

## Review Article

# Assessment of Chaves Low-Temperature CO<sub>2</sub>-Rich Geothermal System (N-Portugal) Using an Interdisciplinary Geosciences Approach

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This paper reviews the results of a multi- and interdisciplinary approach, including geological, geomorphological, tectonic, geochemical, isotopic, and geophysical studies, on the assessment of a Chaves low-temperature (77°C) CO<sub>2</sub>-rich geothermal system, occurring in the northern part of the Portuguese mainland. This low-temperature geothermal system is ascribed to an important NNE-trending fault, and the geomorphology is dominated by the “Chaves Depression,” a graben whose axis is oriented NNE-SSW. The study region is situated in the tectonic unit of the Middle Galicia/Trás-os-Montes subzone of the Central Iberian Zone of the Hesperic Massif comprising mainly Variscan granites and Paleozoic metasediments. Chaves low-temperature CO<sub>2</sub>-rich geothermal waters belong to the Na-HCO<sub>3</sub>-CO<sub>2</sub>-rich-type waters, with pH ≈ 7. Total dissolved solids range between 1600 and 1850 mg/L. Free CO<sub>2</sub> is of about 500 mg/L. The results of SiO<sub>2</sub> and K<sup>2</sup>/Mg geothermometers give estimations of reservoir temperature around 120°C. δ<sup>18</sup>O and δ<sup>2</sup>H values of Chaves low-temperature CO<sub>2</sub>-rich geothermal waters indicate a meteoric origin for these waters. No significant <sup>18</sup>O-shift was observed, consistent with the results from the chemical geothermometry. δ<sup>13</sup>C<sub>CO2</sub> values vary between -7.2 and -5.1‰ vs. V-PDB, and CO<sub>2</sub>/<sup>3</sup>He ratios range from 1×10<sup>8</sup> to 1×10<sup>9</sup>, indicating a deep (upper mantle) source for the CO<sub>2</sub>. <sup>3</sup>He/<sup>4</sup>He ratios are of about 0.9 (R/Ra). The Chaves low-temperature CO<sub>2</sub>-rich geothermal waters present similar <sup>87</sup>Sr/<sup>86</sup>Sr ratios (between 0.728035 and 0.716713) to those of the plagioclases from granitic rocks (between 0.72087 and 0.71261) suggesting that water mineralization is strongly ascribed to Na-plagioclase hydrolysis. Geophysical methods (e.g., resistivity and AMT soundings) detected conductive zones concentrated in the central part of the Chaves graben as a result of temperature combined with the salinity of the Chaves low-temperature CO<sub>2</sub>-rich geothermal waters in fractured and permeable rock formations. This paper demonstrates the added value of an integrated and multi- and interdisciplinary approach for a given geothermal site characterization, which could be useful for other case studies linking the assessment of low-temperature CO<sub>2</sub>-rich geothermal waters and cold CO<sub>2</sub>-rich mineral waters emerging in a same region.

## 1. Introduction

The aim of this paper is to present an overview of the results achieved on the assessment of the Chaves low-temperature CO<sub>2</sub>-rich geothermal system, occurring in the northern part of the Portuguese mainland. Low-temperature geothermal systems are those where the reservoir temperature is below 150°C and often characterized by hot or boiling springs (see [1, 2]). A multi- and interdisciplinary approach, including geological, tectonic, geochemical, isotopic, and geophysical studies, has been established in order to update the conceptual circulation model of a Chaves low-temperature CO<sub>2</sub>-rich geothermal system. The Chaves low-temperature CO<sub>2</sub>-rich geothermal waters flow from natural springs (66°C) and boreholes (77°C) and are mainly used, in a cascade system, for space heating (municipal swimming pool and a hotel) and balneotherapy (at the local spa). At Chaves, the depth reached by the exploitation boreholes is around 150 m depth.

In both high- and low-temperature geothermal systems, surface manifestations of geothermal fluids circulation are usually a subject of large scientific importance. Hot mineral waters discharging in a given area, hydrothermal alteration features identified in drill cores from boreholes, and deposition materials around springs can be detected and carefully studied providing a lot of data with rather low costs (e.g., [3, 4]). Usually, travertine depositions around springs are indicators of geothermal reservoir temperatures that may be too low to generate electricity but may have direct-use applications such as for greenhouses or hot-water heating for nearby communities. As described by [5], potential problems with well-scaling may also be present. Such type of information should be used in geothermal resource assessment of a possible area for development. Exploration-data (e.g., geological, geotectonical, hydrogeological, geochemical, isotopic, and geophysical) should be used to develop a “clear picture” of a given low-temperature geothermal system and, when used in parallel, can provide key information on the origin and “age” of the geothermal waters, underground flow paths, and water-rock interaction occurring at depth and could assist in selecting future drilling sites (e.g., [2]).

In the map of Figure 1, we can observe the distribution of the geothermal heat flow density ( $\text{mW}\cdot\text{m}^{-2}$ ) in Europe [6]. According to [7], the thermal models for the study region indicate a mean heat flow value of  $95\text{ mW}\cdot\text{m}^{-2}$ , derived from borehole measurements. Heat flow measurements and the estimation of geothermal gradients are essential aspects of geothermal resource research, providing a good approximation of the temperature at the top of the reservoir (e.g., [2]).

Carbon dioxide (CO<sub>2</sub>-rich) geothermal waters have been of interest to people, historically since the Roman times and possibly beyond, and surface manifestations in the form of springs are an important resource, exploited for health, consumption, and industrial use as well as having religious and political importance to certain regions of the world [8, 9]. The global prevalence of these waters is widespread, with CO<sub>2</sub>-rich spring waters discharging in a variety of geological and tectonic settings, a source of specific geochemical characteristics (e.g., [10, 11]).

Several studies propose that areas of high heat flow in Western, Central, and Eastern Europe correspond to areas of CO<sub>2</sub> discharge originating from the metamorphism of marine carbonates, as well as a mantle origin (e.g., [12]). The extent of CO<sub>2</sub> production in Europe and central Asia is much larger than that of the Pacific ring, which is proposed to be at least partly due to the extensive orogenic belts of Europe and Asia Minor and the related regional metamorphism (e.g., [13]).

Some important European case studies of reference are here synthetically reviewed, in consideration of the multidisciplinary studies involved and due to the fact that in such hydrogeological systems (as in the Chaves region) both geothermal and cold CO<sub>2</sub>-rich springs are present, with the cold CO<sub>2</sub>-rich springs those presenting the highest mineralization.

Western Germany is home to geological terrains of important volcanic and tectonic activity, with numerous occurrences of naturally emerging CO<sub>2</sub>-rich springs in the Rhenish Massif. The CO<sub>2</sub>-rich waters which emerge in the Rhenish Massif contain gas of mantle origin and discharge in a geological setting of Cenozoic alkali basaltic volcanism, with the CO<sub>2</sub> discharges concentrated in volcanic fields (e.g., [14, 15]). The Massif Central (France), an extensive area of recent volcanism and tectonic activity, is host to many CO<sub>2</sub>-rich geothermal springs. These CO<sub>2</sub>-rich waters also have gas of mantle origin and emerge from Quaternary volcanic rocks or Paleozoic granites at temperatures up to 80°C (e.g., [16–19]). In central Italy, the topographically low-lying hydrogeological setting is composed of several Quaternary volcanic systems, with many geothermal springs. The CO<sub>2</sub>-rich springs have a mixture of mantle and biogenic CO<sub>2</sub> and emerge in volcanic and carbonate terrains (e.g., [20]). Galicia, northwest Spain, is home to CO<sub>2</sub>-rich geothermal and mineral waters. These geothermal and mineral waters range in temperature, from 15°C to 57.2°C with a pH ranging from 5.96 to 9.83. In Ourense, Galicia, high-temperature springs emerge within granitic rocks which form part of the Hesperian Massif. These Spanish springs are located on the same NNE-SSW fault lineament of the Chaves spring’s emergence. The Ourense springs have a temperature ranging from 46 to 69°C, with the origin of CO<sub>2</sub> likely from an upper mantle source (e.g., [21]). The Reykjanes Peninsula, located in southwest Iceland, exhibits a high-temperature basaltic geothermal system with high-temperature (>220°C) CO<sub>2</sub>-rich geothermal fluids at a depth of up to 1200 m. The mantle-based origin of CO<sub>2</sub> is due to mid-ocean ridge spreading, and the presence of water at this depth is due to an influx of seawater (e.g., [22]). Karlovy Vary, Czech Republic, located in the Sokolov Basin, has CO<sub>2</sub>-rich geothermal springs with temperatures of up to 73°C. The recharge of these waters originates in granitic blocks on the sides of the valley, with water deeply circulating (2,000–2,500 m) along faults (e.g., [23]). The CO<sub>2</sub> origin is from a deep source, likely the mantle (e.g., [24]). Hot CO<sub>2</sub>-rich geothermal springs emerge in Kuzuluk/Adapari, northwestern Turkey, an extensional tectonic setting within the seismically active North Anatolian Fault Zone. CO<sub>2</sub> originates from decomposition of marine carbonates and mantle outgassing (e.g., [25]).

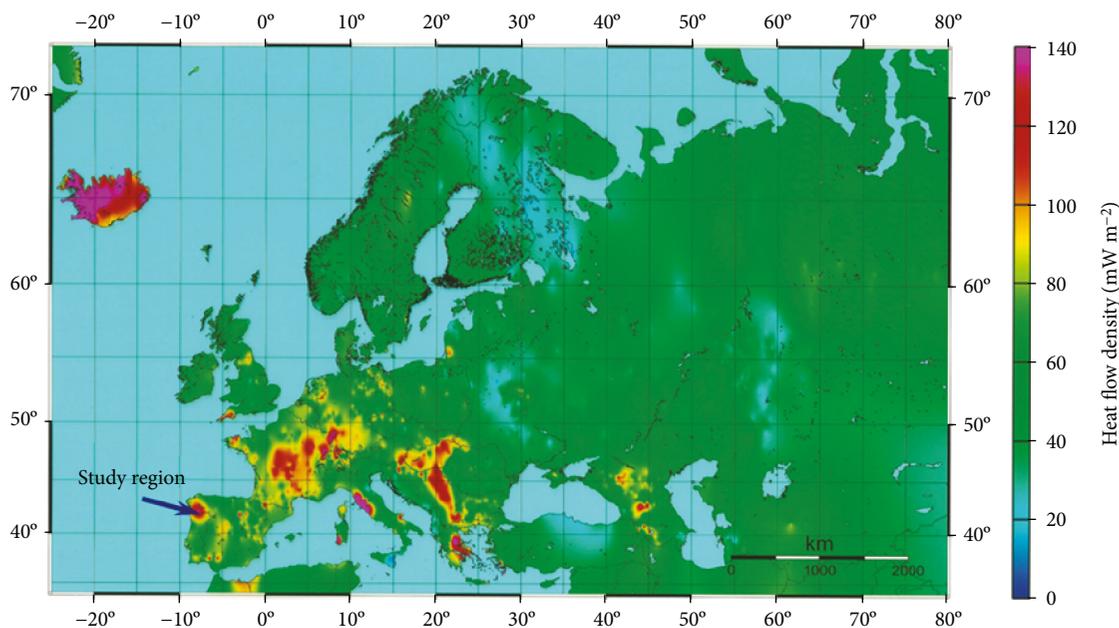


FIGURE 1: Distribution of the geothermal heat flow density ( $\text{mW}\cdot\text{m}^{-2}$ ) in Europe (courtesy Hurter, 1999, taken from [27]).

As already mentioned, in most of the case studies referred above, geothermal and cold  $\text{CO}_2$ -rich mineral waters discharge in the same region, as in the case of the Chaves geothermal area. As discussed by [25, 26], in  $\text{CO}_2$ -rich mineral water systems, water-rock interaction is enhanced at low temperature, since the resulting increased solubility of  $\text{CO}_2$  in water reduces the pH of the waters and increases the water aggressiveness to the rock. This explains the higher total dissolved solids (TDS) in the cold  $\text{CO}_2$ -rich mineral waters of a given hydrogeological system.

Several studies carried out on the northern part of the Portuguese mainland (e.g., [27–38]) have provided a comprehensive characterization of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal system. Several hypotheses have been formulated to assess the origin of the low-temperature geothermal waters and the mechanisms of their being upward from the reservoir towards the surface. In this paper, a review of the results obtained so far will be presented and discussed, with a special emphasis on the multi- and interdisciplinary approaches which enabled the development of the hydrogeological conceptual circulation model of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal system. Geochemical and isotopic signatures of local/regional cold ( $\approx 17^\circ\text{C}$ )  $\text{CO}_2$ -rich mineral waters from Vilarelho da Raia (N of Chaves) and Vidago/Pedras Salgadas (S of Chaves) are also presented and discussed, for comparison with the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters.

## 2. Geomorphologic, Geological, and Tectonic Settings

From the hydrogeological point of view, fractures and discontinuities are amongst the most important of geological structures. Most rocks (like granitic rocks) possess fractures and other discontinuities which facilitate storage

and movement of ascendant fluids through them [39]. The Chaves geothermal area (Figure 2) is located in the tectonic unit of the Middle Galicia/Trás-os-Montes sub-zone of the Central Central-Iberian Zone of the Hesperic Massif [40, 41].

From the hydrogeologic point of view, such terrains are comprehensive archives of the continental crust, including outstanding information on its magmatic, tectonic, and metamorphic evolution. These issues are extremely important to understand where the hottest low-temperature geothermal waters are found in Portuguese mainland (discharge temperature at Chaves –  $77^\circ\text{C}$ ).

The geomorphology is controlled by the so-called Chaves Depression, a graben whose axis is NNE-SSW-trending. The eastern block of Chaves graben is formed by the edge of the Padrela Mountain escarpment (with a 400 m throw). At the west, several grabens, coming in a stair-tectonic configuration from the Heights of Barroso towards the “Chaves Depression,” can be found [42].

The regional geology (Figure 2) has been described by [42–44]. According to those authors, the main geological formations are (i) Hercynian granites (syn-tectonic: 310 Ma and post-tectonic: 290 Ma) and (ii) Silurian metasediments (quartzites, phyllites, and carbonaceous slates). On the W block of Chaves graben, the syn-tectonic granites present a medium- to coarse-grained texture, with abundant biotite and muscovite (approximately 10 to 15% of the modal composition). Quartz appears strongly tectonized. Na-plagioclase (An7–An8) is occasionally intensely sericitized while K-feldspar remains unaltered. Biotite is locally chloritized. On the E block of Chaves graben, the post-tectonic granites have a coarse-grained to porphyritic texture, with biotite and muscovite (with biotite being predominant). Microcline-perthite and Na-plagioclase (near the limit albite/oligoclase) can also be observed. Biotite is

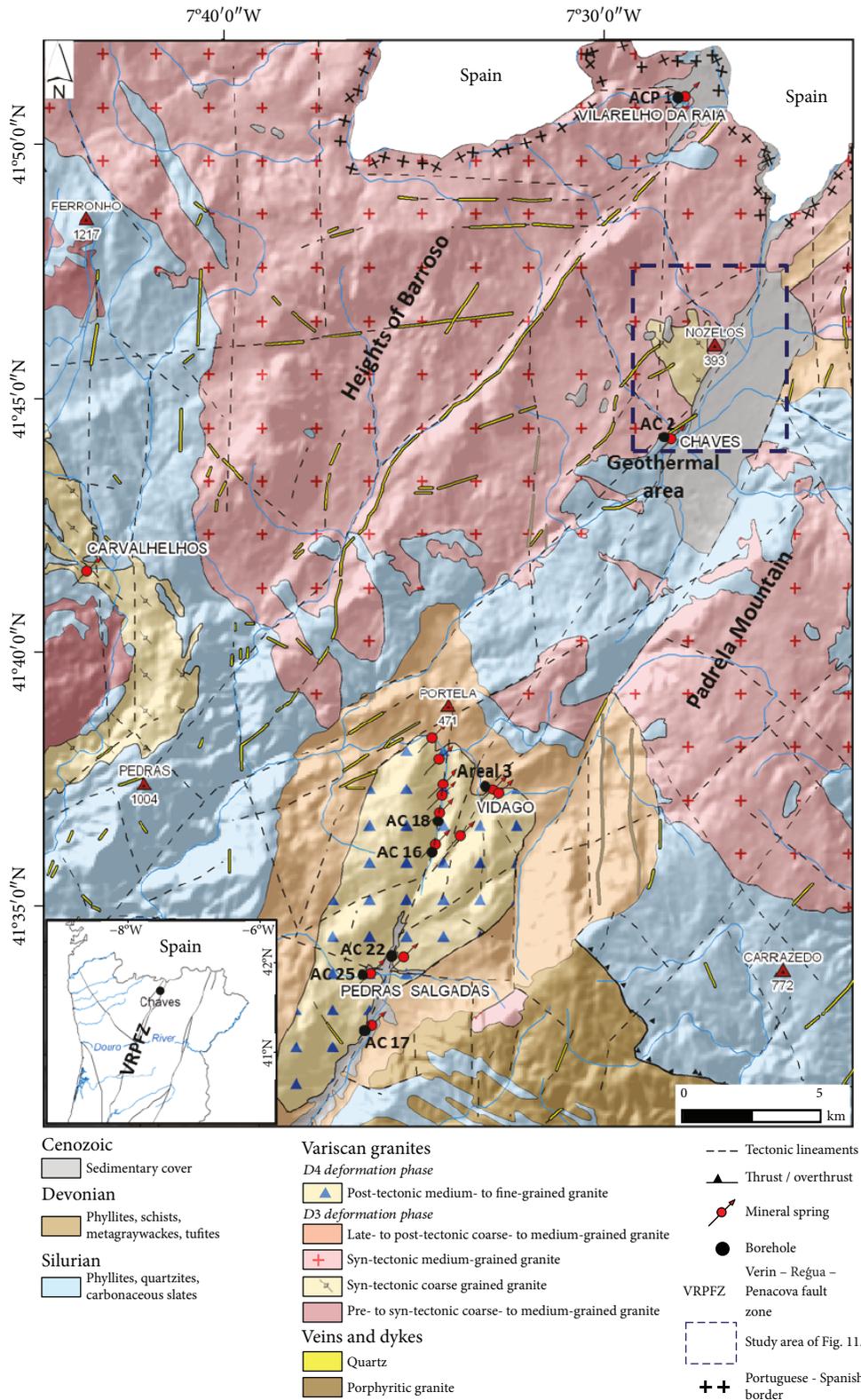


FIGURE 2: Regional geological map of the Chaves region (NW Portugal), showing the location of Vilarelho da Raia, Chaves, Vidago, and Pedras Salgadas CO<sub>2</sub>-rich mineral waters. Adapted from [27].

very chloritized. At Vidago–Pedras Salgadas areas (S of the Chaves geothermal area – Figure 2), the post-tectonic granites present a medium- to fine-grained texture (sometimes

porphyritic). K-feldspar (orthoclase and microcline) quartz, Na-plagioclase, and biotite occur as major minerals. Quartzites comprise a mosaic of fine-grained quartz intergrown

with an intensely indented granoblastic texture, with discrete thin beds of white mica spread in the quartz grains. Sometimes, micaceous films (mainly muscovite) are present, giving a schistose texture enhancing strong tectonization. The phyllites (andalusitic) have a granoblastic texture, showing a silky sheen on schistosity surfaces. The carbonaceous slates present a lepidogranoblastic texture and a well-marked foliation. Graphite (very abundant) alternates with beds of white mica and occurs in continuous beds, sometimes forming small lentils. The most recent geological formations are Miocene-Pleistocene graben-filling sediments with their maximum development along the central axis of Chaves graben [42–44] (Figure 2).

Concerning fracture and structural main features, [45] considered three main Late-Variscan strike-slip fault systems in the northern sector of Iberia: the dominant NE-NNE (always sinistral), the subordinate and conjugate NW-NNW (dextral), and the E-ENE (mainly sinistral). From this geometry and kinematics, [45] concluded that the N-S maximum compressive stress field was responsible for the development of the whole of the fracture/faulting network in Iberia.

In the Chaves region, the ascending low-temperature CO<sub>2</sub>-rich geothermal waters are structurally controlled by the so-called Verin-Régua-Penacova fault zone (VRPFZ – Figure 2) [40, 41, 46], related to Alpine Orogeny, which trends 70°–80°E and is hydrothermally active along a belt extending 150 km through mainland Portugal (Figure 3). Along this tectonic megalineament lie not only the Chaves low-temperature CO<sub>2</sub>-rich geothermal waters (the only geothermal waters in the study region) but also numerous emanations of cold (17°C) CO<sub>2</sub>-rich mineral waters (e.g., Vilarelho da Raia, Vidago, and Pedras Salgadas), with no signs of a geothermal origin as discussed in detail by [27–38], which are used in local spas (see Figures 2 and 3).

As stated by [44], the Chaves low-temperature CO<sub>2</sub>-rich geothermal waters and the cold CO<sub>2</sub>-rich mineral waters discharge preferentially in places where some of 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. It is also important to emphasise that, since the NNE-SSW megalineament reaches great depths ( $\approx$  30 km) in the study region, as referred by [43], it should play an important role, not only on geothermal and mineral waters ascent but also in CO<sub>2</sub> extraction and migration from a deep (upper mantle) source to the surface. In the study region, geothermal waters issue (with discharge temperature of 77°C) only at the Chaves area ascribed to the fact that they emerge within a wide morphotectonic structure (the Chaves Graben – 3 km width by 7 km length – see Figures 2 and 3) with a thickness of graben filling sediments greater than 250 m, as stated by [43, 44]. On the other hand, in the case of Vidago and Pedras Salgadas cold (17°C) CO<sub>2</sub>-rich mineral waters, they issue in locations where local structures (small grabens) do not show such huge structural signatures (see Figures 2 and 3).

In fact, the model proposed by [43] for the Vidago and Pedras Salgadas regions, based on tectonic and geomorphological features, points out the existence of a narrow graben (1 to 2 km wide) related with an also shallow reservoir.

Therefore, as stated by [43, 44], deeper low-temperature geothermal water circulation occurs only in the Chaves area because of (i) high relief, (ii) deep fracturing, and (iii) thickness of graben-filling sediments (see [38]).

As can be observed in Figure 3, the crossed graben-horst system, comprising of the fracture families NNE-SSW and ENE-WSW, is associated to a tectonic lineament originated by the Hercynian fracturing of the Hesperic Massif [43, 44]. This system, which is currently active, was reactivated in the Cenozoic due to the compressional tectonics of the Alpine orogeny, with the local formation of pull-apart basins [43, 44]. The location of the CO<sub>2</sub>-rich springs is mainly determined by the tectonic structures of the region, being situated in the areas of the longitudinal grabens (NNE-SSW) where subsidence is significant and at the intersection of these grabens with the transverse graben-horst systems.

### 3. Geochemistry of the Waters

Water samples for chemical and isotopic analyses were collected from (i) the Chaves low-temperature CO<sub>2</sub>-rich geothermal system (from geothermal springs and boreholes); (ii) the Vilarelho da Raia, Vidago, and Pedras Salgadas cold ( $\approx$  17°C) CO<sub>2</sub>-rich mineral waters (from boreholes), and (iii) the local/regional shallow cold dilute normal groundwater systems (from springs). Temperature (°C), pH, and electrical conductivity ( $\mu$ S/cm) were measured in situ. Chemical analyses were performed at the Laboratório de Mineralogia and Petrologia do Instituto Superior Técnico, Universidade Técnica de Lisboa (LAMPIS), Portugal, using the methodology described in [27]. Chaves low-temperature CO<sub>2</sub>-rich geothermal waters (discharged from springs and exploited from boreholes – AC1 and AC2) are Na-HCO<sub>3</sub>-CO<sub>2</sub>-rich-type waters, which display temperatures between 66 and 77°C, dry residuum (DR) ranging from 1600 to 1850 mg/L, and free CO<sub>2</sub> from 350 to 1100 mg/L (see [29, 33, 36, 38]). The associated gas phase issued from the CO<sub>2</sub>-rich springs at Chaves is practically pure at CO<sub>2</sub>  $\approx$  99.5% volume (O<sub>2</sub> = 0.05%, Ar = 0.02%, N<sub>2</sub> = 0.28%, CH<sub>4</sub> = 0.009%, C<sub>2</sub>H<sub>6</sub> = 0.005%, H<sub>2</sub> = 0.005%, and He = 0.01% in [47]).

In many parts of the world, and Portugal is not an exception, it is not uncommon to find natural springs of CO<sub>2</sub>-rich waters discharging at surface with various temperatures at a distance of few km (e.g., [21, 25, 48]). In fact, in the Chaves region, the tectonic/geomorphological structures (Chaves, Vidago, and Pedras Salgadas grabens – see Figure 3) and the different kinds of granitic and schistose rocks results in the occurrence of the Chaves low-temperature CO<sub>2</sub>-rich geothermal waters and the cold CO<sub>2</sub>-rich mineral waters of Vilarelho da Raia, Vidago, and Pedras Salgadas, discharging along the same NNE-trending fault. According to [29, 33, 36, 38], the Vilarelho da Raia cold ( $\approx$  17°C) spring and borehole CO<sub>2</sub>-rich mineral waters show similar chemical composition comparatively to Chaves low-temperature CO<sub>2</sub>-rich geothermal waters. DR values are between 1790 and 2260 mg/L, and free CO<sub>2</sub> is of about 790 mg/L. Vidago and Pedras Salgadas cold ( $\approx$  17°C) spring and borehole CO<sub>2</sub>-rich mineral waters present higher Ca<sup>2+</sup>, Mg<sup>2+</sup>, and free CO<sub>2</sub> content (up to 2500 mg/L). In the Piper diagram

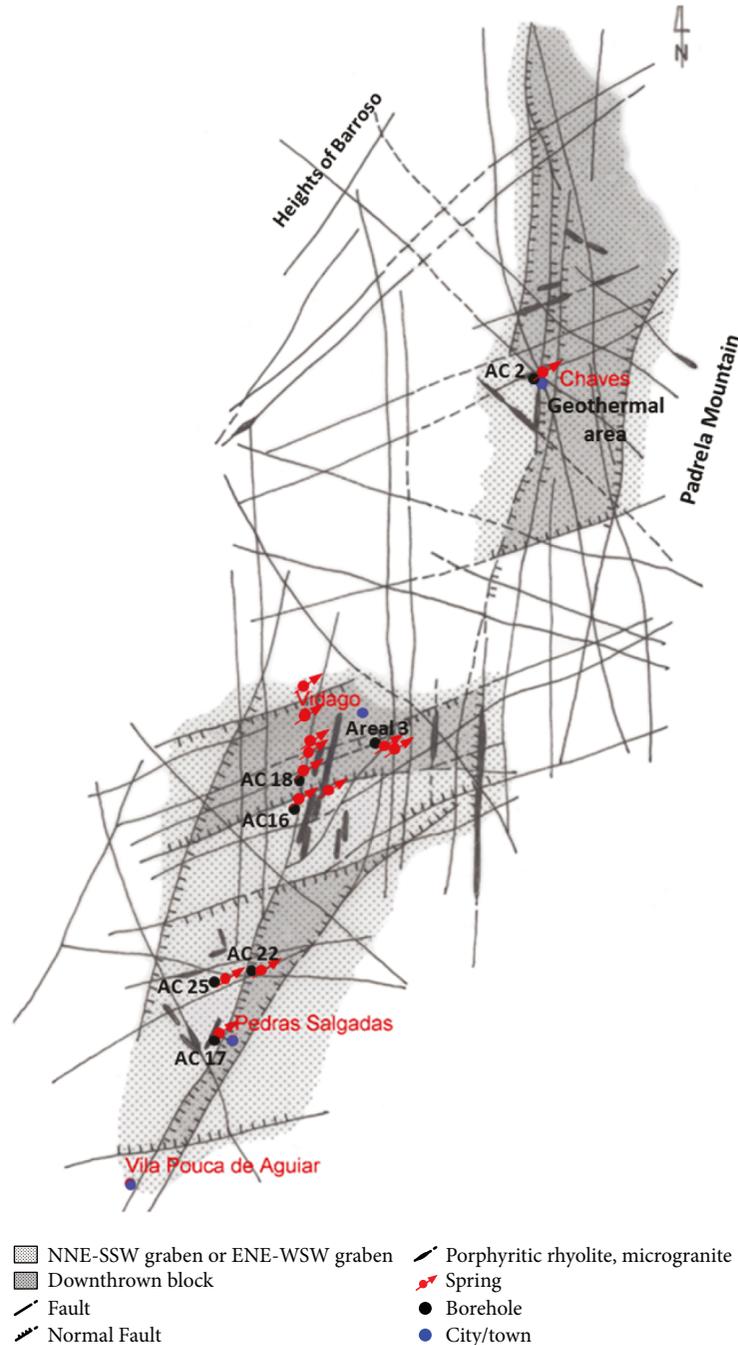


FIGURE 3: Structural lineation map showing the subsidence zones in the Chaves, Vidago, and Pedras Salgadas basins. Adapted from [106].

of Figure 4, one can observe that the cold  $\text{CO}_2$ -rich mineral waters of Vidago and Pedras Salgadas, although strongly dominated by  $\text{HCO}_3^-$  and  $\text{Na}^+$ , present relatively high-alkaline earth metal ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) concentrations indicative of the increasing solubility of these divalent ions with decreasing temperature, as described by [25, 34]. From the observation of the ternary  $\text{Cl-HCO}_3\text{-SO}_4$  diagram of Figure 4, it is possible to conclude that there is no mixing trend between the  $\text{CO}_2$ -rich mineral waters and the local shallow cold dilute normal groundwaters of the region (which commonly belong to the  $\text{Na-HCO}_3$ -type waters).

Like in other parts of the world (e.g., [21, 25, 48]), the studied cold  $\text{CO}_2$ -rich mineral waters show much higher mineralization. In some cases, as in Vidago AC18 borehole waters, DR ( $\approx 4300 \text{ mg/L}$ ) is more than twice the TDS of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters (e.g., [29]). Representative analyses of the studied low-temperature  $\text{CO}_2$ -rich geothermal waters and of the cold  $\text{CO}_2$ -rich mineral waters, as well as of the local shallow cold dilute normal groundwaters, are presented in Table 1.

As described by [25, 48], in  $\text{CO}_2$ -rich hydromineral systems, carbon dioxide is one of the most important

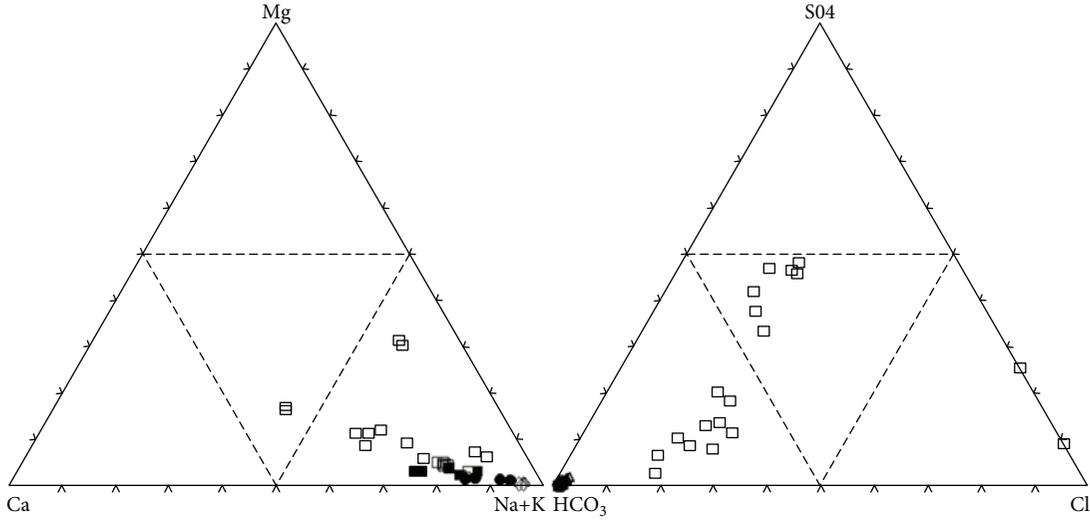


FIGURE 4: Piper diagram for the ( $\Delta$ ) Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters and the ( $\diamond$ ) Vilarelho da Raia, ( $\bullet$ ) Vidago, and ( $\blacksquare$ ) Pedras Salgadas cold  $\text{CO}_2$ -rich mineral waters. For comparison, the ( $\square$ ) local shallow cold dilute normal groundwaters of the region were also plotted. Taken from [30].

TABLE 1: Representative physicochemical data of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal system and the cold  $\text{CO}_2$ -rich mineral waters of the region. Typical physicochemical signatures of the local shallow cold dilute normal groundwaters were also included. Concentrations in mg/L. Table 1 is reproduced from Marques et al. (2006) [under the Creative Commons Attribution License/public domain].

Reference	Local	Type	T ( $^{\circ}\text{C}$ )	pH	Cond.	Na	K	Ca	Mg	Li	$\text{HCO}_3$	$\text{SO}_4$	Cl	$\text{NO}_3$	F	$\text{SiO}_2$	DR
ACP1 ( $\diamond$ )	Vilarelho da Raia	(bw)	17.2	6.6	2350	600	22.8	26.3	5.25	1.20	1579	13.0	21.5	0.3	5.40	54.9	1523
AC2 ( $\Delta$ )	Chaves	(bw)	77.0	6.9	2550	668	62.5	22.1	5.25	2.68	1707	18.3	35.3	n.d.	7.20	86.1	1702
Nas. ( $\Delta$ )	Chaves	(sp)	66.0	6.8	2430	633	63.0	23.4	5.75	2.56	1604	23.8	38.1	0.3	6.90	82.9	1634
Castelões ( $\square$ )	Chaves	(sp)	11.6	5.8	36	5	0.5	1.3	0.40	0.04	12	0.4	2.7	1.8	0.15	21.6	31
AC16 ( $\bullet$ )	Vidago	(bw)	17.6	6.1	1910	423	37.3	73.5	11.50	1.94	1286	7.9	17.3	n.d.	3.50	58.4	1217
AC18 ( $\bullet$ )	Vidago	(bw)	17.0	6.7	6230	1525	106.5	223.0	37.00	6.40	4689	1.9	66.0	1.6	3.40	59.8	4346
Areal 3 ( $\bullet$ )	Vidago	(bw)	12.3	6.9	6250	1585	96.5	132.0	28.00	9.44	5418	n.d.	54.0	n.d.	2.70	68.1	4205
Baldio ( $\square$ )	Vidago	(sp)	11.9	6.4	74	9	0.2	2.8	1.25	0.01	11	10.3	5.3	3.8	n.d.	26.5	76
AC17 ( $\blacksquare$ )	Pedras Salgadas	(bw)	16.1	6.3	2880	580	28.3	183.5	26.00	2.00	2010	10.3	32.0	n.d.	2.50	79.9	1886
AC25 ( $\blacksquare$ )	Pedras Salgadas	(bw)	17.9	6.4	4120	957	48.5	193.0	50.00	3.10	3057	2.3	32.6	n.d.	1.50	73.9	2781
AC22 ( $\blacksquare$ )	Pedras Salgadas	(bw)	14.8	6.5	5340	1285	37.0	227.0	41.00	1.00	4546	n.d.	51.0	n.d.	1.00	61.2	3663

Notes: T: water temperature; Cond. : electrical conductivity in  $\mu\text{S}/\text{cm}$ ; DR: dry residuum; n.d.: not detected (below detection limits). ( $\Delta$ ) Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters; cold  $\text{CO}_2$ -rich mineral waters from ( $\diamond$ ) Vilarelho da Raia, ( $\bullet$ ) Vidago, and ( $\blacksquare$ ) Pedras Salgadas. ( $\square$ ) stands for local shallow cold dilute normal groundwaters. sp: stands for spring waters; bw: stands for borehole waters.

“components/parameters” that influences the physical and chemical signatures of the fluids. Low temperatures enhance water-rock interaction since the solubility of  $\text{CO}_2$  in water increases with decreasing temperature. Therefore, the pH of the cold groundwaters will decrease as the result of the  $\text{CO}_2$  incorporation in a shallow low-temperature environment and the aggressiveness, of the waters will increase leading to a more active water-rock interaction and metal dissolution. This trend could explain the higher mineralization of most of the cold  $\text{CO}_2$ -rich mineral waters found in the region (e.g., Vidago AC18, Areal 3, and Pedras Salgadas AC22 borehole waters).

The mineralization of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters and of the cold  $\text{CO}_2$ -rich

mineral waters is strongly controlled by  $\text{HCO}_3^-$  and  $\text{Na}^+$  (see Table 1), pointing to the hydrolysis of the Na-plagioclases of the granitic rocks as the main water-rock interaction process responsible for the water chemistry (see [26] and Figure 5). Also, as stated by [49], acid hydrolysis of plagioclase and biotite could be the main source of salinity in groundwaters percolating through granitic rocks.

Besides, as stated by [29], the constant ratios of major ionic species (e.g.,  $\text{HCO}_3$  and Na) plotted against a conservative element such as Cl indicate that the chemistry of these waters would be related with a similar geological environment. By observing Figure 5, we can formulate the hypothesis that  $\text{Cl}^-$  present in the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters and in the cold  $\text{CO}_2$ -rich mineral waters

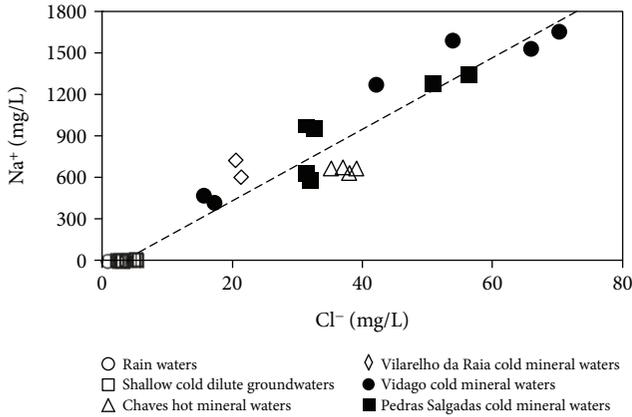


FIGURE 5:  $\text{Cl}^-$  vs.  $\text{Na}^+$  for the studied waters. The dashed line stands for a concentration trend from the regional dilute groundwaters towards the high mineralized waters. Figure 5 is reproduced from Marques et al. (2006) [under the Creative Commons Attribution License/public domain].

is also the result of water-rock interaction, since the increase in  $\text{Na}^+$  concentration in these waters is accompanied by an increase of  $\text{Cl}^-$ .

Chloride is found in small amounts in some silicate and phosphate minerals, usually found in different minerals from granitic rocks, including biotite, amphibole, and apatite (e.g., [50]). In the diagram of Figure 5, the data from Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters (from borehole AC2 and a spring) form a cluster, which is a good indication of the existence of a common reservoir for these waters.

On the other hand, the Vilarelho da Raia, Vidago, and Pedras Salgadas cold  $\text{CO}_2$ -rich mineral waters have different chemical tracer contents, indicating different underground flow paths and/or water-rock interaction with different types of granitic rocks. Higher salinities (e.g., Vidago AC18  $\text{CO}_2$ -rich borehole waters) should correspond to larger residence times associated to shallow underground flow paths, since Vidago AC18 are cold waters.

In the case of Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters, the reservoir fluid may become mixed with cold groundwaters at shallow levels, resulting in the change of the deep fluid chemistry by leaching and reaction with wall rocks during the upflow. Therefore, the results of chemical geothermometers were interpreted with caution and correlated with the results achieved by other disciplines such as isotope hydrology and geophysics.

Many chemical geothermometers have been proposed, both qualitative and quantitative. The most usually used include the quartz and chalcedony geothermometers [51–54], the feldspar (Na-K) geothermometers [55, 56], the Na-K-Ca and Na-K-Ca-Mg geothermometers [57, 58], and the Na-Li geothermometer [59].

As mentioned by [60], in the case of Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters and Vilarelho da Raia, Vidago, and Pedras Salgadas cold  $\text{CO}_2$ -rich mineral waters, the results of  $\text{SiO}_2$  and  $\text{K}^2/\text{Mg}$  geothermometers

are in fair agreement (see Table 2). However, the Na/K and Na-K-Ca geothermometers give higher temperatures, and the Na/Li geothermometer, indicated by [61] as a good thermometric index for  $\text{CO}_2$ -rich waters of the French Massif Central, seems to give rise to an overestimation of the deep temperatures.

As stated by [26, 62], the lower  $\text{SiO}_2$  contents observed in Vilarelho da Raia, Vidago, and Pedras Salgadas cold  $\text{CO}_2$ -rich mineral waters should be faced as a clear indication for rather low water-rock interaction temperatures (see [26]), in a shallow environment, and should not be attributed to silica deposition during ascent of the waters, because precipitation of chalcedony or quartz is very rare at low temperatures.

In order to solve the discrepancies related to silica and some of the cation geothermometers, [60] have adopted a methodology described by [21]. According to that approach, in a  $\log(\text{H}_4\text{SiO}_4)$  vs.  $\log(\text{Na/K})$  diagram, where the equilibrium quartz/chalcedony–adularia–albite was assessed, the whole studied  $\text{CO}_2$ -rich waters lie in the domain of not equilibrated waters. Using the methodology developed by [63, 64], the same authors [60] concluded that, in the classical  $\text{Na}/400\text{-Mg}^{1/2}\text{-K}/10$  diagram, the Chaves, Vidago, and Pedras Salgadas  $\text{CO}_2$ -rich waters are immature waters, while the Vilarelho da Raia  $\text{CO}_2$ -rich waters are located in the area of partial equilibrium with the host rocks at much higher temperatures (between  $160^\circ\text{C}$  and  $180^\circ\text{C}$ ) than those presented in Table 2.

These results seem to indicate that chemical geothermometers should be applied with great caution to the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters and that in the case of the cold  $\text{CO}_2$ -rich mineral waters the circulation depth should be assessed using the results from other disciplines such as hydrogeochemistry and isotope hydrology, namely bearing in mind the presence of tritium in the cold  $\text{CO}_2$ -rich mineral waters (as discussed later in Section 4).

Even considering all restrictions on the applicability of chemical geothermometers to  $\text{CO}_2$ -rich waters, it makes sense to consider acceptable the estimations of deep temperature around  $120^\circ\text{C}$ , for the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters, which are in agreement with the discharge temperature ( $77^\circ\text{C}$ ) of these waters. Considering the mean geothermal gradient of  $30^\circ\text{C}/\text{km}$  [7], a maximum depth of about 3.5 km reached by the Chaves water system was estimated [29]. This value was obtained considering that

$$\text{Depth} = (T_r - T_a)/gg, \quad (1)$$

where  $T_r$  is the reservoir temperature ( $120^\circ\text{C}$ ),  $T_a$  is the mean annual air temperature ( $15^\circ\text{C}$ ), and  $gg$  is the geothermal gradient ( $30^\circ\text{C}/\text{km}$ ).

Accepting that water mineralization is more controlled by the availability of  $\text{CO}_2$  rather than by the temperature (see [26]), the cold ( $\approx 17^\circ\text{C}$ )  $\text{CO}_2$ -rich mineral waters from Vilarelho da Raia, Vidago, and Pedras Salgadas should be faced as different stages of water-rock interaction processes involving local circulation of cold shallow groundwaters. As stated by [65], carbon dioxide waters, if they are not thermal,

TABLE 2: Reservoir temperatures ( $^{\circ}\text{C}$ ) of Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters and of Vilarelho da Raia, Vidago, and Pedras Salgadas cold  $\text{CO}_2$ -rich mineral waters, estimated from chemical geothermometers. Adapted from [29, 60].

Local	Ref.	Chalc. (1)	Quartz (2)	Na-K-Ca (3)	Na-K-Ca (Mg) (4)	Na/K (5)	Na/Li (6)	$\text{K}^2/\text{Mg}$ (7)
V. da Raia	Facha **	70	100	146•	124	101	116	103
	AC1*	90	120	203+	118	188	178	120
Chaves	AC2 *	91	121	210+	132	204	193	125
	Spr. 3 **	92	121	206+	121	191	178	123
Vidago	AC16*	72	102	126•	96	176	211	93
	AC18*	74	104	177•	89	171	188	111
P. Salgadas	AC17*	92	121	106•	92	127	177	80

Notes: (1) Fournier and Truesdell (1974) - in [54]; (2) [56] - cooling by conduction; (3) [57]; (4) [58]; (5) White and Ellis (1970) - in [56]; (6) [59]; and (7) [63]. \*Borehole water; \*\*spring waters;  $^+\beta = 1/3$ ;  $^{\bullet}\beta = 4/3$ .

are not indicative of hydrothermal systems in the subsurface. According to the convention adopted in the “Atlas of Geothermal Resources in Europe” [66], a given groundwater is considered to be thermal if the discharge temperature exceeds  $20^{\circ}\text{C}$ .

#### 4. Isotopic Composition of the Waters and Gas Phase

Isotope geochemistry has greatly contributed to (i) the present understanding of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal system and (ii) the increase in knowledge on the relations with the regional cold  $\text{CO}_2$ -rich mineral waters from Vilarelho da Raia, Vidago, and Pedras Salgadas, discharging along the same NNE-trending fault. In this paper, we review the use of isotope geochemistry to address key questions to update the conceptual model of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal system, in particular to recharge and underground flow paths, emphasising the use of stable isotope data integrated with chemical and other relevant data, such as lithology, geomorphology, and geophysics, in order to achieve important results.

$\delta^2\text{H}$  and  $\delta^{18}\text{O}$  were determined three times for each water sample in order to increase the analytical precision. All isotopic determinations were performed in the former Instituto Tecnológico e Nuclear (ITN) – Chemistry Department, Sacavém, Portugal – presently Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico ( $\text{C}^2\text{TN}/\text{IST}$ ), Universidade de Lisboa, Portugal. The measurements were conducted on a mass spectrometer SIRA 10-VG ISOGAS using the methods described in [67, 68] for  $^2\text{H}$  and  $^{18}\text{O}$ , respectively. The tritium content was determined using the electrolytic enrichment and liquid scintillation counting method described by [69] and by [70], using a Packard Tri-Carb 2000 CA/LL (see [31, 32]). The error associated to the  $^3\text{H}$  measurements (usually around 0.7 TU) varies with the  $^3\text{H}$  concentration in the sample.

With exception of Vilarelho da Raia, all sampled boreholes are  $\text{CO}_2$ -exsolving wells. So, in these cases the gases were collected by using a homemade 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 gas 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 [32] and references therein.

The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters (see Table 3) lie on or close to the GMWL ( $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$ ) defined by [71] and later improved by [72–74]. According to [29, 35, 36, 75], this trend indicates (i) that they are meteoric waters which have been recharged without evaporation, and (ii) that there is no water-rock interaction at very high temperatures, consistent with the results of chemical geothermometers (Figure 6).

As in the diagram of Figure 5, the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  data from Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters form a cluster, supporting the existence of a common system for these waters (see Figure 6). On the other hand, the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  data of Vilarelho da Raia, Vidago, and Pedras Salgadas cold  $\text{CO}_2$ -rich mineral waters, although following the GMWL (also indicating a meteoric origin for these waters), have different stable isotopic ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) composition, indicating different aquifer systems with diverse recharge altitudes and different underground flow paths.

Based on  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of the shallow cold dilute normal spring water samples collected at different altitudes in the Chaves region, the local meteoric water line (LMWL:  $\delta^2\text{H} = 7.01 \pm 0.74\delta^{18}\text{O} + 4.95 \pm 3.9$ ) was calculated ([30] - see Figure 6). The stable isotopic composition of the shallow cold dilute normal groundwaters indicates that the more depleted waters are those related to sampling sites located at higher altitudes (see Table 3), as previously referred by [28–30]. The isotopic gradients obtained for  $^{18}\text{O}$  ( $-0.23\text{‰}$  and  $-0.22\text{‰}$  per 100 m of altitude, respectively) are in good agreement with the values found in Mediterranean regions [76]. The altitude dependence of the isotopic composition of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters has been reported by [28, 30, 76]. As referred by those authors, the depleted  $\delta^{18}\text{O}$  values of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters require that these waters were derived from meteoric waters at more

TABLE 3: Representative stable ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) and radioactive ( $^3\text{H}$ ) isotopic data of groundwaters from the Chaves region. Table 3 is reproduced from Marques et al. (2006) [under the Creative Commons Attribution License/public domain].

Ref.	Local	Altitude	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$^3\text{H}$
ACPI ( $\diamond$ )	Vilarelho da Raia	370	-7.71	-53.2	$1.7 \pm 1.0$
Assureiras ( $\square$ )	Chaves	690	-7.52	-50.7	$6.4 \pm 1.1$
Castelões ( $\square$ )	Chaves	980	-7.72	-50.1	$8.2 \pm 1.0$
Campo de futebol ( $\square$ )	Chaves	360	-5.76	-38.5	$7.0 \pm 1.0$
AC2 ( $\triangle$ )	Chaves	350	-8.03	-55.9	$0.0 \pm 1.0$
Nasc. ( $\triangle$ )	Chaves	350	-7.96	-54.9	$0.5 \pm 0.9$
Baldio ( $\square$ )	Vidago	510	-6.73	-42.9	$4.3 \pm 1.0$
N3 ( $\square$ )	Vidago	480	-6.20	-40.8	$3.6 \pm 1.4$
N6 ( $\square$ )	Vidago	420	-6.42	-41.6	$4.7 \pm 1.0$
N7 ( $\square$ )	Vidago	580	-6.73	-42.5	$7.2 \pm 1.3$
AC16 ( $\bullet$ )	Vidago	355	-6.63	-48.0	$4.1 \pm 1.0$
AC18 ( $\bullet$ )	Vidago	325	-6.81	-44.5	$-0.3 \pm 0.9$
Areal 3 ( $\bullet$ )	Vidago	350	-7.12	-52.2	$-1.6 \pm 1.0$
N1 ( $\square$ )	Pedras Salgadas	660	-6.53	-40.1	$4.2 \pm 1.0$
N2 ( $\square$ )	Pedras Salgadas	1080	-6.79	-40.0	$5.3 \pm 1.1$
N5 ( $\square$ )	Pedras Salgadas	885	-7.20	-45.8	$6.9 \pm 1.0$
AC17 ( $\blacksquare$ )	Pedras Salgadas	580	-7.26	-47.3	$2.2 \pm 1.0$
AC25 ( $\blacksquare$ )	Pedras Salgadas	560	-7.70	-53.1	$0.0 \pm 1.0$
AC22 ( $\blacksquare$ )	Pedras Salgadas	570	-8.27	-53.5	$-0.3 \pm 1.0$

Notes: ( $\square$ ) shallow cold dilute normal groundwaters; ( $\triangle$ ) Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters; cold  $\text{CO}_2$ -rich mineral waters from ( $\diamond$ ) Vilarelho da Raia, ( $\bullet$ ) Vidago, and ( $\blacksquare$ ) Pedras Salgadas. Altitude in m a.s.l..  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in ‰ vs. V-SMOW.  $^3\text{H}$  in TU.

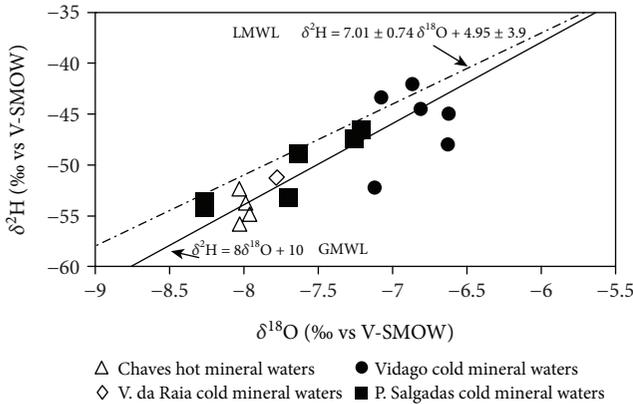


FIGURE 6:  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  relationship of Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters. The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of the cold  $\text{CO}_2$ -rich mineral waters from Vilarelho da Raia, Vidago, and Pedras Salgadas areas are also plotted. Figure 6 is reproduced from Marques et al. (2006) [under the Creative Commons Attribution License/public domain].

than 1150m a.s.l. These elevations are attained in the Padrela Mountain (NE-Chaves), probably the main recharge area for the Chaves low-temperature  $\text{CO}_2$ -rich geothermal system.

As stated by [28–30, 33, 35, 36], the systematic presence of tritium (2 to 4.5 TU) measured in some of the Vidago (AC16 borehole) and Pedras Salgadas (AC17 borehole) cold  $\text{CO}_2$ -rich mineral waters should not be attributed to mixing with shallow cold dilute normal groundwaters (sampling campaign carried out during 2000). Also, as referred by [33, 35, 36], the lower  $\text{Cl}^-$  concentration of Vidago cold  $\text{CO}_2$ -rich mineral waters (AC16 borehole - see Table 1) could be faced as a signature of mixing, which is not consistent with the calculated  $\text{PCO}_2$  values (around 1.20 atm, see [29]). Furthermore, Pedras Salgadas cold  $\text{CO}_2$ -rich mineral waters (AC25 borehole) present similar  $\text{Cl}^-$  contents to the Pedras Salgadas (AC17 borehole) cold  $\text{CO}_2$ -rich mineral waters (see Table 1), but no  $^3\text{H}$  content (see Table 3). So, the systematic presence of  $^3\text{H}$  in Vidago AC16 and Pedras Salgadas AC17 cold  $\text{CO}_2$ -rich mineral waters should be ascribed to shallow (and short) underground flow paths, with the water mineralization being strongly controlled by the  $\text{CO}_2$  content [33, 35, 36, 77].

The income of carbon-14 free  $\text{CO}_2$  (mantle derived) to the studied  $\text{CO}_2$ -rich geothermal and cold mineral water systems must produce erroneous groundwater age estimations [31]. In fact, the radiocarbon content ( $^{14}\text{C}$  activity from 4.3 up to 9.9 pmC) determined in some of the cold  $\text{CO}_2$ -rich mineral waters from Vidago and Pedras Salgadas [31] mismatched the systematic presence of  $^3\text{H}$  (from 1.7 to 7.9 TU), demonstrating the importance of a good knowledge

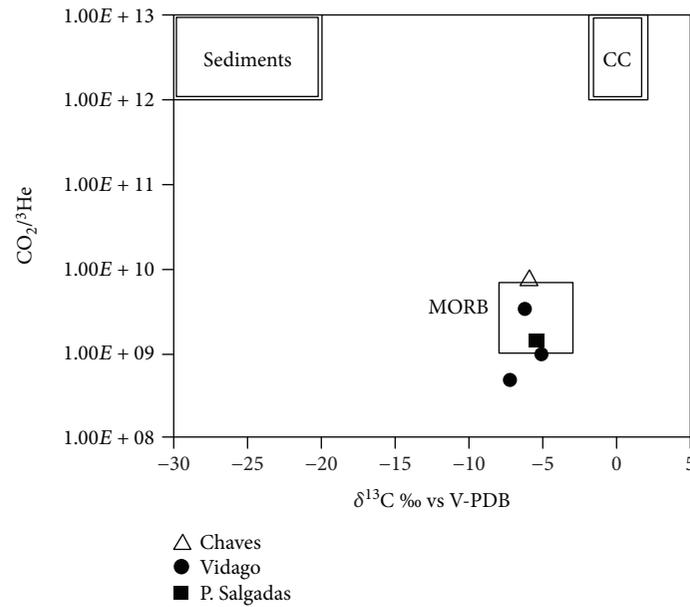


FIGURE 7:  $\text{CO}_2/{}^3\text{He}$  ratio vs.  $\delta^{13}\text{C}$  of the gas phase within the typical MORB formations, the fields were defined based on [104, 107, 108]. The  $\text{CO}_2/{}^3\text{He}$  ratios for crustal and MORB fluids are from [107, 109]. The symbols stand for ( $\Delta$ ) Chaves, ( $\bullet$ ) Vidago, and ( $\blacksquare$ ) Pedras Salgadas. Adapted from [81].

on these cold  $\text{CO}_2$ -rich mineral water systems for the development of the hydrogeological conceptual model of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal system, in which it is very difficult to make sound conclusions on the use of carbon-14 isotopic data for groundwater dating.

In low-temperature geothermal systems, carbon dioxide can be derived from many sources, such as organic matter oxidation, interaction with sedimentary carbonates, metamorphic devolatilisation, and magmatic degassing (e.g., [78, 79]).

According to [77], the  $\delta^{13}\text{C}$  determinations carried out on total dissolved inorganic carbon (TDIC) of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters are in the range of  $-6\text{‰}$  to  $-1\text{‰}$ , corroborating the previous  $\delta^{13}\text{C}$  values ( $\delta^{13}\text{C}_{\text{CO}_2} = -5.72\text{‰}$  vs. PDB) presented by [47] of  $\text{CO}_2$  gas samples of Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters.

Later on, [32] reported  $\delta^{13}\text{C}_{\text{CO}_2}$  varying between  $-7.2$  and  $-5.1\text{‰}$  vs. V-PDB. Given the range of the  $\delta^{13}\text{C}$  values, the deep-seated (upper mantle) origin for the  $\text{CO}_2$  should be considered a likely hypothesis, given the tectonic/fracture scenario of the study region. According to [80], concerning the discussion on the  ${}^3\text{He}/{}^4\text{He}$  and  ${}^4\text{He}/{}^{20}\text{Ne}$  ratios from terrestrial fluids in the Iberian Peninsula, the helium isotopic signatures in a fluid sample from Cabreiroá cold  $\text{CO}_2$ -rich mineral waters, located in Spain at the same NNE-trending fault of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters, are significantly higher than those of typical crustal helium ( ${}^3\text{He}/{}^4\text{He}$  value of 0.69). Those authors estimated that in Cabreiroá fluid sample the helium's fractions from atmospheric, crustal and mantle reservoirs were 0.02%, 91.62% and 8.35%, respectively. The relatively high  ${}^3\text{He}/{}^4\text{He}$  found in the Cabreiroá sample corroborates a significant mantle-degassing component. The isotopic ratios of carbon and helium ( $\delta^{13}\text{C}$ ,  ${}^3\text{He}/{}^4\text{He}$ ) and the geochemical signatures

of the gas phase ascribed to the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters and the cold  $\text{CO}_2$ -rich mineral waters of Vidago and Pedras Salgadas were used by [31, 32, 81], to identify contributions of deep crustal and mantle volatile components associated to the NNE-trending fault (see Figure 7). The  ${}^3\text{He}/{}^4\text{He}$  ratios found in the gas phase of the  $\text{CO}_2$ -rich waters ranged between 0.89 and 2.68 times the atmospheric ratio ( $R_a$ ) at Chaves (AC1 borehole) and Pedras Salgadas (AC25 borehole), respectively, being higher than those expected for a pure crustal origin ( $\approx 0.02 R_a$ ). Also, the  $\text{CO}_2/{}^3\text{He}$  values, from  $5.1 \times 10^8$  to  $7.5 \times 10^9$ , are typical of MORB fluids [32, 81].

In a region where recent volcanic activity is absent, the mantle-derived component of the released deep-seated fluids indicates that extensive neo-tectonic structures (i.e., the NNE-trending fault) are still active [31, 32].

## 5. Water-Rock Interaction and Water/Rock Ratios

Increasing intensity of low-temperature geothermal water use all over the world and possible groundwater-related conflicts between stakeholders (e.g., society, governments, industry, and nature) puts increasing pressure on the natural groundwater environment. At present, 82 countries utilize the low-temperature geothermal water for direct applications with an installed thermal power capacity of 70,885 MW and a thermal energy use of 164,635 GWh/year [82]. For decision-making purposes (e.g., exploitation rates, avoiding overexploitation), indicators such as those presented in this chapter should be accepted as driving forces to simplify complex information (such as the interrelationship between several hydrogeological systems).

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are powerful hydrogeochemical tracers as strontium atomic weight avoids easy isotopic fractionation by any natural process. Commonly, the measured differences in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in waters can be ascribed to Sr derived from different rock sources with different isotopic signatures [83], where the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in waters depend on the Rb/Sr ratios and the age of the percolated rocks [83].

Several studies have used Sr isotope ratios to update knowledge on the chemical evolution of geothermal and mineral waters (e.g., [84–92]). In this paper, we review the use of Sr geochemical and isotopic signatures to improve knowledge on the relation between the Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters and the cold  $\text{CO}_2$ -rich mineral waters from Vilarelho da Raia, Vidago, and Pedras Salgadas, discharging along one of the major NNE-SSW-trending faults in northern Portugal, with special emphasis on (i) identifying the reservoir rocks, (ii) recognizing the existence (or not) of mixing processes, and (iii) improving knowledge on water-rock interaction processes at depth.

Sampling procedures in order to collect representative water and rock samples of the region for Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are described in detail by [38]. Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in waters and rocks were determined by Geochron Laboratories (a division of Krueger Enterprises Inc./Cambridge, Massachusetts, USA), following the methods described in [38]. Sample preparation for isotopic analysis on silicate minerals was performed at Centro de Petrologia e Geoquímica, Instituto Superior Técnico - CEPGIST - Lisbon, Portugal (see [38]).

Strontium concentrations and isotope ratios from waters and rocks (including mineral separates) from the Vilarelho da Raia/Pedras Salgadas region, northern Portugal, are reported in Tables 4 and 5, respectively.

Figure 8 shows a plot of  $1/\text{Sr}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  for the studied low-temperature  $\text{CO}_2$ -rich geothermal waters and cold  $\text{CO}_2$ -rich mineral waters [38]. The  $^{87}\text{Sr}/^{86}\text{Sr}$  of the studied low-temperature  $\text{CO}_2$ -rich geothermal waters and cold  $\text{CO}_2$ -rich mineral waters increase from south to north (Pedras Salgadas  $^{87}\text{Sr}/^{86}\text{Sr} = 0.716713$  to  $0.717572$ ; Vidago:  $^{87}\text{Sr}/^{86}\text{Sr} = 0.720622$  to  $0.72428$ ; and Vilarelho da Raia/Chaves:  $^{87}\text{Sr}/^{86}\text{Sr} = 0.727154$  to  $0.728035$ ) along the NNE mega-lineament of the Verin-Régua-Penacova fault zone (VRPFZ – see Figure 2). This trend could suggest the possible existence of groundwater flow from south to north. However, this assumption is not realistic since according to [28, 36, 93] the studied low-temperature  $\text{CO}_2$ -rich geothermal waters and cold  $\text{CO}_2$ -rich mineral waters have different  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  signatures (see Figure 6).

These Sr isotopic signatures corroborate the idea that the Chaves low-temperature  $\text{CO}_2$ -rich geothermal system is distinct, recharged at high-altitude sites ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values), and ascribed to water-rock interaction within a granitic environment with specific Sr isotopic composition. The fact that there is no hydraulically connection from Pedras Salgadas towards Vilarelho da Raia, along the Verin-Régua-Penacova fault zone, has strong implications for the sustainable management of the Chaves low-temperature  $\text{CO}_2$ -rich geothermal system. In fact, if such hydraulically connected flow path occurred, it would produce a general increase in

TABLE 4: Sr concentrations and isotope ratios from waters in the Vilarelho da Raia/Pedras Salgadas region, northern Portugal. Table 4 is reproduced from Marques et al. (2006) [under the Creative Commons Attribution License/public domain].

Ref.	Local	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$
ACP1 (◊)	Vilarelho da Raia	0.5827	0.728033
CH1Ch. (*)	Chaves	0.0010	0.710599
Assureiras (□)	Chaves	0.0242	0.729536
Castelões (□)	Chaves	0.0059	0.722967
Campo de futebol (□)	Chaves	0.2942	0.723488
AC2 (△)	Chaves	0.4349	0.727191
Nasc. (△)	Chaves	0.4181	0.727154
CH1 V. (*)	Vidago	0.0015	0.710804
Baldio (□)	Vidago	0.0254	0.717003
N3 (□)	Vidago	0.0060	0.722858
N6 (□)	Vidago	0.0089	0.719087
N7 (□)	Vidago	0.0104	0.714352
AC16 (●)	Vidago	0.3424	0.723194
AC18 (●)	Vidago	1.3977	0.724280
Areal 3 (●)	Vidago	1.2130	0.720622
CH1 P.S. (*)	Pedras Salgadas	0.0013	0.711326
N1 (□)	Pedras Salgadas	0.0075	0.715094
N2 (□)	Pedras Salgadas	0.0018	0.730712
N5 (□)	Pedras Salgadas	0.0098	0.731135
AC17 (■)	Pedras Salgadas	0.7001	0.716969
AC25 (■)	Pedras Salgadas	0.8195	0.717572
AC22 (■)	Pedras Salgadas	1.3250	0.716754

Notes: (\*) rain waters; (□) shallow cold dilute normal groundwaters; (△) Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters; cold  $\text{CO}_2$ -rich mineral waters from (◊) Vilarelho da Raia, (●) Vidago, and (■) Pedras Salgadas.

the water mineralization from south to north, which also is not the case (see [28, 36, 93]).

As referred by [34–36], the spreading of the Sr data can be understood through the presence of three end-members ((a) Vilarelho da Raia/Chaves, (b) Vidago, and (c) Pedras Salgadas) of a concentration tendency, from rain waters towards the low-temperature  $\text{CO}_2$ -rich geothermal waters and cold  $\text{CO}_2$ -rich mineral waters ( $1/\text{Sr}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, see Figure 8).

Since the radioactive decay of  $^{87}\text{Rb}$  promotes an emplacement by  $^{87}\text{Sr}$ , which enters more rapidly into solution [83], the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of groundwaters interacting with older granitic rocks (e.g., Chaves low-temperature  $\text{CO}_2$ -rich geothermal waters and Vilarelho da Raia cold  $\text{CO}_2$ -rich mineral waters) are naturally larger than the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of Vidago and Pedras Salgadas cold  $\text{CO}_2$ -rich mineral waters, ascribed to water-rock interaction with younger (post-tectonic) granitic rocks (see Figure 2 and [83–85]).

The presence of low-temperature  $\text{CO}_2$ -rich geothermal waters and diverse groups of cold  $\text{CO}_2$ -rich mineral waters is also corroborated by the structural tectonic environment of the region, namely, by the existence of important structural lineation enhancing the subsidence zones in the Chaves,

TABLE 5: Sr concentrations and isotope ratios of rocks and mineral separates from Vilarelho da Raia/Pedras Salgadas region, northern Portugal. Table 5 is reproduced from Marques et al. (2006) [under the Creative Commons Attribution License/public domain].

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

Note: \*Data from [29].

Vidago, and Pedras Salgadas basins (see [38, 43, 44]). Such features explain the existence of similar but distinct hydrogeological systems rather than a single system (see Figure 3).

Plagioclases and biotite usually supply most of dissolved ions to the water, when compared to K-feldspars and quartz which are slightly attacked [85]. Studies performed in the study region [34, 35, 38] gave emphasis to the fact that although the low-temperature  $\text{CO}_2$ -rich geothermal waters and cold  $\text{CO}_2$ -rich mineral waters sampled at Chaves/Vilarelho da Raia areas, respectively, present the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, Sr isotope ratios of granitic rock samples from the study region (see Table 5) are far higher than the Sr isotope ratios from the water samples (e.g., Vilarelho da Raia granite:  $^{87}\text{Sr}/^{86}\text{Sr} = 0.789683$ ; Vidago granite:  $^{87}\text{Sr}/^{86}\text{Sr} = 0.762890$ ). From these observations, [34, 35, 38] concluded that (i) no equilibrium was attained between the waters and

the whole-rocks and (ii) that the Sr isotope values were achieved from equilibrium between the waters and specific minerals from the granitic rocks. As referred by [38], the mean Sr isotopic ratio of the low-temperature  $\text{CO}_2$ -rich geothermal waters and cold  $\text{CO}_2$ -rich mineral waters ( $^{87}\text{Sr}/^{86}\text{Sr}_{\text{mean}} = 0.722419$ ) is comparable to the Sr isotopic ratios of the plagioclases of the granitic rocks presented by [29]: Vilarelho da Raia<sub>plagioclase</sub>  $^{87}\text{Sr}/^{86}\text{Sr} = 0.72087$  and Vidago<sub>plagioclase</sub>  $^{87}\text{Sr}/^{86}\text{Sr} = 0.71261$ . These results are in good agreement with the chemistry of the studied low-temperature  $\text{CO}_2$ -rich geothermal waters and cold  $\text{CO}_2$ -rich mineral waters which is strongly dominated by the  $\text{HCO}_3^-$  and  $\text{Na}^+$  ions (see Section 3) as the result of the hydrolysis of the Na-plagioclases of the granitic rocks (see [38]).

Concerning water-rock interaction studies, thin sections of drill cores from Vilarelho da Raia AC2 borehole were studied in detail, at LAMPIST, to characterize their

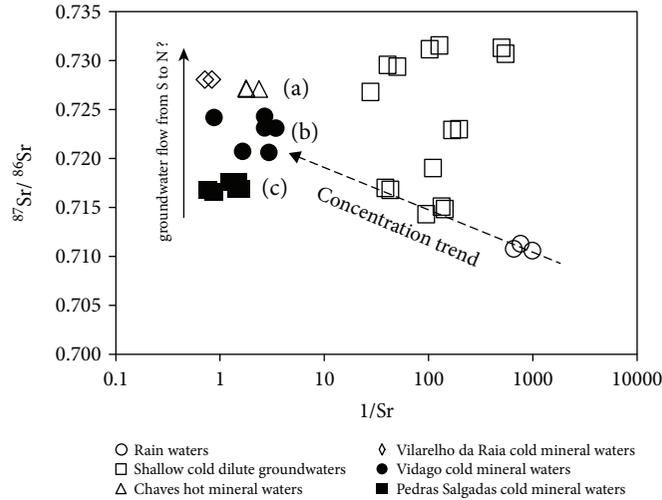


FIGURE 8: Plot of  $1/Sr$  vs.  $^{87}Sr/^{86}Sr$  for the studied low-temperature  $CO_2$ -rich geothermal waters and cold  $CO_2$ -rich mineral waters. Figure 8 is reproduced from Marques et al. (2006) [under the Creative Commons Attribution License/public domain].

mineralogical composition and textural relations (see [37]). Sample preparation for isotopic analysis on granitic rocks and silicate minerals is referred in detail in [37]. Stable isotope analyses of granitic whole-rock samples and selected mineral separates were performed at Delta Isotopes Laboratory (The Netherlands), at XRAL Laboratories (Canada), and at Geochron Laboratories/USA, respectively, following the methodology described in [37] and references therein.

Joined geochemical and isotopic data to characterize and identify the nature of the water-rock interaction between the low-temperature  $CO_2$ -rich geothermal waters and Hercynian granitic rocks (and host rock minerals) in the northern part of the Portuguese mainland was used by [37]. The origin of the fluids responsible for the hydrothermal alteration and the water-rock (W/R) ratios recorded in the vein alteration zones were assessed using stable ( $^{18}O/^{16}O$  and  $^2H/^1H$ ) isotope analysis of whole rocks and mineral separates from the granitic rocks.

This approach was developed considering that

- (i) the geothermal boreholes at Chaves were not cored
- (ii) Chaves low-temperature  $CO_2$ -rich geothermal waters and Vilarelho da Raia cold  $CO_2$ -rich mineral waters show similar geochemical and isotopic signatures
- (iii) Vilarelho da Raia exploration boreholes also penetrate Hercynian granitic rocks
- (iv) the alteration features observed in the Vilarelho da Raia drill cores could be interpreted as manifestations of a “fossil” geothermal system
- (v) they can be used as an analogue for the Chaves geothermal field

According to [37, 93] in the vein alteration zones of the granitic rock samples (along rock fractures), all minerals

are replaced by secondary quartz and white mica, mainly muscovite  $2M_1$ . Illite, halloysite, chlorite, and vermiculite were also found in the same samples.

In order to characterize the meteoric origin of fluids responsible for the vein alteration observed in the drill cores from the Vilarelho da Raia AC2 borehole (see [37]), these authors estimated the  $\delta^{18}O$  and  $\delta^2H$  values of the water in equilibrium with mineral separates such as muscovite and chlorite (Table 6). Whole-rock samples displaying vein alteration signatures were also analysed for  $\delta^{18}O$  and  $\delta^2H$  to estimate the water/rock (W/R) ratios along vein alteration zones (Table 7).

As proposed by [94], in water-rock exchange processes, the water/rock (W/R) ratios can be estimated by using the equation

$$\frac{W}{R_{\text{closed}}} = \frac{(\delta^{18}O_{\text{final-rock}} - \delta^{18}O_{\text{initial-rock}})}{(\delta^{18}O_{\text{initial-fluid}} - \delta^{18}O_{\text{final-fluid}})}, \quad (2)$$

where  $W$  and  $R$  are the atom percentages in the fluid ( $W$ ) and in the rock ( $R$ ). As mentioned by [37], in an open system, the most reliable situation in this case study, the heated water is lost from the system by escape to the surface, making only a single pass through the system from recharge to discharge areas; we have [94]

$$\frac{W}{R_{\text{open}}} = \ln \left( \frac{W}{R_{\text{closed}}} + 1 \right). \quad (3)$$

According to [37], the main problems regarding the application of the abovementioned equations are related to the initial isotopic composition of the rock ( $\delta^{18}O_{\text{initial-rock}}$ ) and fluid ( $\delta^{18}O_{\text{initial-fluid}}$ ). In the studies presented by [37], the initial oxygen isotope composition of the country rocks is represented by the  $\delta^{18}O$  values of the least  $^{18}O$ -depleted rock samples (AM3 and AM80) from Vilarelho da Raia granitic outcrops outside the spring area (Table 6). These

TABLE 6: Isotopic composition of whole rocks and mineral separates from Vilarelho da Raia AC2 drill cores. After [37].

Sample	Type of alteration	Depth (m)	Whole-rock		Muscovite		Chlorite	
			$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$
AM3	Pervasive (low)	(Surface)	+11.41	-75.0				
AM80	Pervasive (low)	(Surface)	+11.47	-66.1	+9.7	-70		
VR23	Pervasive	81.15			+8.5	-44		
VR27a	Vein	89.70	+10.10	-42.0	+9.1			
VR27b	Pervasive	89.70	+10.18	-69.0	+11.6		+6.3	-53.0
VR32a	Pervasive	100.55	+11.25	-66.4	+8.6			
VR32b	Vein	100.55	+10.91	-44.5	+9.1	-42		
VR39	Vein	129.70	+10.80	-65.0	+10.2	-70	+5.2	-75.0
VR41	Pervasive	140.50			+9.8	-64		
VR70a	Vein	195.30	+10.82	-56.0	+9.4	-45		
VR70b	Pervasive	195.30	+10.91	-44.5	+9.3			

Note: The term “low” means a rock sample displaying low pervasive alteration characteristics (almost an unaltered rock sample).

TABLE 7: Water/rock (W/R) ratios related to vein alteration zones, Vilarelho da Raia AC2 drill cores. After [37].

Sample depth	$\delta^{18}\text{O}_{\text{initial rock}}$	$\delta^{18}\text{O}_{\text{final rock}}$	$\delta^{18}\text{O}_{\text{initial water}}$	$\delta^{18}\text{O}_{\text{final water}}$	(W/R) (*)	(W/R) (**)
VR32b	+11.47	+10.91	-5.76	-0.55	0.10 (a)	0.09 (a)
(100.55 m)	+11.47	+10.91	-6.68	+3.84	0.05 (b)	0.05 (b)
VR39	+11.47	+10.80	-9.26	-0.65	0.08 (a)	0.07 (a)
(129.70 m)	+11.47	+10.80	-10.18	+3.73	0.04 (b)	0.05 (b)
VR70a	+11.47	+10.82	-6.13	-0.64	0.11 (a)	0.08 (a)
(195.30 m)	+11.47	+10.82	-7.06	+3.75	0.06 (b)	0.05 (b)

Notes: \* W/R ratios calculated using the  $\delta^2\text{H}$  values of muscovites along open-space filling zones of the granite, the muscovite-water fractionation equation proposed by [96], and the Global Meteoric Water Line. \*\* W/R ratios calculated assuming that the final  $\delta^2\text{H}$  of the altered rock samples, along open-space filling zones of the granite, has approached the  $\delta^2\text{H}$  of the circulating meteoric waters, and the Global Meteoric Water Line (a) W/R ratios calculated at 150°C; (b) W/R ratios calculated at 230°C.

values ( $\delta^{18}\text{O} = +11.41\text{‰}$  and  $+11.47\text{‰}$ ) fall within the “high- $^{18}\text{O}$  granites” group [37, 94].

A meteoric origin for the water responsible for the vein alteration process was assumed by [37], and therefore, the initial water composition was calculated from the  $^2\text{H}/^1\text{H}$  ratio of the alteration assemblage (along veins) and the Global Meteoric Water Line (GMWL:  $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$ ), defined by [71], assuming that the  $^2\text{H}/^1\text{H}$  ratios of the vein fluids had not been affected by water-rock interaction [37]. According to [94], the final  $\delta^2\text{H}$  of the rocks is dependent upon exactly how the meteoric water enters in the system and, consequently, for small amounts of water the final  $\delta^2\text{H}$  of the rock could approach the  $\delta^2\text{H}$  values of the meteoric waters due to the fact that there is not much H in the rocks (see [37]).

Thus, according to [37], the initial  $\delta^{18}\text{O}$  values of the water were estimated by means of

- (i) the  $\delta^2\text{H}$  values of the muscovites located along veins (see [95] - pages 289 and 290)
- (ii) the muscovite-water fractionation equation proposed by [96]

(iii) the Global Meteoric Water Line ( $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$ ) defined by [71].

According to [37], the values obtained (from  $-10\text{‰}$  to  $-6\text{‰}$ ) are reliable. Those authors stated that considering vein alteration features observed in the Vilarelho da Raia granitic drill cores as manifestations of a “fossil” geothermal system, the methodology used to estimate the water/rock ratios along veins [94, 95] predicted initial  $\delta^{18}\text{O}$  values of the water that are rather similar to the present-day meteoric waters (see Figure 6).

The final  $\delta^{18}\text{O}$  values for the rock used in the calculations (from  $+10.80\text{‰}$  to  $+10.91\text{‰}$ ) were the values measured on core samples from vein alteration bands [37]. The final water composition was estimated by the [97] plagioclase-water isotope fractionation equation [37], assuming that  $\delta^{18}\text{O}_{\text{plagioclase}} \approx \delta^{18}\text{O}_{\text{whole-rock}}$  (final composition), as plagioclase is the main mineral in the rock and exhibits the greatest rate of  $^{18}\text{O}$  exchange with an external fluid phase (corroborated by the Sr isotopic data).

As noted above in discussing the vein alteration zones, vein water-rock interaction temperatures ( $150^\circ\text{C} < T < 230^\circ\text{C}$ )

proposed by [37] were estimated through the stability fields of the alteration minerals (e.g., muscovite, illite, halloysite, chlorite, and vermiculite), as suggested by [98–100]. Given these temperatures, the *W/R* ratios obtained by [37] for the open system are between 0.08 and 0.11 and between 0.04 and 0.06 (Table 7), for 150 and 230°C, respectively, suggesting a rock-dominated system (as indicated by the Sr chemical and isotopic data) where a relatively small volume of meteoric water was involved in vein formation [37].

Based on these results, it was suggested that isotopic data on hydrothermal minerals (e.g., muscovite and chlorite) should be used as a natural analogue for assessing the present-day hydrochemical and isotopic evolution of the Chaves low-temperature CO<sub>2</sub>-rich geothermal system [37].

In granitic environments chosen for Enhanced Geothermal Systems (EGS) development, one of the most important questions is determining the relevance of hydrothermal events and their relationships to the history of the granite. Here, the results of the mineralogical, chemical, and isotopic investigations of the silicates from granitic rocks were used to derive a better understanding of past water-rock reactions in the area and information on conditions leading to hydrothermal alteration and fracture fillings. What was learned could be useful in deciding where to develop an EGS exchanger in the subsurface, as it would help estimate the type and intensity of mineral deposition that is likely to occur during its operation.

## 6. Geophysical Approach

Since 1990, various geophysical methods, mainly gravity, resistivity, scalar audio-magnetotellurics (AMT), and magnetotellurics (MT), have been used to study the shallow and deep structures of the Chaves graben (e.g., [101–103]), mostly associated to the geometry of the shallow groundwater circulation zones related with the deep fracture system (see [27]). In this publication, only results from resistivity and AMT will be presented, since they are the ones that better fit our objectives.

According to [102], the resistivity survey comprised 29 Schlumberger vertical electrical soundings (VES), dipole-dipole lines, pole-dipole-lines, and rectangle surveys. The VES were carried out with current electrodes expanding approximately in the NNE-SSW direction and with a maximum spacing ranging from 1200 to 2000 m (Figure 9).

The VES apparent resistivity curves can be grouped into two main groups, representing the geological and geoelectrical diversity [27, 102, 104]. The first group of soundings, comprising curves showing a decrease in the resistivity up to large AB/2 values, were obtained in the eastern and central part of the graben, where the sedimentary sequences are thick (VES 11, 15, and 29 in Figure 9). The second group of VES comprises curves obtained in areas where the bedrock is shallow, i.e., mainly in the western part of the graben (VES 24 in Figure 9).

The 1D inversion results of the VES data [27, 75] were combined to obtain a map of the low-resistivity layer associated with the geothermal reservoir (Figure 9). Additionally, two resistivity cross sections along N-S and E-W directions were obtained combining the 1D inversion results

(Figure 10). These figures show that low-resistivity zones (resistivity values between 10 and 60 ohm-m) are concentrated in the central part of the graben because of high temperatures combined with the high salinity of the geothermal waters in fractured and permeable rock formations.

There are several shallow groundwater boreholes drilled along the N-S axis of the basin (Figures 9 and 10). None of the boreholes reaches the basement of the basin, and neither touches the high temperature reservoir. The most part of the well drill in the Quaternary overburden is represented by the first layer in the VES models. This layer shows resistivity values varying between 70 and 800 ohm-m (Figure 10).

The deepest part of the basin (basement) is represented by the last layer of the VES models and shows high-resistivity values (greater than 500 ohm-m), except in the central part of the graben where the NNE-SSW and NNW-SSE fault systems cross the area.

An audio-magnetotellurics (AMT) survey including more than 100 soundings, in the frequency range from 2300 to 4.1 Hz, was carried out in the graben area [101]. The 1D models calculated from AMT soundings revealed an excellent agreement with those obtained from the Schlumberger apparent resistivity curves [27, 75]. As derived from the 1D inversion of the AMT data [27, 101, 104], the contour map of the conductance values (the ratio thickness/resistivity at each sounding) in the conductive layer is shown in Figure 11.

The high values roughly match the zones of great depth of the bedrock as determined from 1D interpretation of the VES. The conductance anomalies show a preferential (approximately) N-S direction that seems to be perturbed by WNW-ESE structures. The high conductance zones were interpreted as related to the geothermal aquifer in the Chaves graben and may expose the preferential zones for the hot waters' ascent.

In fact, as stated by [105], in a magnetotellurics survey of the Milos Island (Greece) geothermal prospect, the maximum conductance values approximately agree with the maximum temperature gradient. It should be emphasised that the temperature measurements in boreholes from the Chaves graben [7] point towards a similar behaviour.

As already mentioned in Section 2 (Figure 3), geological and tectonic studies evidence the existence of deep fractures trending approximately NW-SE, ENE-WSW, and N-S either in the Chaves graben or in the surroundings. The geophysical results also confirm the presence of such directions (differences in the directions are due to the scarcity of geophysical data), reflecting the pattern of geothermal fluids circulation along the fault system (Figures 9 and 11). As referred by [27, 101, 104], such faults, and mainly their intersection, would provide an efficient conduit system for geothermal fluids ascending from the reservoir, in the deep part of the Chaves graben.

## 7. Chaves Low-Temperature CO<sub>2</sub>-Rich Geothermal System vs. Cold CO<sub>2</sub>-Rich Hydromineral Systems: Conceptual Models

Low-temperature CO<sub>2</sub>-rich geothermal resources represent somewhat complex systems which are not easy to understand

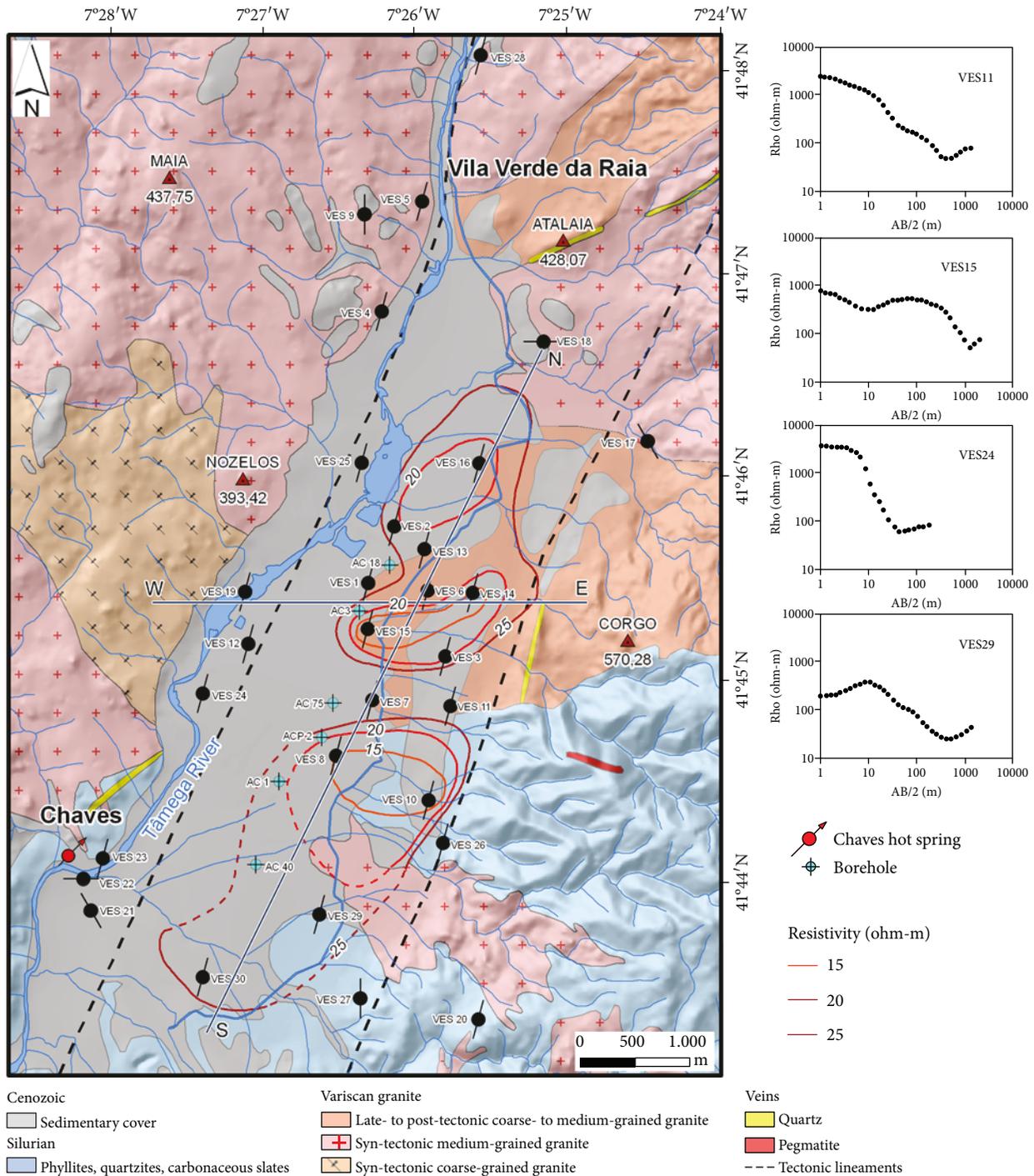


FIGURE 9: Location of the VES carried out in Chaves graben and example of apparent resistivity curves acquired. Geological background adapted from [110, 111]. Lines in the filled circles represent the VES direction. Also shown are the contours of the low resistivity zones in the central part of the graben (approximate depth of 350 m) as determined from 1D interpretation of VES. Adapted from [27].

under multifaceted hydrogeological conditions, particularly in areas where low-temperature CO<sub>2</sub>-rich geothermal waters and cold CO<sub>2</sub>-rich mineral waters discharge a few kilometres apart. According to [9], the conventional description of a groundwater conceptual model is a usually qualitative and often graphic explanation of the groundwater system, including a delineation of the hydrogeologic units, the system boundaries, inputs/outputs, and a description of soils and

rocks. Hydrogeological conceptual models are simplified representations of a given hydrological and hydrochemical cycle within a geological environment ascribed to an aquifer system. These are developed by hydrogeologists normally based on important data sets collected in the scope of regional investigations.

In this paper, a special emphasis was put on the review of the contribution of a multidisciplinary approach

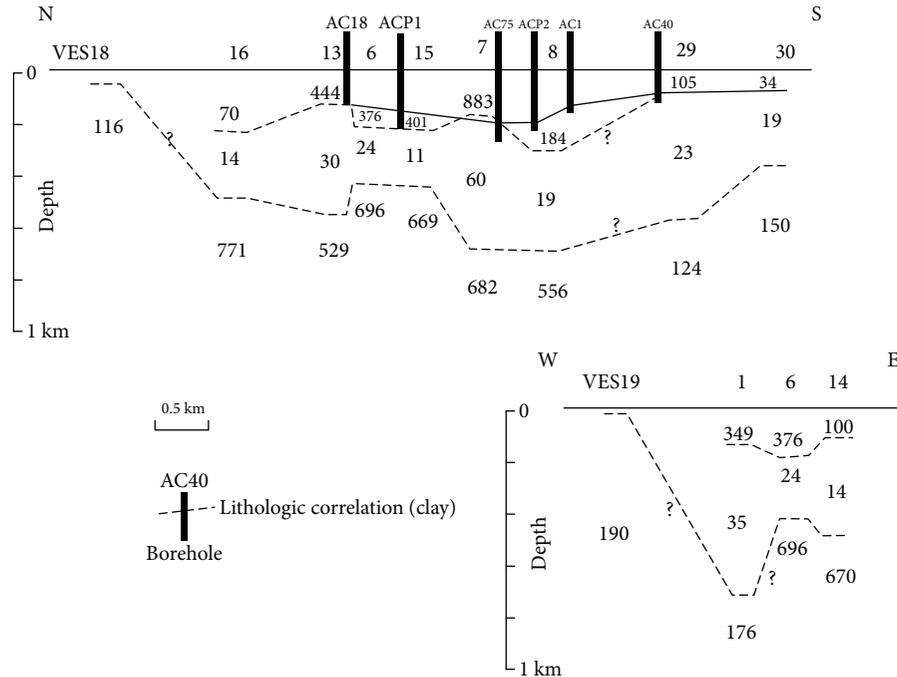


FIGURE 10: Resistivity 1D sections along N-S and E-W directions. Values are in ohm-m. Taken from [27]. AC and ACP stand for diverse boreholes from the Chaves graben.

(geology, geomorphology, tectonics, hydrogeology, geochemistry, isotope hydrology, and geophysics) to the development of the hydrogeological conceptual model of Chaves low-temperature CO<sub>2</sub>-rich geothermal waters, linking to the case of the Vilarelho da Raia, Vidago, and Pedras Salgadas cold CO<sub>2</sub>-rich mineral waters.

As stated by [31–33], chemical and isotopic data reveal that the studied CO<sub>2</sub>-rich waters are part of an open system to the influx of CO<sub>2</sub> gas from a deep-seated source ( $\delta^{13}\text{C}_{\text{CO}_2}$  values and CO<sub>2</sub>/<sup>3</sup>He ratios) and that water-rock reactions are mainly controlled by the amount of dissolved CO<sub>2</sub> (g) rather than by the water temperature. The most probable explanation by which carbon dioxide could be transported from its deep source to the surface involves migration as a separate gas phase being incorporated in the infiltrated meteoric waters (i) at considerable depth in the case of the Chaves low-temperature CO<sub>2</sub>-rich geothermal waters and (ii) at shallow levels in the case of cold CO<sub>2</sub>-rich mineral waters from Vilarelho da Raia, Vidago, and Pedras Salgadas (see [32] and Figure 12). Solutes such as Na and HCO<sub>3</sub> are originated from the local granitic rocks, with their concentration in the waters favoured by the CO<sub>2</sub> dissolution at low temperatures, ascribed to shallow circulation paths (Figure 12), lowering the pH and increasing water-rock interaction, as revealed by the higher mineralization of most of the studied cold CO<sub>2</sub>-rich mineral waters.

The Sr isotopes and Sr concentrations in the waters and rocks provided a clear picture on the influence of varying rock types on the CO<sub>2</sub>-rich water signatures [34, 38]. The Sr-isotope data presented in this study strongly suggest that Chaves low-temperature CO<sub>2</sub>-rich geothermal waters and Vilarelho da Raia, Vidago, and Pedras Salgadas CO<sub>2</sub>-rich

mineral waters should be faced as surface manifestations of different hydrogeological systems and underground flow paths.

Particularly, and ascribed to the updating of the hydrogeologic conceptual model of the Chaves low-temperature CO<sub>2</sub>-rich geothermal system (Figure 13), geological studies evidenced the existence of deep NW-SE- (dextral-) and ENE-WSW- (sinistral-) trending faults, either in the Chaves graben or in the surrounding area, reflecting the pattern of geothermal fluid circulation, which discharge mainly in places where those trending faults intersect at the Chaves graben (see Figure 3).

The ENE-WSW-trending faults provide effective conduits for the meteoric waters ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values) infiltration and deep circulation (chemical geothermometers), while the NW-SE lineaments promote the geothermal fluids ascending from the reservoir to the surface. The meteoric water infiltrates on the highest topography (the altitude effect), where rainfall is important (Padrela Mountain, NE-Chaves), percolates at great depth through granitic rocks (geology, geochemistry of the waters - Na-HCO<sub>3</sub>-type waters, and Sr isotopic data) along the open fault/fracture systems (vein alteration signatures), and then emerges in a discharge area at lower altitude on the Chaves plain (tectonics/geophysics). Solutes such as Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> are originated from the hydrolysis of the plagioclases of local granitic rocks (Sr isotopic data), being favoured by the incorporation of the deep-seated CO<sub>2</sub> in the circulating waters.

In this case, the distance between recharge and discharge areas is relatively large and groundwater flow paths should also be long (i.e., on the order of decades to centuries). However, the determination of the geothermal waters' "age"

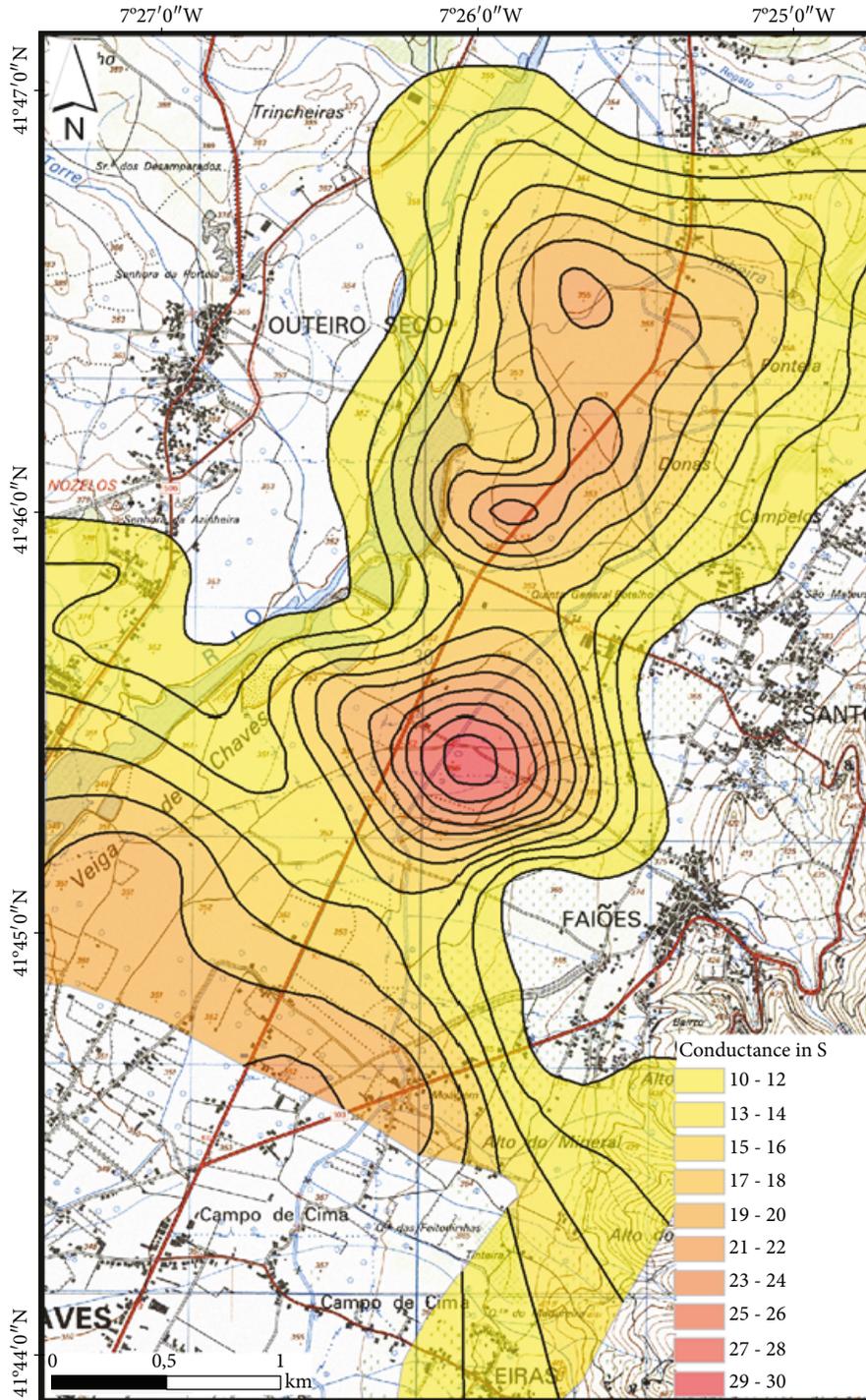


FIGURE 11: Contour map of conductance in the low resistivity layer associated with the geothermal reservoir as derived from AMT data. Taken from [27].

is difficult due to the presence of mantle-derived CO<sub>2</sub> (<sup>14</sup>C free), as described by [31]. Nevertheless, the results from chemical geothermometers seem to indicate a considerable depth reached by the thermal water system, ascribed to long underground flow paths.

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 [32].

### 8. Main Conclusions

This paper review the usefulness of geologic, tectonic, geochemical, isotopic, and geophysical studies on the assessment of Chaves low-temperature (77°C) CO<sub>2</sub>-rich geothermal

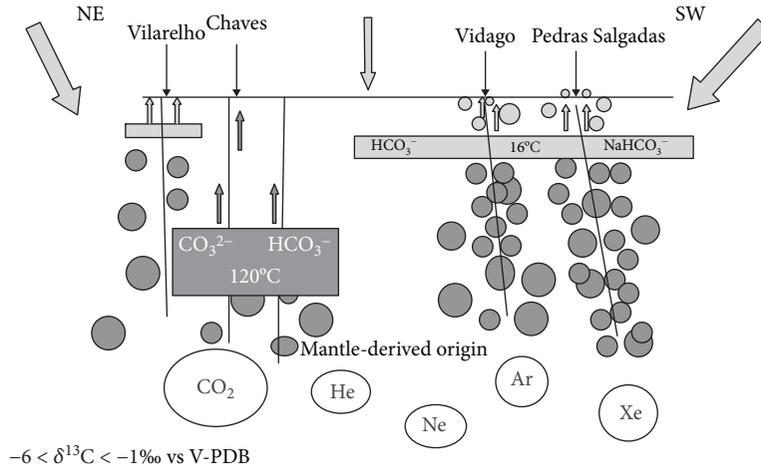


FIGURE 12: Regional conceptual model of the studied CO<sub>2</sub>-rich mineral waters, along the Penacova-Verin fracture zone, between Vilarelho da Raia and Pedras Salgadas (N of Portugal). The filled circles stand for the amount of dissolved deep CO<sub>2</sub> gas; the lines stand for fault systems; down arrows stand for meteoric waters (recharge); up arrows stand for deep/shallow groundwater ascent, boxes stand for a schematic representation of the CO<sub>2</sub>-rich aquifer systems. Adapted from [81].

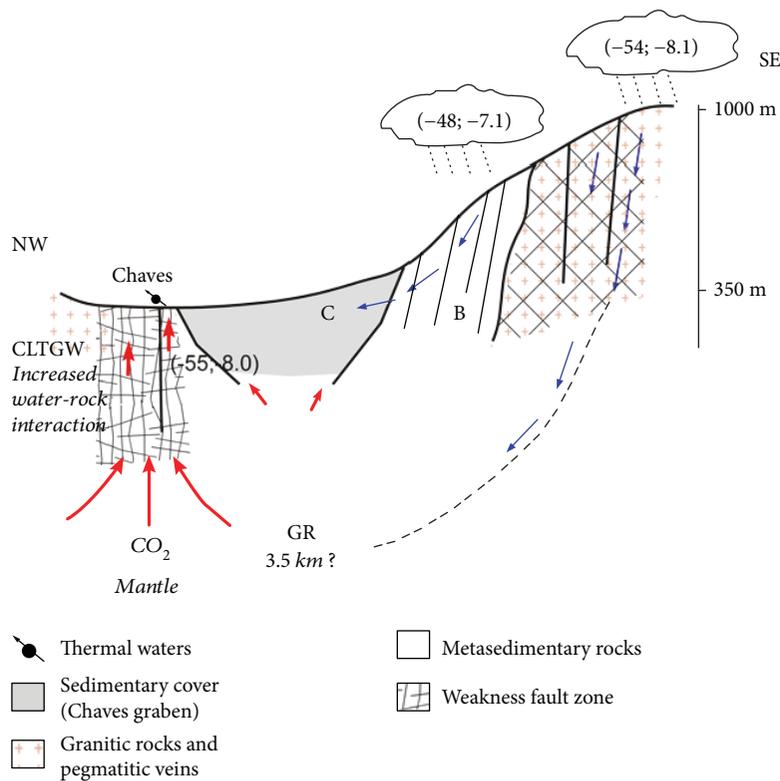


FIGURE 13: Hydrogeological conceptual circulation model of Chaves low-temperature CO<sub>2</sub>-rich geothermal system. B stands for granitic and metasedimentary rocks; C stands for cover deposits; CLTGW stands for Chaves low-temperature CO<sub>2</sub>-rich geothermal waters; GR stands for geothermal reservoir; (-54; -8.1) stands for the isotopic composition ( $\delta^2\text{H}$ ;  $\delta^{18}\text{O}$ ) of the waters. Taken from [27].

system issuing in the northern part of the Portuguese mainland. In this region, a suite of cold (17°C) CO<sub>2</sub>-rich mineral waters (Vilarelho da Raia, Vidago, and Pedras Salgadas) also occur along the same NNE-trending fault. The data reviewed highlight the complexity in studying and linking low-temperature CO<sub>2</sub>-rich geothermal waters

and cold CO<sub>2</sub>-rich mineral waters discharging in the same region. Knowledge of groundwater circulation and possible interactions between the low-temperature geothermal and the cold mineral waters is an important factor to ensure economic use of (i) deep hot waters as a geothermal resource and (ii) shallow cold mineral waters as drinkable

mineral waters, as well as in terms of potential future overexploitation. The integration of the results of studies from different geosciences approaches strongly suggests that the Chaves low-temperature CO<sub>2</sub>-rich geothermal waters and Vilarelho da Raia, Vidago, and Pedras Salgadas cold CO<sub>2</sub>-rich mineral waters should be faced as surface manifestations of different hydrogeological systems ascribed to diverse underground flow paths. This paper is aimed at reviewing the value of an integrated and multi- and interdisciplinary approach for a given geothermal site characterization. The existing integrated model could be useful for other case studies linking the assessment of low-temperature CO<sub>2</sub>-rich geothermal waters and cold CO<sub>2</sub>-rich mineral waters emerging in a same area. The data acquired so far could be extremely useful for future numerical simulation of Chaves low-temperature CO<sub>2</sub>-rich geothermal reservoirs, a very useful instrument for making decisions about the upcoming strategies of field exploitation and for analysing the behaviour of the whole rock-geofluid system. In fact, numerical model construction must be supported by a detailed knowledge of the spatial distribution of reservoir properties in the form of a robust conceptual model. Furthermore, the spas of northern Portugal are of special commercial value and should not be impacted by future water resource development.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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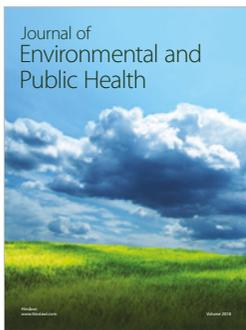
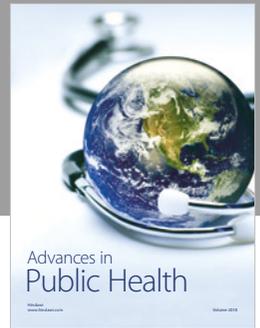
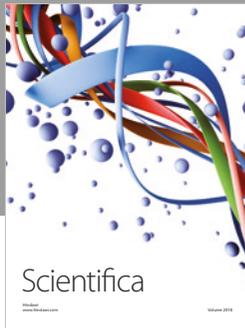
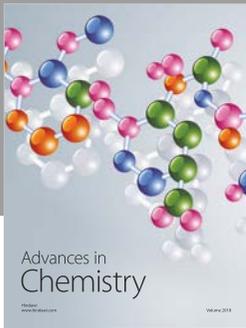
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