Why CO_2-rich mineral waters present peculiar signatures, when compared with other types of mineral waters? Vidago - Pedras Salgadas case study

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Abstract

Numerous studies have analysed the CO_2-rich mineral waters within the Vilarelho da Raia–Pedras Salgadas region of North Portugal, which show marked differences in the geochemical and isotopic signatures of cold (17 °C) and hot (up to 76 °C) CO_2-rich mineral waters in this region. Peculiar signatures in this region are seen through the higher total dissolved solids (TDS mg/L) displayed in the colder Vidago and Pedras Salgadas springs compared to the hot Chaves springs. Typically, in mineral water springs without CO_2, TDS and temperature show a positive correlation due to the increased water-rock interaction at high temperatures. Studies of around thirty CO_2-rich mineral water systems were collated to find further occurrences of this phenomenon. Systems with both hot and cold springs, and a higher TDS in the colder springs, showed the most important factor for this difference may be due to the increased water-rock interaction at low temperatures with the presence of CO_2 in water, particularly in granitic rocks (as in Vilarelho da Raia–Pedras Salgadas region).This study integrated the development of a comprehensive hydrogeological conceptual model of CO_2-rich mineral water systems. Three types of systems: Type 1, dominated by granites, Type 2, dominated by sedimentary rocks, and Type 3, dominated by metasedimentary and metamorphic rocks, were outlined based upon the geology and geochemical characteristics that the water obtains from recharge to discharge. This conceptual model can be used as a base to help define a hydrogeological system, and may be an important tool for the future of hydrogeological studies.

Keywords: CO_2-rich mineral waters, geochemistry, environmental isotopes, water-rock interaction, hydrogeological conceptual models.

1. Introduction

This study will focus on a specific type of mineral and thermal water: CO_2-rich mineral waters. Water rich in CO_2 has been defined by Barnes et al. (1978) as water that contains a minimum of 1 gram per litre of dissolved CO_2, or 1g/L of bicarbonate and with a pH of less than 8.3.

The origin of the CO_2 in CO_2-rich waters has four main sources (e.g. Barnes et al, 1978, Aires-Barros et al., 1998); Organic matter degradation – the decay of organic matter produces CO_2 in soil, which enters thermal and mineral water via recharge pathways through the CO_2 enriched soil; Interaction with carbonates - oxidation of carbonaceous sediments due to water-rock interaction at depth causing dissolution of CO_2 into the groundwater; Metamorphic devolatilization – subduction, and subsequent heating of carbonate-bearing marine sediments due to volcanism leads to CO_2 being released from the rock into the groundwater system; Magmatic degassing - release of gases (e.g. carbon dioxide) into the water when magma is cooled.

CO_2-rich waters mainly discharge in areas of historical or current seismicity, both at a regional and local scale, as well as near areas of active or recent volcanism and areas of high crustal heat flow. These areas mostly fall under localities near or along the boundaries of major crustal plates, with the tectonic activity due to plate boundary movement and interaction. Subduction and igneous intrusion processes create ideal conditions for the release of CO_2 from rocks at depth, as well as deep fracturing related to these processes allowing interaction with the mantle, a common source of CO_2 in CO_2-rich mineral waters (Barnes et al., 1978, Aires-Barros et al., 1998, Cartwright et al., 2001).

1.1 Objectives

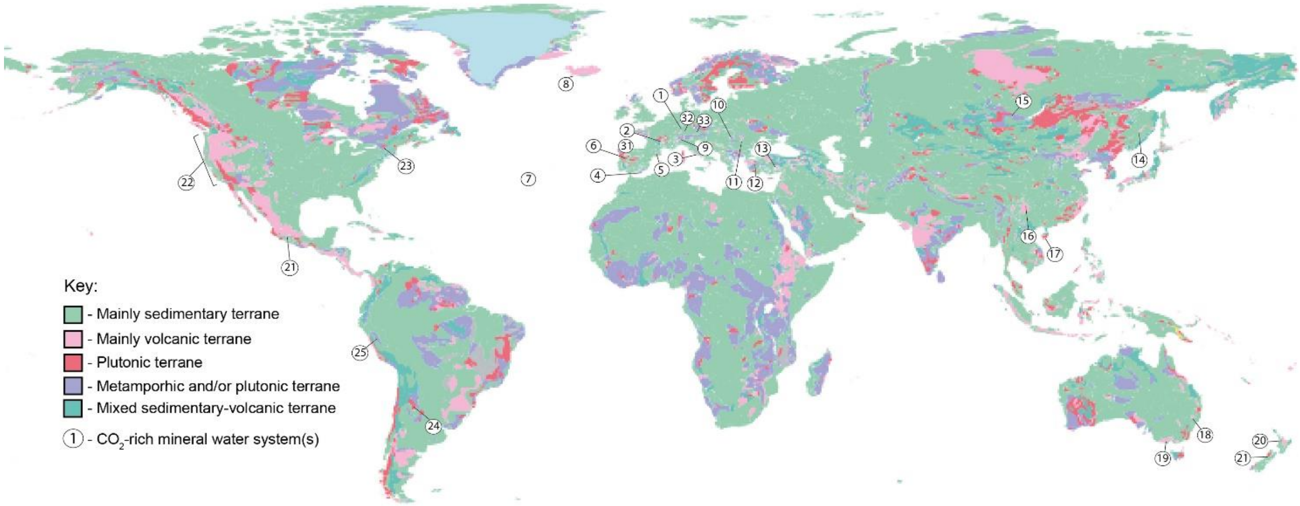
This study aims to increase knowledge on the several multidisciplinary approaches, including geomorphological, geologic, tectonic, geochemical, and isotopic (e.g., $\delta^{2}H$, $\delta^{18}O$, $\delta^{13}C$, $\delta^{87}Sr$, ^{3}H, ^{14}C and $^{3}He/^{4}He$) techniques, that have been advanced successfully to assess the conceptual models of the local/regional CO_2-rich mineral water systems and the mechanisms of their upward movement from the reservoir towards the surface (e.g. Marques et al., 2010, 2012; Carreira et al., 2008, 2010). A comparative study will be made with the Portuguese CO_2-rich mineral water systems of Vidago and Pedras Salgadas (N-Portugal).

This study will be mainly focused on understanding the factors (e.g., geomorphological, geologic, tectonic), controlling the occurrence of this particular type of thermomineral water. Furthermore, a special emphasis will be put on the peculiar geochemical - water-rock interaction processes, and the characterization of the isotopic signatures presented by the CO_2-rich mineral waters will be discussed.

A special focus will be put on the assessment of the hydrogeological conceptual models of the CO_2-rich thermal mineral waters. A conceptual model of a given hydrogeological system should be clear, qualitative, and include a physical description of the operation of the system (e.g. Moore, 2003). The conceptual model consists of maps and cross-sections showing: i) the tectonics and subsurface geology, ii) preferential distribution of recharge, iii) main flow path directions, and iv) discharge areas.

1.2 Distribution and occurrences of CO_2-rich mineral waters worldwide

For the purpose of this dissertation, an updated summary of CO_2 occurrences worldwide has been designed, with a special focus on low-temperature CO_2-rich thermal and mineral water systems, which can be summarised in the map below (Figure 1)



1. Rhenish Massif and Eifel, Germany
2. Massif Central, France
3. Central Italy
4. Betic Cordilleras, Spain
5. Catalonia, Spain
6. Chaves, Vilarelho da Raia and Pedras Salgadas-Vidago, Portugal
7. São Miguel, Azores, Portugal
8. Reykjanes Peninsula, Iceland
9. Swiss Alps, Switzerland
10. Eastern Carpathians, Romania
11. Western Carpathians, Poland
12. North-west Anatolia, Turkey
13. Central Anatolia, Turkey
14. Lastochka and Mukhen spas, Russia
15. Tuva, Siberia, Russia
16. Huanglong, Kangding & Xiage, Sichuan, China
17. Korean Peninsula, South Korea
18. Ballimore, New South Wales, Australia
19. Daylesford, Victoria, Australia
20. Haruaki, New Zealand
21. Southern Alps, New Zealand
22. Western Coast of USA
23. Saratoga Springs, USA
24. Argentinian Alitplano, Argentina
25. Cordillera Blanca, Peru
26. Jungepeao, Mexico
27. Tsamda and Gondasampa, Nepal
28. Jiangxi, China
29. East African Rift Zone, Ethiopia
30. Rwenzori region, Uganda
31. Ourense, Galicia
32. Czech Republic
33. Slovakia

Figure 1 – Geological world map, adapted from Kirkham et al. (1995), showing the locations of the CO_2-rich mineral water systems used in this study.

2. Results

To organize the summary of the diverse case studies in a form which allows the inference of features present in different types of CO_2-rich mineral and thermal water systems, three categories of systems were prepared based on the geological environment in which they occur:

Type 1 – Geologically dominated by granites, with volcanic and sedimentary facies present in some systems. Geomorphologically, massifs are common with related graben structures as well as granitic intrusions.

Type 2 – Sedimentary rocks (limestones, carbonates and sandstones) common, with very thick (> 1 km) sedimentary rocks forming aquifers from which springs emerge.

Type 3 – Volcanic rocks, with systems occurring in areas of active, recent or ancient volcanism. Sedimentary rocks can be present in these systems, such as in the form of metasedimentary complexes.

Synoptic tables were created to categorise each system into these three types, showing the characterising features of each system (geology, tectonic structure, CO_2 origin, flow paths (CO_2 and water), recharge, discharge, geochemistry, and temperature).

The type specific features can be summarised in Table 1.

Table 1 - Summary of the characteristic features of system Types 1, 2 and 3

	Geology	**Tectonic structure**	**CO_2 origin**	**Flow paths (CO_2)**	**Flow paths (water)**	**Recharge**	**Discharge**	**Geochemistry**
Type 1	Granite	Graben/ massif	Mantle/ metamorphic devolatilization	Deep faults	Fractures and faults	Meteoric	Springs	Na-HCO_3
Type 2	Sedimentary rocks	Thick sedimentary aquifers. Basin/graben.	Mantle/ metamorphic devolatilization/ carbonate dissolution	Deep faults/ fractured carbonate lithologies	Fractures and faults	Meteoric	Springs	Ca-HCO_3
Type 3	Volcanic and metasedimentary complexes	Volcanic (active or ancient)	Mantle/metamo rphic devolatilization	Deep faults	Fractures and faults	Meteoric	Springs	Na-Cl-HCO_3 Cl-SO_4-HCO_3

2.1. A comprehensive conceptual model of CO_2-rich mineral water systems

Figure 2, is a comprehensive summary of the key features of each category of low-enthalpy CO_2-rich mineral water system, set in a hypothetical location which contains the three types of systems in one geomorphological setting.

The hypothetical setting is a graben, with the eastern horst composed of granitic rocks. The base of the graben is sedimentary containing limestones and sandstones. The western horst is composed of three lithologies; volcanic complexes, metasedimentary complexes and carbonates.

1. Ca-HCO_3 type water. The water enters through porous/fissured carbonate lithology, and then reaches the graben bounding fault where CO_2-derived from metamorphic devolatilization enters the water. Interaction between the CO_2-enriched water and the carbonate rocks causes the dissolution of Ca into the water. The depth this water circulates is comparatively low, causing a cold-water spring at the surface, where tufa deposition is active around the spring's area due to the high quantity of Ca^{2+} in the water.

2. Na-Cl-Ca-HCO_3 type water. This water infiltrates through fractured metasedimentary complexes, before meeting evaporitic layers, where it gains sodium and chloride. Water-rock interaction between the CO_2-rich water and metasedimentary complexes causes the dissolute of Na^+, Cl^- and Ca^{2+} into the water. A deep fault supplies metamorphic CO_2 to the water. This water does not

reach sufficient depth to be considered hot. Finally, the water passes through a fault through the sedimentary cover to emerge at the surface as a spring.

3. Cl-SO_4-HCO_3 type water. This water infiltrates through volcanic complexes, with volcanism related fractures providing infiltration pathways. The water is deeply circulated, and is heating to a higher temperature than Springs 1 and 2, with mantle upwelling providing a heat source. The CO_2 is supplied to the water via a deep fault, with a metamorphic devolatilization origin. The water-rock interactions between the CO_2-rich water and the volcanic complexes explain the presence of chloride and sulphide, the dominant ions for this type of spring.

4. Na-Ca-HCO_3. The recharging water passes through fractured granite, deeply circulating before reaching a deep fault which is carrying CO_2 from the mantle. The water obtains this CO_2, and water-rock interactions occur within the granitic rocks, causing the dissolution of Na^+ and HCO_3^- into the water. The water then passes through a secondary fault which crosses a limestone layer, where the dissolution of carbonates provides a secondary CO_2 source, as well as adding Ca to the geochemistry of the water. At the surface, the water discharges at a high temperature, with travertine deposition at the surface due to the Ca^{2+} content in the water.

5/6. Na-HCO_3 type. Similarly, to Spring 4, water of Springs 5 & 6 initially infiltrates though fractured granitic rocks. Spring 5 reaches a greater circulation depth than Spring 6, giving it a higher discharge temperature. CO_2 is provided by a deep fault carrying mantle-derived gas. The water-rock interaction occurs between the CO_2-rich water and the granite. Due to the increased water-rock interaction at lower temperatures in CO_2-rich mineral waters, particularly in Na-rich lithologies such as granite, Spring 5 is shown to have a lower TDS than Spring 6.

2.2. Vilarelho da Raia-Chaves/Vidago-Pedras Salgadas region

The Vilarelho da Raia-Chaves/Vidago-Pedras Salgadas is located within the tectonic unit of Middle Galicia/Trás-os-Montes sub-zone of the Central-Iberian Zone of the Hesperic Massif and is dominated by Hercynian granites and Palaeozoic metasediments. A NNE-SSW striking hydrothermally active fault system controls the study area, reaching depths of around 30 km (Baptista et al., 1993) and centres upon the Chaves depression, a major graben post-filled with the greatest thickness of Miocene-Pleistocene sediments in the area.

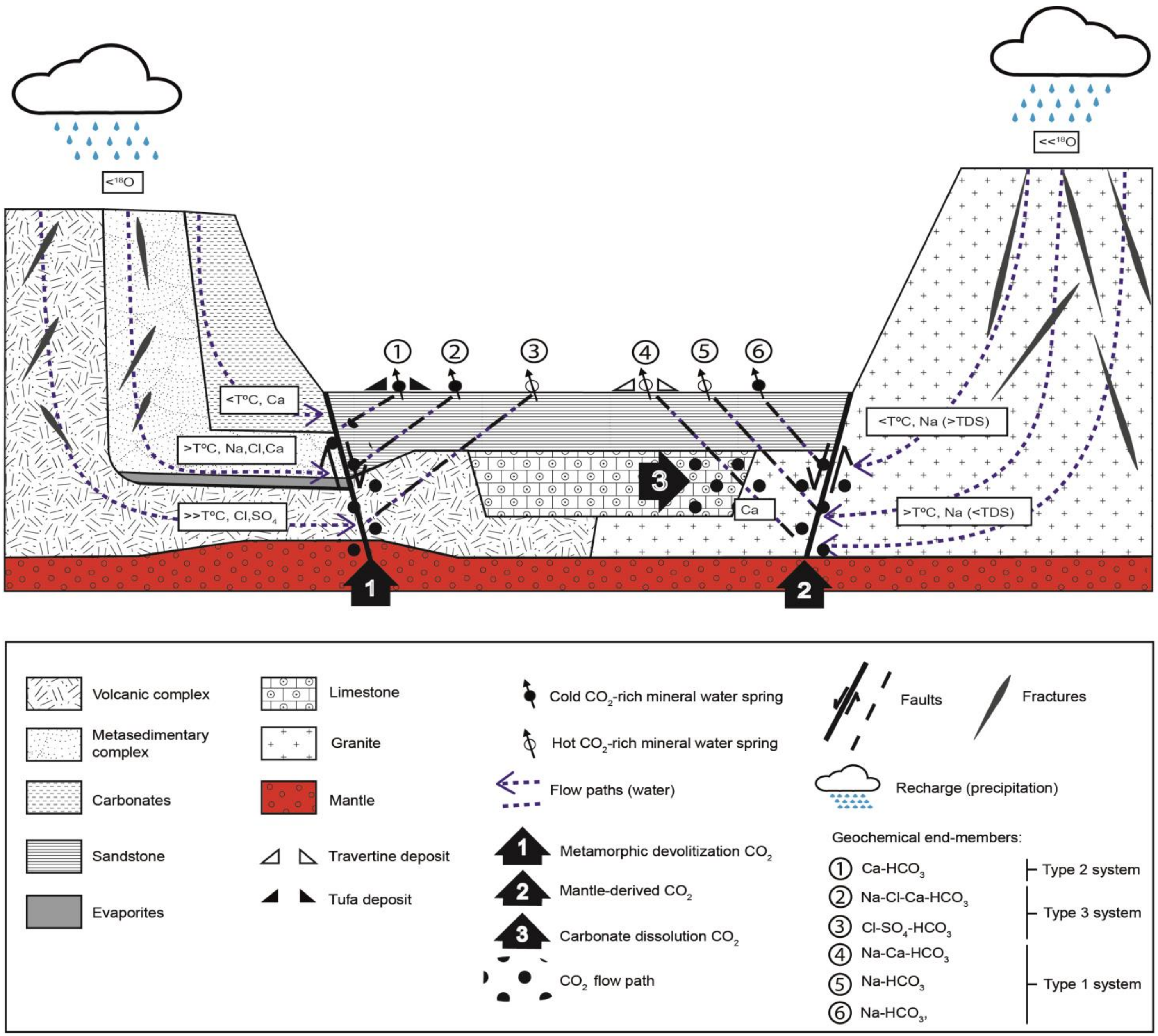


Figure 2 – Comprehensive conceptual model of CO_2-rich mineral water systems.

The Chaves springs are located within a 3 km by 7 km downthrown block, with thick (> 250 m) graben filing Cenozoic sediments. Pedras Salgadas and Vidago are within structures smaller than those seen in Chaves. The size of the graben in Chaves is thought to have given rise to higher discharge temperatures measured at the Chaves thermal spring compared to Pedras Salgadas/Vidago (cold waters), with higher relief and deeper fracturing, along with the thickness of the overlying sediments favouring deeper groundwater circulation. The waters that are issued by these springs have had their geochemical composition extensively analysed, to help determine the origin of the waters. Both hot (76 °C, Chaves) and cold (17°C, Vidago and Pedras Salgadas) mineral waters belong to the HCO_3/Na/CO_2-rich type classification (Marques et al., 2012). Two types of waters are proposed:

Chaves (Type I)

Characterised by temperatures between 48 °C (at the springs) and 76 °C (at the boreholes), pH values close to 7, TDS (Total Dissolved Solids) ranging from around 1,600–1,850 mg/L and CO_2 is about 350–500 mg/L. The gas emitted from these springs is composed of almost pure CO_2. The composition is otherwise Na^+ and HCO_3^- dominated (~ 650 mg/L of Na^+ and 1,500-1,700 mg/L of HCO_3^-). Vilarelho da Raia mineral waters show similar chemical composition, however have lower temperatures (~17 °C) (Marques et al., 2006).

Pedras Salgadas/Vidago (Type II)

These mineral waters have low temperatures (~17 °C), with pH values of ~6. Vidago shows the highest TDS (4,300 mg/L), and both Pedras Salgadas and Vidago have higher Ca^{2+}, Na^+, Mg^{2+}, and free CO_2 (up to 2,500 mg/L) content in comparison to Chaves (Marques et al., 2006).

2.3 What are the peculiar signatures?

The peculiar signatures present in Vilarelho da Raia-Chaves/Vidago-Pedras Salgadas systems can be seen in the relationship between the total dissolved solids present in the CO_2-rich thermal and mineral waters and the temperature of the Type I and Type II waters previously mentioned. Type I waters, found in Vilarelho da Raia (~17 °C) and Chaves (48-76 °C), are of Na-HCO_3 type, and have a TDS of 1,600-1,850 mg/L, with a pH close to 7. Type II waters, which issue in Vidago and Pedras Salgadas at temperatures of around 17 °C, are also of Na-HCO_3 type, and display a TDs of up to 4,300 mg/L, with a pH of ~ 6 (Marques et al., 2012). The Type II waters show a much higher mineralization compared to the Type I waters (Type II – 4,300 mg/L, Type I – 1,600 mg/L), however the temperature of the type II water is much lower (17 °C compared to 76 °C). In mineral waters without CO_2, the relationship between TDS and temperature displays a strong positive correlation; however in these systems the inverse is shown.

This phenomenon can be explained due to the carbon dioxide content. CO_2 content is the most important factor that influences the physical and chemical characteristics of CO_2-rich thermal and mineral waters (Criaud & Fouillac 1986; Greber 1994). The introduction of CO_2 into groundwater will promote chemical changes which can influence the geochemical composition of the water due to the water-rock interactions that the presence of CO_2 creates. Aqueous carbon dioxide reacts with the water to form carbonic acid. Carbonic acid can lose protons to form bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). When this happens, the proton (H^+) is liberated into the water, which causes a decrease in pH, and the salinity of the water increases. This reaction will tend to cause the chemical weathering of silicate minerals present in granite such as feldspars. Calcium (Ca^{2+}) can be present in CO_2-rich mineral waters due to the plagioclase hydrolysis in granitic regions, or groundwater which has come into contact with calcium-rich lithologies such as carbonates (Hem, 1970).

A compilation of hydromineral systems shown in this which display these peculiar signatures (a higher water-rock interaction in cold CO_2-rich waters in comparison to hot or warmer CO_2-rich systems) was made. There is a variety of geological settings, although granite is present and/or the dominant lithology in most of the systems in this summary. The discharge waters are mostly Na-rich type, showing that this increased water-rock interaction at lower temperatures in CO_2-rich mineral waters is mainly due to the aforementioned geochemical reactions. The increased solubility of CO_2 in water at low temperatures seems to be the main responsible for the increased weathering of silicate minerals (Na^+ ions), through feldspar hydrolysis.

2.4 Conceptual model of the Vilarelho da Raia-Chaves/Vidago-Pedras Salgadas region

The main features of the hydrogeological systems of Vilarelho da Raia-Chaves/Vidago-Pedras Salgadas region can be summarized in Figure 3 the conceptual model of region.

The key features which this model aims to display the features of each of the four systems in one model; the difference in circulation depth, temperature, and variations in water-rock interaction seen in the four systems. All four springs of Na-HCO_3-type, and the specific geochemical compositions (TDS, pH, temperature) of the springs are shown in Figure 3.

Meteoric water infiltrates through the fractured granites in the Padrela Mountain with varying altitudes, displayed in the figure, for the Pedras Salgadas, Vidago and Chaves springs, and the Larouco Mountain provides the recharge area for Vilarelho da Raia Spring.

The circulation depth is shown for each spring, with the deeper circulating Chaves waters obtaining a higher discharge temperature due to the proposed presence of a geothermal reservoir at least 3.5 km depth (e.g., Marques et al., 2010). According to Marques et al. (2010), Chaves CO_2-rich thermal waters (76 ºC) are those with a higher discharge temperature due to the proposed presence of a low-temperature (≈ 120 ºC) geothermal reservoir at least 3.5 km depth. The higher TDS due to increase water-rock interaction at low temperatures is displayed in the model, with the fractured nature of the granite reservoirs, and the size of the area denominating the level of water-rock interaction, rather than the size of the reservoir. This high water-rock interaction, and higher TDS in the discharging waters, is shown in the larger fractured areas in Pedras Salgadas and Vidago in comparison to Vilarelho da Raia and Chaves. The mantle origin of the CO_2, as well as the deep faults which allow the water to obtain the gas are displayed.

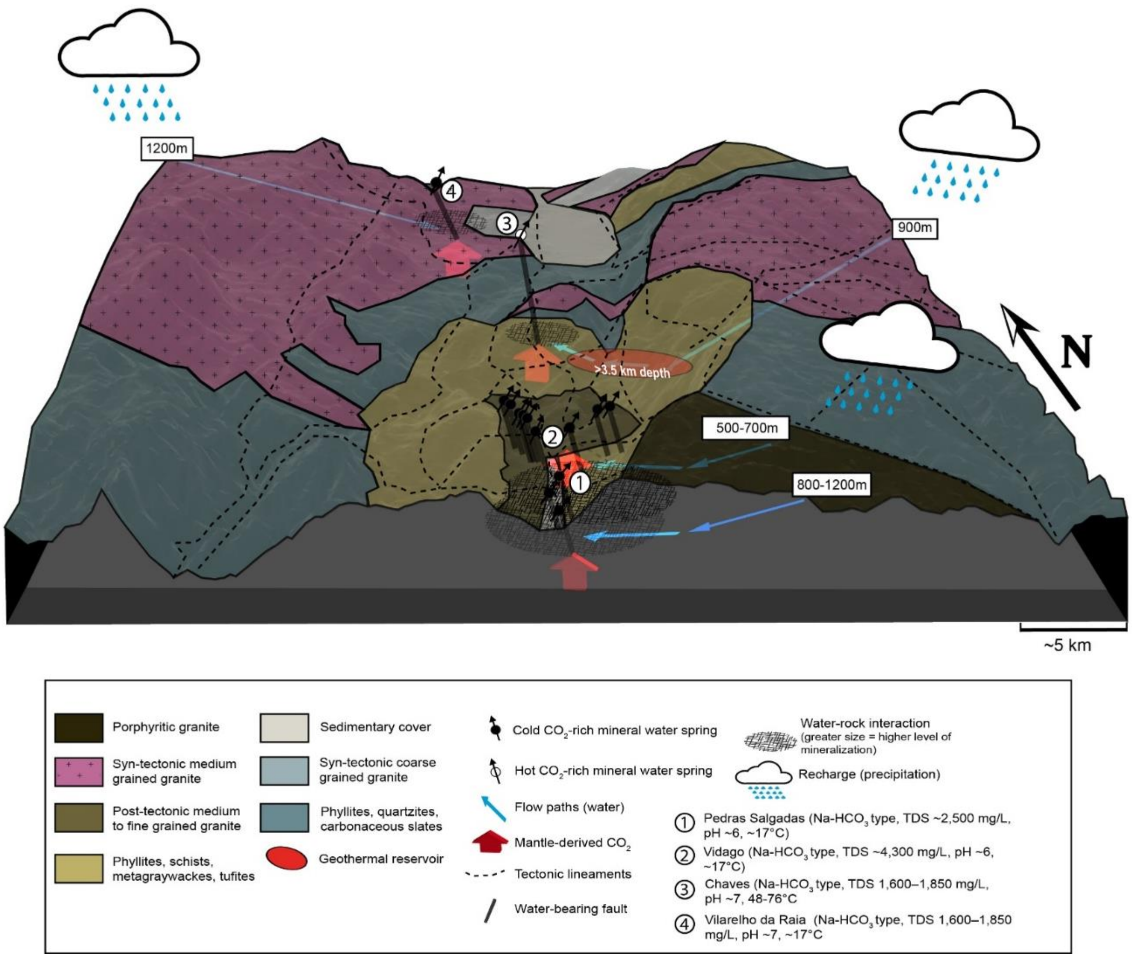


Figure 3 - Conceptual model of the Vilarelho da Raia-Chaves/Vidago-Pedras Salgadas region. Data taken from Marques et al. (2012).

3. Final Remarks

This dissertation involved the compilation of a variety of CO_2-rich thermal and mineral systems worldwide, with the aim of making a comprehensive conceptual model of CO_2-rich thermal and mineral water systems. The formation of this summary of systems allowed the categorizations of these systems into three distinct categories, based on the hydrogeological features characteristic of each type of system: Type 1 (dominated by granitic rocks), Type 2 (dominated by sedimentary rocks) and Type 3 (dominated by volcanic and metasedimentary rocks). This categorization, with the accompanying tables can allow for simplified classification of a CO_2-rich thermal and mineral water system. The tables can be used to display the key features that a study of a hydrogeological system should aim to define to classify the system. These features are geology, tectonic structure, origin of CO_2 flow paths of CO_2 and water, recharge, discharge, and geochemistry (dominant anions and cations, TDS, pH). This taxonomy is the first of its kind, and could be a useful tool when initiating a study of a system, as the most defining features of a system can be entered into the table, giving the researcher a clear idea of what features they need to research to fully comprehend the workings of a given system. For further improvement of this classification system, the distinction between each category can be refined with the addition of further hydrogeological systems, to characterize each system in more detail, or further divide each category into sub-categories. Through the formation of this classification system, the comprehensive conceptual model of CO_2-rich thermal and mineral water systems was formed. This model displays the six most common, or characteristic pathways from recharge to discharge within the three categories (Types 1 to 3), and clearly displays the characteristics defined above and how they attain them. The importance of this dissertation will be shown by those that utilize it in the future, and the wide ranging study of CO_2-rich water systems in this thesis has allowed for the potential concretization of the reasons why the Vidago-Pedras Salgadas CO_2-rich mineral waters display a higher TDS compared to those of Vilarelho da Raia and Chaves.

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