Mineral water resources development in crystalline rocks: challenges and possible solutions

J. M. Carvalho and H. I. Chaminé

Laboratory of Cartography and Applied Geology, Department of Geotechnical Engineering, School of Engineering (ISEP), Polytechnic of Porto, Porto, Portugal; Centre GeoBioTec|UA, Portugal.

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Abstract

The main goal of this work is to present a brief outline on mineral waters resource development in crystalline rocks, particularly focused on challenges, opportunities and solutions. In addition, it will be highlighted the importance of generating dynamics for both territories (North Portugal and Galicia) to launch new transdisciplinary programs in a close cooperation at global scale related to groundwater and hydromineral resources.

1 Introduction

Groundwater which – in any physical and chemical specificity – is distinguished from "normal" water in a given region is considered as mineral in the hydrogeological practice (e.g., Moret [1], Schoeller [2, 3], Albu et al. [4], LaMoreaux and Tanner [5], Carvalho and Chaminé [6], Margat and van der Gun [7]). Mineral water has generally, but not necessarily, deep circulation and/or long hydrogeological circuit. The most common distinguishing characters are mineralization and/ or temperature. Thus, in the stated perspective, mineral water present total mineralization or certain specific characteristics (pH, sulphur, silica, CO_2, etc.) different from the current values, or temperatures higher than the average air temperature.

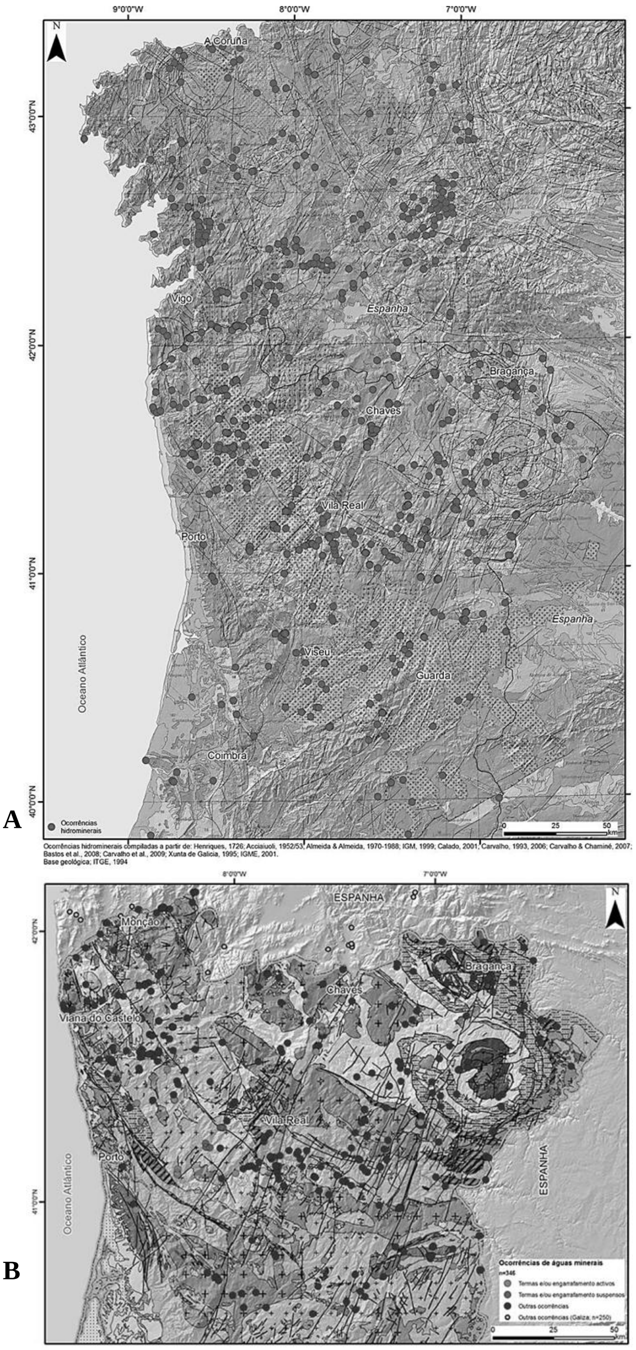
White [8] designated as thermal the water whose temperatures exceed 5°C over the average temperature of the air, option taken up by Schoeller [2] although the latter, instead of 5°C, consider 4ºC. These criteria, virtually identical, are generally followed in the United States of America (Albu et al. [4]). In Europe (CEC [9]) was adopted the solution to consider as thermal the water with temperature exceeding 20°C, returning the systematization of the Mineral Water Symposium of Prague held in 1968 (Malkovsky and Kacura [10]). To the north and central Portugal regions (and also to the Galicia region, in NW Spain) this criterion can be considered acceptable for the average annual air temperature in these areas is less than 16°C (IM and AEMet [11]).

In Medical Hydrology, it is common to designate as thermal water any water (even if not thermal in a hydrogeological sense or similar to the typical water of a given region) as long as it is used in thermal spas (Pomerol and Ricour [12]).

The development and protection of mineral water is often bumped by a variety of difficulties (Carvalho [13], Carvalho et al. [14]), including: (i) Reduced areas of expansion, that is, limited surface available for the exploration activities. The urban explosion drowns everything and the movement of personnel and equipment is extremely difficult; (ii) Effective impossibility of compliance with well head protection areas. Basic sanitation is often poorly attended and industrial activities are still active. In some locations, natural and artificial lakes or dams and weirs that are tourist attraction and sometimes revenue sources, are often hydraulically connected to the discharge areas of the hydrogeological circuit; (iii) The mysticism surrounding mineral waters used in balneotherapy: the aura of mystery and supernatural and the recognized economic value of the resource intimidate the owners, clinical directors and touristic operators, afraid that the exploration and exploitation works will change the therapeutic properties of water and therefore destroy the classical springs and its available flow.

The main mineral water occurences in northern Portugal and Galicia were inventoried recently by the Termared SUDOE project (see details in TERMARED [15], Chaminé et al. [16]). Those occurences (springs, wells and water galleries), as represented in figure 1, are located generally in tectonical nods usually situated in morphotectonical corridors inside geomorphological depression framework (e.g., Choffat [17], Freire de Andrade [18], Acciaiuoli [19], Carvalho [20, 21], Baptista et al. [22], IGM [23], Marques et al. [24], Carvalho and Chaminé [25], Carvalho et al. [26], Delgado et al. [27], Carvalho et al. [28], Oliveira [29], Carvalho et al. [30]). They are all located over the so-called

Ancient Massif and related metasediments (e.g., Ribeiro et al. [31]).



Ocorrências hidrominerais compiladas a partir de: Henriques, 1726; Acciaiuoli, 1952/53; Almeida & Almeida, 1970-1988; IGM, 1999; Calado, 2001; Carvalho, 1993, 2006; Carvalho & Chaminé, 2007; Bastos et al., 2008; Carvalho et al., 2009; Xunta de Galicia, 1995; IGME, 2001.
Base geológica; ITGE, 1994

Figure 1. A) Hydromineral inventory mapping of over 590 occurences (TERMARED project during the period 2009-2011), Northern and Central Portugal and Galicia regions (LABCARGA|ISEP archive); B) Hydromineral resources map of the Northern Portugal, after Carvalho [13]. (Details in Carvalho [13], TERMARED [15], Chaminé et al. [16], and references therein).

Several of those mineral water occurrences correspond to thermal water that may have direct uses for geothermal applications. So, since 1978 (Aires-Barros [32]), following the energy crisis of 1973, in some spas, geothermal direct uses, other than single balneotherapy where initiated. The pioneer site was Chaves (e.g., Carvalho and Silva [33]; Carvalho and Carvalho [34], Carvalho et al. [30]), where, in 1982, a tubular well was performed (AC2) with the specific purpose of heating a municipal swimming pool. This project still operates with full success, now extended to two hotels. A very proactive attempt to put in place a greenhouse complex taking advantage of the geothermal heat was a failure, apparently due to a poor technical and economic makeup of the project.

The systematic occurrence of mineral water springs in geomorphological depressions leads, often, to the coexistence of two or even three types of groundwater circulation generally hydraulically connected between them and with the surface water, as follows:

(i) firstly, mineral water of deep origin percolating fissure permeability materials, which corresponds to relatively lower risk of contamination. In the same formations, "normal water" circulation, whether near or far depth related, is generally also occurring;

(ii) a shallow groundwater circulation over loose deposits with dominant interstitial permeability but without much capacity for self-purification (alluvium, elluvium, colluvium and decomposed rock). This subsystem has generally high vulnerability and risk to contamination.

When designing a new well it is absolutely essential to seal the annular on the shallow subsystem in order to avoid the spreading of contaminants into the mineral water subsystem, say, the mixing of freatic and mineral waters. However the question is not so simple: the mineral water circuit will continue to contact, in the surrounding areas, with the surface water, and other deeper non mineral water percolating the massif. So it is necessary to impose operational rules (regarding dynamic levels and/or pumping extraction) to control flow and mass travel time under appropriate limits.

In most places it is not possible the complete elimination of the surface pollutants given the location in urban areas and also administrative and cultural barriers. So the only way to face the challenge of designing and constructing adequate new wells is to develop comprehensive and robust site conceptual models in the discharge areas integrating mineral and non mineral circuits.

The recommended operational flow in a given well or wells group can be conditioned by the relationship of the potentiometric surface of an alluvial aquifer versus the piezometry of the mineral sub system. Carvalho [35,13] presented the case of Monfortinho, eastern Portugal, near Coria at the Spanish border, were a drainage system was constructed to minimize the flooding and the contamination risks, the abstracted shallow water being used for irrigation.

2 Development of mineral water resources

The development of mineral water resources aims to meet the following objectives which can be cumulative: (i) increase the available flow rate; (ii) maintain the chemical quality and to improve the microbiological quality of the water; and (iii) maintain or increase the temperature.

The specific objectives referred above demonstrate how the practice of the hydrogeology of mineral water imposes higher degree of performance when compared with the common water exploration and exploitation.

2.1 Specificities

At a tactical level, the exploration of mineral water is easier than common water, in the immediate vicinity of known occurrences, because conditioning hydrogeological traps, consistent with adequate site modelling, are best expressed. Furthermore, contrasts with geophysical methods, particularly electrical resistivity, are generally good, namely in hydrogeological systems with high mineralized water. This situation is reinforced by the fact that the hydraulic transmissivity magnitude in mineral and geothermal aquifers is up by one or two orders of magnitude to that of fissured aquifers with normal water in the surroundings, as discussed below. Here, it should be pointed out that the classical geoelectrical methods (and particularly resistivity) continue to be an excellent exploration tool because they give information on the geological structure and some clues about the quality of water can be inferred too. A drawback is the practical difficulty to reach deep targets.

The strategical exploration of mineral water, out of the existing poles, has increased difficulties. Again, consistent hydrogeological conceptual modelling is need with the support of geophysical and geochemical surveys: mineral water is a rare and scarce geological resource.

Mineral water exploration and exploitation have to meet the following difficulties: (i) it is imperative to get the same specific type of water without anthropogenic or other contamination; (ii) the typical occurrence of traditional springs is on valleys where the mineral aquifer is in hydraulic connection with contaminated surface water and/or common groundwater; and (iii) interference with normal shallow and deep groundwater subsystems. This hydraulical interdependence means that, in mineral water wells located along the major rivers, its piezometric levels respond quickly to level fluctuations on the surface water. This has been observed for example, at Chaves, S. Pedro do Sul and Monfortinho (Carvalho [13]).

The basic methodologies of exploration and exploitation of mineral water do not differ substantially from those used in normal water. However, it should be noted that, given the economic value of the geological resources (mineral water), the financial founds for their study are generally more important and more easily available. On the other hand, the requirements in terms of quality and accuracy of the drilling operations and water well equipment, are also significantly higher, tacking in account the particular level of environmental involvement: one must emphasize that this water is to be used, without any kind of treatment or purification, in spas or in the bottled water industry.

The exploration and exploitation works generally interferes with the existing springs or other former structures for water intake. This is a very serious question given the social importance of these structures. The ideal is to perform drilling works during the low season (or closure period at certain spa) and strengthen monitoring (levels, flow rates, chemical and bacteriological quality) on existing springs and wells.

Hydrogeologists and groundwater engineers must understand that mineral water is the "medicine" used in the spa and the commodity inside the water bottling industry, having an added economic value regarding tap water. Cumulatively, it should always be kept in mind that in these natural waters, the resource must be microbiologically pure in origin, which requires significant hygiene and health care throughout all the industrial process.

2.2 Methodologies and technologies

The most widely used techniques include classical photogeological interpretation, remote sensing, geological, geomorphological and hydrogeological mapping from scale 1/25,000 to 1/5,000 or even more detail, if necessary, or if the existing information allows it (Carvalho [21,13]). Using GIS based mapping to integrate all gathered data in mandatory nowadays (e.g., Teixeira et al. [36], Chaminé et al. [37]).

A constant of all technical interventions must be a strong option for an exhaustive bibliographical inventory. This is the formula to better integrate former conceptualization carried out at a time (end of 19th century till the midle of 20th century), with great availability to observe and synthetize field observations. The hydrogeological field inventories should be systematic and extensive and always conducted with the support of local people, acting as contact facilitators and as information providers, sometimes unexpected, perhaps fanciful, but always helpful (e.g., Carvalho [13], Chaminé et al. [37]).

In northern Portugal the investigations have been almost systematically performed with geoelectric surveys, predominantly resistivity rectangle, with emission lines that have reached AB = 1200 m (e.g., Carvalho [38,21,13]). The aim is to make indirect exploration meeting the objectives set for the maximum depth of investigation that was assumed until recently limited to 150, 200 or 250 m

The first boreholes in Portuguese baths were carried out with mechanical classical percussion rigs and also with diamond core drilling (e.g., Seifert and Vicente [39], Seifert [40]) in locations such as Sabroso (Pedras Salgadas) and Caldas de Moledo. The purpose of the angle boreholes, with continuous coring, was to recognize the lithology, faulting zones and, of course, the circulated areas. Recognition of the zones circulated with mineral water (fracturing, joints, discontinuous contacts, etc.) and their orientation with this type of drilling was easy on hydrogeological systems with positive artesianism. But difficulties have emerged in systems with small hydraulic head. In this case the credibility of the method failed: lithological sampling was of excellent quality, but no clear information on circulated zones translated as artesian flows and physical-chemical type of water was available. To solve this difficulty, pumping tests with piston pumps (the ones that was possible to install inside the drilling diameter, 86 and 76 mm) were performed at regular intervals.

An important upgrade was the creation of a pumping chamber at small depths, drilled with "roller-bit" in the weathered zones. Some angle boreholes drilled and completed with this mixed technique (rotary with "roller-bit" and diamond core drilled in depth) were designed as exploration boreholes and are still in operation as exploitation wells. In these boreholes the pumping chamber installed up to 15 to 20m made easier the conduction of pumping tests at regular intervals in depth and the detection of sections with mineral water circulation.

It is important to emphasize that in all of these drilled wells, it was common practice to achieve tight control over the physico-chemical characteristics of the circulation fluid regarding the essential parameters of the water. The pH, conductivity and temperature control is the minimum requirement being usually sufficient in the context of the Portuguese mineral water exploration on the Ancient Massif. The use of inclined boreholes in the mineral water industry is relatively common practice (e.g. Carlovy Vary, Chezoslovakia; Vylita [41]; and Bath, England; Kellaway [42,43]).

The most adequate method available today to the exploration and exploitation of mineral water in cristalline rock is the down the hole hammer (air percussion). Where it was intended to reach great depths (500 to 1000 m) it has been used, aditionally in depth, drilling coring rigs with wire-line. Vertical and angle wells have been drilled and equipped with submersible pumps running without problems. Advantages of the method includes: (i) easy and fast penetration till depths not exceeding 250 m, depending on the drilling diameter, the compressor capacity and the productivity of the drilled rock; (ii) good quality of the cuttings and adequate identification and sampling of the production areas, and, (iii) the air as drilling fluid environmentally friendly, well adapted to precautions regarding the quality of mineral water.

However, it is worth noting some difficulties, namely: (i) the air can disrupt the observations on the quality of the fluid in the aquifer by oxidation of elements or hiding the gas inputs (DNEMT [44]); (ii) over evaluation of the existing resources when drilling, that must be interpreted according to the CRC (Coefficient of Reduced Capacity); Carvalho [13]; (iii) it is a procedure poorly adapted to unconsolidated materials, or very fractured or weathered rock; (iv) there is the risk of formation of "plugs" requiring frequent cleaning of the well; (iv) there is the need to use high power compressors and even "boosters" when the production output is large and/or the water level is located near the surface; (v) identifying each production level is poor because the collected fluid integrates all the well. This last limitation is minimized with the use of down the hole hammer drilling rigs with reverse circulation.

Down the hole hammer rigs show great effectiveness in detecting groundwater levels if drilling is accompanied with the necessary hydrogeological control. The hydrogeological control is essential to achieve the following objectives: (i) compliance with the technical standards of the well design; (ii) systematic adaptation of the planned test program; and (iii) return on the drilling, investment, limiting the multiplication of drilling sites and optimizing data acquisition and interpretation. Today this drilling method is almost unique, being in disuse manual excavation so in vogue until the early 70s of the twentieth century in Portugal.

3 Hydrodinamics of the discharge zones

Given the need to locate new drilling sites with a precision of at least 1m, it is important to know in each case, the geological structures locally responsible for the rising of mineral and geothermal fluids.

Carvalho [13] presented geoelectrical surveys at several selected thermal baths of NW Portugal. These geoelectrical surveys used a rectangle array with appreciable penetration (AB up to 1200 m) at 21 sites as shown in Table 1.

Table 1. Confirmed faulting trends with geoelectrical surveys in selected Portuguese mineral waters (adapted from Carvalho [13]).

Designation	Type	Lithology	Fracture trends
Águas de Bem Saúde	GC	Quartzite + Slate	N-S
Chaves	GC	Slate + granite	NNW / NNE
Corga do Vergueiral	GC	Granite	NW
Melgaço	GC	Granite	ENE
Pedras Salgadas	GC	Granite	NNW
Vidago	GC	Granite	NNW
Vilarelho da Raia	GC	Granite	E-W
Carvalhelhos	S	Granite	NNW
Alcafache	S	Granite	NW
Caldas da Cavaca	S	Granite	NNW / NNE
Caldas da Saúde	S	Granite	NNW
Caldas das Taipas	S	Granite	NNW
Cró	S	Granite	N-S
Entre-os-Rios	S	Granite	N-S
Fonte Santa (Almeida)	S	Granite	NNE
Longroiva	S	Granite	NNW
Manteigas	S	Granite	WNW
Moledo	S	Hornfels	NNE
S. Pedro do Sul (Termas)	S	Granite	NNW
S. Pedro do Sul (Vau)	S	Granite	NNE
Touca	S	Granite	NNE
Unhais	S	Granite	NNE
Vizela	S	Granite	NNW
Monção	S / GC ?	Granite	NNW

(S - Sulphyde; GC - Hydrogenocarbonated)

With the previous surveys it was obtained significant control on mineral water circulated structures consisting of anomalies with electrical resistivity contrasts (resistivity of the enclosing rocks / resistivity core anomaly of the order of 6. These anomalies have horizontal thicknesses up to 20m and a length between a minimum of 10 m to 180m. Therefore, they must be considered as manifestations of hydrogeological faults and hydrogeological traps with adequate connectivity in its core or on the edges.

It appears that the main fracturing direction, confirmed by more than 40% of water occurrences in the sampling analyzed is NNW-SSE. The NNE-SSW (possibly related to the Alpine orogeny stress field; Baptista et al. [22]) accounts for over 20% of the situations and the remaining population are distributed by the directions N-S, NW-SE, E-W, WSE and WSW. Each situation should be considered case by case, but it seems to be confirmed that the direction of regional fracturing is not always the most important in terms of emergency conditions at a local level. NNW-SSE direction should always be porsued. Upcoming E-W directions seem to have an enhancer role, usually being, present in the light of fotogeological interpretation and, as a rule, validated in detailed hydrogeological mapping fieldwork (Carvalho and Chaminé [25]).

In all studied cases it was possible to increase the natural discharge flows. The values of primitive flows (spontaneous flow; Calado [45]) were obtained in Acciaiuoli [18] and unpublished data of the TARH Lda and actual flow rates at drilled wells (Carvalho [13]). The relative increase of flow is largest at locations with smaller initial discharge springs. Thus, for pristine flow rates up to 1 L/s, the actual flow rates reached up to 8 L/s. For flow rates greater than 2 L/s, the increase was moderate. The distribution model tends to follow a logarithmic law. Exploitation yield in each pole ranges from 0, 5 and 12 L/s with a maximum of 18 L/s at S. Pedro do Sul (Ferreira Gomes et al. [46]). Median of the exploitation yield per well is of 1,5 L/s. Considering the lithology, the distribution is indicated in Table 2, which also indicates the same values for “normal” water.

It is confirmed, therefore, that mineral water lie inside preferential circulation areas, particularly evident situation when considering only granite, which, incidentally, constitute the main lithology. The pumping tests and the results of monitoring in Portuguese mineral water fields show that the long term well capacity is not controlled by transmissivity along major fractures, but by associated fracturing degree. Carvalho [20,13] has demonstrated that the relationship between the two transmissivities reaches up to 36 to 1 with a median of 5 to 1, the lower second order transmissivity corresponding to the "transmissivity behavior" of Martínez and Lopez [47].

Table 2. Median of the exploitation yield per well (L/s) in the Portuguese Ancient Massif (adapted from Carvalho [13]).

Lithology	Mineral water (i)	Normal water (Carvalho 2006) (ii)	Relation (i)/(ii)
Granite	1	0,02	50
Metasedimentary Rocks	4	0,5	8
Quartzite	6	0,74	8

The instantaneous flow rate gains achieved by placing wells on major fractures did not match the long-term well capacity. Thus, it is often preferable to locate the exploration and exploitation wells in the vicinity of the main fault but in secondary structures. The location of wells and boreholes (Carvalho et al. [26], Carvalho [13]) will have to be deducted from the conceptual site model of the aquifer and also by logistical conditions (access, water availability for drilling, etc.). Table 3 present the comparison of median transmissivity in mineral water wells with the transmissivity in non-mineral water in the Ancient Massif in NW Portugal. The table 3 shows also that mineral water occur inside the higher transmissive areas. This evidence is clear, either considering, for mineral water, the main transmissivity (T) or the "transmissivity of behavior." (T').

Table 3. Mineral water transmissivity and common water transmissivity by lithology (T: transmissivity; T': "second order transmissivity" (adapted from Carvalho [13]).

Lithology	Mineral water T(m^2/day) (i)	Normal water (Carvalho 2006) T´(m^2/day) (ii)	Ratio (i)/(ii)
Granite	43	1,7	25
Metasedimentary rocks	60	3,1	19
Quartzite	15	4	4

If one considers the higher values, Monção, Chaves, S. Pedro do Sul (Carvalho [21,13]) then the mineral water and normal water transmissivity differs in two orders of magnitude. Storage coefficient (S) determined for depths up to 200m are the order of 10-4 to 10-5, showing a confinement similar to the normal aquifers (e.g., Carvalho [20,21,13], Carvalho et al. [14,26]). In several places there is strong positive artesianism (e.g., Moledo, Manteigas, etc.). This question relates to the location of recharge areas but certainly also with the temperature and the content of waters gases.

4 Concluding remarks

Mineral water exploration is a multi and transdisciplinary task to be carried out with social and economical concerns in order to satisfy the demand.

The hydrogeological conceptual site model is the main tool to solve the hydrogeological and groundwater engineering problems including mineral water exploration (e.g., Bisson and Lehr [48], Carvalho [13], Chaminé et al. [37] and references therein). A key issue is the approach to be carried out: strategic studies (at a regional level) or tactical ones (site level), the most frequent to increase yields in already known thermal baths or mineral water bottling units. A global synthesis mapping at appropriate scale, duly georreferentiated that support the location of drilling sites at metric scale is essential corollary of all the work. That models must be capable of communicating information to all agents (practitioners, researchers, stakeholders and decision makers) involved (figure 2).

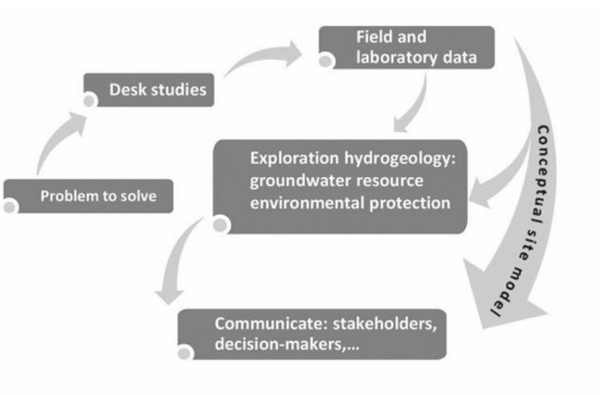


Figure 2. Conceptual site model: a flow path for an integrated exploration hydrogeology approach (after Chaminé et al. [37]).

For Bisson and Lehr [48] groundwater engineering and hydrogeology stopped in time at the level of exploration and it is necessary to embark on a water scarcity future scenario ahead (e.g., Llamas [49], Margat [50], Burke and Moench [51], Diop and Rekacewicz [52], Laimé [53], Custodio [54,55], Llamas and Martínez-Santos [56], Llamas et al. [57]). The sophisticated exploration techniques for oil exploration trying to map megastructures for groundwater purposes – hydrogeological traps – on a regional scale has to be carried out. Bisson and Lehr [48] call this approach the water megawatersheds paradigm that may be justified in Northern Portugal and Galicia for mineral water exploration (see details in Carvalho and Chaminé [6]).

Finally, mineral water management, including exploration and exploitation, are facing the millennium challenge, the global climate change (see for example the report about "climate change impacts in the USA": *http://nca2014.globalchange.gov/highlights/report-aptive strategies*). Mineral water quality and mineral water quantity could be jeopardized by climate change in a variety of ways that affect ecosystems and livelihoods, droughts and flooding may intensify in many regions, even in areas where total precipitation is projected to decline.

Climate change could affect mineral water demand, mineral water withdrawals, and aquifer recharge, reducing availability in some areas. In addition, hazards and risks to coastal aquifers and wetlands are expected. Some of our mineral water aquifers are in hydraulic connection with rivers and the ocean. Changes in precipitation and runoff, combined with modifications in consumption and withdrawal, can affect mineral water. These trends are expected to continue, increasing the likelihood of mineral water shortages

Increasing resilience and enhancing adaptive capacity provide opportunities to strengthen mineral water resources management and plan for climate change impacts. Many institutional, scientific, economic, and political barriers present challenges to implementing a robust transdisciplinary programme to adapt our mineral water resources to a changing climate in a resilient and environmental sustainable perspective.

A last but not least thought: still is a current challenge opportunity for both territories (North Portugal and Galicia, particularly) to launch new programs in close cooperation (scientific, institutional, administrative and societal) at global scale in mapping, characterization, assessment, modelling and protection of the hydromineral and geothermal resources and in the best groundwater management practices to preserve an extraordinary unique, fragile and resilient resource, the *"Mineral Water"*. So, our hope is for next couple of decades must be dedicated to the natural resource under the flag of the Galician–Portuguese language "*Auga–Água Mineral".*

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References

[1] León Moret. Les sources thermominérales. Masson, Paris, 1946.

[2] Henri Schoeller. Les eaux souterraines: hydrologie dynamique et chimique; recherche, exploitation et évaluation des ressources. Masson & cie, Paris, 1962.

[3] Henri Schoeller. Sur les eaux thermominérales et leur origine. In: Romariz, C. (ed.). 3ª Semana de Hidrogeologia, Universidade de Lisboa. pp. 37-43, 1982.

[4] Marius Albu, David Banks & Harriet Nash. Mineral and thermal groundwater resources, Springer, 1997.

[5] Philip E. LaMoreaux, Judy Tanner. Springs and bottled waters of the world: ancient history, source, occurrence, quality and use. Springer, Berlin, 2003.

[6] José Martins Carvalho & Helder I. Chaminé. Uma perspectiva sobre o valor acrescentado das Ciências da Terra nas indústrias do termalismo e do engarrafamento de água. In: Helder I. Chaminé, José Martins Carvalho (editores), O valor acrescentado das Ciências da Terra no termalismo e no engarrafamento da água. Artigos seleccionados do II Fórum Ibérico de Águas Engarrafadas e Termalismo. Edição do Departamento de Engenharia Geotécnica / Laboratório de Cartografia e Geologia Aplicada, Instituto Superior de Engenharia do Porto, Porto, pp. 11-23, 2007.

[7] Jean Margat & Jac van der Gun. Groundwater around the world: a geographic synopsis. CRC Press, Boca Raton, Florida, 2013.

[8] Donald E. White. Magmatic, connate and metamorphic waters. Geological Socitey American Bullettin, 68(12):1659-1682, 1957.

[9] CEC [Comission of the European Communities. Atlas of Geothermal Resources in the European Community, Austria and Switzerland. Comission of the European Communities, DGXII, Brussels, 1988.

[10] Miroslav Malkovsky & Georgij Kacura. Report on the 23rd session of the Internacional Geological Congress. Proceedings of Symposium II, Academia of Prague, 1969.

[11] IM & AEMet [Instituto de Meteorologia de Portugal – Agência Estatal de Meteorologia de Espanha]. Atlas climático Ibérico. Instituto de Meteorologia de Portugal e Agência Estatal de Meteorologia de Espanha, 2011.

[12] Charles Pomerol & Jean Ricour. Terroirs et thermalisme de France. BRGM, Bureau de Recherches Géologiques et Minières, Orléans, 1992.

[13] José Martins Carvalho. Prospecção e pesquisa de recursos hídricos subterrâneos no Maciço Antigo Português: linhas metodológicas. Universidade de Aveiro. (PhD Thesis), 2001.

[14] José Martins Carvalho, Jorge Espinha Marques, Maria José Afonso & Helder I. Chaminé. Prospecção e pesquisa de recursos hidrominerais e de água de nascente no Maciço Antigo Português. Boletim de Minas, 42(2):161-196, 2007.

[15] TERMARED. Catálogo de manantiales termales del espacio SUDOE / Catálogo de nascentes termais do espaço SUDOE / Catalogue des sources thermales de l’espace SUDOE. Xunta de Galicia, Santiago de Compostela, 2011.

[16] Helder I. Chaminé, José Teixeira, José Martins Carvalho, Lourdes Mourelle, Carmen P. Gómez & José Legido. Hydromineral resources inventory mapping (NW Portugal and Galicia): outputs from TERMARED project (INTERREG IV-B SUDOE). In: Resumes del Congreso Internacional del Agua, Termalismo y Calidad de Vida, Campus da Auga, Ourense, 2015.

[17] Paul Choffat. La ligne de dépressions Régua–Verín et ses sources carbonatées. Remarques et considérations. Comunicações dos Serviços Geológicos de Portugal, Lisboa, 12:35-69, 1917.

[18] Carlos Freire de Andrade. Os vales submarinos portugueses e o diastrofismo das Berlengas e da Estremadura. Serviços Geológicos de Portugal, Lisboa, 1937.

[19] Luiz de Menezes Acciaiuoli. Le Portugal hydrominéral. Direction Générale des Mines et des Services Géologiques, 2 volumes, Lisbonne, 1952/1953.

[20] José Martins Carvalho. Mineral and thermal water resources development in the Portuguese Hercynian Massif. In: David Banks, Sheila Banks (editors), Hydrogeology of Hard Rocks, International Association of Hydrogeologists, IAH, Oslo, 24(1):548-561, 1993.

[21] José Martins Carvalho. Mineral water exploration and exploitation at the Portuguese Hercynian Massif. Environmental Geology, 27:252–258, 1996.

[22] João Baptista, João Cabral & António Ribeiro. Seismotectonics of Chaves and Moledo mineral springs in Penacova-Régua-Verin Fault Zone. Comunicações do Instituto Geológico e Mineiro, Lisboa, 84(1):D69–D72, 1998.

[23] IGM – Instituto Geológico Mineiro. Catálogo de recursos geotérmicos. Instituto Geológico Mineiro, Lisboa (Edição CD-rom), 1999.

[24] José Manuel Marques, Jorge Espinha Marques, Paula M. Carreira., Ricardo Graça, Luís Aires-Barros, José Martins Carvalho, Helder I. Chaminé & Frederico Sodré Borges. Geothermal fluids circulation at Caldas do Moledo area, Northern Portugal: geochemical and isotopic signatures. Geofluids, 3(3):189-201, 2003.

[25] José Martins Carvalho & Helder I. Chaminé. O papel da fracturação e da alteração profunda em estudos de prospecção hidrogeológica: os casos das regiões de Oliveira de Azeméis e de Fafe (Maciço Ibérico, NW de Portugal). Geociências, Revista da Universidade de Aveiro, 16(1/2): 13-31, 2004.

[26] José Martins Carvalho, Helder I. Chaminé, Maria José Afonso, Jorge Espinha Marques, Albino Medeiros, Susana Garcia, Alberto Gomes, José Teixeira & Paulo E. Fonseca. Productivity and water cost in fissured-aquifers from the Iberian crystalline basement (Portugal): hydrogeological constraints. In: José Antonio López-Geta, Antonio Pulido Bosch & Juan Carlos Baquero Úbeda (eds.). Water, mining and environment Book Homage to Professor Rafael Fernández Rubio. Instituto Geológico y Minero de España, Madrid, pp. 193-207, 2005.

[27] Jordi Delgado, Ricardo Juncosa, Rosa Meijide, A. Vázquez & V. Barrientos. Características termohidrogeoquímicas de las aguas subterráneas en Galicia. In: Helder I. Chaminé,

José Martins Carvalho (editores), O valor acrescentado das Ciências da Terra no termalismo e no engarrafamento da água. Artigos seleccionados do II Fórum Ibérico de Águas Engarrafadas e Termalismo. Edição do Departamento de Engenharia Geotécnica / Laboratório de Cartografia e Geologia Aplicada, Instituto Superior de Engenharia do Porto, Porto, pp. 281-299, 2007.

[28] José Martins Carvalho, Helder I. Chaminé, José Teixeira, Catarina Rodrigues & Alcides Pereira. Recursos hídricos subterrâneos e águas minerais naturais entre o Rio Douro e o Rio Lis, Portugal Central: breve síntese (Capítulo VI). In: José Simões Cortez, (coord.), Águas Minerais Naturais e de Nascente da Região Centro, Mare Liberum editora, Aveiro, pp. 107-136, 2012.

[29] Alcino Sousa Oliveira. Águas subterrâneas do setor norte de Portugal continental: enquadramentos geográfico e geológico, tipologias e aproveitamentos. Boletin de la Sociedade Española de Hidrología Médica, 30(1): 57-71, 2015.

[30] José Martins Carvalho, Luís Coelho, João Carlos Nunes, Maria do Rosário Carvalho, João Garcia & Rita Cerdeira. Portugal Country Update 2015. Proceedings World Geothermal Congress, Melbourne, Australia, 2015.

[31] António Ribeiro, José Munhá, Rui Dias, António Mateus, Eurico Pereira, Luísa Ribeiro, Paulo E. Fonseca, Alexandre Araújo, José Tomás Oliveira, José Romão, Helder I. Chaminé, Carlos Coke & Jorge Pedro, 2007. Geodynamic evolution of the SW Europe Variscides. Tectonics, 26 (TC6009):1-24, 2007.

[32] Luís Aires-Barros. Aproveitamentos geotérmicos: considerações gerais; a exploração das altas e entalpias no território português. Boletim de Minas, Lisboa, 15(3/4):143-155, 1978.

[33] José Martins Carvalho & Luís F. Silva Pólos geotérmicos de Trás-os-Montes: recursos e metodologias de desenvolvimento. Anais da UTAD, Vila Real, 2:23-45, 1988.

[34] José Martins Carvalho & Maria Rosário Carvalho. Recursos geotérmicos e seu aproveitamento em Portugal. Cadernos Laboratório Xeolóxico de Laxe, A Coruña, 29:97-118, 2004.

[35] José Martins Carvalho. Captação de águas subterrâneas em rochas cristalinas. Tecnologia da Agua, Elsevier, Barcelona. Edição I, pp. 65-74, 2002.

[36] José Teixeira, Helder I. Chaminé, José Martins Carvalho, Augusto Pérez-Alberti & Fernando Rocha. Hydrogeomorphological mapping as a tool in groundwater exploration. Journal of Maps, 9(2):263–273, 2013.

[37] Helder I. Chaminé, José Martins Carvalho, Maria José Afonso, José Teixeira & Liliana Freitas. On a dialogue between hard-rock aquifer mapping and hydrogeological conceptual models: insights into groundwater exploration. European Geologist Magazine, Journal of European Federation Geologists, 35:26–31, 2013.

[38] José Martins Carvalho. Perspectives, prospectives et developpements technologiques. GigaStock, III$^{\text{émes}}$ Journnées Internationalles de Geothermie Apliquée, Versailles, 9(3):1011-1016, 1988.

[39] Hartmut Seifert & António Vicente A. (1968). Caldas de Moledo. Boletim de Minas, Lisboa, 5(3):226-227, 1968.

[40] Hartmut Seifert. Caldas de Moledo. Boletim de Minas, Lisboa, 6(1):66-68, 1969.

[41] Tomas Vylita. New tapping boreholes in Carlsbad. In: Romijn E. et al. (eds.), Geothermics, thermal-mineral waters and hydrogeology. Theophrastus Publications, Athens, pp. 205-218, 1985.

[42] Geoffrey A. Kellaway The hot springs of Bristol and Bath. Proceedings of the Ussher Society, 8:83-88, 1993.

[43] Geoffrey A. Kellaway. Environmental factors and the development of bath spa, England. In: Philip E. Lamoreaux & Judy Tanner, (eds.), Springs and bottled waters of the world: ancient history, source, occurrence, quality and use. Springer, Berlin, 2003.

[44] DNEMT [Division Nationale des Eaux Minérales et Thermales]. Le suivi du forage d'eau minérale: approche methodologique. Division Nationale des Eaux Minérales et Thermales, BRGM, Note Technique, 3:1-17, 1995.

[45] Carlos M. A. Calado. A ocorrência de água sulfúrea alcalina no Maciço Hespérico: quadro hidrogeológico e quimiogénese. Universidade de Lisboa (PhD Thesis), 2001.

[46] Luís Manuel Ferreira Gomes, Afonso de Albuquerque & Henrique Fresco. Protection areas of the S. Pedro do Sul spa, Portugal. Engineering Geology, 60: 341-349, 2001.

[47] Manuel Villanueva Martínez & Alfredo Iglésias López. Pozos y aquíferos: técnicas de

evaluación mediante ensayos de bombeo. ITGE, Madrid, 1984.

[48] Robert A. Bisson & Jay Lehr. Modern groundwater exploration: discovering new water resources in consolidated rocks using innovative hydrogeologic concepts, exploration, drilling, aquifer testing and management methods. John Wiley & Sons, 2004.

[49] Manuel Rámon Llamas. Hydroschizophrenia. Ground Water, 14(3):296-300, 1975.

[50] Jean Margat. The overexploitation of aquifers. International Association of Hydrogeologists Selected Papers 3: 29-40, 1993.

[51] Jacob Burke & Marcus Moench. Groundwater and society: resources, tensions and opportunities. In: Themes in groundwater management for the twenty-first century. ISET, United Nations Publications, 2000.

[52] Salif Diop & Philippe Rekacewicz. Atlas mondial de l’eau: une pénurie annoncée. Autrement éditions, Paris, 2003.

[53] Marc Laimé. Le dossier de l’eau: penurie, pollution, corruption. Seuil, Paris, 2003.

[54] Emilio Custodio. Aquifer overexploitation: what does it means. Hydrogeology Journal, 10:254-277, 2002.

[55] Emilio Custodio. Intensive use of groundwater and sustainability. GroundWater, 43(3): 291-291, 2005.

[56] Manuel Rámon Llamas & Paulo Martínez-Santos. Intensive groundwater use: silent revolution and potential source of social conflicts. Journal Water Resources Planning Management, 131(5):337-341, 2005.

[57] Manuel Rámon Llamas, Emilio Custodio, Africa de la Hera & Juan Maria Fornés. Groundwater in Spain: increasing role, evolution, present and future. Environmental Earth Sciences, 73:2567-2578, 2015.