

Article

Contributions for the Understanding of the São Pedro do Sul (North of Portugal) Geohydraulic and Thermomineral System: Hydrochemistry and Stable Isotopes Studies

Solange Almeida ^{1,*} , Luís Gomes ^{1,2}, Alcino Oliveira ^{3,4}  and Paula Carreira ⁵ 

¹ Departamento de Engenharia Civil e Arquitetura, Faculdade de Engenharia, Universidade da Beira Interior, R. Marquês de Ávila e Bolama, 6201-001 Covilhã, Portugal; limg@ubi.pt

² Geobiociências, Geoengenharias e Geotecnologias (Geobiotec), Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

³ Departamento de Geologia, Escola de Ciências da Vida e do Ambiente, Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5001-801 Vila Real, Portugal; soliveir@utad.pt

⁴ Centro de Geociências (CGeo), Universidade de Coimbra, Rua Sílvio Lima, Universidade de Coimbra—Polo II, 3030-790 Coimbra, Portugal

⁵ Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, ao km 139.7, 2695-066 Bobadela LRS, Portugal; carreira@ctn.tecnico.ulisboa.pt

* Correspondence: sms.almeida@netcabo.pt

Abstract: São Pedro do Sul thermomineral aquifer system is located in the North of Portugal. Hydrogeochemistry and isotopic studies were conducted in order to improve knowledge of this groundwater system, known since ancient Roman times for their therapeutic properties. One thermomineral spring (NT) and three boreholes (AC1, SDV1 and SDV2) have a mean temperature around 68 °C. Currently, these waters are mainly used in thermal spas and for geothermal energy supply. Major cations and anions were used to identify and characterize different water types and sub-systems. Stable isotopes composition, $\delta^{18}\text{O}$ and $\delta^2\text{H}$, have been used to determine the origin and have been used as a first approach to estimate the mean preferential recharge altitude of thermomineral water. The results suggest a single aquifer system with a relative composition of cations and anions and similar mineralization values. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values indicate a meteoric origin with no significant evaporation before infiltration. Besides, the isotopic composition points to recharge areas located at altitudes of about 1000 m a.s.l. This suggests a recharge area in the Freita/Arada mountains located NW of the thermomineral poles.

Keywords: thermomineral water; hydrogeochemistry; stable isotopes (^{18}O and ^2H); water classification; recharge altitude; Portugal



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1. Introduction

Since the Roman occupation, spas have been a tradition in Portugal, owing mainly to the great diversity in the chemistry of its natural mineral waters, which reflect the geological and structural diversity of the territory. The research region is located near the village of São Pedro do Sul, district of Viseu, central Portugal (Figure 1), where this thermomineral aquifer system represents one of the most important sites of thermomineral waters of Portugal. The economic importance of spas for regional development can be inferred by the number of visitors every year to these facilities. According to [1], in 1998, the number of spa users amounted to 20,012. Due to the above reasons (health and economics), protection areas are of vital importance to guarantee the quality of the mineral water and to prevent contamination problems.

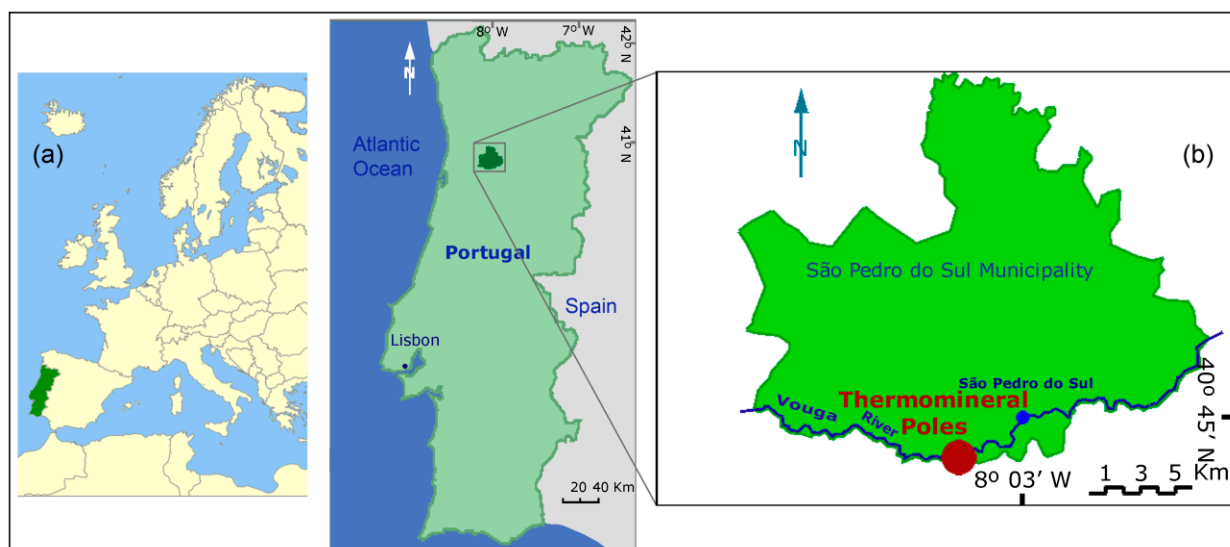


Figure 1. (a) Geographic location of Portugal in Europe (Adapted from: <https://commons.wikipedia.org> (accessed on 3 April 2016)). (b) Geographic sketch location of the thermomineral poles of São Pedro do Sul.

Two mineral water producing poles can be recognized within the area of the study at a distance of around 1.2 km from one another. Termas Pole consists of a bathhouse for medicinal treatments and a geothermal central for the heating of non-mineral waters for domestic use (heating and water supply). This area is supplied by the borehole AC1, with a 500 m depth, and by an ancient spring (Traditional Spring—NT, used for medical treatments since the Roman empire) which together produce, through artesianism, about 18 L/s at 67.6 °C [1]. According to these authors, a small mineral spring and two wells, the SDV1 with a depth of 216 m and SDV2 with a depth of 151 m, characterize the Vouga pole. The water flow of 1.5 L/s at a temperature of 67 °C, mainly produced from well SDV1, was used to heat greenhouses for banana and pineapple production until a few years ago.

The main goals of this investigation were to investigate the characterization of São Pedro do Sul mineral waters through an isotopic and hydrogeochemical approach. A hydrogeochemistry and isotopic study was conducted in order to improve knowledge about the São Pedro do Sul groundwater system: Major cations and anions were used to define different water types and to understand the water–rock interactions of thermal waters; the reservoir temperature was estimated using geothermometers from measured SiO_2 , K^+ , and Mg^{2+} chemical species. In addition, stable isotopes ^{18}O and ^2H were used as indicators of the origin of the thermal water and as a first approach to understanding the recharge areas of the thermomineral water. Numerous studies related to chemistry were performed by many scientists [2–12]. Besides, aspects of geology, hydrogeology, hydrochemistry of geothermal water in the study region were performed during the last decades through conference proceedings, scientific articles, theses and internal reports [3,5,13–20].

Among the frequently used techniques in hydrogeology to characterize aquifer dynamics, environmental isotopes such as ^{18}O and ^2H have been the most useful in terms of providing new insights to understand the changing aspects within aquifer systems, and they are sometimes used as a background tool in the development of conceptual models (e.g., preferential recharge altitudes). In the last decades, isotopic signatures of meteoric waters have become a key tracer, intensively used in hydrogeological studies as a basis for the elaboration of conceptual hydrodynamic models [4,6,21–31].

In most cases, groundwater recharge results from direct infiltration of precipitation (regional precipitation). In this case, groundwater samples will reflect the mean isotopic composition of the regional precipitation. If changes occur between the groundwater and precipitation, an explanation for this deviation should be sought, and different hypotheses

can be formulated, for example, recharge derived from a different source, either from regional precipitation, for example from surface water (rivers, lakes or dams) instead of precipitation; in this case, the groundwater will reflect the mean isotopic composition of the contributing source (river, lake or dam waters), or if evaporation occurs before infiltration, an enrichment in the isotopic composition will be noted.

For this purpose, water samples were collected from different water sources, with respect to different types of rocks and altitudes and were analyzed for important major parameters and isotopic data following standard test procedures. For this purpose, a total of 16 water samples (Figure 2) were collected from a cool spring in June and July 2016 in the surrounding area of São Pedro do Sul site, and a set of major cations and anions results obtained over nine years in NT, AC1, SDV1 and SDV2 was employed in the Piper trilinear diagram plot (Section 4.1). Conversely, 19 samples were used for the isotopic analysis with NT, AC1, SDV1 and SDV2 included (Figure 2). In order to achieve this objective, groundwater samples were collected and analyzed.

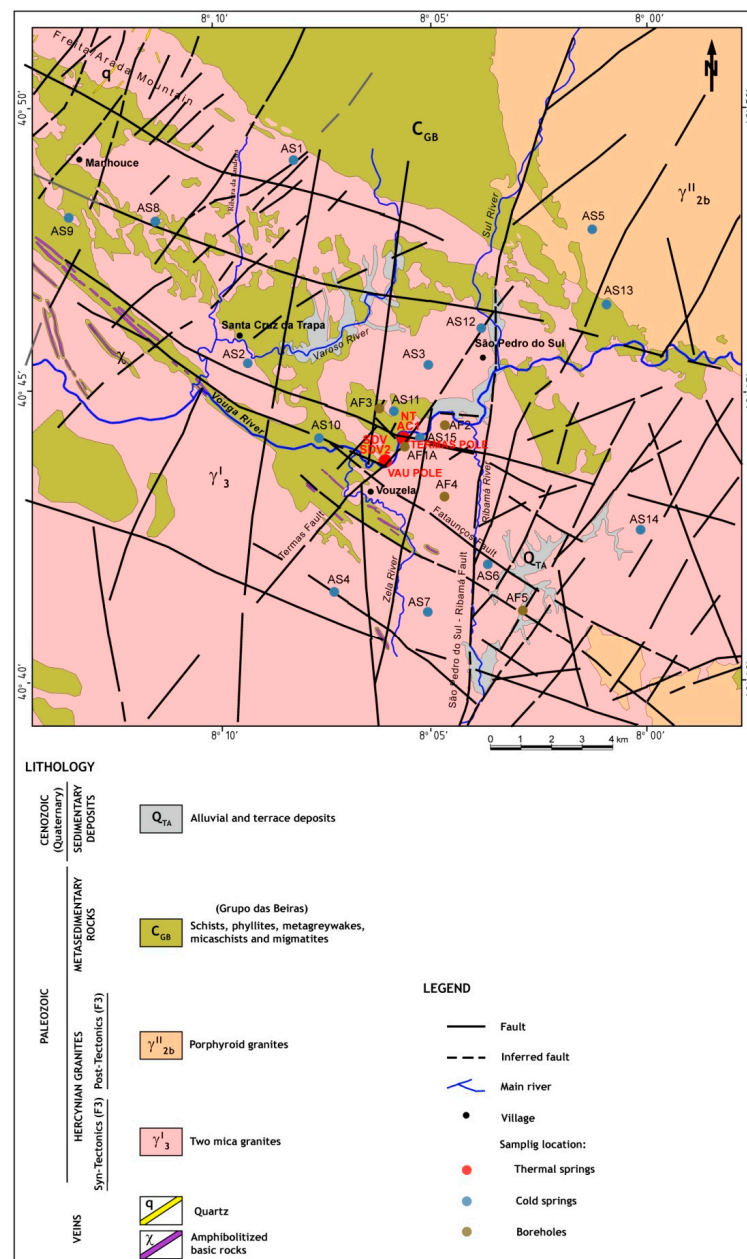


Figure 2. Simplified regional geological and structural map of the study area, with main lithology units, faults and sampling locations.

2. Geological and Hydrogeological Settings

The geological and structural regional map (Figure 2) was built by a combination of different data, which can be summarized in the following resources: geological map of Portugal, sheets 13-D—Oliveira de Azeméis, 14-C—Castro Daire and 17-A—Viseu, scale 1:50,000, as well as the written documents—Notícia Explicativa— which provides detailed and additional information about each geological map [32–37]; geological map of Portugal at 1:500,000 scale [38]; aerial and satellite images available on Google Earth; digital elevation model (DEM), produced from 1:25,000 Portuguese military topographic maps (sheets number 165, 166, 176 and 177) [39]; studies already performed in the area such as internal reports, geological and structural documents [14,17,40] and field geo-structural survey carried out for this work.

The São Pedro do Sul region is characterized by hercynic granite, emplaced between 290 and 321 Myr, in relation to the third phase of Variscan deformation (F_3) occupying extensive areas [19,32,33,35–38]. These hercynian granites can be separated into two outcrops: (1) Syn-tectonics granites in relation to F_3 Variscan deformation [40] peraluminous [41] with two micas. These batholiths occur throughout the Serra da Freita/Arada-São Pedro do Sul corridor, occupying a large area around São Pedro do Sul Thermal Poles (Figure 2). These granites have an anisotropic structure, with a NW–SE direction related to the deformation of the hercynian tectonic axes. (2) Post-tectonics granites in relation to F_3 Variscan deformation that are porphyroid granites composed mainly of biotite, quartz, microcline, plagioclase (andesine and albite) and few muscovite and occur mainly in the NE of São Pedro do Sul.

Metasedimentary rocks are present in the region, although with less importance than granitic rocks. These metasedimentary rocks consist of grey metaquartzites, with calcosilicated rocks layers, schist, phylites, mica schist and metagraywackes of the Cambrian age (and Upper Precambrian). These rocks are intruded by the hercynian granites and present a schist structure with a NW–SE direction.

Amphibolitized basic rock veins occur in metasedimentary rock levels according to the NW–SE orientation. Furthermore, quartz veins are found in association with both granitic and sedimentary rocks related to the NNE–SSW to NE–SW and NW–SE fault directions.

In addition, quaternary sedimentary deposits can be found in a few areas: fluvial terraces, mainly with gravel, are located between 100 and 200 m a.s.l.; alluvial, mainly with sand and gravel, are found in the Holocene floodplains.

The fault pattern of the regional complex is genetically correlated to the Hercynian orogeny and has been reactivated by neotectonic activity [20]. The São Pedro do Sul region appears to be highly faulted as indicated in Figure 2. This regional geological map shows three dominant fault families with orientations: (i) N–S to NNE–SSW; (ii) WNW–ESE to NW–SE; and (iii) NE–SW. The current regional tectonic stress field with maximum horizontal compressive stress trends from NW–SE to WNW–ESE [20] can promote depth fluid circulation from WNW–ESE to NW–SE faults.

Representing the region by a local scale (Figure 3), three main granite facies, which belong to the syn-tectonics granites, were identified in the São Pedro do Sul Thermal Poles area; namely [34,40], Vouzela granite, São Pedro do Sul granite and Fataunços granite. Vouzela granite is a monzonitic granite medium to coarse grained, formed mainly by quartz, albite-oligoclase, potassium feldspar, biotite and muscovite; São Pedro do Sul is a fine to medium grained granite composed mainly of microcline, plagioclase, quartz, muscovite and biotite; Fataunços is a granite close to granodiorite, fine- to medium-grained, with two micas. All these granites are slightly porphyroid textured.

From the structural point of view, the local geologic faults system is mainly represented by NNE–SSW, NE–SW and WNW–ESE structural directions, where, respectively, the São Pedro do Sul-Ribamá Fault, Termas Fault and Fataunços Fault are examples (Figure 3a). These hercynian fault systems are active today and represent tectonic structures with high regional importance. The regional or local fracture networks support the main fractured aquifer systems. Studies developed in the region [7,20] show that there are two types of aquifer systems associated with fractured granites and metasedimentary rocks. The shallow

cold aquifer systems occur throughout the region with lightly mineralized water, while a deeper aquifer system is characterized by higher temperature and strongly mineralized water, to which the thermal poles are closely linked. In addition, a close relationship between this aquifer and São Pedro do Sul-Ribamá Fault was identified. Differences in hydrochemical characteristics are included in Section 4 (Results and Discussion).

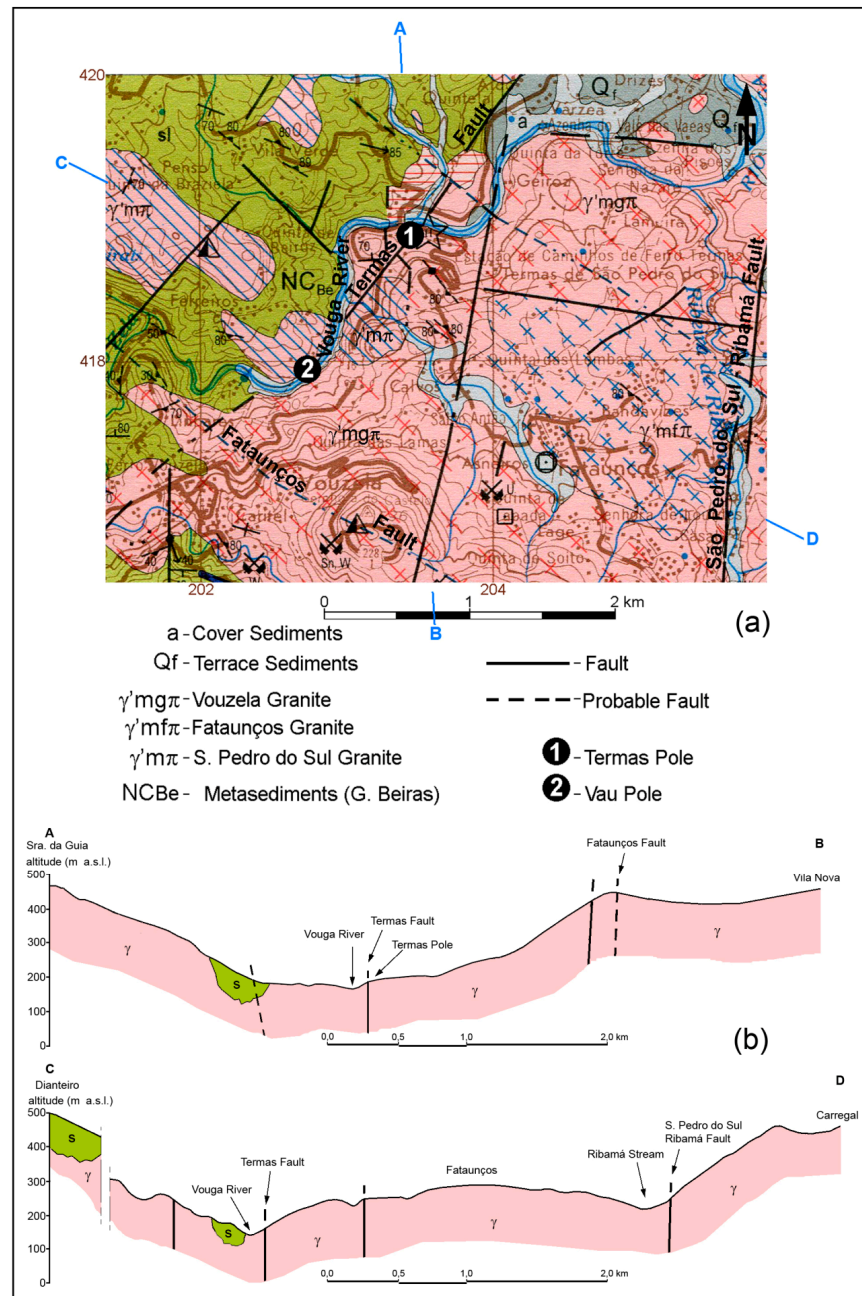


Figure 3. (a) Extract from the geologic map of Portugal, 17-A sheet (Viseu), 1:50,000 scale, with the localization of the São Pedro do Sul thermomineral poles; (b) A–B and C–D cross sections.

Pereira and Ferreira [40] studied the importance of the structural control of the thermomineral springs at São Pedro do Sul, mentioning the positive relation between the active faults and the occurrence of thermal waters and the importance that these structures have in its mineralization and temperature. Furthermore, these authors proposed a schematic cross section important in the conceptual circulation model of São Pedro do Sul thermal waters (Figure 3b). Thermal poles and their hot springs are linked with local fault orientation

and connectivity, namely the Termas Fault oriented NE–SW, the Fataunços Fault oriented WNE–ESE, and the São Pedro do Sul-Ribamá Fault oriented NNE–SSW.

3. Methodology

Groundwater samples were collected from boreholes and springs in order to obtain a representative composition of the thermomineral and cold shallow aquifer systems of the São Pedro do Sul region (Figure 2). The selected cold springs intend to represent the shallow groundwater of the region, characterized by the low mineralization, low temperature, and pH values around 5 to 6 (see Table 1). These selected springs are located at different altitude sites within the surroundings of the research region and represent the initial recharge water composition, “before” water-rock interaction processes, as found in the deep aquifer.

Table 1. Summary of physical, chemical and isotopic parameters of shallow springs and well water samples. Alt., for altitude; EC, electrical conductivity; Temp., temperature values.

Site	Alt.	EC	pH	Temp.	Total min.	SiO ₂	Na ⁺	Ca ²⁺	K ⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	F ⁻	δ ¹⁸ O	δ ² H
	m	µs/cm		°C	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	‰	‰
<i>Thermal Springs</i>																
NT *	156	400.28	8.81	65.0	364.59	76.60	90.90	3.01	3.25	0.03	122.05	27.49	10.24	17.98	−6.44	−36.80
AC1 *	154	399.29	8.84	65.4	365.49	68.55	91.15	2.95	3.24	0.02	122.09	27.71	9.49	18.13	−6.53	−37.10
SDV1 *	142	401.11	8.81	56.0	371.74	70.62	91.28	3.06	3.23	0.02	124.76	28.51	10.11	18.09	−6.45	−36.60
SDV2 *	142	396.06	8.78	62.7	367.73	70.55	91.59	3.08	3.17	0.02	123.98	28.19	10.27	18.08	−6.38	−36.50
<i>Cold Springs</i>																
AS1	1000	14.50	5.84	11.4	12.32	4.56	2.07	0.37	0.10	0.19	1.71	2.83	<0.72	<0.25	−6.22	−35.40
AS2	425	29.50	5.60	14.4	28.64	10.78	4.70	0.26	0.75	0.48	5.25	6.35	<0.72	<0.25	−5.13	−28.50
AS3	350	54.80	6.17	15.8	51.93	17.77	8.72	0.87	0.94	0.92	11.53	11.09	<0.72	<0.25	−5.26	−28.80
AS4	850	25.20	5.36	12.1	20.97	7.36	3.51	0.40	0.08	0.38	4.39	4.78	<0.72	<0.25	−5.60	−30.00
AS5	505	59.90	6.01	13.9	61.03	20.89	9.26	1.57	1.55	0.78	13.36	10.36	1.48	<0.25	−5.43	−28.40
AS6	440	25.20	5.17	15.6	21.21	8.67	3.63	0.33	0.09	0.20	3.17	5.11	<0.72	<0.25	−5.16	−28.40
AS7	725	32.60	5.24	13.3	31.44	12.32	4.79	0.74	0.30	0.25	5.55	6.07	<0.72	<0.25	−5.81	−32.30
AS8	850	–	–	12.7	–	–	–	–	–	–	–	–	–	–	−5.51	−28.50
AS9	700	–	–	12.9	–	–	–	–	–	–	–	–	–	–	−5.01	−25.50
AS10	270	–	–	14.8	–	–	–	–	–	–	–	–	–	–	−4.87	−26.90
AS11	275	–	–	14.7	–	–	–	–	–	–	–	–	–	–	−5.09	−28.20
AS12	320	–	–	13.9	–	–	–	–	–	–	–	–	–	–	−5.03	−27.80
AS13	445	–	–	13.3	–	–	–	–	–	–	–	–	–	–	−5.37	−29.50
AS14	510	–	–	15.0	–	–	–	–	–	–	–	–	–	–	−5.19	−29.30
AS15	250	–	–	16.7	–	–	–	–	–	–	–	–	–	–	−5.00	−27.70
<i>Boreholes</i>																
AF2		115.80	4.70	18.0	81.51	17.09	12.55	1.85	3.65	2.20	<0.50	15.84	<0.72	<0.25	–	–
AF3		81.00	5.98	22.7	84.73	27.24	9.87	1.66	1.36	3.00	27.57	9.21	3.92	<0.25	–	–
AF4		33.10	5.21	14.3	26.65	9.15	4.92	0.53	0.22	0.30	4.58	6.94	<0.72	<0.25	–	–
AF5		63.90	5.75	12.8	52.06	9.16	7.10	3.75	0.90	1.20	15.86	7.41	6.24	<0.25	–	–
AF1A		88.30	5.43	15.5	64.77	14.32	11.82	2.06	0.62	1.70	6.34	14.05	8.40	<0.25	–	–

* Mean values obtained over nine years (2005–2013) by physico-chemical and chemical analyses programs established by legal authorities, except for δ¹⁸O and δ²H values.

The sampling procedures, such as collection, handling, storage and transport, were carefully planned and applied to ensure the safety and quality of sampling. All the processes took place in line with the relevant specifications or standard practices. Thus, the bottles were cleaned with distilled water before sampling and then pre-rinsed with water from the sampling site two or three times before collecting. The water samples were collected in wide-neck high-density polyethylene (HDPE) bottles (filled without leaving any air bubbles), stored in the absence of light and refrigerated at a constant low temperature

of 4 °C until analysis in the laboratory. Water samples for cations were acidified with concentrated nitric acid to keep a pH < 2 and were reserved in 500 mL bottles. For anion analysis, 500 mL bottles were used, while samples for oxygen-18 and deuterium were stored in 50 mL bottles. All water samples were marked, sealed, and stored, and then sent to the laboratory for analysis as soon as possible after collection. In addition, field-measured parameters of pH, electrical conductivity (EC) and temperature were performed in situ using a portable multiparameter WTW Multi 3420 calibrated with a standard solution.

The chemical analyses were performed at LNEG (Laboratório Nacional de Energia e Geologia), Portugal, for major dissolved species determination using the following methods: atomic absorption spectrometry for Ca²⁺ and Mg²⁺; emission spectrometry for Na⁺ and K⁺; colorimetric methods for SiO₂, F⁻; ion chromatography for SO₄²⁻ and Cl⁻; potentiometry for alkalinity, here referred as HCO₃⁻ (Table 1). The stable isotope composition of all groundwater samples was determined at C²TN/IST (Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa) Portugal. The δ²H and δ¹⁸O content is reported in per mil (‰) vs. V-SMOW and was obtained by Laser Spectroscopic (LGR 24d).

As mentioned before, a hydrogeochemistry and isotopic study was conducted in order to improve knowledge about the São Pedro do Sul thermomineral groundwater system. From chemical data, the cations and anions content was used to identify the different water facies and possible evolution trends within the groundwater flow, namely using: (i) the Piper diagram to identify different water types; (ii) Schoeller–Berkaloff diagram to highlight the hydrogeochemistry profile of water samples and to evaluate the main similarities and differences between them.

The groundwater recharge in both aquifer systems (shallow and deep) derives from direct infiltration of precipitation; groundwater samples in both units will reflect the mean isotopic composition of that regional precipitation. Using the “relation”, besides for stable isotopic composition, δ¹⁸O and δ²H content were used to determine the origin and a first approach to estimate the mean preferential recharge altitude areas of the thermomineral water.

A total of 12 groundwater samples were collected inside of the investigated region, among these, 7 cold springs (AS1, AS2, AS3, AS4, AS5, AS6, AS7) and 5 wells (AF2, AF3, AF4, AF5, AF1A) with a mean depth of around 70 m were sampled between June and July 2016 in the surrounding areas of the São Pedro do Sul site.

4. Results and Discussion

4.1. Hydrogeochemical Approach

At São Pedro do Sul, the geological and tectonic environment seems to control some of the major hydrogeological features and processes of the thermomineral waters, such as infiltration, aquifer recharge, groundwater flow paths, and hydrogeochemical evolution. In Table 1, the chemical data presented related to the thermomineral water composition represent the mean composition. The set of major cations and anions results was obtained over nine years of survey in NT, AC1, SDV1 and SDV2. This option (mean values) was chosen considering the high stability in the composition of this group of sites along the years. Besides, from Table 1, it is also possible to note the minor dissimilarity of content in the different parameters within the four sampling sites, presenting similar physico-chemical composition.

Considering the data of Table 1, the chemical characteristics of the thermal water of São Pedro do Sul can be classified as sulfurous waters, with high chemical composition stability. The major elements in these waters are hydrogen carbonate, sodium, silica, chloride and fluoride. Hydrolysis of Na-plagioclase should be considered as the main process responsible for the occurrence of the HCO₃-Na waters because Na-plagioclase is the main mineral of the dominant granitic rock of the regional hydrogeological system.

The water samples collected in shallow cold aquifer systems are characterized by the low total mineralization content. These waters should be considered as a signature of

local recharge associated with a shallow and short flow path regimen, explaining by this assumption, the development of the Na–Cl waters.

The thermomineral system is characterized by a mean output temperature of around 67 to 68 °C (spring and boreholes) and high pH values around 8.8. Besides the total mineralization values in the range of 365–370 mg/L and the waters showing a HCO₃–Na facies; the high silica and fluoride contents, with values around 70 mg/L and up to 18 mg/L, respectively, also represent distinct parameters if they are compared with the shallow cold dilute waters. An important contribution of reduced species of sulfur ≈ 10 mg/L was also determined in this group of waters.

On the contrary, the shallow cold waters present low mineralization, low pH (around 6), and a HCO₃–Cl–Na facies with lower silica, fluor and sulfur content. Nevertheless, focusing only on the cold groundwaters systems, a difference in the chemical and physical parameters is noted when the springs are compared with the boreholes. With the exception of AF4 (see Table 1), all springs present lower mineralization, $EC_{\text{mean}} = 34.5 \pm 16.6 \mu\text{S}/\text{cm}$, while for the boreholes, $EC_{\text{mean}} = 87.3 \pm 21.6 \mu\text{S}/\text{cm}$. This difference probably indicates a not-so-deep circulation of the springs, with shorter residence time allowing for minor water–rock interaction processes.

The chemical signatures found in the deep water system suggest that the thermomineral fluid's composition is mainly dominated by the hydrolysis of Na plagioclase within the granitic reservoir. Groundwater at this depth shows an increase in salinity and in pH, with an increase in sodium over calcium compared with the shallow groundwaters. Moreover, considering the dominant lithology of the research region (Hercynian granitoids), oxidation of sulfide minerals (such as pyrite) at this depth should explain the sulphate content increase in the thermomineral groundwater system.

Granitic rocks dominate the research area, where the feldspars hydrolysis represents an important water–rock interaction process, contributing to a high percentage of dissolved silica. The silica content represents about 20% of the total mineralization of the thermomineral water samples (see Table 1), and higher than 30% in the shallow cold aquifer systems.

The direct application of chemistry predicted that the water–rock interaction processes involved in the geochemical evolution of the groundwaters and these parameters were applied in the estimation of the reservoir temperature and the depth of the thermomineral waters [42,43]. To estimate this, the chemical geothermometers SiO₂ and K²/Mg proposed by Truesdell (1975) and Giggenbach (1988), respectively, (Equations (1) and (2)) [44,45] were selected based on the acceptable and consistent estimation of reservoir temperature in low enthalpy systems:

$$T (^{\circ}\text{C}) = [1315/5.205 - \log \text{SiO}_2] - 273.15 \quad (1)$$

and

$$T (^{\circ}\text{C}) = (4410/14 - \log (\text{K}^2/\text{Mg})) - 273.15 \quad (2)$$

In both equations, the concentrations of K, Mg and SiO₂ is in mg/L. The results obtained at São Pedro do Sul thermomineral waters point to a mean reservoir temperature between 119 °C (SiO₂) and 116 °C (K²/Mg), indicating a maximum depth from 3.10 to 3.19 km. The results obtained are very consistent (Table 2). To calculate the maximum depth “reached” by the thermomineral waters”, the following equation was considered: $\text{depth} = (\text{Tr} - \text{Ta})/\text{gg}$, where Tr stands for the reservoir temperature (°C), Ta for the mean regional annual temperature (13 °C), and gg the regional geothermal gradient of 30 °C/km [46].

Using the available data of the deep and shallow aquifer systems, the data were plotted in a Piper diagram (Figure 4) and in a Schoeller–Berkaloff diagram (Figure 5).

Table 2. Reservoir temperature using the K^2/Mg and SiO_2 geothermometers and maximum depth reached by São Pedro do Sul thermomineral waters.

Ref.	Geother. K^2/Mg ($^{\circ}C$)	Maximum Depth (km)	Geother. SiO_2 ($^{\circ}C$)	Maximum Depth (km)	Average Maximum Depth (km)
NT	111.9	3.00	122.8	3.33	3.17
AC1	117.8	3.18	117.2	3.16	3.17
SDV1	117.7	3.17	118.7	3.20	3.19
SDV2	117.2	3.16	118.6	3.20	3.18
Average	116.1	3.13	119.3	3.22	3.18

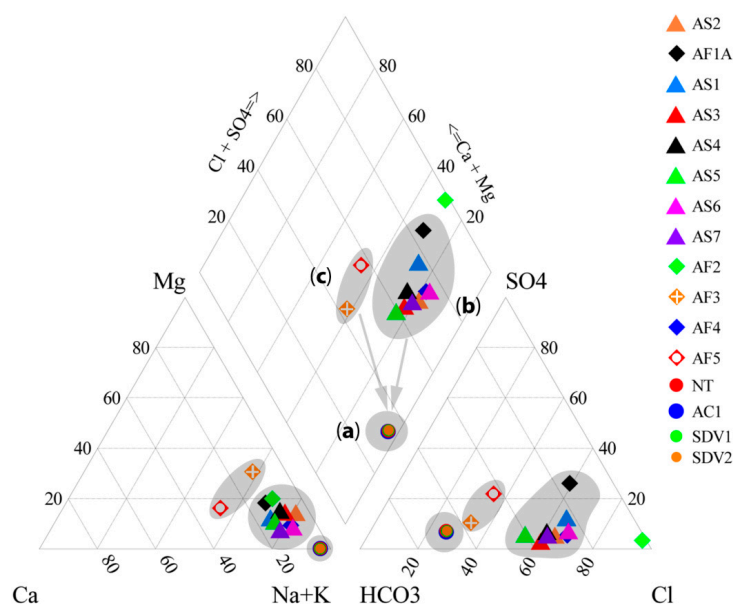


Figure 4. Piper diagram for the 16 water samples of the São Pedro do Sul region. (a) Standing for the thermomineral waters; (b) Composed of sodium chlorinated waters; (c) Composed of sodium, calcium or magnesium bicarbonate waters.

The Piper diagram [47] shows three different domains: cluster (a), standing for the thermomineral waters that are sodium bicarbonate; the second and third groups of water are composed of the water samples from the shallow cold aquifer systems. The non-mineral waters are represented in this diagram by two clusters: the first is cluster (b), composed of sodium chlorinated waters, mainly associated with water–rock interaction processes with granitic rocks, while cluster (c) is composed of sodium, calcium or magnesium bicarbonate waters. The increase in Ca^{2+} and/or in Mg^{2+} is associated with interaction processes with granitic and metasedimentary rocks or cover deposits where there is agricultural land use. The borehole AF2 reveals a chloride value significantly distinct from the other samples, probably resulting from local anthropogenic activities.

From Figure 5 (Schoeller–Berkaloff diagram), the first impression is that all thermomineral and cold waters samples seem to present the same evolution pattern, although with different contents. However, the deviation in Mg content observed in NT, AC1, SDV1 and SDV2 thermomineral waters can most probably be ascribed to lithology heterogeneities, such as absence or presence along the groundwater flow of amphibolite veins, in which its existence can increase Mg content.

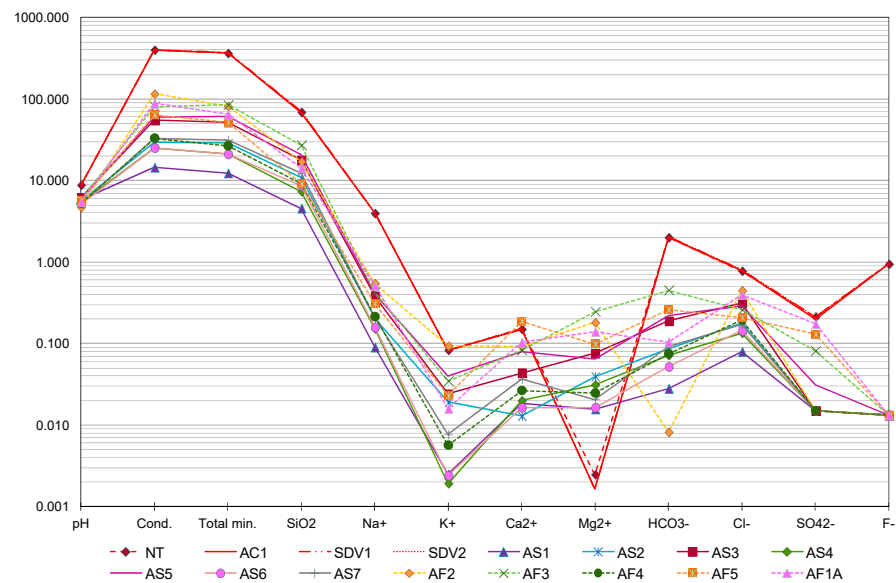


Figure 5. Schoeller–Berkaloff diagram for the 16 water samples of São Pedro do Sul region. Parameters units: conductivity— $\mu\text{s cm}^{-1}$; total mineralization and SiO_2 — mg/L ; other parameters— meq/L .

The hydrogeochemical signatures identified in the two water systems (thermomineral and shallow cold aquifer systems) are ascribed to the regional/local lithological differences, together with the anthropogenic action (pollution) in the region. The different chemical type of waters is well observed when the $\text{Na} + \text{K}$ or $\text{Ca} + \text{Mg}$ content is plotted as a function of the hydrogen carbonate (Figure 6a,b). Besides, the possible existence of mixing between the thermal fluids with the local shallow cold dilute groundwater systems or even with surface waters (river Vouga that cross the area) was not identified.

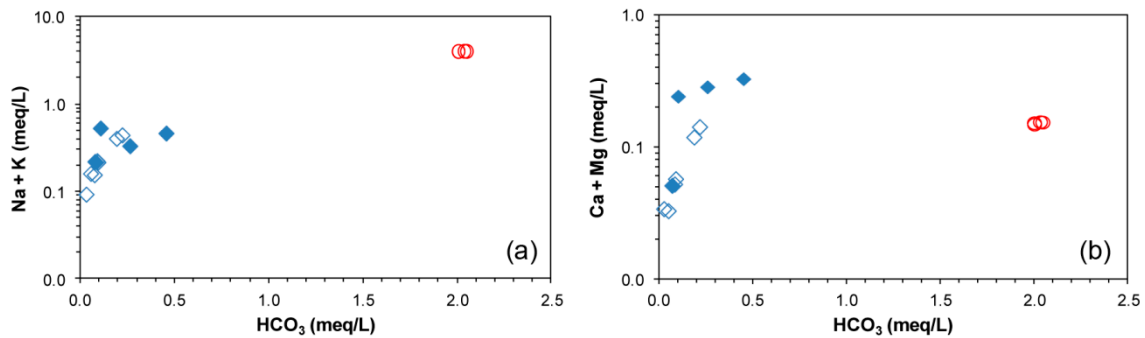


Figure 6. (a) $\text{Na} + \text{K}$ vs. HCO_3 ; (b) $\text{Ca} + \text{Mg}$ vs. HCO_3 of São Pedro do Sul groundwater. (○), thermomineral waters; (◆), shallow cold aquifer system boreholes; (◇), shallow cold aquifer system springs.

The same conclusion of the absence of mixing with the thermomineral waters is also supported as shown by Figure 7; the deeper waters are plotted apart from all the other samples. No transitional water sample compositions were found in the region, corroborating the hypothesis of no mixing between the different aquifers. Conversely, the dispersion within the shallow cold diluted groundwater samples is enhanced when the $\text{Ca} + \text{Mg}$ content is plotted as a function of HCO_3 or as a function of SiO_2 content, which is probably related to metasedimentary formations. The same dispersion is noted in the Cl content. (Figure 7a), however this increase is associated to anthropogenic activities in the surrounding area (agricultural activities). Conversely, it is also noted that the majority of the springs exhibits lower mineralization when compared with the boreholes. This suggests

shallow circulation pathways and smaller residence time, which is important in water-rock interactions processes.

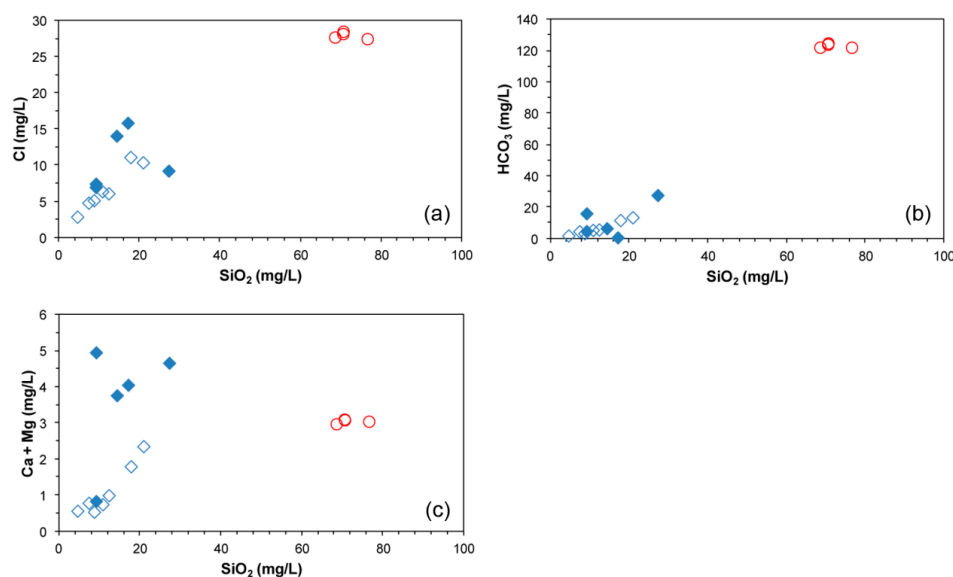


Figure 7. (a) Cl vs. SiO₂; (b) HCO₃ vs. SiO₂ and (c) Ca + Mg vs. SiO₂ of São Pedro do Sul groundwaters. (○), thermomineral waters; (◆), shallow cold aquifer system boreholes; (◇), shallow cold aquifer system springs.

Furthermore, Figures 6a and 7a,b suggest an evolution of the hydrochemical process from the non-mineral waters to thermomineral waters, dominated by hydrolysis of Na plagioclase present in the regional granitic rocks.

The thermomineral waters together with the non-mineral water samples exhibit identical hydrochemical profiles, but they present an enrichment of the component concentrations, with the exception of magnesium concentration, which decreases in absolute terms (Figure 5). There is a considerable increase in sodium and hydrogen carbonate concentrations in the mineral water composition, which may be associated with hydrolysis of Na plagioclase of granitic rocks of the São Pedro do Sul region [7]. The concentrations of sodium, hydrogen carbonate and SiO₂ results from a major residence time of these mineral waters. In relation to non-mineral waters, in general, the hydrochemical profile is similar, except for the samples whose composition is influenced by anthropic activities.

4.2. Stable Isotopes ²H and ¹⁸O

At the research area, 19 groundwater samples were collected for stable isotopic determinations (see Table 1), from AS1 to AS15 cold shallow diluted springs and from NT, AC1, SDV1 and SDV2, thermomineral waters. The isotopic values were plotted in the orthogonal diagram (Figure 8); besides, in this diagram, the Global Meteoric Water Line (GMWL) defined by Craig (1961) [48] and the Local Meteoric Water Line are plotted.

The isotopic composition of all groundwater samples (thermomineral and cold diluted groundwater samples) were used to establish the Local Meteoric Water Line (Local-MWL). The obtained equation ($\delta^2\text{H} = 6.5\delta^{18}\text{O} + 5.6$; $n = 19$; $r^2 = 0.95$) was used since no isotopic precipitation record of this region is available and to observe the difference between the Local-MWL and the Global MWL established by Craig (1961). The local $\delta^{18}\text{O}$ - $\delta^2\text{H}$ relationship for precipitation often varies from the G-MWL in the slope and the intercept, since they are a function of meteorological and geographic characteristics of the region.

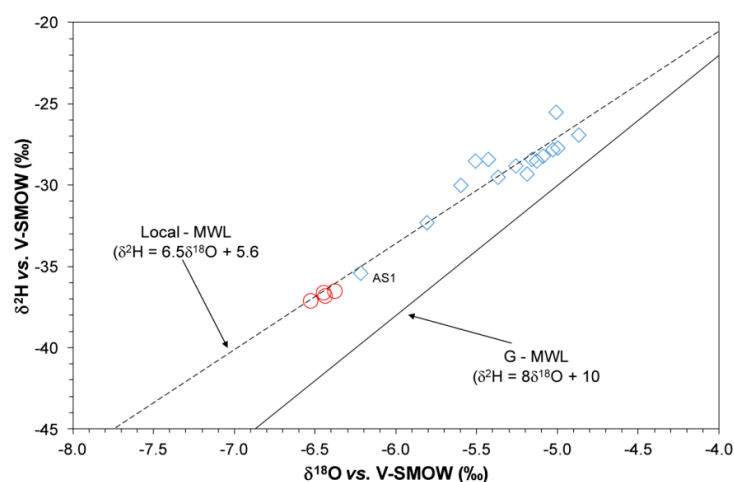


Figure 8. $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ for the São Pedro do Sul thermomineral and cold dilute shallow aquifers. (○), thermomineral waters; (◇) shallow cold aquifer system springs.

From the distribution of the groundwater samples, a common origin of the water vapor masses responsible for the precipitation and aquifers recharge seems to be present, based on strong correlations between ^{18}O and ^2H content and similar deuterium excess content. Yet, it is well noted that there is an isotopic gap between the cold water mean composition ($\delta^{18}\text{O}_{\text{mean}} = -5.25 \pm 0.26\text{‰}$ and $\delta^2\text{H}_{\text{mean}} = -28.6 \pm 1.6\text{‰}$) and the thermomineral waters ($\delta^{18}\text{O}_{\text{mean}} = -6.5 \pm 0.06\text{‰}$ and $\delta^2\text{H}_{\text{mean}} = -36.8 \pm 0.3\text{‰}$). This difference is in the order of 1.2‰ in ^{18}O and around 8.2‰ in ^2H . No evidence of evaporation previous to infiltration is noted in the isotopic content, based on the graphic distribution of all water samples along the Local Meteoric Water Line and in the deuterium excess values ($d = 12.1\text{‰}$ in AS10 to 15.6‰ in AS8); in addition, a common water vapor mass is assumed to be present. In the estimation of the mean isotopic composition of the cold groundwater samples, the spring AS1 was excluded. The isotopic difference observed between these two groups should be an altitude effect.

Several authors [4,6,23,24,27,49–51] use this isotopic shift as a natural tracer for the natural recharge of the water systems and in the establishment of the preferential recharge altitudes of the aquifer systems. Since one of the aims of this study is the identification of any differences/similarities in isotopic input to the water systems, thermomineral and cold dilute aquifers would lead to characterization of its isotopic signatures (mean isotopic composition). In São Pedro do Sul, this “gap” can be used to estimate the preferential recharge altitude of the thermomineral water system.

In general, the distribution of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ mimics the topography of the continents; the waters of mountain chains is marked by more negative δ values. This feature is known as the “altitude effect” and was first mention by Dansgaard (1964) [52,53]. The lowering of temperature with increasing elevation in mountain regions usually leads to enhanced condensation and therefore to a progressive depletion in heavy isotopes in precipitation with altitude (Figure 9) [54].

The altitude effect has been used in numerous hydrological conceptual models all over the world, including on continental Portugal and Madeira Island. The groundwater isotopic composition has been applied as a basis of preferential recharge areas and definition of protection of aquifer systems, and to investigate the origin and to identify the interconnection of water bodies [6,22,25,26,55,56]. The vertical isotope gradient in mid-latitudes generally varies between 0.15‰ and 0.50‰ per each 100 m of altitude gained for oxygen-18, and about 1‰ to 4‰ per each 100 m for deuterium [57–59].

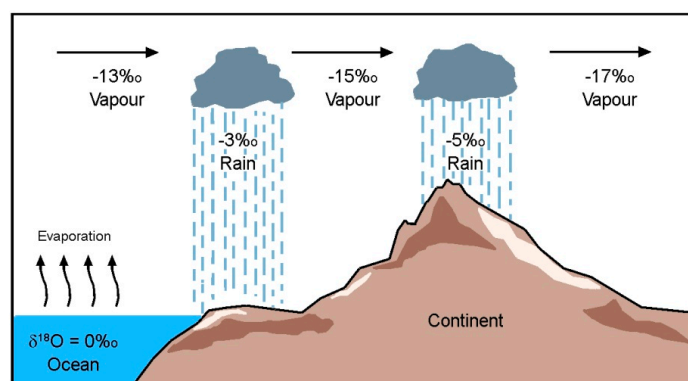


Figure 9. Schematic variation of fractionation in $\delta^{18}\text{O}$ during the hydrologic cycle; the altitude and continental effect in precipitation (water vapor masses) from coastal regions to inland.

At São Pedro do Sul, the assessment of the elevation of the recharge area of the thermomineral system was established based on the $\delta^{18}\text{O}$ values of the shallow cold aquifer systems that are characterized by a short residence time and short circulation pathway. The several springs sampled in the region are located at different altitudes. The results supported the relationship between $\delta^{18}\text{O}$ of these cold shallow springs and the elevation of the sampling site, bearing in mind the conservative behavior of the oxygen isotopic composition of the groundwater from recharge to discharge. The $\delta^{18}\text{O}$ isotopic gradient obtained for the research area was $0.19\text{‰}/100\text{ m}$ of altitude.

Taking into account the isotopic gradient of the region and the isotopic signatures ($\delta^{18}\text{O}$) of the thermomineral waters located at altitudes higher than 1000 m a.s.l., it is suggested that the Freita/Arada mountains, with a maximum altitude of 1120 m a.s.l. and located NW of the thermomineral poles, represent the preferential recharge area of this thermomineral system (Figure 2). This compatibility is corroborated by the close relationship between the isotopic composition ($\delta^{18}\text{O}$) of São Pedro do Sul thermomineral waters and AS1 sample at an altitude of 1000 m a.s.l. (Figure 2 and Table 1).

In addition to the preferential recharge altitude of the thermomineral water, the isotopic composition of these samples also gives information concerning the water flux and potential water–rock interaction processes present along the groundwater flow, such as, for example, dissolution/precipitation processes. Formulating the hypothesis of the isotopic gap observed in the two groups of samples is due to dissolution/precipitation processes. The relation between oxygen-18 and deuterium should not be observed, and the water samples should not be plotted along the Local Meteoric Water Line. This isotopic pattern corroborates that the altitude effect is the main factor responsible for the observed isotopic distribution.

5. Final Remarks

The study performed at the São Pedro do Sul thermomineral pole is the continuity of previous works that have been performed in the region by different authors [1,7,40] in order to understand the conceptual model of these particular waters and their protection. Their knowledge and protection is important since the spa has a strong influence in the regional economy, inferred by the numbers of visitors and by direct and indirect revenue [1].

From the geochemical point of view, according to the Piper diagram, the groundwaters can be classified into two main groups: $\text{HCO}_3\text{-Na}$ and Cl-Na types. Cl-Na water types are generally associated with less mineralized waters (shallow cold diluted systems of local circulation), while $\text{HCO}_3\text{-Na}$ water types are associated with more mineralized waters (São Pedro do Sul thermomineral waters). In the evolutionary context of the typology of Cl-Na to $\text{HCO}_3\text{-Na}$, the sulphureous thermomineral waters of the region represent the maximum of this evolution where HCO_3 and Na ions are the most representative of ionic composition. This evolution results from hydrolysis of silicate mineral processes that occur over time. The four sources of the Termas and Vau poles are similar waters, not only by the

mineralization values of around 365 mg/L, but also in relation to their relative composition of cations and anions. These results suggest a single aquifer system, a hypothesis that is corroborated by the reservoir temperature using the K^2/Mg and SiO_2 geothermometers (119 °C—maximum temperature), and homogenous maximum depths of the aquifer system (3.18 km—maximum depth average).

The $\delta^{18}O$ and δ^2H values indicate that the thermal sources mainly originated from meteoric water, with no significant evaporation before infiltration, and they are mainly recharged from precipitation at altitudes higher than 1000 m a.s.l. In the geohydraulic flow, this suggests a recharge area in the Freita/Arada mountains located NW of the thermomineral poles. The circulation of fluid is believed to happen through the WNW–ESE to NW–SE faults along several kilometers, which flow down into the crust where the water is warmed by the increasing natural temperature and then seeking pathways to reach the surface at the springs. The emergence is controlled mainly by the São Pedro do Sul–Ribamá, Termas and Fataunços faults. The flow-up process in the hydraulic circuit appears to be promoted by the difference in density between cold water inflow and hot water upflow and due to the difference in hydraulic charge between the recharge and discharge zones. Further studies are required to confirm the conclusion we have reached in this work.

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