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Hydrogeological features of the Italian sources included within the European thermal-mineral water inventory developed after the H2020 GeoERA Hover project

Caratteristiche idrogeologiche delle sorgenti italiane riportate nell'inventario delle acque termo-minerali europee derivato dal progetto H2020 GeoERA Hover

Barbara DESSÌ[a], Rossella Maria GAFÀ[a], Lucio MARTARELLI[a], Gennaro Maria MONTI[a], Angelantonio SILVI[a]

[a] Servizio Geologico d'Italia - ISPRA - Via V. Brancati, 48 - 00154 - Roma, Italia -

email: *lucio.martarelli@isprambiente.it; barbara.dessi@isprambiente.it; rossella.gafa@isprambiente.it; gennaro.monti@isprambiente.it; angelo.silvi@isprambiente.it*

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Correspondence to:
Lucio Martarelli
lucio.martarelli@isprambiente.it

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Riassunto

L'Italia è uno dei Paesi più ricchi a livello mondiale rispetto a numerosità e tipologia di acque termo-minerali ed utilizza diffusamente ed ampiamente tale risorsa (e.g. balneazione, riscaldamento di edifici, produzione di energia elettrica). Con questa premessa, il Servizio Geologico d'Italia (GSI) ha partecipato ad un work package del Progetto H2020 GeoERA Hover (programma EU Horizon 2020, grant agreement N.731166) finalizzato alla ricostruzione dei processi idrogeologici responsabili della variabilità qualitativa naturale e della contaminazione antropogenica delle acque sotterranee ed alla costituzione di un geodatabase delle acque sotterranee termo-minerali nell'ambito di una Piattaforma Informativa a livello europeo. Le attività del GSI hanno avuto, inoltre, l'obiettivo di contribuire a definire un aggiornato quadro idrogeologico a scala nazionale delle sorgenti termo-minerali.

Il presente lavoro riporta i primi risultati derivati dal Progetto Hover sulla definizione di uno scenario geologico-idrogeologico generale delle emergenze termo-minerali a scala nazionale (240 sorgenti con temperature all'emergenza >20°C sono state incluse in un database). La maggior parte delle acque termo-minerali studiate sono allineate lungo il margine tirrenico-appenninico e nelle isole, dove sono distribuiti importanti campi geotermici attivi o quiescenti connessi a processi di risalita di magmi. Riguardo alle caratteristiche fisico-chimiche, situazioni estreme di sovra-mineralizzazione ed elevate temperature sono anche state rilevate e corrispondono a siti di importanti SPA e campi geotermici. Alcune considerazioni preliminari di carattere geochimico sono in accordo con una mutua interazione tra fluidi idrotermali ricchi in SO_4-Cl-Na-K, verosimilmente originati da magmi (ultra)potassici/calcalcalini/alcalini, e acque di composizione HCO_3/CO_3-Ca, derivate a loro volta dalla interazione tra rocce calcarea e acque sotterranee. Una preliminare analisi statistica su base regionale delle caratteristiche, tra cui quelle geochimiche, delle acque termo-minerali italiane ha portato a definire che esse non mostrano proprietà pienamente omogenee.

Abstract

Italy is one of the richest countries in the world with regards to number and quality of thermal-mineral waters and has developed a widespread and extensive use of such resource (e.g. bathing, central heating, electric power production). Premised that, the Geological Survey of Italy (GSI) took part in a work package of the GeoERA Hover project (EU Horizon 2020 program under grant agreement N.731166) aimed at defining the interactions involving the geological asset and the hydrogeological processes with natural quality and contamination risk of groundwater and at building a geodatabase of thermal-mineral groundwater within an Information Platform at European level. The GSI activities also aimed at contributing to fill the lack of a comprehensive work dealing with a national scale hydrogeological picture of thermal-mineral waters in Italy.

This paper shows the first results obtained with Hover Project on the definition of a general geological-hydrogeological scenario of thermal-mineral occurrences at an Italian national scale (240 occurrences with cropping temperature >20°C have been included in a database). Most of exploited thermal-mineral water resources are aligned along the Tyrrhenian-Apenninic margin and in the Italian islands, where the most relevant active or quiescent geothermal fields related to magma ascent processes occur. As concerns physical-chemical features, extreme situations of over-mineralized and very-high temperature waters are not uncommon throughout Italy and correspond to a cluster of important SPA and geothermal field sites. Some preliminary geochemical considerations agree with mutual interaction between hydrothermal fluids rich in SO_4-Cl-Na-K, likely originated from (ultra)potassic/calcalkaline/alkaline magmas, and HCO_3/CO_3-Ca waters, originated from leaching of calcareous rocks by groundwater. A preliminary statistical analysis on geochemical and other features of the Italian thermal-mineral sources on a regional basis envisaged that they do not display fully homogeneous characteristics.

Introduction

ISPRA - Geological Survey of Italy (GSI) was involved (July 2018-June 2021), together with other 33 national and regional/federal European Geological Surveys Organizations, in the Hover Project (Hydrogeological processes and geological settings over Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystems) in the framework of the H2020 GeoERA Programme (2018-2021; funded from the European Union's Horizon 2020 research and innovation program under grant agreement N.731166).

Within this framework, the GSI took part in the GeoERA Hover project Work Package 3 dealing with "Hydrogeochemistry and health: Mapping groundwater characteristics for the management of aquifers naturally enriched in dissolved elements", aimed at defining the interactions involving the geological asset and the hydrogeological processes with natural quality and contamination risk of groundwater (Guerrieri et al., 2020). The final data and information products have been organized in an Information Platform developed for the GeoERA Programme.

Over the years, Italy has developed a widespread and extensive use of groundwater at different temperatures, ranging from bathing to central heating and electric power production plants. Italy is one of the richest countries in the world with regards to thermal-mineral springs, distributed throughout its territory. Furthermore, when water yield and temperature are very high, they may be used for central heating and electric power production, as in the worldwide known site of Larderello, Tuscany. Italy has an ancient thermal bath tradition dating back to Roman's time and well-known all over the world also for the attractive natural landscapes which springs are located in. In the last decades the SPA (Salus Per Aquam) tourism has grown all over the world, also due to the increasing necessity of relaxing, deriving from stress of modern life, thus increasing the interest on thermal-mineral waters (e.g. Porowski, 2019; Valeriani et al., 2018; Szocs et al., 2017; Elster et al., 2016; Retike et al., 2016; Rman, 2016; Dessì et al., 2015; Marrero-Diaz et al., 2015; Balderer, 2014; Rajapaksha et al., 2014; Petrović et al., 2010; Li Castri, 2009; Albu et al., 1997; Cataldi et al., 1995; Boni et al., 1982).

National definitions of thermal water are mentioned in the Italian Governmental Law N.323 of 24/10/2000 (Repubblica Italiana, 2000), but this act mainly deals with exploitation permits and medical aspects and not with technical-scientific and hydrogeological issues. Moreover, thermal-mineral water is not defined within any specific Act. At present, the administrative management of thermal-mineral waters in Italy is in charge of the Regions. Besides, though some thermal-mineral water information is managed at a local or regional scale (e.g. Mantelli et al., 2014; Baiocchi et al., 2012; De Nardo et al., 2010; Della Vedova et al., 2001) and some studies on various aspects of this topic have been conducted at Italian interregional scale (e.g. Minissale, 2004; Vuataz, 1997) or at national scale (e.g. Minissale, 1991; Boni et al., 1982), a comprehensive work dealing with a national scale hydrogeological picture of thermal-mineral water in Italy is at present still lacking.

The GSI activities within the Hover Project also aim at contributing to fill this gap by the organization of a representative database of the main Italian thermal-mineral occurrences, based on literature data on about 240 sources (Minissale et al., 2016; Cinti et al., 2014; Di Napoli et al., 2009; Grassa et al., 2006; Angelone et al., 2005; Minissale, 2004; Federico et al., 2002; Boni et al., 1982).

This work shows the first results of the discussion, also based on literature data on water temperature, total dissolved solids, pH, yields and some chemical data, of the whole collected information aimed, at this stage, at the definition of a general geological-hydrogeological scenario of thermal-mineral occurrences at an Italian national scale. These first results will be submitted to an in deep next investigation stage to allow a reconstruction in a comprehensive geological scenario of features of the Italian thermal-mineral sources.

Research area and geological framework

It is here pointed out again that the aim of this study is the collection of information on the main thermal-mineral waters throughout the Italian territory.

The geological history of Italy can be traced from the Early-Paleozoic Hercynian orogen, throughout the Mesozoic opening of Tethys oceans, to their later closure during the Alpine and Apennine subductions. The latter was caused by the collision between the African and the Eurasian plates, in a continental margin characterized by very active crustal dynamics. The forelands of these orogens are represented by the Apulia region, part of the Iblean Plateau (SE-Sicily), a few areas in the Po and Venetian plains, and the Sardinia Island. These foreland sectors, in any case, underwent subsidence or uplift movements because of the migration of the Alpine or Apennine fronts. Moreover, the Apennine foredeep runs on the external side of the Apennine chain from Southern Apennines to the Po Plain, where it meets the older Southalpine foredeep. At the west side of the Apennines, the presence of the Tyrrhenian Sea back-arc basin, starting from Miocene, is evident. Furthermore, Sardinia represents a micro continent drifted away from Central Europe during a rift phase started in Oligocene (e.g. Scrocca et al., 2003; Carmignani, 2001; Vai and Martini, 2001; Mariotti and Doglioni, 2000; Dal Piaz, 1997; Bigi et al., 1992).

Due to the youngness of Italian territory, recent and active morphological, seismic-tectonic, and volcanic processes may be directly observed, like eruptions of Etna (Sicily), the highest European active volcano (e.g. Serri et al., 2001; Wilson and Bianchini, 1999; Cataldi et al., 1995).

The Italian main morphological lineaments are the Alps (to the North; crystalline, ophiolitic, metavolcanic, calcareous-dolomitic, and turbiditic-flysch sequences), the Apennines (along the peninsula and Sicily; mainly calcareous-marly-arenaceous-siliceous sequences, but also volcanic and crystalline rocks are represented), the wide Po-

Veneto-Friuli Plain and the minor and fragmented coastal plains (e.g. Compagnoni et al., 2011; Scrocca et al., 2003) (Fig. 1). The Apennines are geologically younger than the Alps and tectonically very active. Furthermore, beneath central-southern Italy, along the Apennine ridge, geothermal fields occur, probably originated from hot fluids deriving from mantle through the oceanic crust of the Tyrrhenian Sea basin, interfering with meteoric water infiltrated and circulating at deep levels (e.g. Minissale, 2004; Minissale, 1991).

Geological structures like both large and small alluvial, intermountain, and coastal plains host groundwater resources in porous sediments. The carbonate fissured and often karst structures in Alps, Apennine and Sicily have potentially high hydraulic heads and yield large amount of groundwater from springs. Furthermore, quite large amounts of groundwater are hosted by volcanic sequences composed of alternating alluvial, lavic and pyroclastic deposits. Instead, the crystalline complexes of Alps, Calabria and Sardinia display scarce groundwater resources and groundwater of local interest is in the large areas with terrigenous and flysch deposits, like in Northern Apennine, Adriatic side of the Central-southern Apennine and in Central Sicily (e.g. Celico et al., 2005; Civita et al., 2004; Regione Lombardia and ENI-AGIP, 2002; Giuliano et al., 1998; Regione Emilia Romagna and ENI-AGIP, 1998; Boni et al., 1986; Boni et al., 1982; Pietracaprina et al., 1980).

The great variety of geological, morphological, and climatic environments characterizing the Italian territory transmits to groundwater unique and special properties.

The presence of active volcanoes witnesses uplift processes of hot vapor and gas from deep subsurface levels along tectonic elements cutting terrain in a network of discontinuity. Vapor and gas phases of hydrothermal origin interact with both host rocks and groundwater and lead to cropping out of thermal-mineral sources and geothermal fields. The circulation path of thermal-mineral waters may have origin from meteoric waters hosted in carbonate rocks featured by deep circulation. It may also happen under convective karst aquifer systems and flowing out in topographically low areas, like at the boundary of Neogene basins, where may occur mixing with cold mineralized waters. In this scenario, water temperatures may depend on local variations in heat flow and geothermal gradients, mixing phenomena between thermal aquifers and fresh waters from shallow aquifers or different depths of heat sources (e.g. Dessì et al., 2015; Minissale, 2004; Cataldi et al., 1995; Minissale, 1991; Boni et al., 1982).

Groundwater may have different compositions depending on the host rocks of the hydrogeological basin: oligomineral, arsenical/ferruginous, sulphate, sulfide, bicarbonate, carbonic, radioactive, sodium-chloride-bromine-iodine, etc. (e.g. Cantonati et al., 2016, Boschetti et al., 2013, Dewandel et al., 2005, 2006). The presence of substances such as sulphur, iodine, chlorine, bromide, arsenic, lithium, calcium, gas, and radioactive elements may give water therapeutic virtues. These waters, which may also contain colloidal silica, aluminum, lithium, and gas, are often used at different temperatures for therapeutic purposes (crenotherapy, an ancient practice still today used in the modern medical science) which consist in drinking (hydropinotherapy), breathing, bathing and/or mud-bathing with these waters. Thermal treatments have anti-inflammatory, analgesic and relaxing effects and stimulate the metabolic processes (e.g. Valeriani et al., 2018; Matsumoto, 2018; Morer et al., 2017; Fazlzadeh et al., 2016; Li Castri, 2009).

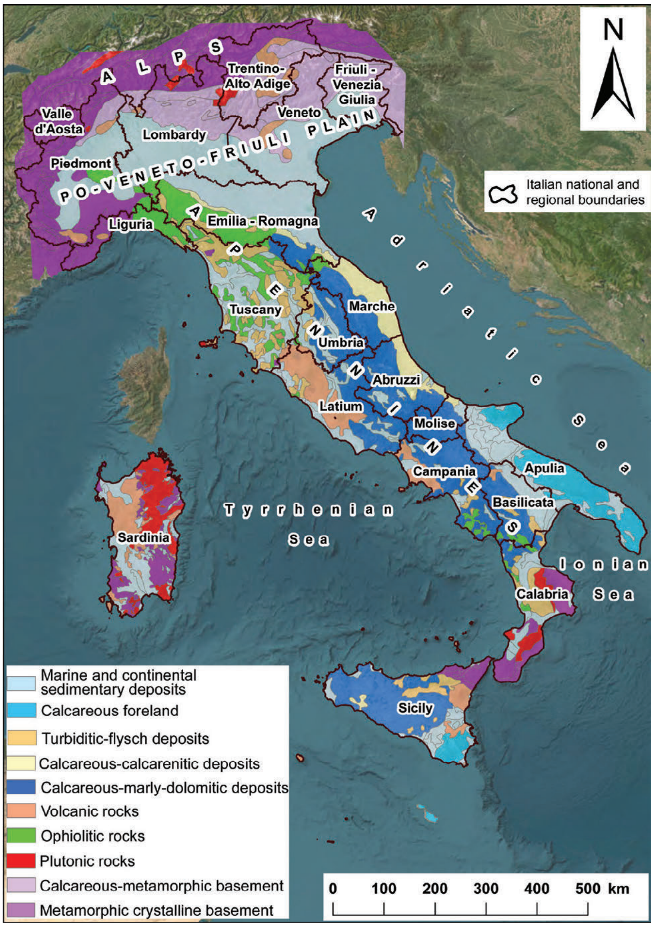

Fig. 1 - Geographical and geological framework of the Italian territory. Italian Region names are also indicated for reference.

Fig. 1 - Schema geografico e geologico del territorio italiano. Sono indicati per riferimento anche i nomi delle Regioni Italiane.

Data and methods

The main Italian thermal-mineral waters with temperature >20°C at the cropping area have been included in a database counting about 240 sources (springs or wells) or groups of sources. The mineralized sources with temperature <20°C were not considered in the present inventory, since they cannot be properly classified as thermal waters (e.g. Porowski, 2019).

This representative database, implemented within the above mentioned WP3 Hover Project, is not exhaustive of all Italian thermal-mineral occurrences and of all their available features. In any case, some characterizing information, like coordinates, usage, yield, hydrogeological settings, aquifer typology, associated lithology, temperature, and main geochemical parameters, is reported for the most important

Italian thermal-mineral occurrences. Furthermore, the number of springs and wells of thermal-mineral waters in Italy is indeed higher than that reported in this manuscript, but here only the main occurrences which were considered valuable to define a general geological-hydrogeological scenario of thermal-mineral occurrences at an Italian national scale were reported.

Out of the about 240 sources, about 200 are from the national scale inventory by Boni et al. (1982) and 40 have been integrated from some regional inventories (e.g. Minissale et al., 2016; Cinti et al., 2014; Di Napoli et al., 2009; Grassa et al., 2006; Angelone et al., 2005; Minissale, 2004; Federico et al., 2002).

In addition, the acquisition of new field data on thermal-mineral sources was not in the purpose of this paper, which only deals with an overview, based on literature data, about both their distribution and featuring in term of lithology of the hosting aquifers, water temperature, total dissolved solids, pH and yields. Then, for a description of methods used to collect the physical-chemical data, please refer to the cited reference literature.

The features regarding the spatial distribution at a regional scale and the geological and hydrogeological background of the collected sources were discussed by analytical calculations and opportunely represented by plotting the corresponding data on appropriate typologies of diagrams.

Available chemical data of the sources were discussed for a hydrochemical classification according to Piper (1944) approach and their hydrochemical characterization and regional distribution was investigated by standard methods of analytical calculations.

A preliminary statistical analysis of geochemical/geological features of the sources was also performed, on a regional basis, by Correspondence Analysis (CA; e.g. Beh and Lombardo, 2014) and Multi-Dimensional Scaling (MDS; e.g. Borg et al., 2018). The statistical hierarchical clustering analyses (e.g. Hastie et al., 2001) of some parameters (e.g. lithological typology, ionic formula, temperature) and some chemical compounds (e.g. SO_4 and TDS) was as well performed.

Results and discussion

In a scenario considering the main Italian thermal-mineral sources having at the outlet water temperature higher than 20°C, it is possible to evidence that they are drawn by 72% from springs and 28% from wells. The total number of this typology of sources within the inventory at a regional scale is as follows: Piedmont = 5; Valle d'Aosta = 1; Liguria = 1; Lombardy = 4; Trentino-Alto Adige = 2; Veneto = 9; Friuli-Venezia Giulia = 2; Emilia-Romagna = 3; Tuscany = 47; Umbria = 4; Marche = 3; Latium = 50; Campania = 20; Apulia = 4; Basilicata = 4 Calabria = 10; Sicily = 35; Sardinia = 37 (please, note that Abruzzi and Molise have not thermal sources). It is evident that the distribution of these sources throughout the Italian territory is not homogeneous, since six regions out of twenty cover in total 83% of exploited thermal-mineral water resource (Tuscany, 25% of total sources; Latium, 16%; Campania, 13%; Sicily, 12%; Sardinia, 9%; Veneto, 8%; Boni et al., 1982). In these regions, mostly aligned along the Tyrrhenian-Apenninic margin and in the Italian islands, the most relevant active or quiescent magmatic bodies occur, as evidenced by the cropping out of recent volcanic rocks (Fig. 2). This is likely due to the previously evidenced geologically young and tectonically active features of the Apennine ridge, which is characterized by hot fluids ascent from mantle through thinned oceanic crust along the Tyrrhenian side (e.g. Minissale, 2004; Minissale, 1991; Calcagnile and Panza, 1979; Boccaletti and Manetti, 1978).

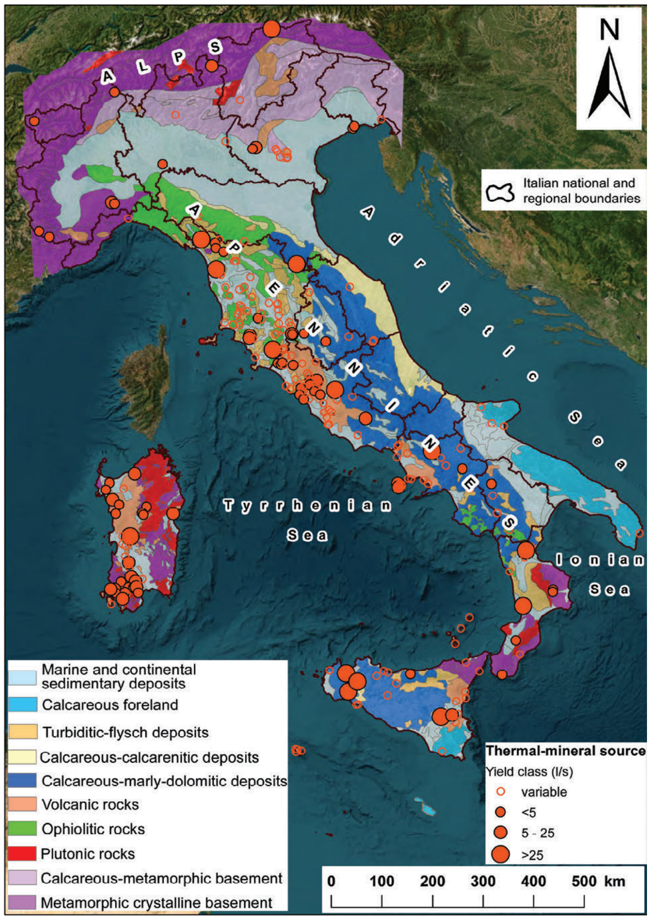

Fig. 2 - Map of the Italian thermal-mineral sources included in the database of the WP3 Hover Project within the Italian geological framework. For further reference toponyms, please, see Figure 1.

Fig. 2 - Mappa delle sorgenti termo-minerali italiane presenti nel database del WP3 del Progetto Hover nello scenario geologico nazionale. Ulteriori toponimi di riferimento sono nella Figura 1.

The main geological background of the sources has been characterized (Tab. 1). As expected, most of thermal-mineral occurrences are directly associated with igneous rocks (about 56% of total occurrences) and especially with volcanic rocks (pyroclastic deposits, about 22%; basaltic lithotypes, about 15%), but also sedimentary (about 26%) and metamorphic rocks (about 17%) are well represented. The latter rock typologies likely correspond to lithotypes where thermal-mineral fluids have ascended through, after groundwater infiltration processes at different depth levels, and which they

Tab. 1 - Main lithological background of the Italian thermal-mineral sources included in the database of the WP3 Hover Project.

Tab. 1 - Principali caratteristiche litologiche delle aree di affioramento delle sorgenti termo-minerali italiane presenti nel database del WP3 del Progetto Hover.

Lithology of the aquifer	N. of occurrences	% of occurrences
IGNEOUS ROCKS		
acidic igneous material	12	5.0
intermediate composition igneous material	16	6.6
basic igneous material	35	14.5
ultramafic igneous rock	2	0.8
granitoid	16	6.6
syenitic rock	2	0.8
pyroclastic material	52	21.6
pyroclastic rock	1	0.4
Total	**136**	**56.4**
SEDIMENTARY ROCKS		
clastic sedimentary rock	22	9.1
carbonate rich mudstone	2	0.8
limestone	19	7.9
travertine	15	6.2
dolostone	3	1.2
peat	2	0.8
Total	**63**	**26.1**
METAMORPHIC ROCKS		
metamorphic rock	7	2.9
gneiss	6	2.5
phyllite	25	10.4
serpentinite	3	1.2
marble	1	0.4
Total	**42**	**17.4**

have interacted with along the hydrothermal fluid circuits. The definition of the source rocks of thermal waters cropping out within these latter rocks is in progress.

As concerns the hydrogeological settings of the terrains which those sources emerge in Table 1, the hydrogeological complexes having a high infiltration rank (e.g. carbonate rocks, calcareous-dolomitic successions) may act as groundwater recharge areas and/or fissured medium for hydrothermal ascending fluids in favourable structural settings. The low permeability complexes (e.g., clayey-marly terrains, terrigenous successions) may serve as a cover for buried geothermal reservoirs. Furthermore, the metamorphic and plutonic rock complexes represent the crystalline basement from which hydrothermal fluids may potentially originate. Finally, the volcanic complexes, mostly aligned along the Tyrrhenian margin, host the most of thermal-mineral sources originated by hydrothermal fluids related to magma ascent processes.

Taking into consideration temperature, TDS and pH values of the main Italian thermal-mineral sources and their distribution among Italian Regions, the following features may be highlighted.

Water temperature of about 70% of thermal-mineral sources have values between 20-40°C, about 20% exhibit 40-60°C and about 10% of total occurrences display >60°C. More in detail (Fig. 3), the thermal-mineral sources with very high temperature (>60°C) have then a minor representativeness. This typology of sources is very distinctive of some Campania sources, likely due to their occurrence in association with igneous/pyroclastic rocks emitted by active volcanic bodies and consequently with local variations in heat flow and geothermal gradients. Very high temperature sources are also present in Piedmont, Lombardy, Veneto, Latium, Sicily, and Sardinia, but with a very subordinate frequency. Piedmont and Lombardy occurrences are associated to calcareous rocks and likely related to local positive anomalies in geothermal gradients and to interaction between the related geothermal field and meteoric waters infiltrated through carbonate successions to deep levels, giving rise to thermal aquifers. For Latium, Sicily and Veneto, thermal waters are associated to igneous/pyroclastic rocks and then the situation is like that of Campania ones, though for Veneto the volcanic bodies are quiescent. Regarding Sardinia, it may be suggested local anomalies in heat flow induced by granitoid basement rocks causing thermal water flows involved in mixing phenomena with meteoric waters infiltrated to different depths.

Concerning total dissolved solids (TDS), about 25% of sources have TDS values <1000 ppm, about 40% are between 1000-3000 ppm, about 20% between 3000-5000 ppm and the remaining 15% display >5000 ppm. TDS values may mainly depend on factors affecting the interactions among geothermal water, groundwater and host rocks occurring within the hydrogeological basin (e.g. rock typology, water composition, presence of gaseous phases, temperature, length of hydraulic pathways). The Italian thermal-mineral emergences with TDS <3000 ppm, representing minimally to very-highly mineralized waters, constitute the 65% of total sources and

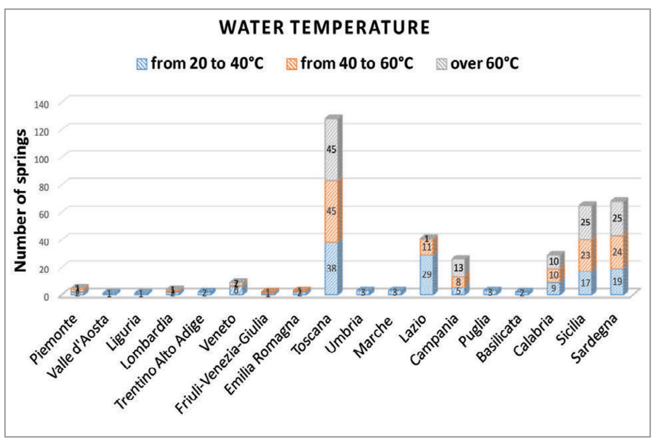

Fig. 3 - Diagram of temperature value ranges of the main Italian thermal-mineral sources and their distribution among Italian Regions.

Fig. 3 - Diagrammi degli intervalli dei valori di temperatura delle principali sorgenti termo-minerali italiane e loro distribuzione su base regionale.

are well distributed among the Italian regions (Fig. 4). Sources having TDS >3000 ppm (over-mineralized waters) are about 35% of total and are represented in Tuscany (where they are associated to metamorphic, travertine, calcareous, clastic and ultramafic rocks), Latium (associated to pyroclastic, igneous, travertine and metamorphic rocks), Campania (igneous and pyroclastic rocks), Calabria (metamorphic and granitoid rocks), Sicily (igneous, metamorphic, granitoid, calcareous and clastic rocks) and Sardinia (igneous, granitoid and metamorphic rocks). These sources within the cited regions are mostly related to metamorphic/igneous/hydrothermal fluids, likely due to the effects on host rocks of geothermal water flow associated with quiescent or active volcanic bodies. In Apulia the over-mineralized waters are associated to calcareous rocks and are likely related to deep geothermal fluid circuits which reacted with calcareous host rocks (e.g. Minissale, 2004, 1991; Cataldi et al., 1995). These typologies of thermal-mineral waters also occur, but with a lower frequency that may be considered as an anomalous condition, in Veneto and Marche (associated to travertine rocks) and Friuli-Venezia Giulia (calcareous rocks) and Emilia-Romagna (clastic rocks), then related to deep geothermal fluids which reacted with calcareous/sedimentary host rocks.

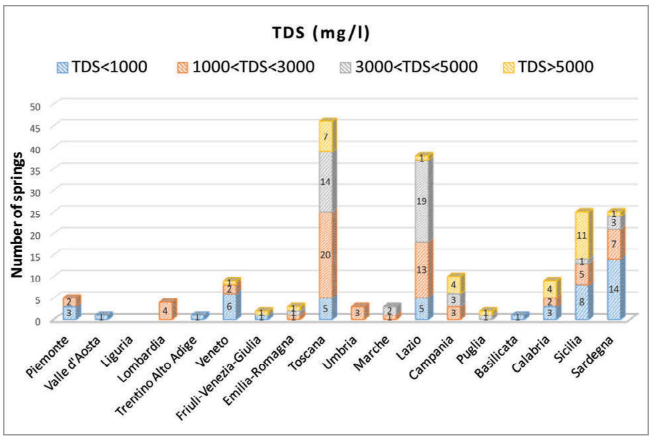

Fig. 4 - Diagram of TDS value ranges of the main Italian thermal-mineral sources and their distribution among Italian Regions.

Fig. 4 - Diagramma degli intervalli dei valori di TDS delle principali sorgenti termo-minerali italiane e loro distribuzione su base regionale.

Sources with pH values from moderately acidic to moderately alkaline (5<pH<9) constitute most of total sources (more than 90%) and are well distributed among the Italian regions (Fig. 5). pH features of groundwater may depend on the chemical features of geothermal fluids (including gaseous phases) which reacted with host rocks within the hydrogeological basins. In any case, thermal-mineral emergences with extreme acidic or basic pH values (<5 or >9, respectively), constitute about the 5% and the 3% of total sources, respectively. Among the Italian regions, extremely acid sources, all associated to igneous/pyroclastic rocks, are mostly distributed in Latium, but also with a lesser extent in Campania and Sicily, likely in agreement with the naturally acidic features of fluids of volcanic origin associated with hydrothermal fluids; while extremely basic sources are very

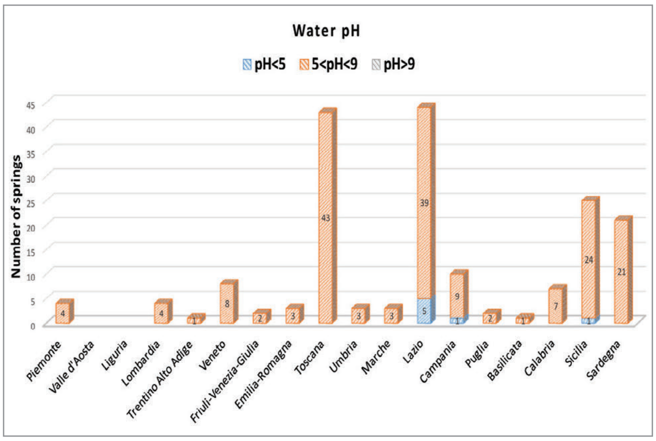

Fig. 5 - Diagram of pH value ranges of the main Italian thermal-mineral sources and their distribution among Italian Regions.

Fig. 5 - Diagramma degli intervalli dei valori di pH delle principali sorgenti termo-minerali italiane e loro distribuzione su base regionale.

few and are represented in Piedmont, Tuscany and Sardinia, likely due to depth and length of pathways along hydrothermal circuits reacting with metamorphic, ultramafic and granitoid host rocks, respectively (e.g. Minissale, 2004, 1991; Cataldi et al., 1995; Boni et al., 1982).

Furthermore, also considering source yields (reliable information for many of the sources is not available due to variable discharge values within a small-medium range), about 65% of sources have yields <5 L/s, about 15% exhibit 5-25 L/s and about 20% show yields >25 L/s (Fig. 2).

As a whole, the diagram of Figure 6 displays that extreme situations of over-mineralized (TDS>3000 ppm) and very-high temperature (>60°C) waters have a limited representativeness, even if are not uncommon, throughout the Italian thermal-mineral sources framework, and they correspond to a cluster of important SPA and geothermal field sites connected with active or quiescent volcanic bodies and/or deep seated hydrothermal circuits (e.g. Minissale, 2004, 1991; Cataldi et al., 1995; Boni et al., 1982), all worthy of further detailed research.

Despite a definitive discussion of available chemical data of the considered thermal-mineral occurrence was not still accomplished, some preliminary geochemical considerations

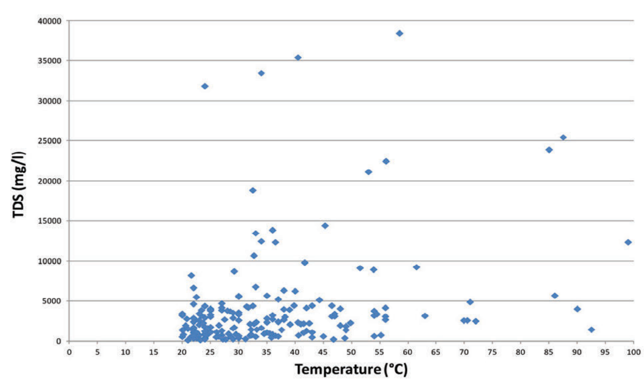

Fig. 6 - Temperature vs. TDS diagram of the main Italian thermal-mineral sources.

Fig. 6 - Diagramma temperatura-TDS delle principali sorgenti termo-minerali italiane.

are here provided. Most part of the waters may be classified, within a Piper diagram (Fig. 7), as HCO_3/CO_3-Ca-Mg to SO_4/Cl-Ca waters (Latium, Tuscany and Sardinia p.p.), HCO_3/CO_3-Na-K to SO_4/Cl-Na-K waters (Campania p.p.), HCO_3/CO_3-Na-K to Cl-Na waters (Campania p.p. and Sicily) and SO_4/Cl-Ca-Mg to Cl-Na waters (Veneto and Sardinia p.p.). This agrees with mutual interaction in different degree between hydrothermal fluids rich in SO_4-Cl-Na-K, having their origin from (ultra)potassic/calcalkaline/alkaline magmas, and HCO_3/CO_3-Ca waters, having origin from leaching of calcareous basement rocks by groundwater, which induced distinctive hydrochemical features to water occurrences within the cited different districts.

Furthermore, in the cation triangle of the Piper diagram (Fig. 7) it is shown that all springs are distributed along a strip aligned from the Na-K vertex to a position next to the Ca vertex along the Ca-Mg side. This is also in agreement with an (ultra)potassic to calcalkaline/alkaline affiliation of magmas and related hydrothermal fluids and calcareous aquifer waters which likely the thermal-mineral waters formed from and interacted with, respectively.

Single springs or minor groups may be allocated in various different areas of the diagram and their affiliation needs a more in deep discussion (e.g. the few Latium and Campania springs allocated in the HCO_3/CO_3-Ca sector are probably due, as already supposed, to mixing with calcareous aquifer waters).

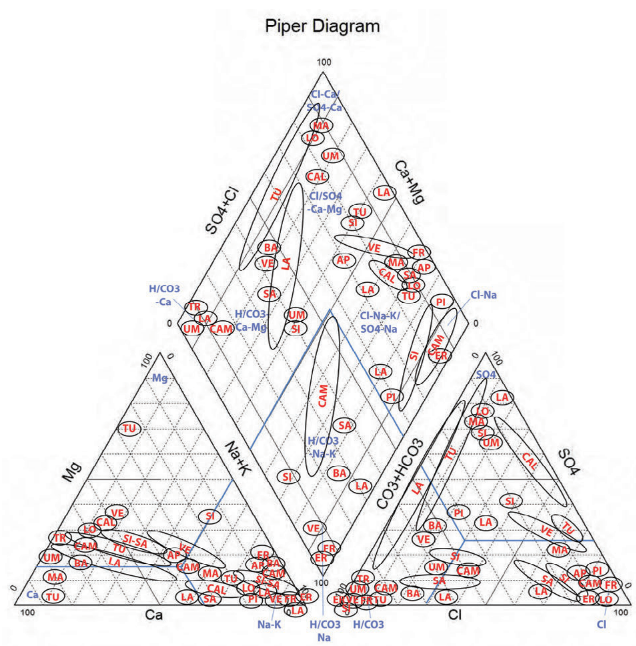

Fig. 7 - Piper diagram on regional base of the Italian thermal-mineral sources included in the database of the WP3 Hover Project. Hydrochemical facies fields are also shown (in blue letters; H/CO_3: HCO_3/CO_3). PI: Piedmont; LI: Liguria; LO: Lombardy; TR: Trentino-Alto Adige; VE: Veneto; FR: Friuli-Venezia Giulia; ER: Emilia-Romagna; TU: Tuscany; UM: Umbria, MA: Marche; LA: Latium; CAM: Campania; AP: Apulia; BA: Basilicata; CAL: Calabria; SI: Sicily; SA: Sardinia.

Fig. 7 - Diagramma di Piper su base regionale delle sorgenti termo-minerali italiane incluse nel database WP3 del Progetto Hover. Sono anche indicati i campi delle facies idrochimiche (in lettere blu; H/CO_3: HCO_3/CO_3). PI: Piemonte; LI: Liguria; LO: Lombardia; TR: Trentino-Alto Adige; VE: Veneto; FR: Friuli-Venezia Giulia; ER: Emilia-Romagna; TU: Toscana; UM: Umbria, MA: Marche; LA: Lazio; CAM: Campania; AP: Puglia; BA: Basilicata; CAL: Calabria; SI: Sicilia; SA: Sardegna.

A preliminary statistical analysis of geochemical/geological features of the Italian thermal-mineral sources included in the database of the WP3 Hover Project, on a regional basis, was also performed. The most interesting results were obtained from data processing by Correspondence Analysis (CA) and a statistical process known as Multi-Dimensional Scaling (MDS; e.g. Borg et al., 2018). These processes led to the drawing of a multi-attribute map which allowed assessing of association, similarity, and interrelation among the examined elements (Fig. 8).

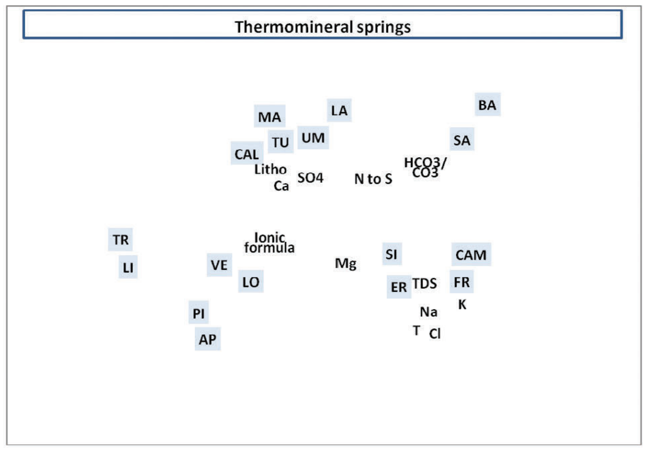

Fig. 8 - Multi-attribute dimensional map of geochemical (Ca, Mg, Na, K, HCO_3/CO_3, SO_4, Cl, TDS contents) and other features (T: water temperature; Litho: lithological typology; ionic formula patterns; N to S: north to south geographical position) of the Italian thermal-mineral sources included in the database of the WP3 Hover Project, on regional basis (regional acronyms as in Figure 7; evidenced in blue).

Fig. 8 - Mappa dimensionale multi-attributi, su base regionale, dei parametri geochimici (contenuti in Ca, Mg, Na, K, HCO_3/CO_3, SO_4, Cl, TDS) e di altra tipologia (T: temperatura dell'acqua; Litho: tipologia litologica; schema della formula ionica; N to S: posizione geografica da nord a sud) delle sorgenti termo-minerali incluse nel database del WP3 del Progetto Hover (acronimi regionali come in Figure 7; evidenziati in blu).

It was stressed that thermal-mineral sources from Friuli-Venezia Giulia, Emilia-Romagna, Campania and Sicily are in good mutual association and have a good similarity and interrelation with water temperature, TDS and Mg, Na, K and Cl contents. Then, these physical-chemical parameters seem to have common features for springs from the former regions.

Furthermore, Piedmont, Lombardy, Trentino-Alto Adige, Veneto, Liguria and Apulia sources seem in some extent to show a degree of mutual association and have similarity and interrelation with ionic formula patterns. Springs from these regions have then a quite similar reference chemical composition.

Thermal-mineral occurrences from Tuscany, Marche, Umbria, Latium, and Calabria have as well some mutual association degrees and have similarity and interrelation with lithological typology and Ca-SO_4 values, probably reflecting that they crop out in similar geological-hydrogeological scenarios.

Besides, Basilicata and Sardinia sources display some reciprocal association degree and similarity and interrelation with HCO_3/CO_3 contents, so probably their waters extensively interacted with calcareous rocks.

Only the north to south geographical position seems to have no association, similarity and interrelation with any other element and source from any regions.

A further discussion arose from the results of a statistical hierarchical clustering analyses of some elements, like lithological typology, ionic formula, temperature and some chemical compounds (e.g. SO_4 and TDS), exhibited by the Italian thermal-mineral sources on regional basis. As an example, the dendrograms of Figure 9 show the hierarchical relationships considering the cited elements evidenced on regional basis and the corresponding allocation to distinctive clusters.

As a whole, it is envisaged that there is not an immediate understanding of the obtained clusters and there is only a partial correspondence among the clustering results from the cited dendrograms and the results obtained from the former statistical method (CA-MDS). This is probably due to the huge and not really homogeneous distribution at the regional scale of the different displayed features. Consequently, it will be likely opportune a more exhaustive geological and geochemical approach at a more detailed scale (e.g. geochemical province, geothermal system, geostructural domain) which may give evidence of geostatistical proximity or distance with respect to the local occurrence of thermal-mineral sources. These aspects will be examined in deep in a next detailed investigation stage.

Conclusions

Geological Survey of Italy of ISPRA (GSI) took part in the H2020 GeoERA Hover Project. The project approach is to link knowledge of geological settings and understanding of hydrogeological processes to natural variability of groundwater quality and to risk of aquifer contamination by anthropogenic dissolved compounds.

Despite some thermal-mineral water information is managed at local or regional scale, a comprehensive updated work dealing with a national scale hydrogeological picture of thermal-mineral water in Italy is at present still lacking. The GSI activities within the Hover Project are also aimed at contributing to fill this gap.

The main Italian thermal-mineral waters with temperature >20°C at the cropping spot have been included in a database counting about 240 sources or groups of sources. This not exhaustive but representative database includes information like coordinates, usage, yield, hydrogeological settings, aquifer typology, lithology, temperature, and main geochemical parameters.

The collected hydrogeological information allowed to define the features of the Italian sources included within the European thermal-mineral water inventory and to date we can propose the preliminary remarks in the followings.

1. The main Italian thermal-mineral sources are drawn by 72% from springs and 28% from wells. The distribution of these sources throughout the Italian territory is not homogeneous, since six regions out of twenty cover in total 83% of exploited thermal-mineral water resource (Tuscany, 25% of total sources; Latium, 16%; Campania, 13%; Sicily, 12%; Sardinia, 9%; Veneto, 8%).
2. Most of thermal-mineral occurrences are directly associated with igneous rocks (about 56% of total occurrences) and, out of them, especially with volcanic rocks (about 37%), but also sedimentary (about 26%) and metamorphic rocks (about 17%) are represented.
3. Considering source yields, about 65% of sources have yields <5 L/s, about 25% exhibit 5-100 L/s and the remaining 10% show yields >100 L/s.
4. The thermal-mineral sources with very high temperature (>60°C) represent around the 10% of total occurrences. This is likely due to their occurrence in association with igneous/pyroclastic rocks emitted by active or quiescent volcanic bodies and their consequently link to local variations in heat flow and geothermal gradients or to local anomalies in heat flow induced by granitoid basement rocks. All these elements favoured forming of thermal water circuits featured by mixing phenomena with meteoric waters infiltrated to different depths.
5. Sources having TDS >3000 ppm (over-mineralized waters) are about 35% of total and are also likely due to association with quiescent or active volcanic bodies and to deep geothermal fluids which reacted with calcareous/sedimentary host rocks.
6. Thermal-mineral emergences with extreme acid or basic pH values (<5 or >9, respectively), constitute about the 5% and the 3% of total sources, respectively. Extremely acid sources are likely in agreement with the volcanic origin of the associated naturally acidic hydrothermal fluids, while extremely basic sources are probably due to deep and long pathways of hydrothermal circuits along host rocks.
7. Extreme situations of over-mineralized (TDS>3000 ppm) and very-high temperature (>60°C) waters are not common throughout the Italian thermal-mineral sources framework, but they correspond to a cluster of important SPA and geothermal field sites, all worthy of further detailed research.
8. Most of waters may be originated by mutual interaction in different degree between hydrothermal fluids rich in SO_4-Cl-Na-K, having their origin from (ultra)potassic/calcalkaline/alkaline magmas, and HCO_3/CO_3-Ca waters, originated from leaching of calcareous basement rocks by groundwater, which induced distinctive hydrochemical features to waters from different districts.
9. It was not possible to achieve an immediate understanding of the preliminary results obtained by some applied statistical methods (Correspondence Analysis, Multi-Dimensional Scaling, Hierarchical Clustering Analyses). The only partial correspondence among the clustering results was likely due to the huge and not homogeneous distribution of the different hydrogeological and geochemical features at the investigated scale. A more exhaustive geological and geochemical approach at a more detailed scale (e.g. geochemical province, geothermal

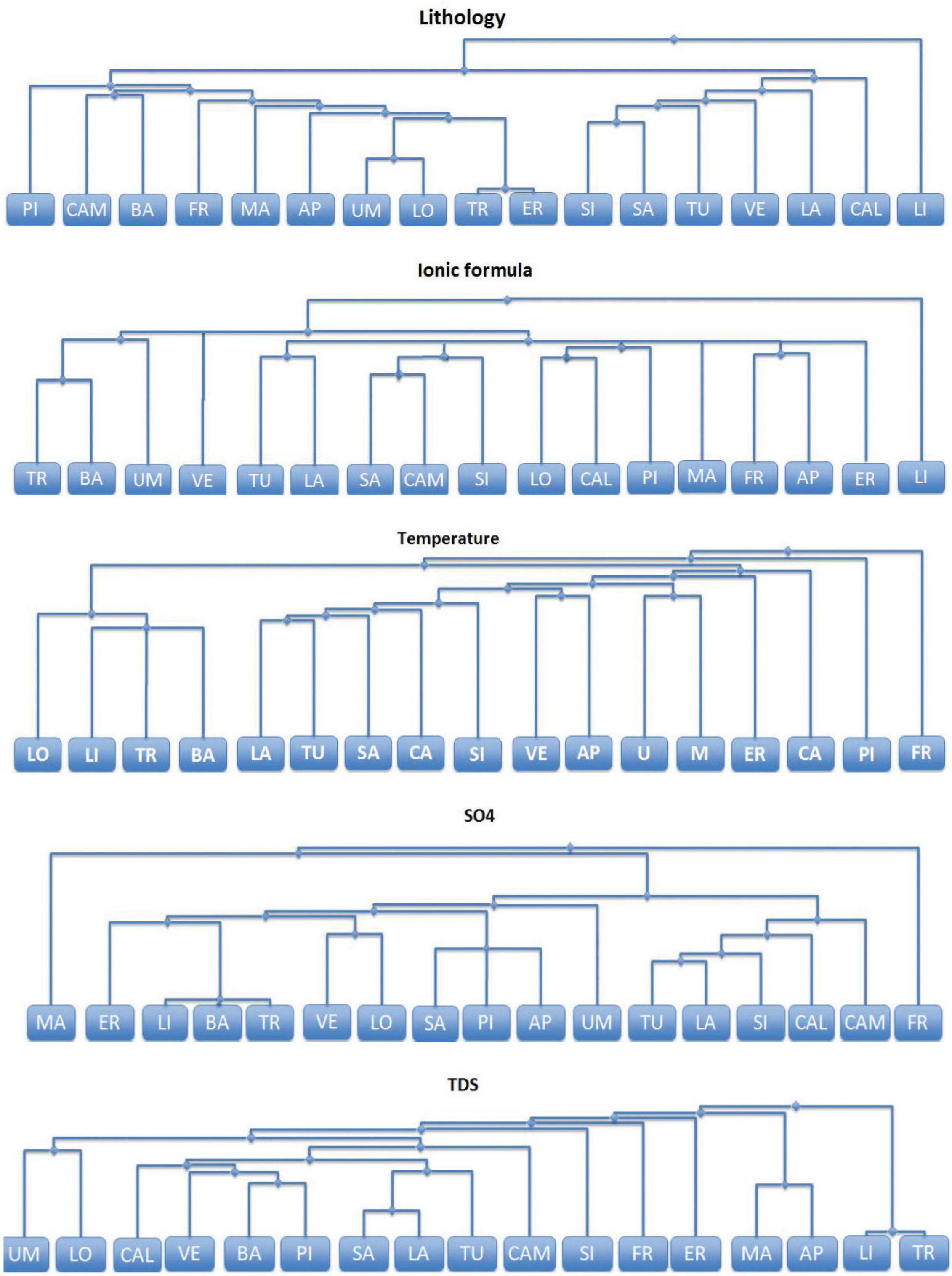

Fig. 9 - Dendrograms showing the results of the hierarchical clustering of some selected features associated to Italian thermal-mineral sources on regional basis (regional acronyms as in Figure 7).

Fig. 9 - Dendrogrammi dei risultati dello *hierarchical clustering* di una selezione delle caratteristiche associate alle sorgenti termo-minerali italiane su base regionale (acronimi regionali come in Figure 7).

system, geostructural domain) is likely envisaged for evidencing the geostatistical proximity or distance with respect to local occurrences of thermal-mineral sources.

Finally, it is opportune to highlight that the cited preliminary results will be submitted to an in deep examination in a next detailed investigation stage to allow a reconstruction in a comprehensive scenario of the Italian thermal-mineral sources.

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Author contributions
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