“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.

Resumo

Numerosos estudos hidrogeológicos e hidrogeoquímicos incidiram sobre as águas minerais ricas em CO_2 na região de Vilarelho da Raia-Pedras Salgadas do Norte de Portugal, que apresentam diferenças marcantes nas assinaturas fisicas, geoquímicas e isotópicas das águas minerais frias (17°C) e quentes (até 76°C) ricas em CO_2 nessa região.

As assinaturas peculiares nessa região são observadas através do total de sólidos dissolvidos (TDS mg/L) mais elevados exibidos nas nascentes frias de Vidago e Pedras Salgadas em comparação com nascentes quentes de Chaves. Tipicamente, nas nascentes de água mineral sem CO_2, os valores de TDS e temperatura mostram uma correlação positiva devido ao aumento da interação água-rocha a altas temperaturas.

Estudos de aproximadamente trinta sistemas de água mineral rica em CO_2 foram coligidos para encontrar similaridades nas ocorrências deste fenómeno. Os sistemas com nascentes quentes e frias, e com valores de TDS mais elevados nas nascentes mais frias, mostraram que o fator primordial para essa diferença pode ser devido ao aumento da interação água-rocha a baixas temperaturas com a presença de CO_2 na água, particularmente em rochas graníticas (como na região de Vilarelho da Raia-Pedras Salgadas).

Este estudo integrou o desenvolvimento de um modelo conceitual hidrogeológico abrangente de sistemas de água mineral ricos em CO_2; Tipo 1, dominado por granitos, Tipo 2, dominado por rochas sedimentares, e Tipo 3, dominado por rochas metasedimentares e metamórficas; nesse modelo foram delineados com base na geologia e nas características geoquímicas que a água obtém desde a recarga até à zona de descarga.

Palavras-chave: águas minerais ricas em CO_2, geoquímica, isótopos ambientais, interação água-rocha, modelos hidrogeológicos conceptuais.

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1. Introduction

Water is one of, if not the most important resource for humans, possessing enormous value in terms of human health, economy, environmental and social factors. Water is key for the development and continuation of life on Earth, and with the ever-increasing demand for water with population increase, the management and preservation of water resources becomes even more important.

Most water on Earth is found in the oceans (97.2%), with the rest mostly found as ice in glaciers and on land (2.15%). The remainder is composed of atmospheric water, groundwater, lakes, humid zones and rivers. 2.5% of all water on earth corresponds to fresh water and within this percentage, only 30.8% corresponds to groundwater (Fetter, 2001).

The continued exploitation of these resources in a sustainable manner, aiming to prevent the contamination of soil and aquifers is vital, with groundwater supplying water for more than half of the world's population

Water is in a constant state of flux, from the hydrosphere to the atmosphere and passing through underground reservoirs. This process is known as the hydrological cycle, starting from evaporation of water through solar heating, followed by precipitation which either stays on the surface and is evaporated or enters the soil and moves into aquifers (Fitts, 2002).

The cycle of subterranean waters can be divided into three stages; recharge, circulation of water underground, and discharge. The recharge is the entrance of the water into the hydrogeological system, principally due to precipitation, but can also be due to rivers of lakes that feed the aquifer, or by artificial injection. The composition of the water underground (without human intervention) depends on the composition of the precipitated water, composition of soil, geology of the aquifer, and the physical, chemical and biological interactions between the water and the media that it encounters (Monroe & Wicander, 2009).

The movement of the water underground and the initial infiltration is mostly through the porosity and permeability of the rocks and faults/fractures present in the rocks. Porosity is a function percentage of pores present in the total volume of a rock, with the pores due to the inherent nature of the rock or through faults and fractures in the rock. Permeability is a function of the pore size and the interconnectivity between the pores (Fitts, 2002).

Mineral and thermal waters are types of groundwaters, issuing at the surface in the form of springs and through abstraction by wells.

These waters are defined by unique physical and chemical characteristics, including temperature, the level of mineralisation, geochemical composition, and dissolved gas. These unique characteristics found in these waters can be attributed to geological and tectonic features and structures within the hydrogeological system, such as different lithologies and faults and fractures present in the rock.

Mineral water can be defined as water containing higher concentration of one or more mineral salts or gas, and thermal water is water with temperature above the average temperature of superficial rock, generally agreed to be greater than 20°C (Barnes et al., 1978).

Carbon dioxide (CO_2) rich mineral waters have been of interest to people historically the Roman times and possibly beyond, 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 (Fetter, 2001, Moore, 2003). .

The global prevalence of these waters is widespread, with CO_2-rich spring waters issuing in a variety of geological and tectonic settings, and the geochemical characteristics can vary between hydrogeological systems, and within specific systems (Barnes et al., 1978, Schofield & Jankowski, 2004).

These incredibly intricate systems are a vital resource, and therefore detailed knowledge on the inner workings and complexities of these systems is paramount to the continued sustainable exploitation of CO_2-rich mineral water systems.

Mineral and thermal waters can be used for a range of applications, including human consumption of mineral water, use of the waters for spa treatments and balneotherapy, and geothermal power systems. In the Vilarelho da Raia-Pedras Salgadas region, the Chaves, Vidago and Pedras Salgadas CO_2-rich thermal and mineral waters are used for spa treatments (Pedras Salgadas Spa & Nature Park) and bottled sparkling water (Água das Pedras) amongst others.

1.1. CO_2–rich mineral waters; an overview

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 was initially suggested by White (1957) to have been of metamorphic origin, specifically the metamorphism of carbonate-bearing rocks at depth, liberating the CO_2 from carbonate and silicate rich rocks at high temperatures. More recent understandings present four main sources of CO_2 (e.g. Barnes et al, 1978, Aires-Barros et al., 1998);

1. 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;
2. Interaction with carbonates - oxidation of carbonaceous sediments due to water-rock interaction at depth causing dissolution of CO_2 into the groundwater;

3. 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;

4. 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).

1.2. 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. 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.

1.3. Structure of the thesis

1. Introduction – Present the concepts, objectives and the structure of the thesis.
2. Methodology – Outline the processes by which the thesis will be undertaken, along with a summary of low temperature CO_2-rich mineral water systems worldwide used to form the conceptual models.
3. Results; creation of the conceptual models - assessing case studies of CO_2-rich mineral and thermal water systems worldwide to categorise the different types of systems and form a 'global' conceptual model of CO_2-rich mineral water systems. Using the summary of systems, outline the potential reasons for peculiar signatures at Vidago-Pedras Salgadas, and following this form a conceptual model for the Vilarelho da Raia-Chaves/Vidago-Pedras Salgadas systems.
4. Discussion – Discuss the potential implications and limitations of the conceptual model CO_2-rich mineral water systems.
5. Final remarks.

2. Methodology

The thesis will be a comprehensive literature review based on previous studies, and attempt to assimilate typical characteristics of CO_2-rich mineral water systems to create a conceptual model of these systems. The complexity of CO_2 rich mineral waters systems has been well defined in previous studies (Greber, 1994, Cartwright et al., 2001), as the factors which control and determine the nature of CO_2-rich mineral water springs and systems are numerous and involve interrelated information from a number of scientific disciplines.

To this effect, the review of studies that this thesis will undertake must be widespread, and attempt to attain specific information about each relevant CO_2-rich mineral water system to normalise the characteristic features of these systems into an all-encompassing conceptual model. The key features that will be established in a selected CO_2-rich mineral water system, and then displayed in the conceptual model, are:

i) Tectonic structure of the region - displays the pathways by which the water will flow (both surface and groundwater), the structures affecting geomorphology such as anticlines/synclines, relief, faults etc.), as well as reservoir/aquifer structure (structural traps);
ii) Subsurface geology - the lithological makeup of the area will have an impact on the thermal and mineral water composition (water-rock interaction processes), as well as burial depth, nature and location of the reservoir/aquifer (permeable/impermeable rock);
iii) Recharge – the distribution of the recharge, the direction and preferential pathways through which the water evolves from surface water to groundwater;
iv) Discharge – the direction and way through which the groundwater rises to the surface;
v) Flow paths – the mechanisms and direction through which surface, shallow and groundwaters will travel;
vi) Isotopic and geochemical characteristics of the water – the thermal and mineral water facies, the origin of dissolved CO_2, temperature of the water, and origin and apparent age of the water.

Furthermore, the research must also have a focus on systems which are similar (with respect to the features outlined above) to the titular case study of Vidago-Pedras Salgadas, as the comparison of the characteristics of this system with other similar systems will help determine the reasons for the ‘peculiar’ signatures found in the of Vidago-Pedras Salgadas system (to be defined in Section 2.5).

2.1. Two cases of the evolution of the assessment of CO_2-rich mineral water systems

A wide range of approaches are used to analyse CO_2-rich mineral water systems, involving different scientific disciplines. The evolution of the assessment of these systems in mainly due to the greater integration of studies involving these disciplines to better the understanding of these systems.

The following case studies illustrate the evolution of the assessment of CO_2-rich mineral water systems over time, with examples of how the incorporation of studies from several disciplines, as well as the extension and elaboration of previous studies allow for a clearer picture of the processes within a system.

Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas region, Portugal

The Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas region of Northern Portugal has been intensively studied of over the past 30 years, with each new study involving a different discipline or method to further the overall understanding of the system itself.

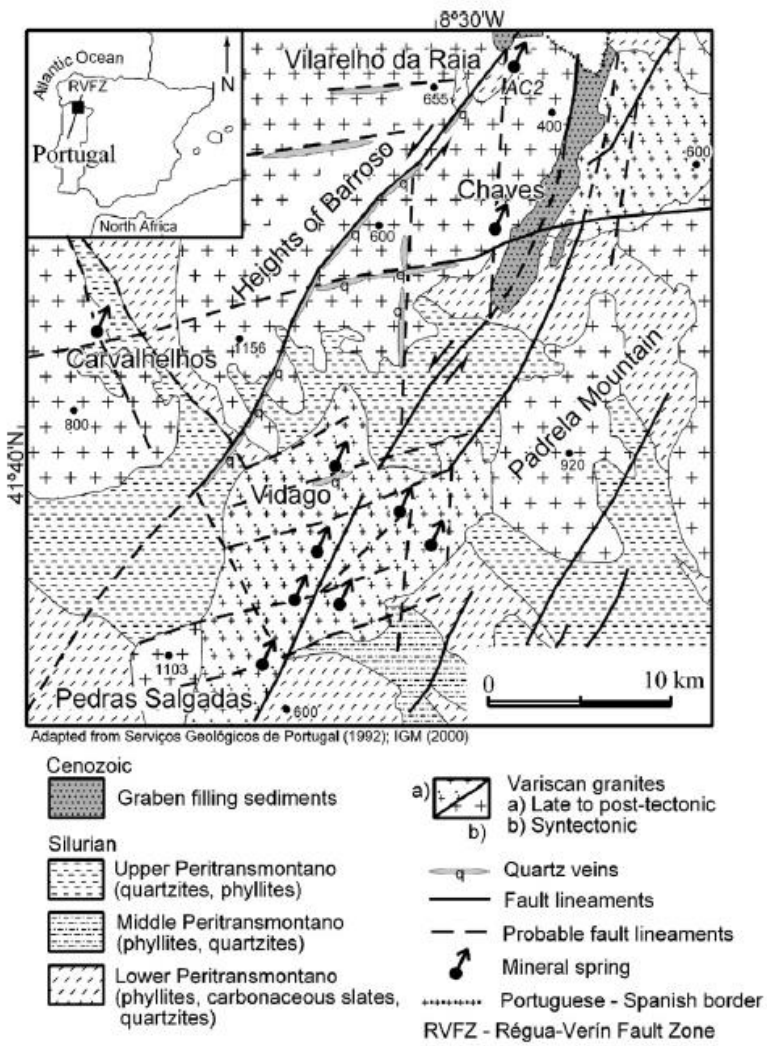


Figure 1 - Schematic geological map of the Vilarelho da Raia-Chaves/Vidago-Pedras Salgadas area (Marques et al., 2010)

Initial geological and tectonic studies of the area were bolstered by stable isotope determinations, with more in-depth geochemical approach of the waters, and more recently further isotopic and geochemical investigations allowing for an in-depth, multidisciplinary picture of the region.

The earliest attempts at understanding the nature of the CO_2-rich mineral waters present in the Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas region were undertaken by Moitinho de Almeida (1982), with a geothermometric study of the waters and determining a potential mantle origin of the CO_2 in the Chaves spring waters. Studies of the geology of the region (Ribeiro and Moreira, 1986; Moreira and Simões, 1988), as well as geological and tectonic studies of the area by Portugal Ferreira et al. (1992) and Baptista et al. (1993) describe the geological setting in which the hydrogeological system lie.

Detailed hydrogeological studies initiated by Moitinho de Almeida (1982), and followed by Aires-Barros et al., (1991, 1994), with compilation by Aires-Barros et al. (1995). These studies, utilising the environmental isotopic composition (oxygen-18, deuterium, and tritium) of the Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas hot and cold waters, aimed to determine the characteristics of the hydrogeological systems with respect to the origin and mean residence time of the waters, preferential recharge areas, and underground flow paths.

Further updates to the hydrogeological model of the Chaves geothermal area using new isotopic and geochemical data (Moitinho de Almeida, 1982; Aires-Barros et al., 1998, Marques et al., 1999) allowed the classification of the thermal and mineral waters to the HCO_3/Na/CO_2-rich type, with division of the waters into two distinct groups (hot spring waters of Chaves and cold spring waters of Vilarelho da Raia). The shallow underground flow paths of Vidago-Pedras-Salgadas and lack of mixing with deep mineralized waters, based on ^3H isotope data, as well as information on the degree of water-rock interaction at depth was also proposed, alongside further data confirming the mantle based origin of the CO_2 in the thermal and mineral water (based on the ^{13}C content).

A key question which arose from these studies was if the hot and cold CO_2-rich mineral waters are surface manifestation of the same hydrogeological system. Through further isotopic, geochemical and geophysical studies by Marques et al. (2001), these hot and cold CO_2-rich mineral waters were determined to be manifestations of similar but not the same hydrogeological systems. The use of Sr and Cl isotopes was then introduced to determine the level of mixing and further solidify the hypothesis of the presence of two separate systems (Marques et al., 2001, Andrade, 2003).

Marques et al. (2006, 2010) continued to update the knowledge of Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas CO_2-rich mineral water systems with research on the level of mineralisation of both hot and cold water, and theorising the reasons behind the higher mineralisation in the colder waters (enhanced water-rock interaction at low temperatures due to increased solubility of CO_2 at low temperatures, further elaborated in Section 3.5).

To summarise the evolution of the assessment of these systems based on the studies undertaken, Figure 2 has been produced to help display how the knowledge of the system has evolved over time. The initial model by Aires-Barros et al. (1995), displays the same recharge source for both the Vilarelho da Raia and Chaves springs, which in the updated model of Marques et al. (2001), is shown to be inaccurate. This updated model shows the two systems having separate recharge areas and pathways. In the most recent model, by Marques et al. (2010), more detailed information about the geology, tectonic structure, circulation depths, and water-rock interaction has been included in the model of the Chaves springs. For example, two separate recharge areas on the Padrela Mountain have been identified for both shallow and deep groundwater circulation, along with the areas of intense rock fracture zones, increasing water-rock interaction.

1995 [1]

2001 [2]

2010 [3]

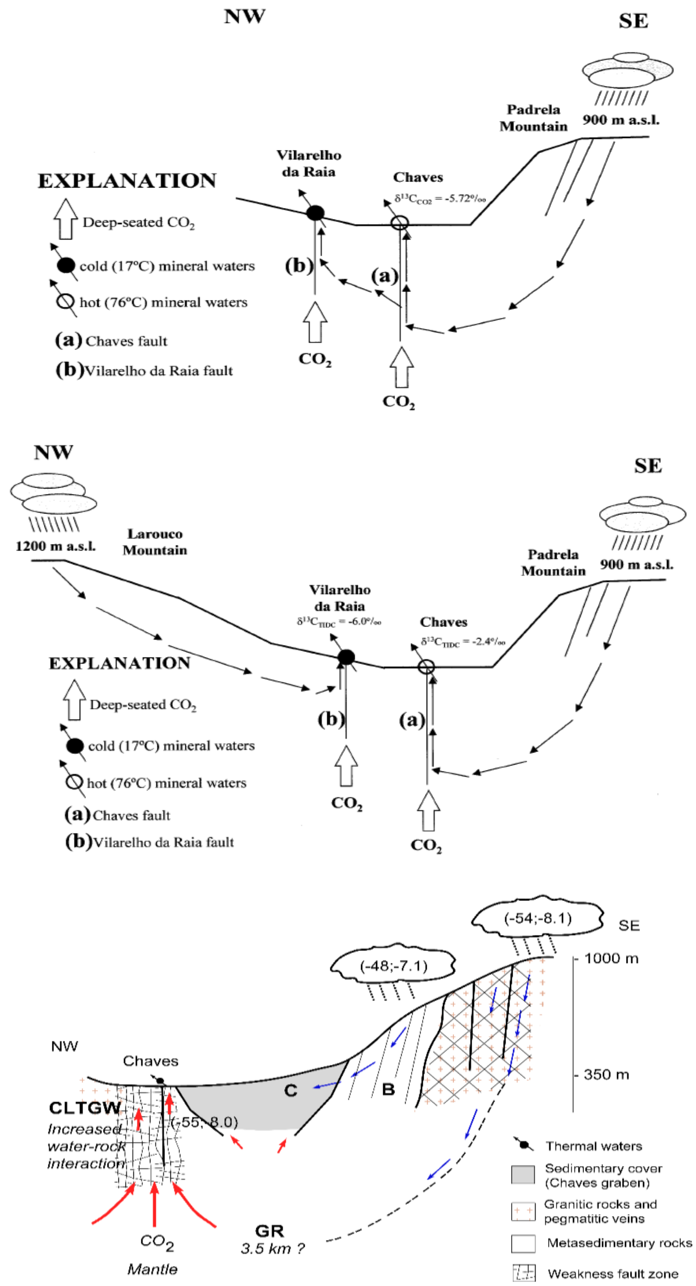


Figure 2 - Evolution of a conceptual model, [1] Conceptual circulation model by Aires-Barros et al. (1995) for the Chaves and Vilarelho da Raia CO_2-rich mineral waters. [2] Conceptual circulation model for the Chaves and Vilarelho da Raia CO_2-rich mineral waters, derived from more recent geochemical and geophysical studies (Marques et al., 2001). [3] Hydrogeological conceptual circulation model of Chaves CO_2-rich thermal waters system, adapted from Marques et al. (2010). ***B*** *stands for granitic and metasedimentary rocks;* ***C*** *stands for cover deposits;* ***CLTGW*** *stands for Chaves low-temperature geothermal waters;* ***GR*** *stands for geothermal reservoir; (δ^2H; $\delta^{18}O$) stands for the isotopic composition of the waters. Adapted from Marques et al. (2010).*

Massif-Central, France

Another CO_2-rich mineral water system which has shown a similar evolution in its assessment is the Mont-Dore region of the Massif-Central in France (Pauwels & Fouillac, 1997). The study of the thermal and mineral waters of this area started in 1974 with geochemical studies of the mineral and thermal springs involving the collection of samples from 52 different springs and shallow boreholes for use in geothermal exploration. The geological and tectonic environment was also studied during this period (Brousse, 1971, 1984).

Following these initial sample collections and geological studies, the isotopic and chemical composition of the fluid samples collected were analysed by Pauwels & Fouillac (1997). This study was used in conjunction with the geological studies to classify the types of thermal waters present in the Mont-Dore region of the Massif-Central, as well as to determine the temperatures the fluids reach at depth and the types of water-rock interaction present in the system.

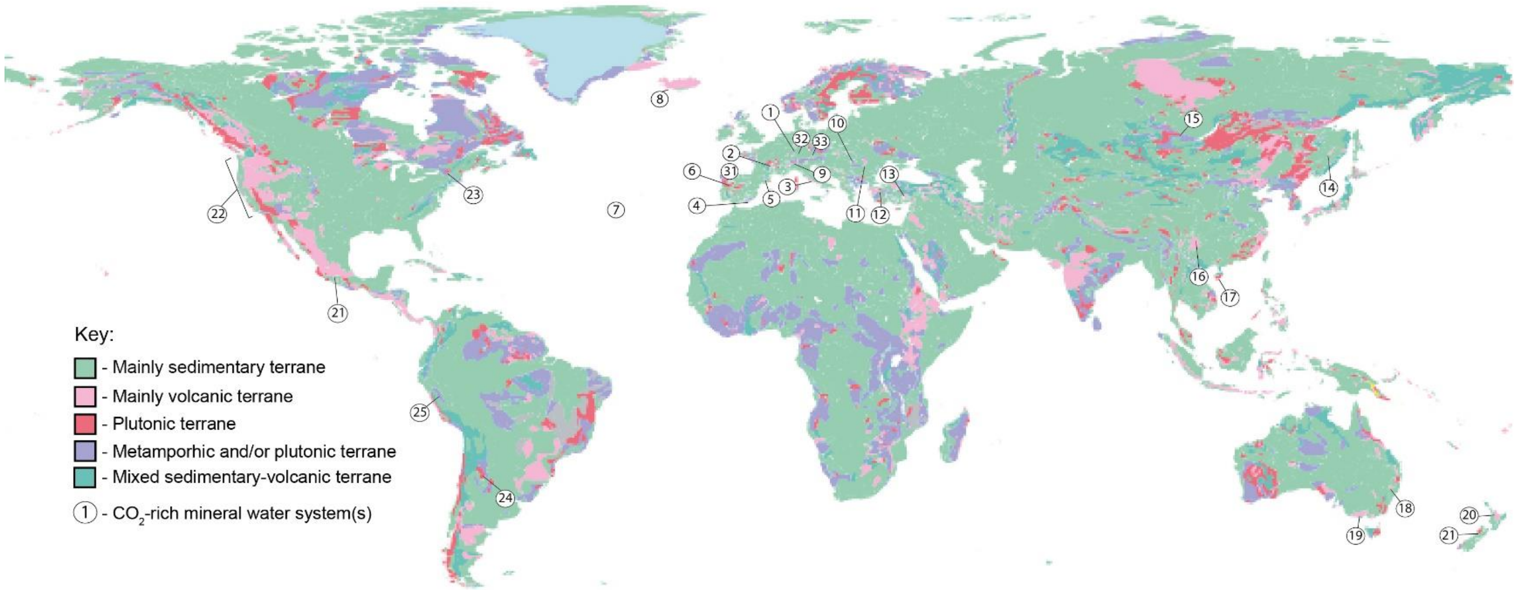
2.2. Distribution and occurrences of CO_2-rich mineral waters worldwide

Barnes et al. (1978) summarise the known occurrences of CO_2 leakage worldwide. They show CO_2 discharges (both in spring waters and solely gas emanations) issue mostly along a > 30,000 km belt, circling from southern South America, up through central and north America and round to Japan and New Zealand (otherwise known as the Pacific ring of fire).

This summary shows that CO_2 discharges along this Pacific ring mostly originate from mantle derived sources and metamorphism of carbonate-bearing rocks. In Europe and central Asia, a trend can be observed.

The summary proposes that areas of high heat flow in western, central and eastern Europe correspond to areas of CO_2 discharge, and the sites evaluated show a CO_2 originating again from the metamorphism of marine carbonates, as well as an igneous, mantle origin (Cartwright et al., 2001). The extent of CO_2 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 (Bissig et al., 2006).

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 Figure 3, as well as the following Section (Section 2.3), where the characterisation of these systems in relation to the geology, tectonics, geochemistry of the waters, recharge and discharge has been described based on the information available for each system. In Figure 3, the distribution of the systems generally lies within areas of metamorphic or plutonic terrains, with these areas being regions of active or historical tectonic activity, and therefore facilitating the emergence of CO_2-rich thermal and mineral water systems.



(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 3 – Geological world map, adapted from Kirkham et al. (1995), showing the locations of the CO_2-rich mineral water systems summarized in this thesis.

2.3. Summary of CO_2-rich mineral water systems worldwide

Europe

Germany

Western Germany is home to geological terrains of recent volcanic and tectonic activity, with numerous occurrences of naturally emerging CO_2-rich springs in the Rhenish Massif and Eifel. The CO_2-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_2 discharges concentrated in volcanic fields (Greisshaber et al., 1992; May, 2005). In the Eifel area, the occurrences of CO_2-rich waters are linked with Quaternary volcanic activities, with a magmatic origin of the gas, ascending through deep faults (Weinlich, 2005). The HCO_3-Mg-Ca-CO_2-rich waters from the East and West Eifel display low discharge temperatures (<15°C) with a TDS of 3,000-4,500 mg/L (Greisshaber et al., 1992).

France

The Massif Central, an extensive area of recent volcanism and tectonic activity, is host to many CO_2-rich mineral springs. These CO_2-rich waters have gas of mantle origin and emerge from Quaternary volcanic rocks or Palaeozoic granite at temperatures between 4 and 62°C (Batard et al., 1981, Pauwels & Fouillac, 1996, Weinlich, 2005). Figure 4 displays a location map of this area.

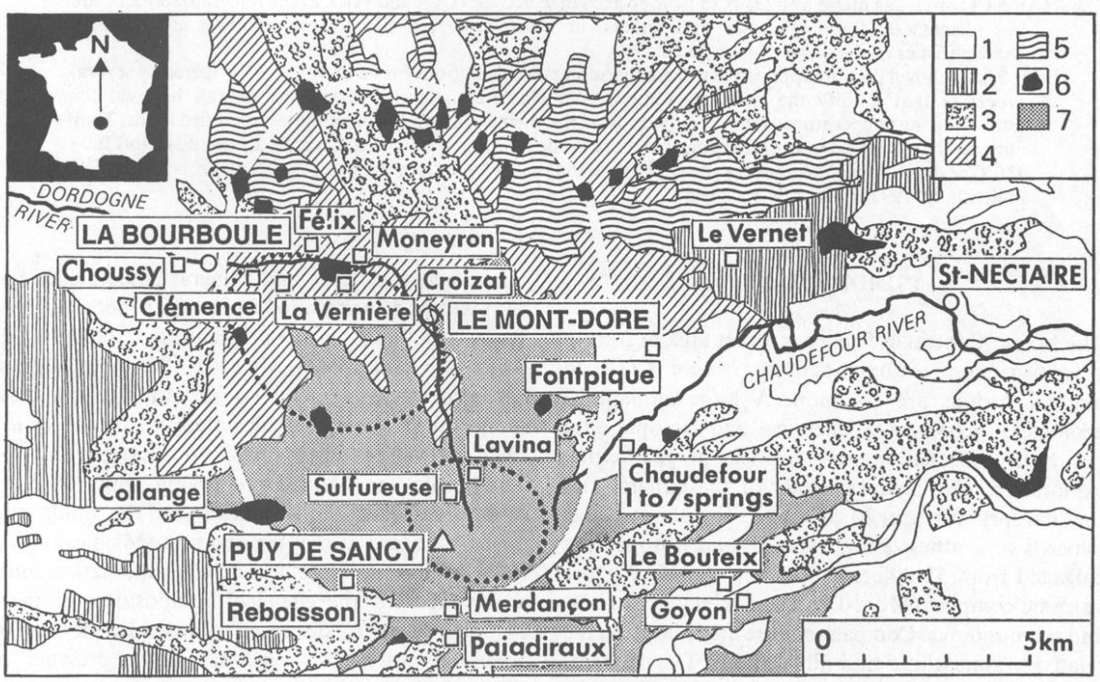


Figure 4 - Map of the Mont-Dore: 1) granite and gneiss basement; 2) ante-caldera basalts (6-3 Ma); 3) undifferentiated Mont-Dore basalt; 4) trachy-andesite, rhyolite, and pumice; 5) hawaiite and tephrite; 6) comendite, quartz trachyte, phonolite; 7) Sancy volcanism: trachy-andesite and pumice. Dotted lines indicate limits of the Haute-Dordogne caldera and outlines of the Sancy 'Structure'. White line indicates the outer limit for differentiated lavas of the central area. (Pauwels & Fouillac, 1996)

The springs and boreholes of Saint-Necaire, which discharge in granite, show a range of temperatures from hot (58.1-62 °C - in boreholes) to colder (15-40 °C - springs) and are of Na-HCO_3-Cl type. These waters are of local meteoric origin.

In Vichy-St Yorre (Massif Central), waters rise from the granitic basement of a graben, through overlying sedimentary rocks, to emerge as springs showing a range of temperatures (<16-64 °C). These waters have a pH ranging from 6.26-7.11, with a Na-HCO_3 geochemistry. Notably, the colder (<30 °C) waters of this area show a similar concentration of dissolved solids to the warmer (41.5-63.7 °C) waters (Sanjuan et al., 1988). This phenomenon is further elaborated in Section 3.5.

Italy

The topographically low-lying hydrogeological setting of central Italy is composed of several Quaternary volcanic and geothermal systems, with many thermal and non-thermal springs. The CO_2-rich springs have a mixture of mantle and biogenic CO_2, and emerge in volcanic and carbonate terrains. Figure 5 shows the conceptual model for this region (Minissale, 2004).

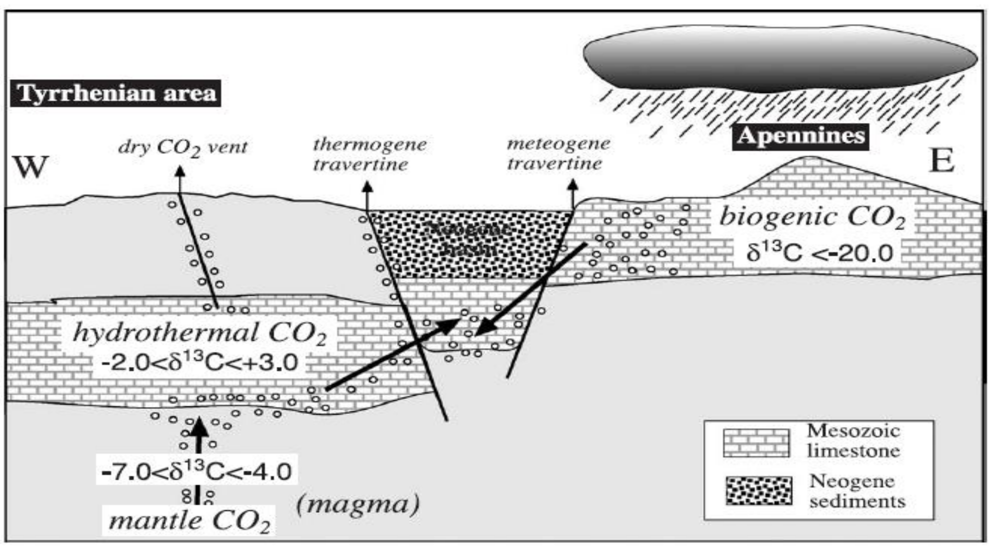


Figure 5 - Fluid circulation model of western and southern Italy (Minissale, 2004)

In the Suio region of central Italy, the thermal and mineral springs emerge in a boundary between the Roccamonfina volcano, a volcanic complex composed of leucite and alkali-trachyte lavas, and a thick series of limestones and dolomites. The waters have a geochemistry of Ca-HCO_3 type, which reflects the waters circulation in a carbonate complex, with a TDS of 2,568-4,213 mg/L and pH of 6.1 (Saroli et al., 2015). The CO_2-rich thermal and mineral waters of Mondragone, which emerge on the southern side of the same volcanic complex also circulate within carbonate formations. These waters have a different geochemistry, Na-Ca-Cl-HCO_3, with a temperature of 52 °C, TDS of 4,616 mg/L and pH of 6.6. The presence of Na-Cl is ascribed to either the mixing of deep magmatic brines, or trapped fossil waters. The origin of the CO_2 in the Suio and Mondragone waters are from deep magmatic sources (Duchi et al., 1994).

Spain

The Betic Cordilleras, in southeastern Spain, are formed of a basement of Paleozoic and Triassic volcanics, with more recent overlying sedimentary Neogene rocks. Paleozoic and Triassic over thrust sheets, delineated by large faults, dominate the tectonic setting of the area. The CO_2-rich waters are of temperatures between 20 and 41°C, with high bicarbonate concentrations (1,100-3,424 mg/L). The emergence of the water bound to the fault systems. The source of the CO_2 is thought to be of either mantle or carbonate rocks in the metamorphic substratum. Figure 6 displays a model of the system (Cerón et al., 1998, 2000).

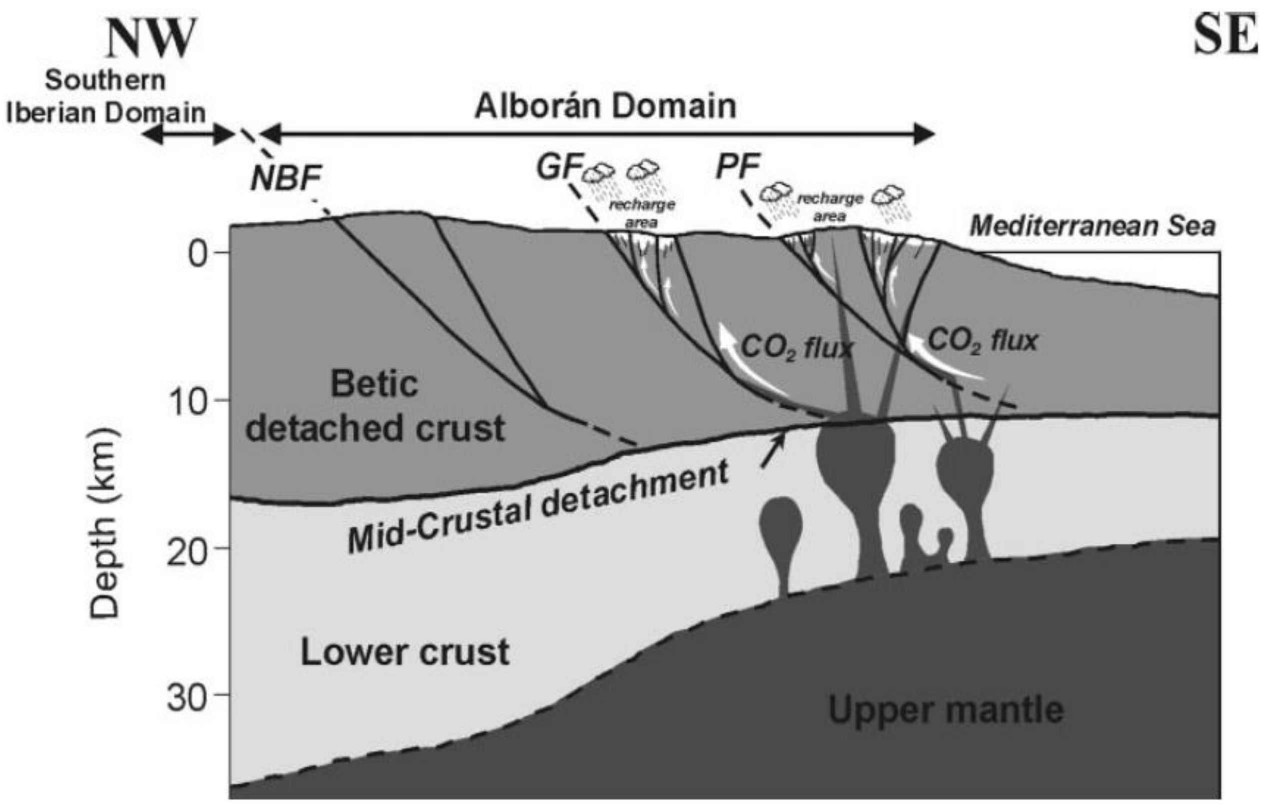


Figure 6 – Cross-sectional model of the Betic Cordilleras (Cerón et al., 2000).

In Catalonia, CO_2-rich waters issue within the Cordillera Costero Catalana, formed of low-grade metamorphic rocks and sedimentary rocks of Paleozoic age, with intrusions of granitic bodies. Faults and fractures related to Miocene-Quaternary volcanism form the flow path for the manifestations of the CO_2-rich waters. The waters are cold (13.5-17.4°C), with one occurrence of hot CO_2-rich water (50°C), and are of two types Ca-HCO_3 water, Na-HCO_3, with a deep-seated origin of the CO_2 (Redondo & Yelamos, 2000).

Galicia, northwest Spain, is home to CO_2-rich thermal and mineral waters. These thermal 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 in this area emerge in granites which form part of the Hesperian massif. These springs are located on the same NNE-SSW fault lineament that the Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas springs emerge in. The Ourense springs have a temperature ranging from 46 to 69°C, with a geochemistry of Na-Ca-HCO_3 type water, due to the water-rock interaction between the granites and the CO_2-rich water. The mineralisation is around 1,500 mg/L in the CO_2-rich waters, with the origin of CO_2 likely from a deep mantle source, similar to the Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas springs (Michard & Beaucaird, 1993).

Portugal

The Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas region, in Northern Portugal is home to several hydrogeological systems displaying both hot (48-76°C, Chaves) and cold (17°C, Vilarelho da Raia and Pedras Salgadas-Vidago) waters of Na-HCO_3 waters, emerging through graben faults ascribed to Hercynian granitic systems (Marques et al., 2012). A detailed case study of these systems can be found in Section 2.5.

On the island of São Miguel, Azores, CO_2-rich mineral water springs present at the Furnas volcano are directly related to the areas volcanic activity. These hot carbonated waters, originating from a shallow steam-heated aquifer, are heated by this volcanism to temperatures of up to 160°C, and issue above a carbon dioxide anomaly on the caldera floor, with a fracture system creating flow paths for the CO_2 and water. Geochemically, the waters present a low pH (~4.7), and are silica and sodium-rich waters (Cruz et al. 1999).

Iceland

The Reykjanes Peninsula, located in southwest Iceland exhibits a high temperature basaltic geothermal system with high temperature (>220°C) CO_2-rich geothermal fluids at a depth of up to 1200 m. The mantle based origin of the CO_2 is due to mid-ocean ridge spreading, and the presence of water at this depth is due to an influx of seawater (Freedman et al., 2010).

Switzerland

These springs are in the Scuol-Tarasp region of the Lower Engadine, Swiss Alps. The geological setting of this cold (2-9°C) CO_2-rich spring water is mostly metamorphic basement rocks with a thick sedimentary cover of platform carbonates, with CO_2 of crustal origin.

Three geochemical water types are present: Ca-HCO_3 water, Na-Cl-HCO_3 water and Na-Mg-HCO_3-SO_4 water. In the Na-Cl-HCO_3 water, the high concentration of dissolved CO_2 has enhanced the water-rock interaction with a Na and B-rich silicate rock. All three types of groundwater are of shallow circulation and recharge directly from local precipitation, as well as displaying enhanced water-rock interaction with increased concentration of dissolved CO_2 (Wexsteen et al., 1988).

Figure 7 shows the location of the different types of springs in the region as well as a cross section showing the geomorphology and geology of the system (Bissig et al., 2006).

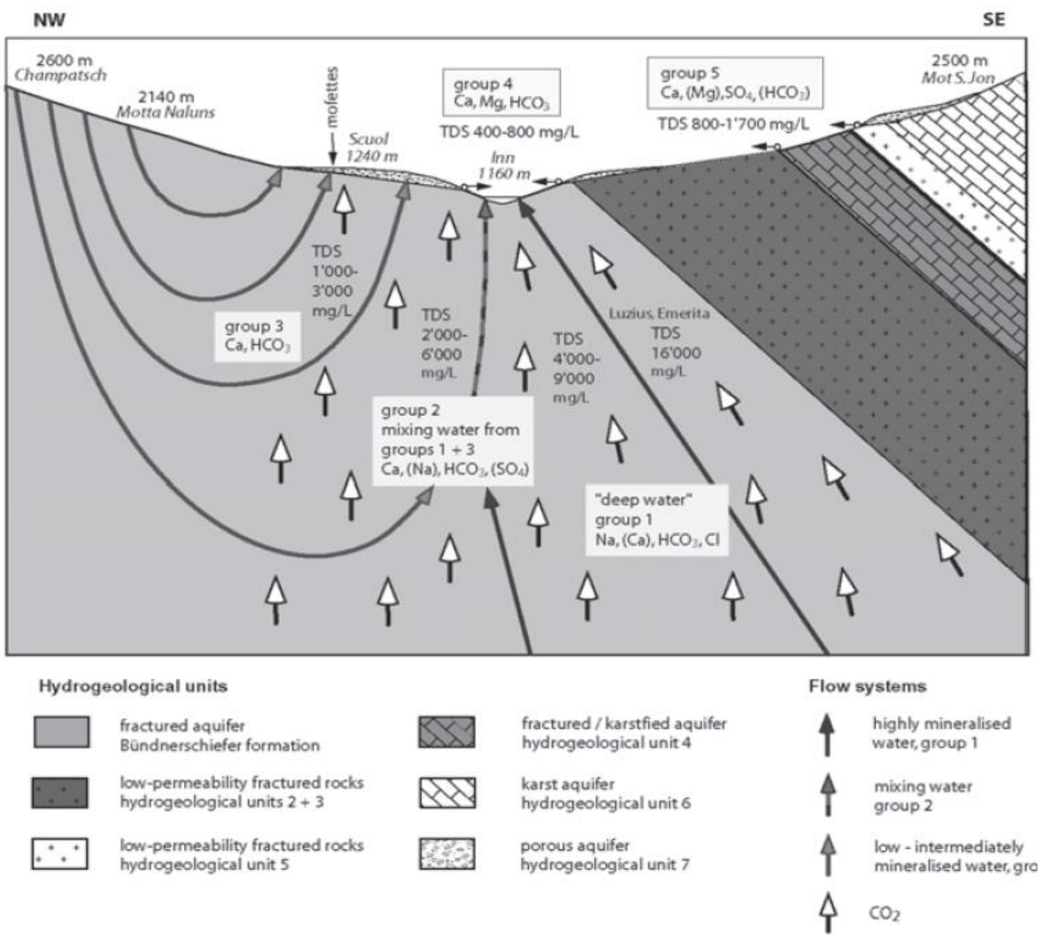


Figure 7 - Conceptual model of the CO_2 and groundwater fluxes in the region of Scuol-Tarasp (Bissig et al., 2006).

Eastern Europe

The Carpathian Flysch of the West Carpathians, Poland is within a longitudinal depression related to plate collision tectonics, with deep faulting forming possible flow paths for the waters. CO_2-rich spring waters have temperatures of about 10°C and are mostly of Ca-Mg-HCO_3 type, with the CO_2 derived from the deep crust (Lesniak, 1998). The springs in the Eastern Carpathians are related to regional Neogene magmatic activity and are located on the eastern and western slopes of the Neogene to Quaternary volcanic chain. The mineral waters are of Ca-Mg-HCO_3 and Na-K-HCO_3 type. The flow paths for the fluids in this area are caused by the nature of the rocks (Boglárka-Mercedesz, 2013).

Czech Republic

Karlovy Vary, located in the Sokolov basin has CO_2-rich thermal and mineral springs of Na-HCO_3-SO_4-Cl, with a TDS of 6,400 mg/L and temperatures of up to 73°C. The recharge of these water originates in granite blocks on the sides of the valley, with water deeply circulating (2,000-2,500 m) along faults (Krejbichová, 1999). The CO_2 origin from a deep source, likely the mantle (Weinlich et al., 1998). Important works have also been performed in the region by Krásný (2001).

Slovakia

The CO_2-rich mineral water Fatra in Slovakia discharges in a basin filled with Neogene sediments, surrounded by granites and gneisses in the Western Carpathians. This water is of Na-HCO_3 type, and enters the system through faulted Hercynian granodiorites, gaining CO_2 at depth through faults, with a slow, deep circulation, before rising through the sedimentary infill of the basin to emerge as springs. Water from a borehole 909 m deep found Na-HCO_3 water with a TDS of 5,980-10,650 mg/L present at increasing depths (Bodiš et al., 2017).

Central & South-East Asia

Turkey

Hot and cold mineral springs of Na-(Ca)-(Mg)-HCO_3-Cl types emerge in Kuzuluk/Adapari, North-western Turkey, an extensional tectonic setting within the seismically active North Anatolian Fault Zone. The cold waters show a distinctly higher level of TDS in comparison to the hot waters, and CO_2 originates from decomposition of marine carbonates and mantle outgassing. This case study is described in greater detail in Section 3.7 (Greber, 1994).

The Nevsehir region shows three types of cold and hot (18-43°C) CO_2-rich spring waters; Na-Ca-HCO_3, Ca-HCO_3 and Na-Cl-HCO_3. The region is geologically composed of metamorphic marbles which create a confined aquifer for these springs. The springs are meteoric in origin and show a high level of electrical conductivity (up to 6,300 µS/cm) in the cold CO_2-rich spring waters, and a hot CO_2-rich spring water displaying an electrical conductivity of 1,610 µS/cm (Afsin, 2002).

In Kemerhisar, low-temperature (14-16°C) CO_2-rich Na-Cl waters emerge, with a deep circulation system related to the basin structure of the area. The Na-Cl waters emerge in mainly volcanic terrain, with evaporites providing the source of chloride. The CO_2 spring waters are recharged meteorically, with CO_2 of mantle origin, and display an increased electrical conductivity in waters with lower water temperatures of the CO_2-rich waters (Afsin, 2003).

The CO_2-rich waters of Kayseri, Central Anatolia are located within the Erciyes basin in the Central Anatolian Crystalline Complex. Granites and syenites are presumed to be the heat source for the thermal waters. The source of the CO_2 in the waters is possibly a combination of organic and mantle origin. There are five different types of waters, with temperatures ranging from 12 to 46.5°C, with different physical and chemical compositions. Notably, some of the low temperature springs have significantly (>10 x) higher electrical conductivity than the other waters (Afsin et al., 2006). This system is described further in Section 3.7.

Russia

In the east of Russia, and Siberia, cold and low-temperature CO_2-rich mineral springs issue within a variety of geologic and tectonic settings. In the Latochka and Mukhen spas in Eastern Russia, Na-HCO_3 and Ca-Mg-HCO_3 waters emerge from sedimentary dominated shallow aquifers along fractures and deep-seated fault systems (Shand et al., 2005, Kharitonova et al., 2007, 2015). The CO_2 in these systems is mantle derived, and supplied along deep-seated faults. The Latochka spa shows elevated mineralization within the CO_2-rich waters of the area (Shand et al., 2005, Kharitonova et al., 2007). In the Tuva region of Siberia, cold (17°C) CO_2-rich groundwaters are located within the Choigan complex (metamorphic and granitic rocks), discharging through graben-related faults. CO_2-rich waters in this complex show higher water-rock interaction in comparison to the ‘normal’ groundwater (Kopylov et al., 2014). Figure 8 shows the location map and cross section of the springs.

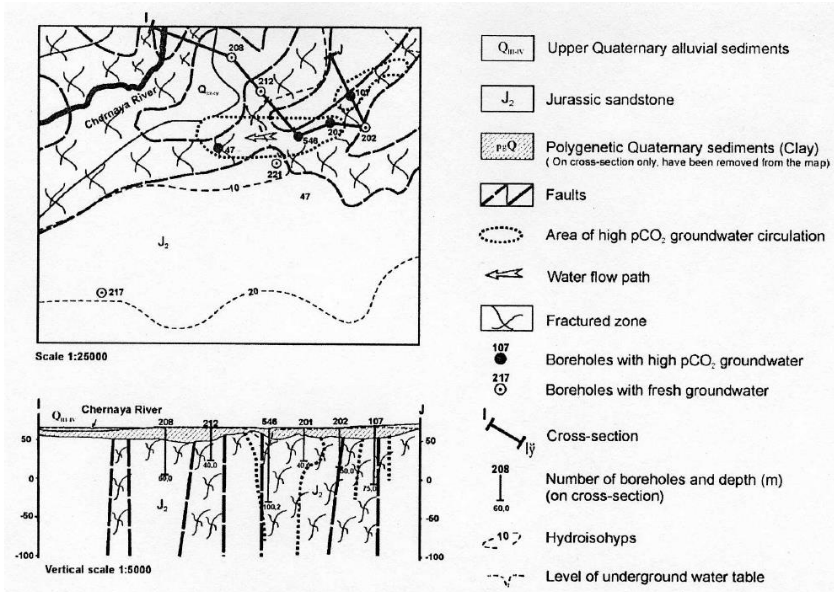


Figure 8 - Hydrogeological map with location of sampling sites and schematic cross-section (Kharitonova et al., 2007).

China

The cold (< 10°C) CO_2-rich, $Ca\text{-}HCO_3$ type spring water of the Huanglong Ravine, Sichuan, is a mix of two waters: fault-driven CO_2-rich spring water, and glacial melt water. The faults give the majority supply of CO_2 to the spring water, which is mostly of mantle origin, with some CO_2 from the dissolution of carbonate rocks. The area displays extensive tufa deposits as the CO_2-rich nature of the water gives rise to a much greater dissolution of carbonates and silicates than is normally seen in karst springs (Yoshimura et al., 2004).

In the Kangding geothermal system there are two categories of spring: lower temperature (29 – 42°C), low pH (6.4), $Ca\text{-}HCO_3$ type water, and higher temperature (60-73°C), high pH (7.2), $Na\text{-}HCO_3$/ $Na\text{-}Cl\text{-}HCO_3$, signatures. The hydrogeochemical features of the first group are attributed to the influence of Paleozoic limestone, while those of the second group (high pH and higher temperature) are related to the granitic body present, with faulting allowing the transport of water and CO_2.

In the Xiage geothermal system, the hot (47–58°C) CO_2-rich waters are $Na\text{-}Ca\text{-}HCO_3$ type waters, with a geological setting of andesites and igneous clastics with limestones. The CO_2 of the geothermal CO_2-rich $Na\text{-}Ca\text{-}HCO_3$ waters is a mixture of metamorphic CO_2 and magmatic CO_2, with faults providing the flow paths for the water and CO_2 (Liu et al., 2000).

The Jiangxi Province of south-east China contains springs which issue in granitic and acid volcanic rocks, with three distinct geochemical end-members; $Na\text{-}HCO_3$, $Ca\text{-}HCO_3$, and SO_4-rich carbon dioxide hot and cold springs. There is a correlation displayed in these springs between the TDS and temperature, particularly in the Na-rich springs, which is further discussed in Section 3.7 (Sun et al., 2017).

South Korea

The occurrences of CO_2-rich spring waters in South Korea generally arise in the plutonic rocks of the eastern part of Korea within granitic terrains, with extensive fracture systems. The hydrogeological systems are low-temperature, related to the tectonic inactivity of the region. The CO_2-rich waters are of three types: Na-HCO_3, Ca-Na-HCO_3 and Ca-HCO_3 types, displaying low pH (5.5-6.5), with varying concentrations of Ca, Na, and HCO_3 (up to 3,300 mg/L, TDS). The origin of CO_2 is predominantly from a deep-seated magmatic source (Koh et al., 2002; Jeong et al., 2005; Kim et al., 2007; Choi et al., 2014). Figure 9 shows a conceptual model of the Na-HCO_3 and Ca-HCO_3 water types that issue in the Kangwon district of South Korea. The water-rock interaction at depth between the granite and groundwater is responsible for the Na-rich type while the Ca-rich type is a shallow groundwater that interacts with gneiss. The mixing between the Na-rich water and shallow groundwater as well as reverse ion exchange contributes to the Ca-rich signature (Choi et al., 2014).

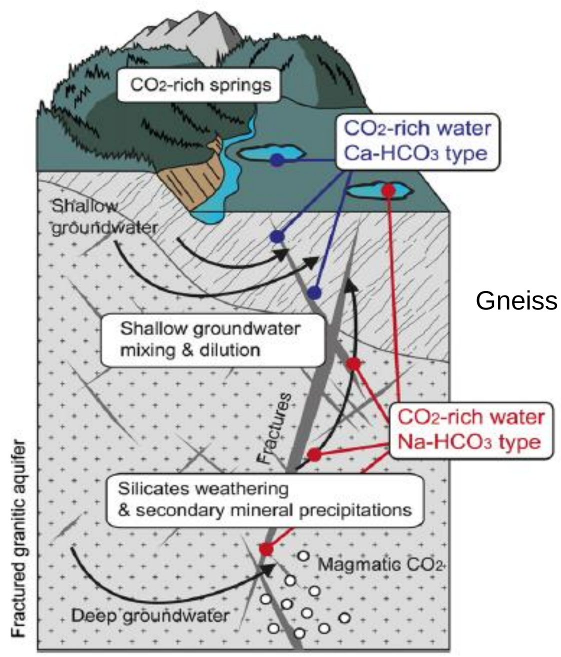


Figure 9 - Conceptual model of the Kangwon CO_2-rich mineral waters (Choi et al., 2014)

Nepal

CO_2-rich mineral springs in the Tibetan Plateau, specifically Tsamda and Gondasampa, emerge in the Tingri Graben, a ~17 km wide structure filled with fractured limestone. Travertine deposits at the surface are associated with the springs. Geochemically, the waters are classified as Na-HCO_3 type, with a pH of 6.34-6.76, TDS of 957-1,850 mg/L and temperatures ranging between 19.2 ºC and 42.6 ºC. Notably, the colder (19.2-24.2 ºC) Gondasampa CO_2-rich waters show almost double the TDS compared to the hotter (42.6 ºC) Tsamda CO_2-rich waters (Newell et al., 2008) (further elaborated in Section 3.7.).

Australasia

Australia

In the Paleozoic fold belt metamorphic rock of the Ballimore region, central New South Wales, CO_2-rich Na-HCO_3 type waters emerge after recently infiltrated groundwater becomes saturated with mantle-derived CO_2 (Schofield & Jankwoski, 2004). The mineral springs of Daylesford, Victoria are CO_2-rich, low pH (5.8-6.9), low temperature (7–16°C), and issue within volcanic rocks, with volcanic activity in this region ceasing thousands of years ago. Deep circulation through heavily fractured basement rocks, combined with post-volcanic intrusions provides the setting for the occurrence of these springs (Cartwright et al., 2001).

New Zealand

CO_2-rich waters issue related to the active volcanism and tectonics of the islands of New Zealand. In the Hauraki Rift Zone geothermal system, where carbonate dissolution provides a source of CO_2, the high-temperature (<200°C) waters are Na-Cl-(SO_4)-HCO_3 type and rise along deep faults. Water-rock interactions (silicate hydrolysis) occur at depth, as well as the influx of seawater (adding Cl^- and SO_4^{2-}) to gain the geochemical characteristics. Figure 10 shows the conceptual model of the Haruaki Rift Zone geothermal system (Reyes, 2009).

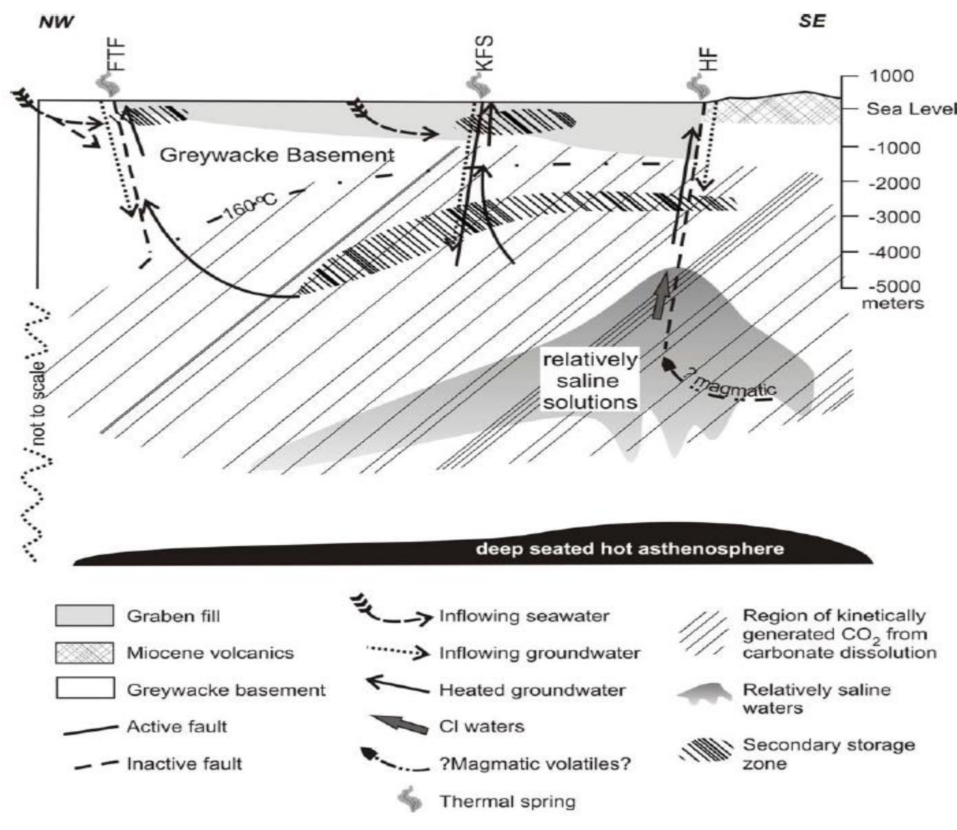


Figure 10 - Haruaki Rift Zone geothermal system (Reyes, 2009)

The Copland spring, a CO_2-rich thermal spring in the Southern Alps occurs in an area of high thermal activity caused by local tectonic activity and faulting. The deep circulation of meteoric water combined with deep faulting and fault-related mantle upwelling provides the heat source and CO_2 source for this travertine-depositing hot spring. The spring waters are of low pH (6.1-6.6), with a temperature of 56°C, and have a high level of mineralization (electrical conductivity of ~2,000 µS/cm). The hydrogeological circulation model of the Copland spring can be seen in Figure 11 (Cox et al., 2015).

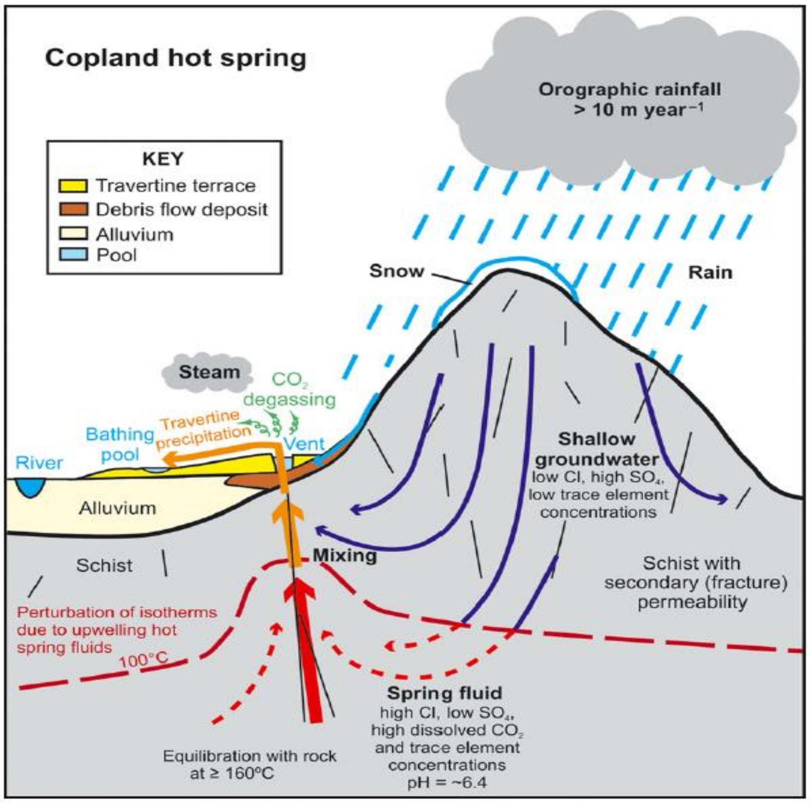


Figure 11 - Copland hot spring geothermal system (Cox et al., 2015)

North America

Mexico

The CO_2-rich springs of Jungapeo, Central Mexico, are part of a low-temperature geothermal system within a volcanic shield, with geological terrains of basaltic andesite lavas. The waters present issue temperatures between 28 and 32°C, with a pH of 5.5-6.5, and have a mostly mantle origin for the CO_2 itself. Meteoric water percolates through the overlying volcanics and is heated at depth by the remnant heat of magma bodies, with deeply penetrating faults providing the pathways for mantle derived gases. Figure 12 shows the hydrogeological circulation model of the system (Siebe et al., 2007).

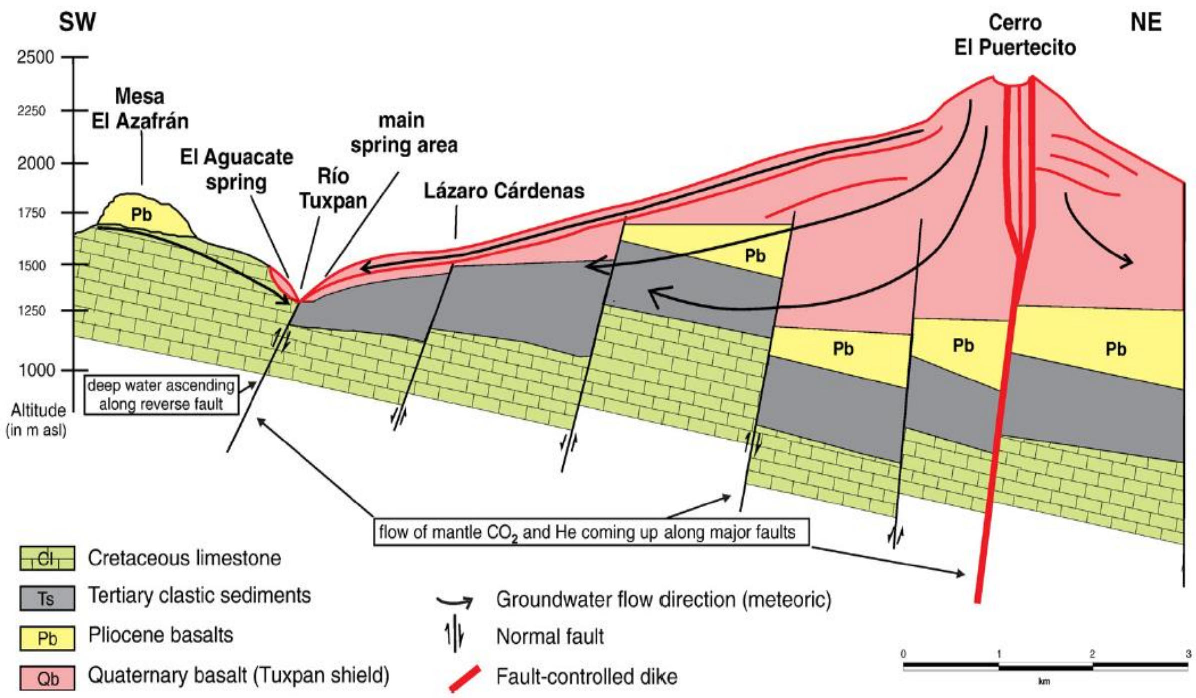


Figure 12 - Cross-section of the Jungapeo geothermal system conceptual model (Siebe et al., 2007).

USA

Throughout western North America, mantle tectonics caused by the deformation of the western margin of the North American plate has produced several hot and cold CO_2-rich mineral springs and related travertine deposits. The evolution of these springs and acquisition of gases is associated with crustal-penetrating deep faults, as well as the high crustal heat flow, an effect of the large-scale plate tectonics of the region. The mantle tectonics, and related mantle degassing has also shown to be a major source for the CO_2-rich springs along western USA (Newell et al., 2005).

On the east coast of the USA, the cold (12°C) CO_2-rich spring waters of Saratoga Springs issue through thick sedimentary deposits (shales) along normal faults (Siegel et al., 2004). The source of CO_2 for these springs is either of mantle origin or igneous melting, and the springs are recharged with a mix of brines as well as local meteoric waters (Hollocher et al., 2002). The schematic geological model of the system is displayed in Figure 13.

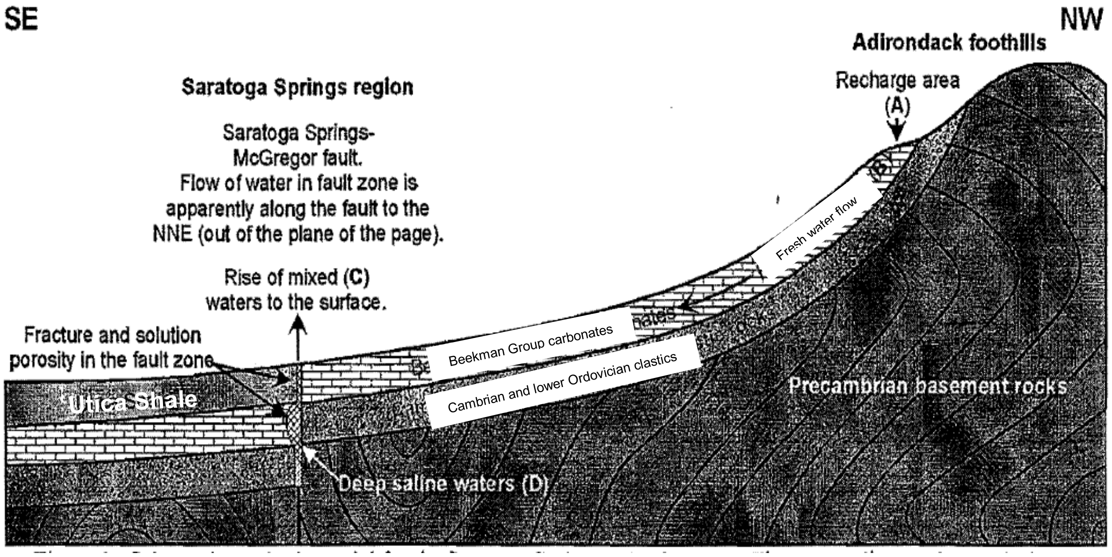


Figure 13 - Schematic geological model of the Saratoga Springs system (Hollocher et al., 2002)

The Grand Canyon hydrologic system (Figure 14) is home to CO_2-rich springs which emerge in Paleozoic sedimentary rocks as well as karstic aquifers, with waters emerging along faults, and depositing travertines at the surface. The waters are between 20 and 35ºC and have CO_2 which is of mixed biogenic and mantle origin, with mantle dominant, and meteoric recharge occurring in the San Francisco Peaks area (Crossey et al., 2006).

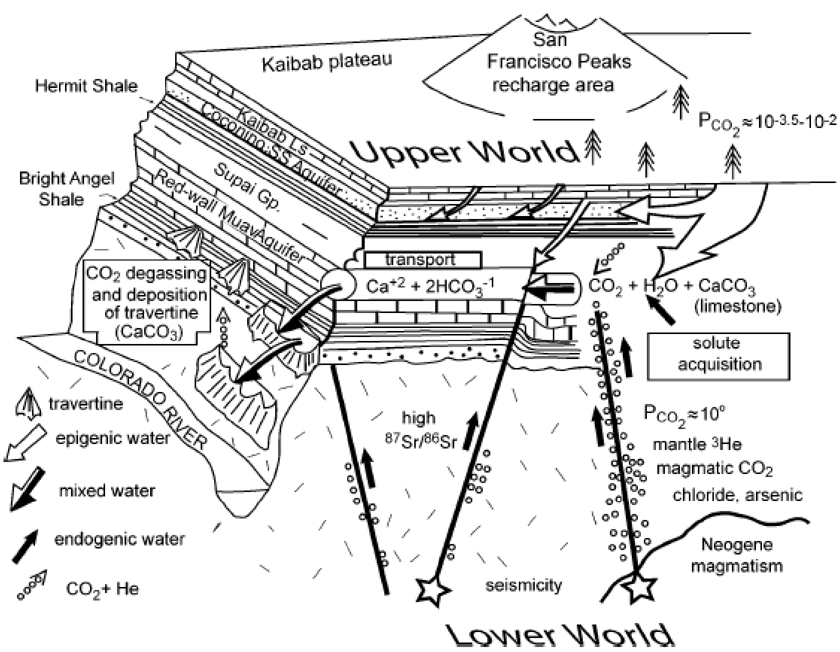


Figure 14 - The Grand Canyon hydrologic system (Crossey et al., 2006)

South America

Argentina

The Northern Argentinian Andes displays CO_2-rich springs which emerge within a hydrothermal travertine deposit. The origin of the CO_2 is from deep-seated magmatic sources, with the deep, fault bound flow of fluids and gas in the system related to active volcanism in the area. The water has a surface temperature of 25°C, a pH of 6.3, and is of the Na-Cl-SO_4 type. The reservoirs are recharged by regional precipitation, with no evidence of mixing of waters at depth. The low-temperature at surface is thought to be because of limited heat transport due to lack of water in the system (low availability of meteoric water in the region (Gibert et al., 2009).

Peru

CO_2-rich hot springs in the Cordillera Blanca occur within a fault zone of the Peruvian Andes, an area of slab subduction (low-angle subduction with absence of active arc magmatism). The waters have temperatures up to 78°C, and the mantle derived origin of the CO_2 in the water is related to the subduction. The waters are of Ca-Cl-HCO_3 composition, and mixing of hot saline waters with cold meteoric waters occurs in the fault zone (Newell et al., 2015).

Africa

Ethiopia

The East African rift area aquifers are formed of fractured, interlayered basalts and ignimbrites, where CO_2-rich springs emerge at the surface. The Na-Cl-SO_4-HCO_3 waters of the Filwuha graben have temperatures ranging from 27.3-78°C, with a TDS of 2,820 mg/L and pH of 6.6-8.11. The origin of the CO_2 is from the mantle and/or metamorphic devolatilization, with faulting related to the graben structure providing the flow paths for water and gas (Kebede et al., 2008).

Uganda

The Rwenzori region is home to hot (25-94°C) CO_2-rich springs which emerge in an area of crustal uplift and volcanism. The lithologies present include banded gneiss, granite and schist at the volcanic centre, with the topographic highs composed of amphibolites, hornblende, gabbros and metasediments. The springs are structurally controlled by faults, with the presence of active travertine/tufa deposition. The waters are mostly Cl-SO_4-HCO_3 type with a total mineralization ranging from 3,640-17,900 mg/L (Kato & Kraml, 2005).

2.4. What is a hydrogeological conceptual model?

To create a hydrogeological conceptual model of CO_2-rich mineral water systems, one must first define what the model must contain.

A hydrogeological conceptual model aims to qualitatively display the processes and mechanisms by which the water within the CO_2-rich mineral water systems obtains its chemical composition, and the pathways through which the water rises from reservoir to surface. There are key features that must be explained in a hydrogeological conceptual model:

i) Tectonic structure of region

The tectonic structure of a region displays the pathways by which the water will flow, both at the surface and at depth (structures affecting geomorphology such as anticlines/synclines, relief, faults etc.), as well as reservoir/aquifer structure (structural traps). An example of this is the Kemerhisar springs in Turkey, where the basin structure of the system provides deep faults and allow deep circulation of the water (Afsin, 2003).

Knowledge of whether a system is active tectonically, or when it was previously active, as well as subsequent intrusions of geological bodies (e.g. granitic intrusions), can help determine the circulation depth and heating source of the water. An example of this can been seen in the Daylesford mineral springs in Australia, where the waters issue in a formerly active volcanic setting, with post-volcanic magmatic intrusions providing the CO_2 and heat source for the spring waters (Cartwright et al., 2001).

Flow paths through faults and fractures are one of the key drivers for movement of both the water and gases within a CO_2-rich mineral water system. Deep crustal faulting typically provides the spring water with gases such as carbon dioxide, with the same deep faults, as well as more shallow faults and fractured rocks providing pathways for the water flow paths.

ii) Subsurface geology

The lithological signatures of the area/region will have an impact on the thermal and mineral waters composition, as well as influence the burial depth, nature and location of the reservoir/aquifer (permeable/impermeable rock).

The geological setting is key in influencing the geochemical nature of the thermal and mineral waters, due the level of water-rock interaction. An example of this is in the Kangding geothermal system in China. There are two types of waters that issue, thought to be due to the geology in through which they emerge; Ca-HCO_3 type water in calcium-rich rocks (limestones), and Na-HCO_3 in Na-feldspar-rich rocks (granites) (Liu et al., 2000).

Burial depth, and the geothermal gradient of a hydrogeological system are important factors in determining the circulation depth of thermal and mineral waters based on the temperatures that they attain at depth.

These factors are based on both the tectonic history and thickness of geological units in a system (Henley & Ellis, 1983).

The geology can also affect the structure of the hydrogeological system, specifically the nature of the reservoir/aquifer, due to the permeability of the rocks in the system. In the Nevsehir region in Turkey the impermeable metamorphic marbles contributed to the existence of a confined aquifer for the springs issuing in the area (Afsin, 2002).

iii) Recharge

The recharge area of a hydrogeological system is defined as where the water infiltrates before entering the aquifer system.

This can be through precipitation, or through mixing of seawater with groundwater from the reservoir. Along with this, the pathways through which the recharge moves from surface to groundwater, such as faults and fractures, are an important factor to consider.

Hydrogeological systems typically recharge in areas of high precipitation, which tend to be those of high altitude. The precipitated water infiltrates at the surface then percolates through faults, fractures, or due to the permeability of the rock, and enters the system as groundwater. Therefore, knowledge of the recharge area can help determine, or add to the knowledge of the tectonic and geological factors of a system, thus contributing to the formation of a conceptual model of a system.

The importance of the correct recharge information can be seen in the Chaves/Vilarelho da Raia springs. These springs were thought to have the same recharge area for the springs. However, isotopic data proved to show that they had separate recharge areas at different altitudes, and therefore can be considered springs emerging from two separate hydrogeological systems (Marques et al., 2001).

iv) Discharge areas

Discharge areas involve the direction, way and area in which the groundwater rises to the surface. This is typically through faults and fractures, with knowledge of the direction and pathway of the discharge giving information on which rocks the water has reacted with, as well as the depth that the water has reached. In some cases, the discharge areas are ascribed to geological contact zones (impermeable/permeable geological formations) (Albu et al., 1984). The location of the discharge area within a system can affect the geochemical composition of the water as it issues at the surface.

v) Flow paths

Flow paths are the preferential mechanisms and direction that all water within the system travels. This can be through faults, fractures, impermeable horizons or lithologies, and well as topography and underground structural traps.

Flow paths of both waters and gases typically occur through faults, which can vary in depth. Deep seated faults, such as those seen in Jungapeo, Mexico, carry gas from the mantle to the water, whereas more shallow faults and fractures control the depth of water circulation as well as the location of the surface manifestations of spring water (Siebe et al., 2007).

The temperature of the water is also related to the depth and nature of the faults and fractures. Heavily fractured rocks, such as the granites seen in South Korea (Koh et al., 2002) provide a slow journey for the water from depth to surface, therefore decreasing the temperature until it is discharged at the surface. Faults can provide a shorter travel time for water, with the surface discharge being high temperature, as the water has had less time to lose heat in its flow path. This can be seen in the Southern Alps of New Zealand, where there is one major fault with related magmatism, creating high-temperature springs at the surface (Cox et al., 2015).
The degree of water-rock interaction is also greatly influenced by the depth of flow paths, as well as the travel-time from infiltration to discharge. A deep underground flow path can create an environment more conducive to water-rock interaction, with increased mineralisation in deeper circulating waters compared to shallow groundwaters. This is seen in the CO_2-rich spring waters of the Mukhen Spa, Eastern Russia, where the shallower circulating water has lower TDS (400 mg/L) than the deeper circulating waters (14,000 mg/L) due the increased water-rock interaction at depth, in this case due to the increased partial gas pressure depth during the reactions (Kharitanova et al., 2015).

vi) Geochemical and isotopic studies

The most traditional, widespread methods of analysing a hydrogeological system and the nature of its waters involve the use geochemical and isotopic data attained from water samples from springs and boreholes. These results are used in combination with geological and geophysical information to obtain a hydrogeological overview of the system, including origin and recharge area, flow paths, and apparent age of the water.

The interaction between CO_2-rich water and the rocks is a process which significantly affects the geochemistry the water possesses. The geochemical signature of a CO_2-rich thermal and mineral water can be defined by the dominant anions and cations, minor constituents (e.g. iron, borate), tracers (for example, stable isotopes, radioactive isotopes, rare-earth elements) and the level of mineralisation (TDS). These factors can give insight into the circulation pathway of spring water. 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).

For example, in granitic areas this low temperature water rock interaction is based upon 2 key factors;

- The solubility of CO_2 increases with decreasing temperature (Greber, 1994).
- The solubility of albite (plagioclase feldspar mineral) increases significantly with an increase of partial pressure of CO_2 (Stumm & Morgan,1981)

As defined by Sillen & Martell (1964), complex ions such as $NaCO_3$ and $NaHCO_3$ (aqueous) are formed in solutions with a mineralization of greater than 1 g/L such as those in this study (Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas, amongst others). Sodium bicarbonate ($NaHCO_3$) can only become soluble in particular conditions, for example with the presence of CO_2 in the water.

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.

CO_2 can enter the water through a variety of methods (metamorphic devolatilization, magmatic, dissolution of carbonates, organic matter).

Aqueous carbon dioxide reacts with the water to form carbonic acid. This can be displayed in equation 1 (Hem, 1970).

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3^- \qquad (1)$$

Carbonic acid can lose protons to form bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}), as seen in equations 2 and 3 below. When this happens, the proton (H^+) is liberated into the water, which causes a decrease in pH.

$$H_2CO_3(aq) \leftrightarrow H^+(aq) + HCO_3^- \qquad (2)$$

$$HCO_3^-(aq) \leftrightarrow H^+(aq) + CO_3^{2-} \qquad (3)$$

With this reaction, the pH of the water decreases, and the salinity of the water increases. This reaction will tend to cause the chemical weathering of silicate minerals present in granite such as feldspar (Hem, 1970).

This chemical weathering of Na-feldspar (plagioclase) can be expressed by equation 4.

$$2\ NaAlSi_3O_8 + H_2O + 2\ CO_2 \longrightarrow 2\ Na+ + 2\ HCO_3 + 4\ SiO_2 + Al_2Si_2O_5(OH)_4 \qquad (4)$$

Calcium (Ca^{2+}) can be present in CO_2-rich mineral waters due to the plagioclase hydrolysis in granitic regions, or groundwater that have come into contact with calcium-rich lithologies such as carbonate, as described in equation 5 (Hem, 1970).

$$CaCO_3 + CO_{2(gas)} + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (5)$$

The presence of sulfate (SO_4) in CO_2-rich mineral waters can be ascribed to the interaction of lithologies rich in pyrite and/or gypsum, as well as release of sulphur present in mantle volatiles, seen in areas of active volcanism (Cruz et al., 1999; Cox et al., 2015)

Chloride (Cl) can be dissolved into CO_2-rich mineral waters due to the presence of evaporites in the hydrogeological system, and the intrusion of saline waters (seawater or brines) (Duchi et al., 1994).

Carbon isotopes ($\delta^{13}C$ and ^{14}C)

$\delta^{13}C$ isotope analysis can be used to determine the origin of the CO_2 in the CO_2-rich mineral waters studied, with the isotope values below displaying the range of values for each gas origin (Truesdell & Hulston, 1980);

- Metamorphic devolatilization (3 – 5‰)
- Interaction with carbonates (–2 to 2‰),
- Magmatic degassing (–8 to –5‰),
- Organic matter degradation (–26 to –22‰)

The $\delta^{13}C$ isotope data obtained by Marques et al. (1998) for the Chaves geothermal area shows values ranging from -6 ‰ to -1 ‰. These values obtained in the TDIC (Total Dissolved Inorganic Carbon) strongly suggest an inorganic source of CO_2 specifically a deep-seated upper mantle-derived origin (Aires-Barros et al., 1998).

The origin of CO_2 in CO_2-rich mineral water systems is not always from a singular source. In the central Appenines, in central Italy, studies on the TDIC of CO_2-rich carbonate aquifers showed results of mixture of 23% biological sources, 36% from carbonate dissolution, with the remaining 41% from deep seated sources (Chiodini et al., 2000). CO_2-rich spring water in the Huanglong Ravine, China, and the Mesozoic granitoids of the Korean Peninsula contain gas that is a mix of mostly mantle origin, with some CO_2 from the dissolution of carbonate rocks (Yoshimura et al., 2004, Jeong et al., 2005). The Rocky Mountain Front Range in Colorado, USA, is an example of a system that displays three different sources of CO_2; mantle derived, metamorphic and from oxidation of carbonaceous sediments (Crossey et al., 2006).

Carbon-14 can also be used for groundwater dating. Carbon-14 dating is an important groundwater dating tool due to its particularly long half-life (5730 years). However, ^{14}C dating can be complex in CO_2-rich hydrogeological systems, as small concentrations of atmospherically derived CO_2 in the recharge waters can be hidden by large amounts of ^{14}C-free CO_2 from magmatic degassing/metamorphic sources (Mook, 2000).

In the Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas systems, Aires-Barros et al. (1998) found radiocarbon values of 7.9 and 9.9 pmC, which indicate an old groundwater system. In some samples tritium was detected which is not in agreement with the ^{14}C content, and points to a different source of carbon to the system, either from the atmosphere or soil CO_2. Carbon-14 age calculations were made for both the hot and cold mineral waters; Vilarelho da Raia 4.97 ± 3.07 ka BP, Pedras Salgadas 8.58 ± 4.33 ka BP, and Chaves 13.29 ± 2.65 ka BP (Carreira et al., 2001).

Analysis of groundwater samples for carbon-14 and tritium were made in the Ballimore region of Australia to determine the relative age of the groundwater. The values, which were lower than detection limit for both carbon-14 and tritium, gave two conclusions. The low tritium values show that the groundwater was recharged before 1952, and the carbon-14 values (which lack modern carbon) indicate the groundwater may be older than 35,000 years (Schofield & Jankowski, 2004).

$\delta^{18}O$ and $\delta^{2}H$

Measurements of the $\delta^{2}H$ and $\delta^{18}O$ isotope ratios of CO_2-rich mineral waters are a key method in the identification of the origin of waters within a system and the tracing of their pathways with respect to recharge and underground flow paths and in the identification of possible mixing with different aquifer systems.

Variations of $\delta^{2}H$ and $\delta^{18}O$ ratios occur with latitude, altitude and distance from the ocean. The latitude effect occurs as the water vapour masses loses heavier isotopes by isotopic fractionation when the vapour masses are moving to areas with higher latitude and lower temperatures. The continental effect (distance from the ocean) describes how the concentration of heavy isotopes decreases as water vapour moves inland. The altitude effect causes an isotopic fractionation leading to a decrease in concentration of heavy isotopes with increasing altitude. These variations can be measured against the international standard V-SMOW (Vienna Standard Mean Ocean Water). The V-SMOW intends to represent the average value of the isotopic composition of the oceans (begin and end of the Hydrological Cycle), and has for both hydrogen and oxygen a value of close to 0‰, whereas freshwater generally has more depleted values (Gat & Gonfiantini, 1981, Clark & Fritz, 1997, Mook, 2000).

Examples of the uses of these isotope ratios are shown in the Mont-Dore region of the Massif-Central, France, and Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas, Portugal. The $\delta^{18}O$ and $\delta^{2}H$ data collected from the thermal and mineral waters of the Mont-Dore region all plot close to the Local Meteoric Water Line, indicating a local meteoric origin for these waters (Pauwels & Fouillac, 1997). Analysis of the isotopic composition of the Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas region CO_2-rich mineral waters shows that both the hot (Chaves) and cold (Vidago, Pedras Salgadas) mineral waters share similar isotopic compositions ($\delta^{2}H$ and $\delta^{18}O$) to the shallow dilute groundwater. This can be inferred as the groundwater and mineral waters having been recharged under similar climatic condition and, in the case of the hot waters, with no detectable water-rock interaction at elevated temperatures.

The values obtained from samples of varying locations within a hydrogeological system can give information on the preferential recharge altitudes of the water. $\delta^{18}O$ values become more depleted with an increase in recharge altitude, therefore a comparison of isotope samples at springs with different altitudes can be used to determine the recharge area of a hydrogeological system. In the Chaves region, North Portugal, water samples that were collected from springs located at various altitudes enabled the estimation of the regional isotopic gradient (the change in $\delta^{18}O$ /100 m in altitude). The regional isotopic fractionation with the altitude can be used to determine the preferential recharge altitude for the mineral waters. Using this information, along with the geomorphology of the region, the recharge areas of the region were determined (Marques et al., 2001). The values obtained from samples of varying locations within a hydrogeological system can give information on the preferential recharge altitudes of the water. $\delta^{18}O$ values become more depleted with an increase in recharge altitude, therefore a comparison of isotope samples at springs with different altitudes can be used to determine the recharge area of a hydrogeological system.

Temperature is also a factor in the variation of $\delta^{18}O$ isotope values. An increase in temperature at depth can cause an enrichment in $\delta^{18}O$ (due to the establishment of an isotopic equilibrium between the aquifer matrix and the water), allowing for inference of the underground depth and pathways of water based on $\delta^{18}O$ ratio comparisons to the local meteoric water. An enrichment of $\delta^{18}O$ in this manner is usually an indication of a current or former high-temperature (> 250°C) geothermal system (Mook, 2000).

Tritium (^{3}H)

Tritium, with its short half-life (50-60 years) (Lucas & Unterweger, 2000) can be useful in the dating of CO_2-rich thermal and mineral water, allowing the ability to differentiate between old and young water (based on the presence or lack of Tritium), and can also provide information on whether or not mixing between these waters has occurred. There is a marked difference between post nuclear bomb tests (post-1945 onwards) and pre nuclear bomb tests (pre-1945) tritium, allowing a differentiation in age. However, this bomb effect is not visible in present days due to the tritium radioactive decay and dilution by the ocean masses.

In the Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas region, tritium was used to help establish the difference in age for the springs in the region, with the lack of tritium in the Chaves spring meaning an older recharge, and higher mean residence time compared to the Pedras Salgadas springs, which contain tritium, and are therefore younger (Carreira et al., 2008). In the Jungwon area, South Korea, the zero to very low amount of tritium (<2 TU) of the CO_2-rich thermal waters show a long residence and circulation time in comparison to the shallow groundwater which has much higher tritium contents (6.6-10.5 TU) (Koh et al., 2008).

The CO_2-rich mineral water springs of the Lower Engadine, Switzerland, display a negative correlation between the tritium concentration and the dissolved ions concentrations, and have tritium values ranging from 0.7TU to 50TU. The negative correlation was interpreted having two possible causes. The first is the dilution of the CO_2-rich mineral water by fresh water, which gives the high tritium value. The second is that the cold CO_2-rich mineral water is young (with high tritium values) and the high dissolved ion concentration is caused by rapid dissolution of ions due to the increased water-rock interaction with the presence of CO_2 at low temperatures (Wexsteen et al., 1988).

$^{87}Sr/^{86}Sr$ ratios and Sr geochemistry

Strontium isotope ratios can be used to help identify the characteristics and changes that occur to thermal and mineral water systems during their development through a hydromineral system. $^{87}Sr/^{86}Sr$ ratios have been used in studies to help determine this evolution of waters through hydrogeological systems, with the high atomic weight of strontium preventing natural fractionation and facilitating the use of Sr isotopes as a hydrogeochemical tracer (Marques et al., 2012).

The $^{87}Sr/^{86}Sr$ ratios of a given water is dependent of the Rb/Sr ratios and age of the rocks that the water has interacted with (Faure, 1986). Analysis and subsequent comparisons of samples of thermal and mineral water and rocks present in the hydrogeological system therefore allow for inference of the lithology of reservoir rocks, presence or extent of mixing of waters underground flow paths, and degree of water interaction at depth.

Analysis of the $^{87}Sr/^{86}Sr$ ratios and Sr geochemistry by Marques et al. (2012) in the Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas systems gave three main conclusions: the meteoric waters are locally recharged, the systems have different preferential underground flow paths, and each system is influenced by granitic bodies of different ages. The study indicates that the Sr isotope data shows strong evidence that Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas CO_2-rich mineral waters originate from different hydromineral systems, and mixing between the systems does not occur.

Another example of the use of strontium isotopes is shown in the CO_2-rich mineral water springs of the Korean Peninsula. Analyses of the strontium isotopes in the CO_2-rich water show similar strontium isotope ratios in both the water and the local granite. Alongside this, the calcium content of the Ca-HCO_3-type water originating from plagioclase, which is abundant in the local granite, gave the inference that the chemistry of the CO_2-rich water is influenced by the water-rock interaction with the local granite at depth (Koh et al., 2002).

2.5. CO_2-rich thermal and mineral waters of the Vilarelho da Raia-Chaves/Vidago-Pedras Salgadas region (N Portugal)

Geology and tectonic setup of the study area

The Vilarelho da Raia-Chaves/Vidago-Pedras Salgadas region 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 (Marques et al., 1999).

Main Geological Units:

i) Hercynian Granites:

Syn-tectonic – 310 Ma

Late to post tectonic – 290 Ma

ii) Silurian metasediments: quartzites, phyllites and carbonaceous slates.

iii) Miocene-Pleistocene sedimentary formations mainly composed of lacustrine, alluvial and detritic layers (Sousa Oliveira & Portugal Ferreira, 1996).

Geology of Chaves

According to Sousa Oliveira & Portugal Ferreira (1996), outcrop samples in the Chaves graben show three types of granites - Chaves, Outeiro Seco and Faiões, as well as quartzites, and andalusitic and graphitic slates.

The Chaves and Outeiro Seco granites are syn-tectonic and display a medium to coarse grained texture, dominated by biotite (which displays some local chloritization) and muscovite. K-feldspar is unaltered, Na-feldspar shows some hydrothermal replacement into sericite, and quartz displayed strong tectonic alteration. The Faiões granite is post-tectonic with a coarse-grained to porphyritic texture. The mineralogy of this granite is composed mostly of biotite and muscovite (biotite dominant). Biotite is highly chloritized, with microcline-perthite and Na-plagioclase also present. The quartzites are composed of a fine-grained quartz matrix interbedded with coarser quartz grains (displaying granoblastic texture) with thin beds of white mica interspersed within the quartz grains. Schistosity shows tectonic alteration of the rock. The andalusitic slates show a granoblastic texture, with a banded matrix of quartz and graphite. Graphitic slates contain both continuous and lenticular beds of graphic interbedded with layers of white mica, with a lepidogranoblastic fabric (Marques et al., 2012).

Geology of Pedras Salgadas and Vidago

Post-tectonic Hercynian medium to fine grained granites with K-feldspar (orthoclase and microcline) quartz, Na-plagioclase and biotite occurring as major minerals. Cenozoic sedimentary cover outcrops in Pedras Salgadas. The emergence of mineral water corresponds to the intersection of sub-vertical facture systems, with quartz veins related to the faulting shown in Figure 15 (Sousa Oliveira & Portugal Ferreira, 1995).

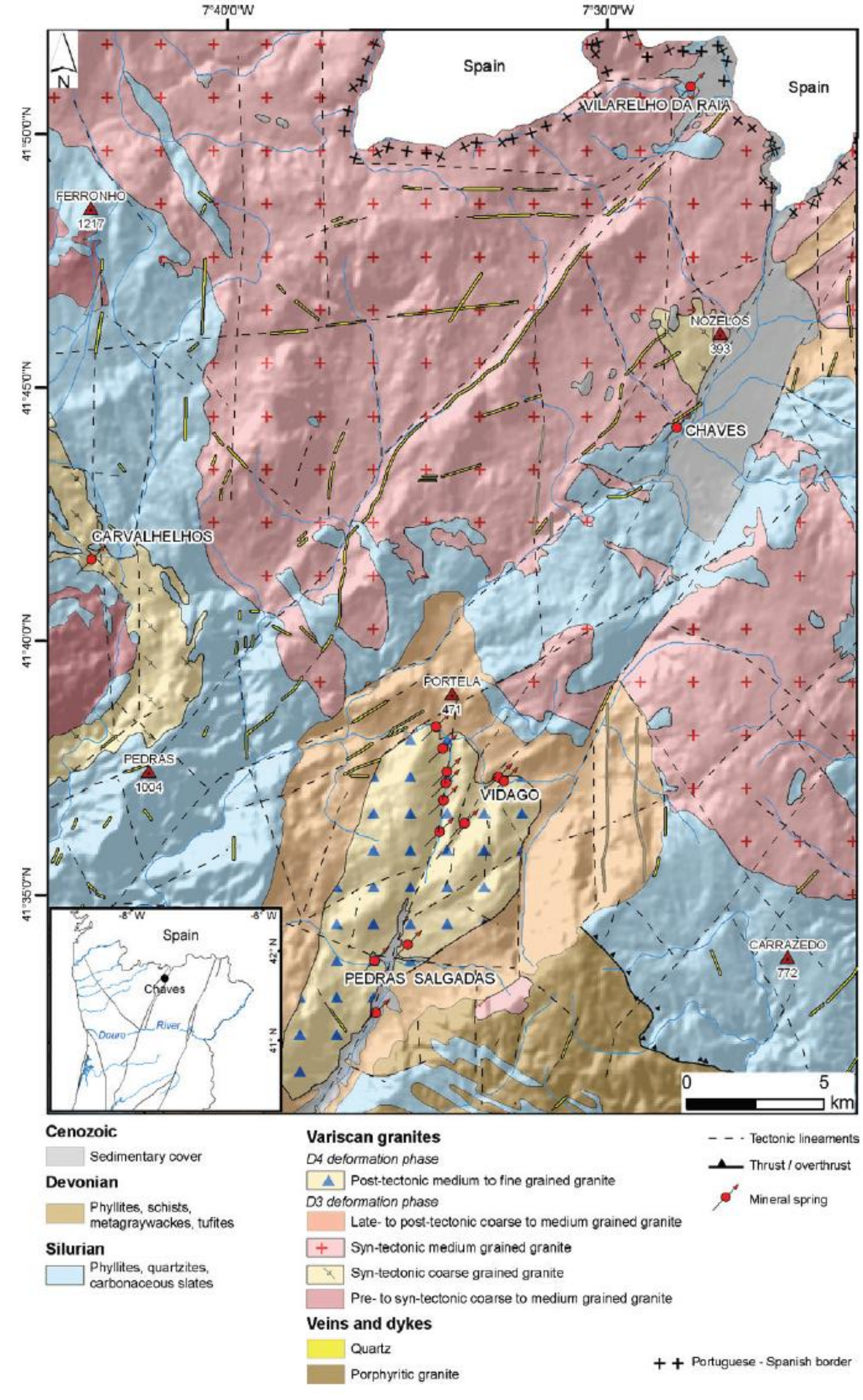


Figure 15 – Regional geological map of the Vilarelho da Raia–Pedras Salgadas region (Marques et al., 2012).

Structural geology and geomorphology

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 15) (Marques et al., 2001). Notably, the Miocene-Pleistocene sediments do not appear to have overlain the post tectonic granites where the Pedras Salgadas and Vidago thermal springs reside. This fault system is intersected by ENE–WSW fracture systems, and these points of intersection give rise to the emergence of mineral waters at Chaves, Vidago and Pedras Salgadas (Sousa Oliveira & Portugal Ferreira, 1996).

Chaves, Vidago and Pedras Salgadas are located inside graben structures. The Chaves springs are located within a 3 km by 7 km downthrown block, with thick (>250m) 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 Vidago/Pedras Salgadas (cold waters), with higher relief and deeper fracturing, along with the thickness of the overlying sediments favouring deeper groundwater circulation (Duque et al., 1998).

Geochemistry of the thermal and cold mineral waters

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.

Two types of waters are proposed:

Chaves-Vilarelho da Raia (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 phase composition emitted from these springs is composed of almost pure CO_2 (> 97% of the gas phase). The groundwater (liquid phase) composition is otherwise Na and HCO_3 dominated (~650 mg/L Na and 1,500-1,700 mg/L HCO_3). Vilarelho da Raia mineral waters show similar chemical composition, however have lower temperatures (~17°C) (Marques et al., 2006).

Vidago-Pedras Salgadas (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, and free CO_2 (up to 2,500 mg/L content in comparison to Chaves (Marques et al., 2006).

The relationship between Cl^- and Na^+, HCO_3^- and Sr content has been analysed by Marques et al. (2006). A positive correlation is found between increasing concentrations of Cl^- and Na^+, HCO_3^- and Sr (Figure 16).

This suggests that the Cl^- content in the waters is derived from leaching of granitic rocks through acid hydrolysis of biotite and plagioclase (Edmunds et al., 1985). This data has also been used to infer the presence of different hydrogeological systems in the region. The Chaves plots in a cluster, suggesting a common origin for the spring and borehole waters due to similar water mineralization, whereas the Pedras Salgadas and Vidago data plots are scattered, showing different levels of mineralization in the waters, which could be interpreted as these waters having different origins of water through separate underground pathways.

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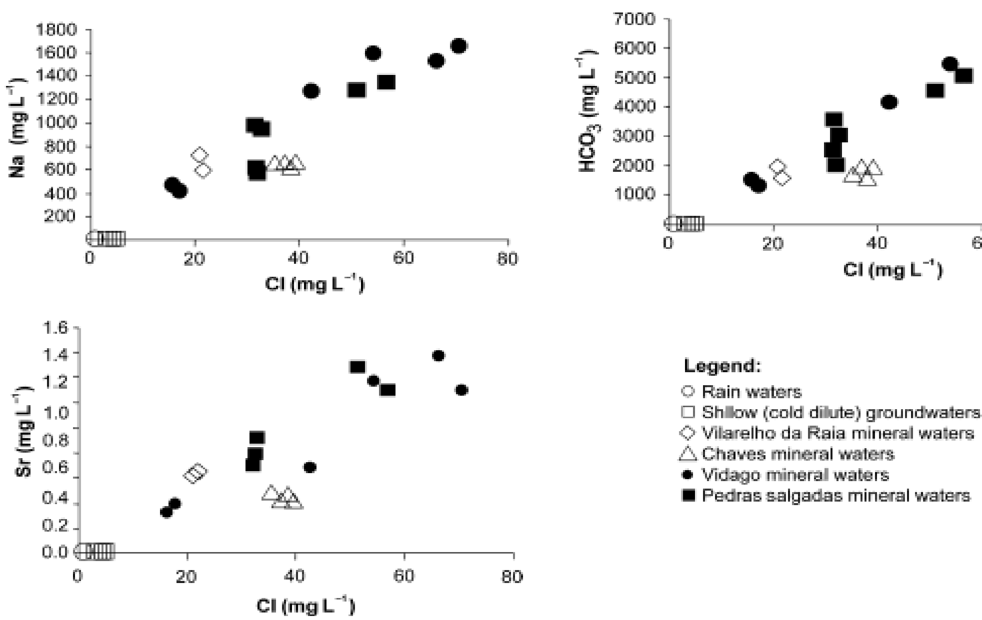

Figure 16 - Cl versus HCO_3^-, Cl^- versus Na^+ and Cl^- versus Sr (mg/L) for the waters from Vilarelho da Raia–Pedras Salgadas region, Modified from Andrade (2003).

Isotopic signatures of mineral waters

$\delta^{18}O$ and δ^2H

To analyse the isotopic composition of the mineral waters, a local meteoric water line was calculated by Andrade (2003), based on $\delta^{18}O$ and δ^2H values of shallow cold dilute groundwater samples collected from springs in the Vilarelho da Raia–Pedras Salgadas region of various altitudes.

Data collected by Marques et al. (2006) indicates that both the hot and cold mineral waters share similar isotopic compositions ($\delta^{18}O$ and δ^2H) to the shallow dilute groundwater. This can be inferred as the shallow groundwater and mineral waters having been recharged under similar climatic condition, with no detectable water-isotope interaction at elevated temperatures or evaporation before infiltration.

Analysis of isotopic composition can help ascertain the preferential recharge altitude of the infiltrated waters. Water samples that were collected from springs located at various altitudes enable the estimation of the regional isotopic gradient (the fractionation in $\delta^{18}O$/100 m). The regional isotopic fractionation with the altitude can be used to determine the recharge gradients (preferential recharge altitude) for the mineral waters. Using this information, along with the geomorphology of the region, the recharge of Chaves, Pedras Salgadas and Vidago appears to be on the Padrela Mountain, with the recharge of Vilarelho da Raia from Larouco Mountain (Marques et al., 2001). Figure 1 displays the location of Padrela Mountain in relation to the studied springs.

$^{87}Sr/^{86}Sr$ ratios and Sr geochemistry

$^{87}Sr/^{86}Sr$ ratios and Sr geochemistry is an important tool in determining the origin of CO_2-rich mineral waters, as this data is directly related to the bedrock that the groundwater has interacted with. Analysis of the $^{87}Sr/^{86}Sr$ ratios and Sr geochemistry by Marques et al. (2012) gave the following conclusions: the Vilarelho da Raia, Chaves, Pedras Salgadas and Vidago systems have different preferential underground flow paths, and each system is influenced by granitic bodies of different ages. The study indicates that the Sr isotope data shows strong evidence that Vilarelho da Raia, Chaves, Pedras Salgadas and Vidago CO_2-rich mineral waters originate from different hydromineral systems, and mixing between the systems does not occur.

Carbon isotopes ($\delta^{13}C$ and ^{14}C)

$\delta^{13}C$ isotope analysis can be used to determine the origin of the dissolved carbon in the CO_2-rich mineral waters. The CO_2 in this type of water can originate from a number of sources, such as: atmospheric, organic carbon ascribed to roots respiration metamorphic and magmatic (release of volatile gas), organic matter (oxidation) and geological interaction (carbonates). The $\delta^{13}C$ isotope data obtained in the study by Marques et al. (1998) shows values ranging from -6‰ to -1‰. These values obtained in the TDIC (Total Dissolved Inorganic Carbon) strongly suggest an inorganic source of CO_2 specifically a deep-seated upper mantle-derived origin (Aires-Barros et al., 1998).

Carbon-14 dating is an important groundwater dating tool due to its particularly long half-life (5730 yrs). ^{14}C dating is complex in geothermal systems, as small concentrations of atmospherically derived CO_2 in the recharge waters can be hidden by large amounts of ^{14}C from magmatic degassing/metamorphic sources. Aires-Barros et al. (1998) found radiocarbon values of 7.9 and 9.9 pmC, which indicate an old groundwater system, however, in some samples tritium was detected which is not in agreement with the ^{14}C content, pointing to a different source of carbon to the system, either from the atmosphere and soil CO_2. Based on the geological and structural context of the region these authors point to a deep-seated magma degassing origin. Carbon-14 age calculations were made for both the hot and cold mineral waters; Vilarelho da Raia 4.97 ± 3.07 ka BP, Pedras Salgadas 8.58 ± 4.33 ka BP, and Chaves 13.29 ± 2.65 ka BP (Carreira et al., 2001).

Tritium (^3H)

The Chaves hot CO_2-rich springs have no tritium, which implies they were recharged over 60 years ago, and supports the deeper circulation depth described by other works (Aires-Barros et al., 1995; Marques et al., 1998, 2000). Tritium is also absent in the Vilarelho da Raia cold CO_2-rich spring, with an 'old' recharge and shallow circulation depth, inferred due to the low discharge temperature. The presence of tritium in the cold Pedras Salgadas springs shows that they have been recharged more recently, with a low discharge temperature due to the shallow circulation depth (Carreira et al., 2008).

Conceptual model of the Vilarelho da Raia-Chaves groundwater systems

Currently, a conceptual circulation model exists for the Chaves and Vilarelho da Raia CO_2-rich mineral waters (Marques et al., 2001). Utilizing the available geochemical and isotopic data of several works carried out in the region, geochemical and isotopic data, the model has evolved from a model proposed by Aires-Barros et al. (1995), which showed a single source of recharge from the Padrela Mountain, to a model (Figure 17) which displays two distinct sources of recharge water for the mineral waters of Vilarelho da Raia and thermal waters of Chaves (Larouco Mountain and Padrela Mountain respectively).

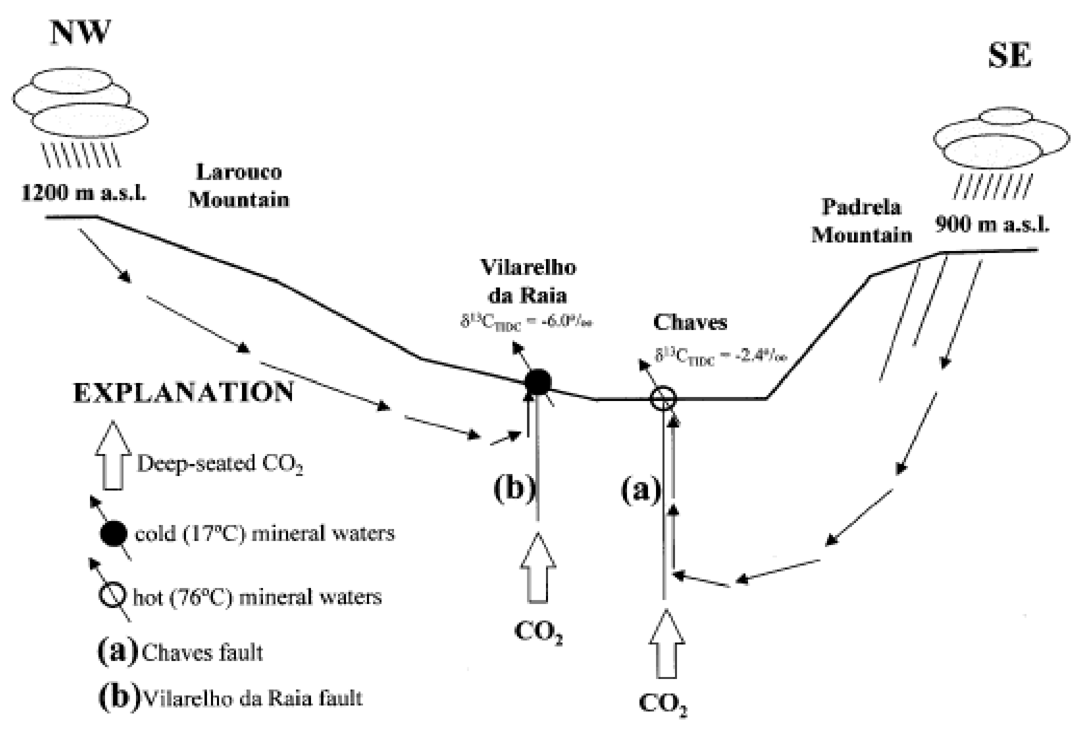

Figure 17 - Simplified conceptual circulation model of the Chaves and Vilarelho da Raia CO_2-rich mineral waters (Marques et al., 2001).

3. 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.

Although systems can contain one or more of these types of lithologies, the dominant lithology, in combination with the tectonic environment of the system was used as the categorising feature. For example, an area with both sedimentary and metamorphic rocks, within an area of active or recent volcanism would be considered a metamorphic system.

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]. These tables allow a concise analysis of each system, with the aim of defining the key characteristics of each category to be then put into the final comprehensive conceptual model.

3.1. Type 1 - Geologically dominated by granites

Key characteristics

The geology of these systems is granite dominated, but can also include sedimentary and volcanic lithologies within the system. The granites can occur as the basement lithology (e.g., Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas, Portugal; Massif Central, France; Kuzuluk, Turkey) or as intrusions (e.g., Russia).

There are a range of geomorphologies in the studied systems in this category, with systems in grabens, basin structures, or within fault zones. The common trend of the systems is that they all have areas of topographic highs and depressions, which dictate the location of the recharge and discharge zones, respectively.

The tectonic features which determine the flow paths of both the water and CO_2 are linked to the geomorphology and geology.

The fractured nature of granite provides some unique features to this category, forming reservoirs with pathways for infiltration of the water recharge at the surface, as well as flow paths for the water to emerge as springs (high mean residence time). Deep faults related to the structural controls provide pathways for the acquisition of CO_2 and flow of water from depth to the surface.

A deep, long circulation time is common in these systems (e.g. Kuzuluk, Massif Central, Tuva). This is probably due to the fractured nature of granite giving a slow infiltration of water deep into the system, with the up flow of water occurring through faults and fractures of varying depths.

Most of the recharge is related to regional precipitation, with the discharge through springs or groundwater from boreholes (e.g. Tuva).

The CO_2 originates from the mantle or from metamorphic devolatilization; carbonate dissolution or organic origins were not seen in these systems or if present are in a very small percentage that will be masked by the CO_2 coming from the mantle or from a metamorphic origin.

The geochemistry shown in these systems is dominated by the presence of Na^+, with Na-HCO_3 type waters the most common. Section 3.6. explains in detail the water-rock interaction between granites and CO_2-rich mineral water.

The key characteristics can be summarised below:

- Fractured granite providing flow paths for water (infiltration and discharge)
- Na-HCO_3-rich geochemical facies
- Graben/massif tectonics

Table 1 - Type 1 CO_2-rich mineral water systems (N.D. = No data available on this category)

Name (country and location)		Geology	Tectonic structure	CO_2 origin	Flow paths (CO_2)	Flow paths (water)	Recharge	Discharge	Geochemistry	Temperature (°C)
Spain	Catalonia (Redondo & Yelamos, 2000).	Granitic basement with overlying sedimentary rocks.	Graben	Mantle	Deep faults	Faults and fractures	Local meteoric	Springs	1. Ca-HCO_3-type; TDS ~1,900 mg/L, pH ~6.5 2. Na-HCO_3-type; TDS ~5,600 mg/L, pH ~6.6	1. ~14 2. 13.5-50.5
	Ourense, Galicia (Michard & Beaucaird, 1993).	Hercynian granites	Massif/Graben	Mantle	Deep faults	Faults	Meteoric	Springs	Na-Ca-HCO_3 tpe, TDS ~1,500 mg/L, pH 6-7	46-69
Portugal	Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas (Marques et al., 1999, 2000, 2001, 2012)	Hercynian granites	Graben	Mantle	Deep faults	Fractures and faults. Deep circulation.	Meteoric	Springs	Na-HCO_3- type; 1. TDS 1,600-1,850 mg/L, pH ~7 2. TDS 4,300 mg/L, pH ~6,	1. 17-76 2. ~17
France	Massif Central (Mont-Dore region) (Batard et al., 1981; Pauwels & Fouillac, 1997; Weinlich, 2005)	Quaternary volcanics or Tertiary granites	Massif	Mantle	Deep faults	Deep circulation, faults.	Meteoric	Springs	Na-HCO_3 type, TDS < 8,000 mg/L, pH 6-7	4-62
Slovakia	Fatra (Boids et al., 2017)	Hercynian granodiorites	Basin	Metamorphic devolatilization /mantle	Deep faults	Fractures and faults	Meteoric	Springs	Na-HCO_3 type TDS 5,980-10,650 mg/L, pH 6-7	Cold
Czech Republic	Karlovy Vary (Krejbichová, 1999; Wienlich et al., 1997).	Granite	Basin	Deep seated	Deep faults	Fractures and faults	Meteoric	Springs	Na-HCO_3-SO_4-Cl type, TDS 6,400 mg/L, pH 6-7	40-73
Turkey	Kuzuluk/Adapari (Greber, 1994),	Volcanic tuffs overlaying andesites and granites	Extensional basin	Metamorphic devolatilization /mantle	Deep faults	Extremely long residence times at depth. Up flow through tectonic fissures. Type 1 waters originate from central reservoir.	Meteoric	Springs	1. Na-(Ca) -(Mg)-HCO_3-Cl type, TDS 4,997 mg/L, pH ~7 2. Na-(Ca)-HCO_3-Cl type, TDS 3,536 mg/L, pH ~6	1. 24.2 2. 40.8
Russia	Tuva (Choigan natural complex (Kopylova et al., 2014)	Gneiss, marbles and schists intruded by granites and diorites	Junction of two grabens	N.D.	Deep faults	Deep circulation, CO_2-rich groundwater.	N.D.	Springs/ground water. Deposition of travertines.	Na-Ca-HCO_3 type; 1. CO_2-enriched groundwaters – TDS ~1,500 mg/L, ph~6.5 2. Fracture-vein carbon dioxide waters, TDS ~2,500 mg/L, pH ~6.5	1. 15-23 2. 21-31

Table 1 -Type 1 CO_2-rich mineral water systems (N.D. = No data available on this category)

China	Kangding (Zaihua et al., 2000)	Granites/limestones	Located an active fault zone, with a large scale granitic mass.	Metamorphic devolatilization /magmatic	Deep faults	Faults	N.D.	Springs	1. Ca-HCO_3 type water, TDS ~2,000 mg/L pH 6.40 2. Na-HCO_3 or HCO_3, Cl-Na type waters, TDS ~2,500 mg/L pH 7.2.	1. 29-42 2. 60-73
	Jiangxi Province (Sun et al., 2017)	Sandstones, schist, migmatites, granites, granitic intrusion.	Tectonically active area	N.D.	Deep faults	Deep faults	Meteoric	Springs	Na-HCO_3 type, TDS < 3,870 mg/L, pH 5.7-7.7	25-71
South Korea	Kangwon (Choi et al., 2014)	Granite (biotitic)	Granite emplaced by syntectonic and continental margin Magmatism. N/E trending normal faults	Magmatic	Deep faults	Springs emerge through faults, with aquifer in fractures.	N.D.	Springs	1. Na-HCO_3 type, TDS 2,030 mg/L, pH ~6 2. Ca-HCO_3 type, TDS 987 mg/L, pH ~6	1. 16.2 2. 10.6

3.2. Type 2 - Geologically dominated by sedimentary rocks

Key characteristics

The geology of these systems is dominated by sandstones (e.g. Lastochka, Russia), limestones (e.g. Tingri, Nepal) and carbonates (e.g. Huanglong, China). Travertine or tufa deposits are common around the spring areas of these systems due to the calcium-rich geochemical composition of the CO_2-rich waters issuing.

The geomorphology of the systems is mostly controlled by basin structures or depressions/anticlines. For some systems, thick sedimentary deposits (>4 km thick) form aquifers (e.g. Suio-Mondragone, Italy, and West Carpathians, Poland).

Flow paths of both the water and CO_2 appear in the form of faults, with deep faults for the attainment of CO_2 and smaller faults related to local deformations or active tectonics providing flow paths for the infiltrating water. Due to the permeable nature of sedimentary rocks such as sandstones, infiltration of water through these rocks into the system can occur; however, in limestones the water circulation is done through cracks in the rock itself and in conduits.

The majority of the recharge is associated with local or regional precipitation, with the discharge through springs or from boreholes.

The CO_2 originates mostly in the mantle or from metamorphic devolatilization with carbonate dissolution origin seen in some systems of this category.

The geochemistry shown in these systems is dominated by the presence of Ca^{2+}, with $Ca\text{-}HCO_3$-type waters the most common, although Na^+ dominated waters are also prevalent, and evaporitic layers or brines can cause chloride to enter the waters of these systems (e.g. Suio-Mondragone, Saratoga Springs).

The key characteristics can be summarised below:

- Thick sedimentary deposits
- Travertine/tufa deposition at surface
- $Ca\text{-}HCO_3$-rich water

Table 2 - Type 2 CO_2-rich mineral water systems (N.D. = No data available on this category)

Name (country and location)		**Geology**	**Tectonic structure**	**CO_2 origin**	**Flow paths (CO_2)**	**Flow paths (water)**	**Recharge**	**Discharge**	**Geochemistry**	**Temperature (°C)**
Italy	Suio-Mondragone. (Minnsale, 2004).	Mesozoic platform carbonates and karsts, volcanic complexes	Thick > 2 km carbonate-karst complex in contact with volcanic conduits. Thermal waters occur in fractured zones with active faults.	Mantle	Deep faults	Fast ascent along the main seismically active faults Bordering the carbonate nuclei.	Meteoric. Infiltration through fractures	Springs	1. Mondragone, Na-Ca-Cl-HCO_3, TDS 4,616 mg/L, pH 6.6 2. Suio, Ca-Mg-HCO_3; TDS 2,568-4,213 mg/L, pH 6.1	1. 52 2. 26-52.
Poland	West Carpathians (Lesniak, 1998).	Shaly sandstones, sandstones and shales.	Longitudinal depression. Thick (up to 10 km) sedimentary deposits.	Deep crustal origin	Deep faults	Deep faulting and water circulation	Meteoric.	Springs	Ca-Mg-HCO_3 type TDS ~5,000 mg/L, pH ~6.2	10
Russia	Lastochka (Shand et al., 2005, Kharitonova et al., 2007).	Highly permeable sandstone.	Anticline structure.	Deep-seated mantle origin.	Deep faults	Deep faults, with accompanying smaller fractures.	Local meteoric origin, low residence time.	Groundwater (boreholes)	Na-Ca-HCO_3 type 1. Deeper borehole; TDS 3,600 mg/L, pH 6.7 2. Shallower borehole; TDS 1,460 mg/L, pH 6.3	Low.
China	Huanglong (Yoshimura et al., 2004).	Thick carbonates (4000m) overlain by clastics (1,000m). Tufa deposition at surface	Thick sedimentary deposits.	Mantle origin (50-70%), the rest from dissolution of carbonates	Deep faults	Local deformations form faults for springs to emerge	Mixture of two source waters; fault-bounded spring water and snow and/or glacier melt water.	Springs	Ca-HCO_3 type TDS ~1,000 mg/L pH 6.4-7.2	3.6-7.2
	Xiage (Liu et al., 2000)	Igneous (andesites and clastics) and Triassic sandstones, limestone and mudstones. Tufa deposition.	N.D.	Mix of metamorphic and magmatic	Deep active faults	Faults	N.D.	Springs	HCO_3-Na, Ca type TDS 1,300 mg/L pH 6.19-6.48,	47-58
Nepal	Tingri (Newell et al., 2008)	Limestone and shale. Travertine deposition.	Graben	Organic matter breakdown and Limestone decarbonation	N.D.	N.D.	N.D.	Springs	Na-HCO3 type 1. Tsamda; TDS 957 mg/L, pH 6.3 2. Gondasampa; TDS 1.720-1,850 mg/L, pH 6.7-6.8	1. 42.6 2. 19.2 – 24.5
USA	Saratoga Spring (Siegel et al., 2004).	Shales	Carbonate aquifer	Mantle/igneous melting.	Deep faults	Faults and fractures	Mix of brines with local meteoric waters	Springs	Na-Cl-HCO_3 type TDS ~18,000 mg/L pH 6.4	12
	Grand Canyon, Arizona (Crossey et al., 2006).	Limestones and shales. Travertine deposition at surface.	Aquifer system in plateau region.	Mantle derived with some biogenic gas.	Deep faults	Deep circulation through faults. Some mixing with shallow groundwater.	Meteoric	Springs	1. Cl-rich 2. SO_4-rich 3. HCO_3-rich TDS > 1,000 mg/L pH 6.0-7.5	22-31

3.3. Type 3 - Geologically dominated by volcanic and metasedimentary rocks

Key characteristics

The geology is a combination of volcanic and metasedimentary complexes, with lithologies such as schists (Copland), ophiolites (Lower Engadine), volcaniclastics and evaporites (Kemerhisar, Dertalan and Ciftehan, Transylvania), basalts (Azores, Jungapeo) present in these systems. Sedimentary lithologies also appear, typically forming the cover deposits or aquifers, as well as granitic rocks as basements (Eifel/Rhine Graben), intrusions (Nevesehir), or banded with other rocks (Rwenzori). Travertine/tufa deposition at the surface (active or ancient) is common (Kayseri, North Argentinean Andes, Peruvian Andes, Rwenzori).

The geomorphology of the systems ranges show alpine orogenic terranes, as well as active and ancient volcanism, and metamorphic intrusions into sedimentary facies.

Flow paths for CO_2 are deep faults, and the flow paths for the water are faults and fractures formed due to the geomorphology and geology of the systems.

The recharge is associated with local or regional precipitation, with the discharge through springs or groundwater from boreholes.

The CO_2 originates from the mantle or from metamorphic devolatilization in most cases, which may be due to the presence of active or ancient volcanism in these systems providing the setting for the metamorphic devolatilization of carbonate rocks as well as mantle upwelling and related faulting.

The geochemistry shown in these systems can be explained by the greater variation in mineral composition compared to the previous two categories. Na^+, Ca^{2+}, Cl^-, and SO_4^{2-} are all dominant in different systems, reflecting the nature of the geology present in these types of systems.

- Chloride-rich waters typically have interacted with evaporitic deposits (e.g. Betic Cordilleras), or mixed with seawater (e.g. Haruaki Rift Zone).
- The presence of SO_4^{2-} can be explained due to the leaching of sulphur from volcanic rocks, seen in the Azores, where the sulphur in the water is thought to have originated due to this process (Cruz et al., 1999) and in the waters of Kayseri, where the source is proposed to be from the dissolution of gypsum, oxidation of pyrite and the coal-bearing layers of volcano-sedimentary complexes (Afsin et al., 2006).
- The silica (SiO_2) occurrences in the waters in this category can be due to the water-rock interaction of CO_2-rich waters and silica-rich rocks, such as those in Jungapeo, Mexico, where the SiO_2-rich waters evolve due to the interaction of the waters with basaltic andesite (Siebe et al., 2007)
- The presence of Na^+ and Ca^{2+} in these waters is due to the same water-rock interactions that occur in the other system types (see Section 3.6), with sodium and calcium minerals common in the lithologies presence in this category (volcanic metasedimentary complexes).

The waters attain higher temperatures where active volcanism or metamorphic terranes with mantle upwelling giving the water higher temperatures, facilitating the release of silicates into the water.

The key characteristics can be summarised below;

- Volcanism (active or ancient)
- Travertine/tufa deposition at surface
- Varied geochemistry – Cl^- and SO_4^{2-} more common than in the other types of systems
- Higher discharge temperatures

Table 3 - Type 3 CO_2-rich mineral water systems (N.D. = No data available on this category)

Name (country and location)		Geology	Tectonic structure	CO_2 origin	Flow paths (CO_2)	Flow paths (water)	Recharge	Discharge	Geochemistry	Temperature (°C)
Germany	Eifel/Rhine graben (Greisshaber et al., 1992, May, 2005).	Quaternary and tertiary volcanics, granitic basement.	Graben and Massif, seismically active	Mantle	Deep faults	Faults	Local meteoric	Springs	1. Ca-Mg-HCO_3 type; TDS < 4,000 mg/L, pH ~6 2. Cl-Na-SO_4-HCO_3 type; TDS < 50,000 mg/L, pH ~6 3. Na-Ca-SO_4-HCO_3 type, TDS < 4,000 mg/L, pH ~6.5	14-52
Spain	Betic Cordilleras (Cerón et al., 1998, 2000).	Meta-sedimentary complexes	Post-orogenic magmatism, crustal thinning basin	Mantle	Deep faults	Faults	Local meteoric.	Springs and CO_2-rich groundwater.	1. Springs; SO_4-(Ca)-HCO_3 type, TDS ~1,100 mg/L, pH ~7.3 2. CO_2-rich groundwater; SO_4-Cl-(Ca)-HCO_3-type, TDS 3,424 mg/L, pH 6.84	1. ~22 2. 26.3
Switzerland	Lower Engadine (Wexsteen et al., 1988, Bissig et al., 2006).	Phyllites and ophiolites	Alpine tectonics-anticlinorium with major (50 km) strike/slip fault and highly imbricated structures near where springs emerge	Mantle	Deep faults	Shallow circulation. Interaction with local groundwater	Local meteoric.	Springs. Fumaroles appear near some springs.	1. Ca-HCO_3 type; TDS 1,400-4,500 mg/L, pH ~6 2. Na-HCO_3, Cl type; TDS 1,800-15,000 mg/L, pH ~6 3. Na, Mg-HCO_3, SO_4 type; TDS ~7,500 mg/L, pH ~6.35	9-11
Portugal	Azores (Cruz et al., 1999).	Basaltic volcanics	Active volcanism	Deep-seated source	Faults	Faults and fractures	Meteoric	Springs	Na-SiO_2/SO_4-rich waters, TDS < 2,900 mg/L, pH 4.8-6.4	15-93
Romania	Transylvania (Boglárka-Mercedesz et al., 2013).	Neogene to Quaternary volcanic chain. Volcanoes and volcaniclastic deposits. Calc-alkaline rocks, andesites, dacites. Some evaporitic deposits.	Intrusive magmatism in sedimentary host rocks. Active post volcanic CO_2 degassing and springs. Border of Transylvanian basin and east Carpathian volcanics.	N.D.	Deep faults	Fractures	Local meteoric	Springs	Na-HCO_3, Ca-HCO_3 and Na-Cl types. TDS 290-10,463 mg/L, pH 5.04-7.68	3.0-12.4
Turkey	Kemerhisar, Dertalan and Ciftehan. (Afsin, 2003)	Metasedimentary complexes. Tuffs, andesites, agglomerates, marls, sandstones	Basin structures	Mantle origin	Deep faults	Faults	Deep circulation. Meteoric recharge	Springs	1. Ca-SO_4 type TDS 590-750 mg/L, pH 5.6-6.4 2. Na-Cl type; TDS 7,970-9,400 mg/L, pH 6.6-6.7 3. Na-SO_4 type; TDS 2,400-2,900 mg/L, pH 7-8.697	1. 30 2. 16 3. 52-54
	Nevesehir (Afsin, 2002)	Marble, tuffs, lahar deposits phyllites, schists, granites	Marbles form confined aquifer	N.D.	Deep faults	Faults	Deep circulation, local meteoric recharge	Springs	1. Na-Ca-HCO_3 type; TDS ~1,000 mg/L, pH 6.7-7.2 2. Ca-HCO_3 type; TDS 2,710-3,400 mg/L, pH 6.39-6.70 3. Na-Cl-HCO_3 type; TDS-11,400-18,000 mg/L, pH 6.5-6.9	1. 15 2. 13-21 3. 15-21

Table 3 (continued) - Type 3 CO_2-rich mineral water systems (N.D. = No data available on this category)

Name (country and location)		Geology	Tectonic structure	CO_2 origin	Flow paths (CO_2)	Flow paths (water)	Recharge	Discharge	Geochemistry	Temperature (°C)
Turkey	Kayseri (Afsin, 2006)	Metasedimentary, overlain be alluvial and terrace deposits with some travertine deposition	Basin, fault zone.	Possibly coal-bearing organic clays.	Deep faults	Faults	Shallow to deep circulation depending on spring. Low (shallow) to high (deep) temp). Meteoric origin.	N.D	1. BTMS; Ca-Na-HCO_3 type, TDS 1,640 mg/L, pH 7.1 2. YMS; Na-Mg-Cl-HCO_3 type, TDS 8,210 mg/L, pH 6.8 3. ACMS; Na-Cl-HCO_3 type, TDS 11,980-14,600 mg/L, pH 6.28-6.70	1. 46.5 2. 14.5 3. 20
Australia	Ballimore region (Cartwright et al., 2001).	Volcanic rocks	Fold belt metamorphics, inactive volcanism, post volcanic intrusion	Mantle	Deep faults	Fractures and faults. Mixing between recharge water and deep aquifer water	Deep circulation through fractured basement rocks. Recharge through river water.	Groundwater	Na-HCO_3 type; TDS 2,000-8,300 mg/L, pH 6.1-7.2	20.3-22.9
New Zealand	Haruaki Rift Zone (Reyes, 2009).	Miocene volcanics with greywacke basement	Back-arc continental Rift Zone	Dissolution of carbonates and magmatic source.	Faults	Faults	Mixing of seawater and groundwater	Springs	Na-HCO_3 and Cl-HCO_3 type	23-57
	Copland (Cox et al., 2015).	Schist with active travertine deposition	Alpine fault zone	Deep seated	Faults	Fractured schist	Local meteoric.	Springs	Na-Cl-SO_4-HCO_3 type, TDS ~2,200 mg/L, pH ~6.4	56-58
Mexico	Jungapeo (Siebe et al., 2007)	Basalt, clastic sediments and limestones.	Shield volcanism	Mantle	Deep faults	Faults	Meteoric water percolates through rocks, heated at depth by the remnant heat of magma bodies	Springs and groundwater	Na-Ca-Cl-SiO_2-HCO_3 type waters, TDS 860-4,784 mg/L, pH 5.5-6.2	28-32
Argentina	North Argentinean Andes (Gibert et al., 2009	Volcanic rocks with travertine deposition (active)	Active volcanism, volcanic belt	Deep-seated magmatic	Deep faults	Deep faults	Meteoric recharge, no evidence of mixing	Springs	Cl-Na,Cl-(SO_4-HCO_3)-Ca group; TDS ~16,000 mg/L, pH 6.3	25
Peru	Peruvian Andes (Newell et al., 2015)	Phyllites, carbonates and igneous rocks. Travertine accumulations	Slab subduction zone. Springs occur along detachment faults	Mantle	Deep faults	Faults	Mixing of hot saline waters with cold meteoric waters within the fault zone	Springs	Na-Cl-HCO_3 type TDS 700-23,000 mg/L, pH 5.0-6.6	38-78
Ethiopia	Filwuha (Kebede et al., 2008).	Ignimbrites layered with basalts	Graben	Mantle/metamorphic devolatilization	Deep faults	Faults	Local meteoric	Springs	Na-Cl-SO_4-HCO_3 type, TDS 2,820-3,640, pH 6.6-8.1	27.3-78.0
Uganda	Rwenzori (Kato & Kraml, 2005)	Banded gneiss, granite and schist at the volcanic center, with the topographic highs composed of amphibolites, hornblende, gabbros and metasediments. Tufa deposition at surface	Area of crustal uplift and volcanism.	Magmatic and carbonate dissolution	Deep Faults	Faults	Local meteoric	Springs	Cl-SO_4-HCO_3 type TDS 1,790-8,460 mg/L, pH 7.2-8-7	25-94

3.4. Summary of tables

To summarise the results obtained, the characteristics defined can be divided into universal features, i.e. those which appear in all the system types, and the Type-specific features.

Universal features:

- The recharge of CO_2-rich mineral systems is in the vast majority of cases meteoric, with water infiltrating preferentially on elevated topography, and entering the system through faults or fractures present in the geological formations;
- The waters of these systems discharge as springs, and in some cases from boreholes used to access the water at depth;
- Following the definitions of CO_2-rich mineral water (Barnes et al., 1978), the mineralisation (TDS) of these waters is over 1,000 mg/L;
- The tectonic structure of these systems is generally a basin-like structure, with a lower topography area where the waters discharge, and topographic highs which provide the recharge location(s);
- Although in some cases the presence of CO_2 derived from carbonate dissolution is noted , the most dominant origin of the CO_2 gas is of mantle/metamorphic devolatilization;
- Following this, in order to come into contact with the CO_2 at depth deep faults are required to provide the flow paths for water and gas, a feature seen in almost all the studied systems;
- In systems with a range of discharge temperatures in different springs, the hotter springs have attained a greater circulation depth than the colder waters.

Features characteristic to type:

- Type 1
  - Granite dominated geology;
  - CO_2 from the mantle/metamorphic devolatilization
  - Na-HCO_3 type waters dominant, pH ~6.5;
  - Flow paths (water) – fractured granite.
- Type 2
  - Geology – Sedimentary dominated (limestones, sandstones, carbonates), travertine deposition at surface;
  - Thick (>4 km) aquifers;
  - Ca-HCO_3-type waters dominant, pH 6.5-7;
  - CO_2 from carbonate dissolution
  - Flow paths from faults and fractures

- Type 3
  - Volcanic and metasedimentary complexes;
  - Volcanic geomorphology with active or ancient volcanism;
  - CO_2 from the mantle/metamorphic devolatilization;
  - Travertine/tufa deposition at surface;
  - Elevated Cl^-, SiO_2 and SO_4^{2-}, higher discharge temperatures (in comparison to Type 1 and 2), pH 6.5-8.4;
  - Flow paths (water) – fractures, porous volcanic rocks/features (lava tubes, etc.).

These features listed above can be summarised in Table 4.

Table 4 - 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	$Na\text{-}HCO_3$
Type 2	Sedimentary rocks	Thick sedimentary aquifers. Basin/graben.	Mantle/ metamorphic devolatilization/ carbonate dissolution	Deep faults/ fractured carbonate lithologies	Fractures and faults	Meteoric	Springs	$Ca\text{-}HCO_3$
Type 3	Volcanic and metasedimentary complexes	Volcanic (active or ancient)	Mantle/metamo rphic devolatilization	Deep faults	Fractures and faults	Meteoric	Springs	$Na\text{-}Cl\text{-}HCO_3$ $Cl\text{-}SO_4\text{-}HCO_3$

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

The conceptual model of CO_2-rich mineral water systems (Figure 18) 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 dissolution 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^{2+} 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 and 6. Na-HCO_3 type. Similar to Spring 4, water of Springs 5 and 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 (Section 3.6-3.7), Spring 5 is shown to have a lower TDS than Spring 6.

Travertine deposition is shown in hot Spring 4, and tufa deposition in the colder temperature calcium-rich Spring 1. In the studies assessed, examples of travertine deposition like that of Spring 4, include Kayseri (Afsin, 2006), Copland, (Cox et al., 2015). North Argentinean Andes (Gibert et al., 2009), and the Peruvian Andes (Newell et al., 2015). All discharge at high (>30°C) temperatures. A tufa is the low-temperature expression of a travertine and examples of tufa deposition described previously include the Type 2 Huanglong (Yoshimura et al., 2004) and Xiage (Liu et al., 2000) systems in China, and the Type 3 Rwenzori system of Uganda (Kato & Kraml, 2005), all with springs which issue at low (<30°C) temperatures.

The geochemical-end members of each spring have been chosen as the most common or most important issues defined in each type. In each system type, almost all geochemical facies displayed on the conceptual model appear due to the complexity of each system. However, with the aim of creating a simplified conceptual model which clearly classifies different types of springs, the main geochemical signatures which define the type were chosen.

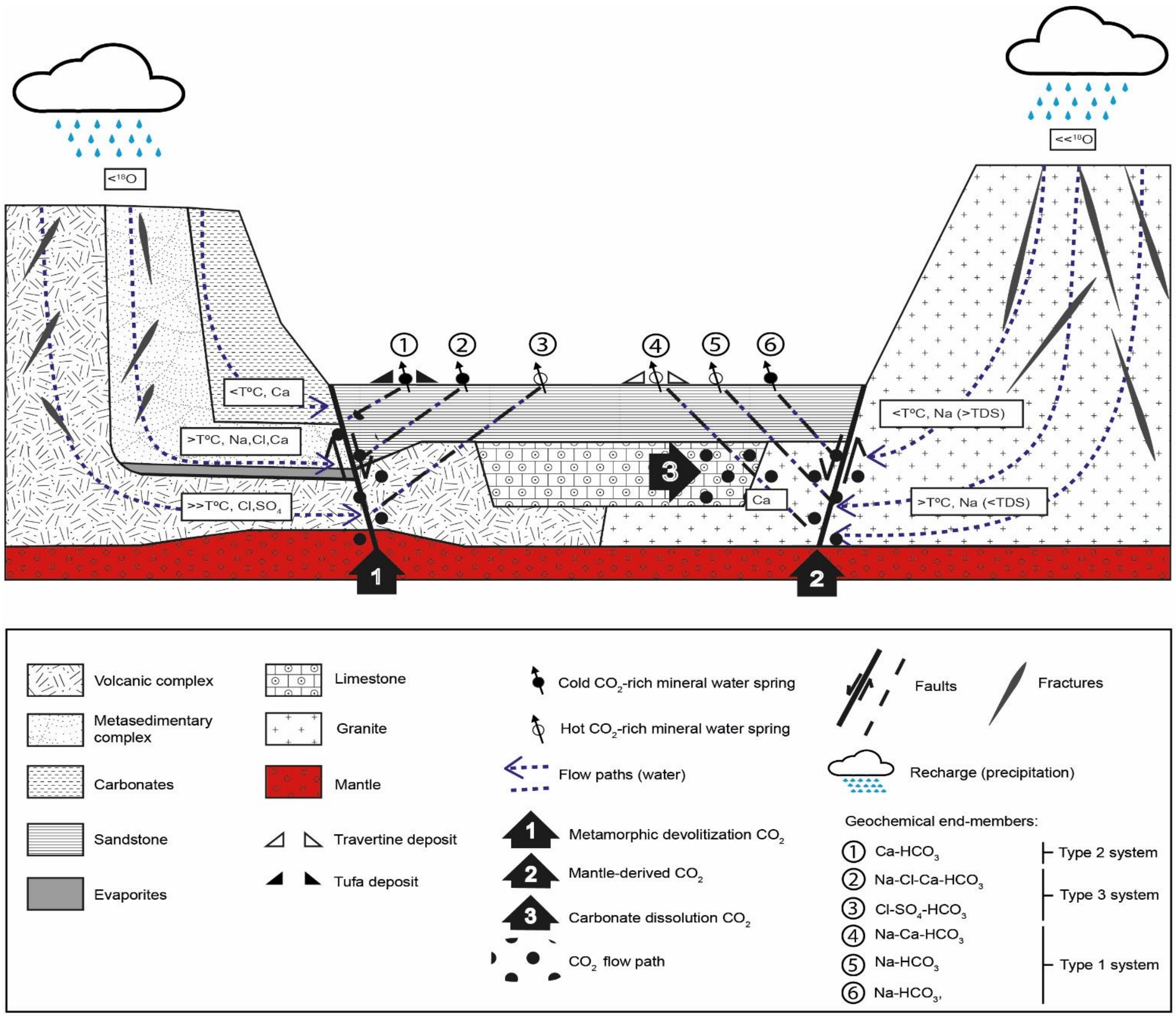

Figure 18 – Comprehensive conceptual model of CO_2-rich mineral water systems

3.5. Peculiar signatures

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 Chapter 3. 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, and the reactions described in Section 2.4 are important factor in the high TDS values observed in CO_2-rich mineral waters, particularly those in the Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas region, as granite rich in Na-plagioclase is abundant where the springs issue (Marques et al. 1998, 1999).

The connection between an increased level of CO_2 in water and a higher level of mineralization in mineral water is a relatively recent discovery (Greber, 1994), and a synopsis of the systems which display this phenomenon has until now not been done.

To further solidify the theory that the reason for the peculiar signatures of Vidago-Pedras Salgadas mineral waters compared to Chaves thermal waters is due to this elevated interaction of water, CO_2 and rock at low temperatures, a summary of the systems found in this study which display these signatures has been made. This summary includes:

- Hot and cold CO_2-rich mineral waters emerging in the same system or region, with the cold waters displaying similar or higher levels of mineralization compared to the hot waters;
- Hot and cold waters emerging in similar geological and tectonic settings within the region;
- Similar recharge source at similar altitudes (meteoric) and circulation pathway (both hot and cold waters pass through similar lithologies), but not necessarily depth;
- Ideally, a Type 1 system, with Na-HCO_3 water emerging in granite, in a graben setting.

The following section (Section 3.6) describes CO_2-rich systems found in this study that display these signatures, and which fulfill some, if not all the above characteristics.

3.6. Examples of the peculiar signatures

Kayseri, Turkey

Springs located in the Kayseri region (previously described in Section 2.3) display the trend of TDS decrease of CO_2-rich thermal waters decreasing with temperature increase.

Figure 19 shows the location of the springs YMS, ACMS and BTMS. These springs all emerge in what could be considered the same (YMS and ACMS), or geologically/geomorphologically similar neighboring system (BTMS), all located in the Sultansazlıgı depression. The waters are located within a confined metacarbonate aquifer (Afsin, 2006).

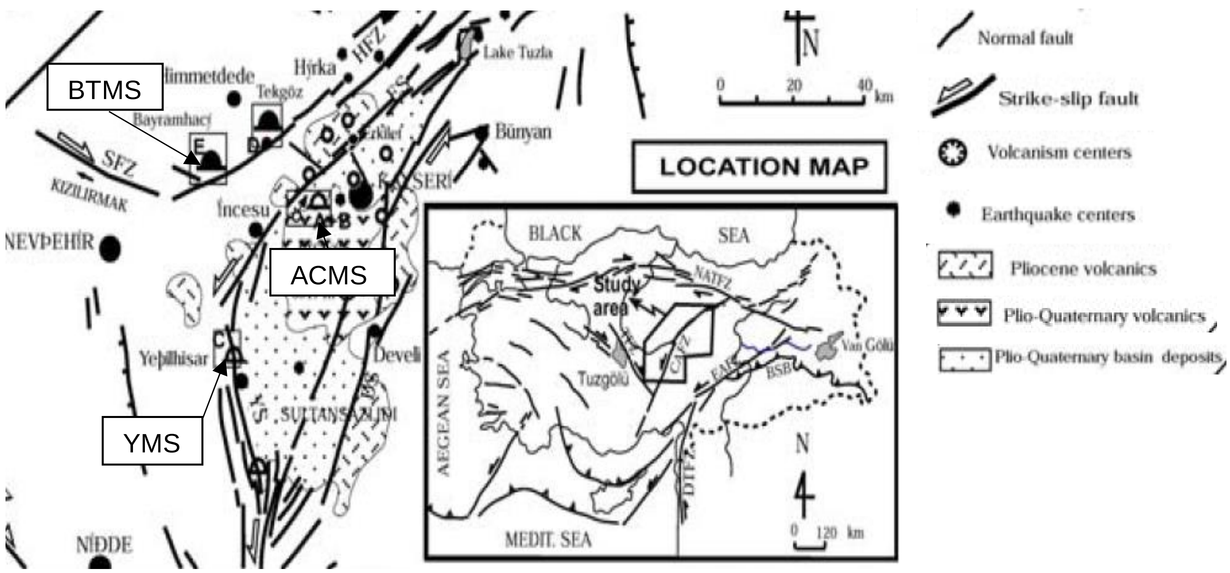

Figure 19 - Location map of the Kayseri region (Afsin, 2006)

The cold CO_2-rich springs of YMS and ACMS show a TDS of 5,600 – 14,600 mg/L and a temperature between 13 and 22ºC. In comparison, the hot (45.0-46.5ºC) CO_2-rich springs of BTMS show a TDS of 1,640 mg/L. A summary of the geochemistry of these springs can be seen in Table 5.

Table 5 - Geochemical signatures of the YMS, ACMS and BTMS CO_2-rich springs of the Kayseri region, Turkey (Afsin, 2006)

Springs	YMS	ACMS	BTMS
Temperature (ºC)	13-16	20-22	45.0-46.5
pH	6.3-6.8	6.3-7.8	7.1-7.3
TDS (mg/L)	5,600-8,750	9,400-14,600	1,058-1,640
Water type	$Na\text{-}Mg\text{-}Cl\text{-}HCO_3$	$Na\text{-}Cl\text{-}HCO_3$	$Ca\text{-}Na\text{-}HCO_3\text{-}Cl$

Isotopic data (^{18}O) shows that all three waters have a similar recharge altitude and are meteoric in origin, with the order of shallow to deep circulation being YMS, ACMS, BTMS. It is possible to conclude that the increased water-rock interaction of CO_2-rich water at low temperature is a key factor in the higher mineralization of YMS and ACMS compared to YMS (Afsin, 2006).

Nevesehir, Turkey

The springs of Nevesehir (Figure 20) emerge in an aquifer confined by marble basement rocks (Afsin, 2002). The location of these springs is very close to the previous case study (Kayseri), with the BTMS spring again featuring in this case to show an example of the TDS-temperature correlation.

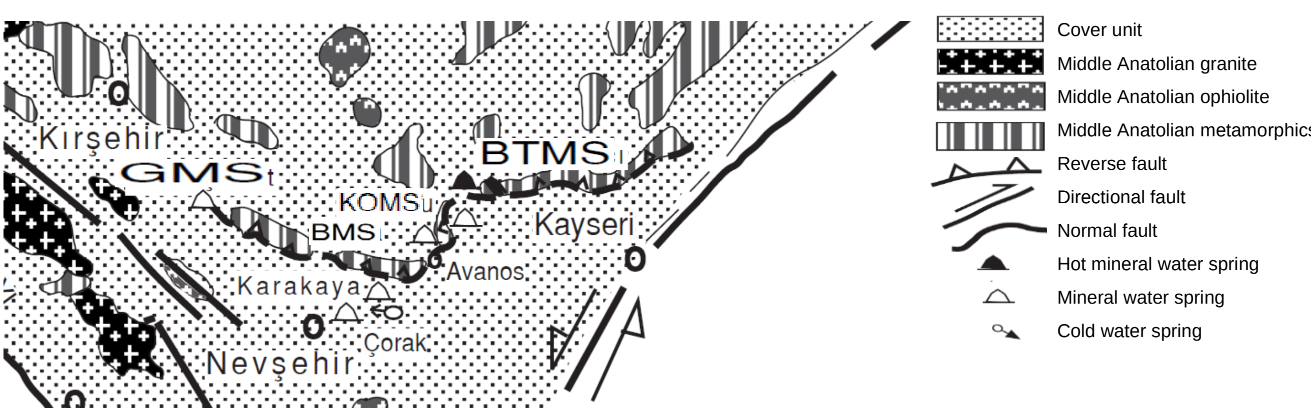

Figure 20 - Location map the Nevesehir region, Turkey (Afsin, 2002).

Environmental isotope ($\delta^{18}O$, $\delta^{2}H$, ^{3}H) and water chemistry analyses give a meteoric origin for the springs. The groundwaters are deeply circulated, with the KOMS and BTMS showing similar values for all environmental isotope values (Table 6).

Table 6- Geochemical signatures of the GMS, BMS, KOMS and BTMS CO_2-rich springs of the Nevesehir region, Turkey. ($_1$ = sample taken in 1998, the rest were taken in 1999 (Afsin, 2002).

Spring	GMS	BMS	KOMS	$KOMS_1$	BTMS
Temperature (ºC)	13-21	15.5	15.5	19	43
pH	6.39-6.7	6.46	6.19	7.1	7.1
TDS (mg/L)	2,710-3400	5,200	2,230	6,300	1,610
$\log_{p}CO_2$	-0.751 - 0.075	-0.097	-0.007	-0.613	-0.492
$\delta^{18}O$ (‰)	-10.5		-10.43		-10.2
$\delta\,^{2}H$ (‰)	-80.26		-78.86		-78.35
^{3}H (TU)	0.6±0.80		0.1±0.80		0±0.80
Water type	$Ca\text{-}HCO_3$	$Ca\text{-}Na\text{-}HCO_3$	$Ca\text{-}Na\text{-}HCO_3$	$Ca\text{-}HCO_3$	$Ca\text{-}Na\text{-}HCO_3$

Table 6 shows that the cold CO_2-rich (13-21 ºC) GMS, BMS and KOMS springs, which emerge in the same confined aquifer as the hot (43 ºC) BTMS spring, have much higher TDS (> 1,000 mg/L). A possible caveat is the significant yearly variation in the composition of the KOMS spring, however despite the variation the difference in TDS and temperature remains (Afsin, 2002).

Kuzuluk, Turkey

The springs of the Kuzuluk system emerge in a graben containing granite overlain by volcanic tuffs. The Kuzuluk system is best summarized in the hydrogeological circulation model by Greber (1994) (Figure 21).

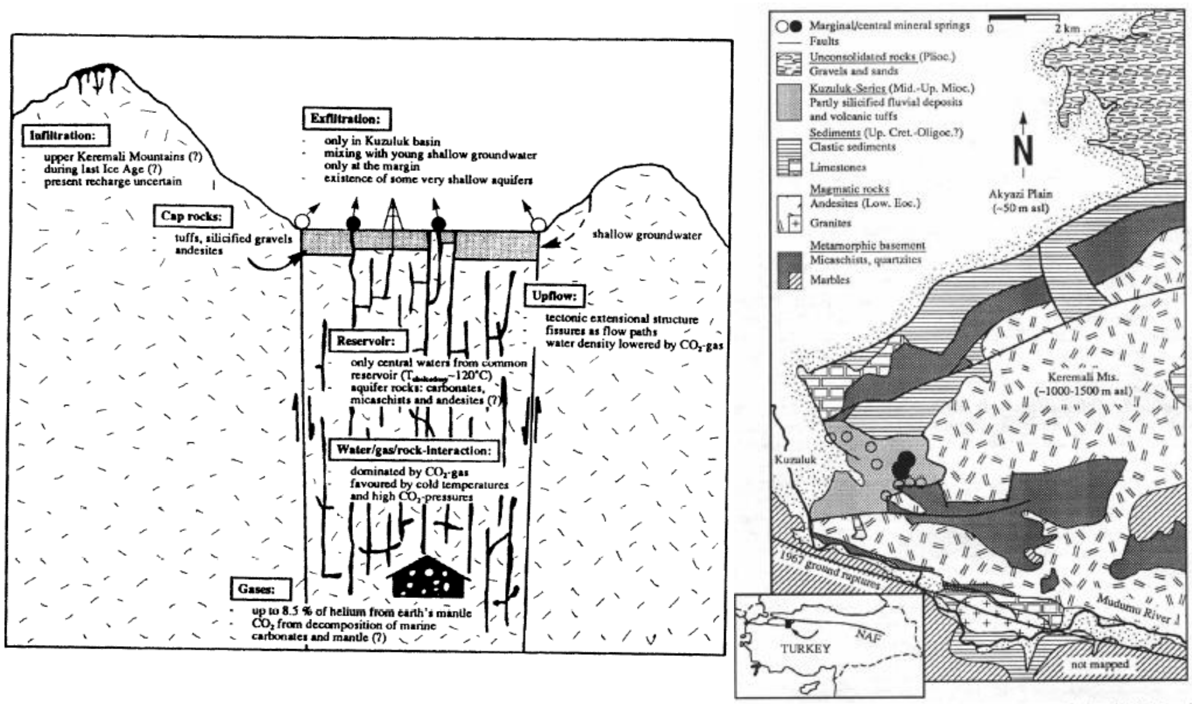

Figure 21 - Hydrogeological conceptual model and location map of the Kuzuluk system (Greber, 1994)

The system is recharged by meteoric water which infiltrated in the mountains bordering the graben, with the water having a long residence time at deep levels where low-temperature CO_2-enchanced water-rock interaction occurred after the water obtained CO_2 at great depths from the decomposition of marine carbonates, as well as possible mantle origin. The central waters have a common origin and are heated to higher temperatures than the marginal waters possibly due to the presence of a central reservoir of fractured carbonates, micaschists and andesites. The colder temperatures of the marginal waters may be due to a shallower circulation path (Greber, 1994).

The two types of CO_2-rich spring waters are marginal spring water and central spring water, geochemically summarised in Table 7. The marginal water is colder than the central (24.2ºC and 40.8ºC respectively) and displays higher level of mineralisation (4,110 compared to 3,200 mg/L) as well as a slightly lower pH.

The increased mineralization seen in the colder marginal waters compared to the hotter central waters is proposed by Greber (1994) to be due to the increased water-rock interaction favored by low temperatures and high CO_2 pressures.

Table 7 - Geochemical signatures of the CO_2-rich springs of the Kuzuluk system, Turkey (Greber, 1994)

Springs	Marginal	Central
Temperature (ºC)	24.2	40.8
pH	6.3-6.4	6.5-7.0
TDS (mg/L)	4,110	3,200
Water type	Na-(Ca)-(Mg)-HCO_3-Cl	

Tsamda and Gondasampa, Nepal

CO_2-rich mineral springs of Tsamda and Gondasampa (described in Section 3.2) emerge in a limestone filled graben and show two distinct types of CO_2-rich mineral waters in terms of TDS and temperature. The geological and geomorphological setting in which these springs emerge can be seen in Figure 22.

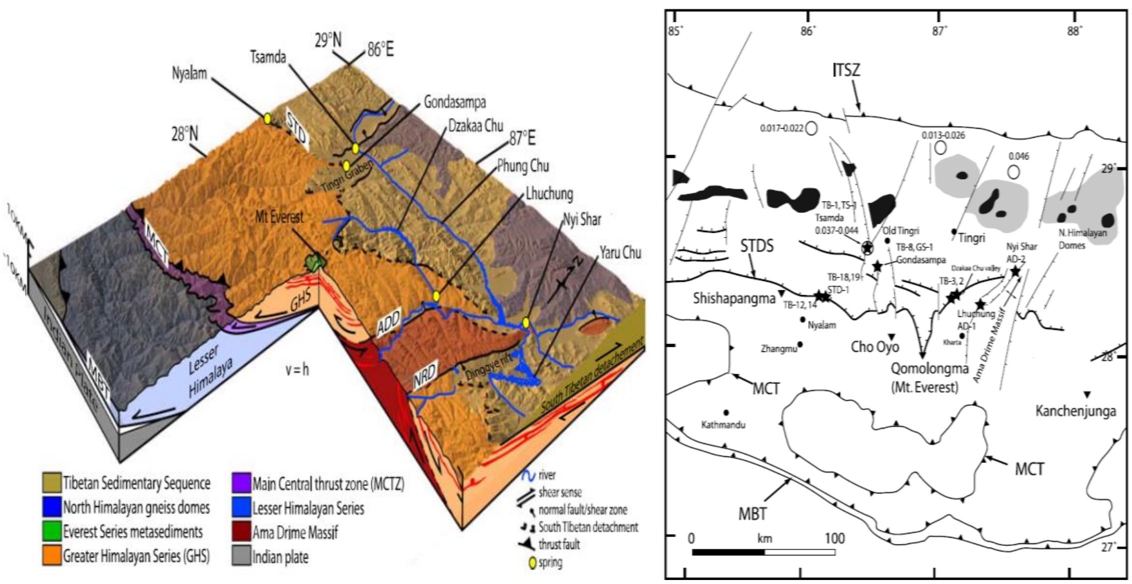

Figure 22 - Geomorphological model and location map of the Tsamda and Gondasampa springs, Nepal (Evans et al., 2008)

The colder (19.2-24.2ºC) Gondasampa CO_2-rich mineral waters show almost double TDS compared to the warmer (42.6ºC) Tsamda CO_2-rich mineral waters, with the geochemical features of each individual spring shown in Table 8.

Table 8 - Geochemical signatures of the TB-1, TS-1, TB-8 and GS-1 CO_2-rich springs

Springs	**TB-1 (Tsamda)**	**TS-1 (Tsamda)**	**TB-8 (Gondasampa)**	**GS-1 (Gondasampa)**
Temperature (ºC)	42.6	33.7	24.5	19.2
pH	6.3	6.4	6.8	6.7
TDS (mg/L)	957	1,275	1,720	1,850
Water type	Na+K-HCO_3			

Both springs have similar circulation depths, with the Tsamba springs probably having a slightly deeper circulation depth to obtain the higher temperature (Evans et al., 2008). As the springs are geochemically of the same type, the controlling factor on the TDS difference is likely due to the water-rock-CO_2 interaction at a lower temperature environment, in the case of the Gondasampa springs.

Catalonia, Spain

These CO_2-rich mineral water springs are located in the La Selva Graben and surrounding areas that form part of the Catalan Coastal Ranges. This Alpine range is formed of horst of Hercynian granite basement rocks and grabens filled with Neogene sediments, with different groups of springs issuing in these horsts and grabens (Pique et al., 2010). Faults related to these tectonic structures form the flow paths for the springs as well as the CO_2, and the recharge is from local meteoric waters.

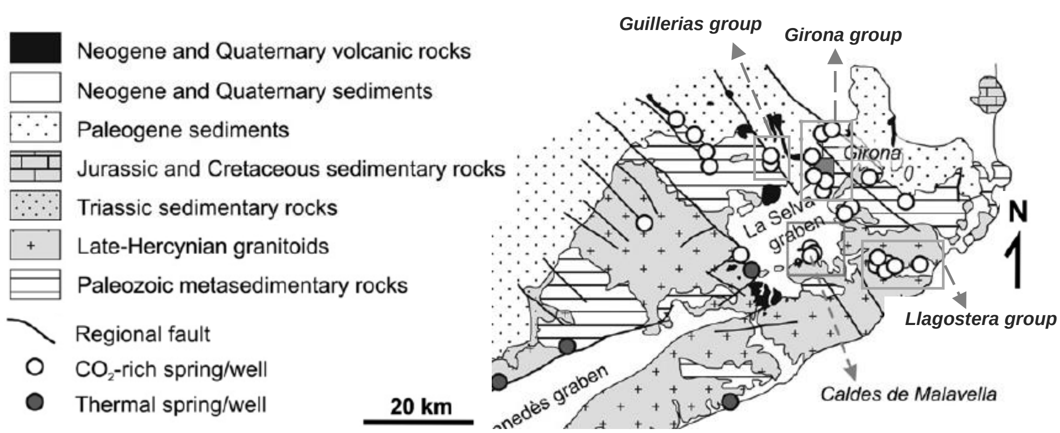

Figure 23 – Location map of the La Selva graben springs (Pique et al., 2010)

The springs in this region have been divided into two facies based on their geochemistry; a Na-rich water and a Ca-rich water. A higher mineralisation is seen in the Na-rich waters compared to the Ca-rich waters, due to a deeper circulation of the Na-rich waters (Redondo & Yelamos, 2000).

There are four groups of CO_2-rich springs defined in this study, with both hot (Caldas de Malavella) and cold (Llagostera, Guillerias and Girona groups) temperatures, with the locations displayed in Figure 23.

- Llagostera group; located in the southern border of the Gabarras horst, these cold (14ºC) springs issue within Late-Hercynian granitoids with a high (up to 4,260 mg/L) TDS, pH of 6.0-6.5, and display both Ca-rich and Na-rich facies. The Ca-rich springs show a markedly lower mineralisation compared to the Na-rich spring (1,900 mg/L compared to 4,260 mg/L).
- Guillerias group; these CO_2-rich cold (14-17ºC) spring waters are highly mineralised (5,970-6,140 mg/L), with a pH of 6.0-6.5, an Na-rich facies, and emerge in the northern horst of the La Selva graben.
- Girona group; situated on the eastern limit of the Gabarras horst, these springs emerge along a large bounding fault. This group contains both Ca-rich and Na-rich cold (14-17ºC) springs, with the Na-rich springs showing a higher mineralisation e.g. the Ca-rich springs has a TDS of ~2,100 mg/L whereas the Na-rich has a TDS of ~3,000 mg/L.
- Caldas da Malavella; the hot (51ºC) springs are of the Na-rich type and display a similar geochemical composition (TDS and pH) compared to the cold Na-rich springs in the region. They emerge along the southern boundary La Selva graben, passing through the crystalline basement and the overlying sedimentary unit.

The geochemical features of these springs are summarized in Table 9.

Table 9 - Geochemical signatures of the Llagostera, Guillerias, Girona and Caldes de Malavella groups (Pique et al., 2010, Redondo & Yellamos, 2000)

Springs	**Llagostera group**	**Guillerias group**	**Girona group**	**Caldes de Malavella**
Temperature (ºC)	~14	14-17	14-17	50.5
pH	6.0-6.5	6.0-6.5	5.5-6.3	6.6-6.70
TDS (mg/L)	1,904-4,260	5,970-6,140	2,000-3,500	3,500-5,570

Remarkably, the hot Na-rich springs of Caldas de Malavella show a similar, or in some cases lower level of mineralization compared to the colder Na-rich springs. Despite the much higher temperature, it appears that given the similar geology, geomorphological setting, and geochemical facies (Na-HCO_3), the higher or similar TDS seen in the colder waters maybe be due to the CO_2 content and the increased water-rock interaction at low temperatures, particularly in granites.

Jiangxi Province, China

The Jiangxi Province is situated in the Southeastern China Active Geothermal Zone and is home to many thermal and mineral springs, issuing in granite and acid volcanic rocks. There are two types of mineral waters in this region, CO_2-rich hot and cold springs and nitric thermal waters (Sun et al., 2017). The springs used for this study show a range of geochemical facies; Na-rich, Ca-rich, and SO_4-rich CO_2 springs, with the majority being the Na-rich type (Sun et al., 2017). Figure 24 shows a location map for this Jiangxi province and the distribution of the springs in the region.

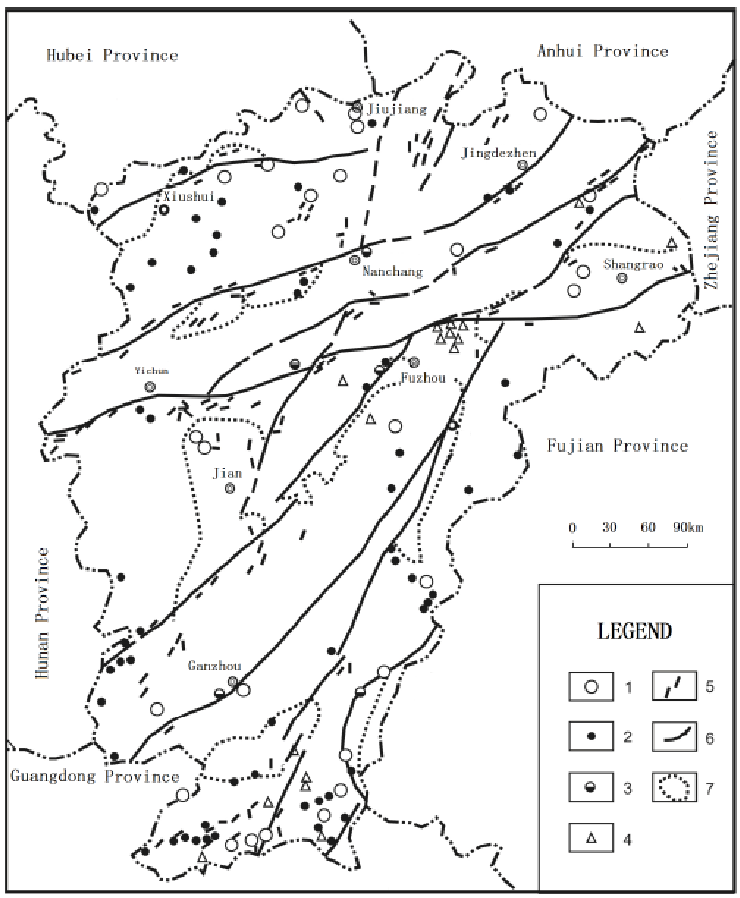

Figure 24 - Location map of the Jiangxi province, China (1-epicenter; 2-hot spring; 3-thermal water bore hole; 4-meozoic crater; 5-intrusive rock; 6-active fault; 7-red basin.) (Sun et al., 2010).

A study by Sun et al. (2017) on the relationship between the total mineralisation and temperature of these springs showed an inverse correlation between the two factors in the CO_2-rich mineral water springs, where higher temperature springs showed a lower TDS. This relationship can be seen in Figure 25.

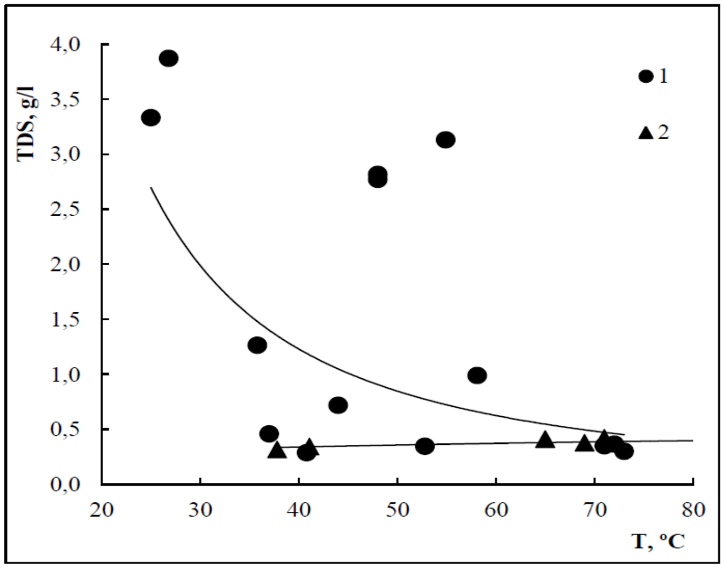

Figure 25 - Dependence of TDS on temperature of thermal waters (1 – carbon dioxide thermal waters; 2 - nitric thermal waters) (Sun et al., 2017)

The correlation seen in this figure is another key example to show the increased water-rock interaction at low temperatures of CO_2-rich waters. The Na-HCO_3 springs show a much higher mineralisation (up to 3,870 mg/L) compared to the other types, which mostly have less than 1,000 mg/L TDS. This may be due to the granitic geology present and the preferential hydrolysis of Na-feldspar (plagioclase) seen in CO_2-rich waters, as described in Section 3.6.

3.7. Conclusion of summary

The hydromineral systems shown in this summary all display to some degree a higher water-rock interaction in cold CO_2-rich waters in comparison to hot or warmer CO_2-rich systems. 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 geochemical reactions described in Section 2.4. 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 hydrolyses.

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3.8. 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 the conceptual model of region (Figure 26).

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 the figure.

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 (76ºC) are those with a higher discharge temperature due to the proposed presence of a low-temperature (≈120ºC) 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 displaying 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.

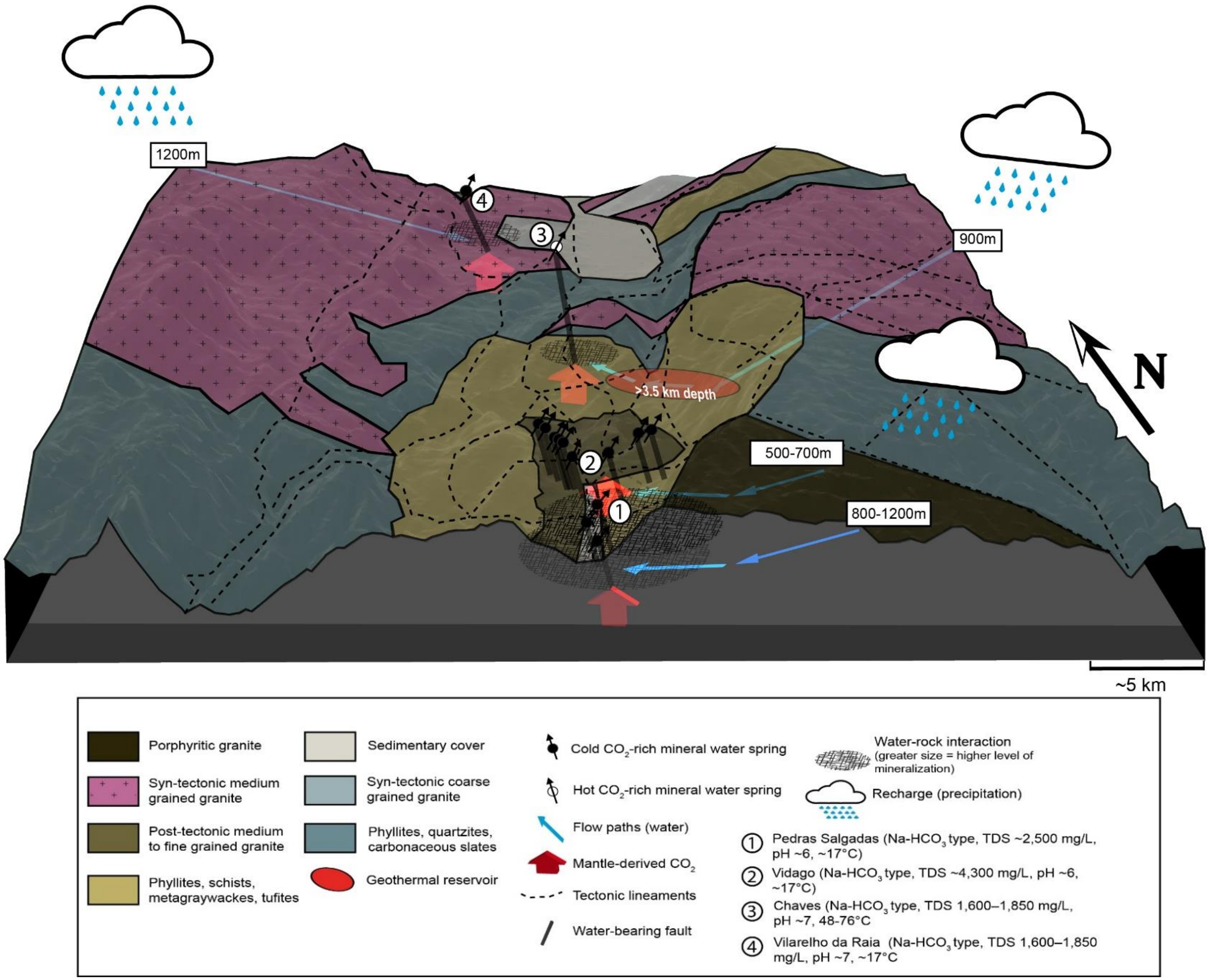

Figure 26 - Conceptual model of the Vilarelho da Raia-Chaves/Vidago-Pedras Salgadas region. Data taken from Marques et al. (2012)

4. Discussion

The comprehensive conceptual model is a form in which to display the different environments that CO_2-rich mineral waters emerge in and the main characteristics they show. These features have been obtained from a wide-ranging literature review of low-temperature CO_2-rich thermal and mineral water systems worldwide, with each key feature (geology, geomorphology, geochemistry, flow paths for CO_2 and water, and isotopic data attempted to be found in each system. The results of this review were summarized in terms of these features into the tables of Chapter 3, with these systems divided into three categories based on the dominant geological setting present in the system. Using the tables, the key characteristics that each system display, as well as features that all systems display were defined, with these features used to form the global conceptual model.

This model of low temperature CO_2-rich mineral water systems is the first that has been produced of its kind. Previous literature from Barnes (1978) produced a summary of the occurrences of CO_2-rich water systems worldwide, however the study was more widespread, and not focused on a certain type (i.e. low temperature), and was without a conceptual model.

The conceptual model is an effective way in which one can easily see the characteristics of the waters that emerge in a hydrogeological system and how they obtain these characteristics, however the inherent complexity of this type of system makes generalisations of the nature of these systems difficult. These systems can have a wide variety of geological settings within the same system (types 1-3), and the size of the system can vary from an area of a few kilometers to 100's, with the difficulty of a boundary definition between different systems.

Through this study of CO_2-rich mineral water system worldwide, the reasons behind the peculiar signatures seen in the Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas systems could be defined with a strong degree of certainty. Through the comprehensive review of the systems, ones which displayed the phenomenon of the inverse correlation between TDS and temperature were further studied (Section 3.6). The correlation was seen in systems which fall into the three different categories (Type 1, 2 and 3), however they were mostly Na-rich waters within the Type 1 category, which interacted at some stage with granitic rocks, and the majority were in a similar geomorphological setting (graben).

In previous works (Stumm & Morgan, 1981, Greber, 1994), this cause of this phenomenon has been defined as due to the increased water-rock interaction at low temperatures due to the increased solubility of CO_2 at lower temperatures. This explanation is accepted as a possible reason for higher TDS in the lower temperature CO_2-rich waters of a hydrogeological system, however a summary of the natural occurrences of this phenomenon, where both hot and cold CO_2-rich waters issue in the same or similar system had not been made.

The summary of the natural occurrences of these peculiar signatures allows for a more concrete establishment of a chemically well-known phenomenon (Stumm & Morgan, 1981) occurring in the natural world, and with this allows the interpretation of the main culprit of the disparity of TDS between the cold CO_2-rich waters of Pedras Salgadas and Vidago, and the hot CO_2-rich waters of Chaves to be the elevated water-rock interaction of CO_2-rich waters at low temperatures.

The conceptual model of the Vilarelho da Raia–Chaves/Vidago-Pedras Salgadas systems allows a clear visualization of the four separate systems, and clearly displays the key features present (e.g. recharge, discharge, flow paths for CO_2 and water, geology, geomorphology, geochemistry).

The limitations of this model are that it is only a graphical depiction, and lack technical detail, for example, the depth of circulation for the Pedras Salgadas, Vidago and Vilarelho da Raia springs, as well as the specific geochemical features of each individual spring (i.e. temperature, TDS, pH), and the subsurface geology. The reason for these omissions is that the information for the estimated depth of circulation for these springs is not available. Alongside this, it is not necessary for the features that are aimed to be shown in the model, only that the circulation depth for the waters of these springs is shallower than the Chaves springs. The specific geochemistry of the individual springs within each system are not displayed, as the general geochemical features of each system are sufficient to display the contrasting geochemistry of each system (i.e. Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas).

Future work could involve the further elaboration of the conceptual model of CO_2-rich mineral water systems, with further research into different systems worldwide to discover new features or further develop the key characteristics of the types of CO_2-rich mineral water systems. A study focusing on CO_2-rich mineral waters which emerge in higher temperatures systems could be made, to where the different water-rock interaction processes that occur in these systems, as well as the variety of geological setting in which they issue, could be defined.

5. Final Remarks

This dissertation involved the compilation of a variety of important information on CO_2-rich thermal and mineral water 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 categorization 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
- Type 3 - dominated by volcanic and metasedimentary rocks

This categorization, with the accompanying tables, can allow for simplified classification of a CO_2-richthermal and mineral water system. The synoptic tables can be used to display the key features that a study of a hydrogeological system should aim to define and classify the system. These features are:

- Geology
- Tectonic structure
- Origin of CO_2
- Flow paths of CO_2
- Flow paths of water
- Recharge
- Discharge
- Geochemistry (dominant anions and cations, TDS, pH)
- Isotopic signatures

This classification system 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 elaborated. 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 value 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.

This compilation of information and comprehensive conceptual model can be used as a base to help define a hydrogeological system, and with further work to help refine the model to create more accurate categorizations using additional studies of CO_2-rich water systems, this model can be an important tool for the future of hydrogeological studies.

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