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Geochemical and Isotope Characterisation of Thermo-Mineral Springs of Corsica Island: From Geological Complexity to Groundwater Singularity

Margaux Dupuy ^{1,2}, Emilie Garel ^{1,2}, Frederic Huneau ^{1,2,*}, Sebastien Santoni ^{1,2}, Maria Di Rosa ³ and Alexandra Mattei ^{1,2}

- ¹ Département d'Hydrogéologie, Université de Corse Pascal Paoli, Campus Grimaldi, BP 52, 20250 Corte, France; margauxdupuy@yahoo.fr (M.D.); garel_e@univ-corse.fr (E.G.); santoni_s@univ-corse.fr (S.S.); mattei_al@univ-corse.fr (A.M.)
- ² Centre National de la Recherche Scientifique, UMR 6134, SPE, BP 52, 20250 Corte, France
- ³ Dipartimento di Scienze della Terra, Università di Pisa, Via Santa Maria, 53, 56126 Pisa, Italy; maria.dirosa.scaglia@gmail.com
- * Correspondence: huneau_f@univ-corse.fr

Abstract: Understanding hydrogeological processes at the origin of thermal and mineral groundwater are necessary to ensure their sustainable management. However, many processes are involved in their genesis and often only one or two processes are investigated at the same time. Here, we propose to use an innovative combination of geochemical, isotopic (³⁴S, ¹⁴C, ¹⁸O, ²H) and geothermometry tools to identify, for the first time in a multi-composite geological context, all processes at the origin of diversified thermo-mineral waters. 19 springs covering a wide range of temperature and chemical composition emerging on a restricted area of Corsica Island (France) were selected. Geochemical results highlight five geochemical provinces, suggesting a common origin for some of them. Geothermometry tools show the unexpected involvement of a common deep groundwater reservoir within this non-active zone. Water stable isotopes highlight a contrasted altitude in recharge areas supplying lowland springs. This suggests that different flow patterns have to be involved to explain the wide geochemical diversity observed and to allow the design of a very first conceptual groundwater-flow model. This paper demonstrates the efficiency of the combination of the selected tools as tracers of water-rock interaction, independently of flow depth, intrinsic water properties, geological conditions and interaction time disparities.

Keywords: hydrochemistry; isotope hydrology; geothermometry; mineral water; thermal water; gaseous springs; CO₂; brines; Corsica

1. Introduction

Mineral and thermal groundwaters are very special water resources characterised by stable and specific geochemical characteristics in terms of dissolved ions and gaseous contents as well as stable, and most of the time, relatively high temperatures. Groundwater circulation in-depth increases the complexity and the multiplicity of groundwater pathways and provides a high diversity of water qualities with potential health benefits such as for thermal, alkaline, CO₂-rich, brines, ferruginous or sulphurous waters [1,2]. These processes can be even more complex in the case of long-residence-time groundwater [3–6]. Geochemical and isotopic tools are very interesting when used together and can provide information on water origins as well as an estimation of the timing of the processes. Nevertheless, most of the time, these processes were studied in regions with only one or two regional geological units [7–14]. Indeed, many regions with a complex and a multi-composite geological structure, such as Corsica, have a wide mineral and thermal water diversity. Their origin and the hydrogeological processes responsible for the thermomineral specificity and diversity are too complex to be clearly understood [1,5,14,15].



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). In such regions, for better water management purposes and to guaranty the economical sustainability of the exploited resources, it can be necessary to understand precisely the water–rock interaction processes to discriminate the flow paths involved in the thermomineral groundwater genesis. Corsica Island (Western Mediterranean, France) is known for its complex geological settings and has an important spa tradition heritage with 43 minerals and thermal springs inventoried, spread over the entire island [16–21].

Motivated by the gap of knowledge about hydrogeological processes and flow patterns at the origin of Corsican mineral waters, new investigations have been carried out on the eastern part of the island, which is well known for displaying the highest mineral groundwater diversity over the island. The main objective was to provide a first conceptual hydrogeological model of the whole hydrosystem. The action was structured along different tasks: (1) describing the diversity of the different springs, (2) characterising water–rock interactions, including the identification of biotic or abiotic processes, as well as mixing processes, (3) assessing the depth of reservoirs and finally, (4) identifying the origin of groundwater and locate the recharge areas. This work provides significant new information on a still under documented region.

2. Study Area Description

2.1. Localisation, Topography and Hydroclimatology

The study area is located on the eastern part of Corsica (France) and is extending over 1500 km². The inland part (2/3 of the area) is mountainous with max 2136 m asl elevation, and the coastal part (1/3 of the area) is a lowland coastal-plain area touching the Tyrrhenian Sea. Three main rivers oriented to west-east drain the zone, the Solenzara River in the south, the Tavignanu River in the middle and the Golu River in the north (Figure 1). In the mountainous part, the climate is considered as sub-alpine, with a mean annual precipitation of 1350 mm and a mean annual temperature of 12 °C [22,23]. In the coastal plain area, the climate is typically Mediterranean with a mean annual precipitation of 650 mm and a mean annual temperature of 16 °C. The potential evapotranspiration is estimated about 2590 mm in the coastal regions of Corsica and the aquifer recharge rate is around 127 mm/y (about 16% of yearly rainfall) [24,25].

2.2. Geological and Hydrogeological Settings

The study area is composed of four geological units (Figure 1) [17]. The Hercynian basement, composed by calc-alkaline granitoid, is extending from the north-west to the southern part. It is overlapped along a N.NW–S.SE axis by two other units resulting from the Alpine orogenesis: the Eocene flysch, a sedimentary detrital unit located on its southern part from Corte to Solenzara cities and the Alpine metamorphic unit, mainly calc-schist, overlapping the Hercynian basement in its northern part. The latter units are separated toward east from Neogene sedimentary deposits by the Saint Antoine fault trending N.NE–S.SW (N020°) [19] (Figure 1). The geology, the mineralogical composition and the hydrogeological functioning of each unit encountered in the study area are described in the following paragraphs.

 The Hercynian basement is mainly composed by biotite-rich monzogranite, tonalogranodiorite or monzogranodiorite [17,26]. Monzogranite, mainly located around Pietrapola (Figure 1), is composed by alkaline quartz [SiO₂] (≈20%), alkaline feldspar [Na, K] (≈50%) and plagioclase [Na, Ca] (≈30%). Tonalogranodiorite and monzogranodiorite, mainly located in the Travu Valley (Figure 1), are, respectively, composed of quartz [SiO₂] (24.4–32.6%), plagioclase [Na, Ca] (52.6–38.2%), alkaline feldspar [Na, K] (7.2–19.7%), biotite [K, Mg, Fe, F] (11.6–7.5%), amphibole [Ca, Mg, Fe] (3.6–1.2%). This basement is intensively fractured and shows many faults NE–SW oriented [17]. Only few hydrogeological studies describe very basic information on the different groundwater types and hydrogeological characteristics of this unit. Deep fractures and discontinuities associated to the superficial weathered levels are favourable to the groundwater storage and flow [16,26–30].

- 2. The Alpine metamorphic units are composed of allochthonous material derived from the exhumation of oceanic and continental tectonic units involved in the Alpine orogeny (from the Late Cretaceous to the late Eocene, e.g., [21]). These tectonic units include meta-granitoid, metasedimentary rocks as serpentinites, meta-gabbros and meta-basalt. Lustrous schists observed were affected by a wide range of metamorphism-induced deformations going from blueschist facies (mainly Inzecca series), eclogite facies (mainly Serra di Pigno and Castagniccia series) to greenschist facies [18,21,31–33]. This geological formation, intensively pleated, is characterised by a lot of discontinuities displaying NS orientation of schistosity in the eastern part of the study site. The hydrogeological favourable zone is located in shallow-eroded parts or through deeper structural discontinuities.
- 3. The Eocene detrital sedimentary flysch is an autochthonous unit structured as a vertical alternation of conglomerates, sandstones and clay, mainly composed by arkose (formed by quartz [SiO₂] (up to 60%), feldspar [Na, K, Ca] (less than 20%), micas (up to 20%)) and pelites rocks. In its western part, this formation rubs along with the Hercynian basement according to the NE–SW contact and is overlapped by sedimentary deposits on the eastern part [16,34]. This heterogeneous geological unit has a low aquifer potential [18].
- 4. The Neogene sedimentary units are very heterogeneous and constituted by lateral deposits of organic matter-rich marls, sandstone and rhyolite conglomerates. Called the "Aghione formation" (Burdigalian and Langhien) these sand-conglomerate sediments are covered by black marls (Miocene) [18]. Locally, these sediments are also composed of limestone and bioclastic sandstone (Tortonian). Due to basin subsidence, Neogene lithology deposits dip to the east and have an approximate thickness of 2 km at the coastline and can reach 8.5 km in the middle of the Corsica Channel. Covered by Quaternary alluvial deposits (Figure 1). Neogene sediments host few shallow local aquifers with very low productivity. However, the thickness of the detrital Miocene layer is in favour of a real hydrogeological potential as a deep multi-layer confined aquifer [19,20].

2.3. Thermal and Mineral Waters in Corsica: Historical Background

At the beginning of the 19th century, the Corsica Island had the highest number of thermal spa in France [35] thanks to its huge hydromineral diversity with thermal, sulphurous, carbogaseous and ferruginous springs. Corsican springs provided access to a wide therapeutic treatment panel and was indicated to treat many diseases, from anaemia to colonial diseases such as malaria [36]. At the beginning of the 20th century, the numerous medicinal and therapeutic recognized advantages from these diversified springs have attracted international spa patients and medical scientists until 1926, when more than 52 doctors were employed in Corsican spas [37,38].

However, the insecurity due to the persistence of the banditry (the Guagno hostage crisis), the insalubrity or the lack of refurbished spa infrastructures, associated to the malaria disease raging in the lowland part of the island, gave start to the decline of the international interest in Corsican thermalism [39]. During the inter-World War period the local and wealthy population sustained the local thermalism. However, at the end of the Second World War, although the activity resumed on few sites (thanks to the universalisation of the French social insurance system) the wars-economic trauma associated to the dismantlement of the French colonial empire (and the end of the "colonial-tourism") lead to the final ending of the Corsican thermalism industry, despite the parallel development of this sector on mainland France at the same time [37–40].



Figure 1. Location of the study area with geology, topography, hydrography and distribution of mineral and thermal waters from the eastern part of Corsica Island (France). Symbols: white square depicts thermal springs, grey hexagon depicts CO₂-rich springs and white hexagon depicts cold springs.

Since, on 43 thermo-mineral springs [34], the Pietrapola site is the only one still exploited, as a thermal spa, in the eastern part of the island. The other famous thermal spa of the Puzzichellu site is now abandoned but the ancestral spring called PUZ-G, PUZ-N and an artesian borehole (PUZ-F) are still emerging. These springs are included in this study (Table 1). However, for a future sustainable exploitation of the Corsican thermo-mineral springs, a scientific characterisation is requested to bring arbitration elements on springs exploitation potential. To this end, this paper aims at characterising their origin and their hydrogeological functioning to document the sustainability and the vulnerability of the resources.

| | | Spring Type | | Location | | Observations | | | | | | | | | | | |
|----------------------|-------------------------------------------------------------------------|----------------------------------------------------------------------------------|---------------------|---------------------|-----------------------|--------------|---------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|------------------------------------------------------|-------------------------------------------------|------------------------------------------|-----------------|------------------|-------------|------------------------------------------------------------------------------------------|--|--|
| Spring's Name | Code | | Altitude (m asl) | GPS Co-C in "Lam | Ordinates bert 93″ | Ten Clas | nperature ssification | Mean Temperature | Mean TDS | Mean Discharge | Water Type | CO ₂ | H ₂ S | Beggiatoa | Local Geology | | |
| | | | (111 (131) | X (m) | Y (m) | Cold | Hot | (°C) | (mg/L) | (L/h) | | | | Dacterra | | | |
| Acqua Acetosa | ACQ | Modified | 47 | 1,227,704 | 6,119,786 | x | | 16.6 | 2222 | 89 | Ca-Na- HCO ₃ | x | - | - | Contact zone between Eocene Flysch and Neogene sediments (marls and conglomerates) | | |
| Caldaniccia Travu | CALD | Natural | 284 | 1,220,621 | 6,111,726 | | Hypothermal | 33.5 | 1925 | - | Na-HCO ₃ | - | - | - | Hercynian basement (granitoids) | | |
| Campo- Favajo | CAM-F | Modified | 25 | 1,231,885 | 6,137,973 | x | | 16.7 | 1038 | 729 | Na-HCO ₃ | - | x | x | Neogene sediments (conglomerates and marls) | | |
| Fontanella | FONT | Natural | 1 | 1,231,781 | 6,107,000 | х | | 17.9 | 8584 | - | Na-Cl | x | x | - | Flysch Eocene (sequence of conglomerates, sandstone and marls) | | |
| Pietrapola | P-MUR3 P-LAV P-LEC P-LUC P-MUR1 P-ESC P-RAST P-SOA | Modified Modified Modified Modified Modified Borehole Modified | 190 | 1222,834 | 6119,744 | | Hyperthermal Hyperthermal Mesothermal Hypothermal Mesothermal Acrothermal Hypothermal | 47.0 49.3 39.0 32.3 46.6 38.3 54.5 50.3 | 243 243 249 239 234 233 227 242 | 1388 571 - 244 353 - - 147 | Na-HCO3 | | | | Hercynian basement (granitoids) | | |
| Puzzichellu | PUZ-F PUZ-N PUZ-G | Borehole Modified Modified | 19 60 60 | 1,230,383,109 | 6,135,227,581 | X X X | | 16.9 15.6 14.6 | 837 1234 1105 | 627 | Ca-SO ₄ - HCO ₃ | - - | X X X | X X X | Neogene sediments (conglomerates and marls) | | |
| Fajo- Quarcio | QUAR-D QUAR-G | Modified Modified | 110 110 | 1,228,745 | 6,142,058 | x x | | 15.8 15.9 | 589 584 | - | Ca-Na- HCO ₃ | - | x x | x x | Jurassic and Cretaceous metamorphic rock (schist and limestone) | | |
| Vadina | VAD | Natural | 18 | 1,234,335 | 6,129,575 | x | | 17.9 | 475 | - | Ca-HCO ₃ | - | x | - | Miocene sediment (sandstone and limestone) | | |
| Vignola Travu | VIGN | Natural | 190 | 1,223,001 | 61,121,348 | | Hypothermal | 27.7 | 1424 | 1394 | Na-Cl | - | x | x | Contact zone between Eocene flysch and Hercynian basement (granitoids) | | |

Table 1. Background information on sampling sites: spring codification, location and observations. Spring type is described as "Natural" for spring without equipment to channel water flows; "Modified" for springs with equipment to channel water flows; "Borehole". (X) Presence, (-) Absence.

3. Methods

3.1. Sampling Network

On the study area, 19 mineral springs emerging at low altitude (<284 m asl), and were monthly sampled from January to June 2014: (Table 1, Figure 1):

- 8 springs of the Pietrapola group: P-SOA, P-MUR1, P-MUR3, P-LAV, P-LUC, P-RAST, P-ESC, P-LEC;
- 3 springs of the Puzzichellu group: PUZ-N, PUZ-F, PUZ-G, including the near-by Campo-Favajo site (CAM-F) and the "Fajo-Quarcio" site labelled: QUAR-G, QUAR-D;
- The Travu River Valley with a Vignola single spring (VIGN) and Caldaniccia single spring (CALD);
- 2 single isolated CO₂-rich springs of Acqua Acetosa (ACQ) and Fontanella (FONT);
- The single cold spring of Vadina labelled as VAD.

In order to identify the regional rainfall input, we collected water stable isotopes at 5 stations of the Corsica rainwater monitoring network [41]: Aleria (9 m), Bastia (1 m), Bonifacio (99 m), Corte (486 m), Campana (760 m) and Palneca (785 m).

3.2. Groundwater Sampling and Analytical Methods

Electrical Conductivity (EC) and Temperature (T) were measured with a WTW cond 3410 and the redox potential (Eh) and pH were measured with a WTW multi 3410 (WTW gmbH, Weilheim, Germany). Bicarbonate concentration (HCO₃) was determined, in the field, using a HACH digital titrator (HACH Company, Loveland, CO, USA).

Major ions samples were filtrated through 0.45 μ m nitrocellulose membranes in two 50 mL polyethylene bottles before storage at 4 °C. One bottle was acidified using ultrapure nitric acid for cation analysis, A Dionex ICS 1100 chromatograph (Thermo FischerScientific, Waltham, MA, USA) was used to determine ionic concentrations at the Hydrogeology Department (CNRS UMR 6134 SPE) of the University of Corsica. The analysis was checked and validated with an ionic balance under 5%.

Silica concentration (SiO₂) was sampled from a 150 mL PEB bottle, quantified with the Molybdosilicate method and analysed with a spectrophotometer Genesys 10S UV–VIS (Thermo Fisher Scientific, Waltham, MA, USA) at the Hydrogeology Department (CNRS UMR 6134 SPE) of the University of Corsica, France.

Trace elements were collected in 50 mL HDPE bottles after filtration through a 0.20 μ m pore size nitrocellulose membrane filter, then acidified with ultrapure nitric and stored at 4 °C. They were analysed by the Q-ICPMS X series II (Thermo Fisher Scientific, Waltham, MA, USA) at the AETE technical platform of the University of Montpellier, France.

Stable isotopes of the water molecule ($\delta^{18}O/\delta^2H$) were collected in a 20 mL amberglass bottle filled without no filtration and no headspace to ensure perfect conservation and stored at 4 °C. They were determined using a Liquid-Water stable isotope analyser DLT-100 (Los Gatos Research, San Jose, CA, USA) at the Hydrogeology Department (CNRS UMR 6134) of the University of Corsica, France, following the analytical scheme recommended by the IAEA [42]. The analytical precision was better than 0.5‰ for δ^2H and 0.2‰ for $\delta^{18}O$.

Samples for ³⁴S-H₂S analyses were conditioned in a 125 mL amber-glass bottle after filtration through a 0.45 μ m pore size nitrocellulose membrane and stabilised with the addition of 12 mg of cadmium acetate. To analyse ³⁴S-SO₄, one-litre PEHD bottles were filled with filtered water through a 0.7 μ m pore size glass fibre membrane filter and acidified with HCl. At the laboratory, samples were saturated with 5 mL of BaCl₂ solution to precipitate and settled BaSO₄, then rinsed with 500 mL of distilled water. The precipitate is recovered on the 0.45 μ m nitrocellulose membrane and desiccated before the sending for the analyse by mass spectrometry (IRMS) at the Isotope Science Laboratory, University of Calgary, Canada. The ¹⁸O-SO₄ analyses were performed from the same sample by isotope ratio mass spectrometer Delta+ (Thermo Fisher Scientific, Waltham, MA, USA) at the same laboratory.

For radiocarbon (¹⁴C) and ¹³C analyses from dissolved inorganic carbon, 1 L of groundwater was sampled in a PEHD bottle without headspace and stored at 4 °C. The analysis was performed by Accelerator Mass Spectrometry (AMS) for both isotopes following the analytical scheme recommended by the IAEA [43–46] at the Beta Analytic testing laboratory, London, United Kingdom.

4. Results and Discussion

4.1. Thermal and Mineral Description

4.1.1. Physico-Chemical Parameters

According to literature, the discharge temperature of mineral waters can discriminate waters with a thermal anomaly, called "thermal waters" (T > 20 $^{\circ}$ C) from "cold waters" $(T < 20 \degree C)$ [47]. Among thermal waters, the highest temperature is observed at the Pietrapola springs group (P–X), where their temperatures range from 31 to 54 °C which classifies them from mesothermal to acrothermal waters. The Travu River Valley shows two thermal springs, both classified as hypothermal: Caldaniccia (CALD) with a temperature of 33.5 °C and Vignola (VIGN) with a temperature of 27.6 °C (Figure 2A, Table 2). These temperature anomalies (T > 20 $^{\circ}$ C) suggest deep circulations. The pH of thermal waters is basic and ranges, according to the springs, from 8.9 to 9.9 for Pietrapola, 8.3 for Vignola and 9.2 for Caldaniccia. Electrical conductivity is stable and rather low with \approx 350 µS/cm for Pietrapola and $\approx 150 \,\mu$ S/cm at Caldaniccia and shows a high and unexpected value for Vignola (\approx 3000 µS/cm) (Table 2). Temperature and pH measured in 2014 are consistent with respective measures from 1980 [34]. High temperature and high pH are typical of a deep magmatic rocks circulation [13,48,49]. This 6 months' survey highlights strong mineralisation stability and is characteristic of the involvement of deep groundwater processes controlling the water quality. The temperature stability, observed for decades, expresses an up-flow without surface influence or mixing processes with shallow unconfined groundwater [34]. For two springs (P-LEC and P-LAV), where a 3 °C cooling associated to EC variations is observed compared to 1980, it then probably translates mixing with shallow water.



Figure 2. Time evolution of physico-chemical parameters (T and E.C.) of groundwater, discriminated as thermal (**A**) and cold (**B**) waters (N = 92).

| | | Т | pН | E.C. | Eh | HCO ₃ | SO ₄ | Cl | Br | F | Na | Ca | Mg | К | SiO ₂ | ² H | [| ¹⁸ C |) |
|--------|------------|--------------|------------|--------------|---------------|------------------|-----------------|------------|--------------|------------|--------------|------------|--------------|--------------|------------------|------------------|--------------|------------------|----------------|
| ID | Date | °C | (-) | μS/cm | mV | | | | | mg | g/L | | | | | ‰ | STD | ‰ | STD |
| | Jan | 16.6 | 6.0 | 2400 | 259 | 1535 | 2 | 120 | 0.5 | 0.4 | 254 | 317 | 23.3 | 8.2 | 57 | -40.6 | 0.07 | -6.68 | 0.02 |
| | Feb Mar | 16.5 15.8 | 6.1 6.3 | 2370 2410 | 293 307 | 1525 1543 | 2 13 | 110 114 | 0.4 0.4 | 0.4 0.0 | 243 247 | 328 328 | 15.3 18.3 | 9.1 3.3 | - 55 | -40.2 -42.3 | 0.05 | -6.75 -7.39 | $0.04 \\ 0.02$ |
| ACQ | Apr | 16.1 | 6.0 | 2220 | 148 | 1537 | 2 | 105 | 0.4 | 0.4 | 220 | 297 | 14.0 | 7.6 | 46 | -40.3 | 0.12 | -6.69 | 0.05 |
| | May | 16.8 | 6.2 | 2330 | 181 | 1485 | 2 | 114 | 0.4 | 0.0 | 257 | 323 | 24.8 | 8.2 | 52 | -39.1 | 0.02 | -6.51 | 0.09 |
| | Jun | 17.7 | 6.3 | 2360 | 178 | 1488 | 2 | 113 | 0.5 | 0.0 | 231 | 289 | 21.5 | 9.9 | 46 | -38.7 | 0.10 | -6.86 | 0.03 |
| FONT | Jan Jun | 17.5 18.3 | 6.1 6.5 | 13,430 | 202 165 | 1918 1932 | 26 25 | 3628 | 15.9 14.4 | 1.5 4.5 | 2301 2255 | 463 444 | 84.7 82.9 | 95.9 92.4 | 44 30 | -54.2 -56.2 | 0.09 0.34 | -8.62 -9.50 | 0.02 0.10 |
| | Jan Fob | 27.2 | 8.3 | 3000 | -105 | 39 27 | 6 | 639 605 | 2.5 | 3.7 | 435 | 131 | 0.2 | 15.1 | 36 35 | -39.2 | 0.03 | -6.48 | 0.07 |
| | Mar | 27.0 | 8.5 | 3010 | -104 -5 | 21 | 11 | 913 | 3.5 | 4.3 | 434 | 128 | 0.2 | 14.5 | - | -39.4 -39.6 | 0.08 | -6.50 | 0.03 |
| VIGN | Apr | 27.5 | 8.1 | 2960 | -25 | 32 | 14 | 877 | 3.5 | 4.4 | 423 | 123 | 0.2 | 14.5 | 34 | -40.2 | 0.12 | -6.70 | 0.02 |
| | May | 28.3 | 8.4 | 2950 | 10 | 20 | 13 | 894 | 3.5 | 4.4 | 429 | 120 | 0.2 | 12.0 | 34 | -39.7 | 0.08 | -6.45 | 0.02 |
| | Jun | 32.2 | 93 | 154 | 305 | 53 | 15 | 7 | 1.4 | 0.7 | 28 | 3 | 0.2 | 0.6 | 38 | -42.2 | 0.50 | -6.79 | 0.00 |
| CALD | Jun | 34.9 | 9.1 | 151 | -28 | 54 | 16 | 6 | 0.1 | 0.7 | 28 | 3 | 0.0 | 0.7 | 38 | -42.4 | 0.34 | -7.13 | 0.10 |
| | Jan Fob | 46.7 46.5 | 8.9 8.8 | 344 345 | -182 -26 | 99 120 | 28 32 | 27 27 | 0.1 | 3.6 | 69 69 | 2 | 0.0 | 3.6 | 88 87 | -54.7 | 0.07 | -8.72 | 0.03 |
| | Mar | 46.6 | 9.3 | 350 | $-20 \\ -86$ | 120 | 25 | 27 | 0.2 | 3.5 | 67 | 1 | 0.0 | 3.4 | - | -54.4 | 0.08 | -8.66 | 0.07 0.04 |
| P-MUR3 | Apr | 47.8 | 9.3 | 348 | -108 | 104 | 27 | 27 | 0.2 | 3.2 | 66 | 2 | 0.0 | 3.5 | 77 | -54.6 | 0.19 | -8.76 | 0.07 |
| | May Jun | 46.9 47.5 | 9.4 9.5 | 349 345 | $-89 \\ -63$ | 117 96 | 32 27 | 28 27 | 0.2 0.2 | 3.2 3.5 | 68 67 | 2 2 | 0.0 0.0 | 3.6 3.5 | 75 77 | $-54.5 \\ -53.8$ | 0.11 0.63 | $-8.58 \\ -9.01$ | $0.05 \\ 0.09$ |
| | Jan | 50.1 | 9.0 | 347 | -232 | 107 | 24 | 28 | 0.1 | 3.6 | 69 | 2 | 0.0 | 3.4 | 85 | -54.9 | 0.04 | -8.78 | 0.02 |
| | Feb | 46.8 | 9.3 | 348 | 19 | 129 | 27 | 27 | 0.2 | 3.1 | 68 | 2 | 0.0 | 3.5 | 85 | -54.4 | 0.14 | -8.64 | 0.09 |
| P-LAV | Mar Apr | 49.2 48 7 | 9.3 9.4 | 349 347 | 6 43 | 120 | 26 26 | 27 | 0.1 | 3.3 | 67 | 1 | 0.0 | 3.3 | - 84 | -54.7 -55.8 | 0.21 | -8.77 | 0.07 |
| | May | 50.5 | 9.5 | 347 | -192 | 109 | 27 | 27 | 0.1 | 3.1 | 67 | 2 | 0.0 | 3.5 | 73 | -54.7 | 0.09 | -8.77 | 0.07 |
| | Jun | 50.8 | 9.6 | 348 | -154 | 98 | 24 | 27 | 0.2 | 3.5 | 68 | 2 | 0.0 | 3.4 | 72 | -54.8 | 0.06 | -9.07 | 0.05 |
| | Jan | 32.4 | 9.3 | 342 | -184 | 105 | 24 | 28 | 0.1 | 3.6 | 69 | 2 | 0.0 | 3.5 | 87 | -54.7 | 0.17 | -8.61 | 0.05 |
| | Feb Mar | 31.4 32.2 | 9.5 9.5 | 344 342 | 56 19 | 102 | 32 24 | 27 27 | 0.1 | 3.1 | 69 67 | 2 | 0.0 | 3.5 3.4 | - 84 | -54.7 -54.6 | 0.22 | -8.75 -8.69 | 0.02 |
| P-LUC | Apr | 32.4 | 9.6 | 343 | 114 | 101 | 32 | 27 | 0.2 | 3.3 | 65 | 2 | 0.0 | 3.5 | 62 | -55.0 | 0.30 | -8.77 | 0.09 |
| | May | 32.7 | 9.7 | 343 | -106 | 110 | 32 | 27 | 0.2 | 3.6 | 67 | 2 | 0.0 | 3.6 | 71 | -55.1 | 0.11 | -8.84 | 0.08 |
| | Jun | 50.7 | 9.9 | 344 | -48 | 100 | 26 | 2/ | 0.2 | 3.4 | 67 | 2 | 0.0 | 3.5 | 73 | -54.8 | 0.33 | -9.10 | 0.08 |
| | Jan Feb | 50.7 50.1 | 9.1 9.3 | 348 353 | $-240 \\ -24$ | 115 | 24 25 | 28 27 | 0.2 | 3.8 3.3 | 69 69 | 2 5 | 0.0 | 3.4 3.5 | 89 90 | -54.9 -54.9 | 0.11 | -8.69 -8.92 | 0.08 |
| P SOA | Mar | 49.5 | 9.3 | 348 | -123 | 121 | 24 | 27 | 0.1 | 3.1 | 67 | 1 | 0.0 | 3.5 | - | -54.8 | 0.11 | -8.80 | 0.05 |
| 1-50A | Apr | 49.5 | 9.5 | 350 | 105 | 105 | 25 | 28 | 0.1 | 3.3 | 65 | 2 | 0.0 | 4.5 | 74 | -55.3 | 0.26 | -8.90 | 0.05 |
| | Tun | 50.8 51.1 | 9.4 9.7 | 347 349 | -200 -114 | 102 | 27 | 27 | 0.1 | 3.2 3.5 | 67 | 2 | 0.0 | 3.6 3.4 | 75 76 | -54.4 -54.9 | 0.04 0.50 | -8.85 -9.26 | 0.02 0.04 |
| P-ESC | Apr | 38.3 | 9.4 | 347 | 126 | 106 | 24 | 27 | 0.1 | 3.5 | 65 | 2 | 0.0 | 3.8 | 25 | -38.8 | 0.05 | -6.46 | 0.04 |
| P-MUR1 | Jan | 46.6 | 8.9 | 347 | -151 | 98 | 30 | 28 | 0.1 | 3.8 | 68 | 3 | 0.0 | 3.5 | 84 | -38.9 | 0.13 | -6.49 | 0.10 |
| P-MUR2 | Jan | 46.8 | | 348 | 191 | - | - | - | - | - | - | - | - | - | - | -39.4 | 0.10 | -6.6 | 0.10 |
| | Jan | 39.6 | 9.4 | 346 | -122 | 110 | 28 | 26 | 0.1 | 2.6 | 68 | 2 | 0.0 | 3.4 | 71 | -39.4 | 0.86 | -6.49 | 0.08 |
| | Feb Mar | 36.0 39.0 | 9.4 9.4 | 366 347 | 56 | 131 120 | 33 27 | 29 27 | 0.1 | 3.2 | 70 68 | 2 | 0.0 | 5.2 3.4 | 74 | -38.3 -38.7 | 0.17 0.15 | -6.30 -7.02 | 0.06 |
| P-LEC | Apr | 39.3 | 9.4 | 376 | 166 | 113 | 32 | 28 | 0.1 | 3.7 | 65 | 2 | 0.0 | 4.3 | 76 | -38.2 | 0.09 | -6.33 | 0.02 |
| | May | 39.5 | 9.6 | 347 | -66 | 111 | 32 | 27 | 0.2 | 3.3 | 67 | 2 | 0.0 | 3.5 | 75 | -38.7 | 0.04 | -6.34 | 0.08 |
| | Jun | 40.7 | 9.8 | 349 | -28 | 110 | 31 | 28 | - | 3.5 | 67 52 | 2 | 0.0 | 4.2 | 76 | -38.4 | 0.32 | -6.47 | 0.08 |
| | Mar | 54.6 54.6 | 9.0 9.1 | 348 348 | -212 - 160 | 120 | 25 | 27 | 0.1 | 3.5 | 67 | 2 | 0.0 | 2.9 3.4 | 65 | -38.3 -38.4 | 0.11 | -7.03 -6.33 | 0.07 |
| P-RAST | Apr | 54.3 | 9.4 | 348 | 65 | 113 | 25 | 27 | 0.1 | 2.8 | 65 | 2 | 0.0 | 3.7 | 82 | -38.6 | 0.17 | -6.80 | 0.06 |
| | Jun | 54.7 | 9.6 | 350 | -156 | 98 | 25 | 28 | 0.2 | 3.8 | 67 | 2 | 0.0 | 3.6 | 74 | -51.9 | 0.08 | -8.23 | 0.02 |
| CAM-F | Jan Feb | 16.7 16.7 | 7.7 | 1451 1440 | 59 130 | 483 466 | 18 19 | 242 235 | 1.0 | 0.6 | 265 255 | 31 | 13.2 14.6 | 3.4 3.4 | 24 24 | -54.9 -51.6 | 0.13 | -8.92 -8.23 | 0.05 |
| | Mar | 16.6 | 7.8 | 1446 | 106 | 472 | 20 | 230 | 0.9 | 0.7 | 266 | 31 | 14.0 | 3.4 | - | -51.0 | 0.13 | -8.21 | 0.05 |
| | Apr | 16.6 | 7.8 | 1451 | -15 | 473 | 19 | 230 | 0.9 | 0.7 | 243 | 32 | 14.4 | 3.6 | 22 | -52.4 | 0.02 | -8.20 | 0.05 |
| | May | 16.7 16.7 | 7.7 7.8 | 1436 1435 | -260 -127 | 489 476 | 19 21 | 230 230 | 0.9 | 1.0 | 251 254 | 30 30 | 13.2 13.2 | 3.4 | 23 23 | -55.0 -55.0 | 0.03 0.49 | -9.04 -8.82 | 0.07 0.08 |
| | i | 10.7 | 7.0 | 1025 | -12/ | 402 | <u><u></u></u> | 200 | 0.9 | 0.0 | 2JH | | 15.4 | 1.0 | 2.5 | -55.0 | 0.13 | 0.02 | 0.00 |
| | Jan Feb | 16.8 16.8 | 7.1 73 | 1025 | 165 180 | 483 489 | 96 116 | 48 47 | 0.2 | 0.0 | 51 52 | 99 106 | 37.3 39.5 | 1.9 2.0 | 38 36 | -54.6 | 0.23 | -8.65 | 0.18 0.11 |
| | Mar | 16.8 | 7.1 | 1014 | 77 | 492 | 87 | 47 | 0.2 | 0.4 | 50 | 102 | 38.8 | 1.9 | - | -54.3 | 0.13 | -8.62 | 0.07 |
| PUZ-F | Apr | 16.9 | 7.4 | 1015 | 8 | 490 | 108 | 51 | 0.2 | 0.2 | 50 | 101 | 43.2 | 1.9 | 36 | -54.6 | 0.13 | -8.71 | 0.07 |
| | Iviay | 17.0 17.1 | 7.2 7.5 | 1014 | $-121 \\ -77$ | 486 490 | 112 89 | 52 48 | 0.3 | 0.0 | 52 50 | 99 98 | 49.4 48.3 | ∠.0 1.9 | 34 40 | -54.8 -55.0 | 0.00 | -8.72 -8.70 | 0.08 |

Table 2. Physico-chemical parameters and concentration in major chemical constituents (mg/L) as well as water stable isotopes values for mineral and thermal waters. (-) Non-measured.

| | | Т | pН | E.C. | Eh | HCO ₃ | SO_4 | Cl | Br | F | Na | Ca | Mg | K | SiO ₂ | ² H | ſ | ¹⁸ C |) |
|----------------|-----------|------|-----|--------|-----|------------------|--------|--------|-----|-----|--------|-----|------|-----|------------------|----------------|------|-----------------|------|
| ID | Date | °C | (-) | μS/cm | mV | | | | | mg | ç/L | | | | | ‰ | STD | ‰ | STD |
| | Mar | 14.3 | 7.8 | 1414 | -66 | 488 | 295 | 93 | 0.4 | 0.4 | 50 | 204 | 44.1 | 2.1 | - | -54.0 | 0.13 | -8.64 | 0.05 |
| DUZN | Apr | 15.5 | 7.8 | 1412 | 79 | 483 | 296 | 140 | 0.3 | 0.3 | 49 | 205 | 44.2 | 2.0 | 48 | -54.8 | 0.20 | -9.07 | 0.07 |
| PUZ-N | May | 15.7 | 7.7 | 1432 | -60 | 490 | 315 | 115 | 0.4 | 0.0 | 50 | 202 | 51.3 | 2.2 | 38 | -54.5 | 0.33 | -8.77 | 0.06 |
| | Jun | 17.1 | 8.2 | 1466 | -77 | 559 | 324 | 114 | | 0.5 | 52 | 209 | 52.3 | 2.2 | - | -54.7 | 0.30 | -8.78 | 0.08 |
| PUZ-G | Mar | 14.2 | 7.1 | 1386 | -77 | 632 | 100 | 96 | 0.3 | 0.3 | 56 | 168 | 51.6 | 2.1 | - | -54.8 | 0.17 | -8.75 | 0.04 |
| | Apr | 15.1 | 7.2 | 1406 | -33 | 616 | 99 | 111 | 0.3 | 0.2 | 57 | 167 | 47.8 | 2.1 | 34 | -54.4 | 0.19 | -9.09 | 0.04 |
| QUAR- D | Mar | 15.2 | 7.4 | 698 | -7 | 400 | 19 | 26 | 0.2 | 0.4 | 63 | 83 | 11.3 | 1.7 | - | -40.7 | 0.07 | -6.76 | 0.05 |
| | Apr | 15.8 | 7.4 | 699 | 213 | 370 | 18 | 26 | 0.2 | 0.5 | 60 | 82 | 10.7 | 2.4 | 9 | -41.5 | 0.35 | -6.90 | 0.08 |
| | May | 16.0 | 7.4 | 669 | 7 | 400 | 18 | 26 | 0.2 | 0.4 | 62 | 76 | 11.2 | 1.7 | 10 | -40.8 | 0.03 | -6.84 | 0.05 |
| | Jun | 16.1 | 7.6 | 694 | -74 | 392 | 16 | 26 | 0.2 | 0.5 | 62 | 76 | 11.0 | 1.7 | 10 | -40.8 | 0.11 | -7.52 | 0.17 |
| | Mar | 15.7 | 7.3 | 699 | -17 | 403 | 18 | 26 | 0.2 | 0.3 | 60 | 82 | 10.1 | 1.7 | - | -40.7 | 0.10 | -6.77 | 0.03 |
| QUAR- | Apr | 15.8 | 7.3 | 701 | 213 | 377 | 17 | 26 | 0.2 | 0.5 | 59 | 83 | 10.9 | 1.8 | 9 | -41.1 | 0.05 | -7.05 | 0.07 |
| G | May | 15.9 | 7.3 | 700 | -42 | 405 | 18 | 26 | 0.2 | 0.4 | 60 | 76 | 11.3 | 1.8 | 10 | -41.1 | 0.13 | -6.96 | 0.08 |
| | Jun | 16.3 | 7.6 | 698 | -55 | 364 | 16 | 26 | 0.2 | 0.5 | 61 | 77 | 11.1 | 1.7 | 10 | -40.7 | 0.44 | -7.34 | 0.04 |
| | Jan | 18.0 | 7.2 | 602 | 280 | 254 | 28 | 41 | 0.3 | 0.0 | 25 | 96 | 4.8 | 1.2 | 17 | -37.4 | 0.11 | -6.00 | 0.02 |
| | Feb | 18.0 | 7.1 | 595 | 267 | 260 | 28 | 40 | 0.2 | 0.3 | 24 | 104 | 3.9 | 1.2 | 17 | -37.1 | 0.01 | -6.03 | 0.04 |
| VAD | Mar | 18.0 | 7.3 | 600 | 294 | 262 | 29 | 41 | 0.2 | 0.3 | 24 | 99 | 3.6 | 1.1 | - | -37.2 | 0.07 | -6.16 | 0.05 |
| | Apr | 18.0 | 7.2 | 595 | 251 | 277 | 28 | 44 | 0.2 | 0.2 | 24 | 99 | 4.1 | 1.1 | 17 | -37.1 | 0.34 | -6.17 | 0.09 |
| | May | 17.9 | 7.2 | 593 | 259 | 262 | 28 | 45 | 0.3 | 0.0 | 24 | 97 | 4.5 | 1.2 | 16 | -37.0 | 0.01 | -6.12 | 0.07 |
| | Jun | 17.9 | 7.6 | 592 | 262 | 270 | 31 | 39 | 0.2 | 0.0 | 23 | 93 | 4.5 | 1.3 | 11 | -36.8 | 0.29 | -7.07 | 0.18 |
| Sea Wa Mear | iter n | 18.3 | 8.2 | 57,375 | - | 165 | 2910 | 21,366 | 73 | 0.7 | 11,773 | 574 | 1421 | 328 | - | 6.12 | 0.13 | 1.31 | 0.08 |

Table 2. Cont.

The temperature of cold waters (T < 20 °C) ranges from 14.2 °C (PUZ-G) to 18.3 °C (FONT) (Figure 2B, Table 2). These lower and stable temperatures show that groundwater flows at a shallower depth than thermal waters. Cold waters show a pH ranging from 6.0 to 8.6 with intermediate (600 μ S/cm) to high EC values (13,500 μ S/cm). FONT and ACQ springs, flowing out from the flysch, have an acid pH, respectively, of \approx 6.3 and \approx 6.1 and a clearly visible CO₂-rich content. These bubbling springs show a higher conductivity (ACQ \approx 2300 μ S/cm and FONT \approx 13,500 μ S/cm) compared to springs flowing through the flysch [50] (Figure 1, Table 1). Four springs (QUAR-D, QUAR-G, PUZ-N and ACQ) show a seasonal temperature variation without EC variation. This is probably due to their very low discharge rate, which can favour the influence of the atmospheric temperature on the mineral water temperature (Table 1). Generally, the temperature and the electrical conductivity of the investigated springs is rather consistent with the 1980s data [34]. This underlines the stable characteristics of the different mineral water at the seasonal and decennial time scales.

4.1.2. Diversity of Hydrochemical Water Types

The Piper diagram (Figure 3) displays different water types found over the study area. Thermal waters P-X and CALD, with basic pH and low EC, display a typical HCO₃-Na water type in agreement with the processes of mineralisation coming from groundwater flow through granitoids rocks [14]. The thermal spring VIGN shows a Na-Cl water type, such as the cold spring FONT, indicating a long water–rock interaction time with detrital deposits or a contribution of moderately saline water such as brines. The CO₂-rich spring ACQ shows an intermediate water type, a Ca-Na-HCO₃ water type, which has already been observed as a result of the mixing processes of water flowing through magmatic and sedimentary rocks [14] but it can also be due to a high proportion of aluminosilicates weathering.



Figure 3. Piper diagram of Eastern Corsica thermo-mineral groundwater (N = 84). The spring group of Pietrapola is displayed in red background while Puzzichellu is displayed in yellow background.

VAD and two springs of the Puzzichellu group PUZ-F and PUZ-G (H₂S-rich water) have a Ca-HCO₃ water type. In the same area, a few meters apart, the other spring PUZ-N shows a Ca-HCO₃-SO₄ water type due to a higher concentration in sulphate compared to PUZ-F (borehole tapping groundwater at 41 metres in-depth) and PUZ-G (spring) (Table 1). The geochemical disparity observed at the same site shows that the geochemical signature is influenced by another process than the water–rock interaction time. On a larger scale, the Puzzichellu springs group also shows a Ca-Na-HCO₃ water type (QUAR-D, QUAR-G) and a Na-HCO₃ water type (CAM-F) (Table 1). So, the very local geology only partially explains the geochemical diversity observed.

4.1.3. Mixing Processes during Up-Flowing

To understand the maturity of water and also to discriminate geothermal systems among volcanic (SO_4 -end-member), peripheral (HCO_3 -end-member) or mature waters (Cl-end-member), relative content in major ions Cl, SO_4 and HCO_3 were classified on a ternary diagram (Figure 4B) [51].



Figure 4. Ternary diagram displaying groundwater chemical content (SO₄, Cl, Ca, Mg, Si and HCO₃). The spring group of Pietrapola is displayed in red background while Puzzichellu is displayed in yellow background. The ternary (**A**) displays the main lithology involved in water mineralisation. Indeed, this [Ca-5*Mg-10*Si] diagram is usually used to illustrate the lithology of rocks involved in water–rock interactions [52,53]. Due to the absence of Si value, FONT and CALD are not displayed on this plot. Developed by Giggenbach [54], the (**B**) ternary diagram helps discerning mature and peripheral waters and gives crucial information about fluid mixing.

The FONT and VIGN spring plots close to the Cl-corner which make them as "mature waters". Indeed, both springs provide highly mineralised waters, sodium-chlorite-rich and testifies for brine waters occurrences at depth [55,56]. All other waters plot close to the HCO₃-corner and can be considered as "peripheral waters". Cold waters are related to direct infiltration from meteoric water through soil. For thermal waters, the HCO₃-content observed (P-X and CALD) usually indicates an important distance from the heat source [11,51,57]. So, the natural geothermal gradient is the only process involved in the warming of waters.

4.2. Water-Rock Interactions

The Figure 4A displays a ternary plot of Si, Ca and Mg-proportions according to local lithology and highlights the different water–rock interactions involved in the groundwater mineralisation [52,53].

4.2.1. Granitoid-Rocks Minerals Hydrolysis

The proportion of silica, close to 100% for Pietrapola springs is linked to the very low concentration in Ca and the absence of Mg in the water. For the VIGN spring, Ca amount is relatively more important than in the Pietrapola springs because the geological context is different. Indeed, the VIGN spring emerges at the interface between granitoids and carbonate-rich flysch, which gives to the groundwater a slightly more carbonated fingerprint.

Differentiating granite-minerals involved in the mineralisation processes of thermal water is allowed by considering Figure 5A, which shows the Na/K ratio as a function of SiO₂. Indeed, the alkali–feldspar alteration process is highlighted for the P-X springs which show the highest SiO₂ concentrations (from 20 to 90 mg/L) and the lowest Na/K ratio (\approx 15) [54,58]. This low ratio is characteristic of the cations exchange between albite and alkaline feldspar at high temperature and under deep reservoirs conditions, as it can be found in Hercynian granitoid rocks [57,59]. According to local geology, the Pietrapola springs emerges from monzogranite with high feldspar content, which is able to explain the Na and K concentration observed in the groundwater. CALD and VIGN show a higher

Na/K Ratio (\approx 50) for an intermediate SiO₂-content (between \approx 20 mg/L and \approx 38 mg, respectively) which reveal different interaction kinetics inside the granitic reservoir and another kind of hydrolysis process at the contact with another granitoid type, more enriched in plagioclase in the Travu River Valley. Indeed, this ratio is characteristic of granodiorite and is responsible for the high Na content observed there. Granodiorite or monzogranite show a similar and relatively high SiO₂ content which tend to indicate relatively long water–rock interaction time within the reservoir.



Figure 5. Ions scatter diagram displaying some major ion content or ratio (Na/K, SiO₂, F, Mg/Ca, Ca and HCO₃) associated with trace elements (Li, As, B, Rb/Sr ratio), W.r.: weight ratio. The spring group of Pietrapola is displayed in red background while Puzzichellu is displayed in yellow background and the Travu River Valley in orange background. The (**A**) plot discriminates the Na⁺ and K⁺ content according to granitoid type; the (**B**) plot illustrates the shallow influence at the origin of HCO₃⁻, Mg²⁺ and Ca²⁺ content; the (**C**) plot corresponds to fluorite weathering in hydrothermal waters.

All thermal groundwaters are Mg-depleted with a low HCO₃ content (Figure 5B). This shows the influence of a deep and high temperature reservoir on the hydrolysis reactions, followed by a fast up-flowing process [60,61]. The Figure 5C displays the Ca as a function of F-content and highlights water–rock interaction processes between the basement-rocks and the following direct upwelling of geothermal fluids [62,63]. Indeed, F-content in groundwater is linked to Hercynian granitoid interactions [64] due to its enhanced mobilisation at a high temperature. Hydrothermal waters are marked by high F-content and low Ca-content and plot close to the granitoid end-member [65]. Due to the

temperature-dependency of fluorite CALD, the coldest springs (\approx 32 °C), is less enriched in F than other thermal waters.

4.2.2. Detrital Sedimentary Rocks Weathering

The VAD spring (Figure 4A), shows the highest Ca-concentration, which is linked to its flows through local limestone and calcareous sandstone. A carbonated signature of groundwater is also observed for the ACQ spring with its Ca-HCO₃ water-type emerging at the interface of the Eocene flysch and Miocene sedimentary rocks. Within the Puzzichellu springs group, QUAR-D and QUAR-G plot close to the carbonate rocks end-member due to their local metamorphosed calc-schist geology (Figure 1, Table 1) which explains their water type (Ca-HCO₃). Considering its sedimentary context, CAM-F displays an unexpected Si-content (Figure 4A). This high SiO₂ amount [\approx 22 mg/L] associated to a high Na/K ratio (\approx 75) suggest a mixing process occurring with deep flow from granitoid, which is able to explain the Na-intake.

The Figure 5B displays the Mg/Ca ratio as a function of HCO₃ concentration in order to discriminate dilution processes during the up-flow from water–rock contact time influence. QUAR-D, QUAR-G, VAD and FONT show proportional increase in Mg, Ca and HCO₃ without significant seasonal variation. This trend suggests mixing with phreatic water in sedimentary rocks providing a proportional income of Mg, Ca and HCO₃ with a low ratio (<0.2) and low HCO₃ (<10 meq/L). FONT and ACQ, both bubbling springs, show the highest HCO₃ content (up to 35 meq/L). Their high mineralisation is due to the intensive water–rock interactions boosted by the aggressiveness of low pH induced by the high CO₂ solubility at low temperatures [48]. However, ACQ shows a seasonal variability of the dissolved content, explained by the surface waters contribution.

Despite the Puzzichellu site hydrofacies disparity (Figure 4A), all springs seem to flow through the same aquifer composed of detrital conglomerates from the heterogeneous Miocene sedimentary deposits [18]. The Puzzichellu spring group shows a seasonal variability of the Mg/Ca ratio without any effect on the HCO_{3-} content. The absence of seasonal HCO_3 variation discredits any HCO_{3-} mobilization due to phreatic flow through sedimentary rocks but translates disparities in water–rock interaction times, explained by the relative stability of ferromagnesian minerals (Mg-rich) and plagioclase feldspar (Ca-rich).

4.2.3. Evidence of Brine Waters Occurrence

FONT (CO₂-rich) and VIGN, both mature waters, display the same signature in fluoride with an intake of Ca-content, probably given by the carbonate signature of the flysch (Figure 5C). Those values plot close to the seawater end-member, their Na-Cl hydrofacies combined with the high E.C. and high amount of chlorite and fluoride indicates residual brines, probably due to a dissolution of interstitial seawater residue, or connate waters occurrence. This saline water is emerging mixed with infiltrating meteoric waters, and after having leached the upper part of the brines out from the sediments, this process is well referenced around the Mediterranean basin [66–68].

4.2.4. Mixing Processes

Principal component analysis (CPA) was performed from major and trace elements (Figure 6, Table 3). The first two axis explain 72.78% of the total variance of the population, F2 is positively correlated to F, K and Rb (magmatic elements) and negatively to Mg, HCO₃ and Ca (sedimentary elements) and discriminates them. While F1 is negatively correlated to As and SiO₂ (hydrothermal elements) and positively correlated with Sr and E.C. This axis discriminates magmatic influences, with its high As-content related to the presence of geothermal fluids [63], from mixing flows involving different flow pattern with high Sr-content due to the increase in combined sedimentary and granitoid rocks hydrolysis [69].



Figure 6. Principal Component Analysis (PCA) discriminating the origin of trace elements and the geological influence on spring water composition. The spring group of Pietrapola is displayed in red background while Puzzichellu is displayed in yellow background. (A) This figure displays both correlation factors (F1 and F2) according to variables (parameters) and observations (springs contents); (B) table displaying the correlation matrix associated to (A), according to Pearson (n - 1).

The Figure 6 highlights the main reservoirs involved in the mineralisation of cold waters (except ACQ and CAM-F), which are flowing mainly through sedimentary rocks and are influenced by shallow waters mixing, while thermal waters (except VIGN) flow mainly through magmatic rocks without shallow water mixing and dilution. Both exceptions (VIGN and ACQ) seem to be influenced by more complex mixing processes, combining deep brines up-flowing and then mixing with phreatic flow through sedimentary and/or magmatic rocks. This is clearly observable on VIGN, which is influenced by brines and waters flowing through magmatic rocks at the same time. This flow pattern is able to dilute magmatic As concentration [up to $0.03 \ \mu g/L$] and cause an intake in Li [1440 \ \mu g/L] and B [1824 \ \mu g/L] (Table 3). The dissolved CO₂ increases rock-hydrolysis, and then the amount of dissolved elements in water which can explain Ca, Mn and Fe concentrations observed in ACQ [70,71]. CAM-F, which springs out from the sedimentary plain, is mainly influenced by deep regional flow influenced by magmatic abiotic interactions.

| Sampling Point | | Traces Elements (µg/L) | | | | | | | | | | | | | |
|------------------|------------------------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------------------|----------------------------------------------|-------------------------------------------|--------------------------------|---------------------------------|-----------------------------------|----------------------------------------------|----------------------------------|-----------------------------------------------------------------------|----------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|
| | ID | Li | В | As | Rb | Sr | Fe | Mn | Ba | F | Al | Cs | Si | Cr | U |
| Acqua Acetosa | ACQ | 624 | 1508 | 0.262 | 20.6 | 2194 | 2947 | 953 | 317 | 190 | 2 | 5.3 | 34,820 | $4.7 	imes 10^{-2}$ | $3.0 	imes 10^{-2}$ |
| Travu | VIGN | 1440 | 1824 | 0.031 | 165.3 | 3867 | 8 | 4 | 59 | 4273 | 26 | 56.4 | 18,810 | $0.0	imes10^{0}$ | $2.3 	imes 10^{-1}$ |
| Pietrapola | P-LAV P-LEC P-MUR3 P-LUC P-RAST P-SOA | 115 112 110 110 111 111 | 143 138 137 137 138 140 | 1.621 1.772 1.413 1.878 1.280 1.587 | 32.8 33.0 31.9 32.2 33.1 33.3 | 56 51 52 50 53 53 | 5 3 13 6 2 | 0 0 0 1 0 | 1 1 1 0 1 1 | 3286 3521 3465 3295 3547 3067 | 17 12 19 13 26 20 | 10.2 10.2 9.7 10.0 10.2 10.2 | 48,391 47,408 46,980 48,086 47,751 47,270 | $\begin{array}{c} 6.0\times10^{-3}\\ 4.2\times10^{-3}\\ 1.5\times10^{-2}\\ 2.4\times10^{-2}\\ 3.5\times10^{-2}\\ 4.3\times10^{-3} \end{array}$ | $\begin{array}{c} 8.9\times 10^{-3}\\ 1.5\times 10^{-3}\\ 6.6\times 10^{-3}\\ 3.0\times 10^{-3}\\ 6.8\times 10^{-3}\\ 4.0\times 10^{-4} \end{array}$ |
| Puzzichellu | PUZ-F PUZ-G PUZ-N CAM-F QUAR-D QUAR-G | 37 37 38 122 39 38 | 62 43 32 468 1206 1200 | 0.028 0.060 0.091 0.003 0.021 0.010 | 2.8 3.5 3.7 5.0 1.8 1.7 | 1880 1583 1497 943 769 752 | 5 39 467 5 18 9 | 3 24 108 6 25 25 | 96 116 47 18 44 42 | 367 349 450 730 364 283 | 1 6 36 3 4 3 | $\begin{array}{c} 0.0 \\ 0.0 \\ 0.0 \\ 0.3 \\ 1.1 \\ 1.1 \end{array}$ | 20,691 24,114 21,129 14,351 5778 5662 | $\begin{array}{c} 1.7\times10^{-2}\\ 1.3\times10^{-1}\\ 8.1\times1\\ 1.6\times10^{-2}\\ 2.3\times10^{-2}\\ 1.1\times10^{-2} \end{array}$ | $\begin{array}{c} 1.5\times10^{-3}\\ 1.5\times10^{-1}\\ 3.2\times10^{-1}\\ 1.1\times10^{-1}\\ 5.6\times10^{-1}\\ 5.8\times10^{-1} \end{array}$ |
| Vadina | VAD | 4 | 30 | 1.132 | 0.5 | 123 | 3 | 0 | 27 | 283 | 1 | 0.0 | 9026 | $4.3	imes10^{-1}$ | $1.6	imes10^{0}$ |
| · | Detection limit | 0.030 | 0.210 | 0.003 | 0.007 | 0.111 | 0.035 | 0.002 | 0.030 | 100 | 0.4 | $6.3 	imes 10^{-5}$ | 17 | 0.008 | $1.7 	imes 10^{-4}$ |

Table 3. Concentrations in trace elements.

4.2.5. Elements Prevalence at Depth

A pH–Eh diagram (Figure 7) was used to characterise the reservoirs conditions affecting the trace elements prevalence in groundwater. All springs are under reducing conditions and highlight that most flow paths are mainly under anoxic geological confinement, except for the two cold springs of VAD and ACQ. VAD, which plots under oxidative conditions during all the monitoring, is influenced by surface waters mixing with phreatic flow through locally karstified limestone able to oxidise and equilibrate water during the flow path. ACQ shows oxidative conditions only during the wet period, which is probably due to the major contribution and mixing with surface waters at this time. For thermal waters, some springs (P-LUC, P-LEC, P-ESC and P-SOA) present oxidising conditions only during the April campaign. According to other values obtained during the monitoring, this oxidation is not significant and is probably due to the probe's wear and its sensibility to high temperature. As observed on the PCA, this diagram confirms a favourable condition allowing the occurrence of $HAsO_4^{2-}$ (aq) for Pietrapola (granitic) but also for VAD (sedimentary). The iron ionic predominance allows confirming the FONT and ACQ springs as ferruginous springs (Fe²⁺ iron form prevalence) (Table 1). These two springs are Cl-rich. According to the alteration state of biotite contained in granite, the Cl and Fe content increased consequently in water [72]. All springs display conditions favouring dissolved sulphate content. However, CAM-F, which flows under reducing condition, shows a temporal trend to sulphate reduction in H₂S_(g) during the dry period (Figure 7). Despite the diversity of the geological conditions, this homogeneous content in sulphate is asking about a possible common origin.

4.3. Reservoir Conditions and Depth Assessment

4.3.1. Water Equilibration in the Reservoir

The Na-K-Mg ternary diagram (Figure 8), proposed by Giggenbach [54], can be used to estimate geothermal reservoir temperatures, to distinguish equilibrium status and to classify geothermal waters as immature, partially equilibrated and fully equilibrated waters.



Figure 7. Pourbaix diagram of sulphur, arsenic and iron elements. The spring group of Pietrapola is displayed in red background while Puzzichellu is displayed in yellow background.



Figure 8. Distribution of thermo-mineral springs water on a Na-K- \sqrt{Mg} Giggenbach diagram [54], which allows determining reservoir temperature and equilibration status of rock with water. The spring group of Pietrapola is displayed in red background while Puzzichellu is displayed in yellow background and the Travu River Valley in orange background.

All cold waters plot within the immature zone, Mg-corner, which means these waters aren't equilibrated with rocks and show a relatively low residence time as confirmed by the ¹⁴C age estimated at PUZ-F (4720 year, apparent radiocarbon age, Table 4). Indeed, the presence of Mg content in the water induces shallow flow influence or indicates reequilibration by mixing with phreatic-water during the up-flow as observed for partially equilibrated waters of VIGN and FONT, which plots within the mixed zone [11,54,73,74]. Indeed, Mg dissolution appears under low temperatures, this process explains why all thermal waters, except VIGN, plot above the full-equilibrated line and highlight waters emerging fully equilibrated without geochemical modifications due to dilution, mixing or any other cooling phenomenon. This tends to indicate a full equilibration of water with rocks due to a very high residence time confirmed by ¹⁴C apparent age estimations on P-MUR3 (8260 year, apparent radiocarbon age) (Table 4).

Table 4. Radiocarbon data and related physico-chemical parameters on non-gaseous thermal (P-MUR3) and cold (PUZ-F) springs. The "apparent age" refers to Stentröm, 2011 calculations [75]. The mention "not corrected" refer to radiocarbon age that is not adjusted for any hydro-geochemical effects on meteoric water ¹⁴CO₂ or neither adapted for hydrologic flow model.

| Comulius Doint | Samula ID | Т | pН | HCO ₃ | δ13C/12C | Fraction | Modern | Americant Acc (Nict Connected) |
|---------------------------|-----------------|--------------|--------------|------------------|--------------------|----------------|----------------------------------------------------|--------------------------------|
| Sampling rollit | Sample ID | °C | - | (meq/l) | ‰ | рМC | Sd | Apparent Age (Not Corrected) |
| Pietrapola Puzzichellu | P-MUR3 PUZ-F | 46.6 16.8 | 9.27 7.11 | 2.08 8.06 | $-16.20 \\ -22.00$ | 35.80 55.60 | $egin{array}{c} \pm \ 0.2 \ \pm \ 0.2 \end{array}$ | 8260 y 4720 y |

The absence of Mg-content does not allow the use of K-Mg geothermometer on thermal water, so other types of geothermometry calculations should be used. The estimated Na-K temperature varies from 120 to 140 °C for CALD and from 180 to 220 °C for Pietrapola. The temperature gap, observed despite being part of the same geological reservoir, highlights that water at the origin of CALD spring flows at a shallower depth than groundwater emerging at Pietrapola. Figure 8 confirms also that VIGN is a mixed water between deep fully-equilibrated water with a highly mineralised, Cl-rich, shallower non-equilibrated water. This mixing explains the seasonal variability of mineralisation. Because of this upflow dilution, the geothermometry calculation does not allow to conclude on the reservoir temperature.

4.3.2. Sulphur Origin and Geothermometry

To discriminate sulphate origin, Figure 9 displays the δ ³⁴S-SO₄ content as a function of δ ¹⁸O-SO₄. Thermal waters show δ ³⁴S-SO₄ and δ ¹⁸O-SO₄, respectively, ranging from 14.1% (P-MUR3) to 19.8% (VIGN) and 1.6% (VIGN) to 7.2% (P-SOA) (Figure 9A, Table 5). Cold waters show δ ³⁴S-SO₄ and δ ¹⁸O-SO₄ values, respectively, ranging from 5.0% (VAD) to 14.8% (PUZ-F) and 3.9% (VAD) to 13.1% (PUZ-F) (Figure 9A, Table 5).



Figure 9. Sulphur isotopes data displayed as: (**A**) Origin of sulphate components thanks to $\delta^{18}O(SO_4)$ versus $\delta^{34}S(SO_4)$ content in mineral waters according to bibliography values associated to their SO₄-content. (**B**) Abiotic or biotic sulphate origin determination thanks to $\delta^{18}O(SO_4)$ versus $\delta^{18}O(H_2O)$ values observed. Dashed straight and solid lines delimit the area where dissolved sulphate (SO₄²⁻) is obtained from inorganic redox processes, from sulphur (S⁻) or sulphite (SO₃²⁻) [76]. (**C**) Geothermometers determination thanks to $\delta^{18}O(SO_4)$ versus $\delta^{18}O(H_2O)$. Dark lines show temperature reservoir determination obtained for low enthalpy reservoir only [77]. The spring group of Pietrapola is displayed in red background while Puzzichellu is displayed in yellow background.

| | | δ^3 | ⁴ S | δ ¹⁸ Ο | | | | |
|-------------|-----------|-------------|----------------|-------------------|------------|--|--|--|
| Samplir | ng Point | Sulphate | Sulphide | Sulphate * | Water * | | | |
| | Sample ID | ‰ VS. V-CDT | ‰ VS. V-CDT | % VS. SMOW | % VS. SMOW | | | |
| | CAM-F | - | 5.6 | - | - | | | |
| Puzzichellu | PUZ-F | 14.8 | -27.7 | 13.05 | -6.62 | | | |
| | QUAR-G | 8.9 | - | 10.22 | -6.77 | | | |
| Vadina | VAD | 5.0 | - | 3.93 | -6.62 | | | |
| | P-MUR3 | 14.1 | 0.1 | 6.33 | -8.66 | | | |
| Pietrapola | P-LUC | 14.9 | - | 7.11 | -8.69 | | | |
| - | P-SOA | 16.1 | 0.6 | 7.24 | -8.80 | | | |
| Travu | VIGN | 19.8 | - | 1.59 | -8.23 | | | |

Table 5. S isotopes values from sulphate (SO₄), sulphide (H₂S) and ¹⁸O-SO₄, ¹⁸O-H₂S values. (*) Values used in isotope geothermometry calculation.

All springs (except VIGN and VAD) show a positive correlation between δ^{34} S-SO4 and δ^{18} O-SO₄ values. This highlights a similar source in dissolved sulphur and confirms the common origin suggested previously (Figure 9) [78]. The lowest δ^{34} S-SO₄ value is observed at VAD and plots on the atmosphere precipitation zone close to the Italian precipitation (mean = +2.1‰ and values ranging between -2.5 to +8.3‰) [79]. VIGN, with its low δ^{18} O, is associated with a high δ^{34} S content and plots close to seawater (δ^{34} S-SW ~

+21‰) [80]. This is explained by the occurrence of brines waters coming from the flysch formations. Indeed, δ^{34} S-SO₄ varies in relation with the geological context. The absence of negative values allows excluding pyrite oxidation as a source of dissolved sulphate [81].

Abiotic Origin of Sulphate

To discriminate oxidation among processes at the origin of abiotic dissolved sulphate, the Figure 9B displays the δ ¹⁸O-SO₄ and δ ¹⁸O-H₂O signatures according to sulphide (S⁻) or sulphite (SO₃) oxidation [82]. To distinguish them, it is commonly accepted that sulphate formed by oxidation of the sulphide must show a proportional correlation between δ ¹⁸O-SO₄ and δ ¹⁸O-H₂O [78]. According to [73], fractionation is usually minor during the oxidation of mineral sulphide to sulphate. Figure 9B specify that six springs present an abiotic origin of sulphate: coming from Sulphide (S-) oxidation (VAD, VIGN) or sulphite (SO₃²⁻) oxidation (QUAR-G, P-LUC, P-MUR3 and P-SOA) and only one (PUZ-F) has a potential biotic origin [76,78,82].

Biotic Origin of Sulphate

Sulphide isotopic measurements (δ^{34} S-H₂S) were performed on four springs (CAM-F, PUZ-F, P-MUR3, P-SOA) (Table 5). Results show that thermal waters (P-MUR3, P-SOA) and the cold water (VAD) have positive values while the other spring of the Puzzichellu site has a negative value (PUZ-F). This negative δ^{34} S-H₂S associated to an increasing dissolved sulphate content at the spring reveals an intensive bacterial activity [81] (Figure 9A,B). Indeed, PUZ-F is very depleted in δ^{34} S-H₂S (negative values) and is the most concentrated in SO₄ (\approx 87 mg/L) (Table 5). The biotic sulphate reduction process creates δ^{34} S-H₂S depletion and residual sulphate enrichment in δ^{34} S-SO₄ [83,84]. In case of high organic matter content in the aquifer associated with low availability of Fe, biotic activity creates a significant amount of H₂S with negative values [81]. The negative value measured at PUZ-F (δ^{34} S-H₂S = -27.7‰) specify the bacterial origin of sulphate as both chemolithotrophic sulphide oxidising bacteria (e.g., Thiobacillus hydrothermalis, *Thiomicrospira* spp., Achromatium volutans) and thermophilic sulphate-reducing bacteria (e.g., *Desulfacinum* spp., Desulfovibrio) [84]. These biological processes explain the high amount of dissolved H₂S and SO₄ observed in the Puzzichellu group springs (Tables 1 and 2).

4.3.3. Reservoir Temperature and Depth Assessment

Thanks to the identification of S-bearing minerals responsible for sulphur origin in water for Mg-devoid springs (VIGN, CALD, P-X), it is possible to refine geothermal temperatures evaluated with the SO₄-H₂O oxygen isotope geothermometry [56,77,85] (Table 6, Figure 9C). Considering a geothermometric gradient of 30 °C/km, these calculations also allow determining the reservoir depth following the Marques et al.'s Equation [48]. Figure 9C highlights the involvement of only low-temperature geothermal reservoir (T < 150 °C). Only VIGN plot into the high-temperature geothermal reservoir but the estimated temperature should not be taken into account because of the mixing processes previously identified.

Three isotopic geothermometry calculations were performed on thermal springs (P-X and CALD) (Table 6). Lloyd et al. as well as Mizutani and Rafter isotopic calculations show good correlation with each other [77,85]. The new isotopic calculation proposed by [67] for low-temperature geothermal application is overestimated (30%) compared to [68,76]. The [76] isotopic calculations are underestimated (80%) compared to the geochemical methods [54]. However, this comparison of isotopic geothermometry applications confirms that low-temperature geothermal method is not a good tool to estimate reservoir temperature of alkaline water flowing through granitoids [76]. However, this comparison allows to specify that a common geothermal reservoir might be at around 3 km in-depth.

| | | | C | old Waters | | | Thermal | Waters | |
|-------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------------------------------|--------------------------------------|--------------------------------------|---------------------------------|
| | | | Puzzic | hellu | Vadina | Travu Pietra | | Pietrapola | |
| | | Sample ID | QUAR-G | PUZ-F | VAD | VIGN | P-MUR3 | P-LUC | P-SOA |
| Isotope values Geochemical Geothermometry calculation | ¹⁸ O-SO ₄ ¹⁸ O-H ₂ O Giggenbach (1988) [54] | (‰) (‰) Na-K K-Mg | 10.22 -6.77 100 | 13.05 -6.62 - | 3.93 -6.16 - 100 | 1.59 -8.23 160 150 | 6.33 8.66 200 | 7.11 -8.69 200 | 7.24 -8.80 200 - |
| Isotope Geothermometry calculation | Lloyd (1968) [85] Mizutani and Rafter (1969) [77] Boschetti (2013) [76] | T (°C) T (°C) Empirical T (°C) Theorical T (°C) | 106 97 53 58 | 86 75 35 42 | 182 177 117 118 | 186 181 120 121 | 124 115 68 72 | 116 107 61 66 | 114 105 59 65 |
| Depth assessment | Giggenbach (1988) [54] Lloyd (1968) [85] Mizutani and Rafter (1969) [77] Boschetti (2013) [76] | Na-K depth (km) K-Mg depth (km) (km) (km) Empirical depth (km) Theorical depth (km) | 2.8 3.0 2.7 1.2 1.4 | 2.8 2.3 2.0 0.6 0.9 | 2.8 5.5 5.4 3.4 3.4 | 4.8 4.5 5.7 5.5 3.5 3.5 | 6.1 - 3.6 3.3 1.7 1.9 | 6.1 - 3.3 3.0 1.5 1.7 | 6.1 3.3 3.0 1.4 1.6 |

Table 6. Sulphates isotopes geothermometers calculation compared to geochemical geothermometry and flow depth estimation.

4.4. Groundwater Origin and Recharge Conditions

The stable isotopic composition of groundwater displays values between -55.8% and -37.0% for δ^2 H, and between -8.92% and -6.00% for δ^{18} O (Figure 10, Table 2). According to Figure 10A, all samples plot between the Global Meteoric Water Line (GMWL) [86] and the Western Mediterranean Meteoric Water Line (WMMWL) [87]. It clearly means that groundwater has a local meteoric origin and completely excludes any seawater or magmatic contribution, even for the most mineralized springs. The isotopic signature of the different springs is very coherent with values observed punctually in previous studies [88] and highlights the stability of the spring water recharge conditions.

An enrichment in δ^2 H without any effect on δ^{18} O is observed during H₂S, CH₄ or H₂ exchange [89]. Because variation of the δ^2 H value is only observed at VIGN, Figure 10B confirms that brine waters involved in the mixing have a high gaseous content. Figure 10C displays cold waters, which are more enriched in δ^{18} O and δ^{2} H value than thermal waters. With values ranging from -8.92 to -6.00% in δ^{18} O and from -54.9 to -37.0% in δ^{2} H shows that water is infiltrated at a lower altitude (<150 m asl), CO₂-rich waters are characterised by a depletion in δ^{18} O, which leads to horizontal deviation from the GMWL [89–91]. As expected, ACQ and FONT are also affected by this fractionation. The stable isotope value confirms that the high EC and the high Cl-content observed in FONT are exclusively due to water-rock interactions and not to seawater intrusion. The weighted mean of water stable isotope signal measured (N = 63) at each rainfall stations are as follows: Bastia ($\delta^{18}O = -6.28\%$, $\delta^{2}H = -37.70\%$), Corte ($\delta^{18}O = -7.29\%$, $\delta^{2}H = -46.57\%$), Aléria $(\delta^{18}\text{O} = -6.50\%, \delta^2\text{H} = -37.79\%)$, Bonifacio $(\delta^{18}\text{O} = -6.65\%, \delta^2\text{H} = -41.59\%)$, Campana $(\delta^{18}\text{O} = -8.17\%, \delta^2\text{H} = -52.33\%)$ then Palneca $(\delta^{18}\text{O} = -8.38\%, \delta^2\text{H}_{Palneca} = -53.63\%)$. The mean of seven measures on the Mediterranean seawater is $\delta^{18}O_{Seawater} = +1.35\%$ and $\delta^2 H_{\text{Seawater}} = +6.31\%$ (Table 2) [41,92].

Figure 10B displays all thermal waters, these waters are isotopically depleted with values ranging between -8.92 and -8.20% for δ^{18} O and between -55.8 and -51.4% for δ^{2} H. Compared to the rainwater values observed, thermal waters are more depleted than Campana, meaning that waters infiltrate at a higher altitude than 800 m asl [93]. Except for VIGN, which is more enriched than the other thermal waters (Pietrapola and CALD) and confirms the involvement of mixing processes. This spring-water is a mixed water between a hot, low mineralised, deep and full-equilibrated water with colder, acidic, highly mineralised waters (brines). Considering this mixing process, the recharge altitude could not be estimated. As Sardinia's geothermal waters [94], no δ^{18} O enrichment from high-temperature water–rock interactions is observed, which is usually expected for thermal



waters (Figure 10A) [89,95]. It is due to the involvement of low-temperature geothermal processes (<150 °C).

Figure 10. δ^2 H Vs. δ^{18} O plot of all minerals and thermal groundwaters. The mean stable isotopic composition of the rainfall at Bastia, Aléria, Bonifacio, Campana and Palneca are also plotted as grey squares, with their respective altitude [41]. The dotted black line is the WMMWL [87] and the black line is the GMWL [86]. (B) and (C) are zoom of (A).

4.5. Conceptual Model

Analyses and comparison of hydrogeochemical, geothermometric and isotopic characteristics of thermal and cold mineral waters of Eastern Corsica reveal the involvement of, at least, three groundwater-flow processes at the origin of the observed geochemical diversity. These results are illustrated on a regional conceptual model of the different flow-paths and geological units (Figure 11). Thermal waters (from 27 to 54 °C at the discharge-point), weakly mineralised (<300 μ S/cm) Na-HCO₃ alkaline waters, which are hosted in deep (mainly granitoid) fractured reservoirs and are influenced by low-temperature geothermal processes (<150 °C). Major faults and shear zones provide preferential pathways for rainfall infiltration from the mountainous relief (recharge > 800 m asl) and for fast up-flowing of deep water (high-temperature and Mg absence). This fully equilibrated groundwater, associated with high F-content and low ¹⁴C activity, indicates long residence times (8300 year) at depth (at least 3 km) (Table 6).



Figure 11. Hydrogeological conceptual model of mineral waters from the eastern part of Corsica except for Vadina and Fontanella springs (out of the perspective). The primary source of water (blue arrows) is meteoric water that is heated at depth by the geothermal gradient, and which ascends as thermal fluid (red arrows) through faults (black lines).

Cold waters (14–18 °C) from shallower reservoirs, mainly made of sedimentary rocks with marly interlayers rich in organic matter, are characterised by a Ca-HCO₃-(SO₄) water type. These complex sedimentary deposits act as a multilayer aquifer (up to 3 km), favourable to a multiplicity of flow pattern increasing residence times disparities (4700 y). Local rainfall recharge (<150 m asl) infiltrates at a shallow depth and, thanks to the different local faults (graben and horst), can up-flow very locally. Some of these waters are not equilibrated with rocks (immature waters) and are influenced by surface waters infiltration (non-perennial, seasonal flow variation). The presence of organic matter in depth promotes the development of a bacterial activity responsible for the increase in SO₄-content in water and the H_2S gaseous release. This study also highlights that many springs appear at the interface between the main geological units inducing specific and complex mixing processes. Indeed, interface flow-paths favour interactions between different geological units and entail important singular geochemical and isotopic modification of water. These modifications create complex water types, depending on the mixing proportion. This study also highlights for the first time the existence of brine-type waters in the southern part of the study area, these mature waters, cold CO₂-rich (acidic water), are highly mineralised $(2000-12,000 \ \mu\text{S/cm})$ and are characterised by a Na-Cl water type.

5. Conclusions

Measurements, analyses and comparisons of the physico-chemical, hydrogeochemical and isotopic composition of thermal and cold mineral waters of Eastern Corsica reveals that these groundwaters have dramatically different hydrogeological flow conditions. Stable isotope data suggest that the recharge is due to rainfall infiltration at two distinct altitudes involving different hydroclimatic recharge conditions. The high concentrations of trace elements in water also provide evidence for long residence-time, complex rock–water interactions and reveals the occurrence of gaseous rich brine waters. The presence of this gaseous content in water complicates the understanding of the water–rock interaction processes and should be the subject of a further investigation to strengthen the hydrogeological model established here. In addition, the use of geothermometry allows specifying reservoir conditions and helps to improve the conceptual model of regional hydrogeology. Improving knowledge of these very complex hydrosystems will now allow adapting their management and improving their protection. Further investigations, including the characterisation of the gaseous content, will help, in the future, in identifying the origin and processes of the gaseous release as well as the mixing processes occurring during the up-flow.

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