Therapeutic characteristics of Galician mineral and thermal waters (NW-Spain) ascribed to their local/regional geological setting

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Abstract

Galicia is located in the NW corner of the Iberian Peninsula (Spain). From a geological point of view, the territory belongs to the Hercynian chain and, more specifically, to a large outcrop dominated by igneous and metamorphic rocks called the Hesperian Massif or Iberian Massif. In some sectors the Hesperian Massif is partially covered by more recent sedimentary deposits. The geology of Galicia is very complex due to the age of the rocks that make up its substrate and their diversity. Thus, the hydrogeological behaviour of the underground medium (hydrodynamic and hydrogeochemical characteristics) will determine the therapeutic properties of the water emanating from the surface. In Galicia, aquifers are generally shallow with low mineralization, except for those whose waters come from deep fractured mediums. The chemical characteristics of the water are directly related to the geological matrix. The groundwater flows through the geological medium and is mineralogically enriched by heterogeneous chemical reactions. Galicia turns out to be an area rich in the potential exploitation, applications and use of different water resources. These resources are thermal, mineral-natural and mineral-medicinal waters. In this work, we have developed a study that relates the geology, hydrogeological and hydrogeochemical characteristics of the Galician substrate and their potential therapeutic indications. To achieve that, we have chosen to study the exploited waters with higher flow rates, including the natural mineral waters for human use.

Keywords

Water quality; Minerals waters; Thermal waters; Medicinal waters

Introduction

A very limited number of comprehensive studies have analysed the hydrochemistry, medical hydrology and hydrogeology in Galicia. The only studies available are focused on local areas. Regional and local studies of certain characteristics have been conducted (Juncosa et al. 2012, 2015; Delgado et al. 2007, 2011, 2013), including hydrogeochemical studies developed in specific basins. There are similar studies in NW Portugal (Carvalho 1996; Marques et al. 2012). Hernández et al. (2012), Corral et al. (2012), and Martínez-Pledel et al. (2012) can be cited, among others, as hydrogeological studies. Other studies are focused to geothermal resources (Craig 1963; Giggenbach 1992; Marques et al. 2010; Chamorro et al. 2014), although the state of knowledge of the geothermal potential of Galicia remains essentially unexplored. In terms of medical hydrology, there is extensive literature about water uses (for instance Comstock 1979; Harper 2008; Luft et al. 1990; Matz et al. 2003; Meyniel 1975; Morris et al. 2008; Valitutti et al. 1990). However, a comprehensive and global study of the hydrogeochemistry, hydrogeological and medical hydrology has not been developed for all of Galicia.

For this reason, the purpose of this study is to analyse the therapeutic characteristics of the Galician groundwater taking into account the relationship between the geology, hydrogeology and hydrochemistry of its substrate.

Geological background

Galicia is located in the NW corner of the Iberian Peninsula (Spain). Geologically, the territory belongs to the Hercynian chain. The geology of Galicia is very complex on a smaller scale, due to the ages of the rocks that make up its substrate and the diversity of the materials. Thus, it is possible to find rocks ranging from the Precambrian to the present in Galicia. Additionally, from the tectonic point of view, some of these rocks have been subjected to stresses associated with different orogenies: the Caledonian, Hercynian and Alpine. Of these orogenies, the Hercynian has left the most significant mark (e.g., Gibbons and Moreno 2002; Vera 2004; Ribeiro et al. 2007; Martínez Catalán et al. 2008).

The main outcrop lithologies in Galicia can be summarized by the following categories (Juncosa et al. 2012):

1. Metasedimentary rocks Limestones and dolomites (transformed into marbles), quartzite, shale, schist (with muscovite, biotite, and chlorite) and paragneisses. These rocks were originally sedimentary rocks that were affected by metamorphic processes related to the orogenic periods.
   a. Limestones and dolomites These are located in the eastern part of Galicia, following bands from Mondoñedo (North) to Valdeorras (South).
   b. Quartzites These are located in the central-eastern part of Galicia.
   c. Shales These are very well developed in many areas of Galicia; but are mainly in the eastern area.
   d. Schists These are also very well developed in Galicia; but are mainly in the central-western area.
   e. Paragneisses The most prominent location of these rocks is the Ollo de Sapo formation, which emerges in antiformal structures from O Barqueiro to Zamora.
2. Granitic rocks These rocks are found in Galicia, especially in the central and eastern areas.
3. Basic and ultrabasic rocks (amphibolites, gabbro, diorite, peridotite, serpentinites, dunite, granulites and eclogites): These rocks are located in Cabo Ortegal, Bergantiños, Santiago, Lalin and Sobrado-Melide.

4. Tertiary basins filled with detrital materials (clays, silts, conglomerates and, sometimes, lignite). The main basins are: As Pontes, Meirama, Vilalba, Guitiriz, Sarria, Monforte, Quiroga, Valdeorras, Maceda, Xinzo de Limia and Verín.

5. Quaternary deposits: alluvial sediments, glaciers, hillside deposits, beach and wind deposits (Corrubedo), etc.

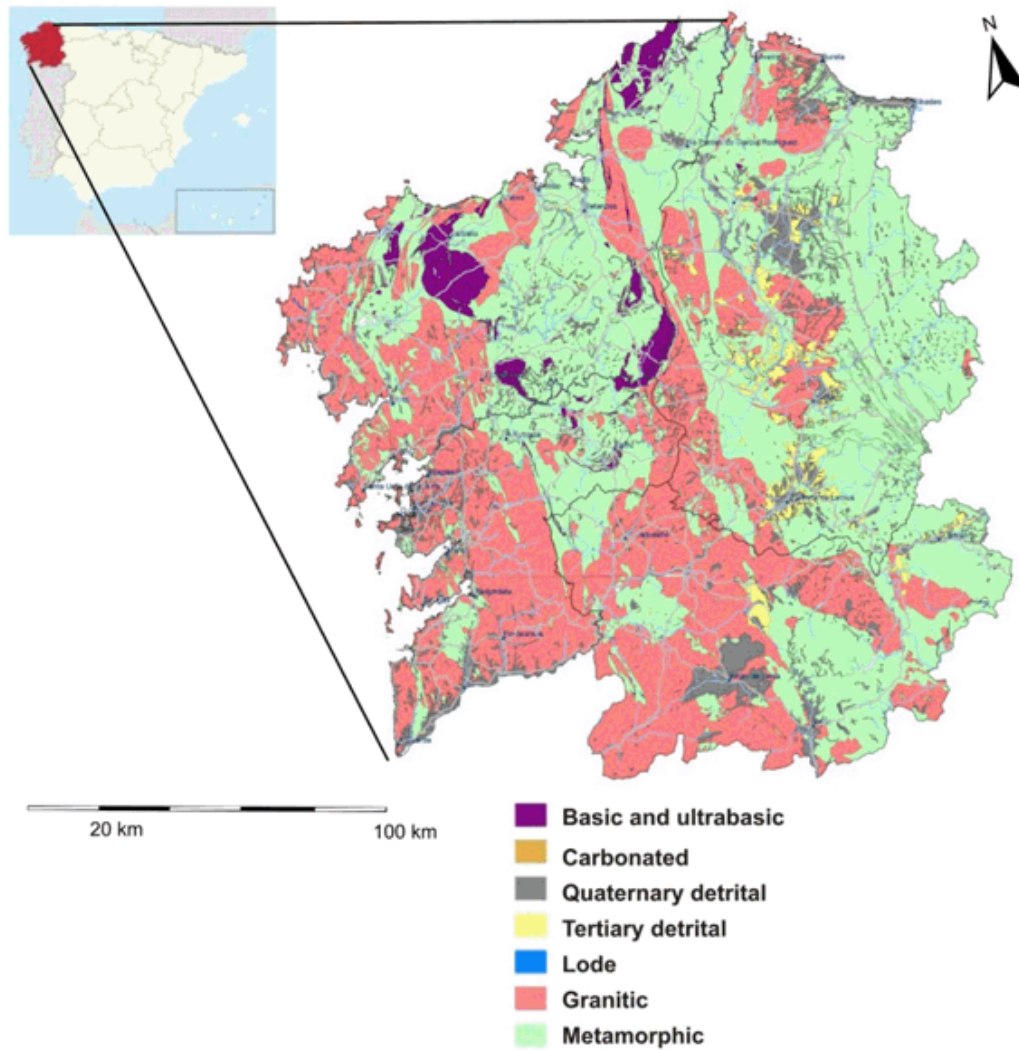Figure 1 shows a geological map of the main groups of rocks in Galicia.

Fig. 1. Geological map of Galicia. SITGA (http://sitga.xunta.es/)

Hydrogeological characteristics

The movement of water through the crust is the result of a number of mechanisms, such as sediment compaction, the existence of topographic gradients, variations of the water density, seismic "pumping", diagenesis, metamorphism and magmatism (Young 1995).

Groundwater flow can develop at very different time scales according to the hydrodynamic and geological features. Similarly, groundwater can move across very different distances before emerging at surface discharge points.

Fractured igneous and metamorphic rocks (crystalline rocks) are the most abundant rocks in Galicia, presenting heterogeneity and anisotropy, coinciding mainly along flow zones with cracks and fractures. The permeability of the undisturbed rock matrix is very low, as it is conditioned by the morphometry of fractures, connections and filling. The potential to transmit and store water is very small. Therefore, the dominant hydrogeological model in Galicia depends on phreatic aquifers.

The hydrodynamic characteristics of the main Galician outcrops can be summarized as follows:

1. Carbonate formations (limestone and dolomite) and quartzite formations The secondary porosity of these formations is important (dissolution porosity in carbonates and fracture porosity). These are the formations that have the highest permeabilities in Galicia and are commonly karstified. The water flows quickly and along "channels" (Vegadeo Formation, the old mine of Pb–Zn in Pedrafita do Cebreiro and the carbonated formation associated with Candana Group in Riotorto, Tricastela and Sarria).
2. Igneous and metamorphic lithologies Their porosity is associated with intense development of fractures. In the case of metamorphic rocks, the existence of one or more foliation families can occur. The weathering of these rocks leads to the development of superficial alterations (regolith) of variable thicknesses. The regolith can have a thickness greater than 10 m, and its hydrodynamic behaviour is very different from the rest of the rock mass, resembling sands and gravels. The recharge occurs through massive discontinuities, so the response of the water table is usually very quick. These discontinuities can be filled by minerals (frequently clays) that limit access to water. The geometry and distribution of these aquifers are much more difficult to assess. Overall, the average permeability of these materials is low, but it can be high near the surface, where there is more intense fracturing and the discontinuities are more open.
3. Tertiary basins These basins are relatively large and discontinuous. Specially, they are sedimentation basins that currently take up the depressions in the relief (As Pontes de García Rodríguez, Meirama, Maceda, Quiroga, Monforte de Lemos, Sarria, Junceda, Visantoña, Guitiriz, Pastoriza and Vilalba). These depressions are filled with sand, clay, gravels and, sometimes, lignite layers. Hydrogeologically, the aquifers are small, but they are of interest from the point of view of the local operations. The average permeability of these units is rather low due to the existence of a high proportion of clay and silt. Its porosity is mainly an intergranular type.
4. Quaternary sediments They are continental deposits which are related to the current rivers (alluvium) and the partial erosion of Tertiary materials and continuous denudation of mountain boundary (colluviums) at certain points, and, even, sediments of glacial environment (Rey et al. 2004, Vidal Romaní and Yepes 2001).

The permeability map of Galicia can be seen in Fig. 2. This map is related to the geological map.
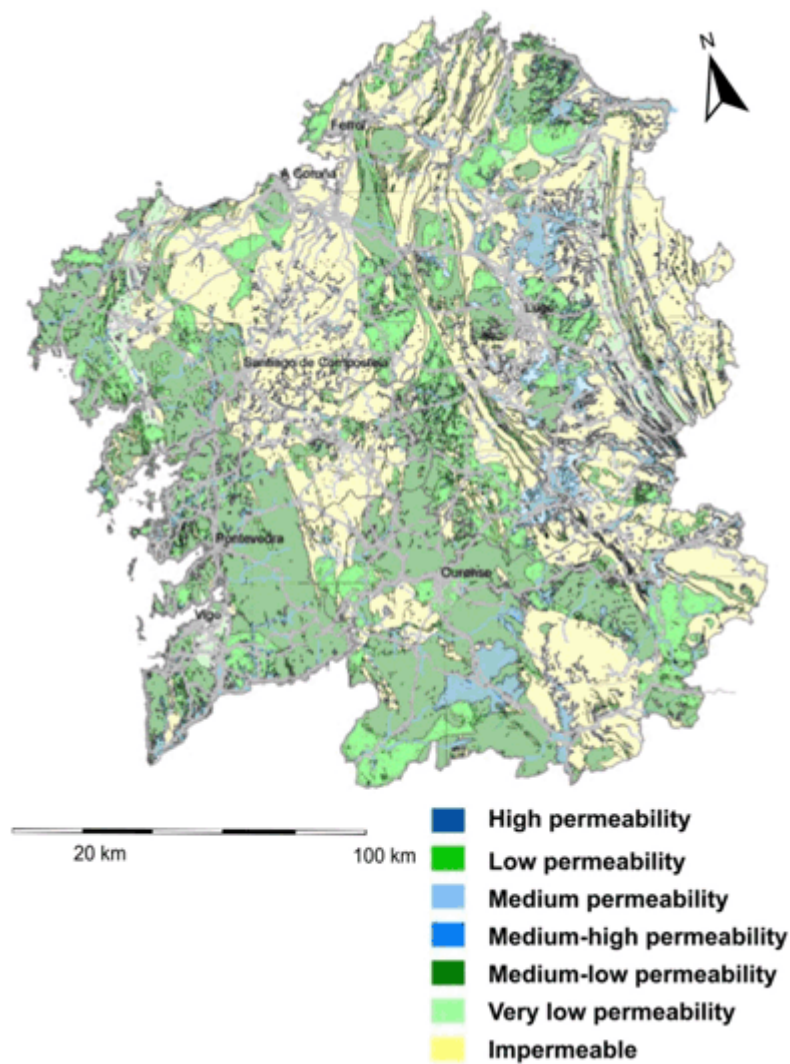
High permeability
Low permeability
Medium permeability
Medium-high permeability
Medium-low permeability
Very low permeability
Impermeable

Fig. 2. Hydrogeological map of Galicia. SITGA (http://sitga.xunta.es/)

Chemical and thermal characteristics of groundwater

The chemical composition of natural waters is influenced by many factors, including aerosols and atmospheric gases, surface erosion and the weathering of rocks and sols (with biological component), the dissolution and precipitation of minerals far from the surface and human activity Stumm and Morgan (1995). The study of the processes that occur in the aqueous phase is usually performed by applying chemical thermodynamics principles. Some of these processes occur very near chemical equilibrium, although it is also necessary to consider the mechanism and reaction rates of chemical kinetics (Hounslow 1995).

Water solutes are also part of the geochemical cycle (Hem 1991). This cycle starts with the weathering of rocks, which is the process that breaks down rocks and many of the minerals that they are made from. In this process, according to different chemical reactions, some constituents with solid phases pass through the water as solutes Henley et al. (1984). On the other hand, the decomposition of organic matter in soils releases acids that dissolve minerals. This process is called the biogeochemical cycle.

Weathering is more intense when the climate is warmer and wetter, but it is equally effective in latitudes with moderate climates, which includes Galicia. However, not all the minerals are weathered at the same speed, so the chemical fraction transferred into the water is restricted. This weathering process can be expressed by the Goldlich series (Fig. 3). As such, the concepts of flow scale and residence time are fundamental to understanding the evolution of groundwater chemistry.
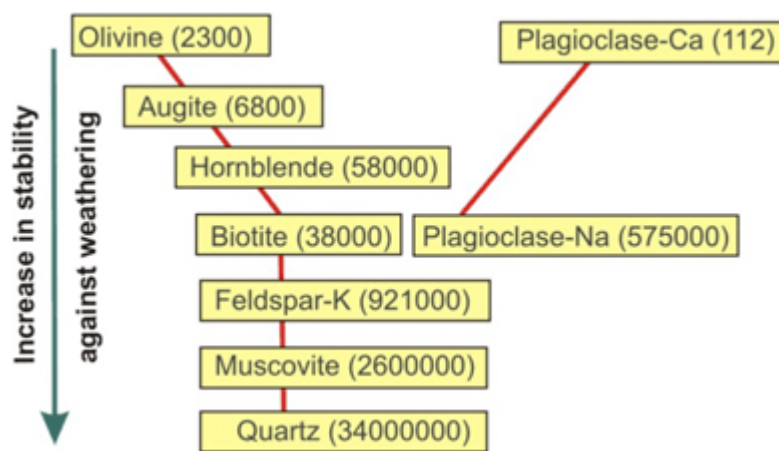

Fig. 3 Goldich series of weathering. The numbers correspond to the years required to dissolve a volume of 1 mm3, at pH 5 and 35 °C (adapted from Langmuir (1996))

Chemical quality

Groundwater composition is quite variable. However, the number of major components in the water is very limited and variability (in terms of the concentration ranges) is not as important as we might have expected it to be for many of the existing lithologies and interaction processes (organic and inorganic). Thus, according to Davis and De Wiest (1966), seven elements are normally found in water at concentrations greater than 1 mg/L (Ca, Mg, Na, HCO_3, Cl, SO_4 and SiO2), although there are 22 elements that make up 99.8% of the upper lithosphere, oceans and atmosphere. These 7 elements make up 95% of the chemical components of groundwater. In addition, there are eight minor components often found in groundwater, at lower concentrations (0.01–10 mg/L) (K, Fe, Mn, Sr, B, F, CO3 and NO_3). The rest of chemical elements are typically present as trace constituents (0.01 mg/L).

The movement of water through the unsaturated zone determines the concentrations of the major constituents and how they tend to increase. Thus, Chebotarev (1955), in a work in which he took into consideration more than 10,000 Australian groundwater analyses, concluded that these concentrations tend to chemically evolve towards the composition of seawater. He observed that this evolution is usually accompanied by regional changes in the dominant anion according to the pattern indicated by Fig. 4. Figures 5 and 6 also illustrate this observation.
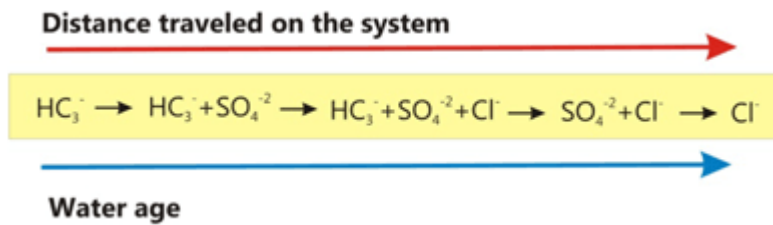
Distance traveled on the system

$$HC_3^- \rightarrow HC_3^- + SO_4^{-2} \rightarrow HC_3^- + SO_4^{-2} + Cl^- \rightarrow SO_4^{-2} + Cl^- \rightarrow Cl^-$$

Water age

Fig. 4. Hydrochemical evolution sequence of natural groundwater
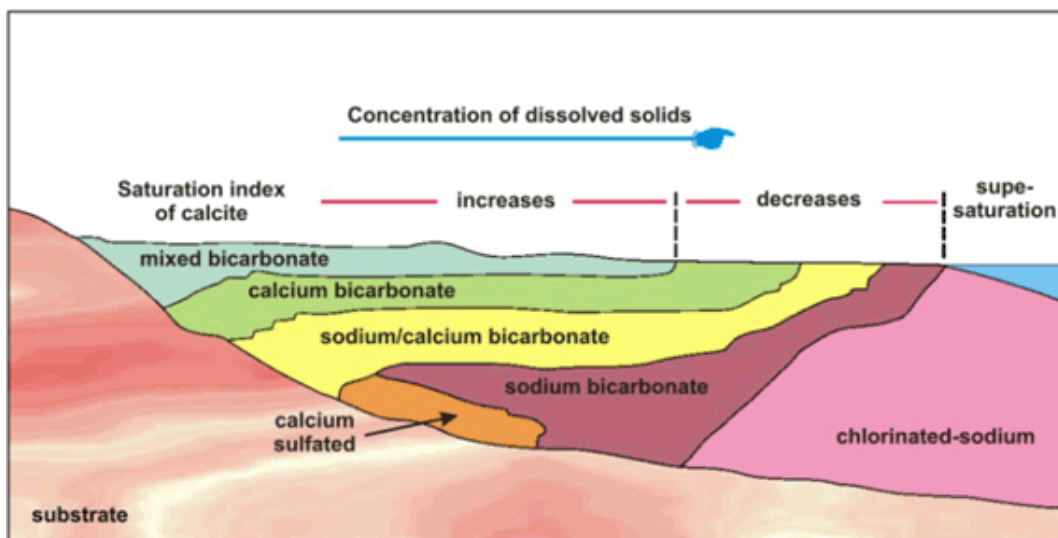(Chebotarev 1955)

Fig. 5. Evolution of the geochemical characteristics of groundwater in the context of
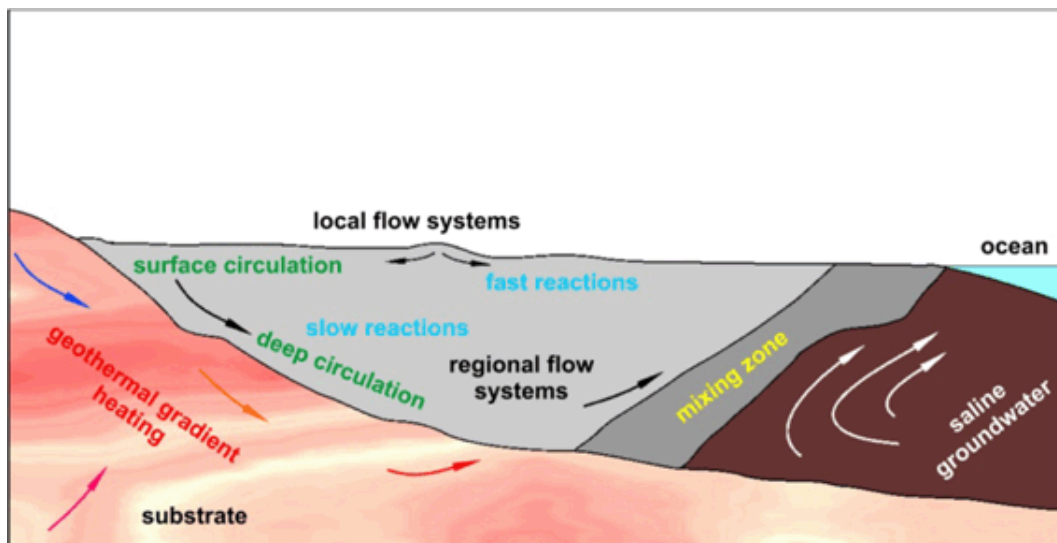a coastal plain (Winter et al. 1998)

Fig. 6. Hydrogeothermal processes capable of modifying the chemical characteristics of groundwater (Winter et al. 1998)

Therefore, the hydrochemistry is associated with lithology and it is possible to establish the following groups of waters (Fig. 7):

1. Crystalline silicate rocks with coarse and medium grains This group of rocks includes igneous and metamorphic lithologies. The waters tend to be bicarbonate-sodium/potassium although springs close to the coast can have an important chlorinated component (thermal spring of A Toxa, Caldas de Reis, etc.). On the other hand, many igneous and metamorphic rocks contain potentially important amounts of sulphides, especially pyrite (FeS_2). The rise of deep water to the surface can occur such that the dissolved sulphur species do not oxidize to sulphates, leading to the formation of sulphurous springs or sources of waters (Guitiriz Spa, Baños da Brea, Termas de Cuntis, Baños Viejos de Carballo, etc.).

2. Schistose silicate (shale and phyllite) and carbonaceous rocks with low solubility These rocks have a very small primary permeability but, during their deformation, often develop a good secondary porosity (fracture porosity). They are composed of aluminium silicates, mica, quartz and iron oxides (ferruginous waters; for instance, O Incio Spa). These minerals have relatively low solubilities. Therefore, their weathering usually provides few solutes. Some of these rocks (for instance, ampelitic shales) may contain significant amounts of pyrite or other sulphide minerals capable of releasing sulphur species into the water (sulphurous waters) or, after oxidation, may provide appreciable amounts of sulphate.

3. Carbonate rocks (limestones and dolomites) These rocks provide calcium or magnesium bicarbonate waters (Vegadeo Formation, some units of Candana group).

4. Terrigenous sediments (clays, silts, sands, etc.) These sediments are poorly mineralized and are composed of sodium/ calcium bicarbonate. Most of these lithologies have a detrital origin.

5. Thermal springs and balnearies Michard and Beucaire (1993) have carried out a study of waters of different compositions and temperatures in Galicia.

6. Rainfall, river and seawater The waters of the rivers and rain in Galicia have very diluted compositions, and are slightly acidic.

On the other hand, waters from the same type of geological massif can have very different hydrochemical characteristics. Thus, the waters with deeper circulation paths (longer residence period) have higher mineralizations than the shallow circulation waters. Additionally, at mixture of the two types of paths can occur at points of surface discharge, so it is more common to talk about families of waters with similar hydrochemical characteristics than pure waters. Mineralogy plays an important role in the chemistry of many of the components of groundwater (Chebotarev 1955; Giggenbach 1988; Coudrain-Ribstein et al. 1998).
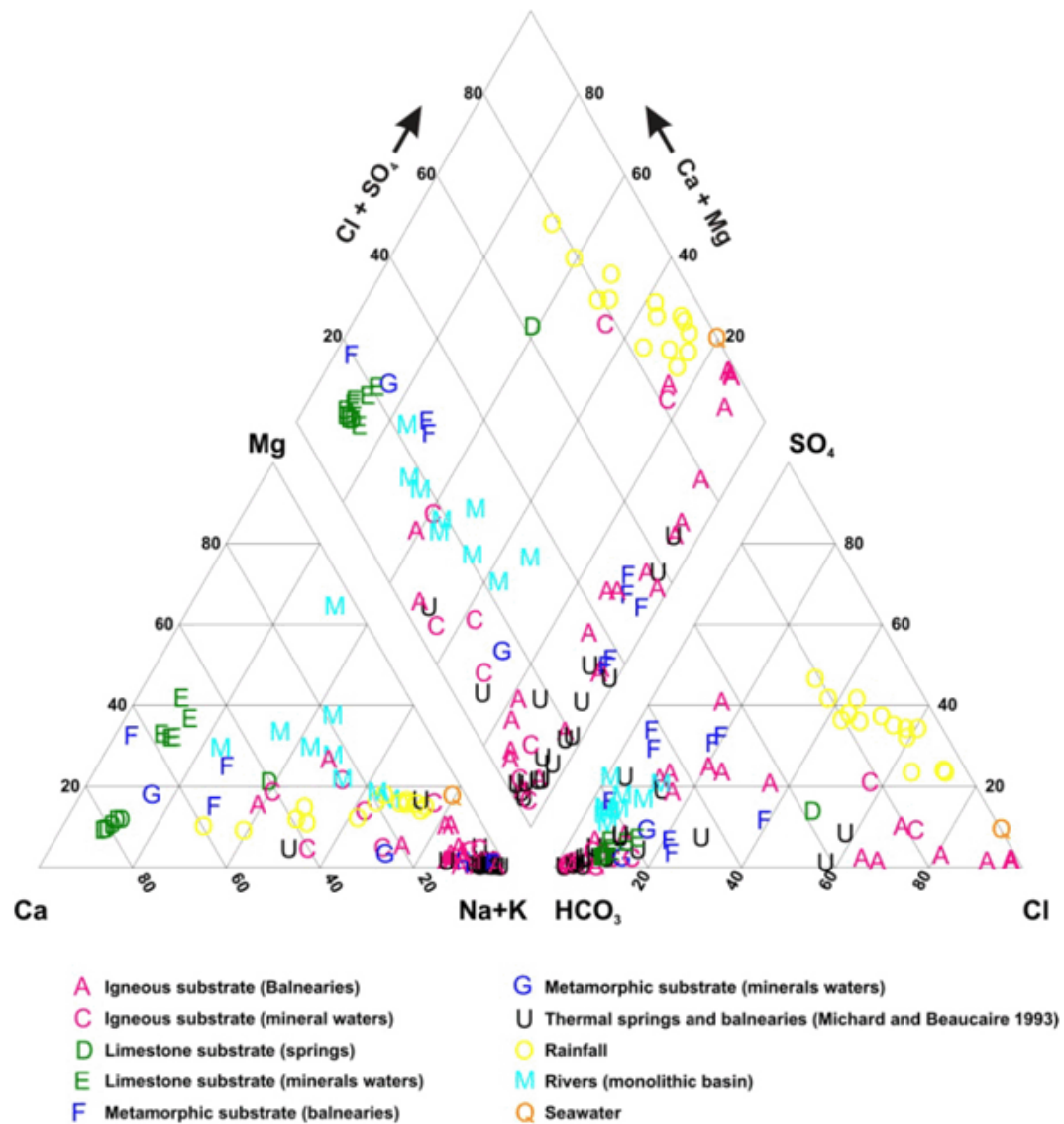

Fig. 7. Piper–Hill diagram. Data concerning the chemical compositions of the groundwaters, thermal waters, mineral waters, rivers and rainfall associated with different lithologies of Galicia

Hydrothermal quality

Galicia is a land rich in thermal springs. Many of them have been known since ancient times and, at present, are a source of wealth. An important network of spas has developed in recent years (Fig. 8).

With regard to thermal water quality, Galicia is a region in Spain where there is a "thermal anomaly": There are zones in the South and on the border with Portugal where there are springs with the highest temperatures.

Fig. 8. Main spas and thermal springs in Galicia. Red located in an igneous substrate.
Blue located in a metamorphic substrate

Michard and Beaucaire (1993) developed a study of 21 thermal springs with granitic lithologies in Galicia. Their study ignores important thermal manifestations (the cases of A Toxa, Baños Viejos de Carballo, Arteixo, etc.) and focuses on verifying a reactive model widely that has been applied to other geological contexts (French Central Massif, Corsica, Bohemian Massif, Pyrenees, Alps, etc.). Thus, these authors suggest that the composition of the different waters they studied (from carbogaseous to alkaline) can be justified by a varying original CO_2 concentration and by different degrees of water/rock interaction. Thus, according to these authors, the waters in Galicia can be classified in four categories:

Group I This group has a high pH (alkaline) and low concentration of magnesium. It has a composition close to equilibrium with a mineral paragenesis characterized by the presence of calcite, albite, potassium feldspar, laumontite, prehnite, chlorite and chalcedony. This water would

be the type that prevails in calc-alkaline granitoids. An example of this group would be the waters of the Termas de Cuntis.

Group II This group is similar to Group I but it would be in equilibrium with mineral paragenesis made up of calcite, albite, potassium feldspar, muscovite, laumontite, chlorite and chalcedony. Examples of this group include the water sources near Ourense, O Canedo and O Tinteiro.

Group III This group is represented by the springs located in the vicinity of Ourense (for example, Baños de Molgas, Laias Spa and As Burgas de Ourense). Concentrations of sodium, potassium, magnesium and silica are related to a mineral association similar to that described in Group II. Calcium would not be controlled by the presence of laumontite (which is absent from the mineral association) and the high bicarbonate content would not be compatible with the equilibrium with calcite. Group III represents waters with a lower degree of interaction with rocks and a greater chemical imbalance due to this.

Group IV This group includes carbogaseous waters (Mondariz Spa and Cabreiroá Spa) that demonstrate a greater chemical imbalance with the host rocks (Fig. 9).
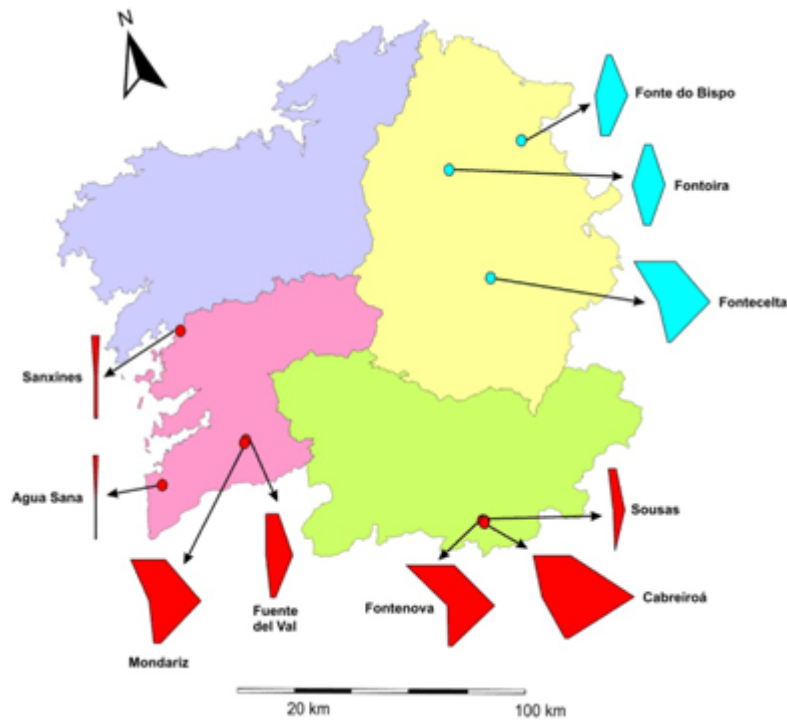
Fig. 9. Springs of mineral waters in Galicia and their stiff diagrams. Red located in an igneous substrate. Blue located in a metamorphic Substrate

The temperatures measured at the points of thermal water upwelling do not usually coincide with the temperatures at the maximum depth at which the waters are heated. This lack of similarity is due to many of processes that cause cooling. According to D'Amore (1991) the most important processes are: (1) adiabatic boiling (i.e., the physical separation of a vapor phase without heat exchange with the rock), (2) heat dissipation by thermal conduction to the rock, (3) mixing with cold surface waters, and (4) a combination of the previous processes.

Chemical analysis of the thermal waters provides useful information for identifying these processes. Waters that rise quickly from deep aquifers with no conductive cooling often have a chemical composition that reflects the water/rock equilibrium at the aquifer temperature. However, the cooling of the waters by conduction is produced when the ascent to the surface is slow (D'Amore 1991). These slow-moving waters can even travel horizontally before surfacing. As a result, rows of springs can be found with very similar chemical compositions but with very different temperature (Mahon 1966; Fournier and Rowe 1966; Fournier and Potter 1982). Moreover, when the rising hot water is cooled via mixing with surface waters, the springs can show different chemical and thermal characteristics.

Classification of groundwater in Galicia

Typology of water

The planning and management of mineral and thermal waters in Galicia is performed by a set of management criteria. Therefore, the following water classification has been developed into a law, D1798/2010, as shown in Table 1.

Regulation of mineral waters and thermal waters			
Type	Mineral waters		Thermal waters
	Mineral-medicinal waters		Mineral-industrial waters
	For therapeutic purposes	Springs waters	Natural waters

Table 1. Classification of waters according to Law D1798/2010

The different categories can be defined as follows:

- Mineral-medicinal waters for therapeutic purposes The naturally or artificially occurring waters that are declared of use to the public and that are suitable for therapeutic treatments. For this, they must have certain qualities.
- Spring waters Those waters of underground origin that emerge spontaneously or are captured by labors made for this purposes. They are naturally pure.
- Natural waters Waters that are healthy bacteriologically, with underground origins, that emerge at one or more points of upwelling. They can be clearly distinguished from drinking water by their nature and original purity, characterized by their mineral contents, trace elements and favourable effects. They can be drunk.
- Mineral-industrial waters Waters that allow the safe use of the contained substances. The sea water used for this purpose is included.
- Thermal waters Waters whose upwelling temperature is four Celsius degrees higher than the average annual temperature of the area where they emerge, that are declared of use to the public and that are suitable for therapeutic uses in spas.

Several authors (Souto 1990; Baeza et al. 2001) have inventoried the mineral waters and thermal waters in Galicia.

Classification of water according to physical and chemical characteristics

Of the physical characteristics of the water, temperature is the most widely used criterion for classifying mineral water. The most useful classifications, from a medical point of view, are those that consider the water temperature in relation to body temperature, since external applications of mineral-medicinal water will almost always take body temperature into account.

From a therapeutic point of view, the criteria used to classify the mineral-medicinal waters in Spain are also used in other countries. The most common classifications are those that take into account the total mineralization and the predominant anion and cation content, those that account for the presence of special components, or those that classify by physical properties, such as temperature.

In Spain, the classification proposed by Armijo and San Martín, and published by Maraver (Maraver 2002), is used for medical hydrology. For this study, the different criteria developed in the different European countries have been considered. There is the Latin approach, in which a mineral-medicinal water is water with therapeutic properties, regardless of the total amount of minerals, and the Germanic criterion, in which it is necessary to have a minimum amount of dry residue and chemical components to be considered mineral-medicinal water; meanwhile, Spain has followed a mixed approach (Table 2).

Classification of mineral-medicinal waters according to mineralization and chemical composition	
Mineral-medicinal waters with more than 1 g/L of mineralizing substances	

Chlorinated (>20% mEq of chloride)	• Sodium
	• Calcium
	• Mixed
	  ◦ Sulphated
	  ◦ Bicarbonated

Sulphated (>20% mEq of Sulphate)	• Sodium
	• Magnesium
	• Calcium
	• Mixed:
	  ◦ Chlorinated, Bicarbonated
	  ◦ Sodium, Magnesium

Bicarbonated (>20% mEq of Bicarbonate)	• Sodium
	• Calcium
	• Mixed
	  ◦ Chlorinated, Sulphated
	  ◦ Sodium, Calcium

Mineral waters with special mineralizing elements	
Carbogaseous	>250 mg of CO_2/L
Sulphur	l mg of reduced S/L • Sodium • Calcium
Ferruginous	(more than 5 mg/L of Fe bivalent)
Radioactive	(more than 67.3 Bq/L)

Table 2. Classification of the mineral-medicinal waters according to chemical composition (D1074/2002)

Classification of water in Galicia according to temperature

According to the criteria described, the waters of the Galician spas and springs with mineral-medicinal contents can be categorized from a thermal point of view as shown in Table 3.

Designation	Temperature ºC	Spas and springs
Cold	<19.9	Augas Santas-Pantón Agua de Fonte Nova: main spring Agua Cabreiroa with Gas 2 Sousas: spring 1 O Tremo Mondariz (Gándara) Guitiriz Rio Pambre O Incio
Hypothermal $T < T_{aa} + 4$ °C	20–34.9	Baños de Berán O Carballiño Ponte Caldelas Acuña Charca do Allegal Baños de Brea Arnoia Fonte do Bañiño
Mesothermal $T = T_{aa} + 4$ °C	35–36.9	Caldas de Partovia Arteixo
Hyperthermal $T > T_{aa} + 4$ °C	37–60	Baños de Loureda Baños Viejos de Carballo Laias Baños de Molgas Dávila Caldelas de Tui Cortegada Lugo A Toxa
	>60	Lobios Xardin das Burgas Termas de Cuntis

T spring temperature, T_{aa} average annual temperature
Table 3. Classification of waters according to upwelling temperature

Classification of water in Galicia according to mineralization and chemical components

From the point of view of overall mineralization, mineral-medicinal waters can be classified by their dry residue at 180 °C. The mineral-medicinal waters with low mineralization (250–500 mg/L) are predominant in Galicia (36% of the total). Medium mineralization waters (500–1000 mg/L) account for 24% of the total. High mineralization waters (>1000 mg/L) also account for 24% of the total. Finally, the waters with very low mineralization represent 16% of the total.

From a standpoint of special mineralizing elements, spas using carbogaseous waters with more than 250 mg/L free CO2 include the Mondariz Spa (Gandara) (988.9 mg/L), Agua de Cabreiroá with Gas 2 (705 mg/L) and Agua Fonte Nova - main spring (631 mg/L).

The waters of the Galician spas are, in general, very soft waters (0–100 mg/L of $CaCO_3$), as expected for terrain with high calcium contents. The Arteixo spa is an exception, with waters that are soft (100–200 mg/L of $CaCO_3$), as is the A Toxa spa, which has extremely hard waters (>400 mg/L of $CaCO_3$).

The A Toxa spa waters are unique due to their high concentrations, moderate temperatures (40–47 °C) and their sodium-chloride contents. The waters here have a significantly lower magnesium content (also potassium and sulphate) and a higher fluorine, calcium and carbonates content than seawater. Thus, the origin of the water of A Toxa is due to seawater and intense interactions with the surrounding rocks. The reduction in the sulphate content could be caused by the precipitation processes associated with the electrochemical reductions at depth ($SO_4 \rightarrow HS$) and the increase in the carbonates due to the dissolution of calcites under the partial pressure conditions of a higher CO_2 value than the partial pressure of the atmosphere, fixing magnesium and potassium (predictably by forming phyllosilicates) and leaching some amount of fluoride and calcium. (Coudrian-Ribsterin et al. 1998).

Moreover, one characteristic of the Galician waters is the presence of high silica and fluoride concentrations, which results from the geomorphology of the reliefs. The pH of the Galician springs is acidic in the carbogaseous bicarbonate waters (Gandara in Mondariz, Cabreiroá, Fontenova, Sousas and A Toxa) and is alkaline or highly alkaline elsewhere.

A preliminary inspection of the water from different Galician spas show that, except for the A Toxa spa (and the Arteixo spa and springs "Troncoso" and "Estrella" from Mondariz), most of the waters are relatively diluted (Figs. 10, 11). This dilution could imply a relatively short residence time in the substrate. Additionally, the waters are mainly bicarbonate-sodium type (including Mondariz), with notable sodium-chloride exceptions, (A Toxa, Arteixo, and springs and sources of Caldas de Reis) and one bicarbonate-calcium type (O Incio). O Incio is not really a thermal system, but rather is a ferruginous source that takes its composition from a relatively shallow trip through shale.

Figure 12 shows a triangular diagram of the most representative anions of the typical thermal springs. This scheme, proposed by Giggenbach and Goguel (1989), was originally intended for magmatic-hydrothermal systems but it has been used in a generalized form to classify the thermal springs preliminarily. In summary, the diagram divides the waters according to their relative chloride, sulphate and bicarbonate contents.

Most of the thermal springs are projected in the lower right section of the figure, within the domain called the "peripheral waters." According to Giggenbach (1988, 1997), this area is characterized by the existence of water that, having interacted with the bedrock, would not have reached chemical equilibrium with it. On the other hand, the water compositions near the vertex of chloride would be in the domain of "mature water", i.e., those who have interacted with rocks enough to have approached significant chemical equilibrium with them. Several water samples are located in the field of "mature water", particularly those belonging to the Arteixo spa, Caldas de Reis (Davila Acuña) and A Toxa (Juncosa et al. 2011).

Figure 13 shows a Giggenbach triangular diagram (Giggenbach 1988) for cations of K, Na and Mg in the waters of the spas and thermal springs in Galicia, as well as for some of northern Portugal, which distinguishes whether the springs are located on igneous or metamorphic substrates, if the springs has carbogaseous waters and the particular case of A Toxa. In two curves are represented in Fig. 13.
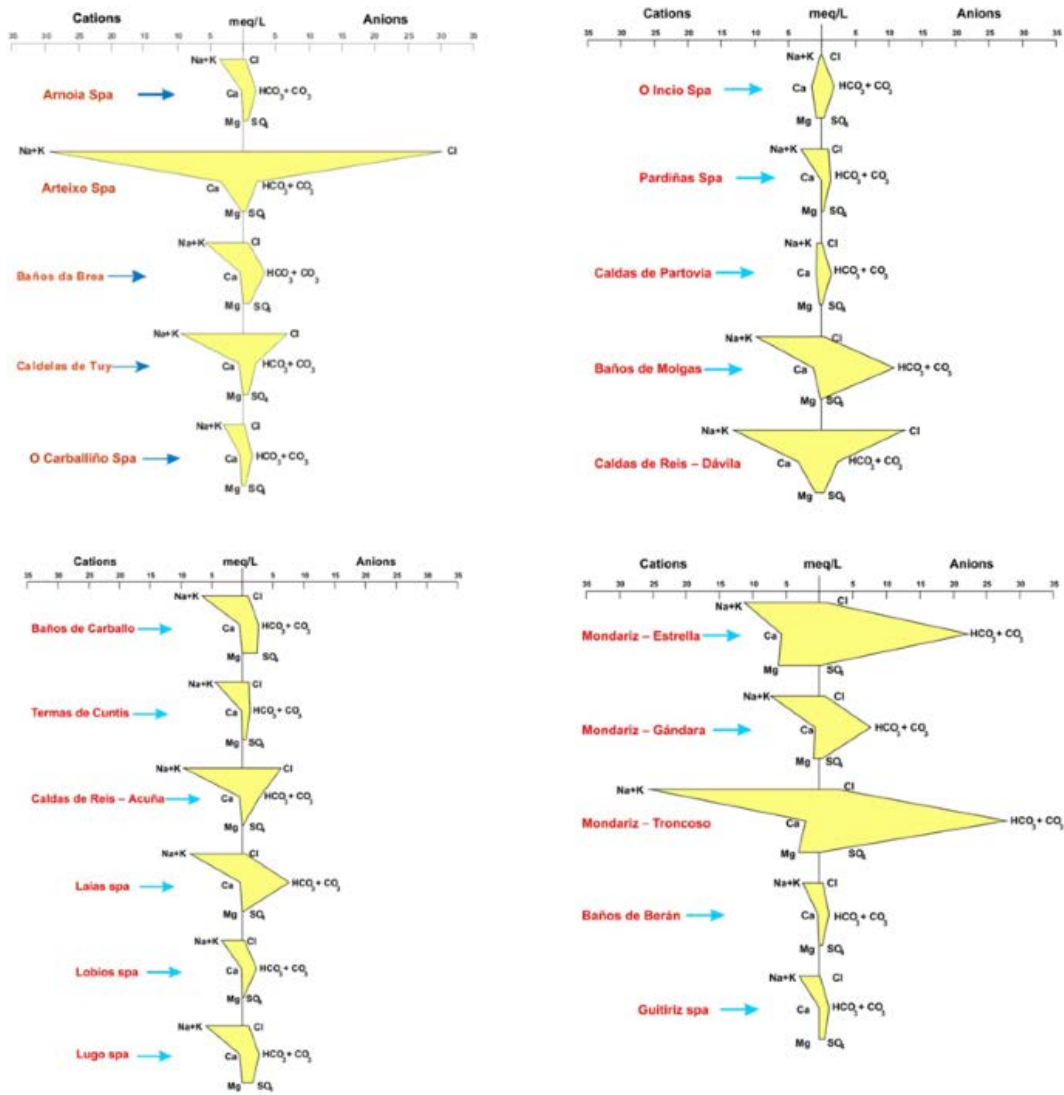
Fig. 10. Stiff diagrams of the mineral waters in Galicia
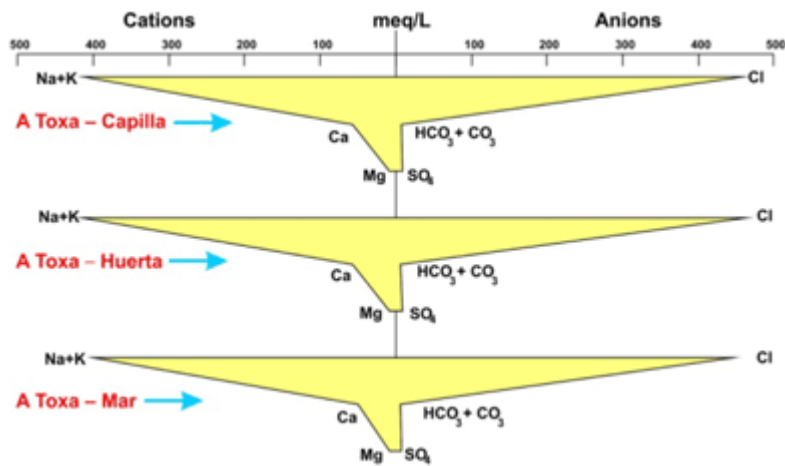
Fig. 11. Stiff diagrams of some springs from the A Toxa spa
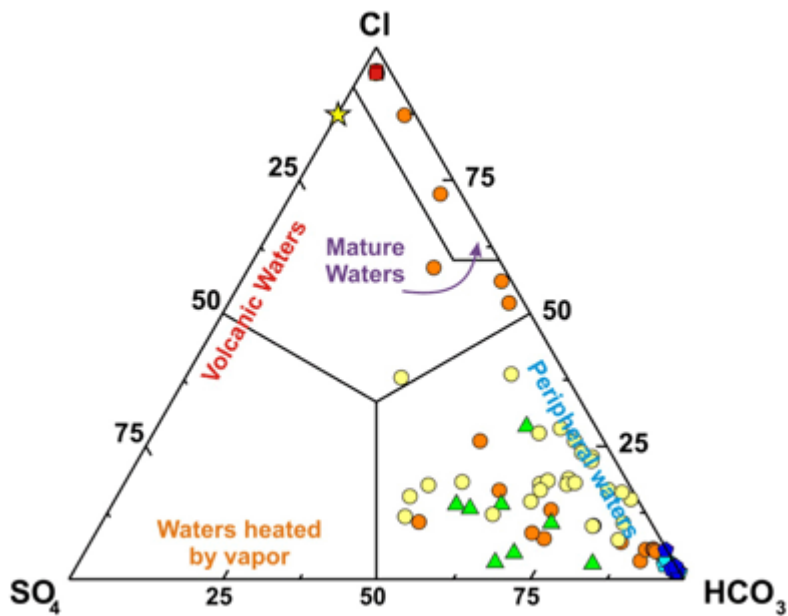
Fig. 12. Diagram of Cl–HCO3–SO4 (mg/L) of Giggenbach and Goguel (1989) of the spas and thermal springs of Galicia and northern Portugal. Igneous substrate the orange circles (Galicia) and yellow circles (northern Portugal: Vilarelho da Raia, Chaves, Pedras Salgadas, Vidago, São Lourenço, Carlão y Caldas do Moledo). Metamorphic substrate green triangles. Carbogaseous waters dark blue pentagons (Verín and Mondariz) and light blue pentagons (northern Portugal). Waters of A Toxa spa red squares.

Fig. 13. Giggenbach triangular diagram (Giggenbach 1988). Spa water composition and thermal springs in Galicia are plotted. Igneous substrate brown circles (Galicia) and yellow circles (northern Portugal: Vilarelho da Raia, Chaves, Pedras Salgadas, Vidago, São Lourenço, Carlão y Caldas do Moledo); metamorphic substrate green triangles; carbogaseous waters dark blue pentagons (Verín) and light blue pentagons (northern Portugal); waters of A Toxa spa red squares. The average compositions of basalts, granites and rocks of the upper crust are also plotted.

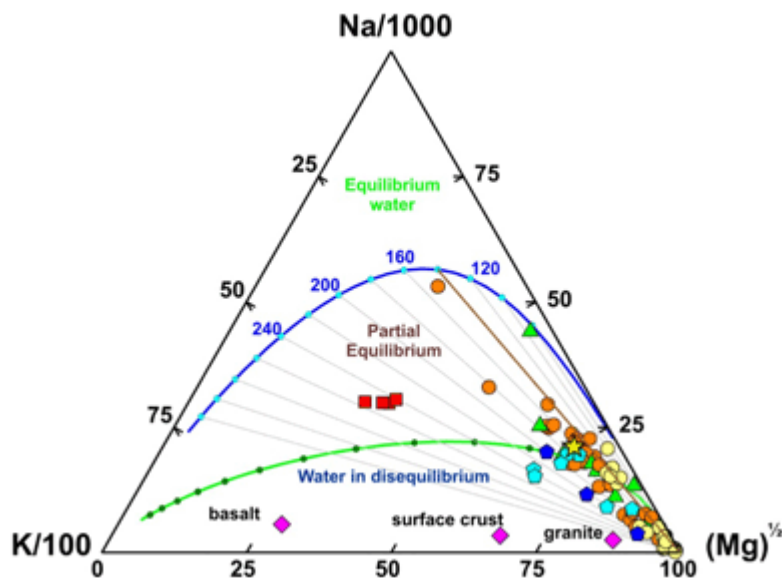In the triangular diagram, Giggenbach usually showed two curves that divide the area of the plot into three main domains: overall balance, partial equilibrium and disequilibrium. The equilibrium curve is calculated from the geothermometric relationships that Giggenbach suggested for K/Na and K/Mg ionic pairs, which represent the interactions of the natural waters with the minerals of crustal rocks. Similarly, since the equilibrium of the K/Mg system is reached faster (at lower temperature) than that of the K/Na system, Giggenbach proposed a second curve that would show the waters that have not reached total K/Mg and K/Na equilibrium. These waters would be in transit towards this equilibrium.

The area of water in disequilibrium (i.e., immature water) represents those waters with compositions that are the product of the dissolution of minerals present in the rocks without reaching equilibrium. According to Giggenbach (1997), high magnesium content is incompatible with high temperatures, which denotes the acquisition of this element at low temperatures (for example, via water/rock interactions at low temperature or via mixing with colder fluids) or a high degree of immaturity.

On the other hand, most of the analysed waters define a linear trend (brown line) that would suggest a partial equilibrium at a maximum temperature of approximately 140 °C. That is, a significant portion of the water could come from at mixture of deeper water (with reservoir temperatures of approximately 140 °C) with surface water. Assuming a normal geothermal gradient (~32 mK/m), the depth of the thermal water reservoir would be located 3–4 km. However, using the Iberian Massif gradient (~25 mK/m) gives a depth of 4–5 km.

Furthermore, A Toxa waters are outside of the range of the other waters, within the scope of partial equilibrium and are apparently associated with a reservoir of a higher temperature. It is worth noting that the magnesium content of the waters of A Toxa is much lower than in other waters, with concentrations close to the equilibrium values for basaltic rocks. In this case, it is difficult to establish a link between these waters and the deep circulation of seawater through a basaltic oceanic crust.

The K/Ca and K/Mg ratios of the thermal springs generally reach equilibrium faster than those associated with other geothermometers (for example K/Na) (Giggenbach 1988). It is an accepted fact that the presence of calcium in water is associated with the presence of calcite in rocks. The solubility of calcite depends on temperature, pH and the partial pressure of CO_2 (Fig. 14). However, these ionic ratios are also likely to reflect situations of rebalancing. In this case, the temperatures would reflect lower thermal conditions than the reservoir temperatures where the thermal waters originated. Additionally, mixing with surface water (which is richer in magnesium and bicarbonate) can distort their meaning.
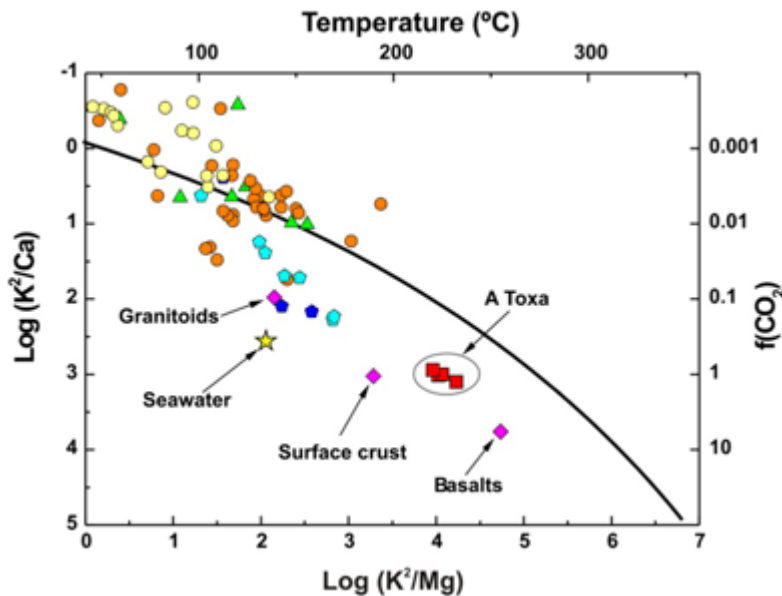
Fig. 14. Spas and thermal springs of Galicia and northern Portugal. (V). The log (K^2/Mg) vs. log (K^2/Ca) (or temperature vs. fugacity of CO_2) diagram corresponding to the igneous substrate (Galicia, orange circles; northern Portugal: Vilarelho da Raia, Chaves, Pedras Salgadas, Vidago, São Lourenço, Carlão y Caldas do Moledo, yellow circles) and the metamorphic substrate (green triangles). A Toxa waters red square. Carbogaseous waters pentagons (Verín, in dark blue, and northern Portugal, –Chaves, Vilarelho da Raia, Vidago, Pedras Salgadas- in light blue).

Figure 14 shows the K/Ca and K/Mg relationships of the waters analysed in this paper. A curve representing the linkage of bicarbonate to granitic rocks is also shown. The precipitation of calcite is promoted by higher temperatures. This reaction can be expressed as follows:

Silicate−Ca−Al+CO_2+H_2O→$CaCO_3$+clays
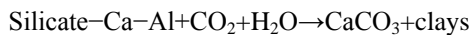
It is interesting that most of the water fit the above theoretical trend reasonably well. In fact, there is a remarkable similarity between these data and the data provided by Coudrain-Ribstein et al. (1998) (who proposed analogous reactions in relation to the natural CO_2 content in groundwater). This does not occur in the A Toxa waters and in carbogaseous waters.

The carbogaseous waters represented in Fig. 14 demonstrate that CO_2 fugacities are higher than those described by the reaction of carbonate fixation. Many authors have suggested a deep origin (in the mantel) for the CO_2 of some of the next thermal sources (Marques et al. 2000, 2001, 2003). The presence of CO_2 in the upper mantle has been inferred from decarbonation reactions of $MgCO_3$ and $CaCO_3$. The CO_2 fugacities for the decarbonation reactions indicate that CO2 is more compressible at high pressures than previously predicted (Haselton et al. 1978). A Toxa waters are significantly different from the rest of the waters in this study. In Tables 4, 5, 6 and 7 the main chemical compositions of Galician waters are shown.

Spas/springs	Dry residue	Anions					Cations						Gas phase		Silica
Strong mineralization water (>1000 mg/L)		HCO_3	SO_4	Cl	F	HS	Na	Ca	K	Li	Fe_{total}	Mg	CO_2	H_2S	SiO_2
Sodium bicarbonate waters															
Agua de Fonte Nova-Main spring	1952	1610	11	29	18	1.80	552	8	48.0		0.89	7	631		62
Agua Cabreiroa with Gas 2	1565	1490	10	28	5.22	1.80	485	17	54.0		1.39	15	705		63
Mondariz (Gándara)	1140	980	12	92	2	0.20	266	59	30.0	1.4	0.02	40	988		53
Sousas–Spring 1	1254	1180	8	25	9.35	1.80	408	13	30.0		0.90	8	7.9		64
Sodium chlorinated waters															
A Toxa	36,760	268	728	17,900	3	11	10,200	1180	1200	31	4.20	126	165	0.02	85
Arteixo	2473	106	29	1010	8	4	590	43	30.0	3	0.02	2	1.1	0.00	64
Baños de Loureda	2100	129	23	1120	4.4		724	60	26.0		0.0003	3			58.4

Table 4. Chemical compositions of the mineral-medicinal waters of high mineralization (mg/L)

pas/springs	Dry residue	Anions					Cations						Gas phase		Silica
Medium mineralization (500–1000 mg/L)		HCO_3	SO_4	Cl	F	HS	Na	Ca	K	Li	Fe_{total}	Mg	CO_2	H_2S	SiO_2
Sodium bicarbonate waters															
Baños de Molgas	706	636	7	22	14	2.2	250	10	11		0.096	1	40.7	9.10	66
Laias	539	400	28	35	16	11	172	5	7	0.7	0.02	1	1.1	0.40	72
Fonte de Bañiño	697	684	29	22	11	2.0	276	12	8		0.18	3	1.1		58
Burgo de Arriba	617	516	3	23	12.55		207	5	10		0.039	1	19.8		85.6
Sodium chlorinated waters															
Caldelas de Tui	713	98	37	281	14	26	226	11	10	0.5	0.02	1	1.1	0.00	99
Acuña	728	152	19	269	21	3	243	5	7	0.7	0.02	1	1.1	0.10	53
Dávila	720	164	17	268	17	5	247	4	7	0.7	0.02	1	1.1	0.02	58
Xardin das Burgas	617	9	2.882	24.11	10.26		203.69	12.02	8.68	1.29	0.14	0.71			16.2

Table 5. Chemical compositions of the mineral-medicinal waters of medium mineralization (mg/L)

Spas/springs Weak Mineralization (250–500 mg/L)	Dry residue	Anions					Cations						Gas phase		Silica
		HCO_3	SO_4	Cl	F	HS	Na	Ca	K	Li	Fe_{total}	Mg	CO_2	H_2S	SiO_2
Sodium bicarbonate waters															
Cortegada	351.6	220	10	47	34.4	7.63	120	1	3	2.10	0.036	1	1.1		66
Baños de Brea	412	207	31	64	23	28	112	5	7	1.90	0.036	3	4.4	12	106
Lugo	421	186	78	47	18	17	135	5	6	0.60	0.020	1	1.1	3.20	75
Arnoia	273	124	35	45	24	28	3.958	0.25	0.054	0.54	0.020	0.082	0	0.10	65
Augas Santas-Pantón	461.4	188	80	39	28.8	20.73	129	7	5	3	0.0001	3	1.1		41.9
Baños Viejos de Carballo	450	117	75	57	25	36	144	1	4	1.60	0.020	1	1.1	0	67
O Tremo	251	138	36	36	11	16	96	2	1		0.027	1	1.1	3.16	29
Guitiriz	262	74	15.3	29.3	14.5	66	83	2.3	0.83	0.62	0.330	0.094			20
Termas da Chavasqueira	403	322	9	19	17.1	2.59	138	2	5		0.030	1	1.1		72.6
Sodium chlorinated waters															
Termas de Cuntis	310.4	91	45	38	20.3	8.45	93	5	2	1	0.020	4	1.1	0	91.4

Table 6. Chemical compositions of the mineral-medicinal waters of weak mineralization (mg/L)

Spas/springs Very weak mineralization (100–250 mg/L)	Dry residue	Anions					Cations						Gas phase		Silica
		HCO_3	SO_4	Cl	F	HS	Na	Ca	K	Li	Fe_{total}	Mg	CO_2	H_2S	SiO_2
Sodium bicarbonate waters															
Ponte Caldelas	247.8	181	12	25	15.6	–	91.9	1	1.49	–	0.040	1	–	–	42.6
Lobios	247	139	17	27	11.5	–	86.45	1	4.3	–	0.048	1	–	–	118.8
Baños de Berán	240	74	14	16	9.8	2.3	49.3	6.7	1.3	0.9	0.02	0.46	–	0.5	43
O Carballiño	198	59	24	32	10	20	56	1	1	–	–	1	–	–	56
Castro Caldelas	186.9	118.3	16.8	3.5	0.2	–	35.1	3.1	0.1	0.08	0.002	1.7	–	5.7	1.6
Partovia	140.2	67	34	3	3.5	–	44	2	–	–		1	1.1	–	37.5
Río Pambre	222	96	24	20	17.1	–	67	1	0.97		0.092	1	–	–	30.6

Table 7. Chemical compositions of the mineral-medicinal waters of very weak mineralization (mg/L)

Therapeutic indications

From the standpoint of medical hydrology, the effects of the mineral-medicinal waters according to their predominant composition are shown in Table 8 (Maraver 2002). Likewise, the distribution of the therapeutic indications of various mineral-medicinal waters is collected in Table 9, taking into account the spatial distribution of the mineral-medicinal waters

.

Mineral water actions due to mineral compositions

Chlorinated	Stimulate organic and metabolic functions Enhance cell tropism; scarring processes and tissue repair Improve blood and lymphatic circulation
Sulphated	Purgatives Choleretic Cholagogues and stimulants of intestinal peristalsis
Bicarbonated	Antacids Increase pancreatic activity To favour the saponifier power of fat by bile Hepatoprotective Favour glycogenesis Favour the mobilization and elimination of uric acid in urine
Carbogaseous	Orally: (more than 1000 mg/L) Aid digestion and mask flavours Stimulate secretions and gastric motility Facilitate intestinal function Topically (more than 400 mg/L) Peripheral vasodilatation Decrease the thermal threshold
Sulphur	Activate metabolic oxide-reducing processes Anti-toxic effects, antiallergics and trophism improvers Regulatory actions of respiratory secretions Immunological effects on the skin
Ferruginous	Activate haematopoiese and cell oxidative functions Improve tissue trophism
Radioactive	Sedative and analgesic Antispasmodic and decontracting Regulators of the vegetative nervous system
With mineralization lower than 500 mg/L	Diuretic Washing and dragging of all kinds of stone

Table 8. Therapeutic actions associated with medicinal mineral waters

Therapeutic indications of the main Galician waters	
A Toxa	Rheumatology
Arteixo	
Baños de Molgas	
Xardín das Burgas	
Laias	
Baños Viejos de Carballo	
Lugo	
Cortegada	
Arnoia	
Lobios	
Baños de Loureda	
Termas de Cuntis	
Caldas de Partovia	
Dávila	Respiratory
Acuña	
Caldelas de Tui	
O Carballiño	Hepatobiliary
Guitiriz	
Pardiñas	
Agua de Fonte Nova–main spring	Gastroenterology
Agua cabreiroá with Gas 2	
Mondariz (Gándara)	
Sousas–Sprinq 1	
O Incio	
Aguas Santas-Pantón	Dermatology
Baños de Brea	
Ponte Caldelas	
Charca do Allegal	
O Tremo	
Río Pambre	
Baños de Berán	

Table 9. Therapeutic indications of Galician waters

Conclusions

This paper presents a study of the chemical characteristics of the mineral and thermal waters of Galicia. The chemical qualities of the different springs are related to the geological mineralizations of the medium, the ascending flow velocity, the depth of the thermal focus, the water paths and the proximity to the coast. Thus, in general, the springs closest to the coastal zones are characterized by being sodium chlorinated, while the inland ones are sodium/potassium bicarbonated.

The more mineralized waters are those that come from greater depths with longer paths. These waters can have high temperatures when upwelling. These waters circulate slowly and follow a regional flow path. In addition, there are some ferruginous springs coming from areas with reduced sulphur waters, where sulphur has not oxidized to sulphate.

Acknowledgements

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