE-trending fault, the so-called Penacova-Régua-Verin megalineament. Along this tectonic structure different occurrences of CO<sub>2</sub>-rich thermomineral waters are found: Chaves hot waters (67 °C) and also several cold (16.1 °C) CO<sub>2</sub>-rich waters. The δ<sup>2</sup>H and δ<sup>18</sup>O values of the thermomineral waters are similar to those of the local meteoric waters. The chemical composition of both hot and cold mineral waters suggests that water–rock reactions are mainly controlled by the amount of dissolved CO<sub>2</sub> (g) rather than by the water temperature. Stable carbon isotope data indicate an external CO<sub>2</sub> inorganic origin for the gas. δ<sup>13</sup>C<sub>CO2</sub> values ranging between –7.2‰ and –5.1‰ are consistent with a two-component mixture between crustal and mantle-derived CO<sub>2</sub>. Such an assumption is supported by the <sup>3</sup>He/<sup>4</sup>He ratios measured in the gas phase, are between 0.89 and 2.68 times the atmospheric ratio (Ra). These ratios which are higher than that those expected for a pure crustal origin (≈0.02 Ra), indicating that 10 to 30% of the He has originated from the upper mantle. Release of deep-seated fluids having a mantle-derived component in a region without recent volcanic activity indicates that extensive neo-tectonic structures originating during the Alpine Orogeny are still active (i.e., the Chaves Depression).

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### 1. Introduction

Sodium bicarbonate–CO<sub>2</sub>-rich thermomineral waters have been described from all continents in different geological environments such as: from France within the Palaeogene sediments in granitic basement (Rihs, et al., 2000), in Germany associated to formations of the Rhine Graben within a volcanic environment varying between alkali basalts, undersaturated nephelinites and leucitites to phonolites and carbonatites (Griesshaber et al., 1992), in the Czech Republic part of the Bohemian Massif, old geological heterogeneous rock from the Proterozoic and lower Paleozoic (Krásný, 2001, 2007) in Romania marls with intercalations of sandstones and volcanic tuffs dominate the lithology (Bacia et al., 2001), in Spain, the work discussed by Pérez et al. (1996) is focus on the Hesperic Massif, consisting mainly of Hercynian granites and Paleozoic metasediments, while in the United States in the Aquia aquifer Maryland basically composed by marine

carbonates (Chapelle and Knobel, 1985) and the study performed in the confined aquifer situated within fractured Permian to Jurassic sediments in Australia (Schofield and Jankowski, 2004).

Understanding the origin of carbon dioxide and other volatiles in this type of groundwater represents a major geological process of Earth degassing. Mantle-derived volatiles escape to the Earth's surface primarily through the mid-ocean spreading ridges (Marty and Tolstikhin, 1998). However, recent studies have reported important contributions of mantle-derived volatiles in continental scenarios associated with active tectonics, volcanism and crustal extension (Xu et al., 1995, Griesshaber et al., 1992, Sherwood Lollar et al., 1997, Caracausi et al., 2005). More recently in Italy, regional-scale studies on deeply-derived CO<sub>2</sub> input in to groundwater have been performed (Chiadini et al., 2000; Chiadini et al., 2004). Furthermore, dissolved gases in waters have been successfully used in geochemical investigations to solve hydrological, geothermal and mineralogical problems (Capasso and Inguaggiato, 1998). Moreover, mineralogical, petrographic and geochemical compositions of fractures fillings in crystalline rocks have provided valuable information on the mechanisms of mineral formation and for reconstruction of past fluid circulation (Sacchi et al., 2004).

In this context, the study of dissolved gas species applied to CO<sub>2</sub>-rich thermomineral waters is important because of the high mobility of

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gases, combined with their different solubility coefficients. Thus, the dissolved gases are excellent geochemical tracers providing additional information to the traditional chemical and isotopic approaches as for gas–water interaction processes.

The present work will focus on the geochemical characterization of CO<sub>2</sub>-rich thermomineral waters in the N part of Portugal approximately between Vilarinho da Raia and Pedras Salgadas areas (Fig. 1). The two-component mixing of the conceptual model of the region hydrogeological system will be presented and discussed. Several hydrogeological studies have been carried out in this region using a multidisciplinary approach based on isotopic, geochemical and geophysical methodologies. The hydrogeochemical features and water–rock reactions have been used to explain the origin and evolution of the CO<sub>2</sub>-rich thermomineral waters (Aires-Barros et al., 1995; Aires-Barros et al., 1998; Marques et al., 1998a,b, 2000, 2001; Monteiro Santos et al., 2002; Andrade, 2003).

## 2. Background

The region is located in the Ante-Mesozoic Hesperic Massif, in the tectonic unit of Middle Galicia/Trás-os-Montes sub-zone of the Central-Iberian Zone of the Hesperic Massif, consisting mainly of Hercynian granites and Paleozoic metasediments (Fig. 1). The main regional geological formations are: (1) Hercynian granites (syn-tectonic–310 Ma and late to post-tectonic–290 Ma) and (2) Silurian metasediments of the Upper, Intermediate and Lower Peritransmontano Group, which consists on a sequence of quartzites and phyllites. Inserted between the schistoid complex, bands of carbonaceous slates are well displayed in Chaves area in a randomly outcrops. The most recent formations are Miocene–Pleistocene graben filling sediments (with variable thickness) showing their maximum development along the central axis of “Chaves Depression”. This graben, whose axis is oriented NNE–SSW is bounded on the east by the edge of

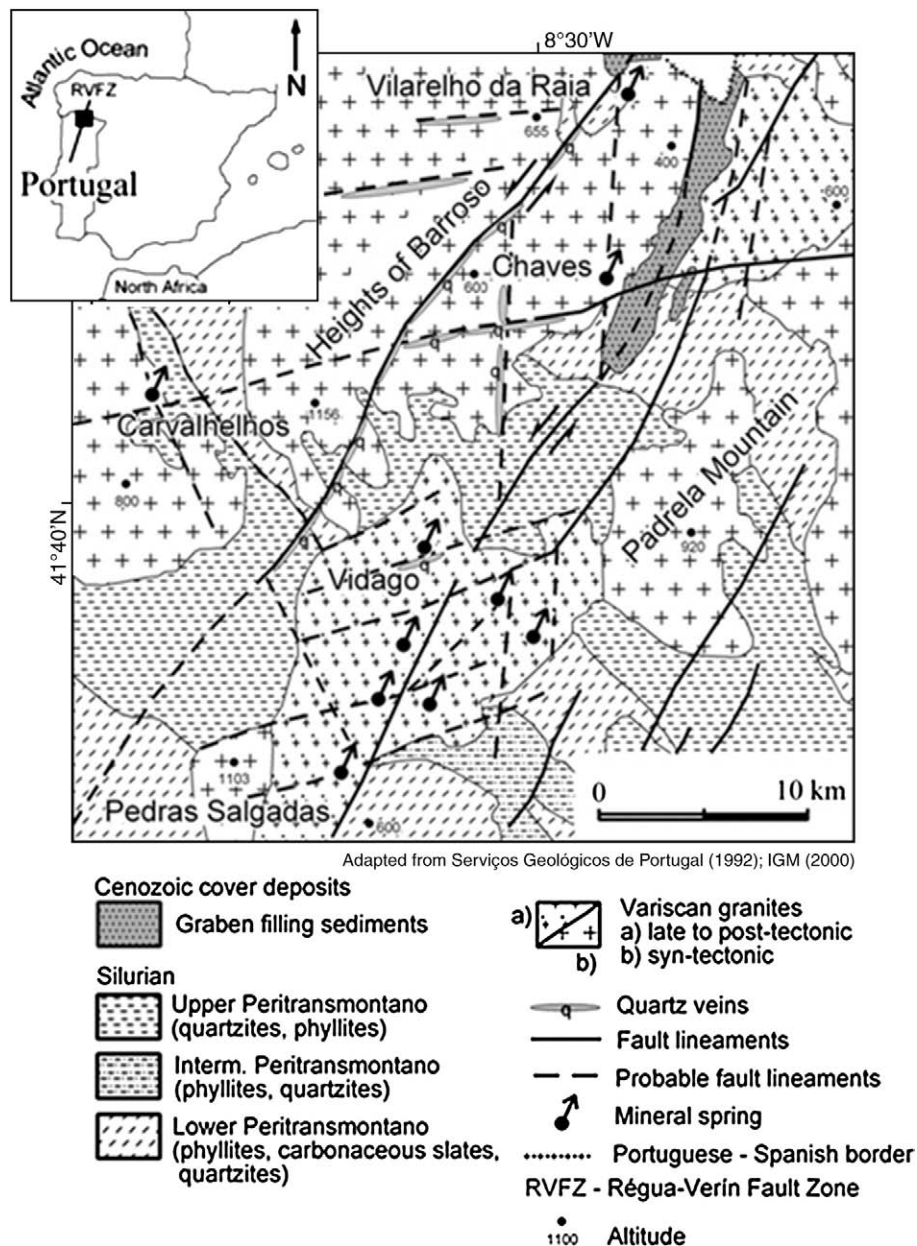


Fig. 1. Geological sketch map of the research region showing locations of the main water and gas sampling sites. Adapted from Sousa Oliveira, 1995).

Padrela Mountain escarpment with a 400 m throw. The western block is formed by several smaller grabens coming from the Heights of Barroso towards the Chaves depression. The Silurian metamorphic formations have been recognised on both eastern and western sides of Chaves graben. The Miocene–Pleistocene series are mainly composed of lacustrine, alluvial and detritic layers (Sousa Oliveira and Portugal Ferreira, 1996).

The region is mainly controlled by the NNE–SSW active fault system, which plays an important role in the thermomineral waters ascent. Sousa Oliveira and Portugal Ferreira (1996) pointed out the fact that the mineral waters emerge in places where the NNE–SSW and ENE–WSW sub-vertical fracture systems intersect (Fig. 1).

To better understand relations between water chemistry and isotopes and coexisting gas geochemistry, water and gas samples were collected in both hot (68 °C) and cold (16.1 °C) systems to characterize the geochemical and isotopic signatures of the associated gas phases. The main objective was to identify the contribution of deep crustal and mantle volatile components associated with the regional tectonic structures. The obtained data (CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, CO, O<sub>2</sub>, Ar, He, Ne, <sup>2</sup>H, <sup>3</sup>H, <sup>13</sup>C, <sup>18</sup>O, <sup>3</sup>He/<sup>4</sup>He, <sup>40</sup>Ar/<sup>36</sup>Ar and <sup>15</sup>N) were used as a hydrogeological tool in the evaluation of the groundwater resources of these areas, increasing our knowledge on groundwater flow circulation paths and on the relation between the hot and cold CO<sub>2</sub>-rich mineral waters. Characterization of these waters is important in the assessment of local/regional low-temperature geothermal resources, to determine whether the hot and cold carbon dioxide waters should be considered (or not) surface manifestations of a large-scale deep-seated hydrothermal system.

### 3. Groundwater sampling and analytical methods

The results presented in this work were obtained during the survey in December 2005. Water samples were collected from seven boreholes, and stored in polyethylene bottles for chemical and isotope analyses while temperature (°C), electrical conductivity (μS/cm) and pH were determined *in situ*. All the sampled boreholes, with exception of Vilarelho da Raia, are CO<sub>2</sub> evolving wells. For these sites, the gases were collected by using a home-made gas–water separator. Separated gas was flown through a glass flask with two-way stopcocks having a volume of about 30 ml. At Vilarelho da Raia, water samples for dissolved gases analyses were collected in glass bottles hermetically sealed in the field with gas-tight Teflon-rubber septa taking care to not include air bubbles. Gases were extracted and analysed at the laboratories of the Istituto Nazionale di Geofisica e Vulcanologia (Palermo, Italy) using the methods described by Capasso and Inguaggiato (1998), Inguaggiato et al. (2005), Inguaggiato and Rizzo (2004).

The δ<sup>2</sup>H and δ<sup>18</sup>O were determined three times for each sample in order to increase the analytical precision. The measurements were conducted on a mass spectrometer SIRA 10 VG-ISOGAS using the methods proposed by Friedman (1953) and Epstein and Mayeda (1953) for <sup>2</sup>H and <sup>18</sup>O, respectively. The tritium content was determined using the electrolytic enrichment and liquid scintillation counting method (IAEA, 1976; Lucas and Unterweger, 2000) using a PACKARD TRI-CARB 2000 CA/LL. The error associated to the <sup>3</sup>H measurements (usually around 0.7 TU) varies with the <sup>3</sup>H concentration in the sample. All isotopic determinations were performed in the ITN–Chemistry Department, Sacavém Portugal.

The chemical analyses were performed at the Laboratório de Mineralogia e Petrologia of IST–Lisbon (Portugal). Total alkalinity was measured a few hours after collection and the following methods were applied for chemical analyses: atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na, K and Li; colorimetric methods for SiO<sub>2</sub>, Al and Fe; ion chromatography for SO<sub>4</sub>, NO<sub>3</sub> and Cl; potentiometry for alkalinity, here referred to as HCO<sub>3</sub>. Dry residuum was estimated following the US Geological Survey procedure (Hem,

1970). The free CO<sub>2</sub> data was obtained through the carbonate alkalinity, determined by the back acid-base titration method.

## 4. Results

### 4.1. Isotopic composition of groundwater

The isotopic composition (δ<sup>2</sup>H and δ<sup>18</sup>O) of the CO<sub>2</sub>-rich mineral waters ranges from −8.42‰ to −6.97‰ for oxygen and from −57.0‰ to −48.0‰ for hydrogen (Table 1). Most of the thermomineral water samples plot along the Global Meteoric Water Line (GMWL, Craig, 1961) or at the right of this line. These isotopic signatures indicate a meteoric origin for these waters and they have not been subjected to sub-surface evaporation (Fig. 2). In this diagram, two long term weighted mean values of precipitation from Bragança and from Vila Real (period 1988–1991 monthly record) meteorological stations are plotted (δ<sup>2</sup>H<sub>Bragança</sub> = −50.0‰; δ<sup>18</sup>O<sub>Bragança</sub> = −7.73‰ and δ<sup>2</sup>H<sub>Vila Real</sub> = −42.5‰; δ<sup>18</sup>O<sub>Vila Real</sub> = −6.40‰; in Carreira et al., 2005). These stations are part of GNIP network (Global Network of Isotopes in Precipitation) and are located in the vicinity of the research region at altitudes of 690 and 481 m.a.s.l., respectively. These values were plotted as reference for the isotopic composition of local meteoric waters.

Frequently, within high-temperature (>150 °C) geothermal systems, a positive “oxygen-shift” is observed that is attributed to exchange of oxygen in the water molecule with the oxygen in silicate or carbonate minerals in confining rocks (Craig et al., 1956). Kharaka and Mariner (2005) show that oxygen mass balance equations together with isotope fractionation factors between water and minerals can be applied to estimate the “oxygen-shift” in both water and rocks. In our research region no evidence of water–rock interaction processes at high temperature have been detected particularly Chaves thermomineral waters. Nevertheless, Kharaka and Mariner (2005) believe that small oxygen-shifts can be observed in old systems where the isotopic composition of the rock have been shifted to equilibrium with the water, and in low-temperature systems where the rate of exchange between the water and the rock is too slow to cause a change in the isotopic composition of water as it passes through the system. In the study region, the isotopic data deviation found within the water samples collected from different groundwater systems (Pedras Salgadas, Chaves, Vidago and Vilarelho da Raia) is due, most probably, to the different recharge altitudes. On the other hand, the low tritium content (close to the detection limit) indicates a relatively long residence time, associated with groundwater circulation paths reaching, in the case of Chaves system, considerable depths (Table 1).

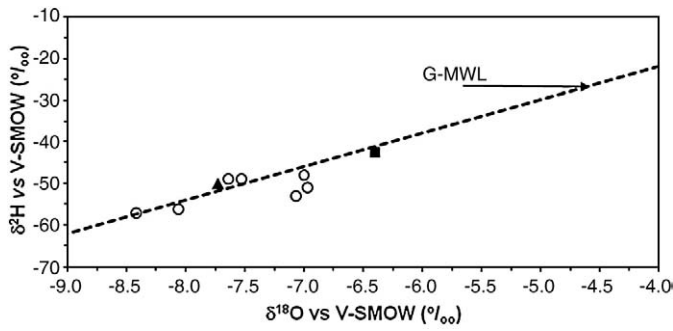
### 4.2. Chemical composition of groundwater

A preponderance of Na–HCO<sub>3</sub> water discharge in the research area. The results identify two groups of waters. The first one is composed of Chaves (67 °C) and Vilarelho da Raia (16.4 °C), characterized by a dry residuum (DR) of 1498 and 1621 mg/L and a Total CO<sub>2</sub> between 2171

**Table 1**

Temperature and isotopic composition (δ<sup>2</sup>H, δ<sup>18</sup>O and <sup>3</sup>H) of the groundwater samples collected in the field campaign of December 2005. The <sup>2</sup>H and <sup>18</sup>O results are reported in ‰-notation with an accuracy of 1‰ for δ<sup>2</sup>H and 0.1‰ for δ<sup>18</sup>O.

Ref.	Sampling date	Temp. (°C)	δ <sup>18</sup> O (‰)	δ <sup>2</sup> H (‰)	<sup>3</sup> H ± σ (TU)
Chaves Termas AC1	December 2005	68.0	−8.42	−57.0	0.0 ± 0.6
Vilarelho da Raia		16.4	−8.06	−56.0	0.0 ± 0.8
Vidago Areal 3		17.5	−6.97	−51.0	0.0 ± 0.7
Vidago 16		16.0	−7.00	−48.0	1.0 ± 0.6
Vidago 18		15.5	−7.07	−53.0	0.0 ± 0.6
Pedras Salgadas 17		13.7	−7.53	−49.0	0.7 ± 0.6
Pedras Salgadas 25		17.7	−7.64	−49.0	0.0 ± 0.6



**Fig. 2.**  $\delta^{18}\text{O}$  vs  $\delta^2\text{H}$  (‰ vs V-SMOW) for the  $\text{CO}_2$ -rich mineral waters (December 2005). GMWL stands for Global meteoric Water Line ( $\delta^2\text{H} = \delta^{18}\text{O} + 10$  Craig, 1961); the symbol (○) stands for the isotopic composition of the thermomineral water samples; (▲) stands for the isotopic composition weighted mean Bragança meteorological station and (■) stands for the isotopic composition weighted mean Vila Real meteorological station (Carreira et al., 2005).

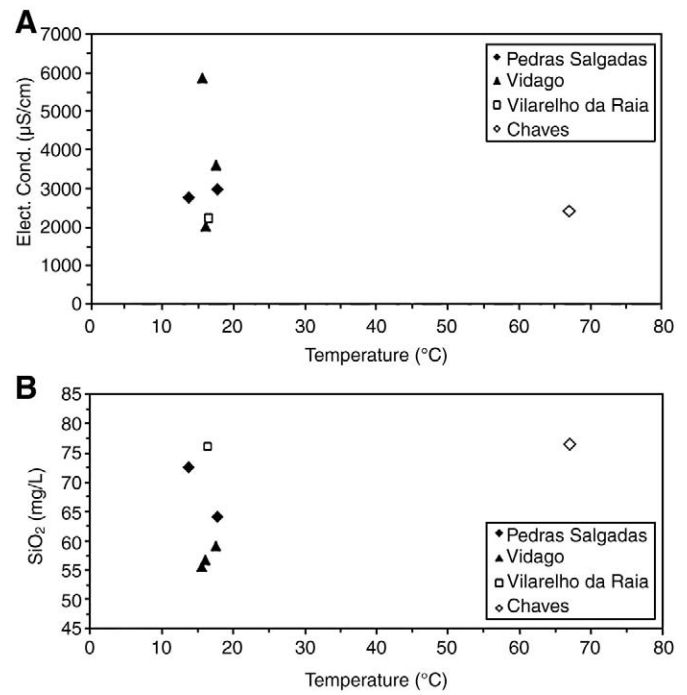
and 2292 mg/L. The second group consists of Vidago and Pedras Salgadas mineral waters showing a mean temperature of 16.1 °C, and highest content in Ca, Mg, and Total  $\text{CO}_2$ , up to 5909 mg/L. Within this group Vidago AC18 mineral waters show the highest mineralization with DR content of 4146 mg/L (Table 2).

This relation is often used in the evaluation of the deep (reservoir) temperatures of hydrothermal systems. The dissolution of most minerals in nearby igneous rocks is thermodynamic dependent having a direct relationship with fluid temperature. In many geothermal regions, surface manifestations consist only of hot ground, acid surface waters and fumaroles. In these cases, water geothermometers cannot be applied. This implies the use of steam (gas) geothermometers. Some studies have been performed in geothermal wells by Arnorsson and Gunnlaugsson (1985) who report good agreement between measured temperatures and the average of the temperatures estimated from the  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2$  and  $\text{CO}_2/\text{H}_2$  geothermometers in nearby fumaroles. However, there are no fumaroles in the study region, just springs and boreholes with gas bubbles, and no temperature dependence is observed between the amount of mineralization and the dissolved  $\text{SiO}_2$  of the waters (Fig. 3). Therefore, silica and possibly other water geothermometers will produce rough reservoir temperatures.

**Table 2**

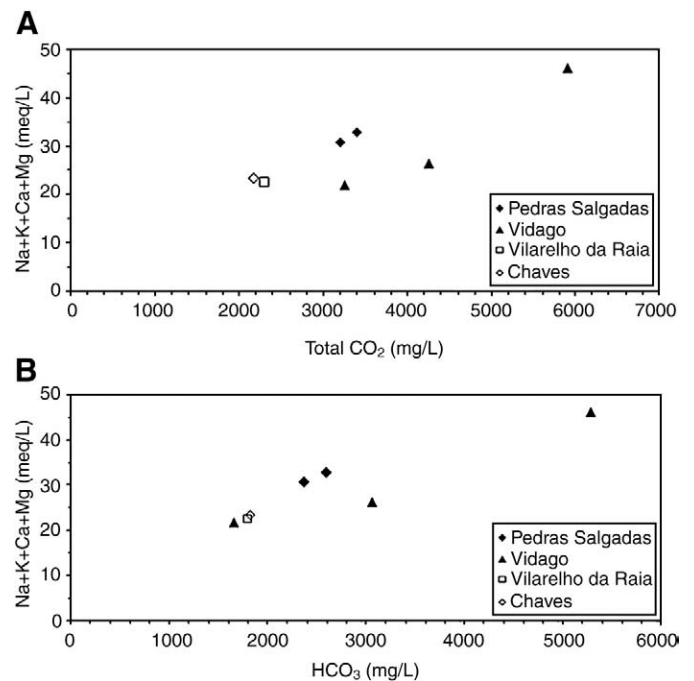
Physical and chemical signatures of the studied mineral waters (December 2005). Temperature (°C), pH, electrical conductivity ( $\mu\text{S}/\text{cm}$ ) and Eh (mV) were obtained *in situ*. Concentrations are in mg/L.

	Pedras Salgadas AC25	Pedras Salgadas AC17	Vidago AC16	Vidago AC18	Vidago Areal 3	Vil. Raia ACP1	Chaves AC1
Temp.	17.7	13.7	16.0	15.5	17.5	16.4	67.0
pH	6.40	6.40	6.10	6.57	6.35	6.45	6.41
Elec. cond.	2990	2780	2030	5850	3610	2230	2420
Eh	106	104	116	67	95	109	151
Ca	83.9	162.5	73.6	183.7	51.9	27.0	18.7
Mg	30.0	26.3	13.9	36.7	13.4	4.8	5.5
Na	581.7	455.4	368.9	722.3	486.1	465.3	470.9
K	35.2	25.4	36.4	101.5	58.1	21.0	59.6
Al	0.13	0.18	0.08	0.37	0.13	0.04	0.05
Fe	3.90	4.40	3.90	2.60	0.95	0.51	0.09
Li	2.57	2.35	2.42	4.91	4.54	1.74	2.63
$\text{HCO}_3^-$	2597	2369	1652	5284	3058	1794	1823
$\text{SO}_4$	5.1	10.3	7.5	3.5	2.78	25.6	28.5
Cl	23.7	31.0	18.4	80.4	29.2	35.7	35.1
$\text{NO}_3$	0.28	1.28	5.49	1.20	0.28	0.28	0.27
$\text{SiO}_2$	64.2	72.5	56.8	55.7	59.1	76.1	76.5
D.R.	2049	2180	1349	4146	2480	1498	1621



**Fig. 3.** (A) Relation between the emergence temperature and the electrical conductivity of the water samples. (B) Dissolved  $\text{SiO}_2$  as a function of the issue temperature.

In addition, the  $\text{CO}_2$  solubility increases with the decrease of the temperature, and so within a  $\text{CO}_2$ -rich system the mechanisms of water-rock interaction will be favoured by low temperatures. This “behaviour” can explain the high TDS of the cold, mineralized waters when compared with the thermal waters (Fig. 4). The difference in salinity of the groundwaters seems not to be related with the water temperature, or with the degree of weathering controlled by long residence time. Instead, mineralization is strongly dependent of the



**Fig. 4.** (A) Relation between the cationic species and the total dissolved  $\text{CO}_2$ . (B) Relation between the cationic species and the  $\text{HCO}_3^-$  content.

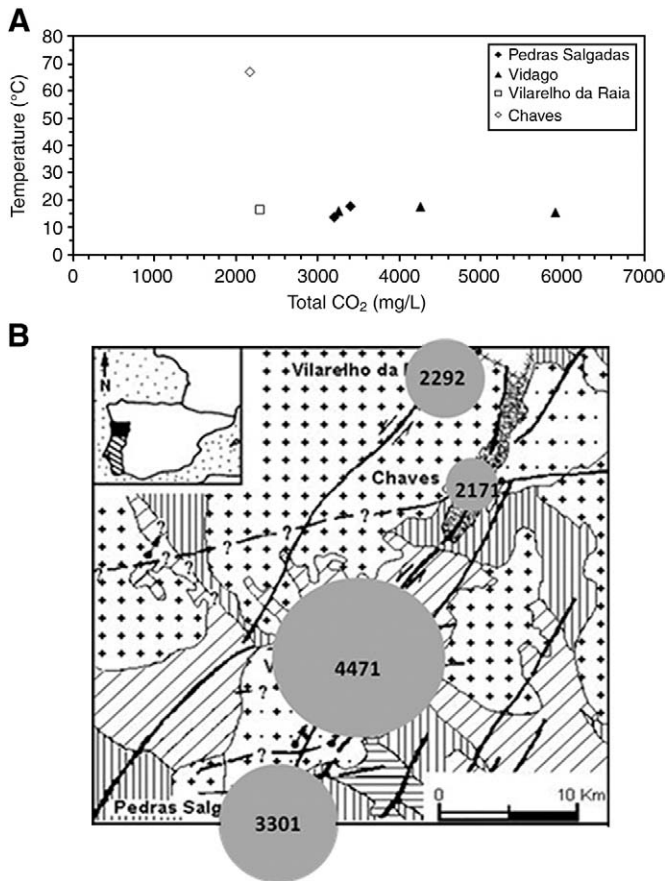


Fig. 5. (A) Groundwater temperature vs the Total dissolved CO<sub>2</sub> (mg/L). (B) Regional distribution of the Total CO<sub>2</sub> (mg/L) dissolved in the mineral waters.

amount of dissolved gases in the groundwaters. The low Ca and Mg content found in Chaves thermomineral water and in Vilarelho da Raia system, is caused by the geological matrix of the aquifers, which plays an important role in the geochemical signatures of the mineral waters. Hydrothermal mineral assemblages from Chaves/Vilarelho da Raia granitic rocks are observed in the drill cores, besides petrographic observations indicate that a pervasive (diffuse) alteration event affected the entire granitic massif (Marques et al., 1998a). Alteration of biotite and plagioclase created secondary chlorite and sericite, respectively. The similarity of the <sup>87</sup>Sr/<sup>86</sup>Sr values between the mineral waters (<sup>87</sup>Sr/<sup>86</sup>Sr=0.728033) and the plagioclases from Vilarelho da Raia granitic rocks (<sup>87</sup>Sr/<sup>86</sup>Sr=0.72087) obtained by

Marques et al. (2006) suggests that mineralization is strongly dominated by water/plagioclase-Na interaction.

The geochemical patterns observed in the CO<sub>2</sub>-rich mineral waters of northern Portugal indicate that the water-rock interactions are controlled by the presence of CO<sub>2</sub> more than by the existence of high temperatures at depth. Similar conclusions were reached by Schofield and Jankowski (2004) in Na-HCO<sub>3</sub>-rich groundwaters from Ballimore region (Australia) where the geochemistry of the mineral waters indicates that the influx of CO<sub>2</sub> gas governs the water-rock interactions controlling in particularly pH buffering.

Near the PGV megalineament CO<sub>2</sub>-rich mineral waters show a regional pattern that can be identified when the total CO<sub>2</sub> content dissolved in the mineral waters is schematically represented in a regional map (Fig. 5). A decrease of total CO<sub>2</sub> gas concentration from South to North is observed.

### 5. Geochemistry of gases

Table 3 reports the analytical results obtained for the free and the dissolved gases measured in the seven groundwater samples. In all, either in the free or in the dissolved gas phase, CO<sub>2</sub> is the dominant gas component, and N<sub>2</sub> the second most abundant one. All water samples are strongly enriched in helium with respect to the air (He<sub>air</sub> = 5.2 ppm) and to Air Saturated Water (He<sub>ASW</sub> ≈ 4.5 × 10<sup>-5</sup> ccSTP/L). In the bubbling gas samples He content ranges from 105 to 1061 ppm, while helium dissolved in the waters of Vilarelho da Raia is about 1.2 × 10<sup>-2</sup> ccSTP/L corresponding to about 7850 ppm vol.

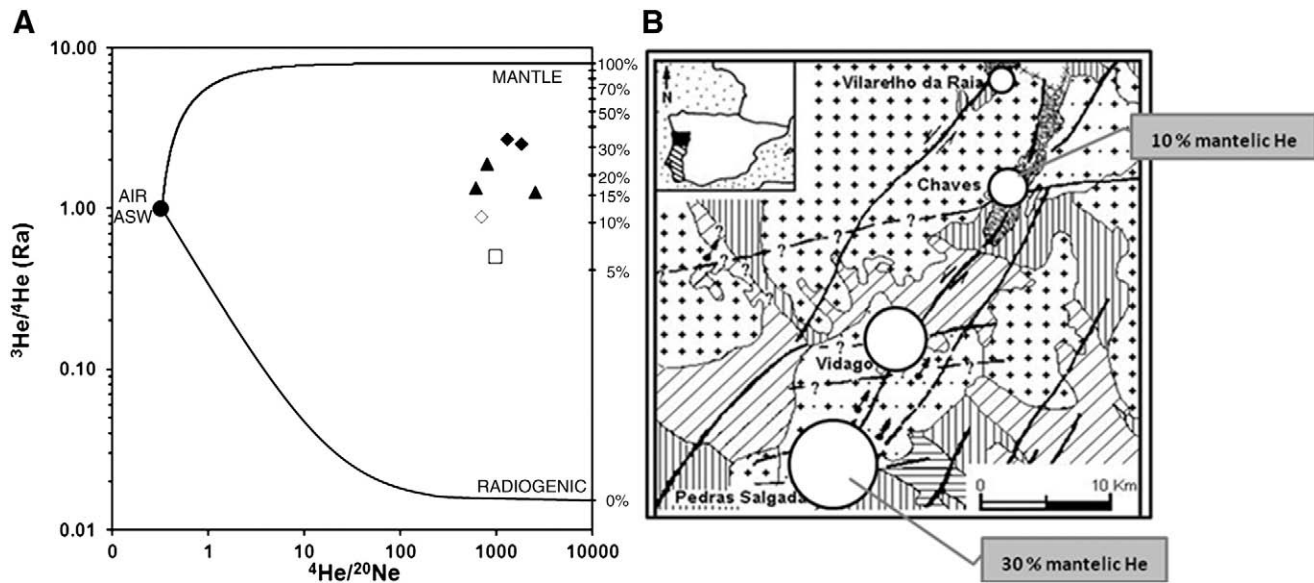
The helium (<sup>3</sup>He/<sup>4</sup>He) and carbon (δ<sup>13</sup>C<sub>CO2</sub>) isotopic ratios of the gas phase associated with the CO<sub>2</sub>-rich mineral waters were used to distinguish between deep crustal fluids and mantle volatiles released along the tectonic lineament ascribed to the “Chaves Depression”. The measured <sup>3</sup>He/<sup>4</sup>He ratio values are higher than those of pure crustal radiogenic helium (≈ 0.02 Ra). The <sup>3</sup>He/<sup>4</sup>He ratio measured in the gas phase of the mineral waters varies between 0.5 and 2.68 times the atmospheric ratio (Ra), at Vilarelho da Raia (ACP1) and in Pedras Salgadas AC25 boreholes, respectively. The obtained ratios are higher than those of pure crustal radiogenic helium (≈ 0.02 Ra). Therefore, an addition of <sup>3</sup>He has to be considered (Fig. 6A).

The main source of <sup>3</sup>He is the mantle, which is characterized by <sup>3</sup>He/<sup>4</sup>He ratios up to three orders magnitude higher than the same ratio in the crust. For example, the typical He% value of the mantle (MORB) is 8 ± 1 R/Ra. High fluxes of mantle-derived helium in continental areas are associated with regions subjected to extensional tectonics, or characterized by rising mantle plumes and magma injections in the crust. Following the equation proposed by Sano and Wakita (1985) the relative contribution of the three main sources of helium (crust, mantle and atmosphere) was computed, based on the <sup>4</sup>He/<sup>20</sup>Ne ratios. A low atmospheric contamination was found in all

Table 3

Gas phase composition (December 2005) and δ<sup>13</sup>C and <sup>3</sup>He/<sup>4</sup>He isotopic ratios of the studied CO<sub>2</sub>-rich mineral waters. b.d.l. stands for “bellow detection limits” and n.m. stands for “not measured”.

Ref.	Gas phase composition									Isotopic ratios		
	Free gases									δ <sup>13</sup> C CITD	<sup>3</sup> He/ <sup>4</sup> He R/Ra	<sup>4</sup> He/ <sup>20</sup> Ne
	CO <sub>2</sub> (%)	O <sub>2</sub> (%)	N <sub>2</sub> (%)	CO (ppm)	CH <sub>4</sub> (ppm)	He (ppm)	Ne (ppm)	Ar (total)	CO <sub>2</sub> (g)			
P. Salgadas AC25	97.45	0.02	1.80	0.6	783	195.9	0.150	330.6	-5.3	-0.88	2.68	1304.8
P. Salgadas AC17	95.66	0.31	2.99	b.d.l.	600	229.6	0.126	283.3	-5.2	-0.92	2.50	1826.9
Vidago AC16	92.31	0.66	5.24	2.2	469	334.0	0.416	711.9	-5.1	-2.32	1.90	803.1
Vidago AC18	97.44	b.d.l.	0.90	b.d.l.	41	149.3	0.243	239.4	-6.2	-0.10	1.34	614.7
Vidago Areal 3	94.41	b.d.l.	5.54	b.d.l.	1021	1061.0	0.417	965.9	-7.2	-2.20	1.26	2545.6
Chaves AC1	97.42	0.04	1.72	1.0	500	105.1	0.150	232.0	-5.8	-2.43	0.89	699.2
Vil. da Raia ACP1	318.60	4.42E-02	2.32E+01	0.0	2.10	1.23E-01	1.25E-04	n.m.	n.m.	-4.81	0.50	984.0



**Fig. 6.** (A)  $^3\text{He}/^4\text{He}$  vs  $^4\text{He}/^{20}\text{Ne}$  ratios plot. The relative percentage of the mantle contribution, computed on the bases of the  $^3\text{He}/^4\text{He}$  ratios, is also reported (right axis). Symbols as shown in Fig. 3. (B) Regional spatial distribution of the  $^3\text{He}/^4\text{He}$  ratio in the gas phase of the water samples.

samples, with a variable proportion of prevailing radiogenic helium produced in the crust and magmatic/mantle-derived helium up to 30% in Pedras Salgadas (Fig. 6B). In the research region, a progressive decrease of the mantle contribution was also noted in the  $\text{CO}_2$ -mineral waters towards the North, reaching a minimum at Vilarinho da Raia area with about 6% of mantle He input.

Truesdell and Hulston (1980), in their study on hydromineral systems, concluded that the carbon dioxide may be released from four main sources having different, even partially overlapping, carbon isotope signatures: (1) dissolution of marine limestone with  $\delta^{13}\text{C}$  values around 0‰; (2) metamorphic processes producing  $\text{CO}_2$  with  $\delta^{13}\text{C}$  slightly above 0‰; (3) organic processes (primary biogenic carbon) with values lower than  $-22\%$ ; and (iv) mantle origin having values between  $-3$  and  $-8\%$  (Javoy et al., 1986; Marty and Zimmermann, 1999; Cartigny et al., 2001).

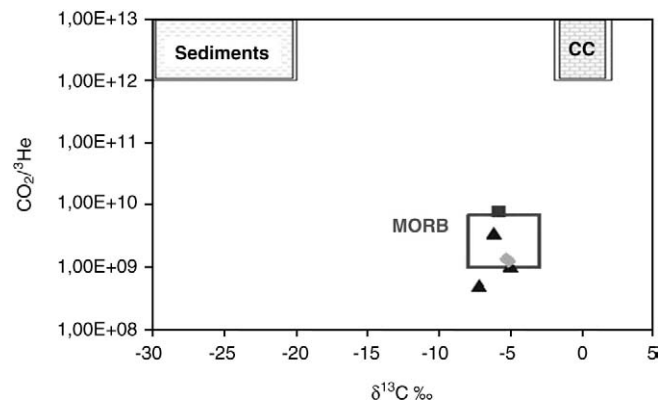
The  $\delta^{13}\text{C}$  of the TDIC (Total Dissolved Inorganic Carbon) with of the  $\text{CO}_2$ -rich waters selected in research region ranges from  $-2.43\%$  (Chaves) to  $-0.10\%$  (Vidago AC18) while in the  $\text{CO}_2$  gas phase isotopic composition varies between  $-7.2\%$  (Vidago Areal 3) to  $-5.1\%$  (Vidago AC16). The research area has been involved in several metamorphic events and such processes ought to release  $\text{CO}_2$  having typically  $\delta^{13}\text{C}$  of around 0‰. Based on the geological setting of the research area and according to Truesdell and Hulston (1980), the origin of carbon dioxide in hydromineral systems may be inorganic or organic. Inorganic carbon dioxide may be released from degassing mantle or may derive from crustal processes such as the dissolution of limestone, clay-carbonate diagenetic reactions (Hutcheon et al., 1990) or thermal decarbonization of carbonate rocks during regional metamorphism (Barnes, 1970; Mayo and Muller, 1997), while the biogenic  $\text{CO}_2$  is released during soil respiration. Each of these processes or reservoirs has different, even partially overlapped,  $\delta^{13}\text{C}$  values. Carbon dioxide deriving from carbonate dissolution and from thermo-metamorphism has  $\delta^{13}\text{C}$  values straddle 0‰,  $\text{CO}_2$  released from mantle have an average value between  $-3\%$  and  $-8\%$  (Javoy et al., 1986; Marty and Zimmermann, 1999; Cartigny et al., 2001) while biogenic  $\text{CO}_2$  is strongly depleted in  $^{13}\text{C}$  ( $\delta^{13}\text{C} < -22\%$ ). This latter source can in part be ruled out (minor contribution), since the organic  $\text{CO}_2$  income to the system from soil and vegetation should be considered negligible with respect to the high DIC contents found in the collected samples.

Furthermore, theoretical experiments on carbon isotope fractionation (Zhang et al., 1995; Szaran, 1998) demonstrated that carbon isotope shift associated to  $\text{CO}_2$ -uptaking or  $\text{CO}_2$ -releasing is minimal (up to 2‰) in acidic waters whereas becomes significant in alkaline solutions since the majority of the DIC species were dissolved as  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions.

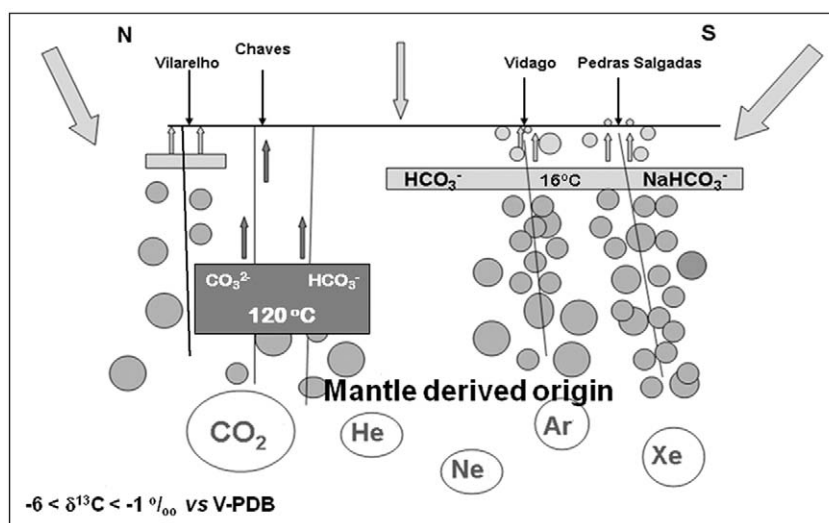
Considering these three origins, the carbon isotope signature of the collected gases should reflect the pristine isotope composition of the carbon source. The measured  $\delta^{13}\text{C}_{\text{CO}_2}$  values around  $-6\%$  seems to be consistent with a mixing between crustal marine plus metamorphic gases and mantle-derived volatiles (Fig. 7). However, all the free gases measured in the  $\text{CO}_2$ -rich mineral waters in the N of Portugal fall very close to the field of the gas typical of a mantle origin.

## 6. Concluding remarks

Chemical and isotopic data reveal that the  $\text{CO}_2$ -rich thermomineral waters of northern Portugal are part of an open system to the influx of



**Fig. 7.**  $\text{CO}_2/^3\text{He}$  ratio vs  $\delta^{13}\text{C}$  of the gas phase within the typical MORB formations; fields defined for sedimentary basins (sediments) and marine carbonated (CC) rocks  $\text{CO}_2/^3\text{He}$  ratios were based on Sano and Wakita (1985);  $\text{CO}_2/^3\text{He}$  ratios for MORB fluids were based on Allard (1983) and Armannsson et al. (1989) data; The symbols stands for: (■) Chaves, (●) Vidago and (▲) Pedras Salgadas. Adapted from Carvalho et al., 2007.



**Fig. 8.** Conceptual model of the CO<sub>2</sub> rich mineral waters system along the Penacova-Verin fracture zone, between Pedras Salgadas e Vilarelho da Raia (N of Portugal). The filled circle stands for the amount of dissolved deep CO<sub>2</sub> gas; the lines for faults systems; down arrows for precipitation (recharge); up arrows for groundwater arise, boxes schematic representation of the CO<sub>2</sub>-rich mineral systems. Adapted from Carvalho et al., 2007.

CO<sub>2</sub> gas from a deep-seated source. The presence of a CO<sub>2</sub>-rich gas phase is responsible for the mineralization of these waters (Fig. 8). The mineralization of these waters is strongly dependent of the amount of dissolved gases in the groundwaters, on the other hand, the low Ca and Mg content measured in Chaves thermomineral water and in Vilarelho da Raia system, is caused by the geological matrix of the aquifers, which plays an important role in the geochemical signatures of the mineral waters. The chemical composition of both hot and cold mineral waters suggests that water–rock reactions are mainly controlled by the amount of dissolved CO<sub>2</sub>(g) rather than by the water temperature.

The <sup>3</sup>He/<sup>4</sup>He and <sup>4</sup>He/<sup>20</sup>Ne ratios measured are (see Table 3) are consistent with those obtained within this study, i.e., with a mixing of two-component the prevailing one of radiogenic origin and noticeable mantle sources. This hypothesis is supported by the stable carbon isotope data that corroborates an external source of CO<sub>2</sub> of inorganic origin. The  $\delta^{13}C_{CO_2}$  values are ranging between  $-7.2\text{‰}$  and  $-5.1\text{‰}$ , and are consistent with a two-component mixture between crustal and mantle-derived CO<sub>2</sub>. The release of deep-seated fluids having a mantle-derived component in a region without recent volcanic activity suggests that active neo-tectonic structures originating during the Alpine Orogeny (i.e., Chaves Depression) tap mantle carbon and helium. Coupling geochemical investigations on the helium–carbon systematic with geophysical studies on local crustal structure should distinguish between mantle heat transmitted through the crust and heat anomalies caused by intrusion of magma (O’Nions and Oxburg, 1988).

The results obtained regarding the characterization of the CO<sub>2</sub> origin is important in the assessment of local/regional low-temperature geothermal resources, since the hot and cold carbon dioxide waters should be considered surface manifestations of a large-scale deep-seated hydrothermal system and the role of the carbonaceous slates (with significant amounts of graphite) that are well displayed in Chaves areas and most probably in Pedras Salgadas, Vidago although not outcropping, do not influence the hydrogeochemical signature of the mineralized groundwaters. These studies are extremely important for sustainable management of local water resources, future water development strategies and drilling plans. Furthermore, the Spas of northern Portugal are of special commercial value and should not be impacted by future water resources development.

## Acknowledgements

This research was developed under the scope of the POCTI/CTA/45159/2002 R&D Project DISGAS—Dissolved gases in sub-surface hydrology—CO<sub>2</sub>-rich thermomineral waters (N-Portugal), funded by the Portuguese Foundation for Science and Technology (FCT) and FEDER EU Programme. The authors would like to thank Fraser Goff and an anonymous reviewer for their comments and suggestions in order to improve the manuscript.

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