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Contribution of Hydrogeochemistry and Isotope Hydrology (δ^2H and $\delta^{18}O$) to Update the Conceptual Hydrogeological Model of the Hyposaline Natural Mineral Waters of Ribeirinho and Fazenda do Arco (Castelo de Vide, Central Portugal)

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Contribution of Hydrogeochemistry and Isotope Hydrology (δ^2H and $\delta^{18}O$) to Update the Conceptual Hydrogeological Model of the Hyposaline Natural Mineral Waters of Ribeirinho and Fazenda do Arco (Castelo de Vide, Central Portugal)

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Abstract

In this paper, the conceptual hydrogeological circulation model of natural mineral waters from Ribeirinho and Fazenda do Arco hydromineral concession (Castelo de Vide) is updated. These waters are exploited by the Super Bock Group, as bottled waters, and are commercially labelled as Água Vitalis. The physico-chemical data (2004 – 2024) of these waters were processed regarding their joint interpretation with recent isotopic (δ^2H and $\delta^{18}O$) data. The study region is dominated by the Castelo de Vide syncline that develops along the southern limit of the Central Iberian Zone. These natural mineral waters have low electrical conductivity (EC) mean values ($42.80 < EC_{mean} < 54.45$ µS/cm) and a slightly acidic pH ($5.14 < pH_{mean} < 5.46$), making them hyposaline waters. The recharge area of this aquifer system coincides fundamentally with the outcrops of Lower Ordovician quartzites. The updated conceptual circulation model presented in this work is essentially based on the chloride-sodium signatures of these waters, explained by the preferential recharge of meteoric waters (δ^2H and $\delta^{18}O$) and low water-rock interaction temperature. Such isotopic results seem to indicate the non-existence of a flow continuity between the two blocks (NW and SE) of the quartzite ridges, separated by a fault with a local orientation approximately N-S, as indicated by the most enriched isotopic values of the waters from borehole AC22 ($\delta^{18}O$ = -5.90 ‰ *vs.* V-SMOW) located in the SE block, compared to the average isotopic value of the waters from the other boreholes (Vitalis I, II, III, IV, V and VI) located in the NW block ($\delta^{18}O_{mean}$ = -6.30 ‰ *vs.* V-SMOW).

Keywords: hyposaline natural mineral waters; quartzite formations; hydrogeochemistry; environmental stable isotopes; updating of the conceptual circulation model; Castelo de Vide; central Portugal

1. Introduction

Across the globe (Portugal included), natural mineral waters originate from precipitation. In some occurrences, the processes of recharge and underground flow paths can be quite complex, needing extensive information gathered to understand the mechanisms involved. The evaluation of a region's hydromineral resources requires a multidisciplinary approach - encompassing geology, tectonics, geophysics, hydrogeology, hydrogeochemistry, and isotope hydrology - to develop a well-

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founded conceptual hydrogeological circulation model. A conceptual hydrogeological circulation model associated with a given hydromineral system must be essentially qualitative and include a physical description of its functioning, comprising the main focus and specific content of the investigation involved ([1]). Such models often consist of maps and/or schematic geological cross-sections showing the location of potential recharge areas, underground flow paths, key water-rock interaction processes at depth, and discharge sites (e.g., [2,3]). This is a topic that should be updated/modified over time, in accordance with recent information, or new approaches, that become available as a result of field work and the use of new laboratory methodologies. These models will act as a base for both future development strategies and the sustainable management of these important and "hidden" geological resources.

Natural mineral waters are a type of groundwaters that are bacteriologically pure and preserves stable physico-chemical properties at its source, within natural variation limits. They are distinct from common groundwaters due to their inherent purity and unique composition, characterized by its mineral content, trace elements, and other specific constituents, which may offer health benefits. These waters acquire their physical and chemical signatures from the mineralogical composition of the geological formations they flow through and the nature of water-rock interactions. Additionally, the temperature at which they emerge reflects (in most systems) the depth of their circulation; higher temperatures indicate deeper and longer underground flow paths, facilitated by rock diaclases / fractures and faults.

In Portugal, most natural mineral waters are utilized as bottled waters and in thermal spas. Some hydromineral systems have been studied, including those similar to Ribeirinho and Fazenda do Arco. A comparative study of two similar hydromineral systems in Central Portugal - Luso and Penacova - was conducted by [4]. According to [4], these systems are supported by early Ordovician quartzites and consist of three primary fractured aquifer systems: (i) an upper aquifer system with "normal" groundwater discharging at approximately 17°C, (ii) the Luso natural mineral aquifer system, which has a discharge temperature of around 27°C, and (iii) the Penacova natural mineral aquifer system, where water emerges at about 20°C. These are hyposaline waters, with total mineralization levels reaching up to 43 mg/L and display a Cl-Na facies. The $\delta^{18}O$ values suggested the presence of meteoric waters originating from similar recharge altitudes [4]. The silica concentration correlates with the depth of circulation and residence time, as inferred from discharge temperatures and ^{3}H values. According to the conceptual hydrogeological circulation model presented by [4], the hydraulic behavior of the aquifers involves recharge through direct precipitation. The upper aquifer exhibits a shallow circulation, whereas the deeper natural mineral aquifer systems follow a NW (Luso) and SE (Penacova) underground flow path.

As per [5], the Monfortinho hydromineral system is situated in central Portugal near the Spanish border. It is a confined aquifer, located between the pre-Ordovician Schist-Greywacke complex below and schist formations of the Llanvirnian-Caradocian above. The water from this system is classified as Na-HCO_3 natural mineral water, hyposaline (total mineralization of 44 mg/L), rich in SiO_2 (accounting for 53 % of the total mineralization), with a pH of 5.8, and emerging at 29.4 °C. The recharge zones for this system include Arenigian quartzite ridges at altitudes between 400 and 600 meters above sea level. After recharge, these waters flow within quartzite formations at depths of approximately 300 - 400 meters [5]. In the discharge zone, the ascent of natural mineral waters is facilitated by intense fracturing of quartzite formations, resulting from both local and regional faults [5].

A study by [3] provided an updated interpretation of the conceptual circulation model for the Ladeira de Envendos hyposaline hydromineral system in Central Portugal. According to these authors, the geology of this region is heavily influenced by the Amêndoa-Carvoeiro synform, which dates back to the Ordovician-Silurian period and features continuous, aligned quartzite ridges on the NE flank that form a series of inselbergs. Stable isotope data ($\delta^{2}H$ and $\delta^{18}O$) suggest that local meteoric waters infiltrate preferably at approximately 400 meters altitude and evolve into Cl-Na facies natural mineral waters as they follow a NW-SE underground flow path through highly fractured and

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permeable quartzite rocks [3]. During their flow from recharge to discharge, these waters acquire silica (approximately 9 mg/L) through interaction with quartzite rocks. The waters emerge at around 21 °C, with their ascent being controlled by fractures and local faults. The estimated residence time of these waters ranges between 25 and 40 years, as inferred from ^{3}H content, indicating an active recharge process within this hydromineral system.

The primary goal of this study was to update the conceptual hydrogeological circulation model of the Ribeirinho and Fazenda do Arco (Castelo de Vide - Central Portugal) hyposaline hydromineral system, emphasizing the importance of conceptual models in assessing and ensuring the sustainable management and protection of such resources. To achieve this, a interdisciplinary approach integrating geology, hydrogeochemistry, hydrogeology, and isotope hydrology was applied. The findings and discussions based on these methodologies will be presented in the following sections.

This study, as the results from the collaboration between Instituto Superior Técnico and Super Bock Group (private stakeholder), represents the first comprehensive investigation of its kind in the region, with a particular focus on the contribution of isotope hydrology ($\delta^{2}H$ and $\delta^{18}O$) alongside other geoscience disciplines. The research aims to characterize the Ribeirinho and Fazenda do Arco hyposaline hydromineral system (the so-called Vitalis natural mineral waters) both quantitatively and qualitatively, addressing key aspects such as i) hydrochemical facies, ii) water-rock interactions processes, iii) origin and recharge altitude, iv) circulation depth and temperature of these natural mineral waters.

The region under study is located in the Serra de São Mamede Natural Park, in the northeast of Alentejo, district of Portalegre.

2. Geomorphological, Climatological, Geological and Hydrogeological Framework

The study region is mostly made up of granite rocks, and is characterized by an extensive plain, where altitudes vary between 300 and 400 m a.s.l. [6]. This landscape is marked, in contrast, by the synclinal structure where two Ordovician quartzite ridges of the Serra de São Mamede stand out, oriented NW-SE along approximately 40 km, reaching altitudes above 820 m a.s.l. [7].

The unique geomorphology of this Alentejo region (Figure 1) influences the local climate, resulting in a decrease in temperatures and an increase in precipitation. In fact, the abundance of water resources in this region is partly related to climatic conditions, with greater precipitation and less evaporation, thus resulting in greater effective infiltration [8]. The hottest months are July and August, and the coldest months are December, January and February. The average local minimum and maximum temperatures are between 2 °C and 32 °C, respectively. As per [7], the average annual precipitation for this region, around 904 mm

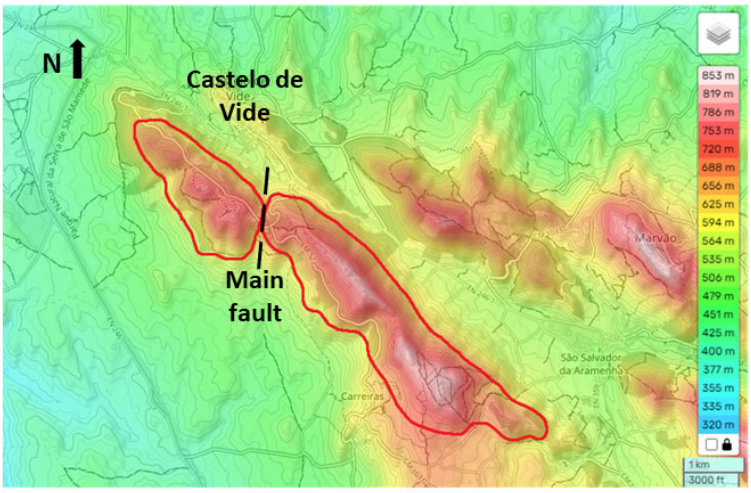

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Figure 1. Geomorphology of the region of Castelo de Vide - Serra de São Mamede (ex. 853 m refers to m a.s.l.). In shades of red, the two important ridge lines are represented, separated by a fault with a local orientation approximately N-S. Adapted from "www.topographic-map.com", retrieved on 05/15/2023.

Castelo de Vide syncline structure (Figure 2) develops along the southern limit of the Central Iberian Zone (ZCI) limited to the SW by the Portalegre-Ferreira do Zêzere thrust fault. The core of the Castelo de Vide syncline is formed by current alluvium, slope and valley floor deposits dating from Holocene, surrounded by a layer of Upper Silurian schists, flanked by Lower Ordovician quartzite formations that contact SW with the arkoses (base layer of the syncline) and with the ante-Hercynian tectonized-granites [9].

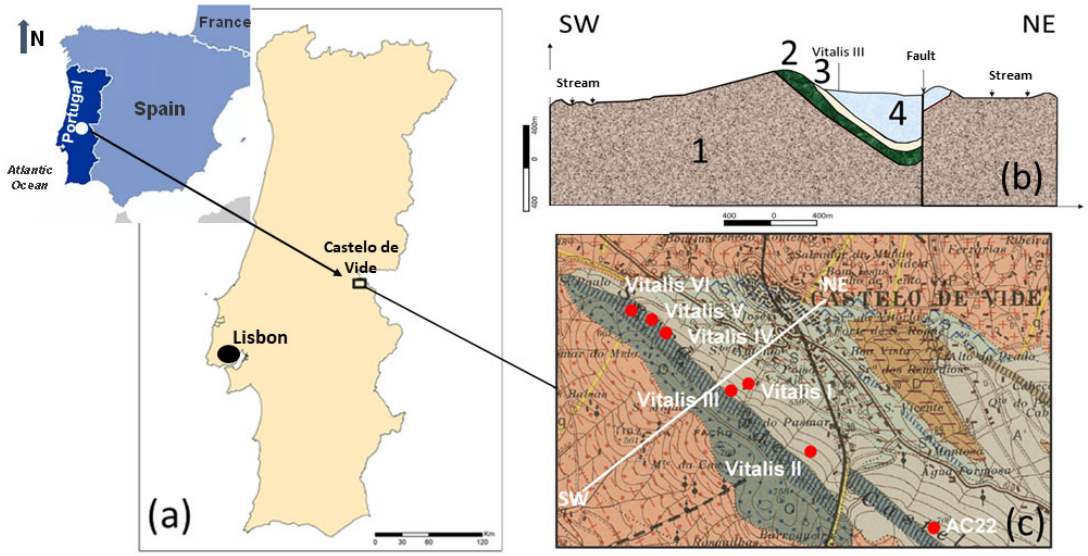

Figure 2. (a) Geographical location of the region under study; (b) Geological cross section 1 - Granites, 2 - Arkoses, 3 - Quartzite ridge, 4 - Schists; (c) Sampling sites (geology taken from [10]. Adapted from [11].

Quartzites are strongly fractured, facilitating the flow of groundwater [10]. The Vitalis water boreholes are found in quartzite ridges (the result of differential erosion), as they are harder and more resistant than the surrounding rocks.

As stated by [11], the recharge area of the aquifer system associated with the Vitalis water must essentially coincide with the outcrop area of the Lower Ordovician quartzites (Figure 3). This formation is strongly fractured, which facilitates the direct infiltration of precipitation, as well as the groundwater flow through the opening of discontinuities, notably existing rock fractures and stratification planes.

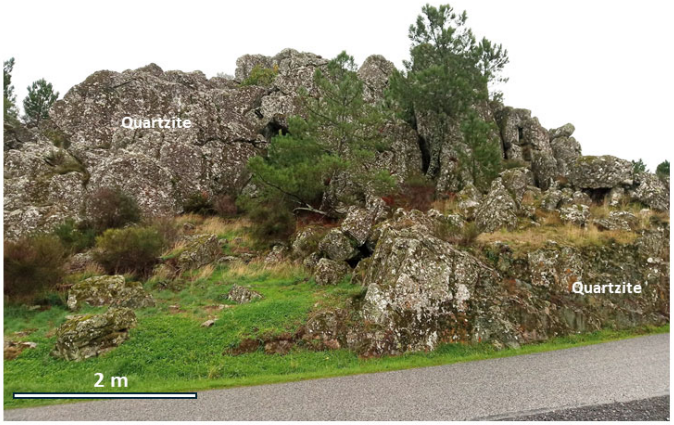

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Figure 3. Example of the quartzite rocks outcropping at the study region. Photo by J. M. Marques (2023).

3. Materials and Methods

To conduct this study, seven representative sampling sites of the Ribeirinho and Fazenda do Arco hyposaline hydromineral system (Castelo de Vide, Central Portugal) were selected: the Vitalis I to VI and AC22 boreholes. A comprehensive physico-chemical database (2004–2024) exists for the Vitalis I to VI boreholes, kindly provided by the Super Bock Group, the concessionaire of these natural mineral waters.

The boreholes vary significantly in depth: Vitalis I – 262.76 m, Vitalis II – 172.65 m, Vitalis III – 102 m, Vitalis IV – 84 m, Vitalis V – 108 m, Vitalis VI – 129.5 m, and AC22 – 91 m. These depth variations are determined by their location within the Castelo de Vide syncline, which determines the drilling depth required to reach the quartzite layers. For each borehole (excluding AC22), concerning the hydrostatic initial level (HsIL) and the exploitation hydrodynamic level (EHdL), we have (Table 1):

Table 1. Hydrostatic initial level (HsIL) and exploitation hydrodynamic level (EHdL) for the boreholes from the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide). Data kindly provided by the Super Bock Group. .

Borehole	Vitalis I	Vitalis II	Vitalis III	Vitalis VI	Vitalis V	Vitalis VI
HsIL (m)	0	13	20.4	32.5	47.6	32.2
EHdL (m)	16	35	44	54	61	60

As a complement to the existing database, a fieldwork campaign was conducted in October 2023 to collect water samples from these boreholes. The fieldwork campaign focused on: i) *in-situ* measurements of temperature (°C), pH, electrical conductivity (EC, µS/cm), and redox potential (Eh, mV, referenced to H^+/H_2) using a portable Hach HQ40D digital multi-parameter meter, and ii) collecting water samples for isotopic analysis (δ^2H and $\delta^{18}O$). No samples were collected for chemical analysis, since all boreholes are regularly monitored by Super Bock Group, with the exception of AC22.

For the Vitalis I to VI and AC22 boreholes, the following analytical standard methods were employed by the Super Bock Group: Bicarbonate – SMEWW 2320 B (titration method). Silica – M.M. 2.2.7 (speciation calculations). Ionic chromatography for: Chloride, sulphate, and nitrate – SMEWW 4110 B. Sodium, potassium, calcium, and magnesium – M.M. 6.1.1.

For the determination of δ^2H and $\delta^{18}O$ values in the natural mineral waters from the study area, 50 mL water samples were collected from each site. The samples were stored in high-density polyethylene bottles with double lids to prevent isotopic fractionation (evaporation). Stable isotope determinations (δ^2H and $\delta^{18}O$) were performed at the Laboratório de Isótopos Ambientais (C^2TN/IST, Centro de Ciências e Engenharias Nucleares from Instituto Superior Técnico) using a Laser Spectroscopic Analyzer (LGR DT-100 24d). The accuracy was ±1‰ for δ^2H and ±0.1‰ for $\delta^{18}O$. The results are reported in delta (δ) notation and referenced to the international standard V-SMOW [12,13].

4. Results and Discussion

4.1. Physico-Chemical Signatures of the Waters

Groundwater is a crucial component of the Earth's hydrological cycle, influenced by complex interactions between meteoric waters and geological formations. Quartzite, a highly resistant metamorphic rock primarily composed of quartz (SiO_2), plays a significant role in shaping the chemical characteristics of infiltrating rainwater. Therefore, hydrogeochemistry plays a crucial role in assessing groundwater systems, particularly natural mineral waters. The physical and chemical characteristics of these waters provide valuable insights into: (i) the groundwater recharge origin and

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type, (ii) the delineation of underground flow paths, (iii) the assessment of water-rock interactions within the aquifer matrix, and (iv) the refinement of conceptual hydrogeological models (e.g., [14,15].

Concerning the comprehensive physico-chemical database (2004–2024) kindly provided by the Super Bock Group, data from 11 different parameters were processed: bicarbonate, chloride, sulfate, sodium, potassium, calcium, magnesium, silica, total mineralization (in mg/L), pH and Electrical Conductivity (EC in μS/cm), by creating time trend diagrams, evaluating the concentration of these parameters over time and analyzing the evolution in the different boreholes. For the study of the hydrochemical analyses provided, less significance was given to the AC22 borehole due to the reduced number of samples (also very concentrated in time) compared to the other boreholes (Vitalis I, II, III, IV, V and VI).

Considering all data series provided by the Super Bock Groupwe can state that these natural mineral waters have average pH values between 5.14 and 5.46. Due to its low solubility, quartzite-dominated aquifers often produce low pH waters (e.g., [3–5]. EC_{mean} values vary between 42.80 and 54.45 μS/cm, with an average value of 49.25±5.15 μS/cm.

Although the EC values are relatively low, through the graphical interpretation of the temporal evolution of EC (Figure 4), it is possible to distinguish 2 groups: the natural mineral waters from boreholes Vitalis IV, V and VI record higher EC values than the natural mineral waters from boreholes Vitalis I, II, and III. The difference in average electrical conductivity between these two groups of mineral waters is 9 μS/cm (mean EC of Vitalis I, II, and III = 44.7 μS/cm while the mean EC of Vitalis IV, V, and VI = 53.7 μS/cm) This trend is in line with what was mentioned by [11] regarding the underground flow direction of the studied natural mineral waters along quartzite formations, from SE to NW, given that the increase in EC values can be related to the average residence time of natural mineral waters in this hydromineral system, promoting water-rock interaction.

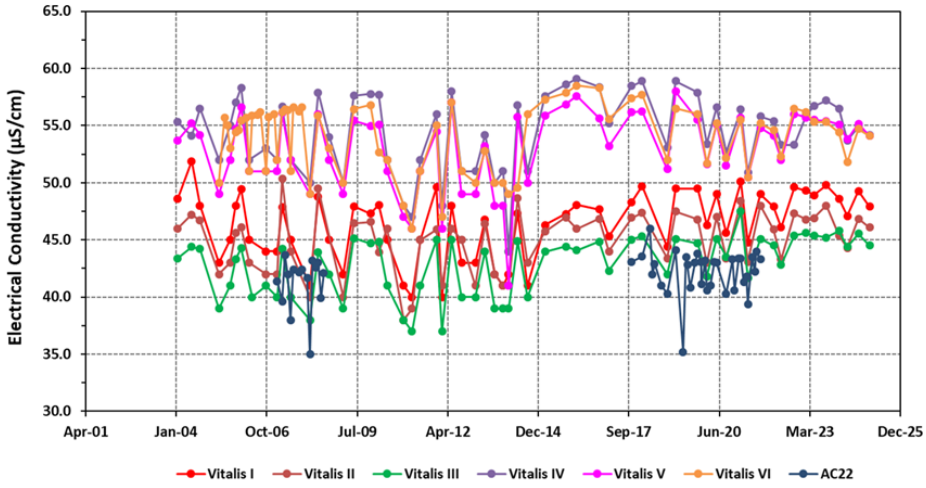

Figure 4. Temporal evolution of EC (μS/cm) in the boreholes of the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide).

According to [16] these waters are hyposaline natural mineral waters, , as they present total mineralization values below 100 mg/L (Figure 5), varying in this case between 31.87 mg/L in AC22 up to 48.06 mg/L in Vitalis IV. The division of the boreholes into the two main groups described earlier (Figure 4) is no longer evident when Total Mineralization is plotted against time. In Figure 5, it is possible to observe a very homogeneous behavior between the 6 boreholes (Vitalis I to VI), presenting the same trend over time.

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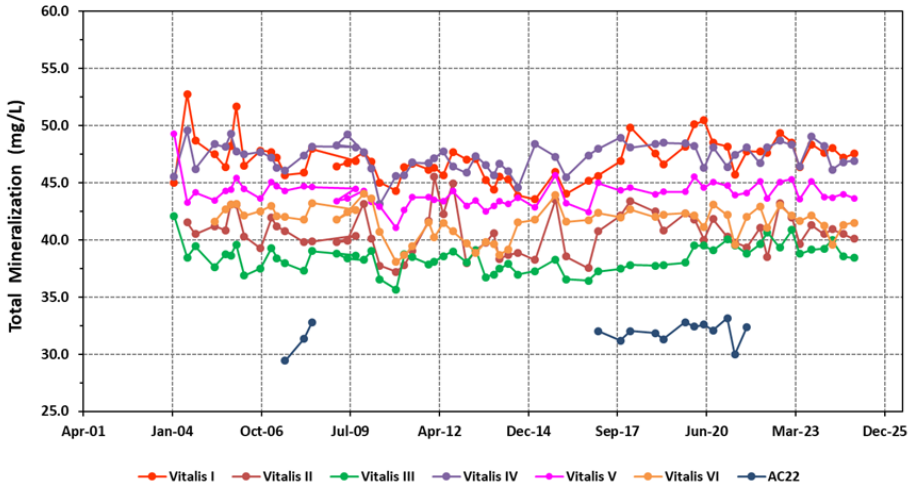

Figure 5. Temporal evolution of Total Mineralization (mg/L) in the boreholes of the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide).

The chemical average composition of all boreholes (see Table 2) was projected on the Piper Diagram, Figure 6. This graphical method allows us to classify the chemical facies of these natural mineral waters, i.e, all of them are Cl-Na *facies*, typical of waters circulating in quartzite rocks, as referred by [3,4].

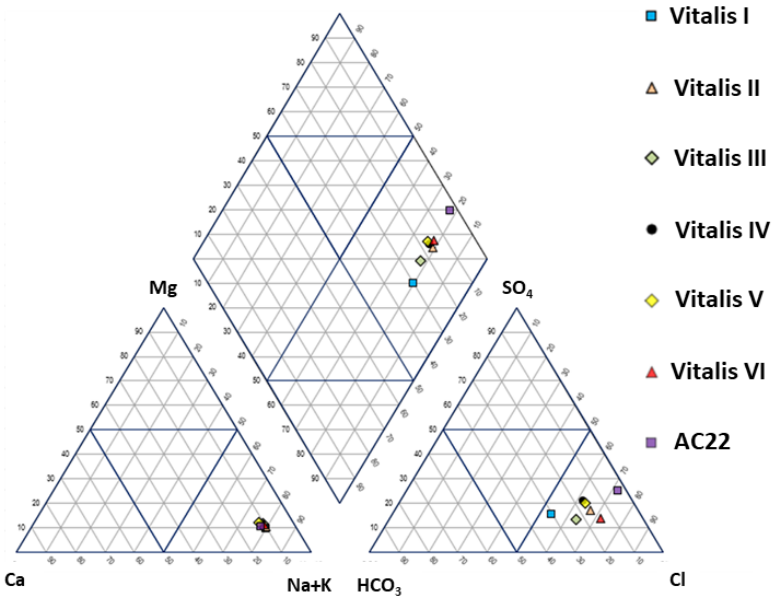

Figure 6. Piper Diagram – projection for the boreholes (Vitalis I, II, III, IV, V, VI and AC22) from the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide).

Table 2. Average chemical composition of the boreholes (Vitalis I, II, III, IV, V, VI and AC22) from the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide). Concentrations in mg/L.

	Vitalis I (n=60)	**Vitalis II** (n=59)	**Vitalis III** (n=60)	**Vitalis IV** (n=61)	**Vitalis V** (n=60)	**Vitalis VI** (n=72)
pH	5.46±0.08	5.17±0.11	5.26±0.07	5.22±0.07	5.18±0.08	5.14±0.09

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EC	46.34±2.95	44.90±2.69	42.80±2.59	54.45±3.36	52.97±3.41	54.02±3.03
HCO_3^-	6.40±0.63	3.05±0.30	4.35±0.24	4.07±0.30	4.08±0.37	3.40±0.44
Cl^-	6.58±0.40	6.97±0.49	6.96±0.25	8.50±0.28	9.00±0.43	9.69±0.58
SO_4^{2-}	2.79±0.44	2.53±0.39	2.09±0.41	4.16±0.49	2.74±0.33	2.67±0.63
Na^+	5.93±0.27	5.17±0.24	5.06±0.18	6.50±0.19	6.24±0.15	6.60±0.18
K^+	2.07±0.08	2.06±0.12	1.91±0.08	2.35±0.10	2.06±0.10	1.85±0.13
Ca^{2+}	0.81±0.06	0.72±0.07	0.71±0.06	0.97±0.07	0.99±0.09	0.89±0.07
Mg^{2+}	0.45±0.03	0.45±0.07	0.50±0.03	0.62±0.03	0.63±0.03	0.59±0.03
SiO_2	19.92±1.15	16.79±1.41	15.04±0.71	17.66±0.83	15.79±0.91	13.72±0.84

Table 2 shows that the natural mineral waters from the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide) are characterized by very low mineralization. Among the dissolved substances, silica (SiO_2) is present in the highest concentration, followed by chloride (Cl^-) and sodium (Na^+). The average dry residue values for these waters range from 37.36 ± 2.89 mg/L (n=60) in Vitalis III to 46.75 ± 3.34 mg/L (n=61) in Vitalis IV. Based on the European Classification [17], these natural mineral waters are categorized as hyposaline waters.

The diagram in Figure 7 indicates that sodium (Na^+) concentrations in the natural mineral water samples from the various boreholes remain relatively uniform over time. The Na^+ content change aproximatly between 4.7 mg/L (Vitalis III) and 7.2 mg/L (Vitalis VI). Although this variations is rather small , it is possible to identify a gap between Vitalis II and Vitalis III, in comparision with the other boreholes. The division between these two groups is in this case less distinct than in Figure 4, i.e., Vitalis I water is now closer to the more mineralized groups of waters.

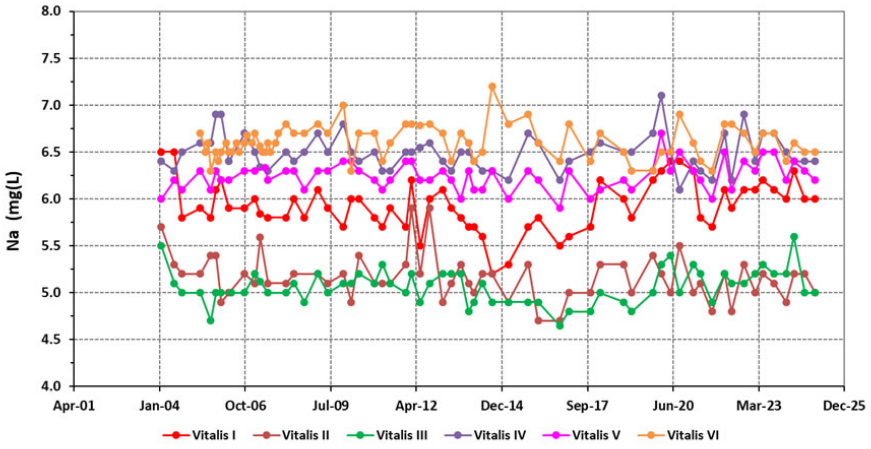

Figure 7. Temporal evolution of Na^+ (mg/L) in the boreholes of the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide).

The presence of slightly higher Cl^- concentrations in the natural mineral waters of the Vitalis IV, V, and VI boreholes (Figure 8), can be explained, as for the case of Na^+ concentrations (Figure 7), as the result of the increase in Na^+ and Cl^- concentrations along the subsurface flow direction of the natural mineral waters, from SE to NW.

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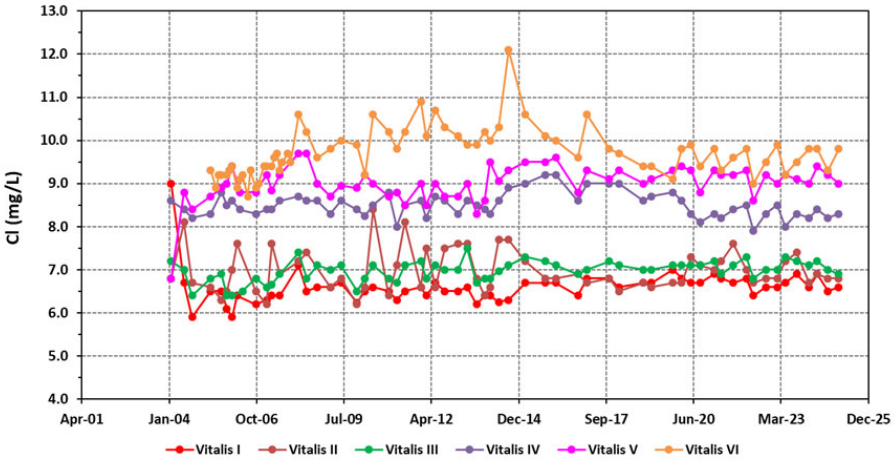

Figure 8. Temporal evolution of Cl^- (mg/L) in the boreholes of the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide).

Given that these are natural mineral waters circulating in quartzite rocks, presenting Cl-Na *facies*, the slightly increase in Na^+ and Cl^- may be associated with the leaching of NaCl salts deposited (either in the soil or in the discontinuities of the quartzite formations – diaclases, fractures, stratification) after the various episodes of atmospheric precipitation (recharging of the hydromineral system). Thus, the natural mineral waters from boreholes Vitalis IV, V, and VI presenting slightly higher Na^+ and Cl^- concentrations seems to corroborate the existence of an underground flow path from SE to NW, as reported by [11].

The studied natural mineral waters present higher silica (SiO_2) concentrations when compared with the other chemical parameters analyzed (Table 2), given that they are natural mineral waters whose recharge, infiltration and underground circulation paths are associated with the main discontinuities of the quartzite rocks in the region, which through water-rock interaction release SiO_2 into the aqueous solution (see [14,15]). In the case of natural mineral waters from Vitalis I borehole, the slight increase in SiO_2 concentration (Figure 9), associated with the increase in the HCO_3^- concentration (Table 2) could be explained by the hydrolysis of feldspars from the granites and arkoses present on the SW flank of the syncline [10] , evidencing the possible existence of lateral recharge through faults and/or higher fracture zones.

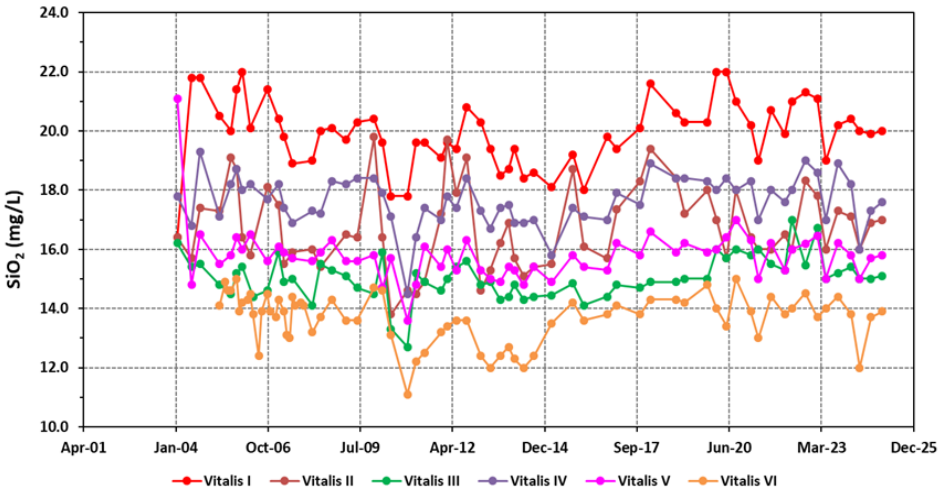

Figure 9. Temporal evolution of SiO_2 (mg/L) in the boreholes of the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide).

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The different SO_4^{2-} concentrations in each borehole do not reflect an increase in content along the groundwater flow path from SE to NW (Figure 10). The Vitalis IV borehole has the highest content (approximately 1 mg/L), with the lowest SO_4^{2-} concentrations observed in the Vitalis III and Vitalis VI boreholes.

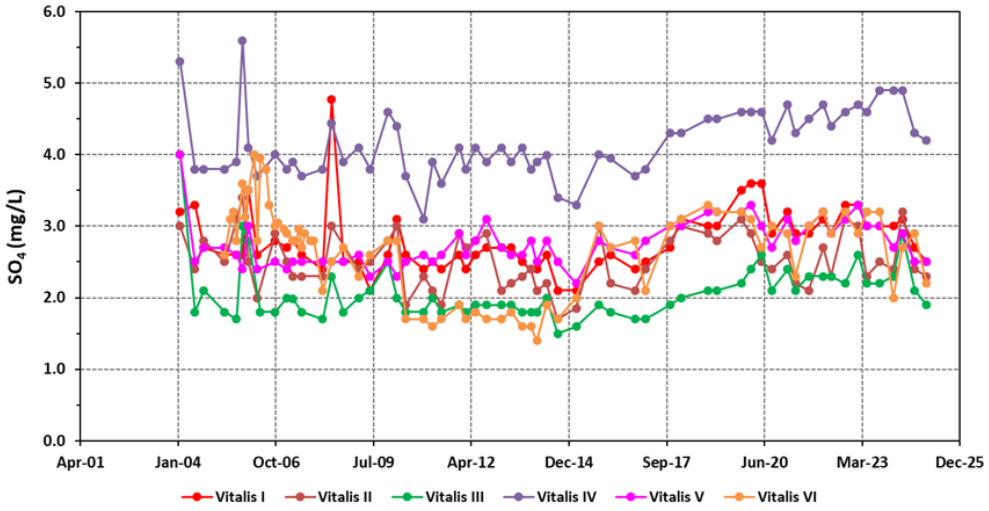

Figure 10. Temporal evolution of SO_4^{2-} (mg/L) in the boreholes of the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide).

One possible explanation for the increase in SO_4^{2-} concentration observed in the natural mineral waters under study could be an anthropogenic source, such as agricultural activities. However, this hypothesis seems to be unlikely, as the difference in SO_4^{2-} levels is minimal (approximately 2 mg/L) and remains relatively constant over time.

A more plausible explanation is the oxidation of pyrite, which occurs as an accessory mineral in several geological formations in the region. These include quartz veins that fill local discontinuities, and granites located on the southwestern flank of the quartzite ridges and Upper Silurian schists [10]. Given the high degree of fracturing in the SW granitic area surrounding the boreholes, it is reasonable to suggest that pyrite oxidation, potentially combined with lateral recharge, is the main source of the SO_4^{2-}. When pyrite comes into contact with water, it leads to the formation of sulfate ions (e.g., [18], supporting this interpretation.

The presence of lateral recharge in the Ribeirinho and Fazenda do Arco hydromineral system, facilitated by E-NE-oriented fractures and faults through granites and arkoses [10] (see Figure 2c), seems to be supported by the geochemical evidence. The levels of HCO_3^-, Na^+, K^+, Ca^{2+} and SiO_2 of the waters from Ribeirinho and Fazenda do Arco likely result from the hydrolysis of feldspars in the granites and arkoses.

4.2. Isotopic (δ^2H and $\delta^{18}O$) Signatures of the Waters

Isotope hydrology, particularly the analysis of stable isotopes such as oxygen-18 and deuterium, is a powerful tool in hydrogeological studies. These isotopes act as natural tracers, enabling the identification of groundwater recharge areas, delineation of underground flow paths, and assessment of mixing processes between water bodies. Their spatial and temporal variations reflect the origin and movement of water through the hydrological cycle, offering critical insights for the development of robust hydrogeological conceptual models [19]. In regions with complex geology or limited hydrochemical contrasts, stable isotope content provides essential data that complements traditional hydrogeological methods, improving the accuracy of aquifer characterization and water resource management [20}.

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In October 2023, a sampling campaign was conducted to determine the isotopic composition (δ^2H and $\delta^{18}O$) of the natural mineral waters from the Ribeirinho and Fazenda do Arco hydromineral concessions. This analysis served as a complementary method to the hydrogeochemical characterization, aiming to refine the conceptual hydrogeological model of the study region. The results are presented in Table 3.

Table 3. - Isotopic composition ($\delta^{18}O$ and δ^2H) and deuterium excess (d) of water samples from the boreholes of the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide).

Sampling site	October 2023 Field work campaign		
	$\delta^{18}O$	δ^2H	d
Vitalis I	-6.31	-30.8	19.68
Vitalis II	-6.13	-30.7	18.34
Vitalis III	-6.13	-31	18.04
Vitalis IV	-6.31	-32	18.48
Vitalis V	-6.4	-32.8	18.4
Vitalis VI	-6.49	-32.5	19.42
AC22	-5.9	-33.5	13.7

Note: $\delta^{18}O$, δ^2H and d (deuterium excess) values in permillage (‰) relative to the V-SMOW standard.

During this field work campaign, *in-situ* measurements - temperature T (ºC), pH, electrical conductivity EC (µS/cm) and redox potential Eh (mV) - were performed using a portable Hach HQ40D Digital two channel multimeter. The results obtained are reported in Table 4.

Table 4. Field parameters determined *in situ*, obtained during the October 2023 field work campaign, for water samples from the boreholes of the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide).

Sampling site	pH	EC (µS/cm)	T (ºC)	Eh (mV)
Vitalis I	4.82	49.8	16.1	96.2
Vitalis II	5.44	48.3	16.2	61.9
Vitalis III	4.76	56.5	15.8	99.4
Vitalis IV	4.69	58.8	16.2	103.5
Vitalis V	4.41	60.0	16.7	119.3
Vitalis VI	4.84	60.1	16.4	95.0
AC22	4.37	45.6	15.5	120.9

The isotopic composition of the natural mineral waters from the Ribeirinho and Fazenda do Arco hydromineral concessions (Castelo de Vide) is presented in the δ^2H–$\delta^{18}O$ diagram shown in Figure 11. The plotted data points align rather closely with both the Global Meteoric Water Line (GMWL: $\delta^2H = 8 \cdot \delta^{18}O + 10$; [21]) and the Portalegre Meteoric Water Line (Portalegre MWL: $\delta^2H = 6.38 \cdot \delta^{18}O + 3.24$; [22], indicating that these waters are of meteoric origin. The Portalegre meteorological station, is located approximately 20 km south of the Castelo de Vide study area at an altitude of 780 m a.s.l., reports an annual weighted isotopic composition of $\delta^{18}O = –5.60$ ‰ and $\delta^2H = –33.2$ ‰ [22]. These values are rather similar to those observed in the natural mineral water samples from Ribeirinho and Fazenda do Arco. However, the samples exhibit a slight shift toward more depleted isotopic values (see Table 3).

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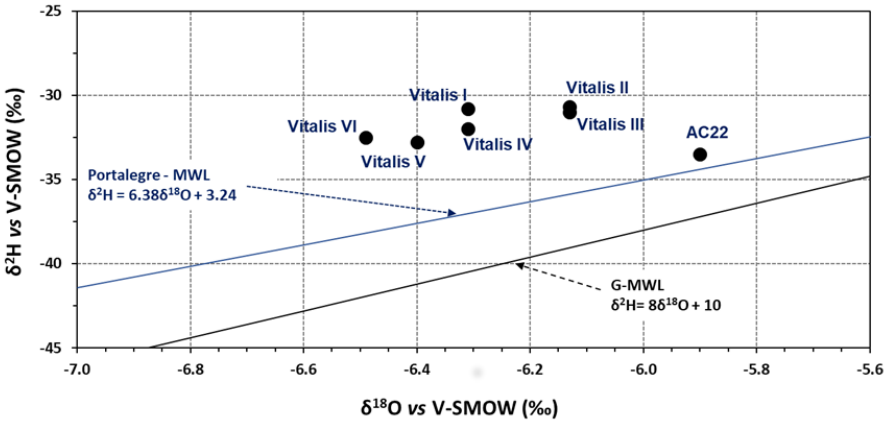

Figure 11. Plot of the isotopic composition of the natural mineral waters from of the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide) on a δ^2H-$\delta^{18}O$ diagram. The lines represent the Global Meteoric Water Line G-MWL $\delta^2H = 8*\delta^{18}O+10$ [21] and the Portalegre Meteoric Water Line Portalegre-MWL $\delta^2H = 6.38*\delta^{18}O+3.24$ [22]. .

The preliminary isotopic results suggest a lack of hydraulic continuity between the two quartzite ridge blocks (NW and SE), which are separated by a fault trending approximately N-S (see Figure 2). This hypothesis is supported by the relatively enriched isotopic signature of water from borehole AC22 ($\delta^{18}O$ = –5.90 ‰), located in the SE block, compared to the average isotopic composition of waters from boreholes Vitalis I to VI in the NW block ($\delta^{18}O_{mean}$ = –6.30 ‰). The isotopic composition of the NW block borehole waters indicates recharge from relatively high altitudes (above 780 m a.s.l.) as inferred from their location (see Figure 2) and the annual weighted averages recorded at the Portalegre Meteorological Station [22]. In contrast, the more enriched isotopic values observed in borehole AC22 suggest a preferential recharge from lower altitudes than those supplying the Vitalis I to VI boreholes.

The relationship between EC values and isotopic composition ($\delta^{18}O$) of the natural mineral waters, based on data collected during the October 2023 field campaign and shown in Figure 12, supports the hypothesis that recharge of the NW block waters occurs along the entire quartzite ridge. The data also suggests an underground flow direction from SE to NW, consistent with the model proposed by [11]. This interpretation is based on the regular increase in EC values from SE to NW, ranging from 48.3 µS/cm at Vitalis II (SE) to 60.1 µS/cm at Vitalis VI (NW). In contrast, borehole AC22, located in the SE block, shows a lower EC value of 45.6 µS/cm, suggesting a relatively short underground flow path. This points to a possible flow direction from NW to SE, opposite to that inferred for the NW block. It is important to note that these interpretations are based on a single sampling campaign for both isotopic analysis and *in-situ* measurements. Additional surveys are necessary to confirm these findings.

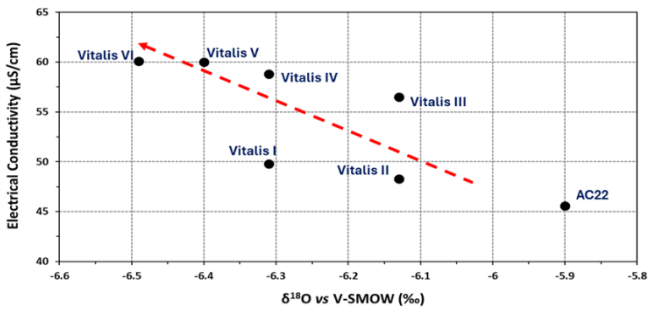

Figure 12. Plot of EC values and the isotopic composition of the natural mineral waters from of the hydromineral concessions of Ribeirinho and Fazenda do Arco (Castelo de Vide) on a EC-$\delta^{18}O$ diagram. Data from October 2023 field work campaign.

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5. Updating of the Conceptual Hydrogeological Model

According to [1], a conceptual hydrogeological circulation model for a hydromineral system should be easy to understand, mostly qualitative, and offer a clear explanation of how the system works. As new data becomes available through recent field work campaigns, such models should be regularly updated to reflect improved understanding. The primary aim of this study was to enhance the conceptual hydrogeological circulation model for the hyposaline natural mineral waters of Ribeirinho and Fazenda do Arco, located in Castelo de Vide, Central Portugal. The updated model is illustrated schematically in Figure 13.

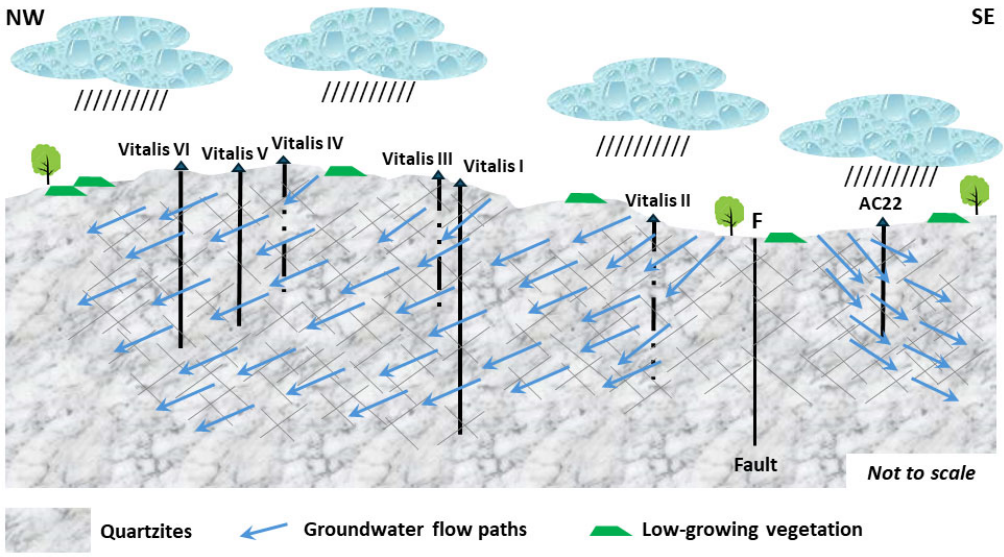

Figure 13. Schematic representation of the updated conceptual hydrogeological circulation model for the hyposaline natural mineral waters of Ribeirinho and Fazenda do Arco (Castelo de Vide, Central Portugal) (not to scale).

The hyposaline natural mineral waters from Ribeirinho and Fazenda do Arco, of the Cl-Na-type, originate from meteoric water that infiltrates the quartzite ridges of the Serra de São Mamede, which trend NW–SE. Recharge occurs at similar altitudes, approximately 780 meters above sea level, and is facilitated by the high degree of fracturing in the quartzites, resulting in preferential SiO_2 dissolution. Impermeable formations, such as upper Silurian schists, direct the groundwater flow along the more permeable quartzite layers. This flow generally follows a SE–NW direction at relatively shallow depths, as inferred from the relatively low temperatures recorded at the boreholes. This flow direction is also supported by the slight NW tilt of the syncline axis [10].

The quartzite ridges are structurally divided into two blocks - northwestern (NW) and southeastern (SE) - by a fault trending N-S. Isotopic analysis (δ^2H and $\delta^{18}O$) indicates limited hydraulic connectivity between these two blocks. The mineral water from AC22 (SE block) displays a more enriched isotopic signature compared to water from boreholes Vitalis I to VI in the NW block. Geological, geochemical, and tectonic evidence further support the hypothesis of lateral recharge within the Ribeirinho and Fazenda do Arco hydromineral system. This lateral input is likely facilitated by E–NE-trending fractures and faults [10]. These structures contribute to localized increases in concentrations of HCO_3^-, Na^+, K^+, Ca^{2+}, and SiO_2 in some boreholes, likely due to feldspar hydrolysis in granitic and arkosic rocks.

As illustrated in Figure 13, the hyposaline natural mineral waters of the Ribeirinho and Fazenda do Arco can be categorized into two distinct subsystems. These differ in recharge altitude and underground flow paths.

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6. Concluding Remarks

The updated conceptual hydrogeological model of the hyposaline natural mineral waters of Ribeirinho and Fazenda do Arco (Castelo de Vide, Central Portugal) provides significant insights into the dynamics of this unique hydromineral system. Dominated by the Castelo de Vide syncline and developed along the southern margin of the Central Iberian Zone, this region hosts natural mineral waters that are characterized by low electrical conductivity, slightly acidic pH, and a characteristic Cl^--Na^+ signature, typical indicators of meteoric origin and limited water-rock interaction. These properties, along with elevated SiO_2 concentrations and very low mineralization, confirm the dominance of Lower Ordovician quartzite outcrops as the primary recharge area and flow medium.

The integration of hydrogeochemical and isotopic data (δ^2H and $\delta^{18}O$) has proven essential for refining the conceptual model, particularly in identifying recharge altitudes, delineating subsystems, and tracing groundwater flow paths. The model confirms that groundwater circulation occurs mainly through fractured quartzites, with minimal interaction with other lithologies, maintaining the physical and chemical stability typical of natural mineral waters.

It should be enhanced the hydrochemical similarities observed between Ribeirinho and Fazenda do Arco and other well-documented Portuguese natural mineral water systems such as Ladeira de Envendos, Luso and Monfortinho. In all these natural mineral systems the presence of quartzite formations controls the recharge and underground flow paths, leading to comparable end-member characteristics: Cl^--Na^+ water facies, "high" silica content and, to hyposaline waters.

These findings not only enhance scientific understanding of the system but also have practical implications. Natural mineral waters, due to their purity and unique composition, are valuable geo-resources with significant social and economic relevance. Thus, improving conceptual models through multidisciplinary approaches is essential to ensure their sustainable exploitation and long-term preservation.

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