Systematic Review of Geochemical Data from Thermal Springs, Gas Vents and Fumaroles of Southern Italy for Geothermal Favourability Mapping

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Abstract

In recent years, two research projects specifically conceived by Italian Institutions of Research to promote the implementation of the use of geothermal energy in Southern Italy has allowed the review of most data on chemical and isotopic compositions of natural thermal manifestations in the territory of Italy. Two large databases, one for thermal springs and CO_2-rich springs, and a second one for fumarolic condensates and associated gas phase have been produced and are available on line, with data spanning in time from the early 70's to the present.

We have used those data, after careful evaluation of the quality and reliability of them, to produce correlation diagrams and isodistribution maps of some relevant geochemical/geothermal parameters, such as: pCO_2 in thermal springs, %CO_2 and $\delta^{13}C$ in CO_2 of gas phases, $^3He/^4He$ ratio and %He. In this way, we have been able to delimit the areal patterns of thermal anomalies potentially related with geothermal reservoirs. The cross correlation among the many parameters (>40) selected has allowed the overview on the circulation of fluids at shallow crust, in one of the most active tectonic boundary of the Earth between the African and the Eurasian continents.

Shallow circulation of hot fluids is particularly active in the Roman Comagmatic Province, the Neapolitan area and Sicily (both at Etna, Aeolian Archipelago and Pantelleria island in the Sicily Channel) where active geothermal systems are already known, whose areal extension is probably much larger than what envisaged at present.

The geothermometric evaluation of data has not allowed to clearly identity new areas apart from those already known but, nevertheless, some areas in the inner Apennines, as well as Sicily and Sardinia have shown anomalous $^3He/^4He$ values that point to the presence of mantle fluids located inside the crust.

Being most of active volcanic islands likely much smaller than the thermal anomaly they are associated with, a futuristic perspective of utilizing geothermal fluids off shore is suggested. Moreover, the database and the proposed maps can be a useful tool both scientific community and

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1 stakeholders to perform geothermal favourability maps and to identify potential new areas

2 interesting from a geothermal perspective.

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4 **Key words:** *Geothermal potential; thermal springs; fumaroles; gas vents; geothermal prospection;*

5 *geochemical prospection; southern Italy.*

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7 **1. Introduction**

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9   In February 2010 the Italian Parliament promulgated a reorganization law, in order to favour

10 the exploitation of geothermal energy by private investors. Following this governmental indication,

11 the Italian Ministry of Economic Development launched a three-years (2011-2014) project named

12 "*VIGOR*" (*http://www.vigor-geotermia.it*) in order to promote innovative actions for geothermal

13 energy exploration in Southern Italy. This was followed by another project, lasted from 2013 to

14 2015, funded by the Italian Council for Research entitled "*Geothermal Atlas of Southern Italy*"

15 (*http://atlante.igg.cnr.it*). These projects served to gather analytical and technical data to be used to

16 locate and categorize all potential geothermal resources in the regions involved (Latium, Abruzzi,

17 Molise, Campania, Puglia, Lucania, Calabria, Sicily and Sardinia; Fig. 3). Some of these regions

18 host active volcanoes (*e.g.:* Vesuvius and Phlegraean Fields in Campania; Stromboli Island and

19 Etna in Sicily) as well as several others in a quiescent state (*e.g.:* Ischia Island in Campania; Alban

20 Hills in Latium; Vulcano and Pantelleria Islands in Sicily). They also host well-known geothermal

21 systems (*e.g.:* at Vulsini Mts., Ischia, Vulcano and Pantelleria Islands) and a very high number of

22 thermal springs, the latter traditionally used for balneotherapy since Roman times.

23   One of the outcomes of both of those projects was the production of a Geochemical Atlas

24 of geothermal manifestations. This included geochemical databases with the chemical and isotopic

25 data available for thermal springs, CO_2-rich waters, fumaroles and gas vents present in the studied

26 territory, as well as maps of their precise location and contour maps of the spatial distribution of

27 geochemical parameters of geothermal interest.

28   The main target of the analysis and use of the chemical parameters acquired with both

29 projects was to provide potential stakeholders with an efficient tool for geothermal prospecting

30 and/or surveying.

31   In the present work we proceeded to: *i)* update all data already gathered in previous similar

32 projects, either published (*e.g.:* CNR, 1982a; 1982b; Cataldi et al., 1995) or unpublished (*e.g.:*

33 INGV, 2006) and *ii)* review the extensive literature data produced in the past 50 years.

34   Careful review of the existing data and production of new ones, where implementation was

35 necessary, were carried out jointly by the Italian Council for Research (CNR) and by the Italian

36 National Institute of Geophysics and Volcanology (INGV). An extensive report on these activities

37 (Minissale et al., 2016) can be downloaded (in Italian) from:

38 *http://atlante.igg.cnr.it/images/stories/volumi/VolumeGeochimicaAtlante-online.pdf.*

39   This paper was primarily intended to share with the international community the results of

the long (more than two years) process of elaboration of all geochemical data from the geothermal areas of Southern Italy, indicating the criteria used to select the parameters that we considered the most relevant for the aims of this study. Secondly, we aimed at providing reliable and robust data for the eventual production of geothermal favourability maps of Southern Italy by national and international investors.

2. Fluid geochemistry as a tool for geothermal investigation and favourability mapping

At the onset of a geothermal exploration project there is usually a high degree of uncertainty on whether the planned activity will be economically viable or not, and/or if it will be technically feasible and environmentally compatible. Best practices in the exploration for any natural resource should aim at reducing the risk of failure prior to significant capital investment. In the case of geothermal resources exploration, the high risk associated with the estimate of the resource capacity is one of the key issues that investors have to face. The principal variables required to define the resource capacity are: *i)* temperature (enthalpy), volume and depth of the resource; *ii)* optimal productivity of extraction wells; *iii)* sustainability of the extraction rate of producing wells; and *iv)* the energy market demand. Each phase of a geothermal exploration program should be clearly determined before its beginning, in order to address all risks, and each type of risk should be accurately evaluated.

Because of the uncertainty involved, in order to minimize the costs and maximize the amount of information available for each component of a geothermal project, it has become a common practice to divide the preparatory work into several separate phases. In this regard, the ESMAP Geothermal Handbook (ESMAP, 2012) provides a guide for developing a geothermal project, indicating seven phases, as follows: *i*) preliminary survey; *ii*) exploration; *iii*) drilling tests; *iv*) project review and planning; *v*) field development; *vi*) power plant construction and *vii*) commissioning and operation. Stage *i)* can be preceded by a *stage zero*, namely a geothermal favourability mapping (Fig. 1). It is in fact useful to identify the location of potential geothermal areas by combining different types of data through a dedicated software, such as Geographical Information Systems (GIS).

In stages *i)* and *ii)*, geochemical prospecting methods are extensively used and act as a valid support for other Earth Sciences disciplines (geological and geophysical, mostly) involved in the geothermal project. In particular, fluid geochemistry plays a major role in understanding: *i)* distribution of permeable zones; *ii)* areal extension of the potential geothermal reservoir; *iii)* typology of geothermal systems (liquid-or vapour-dominated); *iv)* evaluation of the minimum temperature at depth; *v)* chemical features of the geothermal fluid; *vi)* existence, location and extension of water recharge areas.

The preliminary phase involves a work program designed to assess any possible evidence for geothermal resources in a specific area. This is carried out through an extensive literature

review of hydro-chemical data (from hot/thermal springs, mud pools, etc.), data from natural gas manifestations (dry vents, fumaroles, etc.), as well as data from drillings (temperature and resistivity logs, etc.). Once geothermal manifestations have been located, and characterized, new samples of representative fluids should be taken, especially at sites with high fluid temperature and high electrical conductivity. Cold springs or cold wells, with: high electrical conductivity, high gas bubbling, unusual odour or strange taste, are further considered for sampling, in places where no thermal manifestation is evident.

Where geothermal fluids reach the surface, their chemical/isotopic composition is used to deduce their sub-surface temperature through application of geothermometers that are the most used tools in preliminary phases. Geothermometers depend on one or more dissolved component in the geothermal fluid, such as: solutes, gases or isotopic ratios. Accordingly, they have been classified into three groups: *i)* chemical (or solute); *ii)* gas; and *iii)* isotope geothermometers. They are based on the existence at depth of a temperature-dependent mineral-fluid equilibrium that constrains the chemical and the isotopic composition of the system. However, when a geothermal fluid rises to the surface, it becomes subject to a number of physical and chemical processes that change its final composition. Boiling, loss of CO_2, mixing with shallower fluids, conductive cooling, etc., can cause additional mineral dissolution or precipitation, because of changing of the saturation index with respect to mineral phases. For example, the increase of *p*H of pristine fluids may cause precipitation of hydroxides and carbonates. Furthermore, the top part of a geothermal system may be subject to mixing with percolating ground water, with consequent dilution and cooling of the geothermal fluid. This process in particular, among other effects, may significantly alter the temperature values estimated with geothermometers. It is therefore necessary to use geothermometers cautiously, as a suite within their geologic context, in order to properly estimate the resource temperature (Armannsson, 2012).

Besides geothermometers, soil gas studies may provide information about the pathways used by geothermal fluids to reach the surface. Measurement of gas fluxes and concentrations in the soil (Bertrami et al., 1990; Finlayson, 1992; Hernández et al., 2000; Voltattorni et al., 2010; Phuong et al., 2012; Fridriksson et al., 2016) sometimes coupled with measurement of soil temperature (Lan et al., 2007; Skord, 2013; Maucourant et al., 2014), has been extensively used for the exploration of geothermal reservoirs, as well as for the estimate of the location and surface extension of heat sources. Noble gases, as well as Hg, are assumed to be released from active geothermal systems at depth and their high mobility makes them ideal pathfinders for concealed natural resources, as they can escape to the surface along fractures and faults (*e.g.:* Koga, 1982; Fridman, 1990).

Another largely used application of geochemical data in geothermal prospecting is the development of geothermal favourability maps. In general, favourability maps permit to establish a hierarchy among geothermal areas, from low to medium and high enthalpy geothermal resources,

based on their geothermal potential (Carranza et al., 2008; Iovenitti et al., 2014; Trumpy et al., 2015). Input data are given by spatial analysis of multiple parameters (geological, hydrogeological, geophysical and geochemical), performed using a GIS software. Indeed, the use of GIS allows to define spatial associations between different thematic information (layers) for a specific area. Each layer is converted into a reclassified thematic grid (map); each grid is assigned both a weight and an influence (importance) on the basis of statistical criteria or *knowledge-driven* models (based on experts' opinion). In this framework, several authors have used geochemical data (from thermal springs, gas bubbling pools and fumaroles) in terms of distance from potential geothermal reservoirs (Noorollahi et al., 2007; 2008; Yousefi et al., 2010; Aravena and Lahsen, 2013; Moghaddam et al., 2014; Procesi et al., 2015). In particular, some authors have defined that distance by statistical approaches taking into account already exploited geothermal sites (Noorollahi et al., 2007; 2008; Yousefi et al., 2010), whereas others have defined it by *knowledge-driven* models considering a buffer around the geothermal manifestation (Procesi et al., 2015).

A different approach was recently proposed by Trumpy et al. (2015) using geochemical data in a wide regional context, in terms both of partial pressure of CO_2 (Pco_2) in thermal springs and of $^3He/^4He$ ratio in gas discharges. The $^3He/^4He$ ratio is a good indicator of degassing from mantle-derived magma residing in the crust that, coupled with CO_2, can be also a good indicator of degassing from hydrothermal systems fed by deep fluids. Those authors have therefore compiled maps as combinations of *geochemical favourability* layers (based on the distribution of $^3He/^4He$ ratios and dissolved Pco_2 values) and other layers, using a dedicated Index Overlay Model.

3. Geochemical database and data selection criteria

Published and unpublished geochemical and isotopic data of the thermal manifestations were collected and organized in two files, one for the liquid and one for the gas phase, both available as supplementary material at *http://atlante.igg.cnr.it/*.

The basic reference for this collection was the national geothermal database handled by the Italian National Research Council (ENEL, 1988; Barbier et al., 2000; Trumpy and Manzella, 2017). Useful data were also retrieved from the huge scientific literature of the last 50 years. Almost 150 scientific publications were carefully checked, most of which refer to active volcanic areas. Only those data including information on the precise location of the emergence were considered. In addition, new data were acquired in areas where information was lacking. No classification criteria for the waters were applied (*e.g.:* as a function of salinity or chemical composition), and the selection of sites was based on a water temperature threshold set at 20 °C for thermal springs, as usual in temperate regions. The database of selected water sites contains 515 chemical analyses referring to 246 emergence sites; the database of gas sites counts 509 chemical analyses, including 246 emergences.

In the first database, some cold waters, such as those rich in CO_2, were also included. The

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1 presence of relevant CO_2 degassing from secondary superficial aquifers could in fact be an

2 indication of the presence, at an undefined depth, of an active parent hydrothermal system,

3 possibly just masked by the shallower cold water circulation. In addition, in order to give a

4 complete framework of the naturally emitted gaseous fluids in Southern Italy, CH_4-rich emissions,

5 generally cold and associated with the presence of thick Neogene sedimentary formations, were

6 also included in the gas database.

7 A proper screening work was done for water samples: only the analyses showing an

8 electronic balance between cations and anions lower than 5% were selected. For the gas samples,

9 those clearly affected by air (oxygen) contamination were excluded. Analyses, provided with the

10 geographic coordinates of the respective sampling site (in UTM-WGS84 metric units Fuse 33 N)

11 were listed, starting from the most recent ones in case of multiple analyses.

12 As regards thermal waters, each site in the water file displays: *i)* elevation (in m *a.s.l.*); *ii)*

13 flow-rate (in L/sec); *iii)* temperature (in °C); *iv)* pH; *v)* redox potential (as Eh, in mV); *vi)* electrical

14 conductivity (in µS/cm) at 25 °C; *vii)* salinity (TDS=total dissolved solids in mg/kg); *viii)* major

15 elements (Ca, Mg, Na, K, HCO_3, SO_4 and Cl) and *ix)* minor elements (Sr, F, Br, B, NH_4, NO_3 and

16 SiO_2), both expressed in mg/kg; *x)* isotopic ratios of $^2H/H$ (as δ^2H) and $^{18}O/^{16}O$ (as $\delta^{18}O$), both in ‰

17 vs. SMOW; *xi)* tritium (in UT unit); *xii)* $\delta^{13}C$ of carbon in dissolved inorganic carbon (DIC) in ‰ vs

18 PDB; *xiii)* pCO_2 (-$logP{co_2}$) calculated with the PHREEQC speciation program (Parkhurst and

19 Appelo, 1999) and *xiv)* reference to the papers where chemical original data were published.

20 Taking into account the variability of the gas emissions, the classification proposed was

21 made based on the type of emergence. Free gas emissions (*mofette* = mo in the gas table) and

22 *mud volcanoes* (mv) are not so common; more frequently, gases are associated with water

23 emissions or with fumarolic fluids (fu). Bubbling gases can be associated with both cold (and

24 hypothermal water (typically from 15 to 20 °C) from shallow aquifers (sg), and from the thermal

25 regional aquifers hosted in carbonates (tsg). Sometimes, bubbling gases, both in flowing and/or in

26 stagnant (rain-originated) waters, are locally known as ''*acque acetose*'', ''*acque arzenti*'', "*acque*

27 *puzze*", "*acque bolle*", etc. (Minissale, 2004). The values of dissolved gas (stripped) were

28 discarded when analyses of free gases were available in the same area. In areas where no other

29 information was available, the values of stripped gas were kept.

30 Due to its high relevance, the $^3He/^4He$ ratio (as R/Ra where R is the ratio in the sample and

31 Ra is the ratio of air=1.39×10^{-6}, Mamyrin and Tolstikhin, 1984) of both bubbling and stripped gas

32 samples was reported in the gas file, even in the absence of the analysis of the main gas

33 components. The gas table in supplementary material reports both the uncorrected and corrected

34 (Craig et al., 1978) helium isotopic ratio as R/Ra and R/Ra_c, respectively. R/Ra_c was considered

35 when the corresponding He/Ne ratio for correction due to air contamination (Craig et al., 1978) was

36 available.

After reporting name and locality of each sample, columns in the gas file were organized as follows: *i)* type of manifestation, *ii)* year of sampling or year of data publication; *iii)* geographical coordinates; *iv)* elevation (or depth with respect to the ground level if the gas comes from a well, or the depth respect to the sea level in case of submarine emission); *v)* sampling temperature; *vi)* major components (CO_2, N_2, O_2, CH_4, H_2S); *vii)* minor components (H_2, CO, He, Ar, Ne, Rn); *viii)* various isotopic ratios, including: $^3He/^4He$, $^{40}Ar/^{36}Ar$, $\delta^{13}C$ both of CO_2 (gas) and DIC and, finally, *ix)* $\delta^{13}C$ and δ^2H in CH_4.

4. Geochemical mapping

To draw isodistribution maps on a regional scale, we decided to follow the same approach as Trumpy et al., (2015), who selected the pCO_2 in thermal waters and the $^3He/^4He$ ratio in the gas phase, as main chemical parameters in producing geothermal favourability maps. In addition, we have also considered: the CO_2 concentration and the ^{13}C-co_2 in the gas phase, being these parameters strictly related to the pCO_2 in waters. Regarding the $^3He/^4He$ ratio we decided to add also the total helium concentration in the gas phase, being a parameter connected with long circulation and residence time of underground fluids in areas not affected by huge CO_2 degassing/dilution.

5. Criteria

5.1 *Carbon parameters*

Generally, the gas phase associated with hydrothermal fluids in convergent margins is rich in CO_2 and it is related to magma degassing and/or decarbonation reactions (Barnes et al., 1978). CO_2 moves to the surface and is dissolved in shallow aquifers, inducing an increase in their Pco_2 (*soda springs*). When aquifers become saturated in CO_2, the gas leaves them and moves upwards along fractures. The gas eventually emerges at the surface in the form of focused or diffuse soil degassing, or it is further dissolved into shallow cold and thermal waters. Therefore, high Pco_2 values in groundwater are normally associated with geothermal fluids, although at undefined depth, and together with the isotopic signature of carbon they can be effective indicators of geothermal reservoirs at depth (Panichi and Tongiorgi, 1976). Both parameters can be used to map the areal extension of geothermal systems, as already done in central Italy along the peri-Tyrrhenian margin (Minissale, 1991b; Chiodini et al., 1995; Doveri et al., 2010; Giordano et al., 2014), where active geothermal systems discharge huge amounts of CO_2 (Chiodini et al., 2004). The reason why CO_2 works well in central Italy, is that the local geothermal systems are hosted in permeable Mesozoic carbonate rocks often covered by impermeable Quaternary volcanoclastic material and/or Neogene clay-rich post-orogenic sedimentary deposits that act as a good cap-rock for the rising CO_2.

1   In order to define the different classes of P_{CO_2} in waters for the drawing of isodistribution
2 maps we choose a statistical approach through the analysis of data using the Normal Probability
3 Plot (NPP; Sinclair, 1964). Three main classes were recognised: *i)* highly anomalous, with pCO_2 >-
4 0.75 (P_{CO_2}>0.18 bar); *ii)* weakly anomalous, with -1.75 < pCO_2 < -0.75 (0.078 bar < P_{CO_2} < 0.18
5 bar; and *iii)* non-anomalous, with pCO_2 < -1.75 (P_{CO_2}<0.078 bar) (Fig. 2). It is worth of note that
6 these classes, obtained on a regional scale, roughly correspond to those proposed by Doveri et al
7 (2010) for Latium region (north and south of Rome) to define and delimit the areal extension of
8 potential geothermal system.

9   Referring to the CO_2 concentration and the $\delta^{13}C$-CO_2 in the gas phase, classes defined by
10 the NPP analysis have resulted: *i)* <8.0, *ii)* from 8.0 to 50.0, *iii)* from 50.0 to 85.0, *iv)* ≥85.0 percent;
11 and *i)* from +3.0 to -3.0, *ii)* from -3.0 to -7.0, *iii)* from -7.0 to -20.0 and *iv)* ≤-20.0 delta permil,
12 respectively.

14 5.2 *Helium parameters*

16   As well known, the $^3He/^4He$ ratio is a strong indicator of mantle-magma residing in the crust
17 (Mamyrin and Tolstikhin, 1984) that, coupled with CO_2 anomalies, can be a good indicator of
18 degassing from hydrothermal systems and, eventually, converging towards the presence of
19 potential geothermal reservoirs at depth. Helium ratios can also trace crustal and atmospheric
20 sources (or contamination) in different geodynamics contexts (O'Nions and Oxburg, 1988).

21   Typical crustal values of R/Ra are in the range 0.001-0.2, while mantle values range
22 between 0.2 (Marty and Jambon, 1987) and 8.0, according to the degree of crustal contamination
23 of the primary gas rising from the mantle (Poreda and Craig, 1989; Hilton et al., 1993; Hulston and
24 Lupton, 1996). R/Ra value of ~8.0 is entirely derived from mid-ocean ridge basalts (MORB) or
25 upper mantle components. The large difference between crustal and mantle makes the $^3He/^4He$
26 ratio an effective tracer of subducting slabs in areas of arc magmatism (Craig et al., 1978).

27   Relatively high R/Ra values in Southern Italy were measured in gases discharged from the
28 active volcanic areas of: Mt Etna (6.9; Allard et al., 1997), Vulcano island (6.2; Tedesco and
29 Scarsi, 1999), Pantelleria island (7.32; Parello et al., 2000) and from the quiescent Vulture volcano
30 (6.35; Caracausi et al., 2015). Lower R/Ra values were measured in hydrothermal systems in the
31 Neapolitan area: at Campi Flegrei (2.0-3.2; Tedesco et al., 1990), Vesuvius (2.2-2.7; Federico et
32 al., 2002), Ischia island (1.6-3.7; Inguaggiato et al., 2000) and spotty in the inner Apennine chain
33 (*e.g.:* Mefite d'Ansanto, 2.84 (#108); Caracausi et al., 2013).

34   In peri-Tyrrhenian area of Tuscany and Latium gases have lower R/Ra values from 0.4 to
35 0.8 (Hooker et al.1985; Minissale et al, 1997a; Cinti et al., 2011; 2014), although a significant ^3He
36 enrichment was measured in geothermal fluids from Larderello (up to 3.2; Minissale et al., 1997a),
37 Cesano (1.2-2.0; Minissale et al., 1997a; Cinti et al., 2017) and in the gas discharges from the
38 Alban Hills (0.9-1.9; Barberi et al., 2007) and Roccamonfina volcano (1.89; Cuoco et al., 2017).

The variability of the helium isotopic ratio from south to north Italy reflects the complex geodynamic setting of the country. Sano et al. (1989) related the ^{3}He/^{4}He ratios measured in Italy to the upwelling mantle in the Tyrrhenian Bathyal Plain, which is characterized by a very thin oceanic crust (8-10 km; Panza and Calcagnile, 1979) and by heat flow values even higher than 200 mW/m^2 (Della Vedova et al., 1991). Other studies suggested that the low ^{3}He/^{4}He ratios measured in the northern Tyrrhenian sector reflect the composition of the subducted crust enriched in ^{4}He because of northward contamination by metasomatic fluids derived from the partly subducted Apennines (Polyak et al., 1979; Frezzotti et al., 2009).

What reported above highlights that R/Ra ratios lower than those from volcanic areas (*e.g.:* Mt. Etna), can derive from geothermal systems typically affected by meteoric recharge and hence by ^{4}He atmospheric contamination, and in this framework the Larderello geothermal system in Tuscany represents an excellent example. This consideration suggests that the use of the R/Ra ratio for geothermal prospecting purposes must take into account the local geological and geodynamic setting to avoid deceptive evaluations.

In light of the above discussion, we decided to consider five classes of R/Ra (or R/Ra$_c$): *i)* <0.2; *ii)* from 0.2 to 1.0; *iii)* from 1.0 to 3.0; *iv)* from 3.0 to 5.0 and *v)* >5.0, respectively.

6. Mapping methods

The areal data distribution of the selected geochemical parameters *i.e.:* *i)* the partial pressure of CO_2 in thermal springs, shallow wells and cold CO_2-rich waters; *ii)* CO_2 gas content; *iii)* δ^{13}C of CO_2 along with *iv)* the ^{3}He/^{4}He ratio and *v)* total helium in the gas discharges, were interpolated using the Inverse Distance Weight (IDW) method. This deterministic algorithm, available into GIS environment, is a spatial interpolation method for multivariate analysis of points in a defined area. The usefulness of this method arises from the need to extrapolate reliable values where they are missing. Compared to other methods, IDW has the advantage of being easy to use. It requires: *i)* the definition of few contour parameters; *ii)* allows the estimation of the phenomenon at a given point; *iii)* shows anomalous cases attributable to specific situations which should be deepened, from time to time, to produce realistic output isodistribution maps.

Main disadvantages of IDW method are: absence of estimation of the error associated to the interpolation process and the strong dependence of the samples distribution on interpolation reliability. The output cartography, being deterministic, provides for the measured points a value equal to the one actually observed. The result of the interpolation is a surface in raster format, function of the spatial coordinates *x* and *y* which represents the value assumed by each single parameter considered in the interpolation space. Considering the dimensions of the investigated area and the distribution of samples, the size of the output grid cell we have adopted was one km per side.

7. Geological and hydrogeological setting of southern Italy

Southern Italy is located in between the African and Eurasian tectonic plates, whose collisional boundary is located somewhere in the southern Tyrrhenian Sea and the north-east sector of Sicily (*Taormina line*; Fig. 3). Its territory includes all possible geodynamic environments: *i)* trusting chains (*i.e.*, *Apennines* and *Magrebids*), *ii)* stable trusted crystalline Paleozoic block (*i.e.*, *Sardinia-Corsica Massif*), *iii)* trusted-long drifted and still trusting Alpine crystalline blocks (*i.e.*, *Calabrids*), *iv)* back-arc micro oceans still under formation (*i.e.*, the *Tyrrhenian Sea*), *v)* rifting areas (*i.e.*, *Sicily Channel*) and related volcanism (Pantelleria Island), *vi)* active subduction of oceanic crust (*i.e.*, northwestward subducting Mesozoic Ionian basin underneath the Calabrian Arc) *vii)* transpressive faults (among the many, the *Ancona line*, the *Sangineto line*, etc), *viii)* active andesitic arc volcanism (*i.e.*, *Aeolian Arc*) and, finally, *ix)* stable foreland areas (*Iblean*, *Pelagian* foreland in Sicily and *Apulian* foreland along the southern Adriatic Sea). All these tectonic units and geodynamic environments are shown in figure 3.

Apart from stable flat foreland areas, the territory is characterized by a rugged morphology, strong seismicity (*e.g.:* Chiarabba et al., 2005) and active or recent volcanism. The latter produced and still produces rocks of extremely different composition: from calc-alkaline in the Aeolian Arc (Barberi et al., 1974), to strongly silica undersaturated, the latter being K-rich (*leucitites*) in the Roman and Neapolitan volcanic province (Washington, 1906) and Na-rich (*pantellerites*) on Pantelleria Island in the Sicily Channel. New oceanic basaltic crust is actively forming (*e.g.*: *Marsili* and *Palinuro* seamounts; Fig. 3) in the Tyrrhenian Sea (Boccaletti and Manetti, 1978), and recent Quaternary intraplate basalts are present both in Sardinia (*Logudoro*; Peccerillo, 2005) and Sicily (Etna volcano and Iblei Mts; Peccerillo, 2003) islands (Fig. 3).

The continental Apennines, Calabria and Sicily regions are characterized by a general strong tectonic compression, whereas the Tyrrhenian Sea and the Sicily channel are affected by extensional tectonic stresses. Such extension, due to the formation of the Tyrrhenian Sea as a back-arc basin after the south-west-directed subduction of the Adria Plate (Boccaletti and Manetti, 1978), is the ultimate reason for the presence of abundant Pliocene-Quaternary volcanism along the NW-SE trending peri-Tyrrhenian margin of Italy. Geochronological data for the main magmatic centres show that there is a general decrease in age from north to south, where volcanism is presently very active.

The main lithostratigraphic feature of Southern Italy is the presence of potential permeable geothermal regional reservoirs hosted inside widespread and thick Mesozoic platform and pelagic carbonate sequence (Pescatore and Ortolani, 1979). They are in places overlain by allochthonous pelitic low-permeability flysch series and Neogene sediments in the many NW-SW basins present and tectonic troughs, such as the *Bradanic* (Lucania) and *Caltanissetta* (Sicily), respectively (Fig. 3). The carbonate sequences are similar, in lithology, to the coeval unfolded *Apulian* and *Pelagian* (African) foreland sequences. Locally, when buried, the limestone may even host huge magmatic chambers, such as the supervolcano of the Phlegraean (*burning* in Greek) Fields (Armienti et al.,

1 1984) and Vesuvius areas (Barberi et al., 1981) in the Campania region.

2 This active volcanism is clearly associated with a strong geothermal potential and, this led

3 in the past to carry out successful (at least in terms of discovery of anomalous geothermal

4 gradients) geothermal drillings : *i)* in the Roman Co-magmatic Province (Fig. 3), at *Latera* volcano

5 (Bertrami et al., 1984), *Torre Alfina* (Cataldi and Rendina, 1973) and *Sabatini Mts* (*Cesano* in

6 figure 4: Calamai et al., 1976; Funiciello et al., 1979), *ii)* at *Ischia Island* (Penta and Conforto,

7 1951) and in the Neapolitan area (Carlino et al., 2012), *iii)* at *Vulcano Island* in the Aeolian volcanic

8 arc (Sommaruga, 1984) and *iv)* at *Pantelleria Island* in the Sicily Channel (Gianelli and Grassi

9 2001). On the contrary, unproductive ("cold") wells have been drilled in the area between the

10 Roman and the Neapolitan volcanic areas, around the *Alban Hills* (Giordano et al., 2014) and

11 *Roccamonfina* (Watts, 1987) volcanoes, as well as in Sardinia east of the Quaternary basaltic

12 *Logudoro* volcanic area (Regione Autonoma Sarda, 2013).

13 The contemporary presence of buried thick carbonate sequences and shallow magma

14 chambers in many places triggers the formation of huge quantities of hydrothermal CO_2 (Kerrick,

15 2001), whose origin and discharge to the surface have been largely studied in the past (Panichi

16 and Tongiorgi, 1976; Minissale 1991; Chiodini et al., 1995; 2000; 2004;). At the same time, the

17 carbonate sequences form the highest mountains, that act as the main collector of rain (due to

18 their high permeability) in the Apennines, and the regional ground water flow that heads towards

19 the Tyrrhenian Sea apparently lowers the local heat flow. As a matter of fact, many springs that

20 emerge at the foot of the Apennines along the Tyrrhenian coast have huge discharges (up to

21 several m^3/sec) of water of meteoric origin, with temperature of 8-10 °C (Minissale, 2004).

22 However, there are also several meso-thermal springs, with outlet temperature of about 20 °C, and

23 even more springs with higher temperature, whose thermalism is caused by horizontal advective

24 heat flushed along the circuit from the mountains to the sea (*e.g.*: Minissale and Vaselli, 2011;

25 Chiodini et al., 2013). Any eventual presence of active hydrothermal systems affected by such

26 regional circulation can be therefore easily hidden, as it happens, for example, along the southern

27 boundary of the famous Larderello geothermal field in Tuscany. In that case, suspended and

28 relatively cold unconfined aquifers (T° = 90-95 °C) hosted inside the outcropping limestones are

29 very close to the high temperature vapor-dominated (200-250 °C) area isolated from the steam-

30 dominated zone, by an effective sealed barrier (Ceccarelli et al., 1987; Minissale 1991a).

8. Geographical distribution of thermal waters and gases

34 In the European context, Central-Southern Italy is certainly the region with the highest

35 concentration of natural thermal springs, CO_2 emissions and active or fossil travertine deposits

36 (Minissale, 2004 and references therein). Such abundance is paralleled by the presence of several

37 active and dormant volcanic areas, evenly distributed from the Roman Volcanic Province in the

38 north, to the volcanic island of Pantelleria to the south. The position of thermal and gas emissions

considered in the present survey is shown in figure 3. Precise location and relative number in the data bases (in italic for the gas data), region by region, are reported in figures 4 through 6.

In Latium and Campania regions, most springs and gases are located along the Tyrrhenian coast, whereas in the Neapolitan area and in Sicily they are clearly associated with the several volcanic islands at: Ischia, Stromboli, Vulcano, Lipari, Panarea and Salina and Pantelleria. Isolated quiescent volcanoes, either located in the Tyrrhenian coastal sector (such as Roccamonfina, 70 km NW of Naples), or inside the Apennines (Vulture, 90 km ENE of Naples), as well as Iblei Mts in Sicily, and Logudoro basalts in the northern sector of Sardinia have, at their surroundings, some thermal and/or CO_2-rich gas emissions.

Among the thermal springs and the CO_2-rich gas vents not clearly related to volcanic or geothermal areas, two different types need specific attention. The first one refers to isolated manifestations located deep inside the Apennine chain, sometimes at high elevation, clearly related to the several relevant E-W- or SW-NE-directed transpressive faults that cross Italy from the Tyrrhenian coast to the Adriatic and Ionian coasts. Examples are along the Ancona-Anzio (# 22,*33* in Fig. 4; Pizzi and Galadini, 2009), the Roccamonfina-Ortona (*e.g.*: # 55,*97* in Fig. 5; Milano et al., 2008) and the Sangineto (*e.g.*: # 124,*152* in Fig. 6; Totaro et al., 2014) tectonic lines (Fig. 3).

The second group of thermal emissions refers to coastal thermal springs emerging a few meters above the sea level, but sometimes even at sea level along the shoreline. Examples of this group, on moving from north to south are: the Osa spring (# 6,*9*) located 90 km NW of Rome (Fig. 4), the Sineussiane springs (# 58-59,*91*) about 50 km NW of Naples (Fig. 5), the Terme Luigiane (# 125,*163*) in the NW sector of Calabria (Fig. 6) and Ali and Termini Imerese (# 155,*177*) in Sicily (Fig. 6). Sometimes this type of emergence occurs even in a foreland setting, such as the Santa Cesarea spring (# 111-117,*137* in Fig. 5; Santaloia et al., 2016) located at the extreme east heel of Italy.

Both types of emissions, quite common worldwide, have a tectonic origin (*e.g.*: Minissale et al., 2000b) and they are generally not connected with active geothermal areas. In fact, they have generally a N_2-rich associated gas phase reflecting their strictly meteoric origin, or sometimes a CH_4-rich phase when associated with hydrocarbon deposits. In Italy, they represent a minority among the thermal emissions, but, locally, they may be present not far from active volcanoes. Typical is the case of the Etna volcano that host CH_4 rich gas emission at the NW (# 191) and E (# 201) margins of the edifice (Fig. 6). Although these types of emissions, sometimes cold, are not related to active hydrothermalism, they have been included for completeness in the databases and in the following general discussion and diagrams.

9. Geochemistry of waters

As a general principle, the chemical composition of groundwater is largely controlled by the reaction of water with rocks and minerals. Water is a solvent and, as such, is capable of dissolving

1 and interacting with organic and inorganic components of soils, minerals that make up
2 unconsolidated deposits (*e.g.*: sand and gravel), and with various types of bedrock (*e.g.*:
3 limestone, evaporite, crystalline rocks, volcanics). Dissolution of soil minerals from groundwater is
4 a process that can take days, years or centuries, depending on: *i)* the solubility of materials and
5 the kinetic of dissolution processes, *ii)* water/rock ratio; *iii)* groundwater residence time, *iv)* specific
6 surface of material (granulometry) *v)* physical-chemical characteristics, such as temperature, *p*H
7 and redox potential (Eh), *vi)* presence of acidic (*i.e.* CO_2) and/or reducing (*i.e.* H_2S) gases, *vii)*
8 presence of bacteria, etc.. All these factors control cations and anions contents in solution, as well
9 as their ionic ratios and contribute to the amount of the saline content (*i.e.* the total dissolved
10 solids, onward TDS) characterizing the different groundwater.

11 As reported in previous paragraphs, the hydro-geological setting of southern Italy is very
12 complex; aquifers are hosted by and interact with rocks having very different origin and
13 mineralogy. From sedimentary to volcanic and metamorphic environments, groundwater circulates
14 in sectors characterised by anomalous geothermal gradients, corresponding to fractured and/or
15 faulted areas and dissolve huge quantity of deep-originated CO_2 produced both in geothermal and
16 volcanic systems. Accordingly, springs, irrespective of their outlet temperature, display a
17 remarkable variety of chemical compositions as a function of the different geochemical processes
18 occurring along the hydrological paths. Considering these processes, the chemical composition of
19 water samples is described in terms of major ion contents, in: *i)* the Langelier-Ludwig (1942)
20 diagram of figure 7; *ii)* the Ca, Mg and Na+K ternary diagram (Fig. 8, right) and *iii)* the main anions
21 Cl, SO_4 and HCO_3 contents (Fig. 8, left). By comparison, the composition of seawater is also
22 reported. Due to the wide range in their outlet temperature (11-133 °C), the analysed waters were
23 arbitrarily divided into three groups: cold (<25°C), warm (25-50 °C) and hot (>50°C). The
24 classification diagrams indicate the occurrence of the following waters types:

25 <u>Ca-HCO_3</u> - It is the chemical composition showed by the majority of cold waters, several
26 warm waters and few hot waters. Cold waters migrated through shallow hydrological circuits and
27 represent the early stage of the interaction between rain and local soil and bedrock. Ca-HCO_3 is
28 the likely original composition of the groundwater forming the thermal waters in Italy, as results
29 from isotopic data (Minissale, 1991b). Some cold waters (# 39-44, 55) of the Tyrrhenian side of
30 Latium and Campania regions spreading southwards from the Roman Comagmatic Province (RCP
31 onward) receive a huge CO_2 input from depth; they have acidic *p*H and are enriched in Na and K
32 leached from volcanic rocks they interact with. Warm waters # 61, 108, 146, 150, 152, 222, located
33 in Campania, Sardinia and Sicily, dissolve a deep CO_2 gas phase in carbonate environments and
34 circulate in faulted areas. The different (*i.e.* deeper) depths reached by these hydraulic circuits,
35 with respect to the cold ones, are strongly emphasized by their outlet water temperatures (up to
36 37°C).

1   <u>Ca-SO$_4$</u> - It is prevalently due to the dissolution of Triassic anhydrite beds at the base of the

2 Mesozoic carbonate sequence, which is particularly thick in the northern sector of the study area

3 (Patacca et al., 2008). Waters are quite exclusively warm-to-hot, and emerge mainly in: *i)* central

4 Italy (RCP, *e.g.*: # 4-5, 11, 15-21, 32, 35-37), showing high pCO_2, *ii)* main Apennines (# 1) as well

5 as in *iii)* northern and central Calabria (# 123, 126; Duchi et al., 1991). In sample # 126, gypsum-

6 rich formations are contained in the Mesozoic carbonates outcropping in a tectonic window

7 (Italiano et al., 2010).

8   <u>Acidic (*p*H<2.9)-SO$_4$-dominated.</u> They are represented by the near-boiling acidic pool of the

9 *Solfatara* area (# 65, 68; Phlegraean Fields) and # 175 located in the Vulcano island in Sicily. This

10 particular composition originated through rising magmatic gases (mainly H_2S) interacting with (and

11 heating) shallow meteoric waters. The oxidation of H_2S to H_2SO_4 ($H_2S+2O_2 \rightarrow 2H^++SO_4^{2-}$), driven

12 by atmospheric O_2, determines the sulphate signature and the very low *p*H conditions, which is the

13 cause of the absence of HCO_3 converted into volatile H_2CO_3.

14   <u>Na-Cl</u> - This composition contains the largest number of waters, irrespective of their

15 temperature, although hot samples are dominant. They have different salinity but mostly classified,

16 following Freeze and Cherry (1979), as brackish (1,000< TDS ≤10,000 mg/L) or saline (TDS

17 >10,000 mg/L) waters. Several processes, acting sometimes together, can be invoked to explain

18 the salinity. In particular:

19 *i)*   mixing between freshwater and seawater for cold samples discharging along the shore line

20   (*e.g.*: # 47, 82, 109, 110, 112, 113, 117, 158);

21 *ii)*   mixing between seawater, the latter sometimes modified through water-rock interaction at

22   high temperature, and hot deep saline waters [*e.g.*: # 58-59, 89, 97, 100, 141, 169-172, 181,

23   182, 203, 233; these waters discharge in the main hydrothermal basins of southern Italy: in

24   Campania (Ischia Is., Phlegraean Fields), Sardinia (Campidano graben) and Sicilian

25   volcanoes (Pantelleria Is., Panarea Is., Vulcano Is., Stromboli Is. ad Sciacca)];

26 *iii)*   rising magmatic H_2S, SO_2, CO_2 and HCl interacting with shallow meteoric waters.

27   Representative of this group is thermal sample # 64 (Plegraean Fields) where the chemical

28   features suggest a direct ascent of both gases and water from the ''major upflow zone''

29   (Giggenbach, 1988);

30 *iv)*   high saline content (TDS>13,000 mg/L) waters stemming from brines associated with

31   hydrocarbons, as supported by high CH_4 concentrations in the gas phase associated with the

32   springs (Madonia et al., 2011). These weakly thermal samples are emitted by mud volcanoes

33   scattered in the territory, (# 56, 168, etc.);

34 *v)*   interaction with marine sediments and/or mixing with formation/connate waters (<25 °C

35   samples: # 124, 129), as well as extensive and prolonged interaction with both metamorphic

36   and crystalline rocks (warm samples # 122, 125, 127, 128, 130, 131-136). These warm

37   waters discharge diffusely in Calabria (Italiano et al., 2010) mostly along regional fault

1 systems, and hot waters also issuing from the crystalline basement in the central part of
2 Sardinia (# 213 and 215; Angelone et al., 2005).

3 Na-HCO$_3$ - The origin of these waters (top right sector of Fig. 7) in the study area is due to
4 the interaction of CO$_2$-rich fluids with volcanic rocks, in which feldspars are converted to clays,
5 generating aqueous solutions typically rich in Na$^+$(K$^+$) and HCO$_3^-$ (e.g.: Drever, 1982). These CO$_2$-
6 rich samples are representative of the waters discharging at the periphery of the main
7 hydrothermal systems (Giggenbach, 1988). Waters of this group are found in the most known CO$_2$
8 degassing areas of southern Italy: Campania (Phlegaean Fields, Ischia Isl., Vesuvius volcano),
9 Sardinia (Campidano graben, Logudoro), Basilicata (# 119 and # 120), Sicily (Iblei Mts: # 161) and
10 Latium (e.g.: # 45 in the Alban Hills).

11 The Ca, Mg and Na+K triangular plot of figure 8 (right) and the Cl, SO$_4$ and HCO$_3$ triangular
12 plot in figure 8 (left) give an insight into the origin of the constituents of groundwater, highlighting
13 the various processes governing their chemistry. These plots achieve their goals by overcoming
14 the ambiguities presented by the Langelier-Ludwig diagram in where, for example, Cl and SO$_4$, as
15 well as Ca and Mg, are shown in pair. In addition to the information provided by figure 7, the
16 cations triangular plot allows: i) to recognize the progressive enrichment in both Na and K of the
17 CO$_2$-rich calcium-bicarbonate waters of Latium and Campania regions interacting with alkali-rich
18 volcanics; ii) to evidence the Mg peculiar enrichment of samples # 76, # 163, # 166 ad # 167,
19 relatively warm waters circulating in the Vesuvius and Etna volcanic areas where Mg is likely
20 brought into solutions through the leaching, in acidic environment, of ferromagnesian minerals
21 contained in the volcanic rocks; iii) to point out the noticeable differentiation between Ca-rich and
22 (Na+K)-rich hot waters; the former interacting with evaporites, while the latter mix with seawater
23 (samples close to the blue star) and/or undergo alkali enrichment via water-rock interaction
24 (samples towards the Na+K corner). Similar indications derive from warm waters, which result
25 more scattered in the plot due to possible mixing at various degree with freshwater or with the two
26 reported Ca-rich or Na(K)-rich hot end members.

27 According to Giggenbach (1988), the Cl, SO$_4$ and HCO$_3$ triangular plot in figure 8 highlights
28 the presence of characteristic fields, in which waters can be grouped and different chemical
29 processes assessed. Accordingly, we find: i) HCO$_3$ waters, typical of both volcanic (RCP,
30 Plegraean Fields, Ischia Is., Vesuvius, Aeolian Archipelago, Pantelleria Is., Etna) and geothermal
31 (Campidano and Logudoro in Sardinia; Campania region; NE Sicily sector) areas, where
32 dissolution of large amounts of deep-derived CO$_2$ promotes intense leaching of the permeable
33 volcanic rocks (peripheral waters); ii) SO$_4$-dominated samples located in Lipari Is. and Plegraean
34 Fields: waters are interpreted as being heated by H$_2$S-rich vapour exolved from deep geothermal
35 systems; iii) Cl-and-SO$_4$-rich waters characterized by high discharge temperatures, issuing from
36 the main geothermal systems located in southern Italy (Ischia Is., Plegraean Fields, Aeolian

Islands, Pantelleria Is.); mass and heat exchange with hot water-bearing fluids are maximal in these areas.

Summing up, water chemistry, in terms of anion, can be due to hot brines rising from deeper hydrothermal reservoirs or evolving through a complex interplay of several processes, best described as a mixing between a shallow meteoric component, hydrothermal fluids (both steam and brines) and seawater. Na-Cl waters plotting close to the field of mature geothermal waters can be considered the most representative of the deep thermal liquid reservoir (Giggenbach, 1988).

In term of isotopic composition of thermal emergences in southern Italy, the classic $\delta^{18}O$-δD diagram of figure 9 (left) reports, according to the number of available data, the average values for each single site. The figure shows, apart from the Global Meteoric Water Line (GMWL; Craig, 1961), the Mediterranean and east Mediterranean meteoric water lines (Gat and Carmi, 1970) and the recently assessed Sicilian meteoric line (Liotta et al., 2013). The figure also shows, for comparison with samples, the position of the average composition of rainfall in Central Italy (Minissale, 2004) and the average values of the entire set of considered spring data in Southern Italy.

It is evident that the large majority of the samples, both: cold, warm or hot, are constrained in the area delimited by the Global and the eastern Mediterranean water lines. A few samples, especially if with associated vigorous CO_2 emissions (e.g.: #102) are quite shifted to the left of the GMWL due to strong and prolonged ^{18}O exchange between water and CO_2 (Karolyte et al., 2017); others lie to the right of the GWML if located in active volcanic areas [e.g.: # 68 in the Phlegraean Fields (Cortecci et al., 1978); or # 184 in the Isle of Vulcano (Federico et al., 2010)] because of typical high temperature ^{18}O shifts.

As already reported on a regional scale (Minissale, 1991b), several evaporation lines can be drawn in those places where volcanic or geothermal systems are located near the Sea (e.g.: Sciacca in Sicily; Capaccioni et al., 2011). To go a little deeper into this mixing process near the Mediterranean Sea, the δD-Cl diagram is shown in figure 9 (right). The figure shows several possible mixing lines, in particular the mixing lines with low elevation rainfalls and high elevation rainfalls, in the area between which, most samples are located. A few samples are in quite anomalous position, such as the S.ta Cesarea (# 112, 115, 116; location in Fig. 5) and the mud pond inside the Solfatara crater (# 65); the first with excess chlorine with respect to the Mediterranean Sea possibly related to hydrocarbon deposits (Santaloia et al., 2016), the latter for strong local evaporation of steam condensate of the near Solfatara fumarole. It is worth noting that all active volcanic islands [Ischia (e.g # 83), Vulcano (e.g.: # 184) and Pantelleria (e.g.: # 203) islands], where there are sufficient samples to derive local evaporation lines, have relevant portions of seawater inflows into their hydrothermal circuits (systems).

10. Geochemistry of gases

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1   In the regions of Italy under investigation, free CO_2 gas is normally found associated with
2 the ground water (Minissale, 2004 and literature therein cited), as described in the previous
3 section, even at sites located far away from active volcanic areas or from hydrothermal systems
4 associated with volcanism.

5   Apart from CO_2, atmospheric gases (chiefly N_2 and Ar) can also be found in Southern Italy
6 thermal waters, being at times the only gas species dissolved (*e.g.*: Minissale et al., 2000a). This is
7 due to their abundance in rainwater recharging the carbonate aquifers, as well as to the
8 remarkable thickness and the high permeability of the carbonate rocks making up the Apennines.
9 Another common gas continuously forming inside the sometimes very thick Neogene sediments, is
10 CH_4 (Mattavelli and Novelli, 1987). Generally it accumulates and diffuses by escaping from over-
11 pressurized buried hydrocarbon reservoirs, or from bacterial reduction of organic matter in a
12 shallow subaerial environment (Schoell, 1988).

13   Three major components alone of the gas phase above described (*i.e.*, CO_2, N_2 and CH_4)
14 usually represent >98% in concentration of all natural gas manifestations, being either associated
15 with thermal waters or bubbling through cold superficial water or through focused gas vents or
16 diffusely from the soil. The CO_2 vs. N_2 diagram of figure 10 shows that the large majority of the gas
17 samples from hydrothermal areas displays two opposite compositions, one with CO_2 >90% and the
18 other with N_2 > 80%, with a clear mixing line between these two gases. Only a few samples plot
19 along another mixing line between N_2 > 80% and N_2 < 25%, being CO_2 always lower than 10%.
20 These samples show a prevailing CH_4 composition and are mostly from mud volcanoes located
21 into sedimentary basins. The main compositional dualism of hydrothermal gases is a consequence
22 both of the upward convective motion of high-enthalpy fluids rich in CO_2, which is readily released,
23 and of the concurrent downward gravitational motion of cold recharge waters, rich in N_2, mostly
24 coming from the superficial carbonate formations. As the recharge water from the carbonate
25 mountains in the Apennines gets deeper and hotter along the flowing towards the Tyrrhenian
26 coast, it releases N_2 due to its decreased solubility (Minissale et al., 1997a). This explains why
27 most of the N_2-rich samples in figure 10 are from dissolved gases from water springs or wells,
28 whereas most of the CO_2-rich samples are from free gas emissions like mofettes and hot
29 fumaroles.

30   Regarding CO_2, the isotopic $^{13}C/^{12}C$ ratio of carbon helps in discriminating among the
31 different sources (Deines et al., 1974) that may contribute to the total CO_2 released with
32 hydrothermal fluids in Southern Italy. The CO_2 vs. $\delta^{13}C_{CO2}$ diagram of figure 11 (top) shows that, as
33 the CO_2 content increases in concentration, its isotope composition shows a clear trend towards
34 more positive values, up to about +3.0 ‰ (PDB). The most positive $\delta^{13}C_{CO2}$ values are in samples
35 from fumaroles and mofettes, again underlining the more direct connection between free gases
36 and deep hydrothermal sources of CO_2. This trend also suggests an increasing contribution of ^{13}C-
37 rich CO_2 from mantle fluids in samples of -7.0 < ^{13}C < -4.0 range (Rollison, 1993), as well as a

1 contribution of isotopically much heavier CO_2 either from dissolution of limestones or from their

2 metamorphism under hydrothermal conditions (Craig, 1963).

3 Where available, we plotted the C-isotope values of free-gas CO_2 versus those of Dissolved

4 Inorganic Carbon (D.I.C.) in the associated water or condensed steam phase (Fig. 11, bottom).

5 Despite its largely empirical nature (the fractionation between the different species of carbon in

6 solution depends on many parameters, such as pH and temperature), this correlation shows that a

7 large number of samples, including all those from fumaroles and almost all from mofettes and mud

8 volcanoes, have a C-isotope composition in the free-gas CO_2 abnormally enriched in the "heavy"

9 isotope. According to Mook et al. (1974), at temperature above 120 °C the fractionation factor in

10 water between gaseous CO_2 and dissolved HCO_3^- favours ^{13}C enrichment in the residual gas

11 phase, thus shifting the isotopic composition of carbon towards more positive values of $\delta^{13}C_{CO2}$.

12 This points to an excess of free CO_2 in those samples, with the gas phase separated at

13 temperature of up to about 300 °C (considering a maximum isotopic shift of 7-8‰; Mook et al.,

14 1974). The free CO_2 gas would be in isotopic disequilibrium with that dissolved in water and the

15 disequilibrium would be kept in the rising gas, particularly in that eventually issued from mofettes

16 and fumaroles, because of its high velocity of motion towards the surface.

17 If we consider the $\delta^{13}C_{CO2}$ versus $\delta^{13}C_{CH4}$ (Giggenbach, 1982) plot (Fig. 12), the theoretical

18 lines of isotope fractionation at increasing temperatures (Bottinga, 1969), suggest that, as

19 observed for Larderello and in general for central-northern Apennines (Minissale et al., 2000a),

20 the origin of CH_4 for most of the samples in Southern Italy is abiogenic, and in some cases

21 thermogenic. Figure 12 shows also that, as already suggested from literature (Tassi et al., 2012),

22 methane from most of the mud volcanoes of Sicily and, more generally, from CH_4-dominant gas

23 emissions, is biogenic. In fact, both $\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$ values from those samples are highly

24 negative.

25 Another gas species that gives valuable information on the origin of the fluids is helium. In

26 general, high content of He in a gas phase at the surface indicates long residence time of the

27 parent fluid within the crust, due to the α-decay of U-Th radiogenic chains. The relative abundance

28 of ^3He and ^4He in gas samples provides clues to the possible contribution of magmatic/mantle gas.

29 Figure 13 (left) shows the correlation between the two He isotopes. Despite the general good

30 correlation between them, ^3He is clearly enriched in samples of fumarole gases in volcanic areas,

31 as expected. The R/Ra values plotted versus the respective ^3He contents (Figure 13, right),

32 however, show no strong correlation between the two parameters, especially for dissolved gas

33 samples. This is explained by massive input of ^4He constantly produced by radioactive decay in

34 the crust. This isotope, therefore, accumulates in "old" gases, typically associated with long-lasting

35 water circulation into the Mesozoic limestone and emerging as thermal springs prevalently at low

36 topography at the edges of the coastal outcropping areas. In any case, R/Ra values higher than

37 2.0 were found in samples from volcanic fumaroles and the highest values measured were slightly

higher than 7.0 (maximum R/Ra = 7.32 at Pantelleria Island; Parello et al., 2000). These values are very close to those typical of a MORB-type source (8.0 ± 1.0 Ra, according to Gautheron and Moreira, 2002), which once more testifies the marked influence of magmatic/mantle fluids in the development of geothermal conditions in southern Italy.

11. Geothermometry

Brief notes on the geothermometric significance of data are presented in this paragraph with the aim of helping and reinforcing the geothermal assessment of individual areas in Southern Italy.

By following the approach of Giggenbach (1986; 1988) we show in Fig. 14 its popular K-Na-Mg ternary diagram applied to the springs and fumaroles data with temperature > 25 °C only, divided in two groups: <50 °C and >50 °C, respectively. The diagram is based on the assumption that, in a hydrothermal system of average crustal composition, the K/Na ratio increases according to the equilibrium between K-feldspar and plagioclase, and Mg is removed during the precipitation of chlorite and muscovite at high temperature, increasing therefore the K/Mg ratio, as a second geothermometer (Giggenbach, 1991). A full equilibrium line is defined with Na, K and Mg concentrations fixed by temperature, whereas the line of rock dissolution represents the natural evolution, over time, of cold groundwater composition at fixed Na/K ratio, typically at very low temperature. The main drawback of this diagram is that: the addition of even small quantities of cold, Mg-rich, shallow, cold waters (mixing) to deep hydrothermal rising fluids, easily shifts the original compositions from the full equilibrium line towards the Mg corner. This shifting actually strongly reduces the possibility of interpretation of springs data in terms of geothermometry, even in places where the composition of fluids produced by geothermal wells is well known (e.g. Mt. Amiata geothermal field in Tuscany; Minissale et al., 1997b).

The diagram applied to all considered samples, including fumarolic condensates, shows that there is only one sample from Pantelleria Island (# 205; data from Gianelli and Grassi, 2001) that lies along the left side of the full equilibrium curve at high temperature (260 °C), and the reason is that this is the only sample reported in the data base coming from a deep geothermal well, and therefore likely "free" from shallow cold contamination or mineral precipitation. On the cold right side of the equilibrium curve there are several samples, mostly emerging from the crystalline rocks of Calabria (#127, 130, 136) and Sardinia (# 217, 226, 215, 216), in areas of normal thermal gradients. They are all characterized by having nitrogen as associated gas phase, and they really represent fully equilibrating, deep circulating solutions. All of them are associated to relevant fault systems both in Sardinia (Angelone et al., 2005) and Calabria regions (Italiano et al., 2010).

As often happens when applying this diagram to potential geothermal areas, there are a lot of samples lying near the Mg corner, and not much can be derived from them in terms of

1 geothermometric interpretation. In these samples, the mixing with Mg-rich shallow components

2 prevails over the deep Mg-depleted hot component. Then, there are also quite a lot of samples

3 located in the partial equilibrium and/or dilution area, and at least one possible regional mixing line

4 can be drawn, suggesting a common deep component at 180°C in many places, including

5 Pantelleria (p), Ischia (i) and Vulcano (Vu) islands, as well as Phlegraean Fields (s). Two more

6 mixing lines are possible, one pointing to 260 °C, including Pantelleria (# 205), Ischia (# 91) and

7 Phlegraean Fields (# 71), and the other to 320 °C for Vulcano (# 185) and Phlegraean Fields (# 64,

8 69), respectively. Finally, the diagram shows several samples (mostly from shallow hot wells) in

9 the Vesuvius aquifer (Ve) and Vulcano Island aquifer (Vu) lying directly on the rock dissolution line.

10 This is, in general, the best indirect indication of a very high, local conductive heat flux. In fact, a

11 shallow, hot, low salinity, HCO_3 in composition aquifer is likely related to very high secondary

12 conductive heat flow, especially in volcanic areas (Minissale, 2018).

13 As a general comment on this diagram, it seems that all active volcanic areas of Southern

14 Italy have water samples in anomalous positions that suggest high deep temperatures, and that in

15 many places, excluding Calabria and Sardinia regions, there are, possibly in the Mesozoic

16 carbonate reservoir, temperatures around 180°C.

17 A parallel geothermal evaluation to water samples is made using gas compositions in figure

18 15. Again the chosen diagram is one of the several proposed by Giggenbach (1991; 1992; 1993)

19 where the ratio of $log(CH_4/CO_2)$ is plotted versus the $log(H_2/Ar)$. The advantage of representing

20 data with ratios of components is in the fact that ratios are relatively independent by the

21 steam/water ratio, a parameter well known only for samples taken from wells. The diagram is

22 constrained, at temperatures of geothermal interest, by the rock buffer given by the couple

23 Fe^{2+}/Fe^{3+} where the H_2/H_2O ratio ($R_H=log(fH_2/fH_2O$ where f stands for fugacity) is assumed to be

24 independent by temperature and fixed at a value of -2.8 (Giggenbach, 1987). The equilibrium

25 curve, at boiling condition, limits a "*two phase*" area where liquid and vapour phases are

26 coexisting. The large area between the boiling line and the gas compositions constrained by the

27 lower temperature buffer *calcite-anhydrite*, gives an idea of: *i)* how samples are far from the

28 equilibrium line in oxidizing conditions (H_2 converted to H_2O) and/or *ii)* how much is the addition of

29 "shallow" biogenic CH_4 not deriving from the equilibrium $CO_2+H_2=CH_4+H_2O$. Actually, the iso-

30 temperature lines shown in the diagram represent the relative proportions of H_2, CO_2, CH_4 and Ar

31 of the latter reaction at different R_H values.

32 As seen from the figure, there are only few samples taken from fumaroles (# 122, 215, 217,

33 228 and 232) along the equilibrium line and the two phases area. All the remaining samples, either

34 taken from springs, wells, mofettes and fumaroles, including all the fumaroles from the Etna

35 volcano, plot far from the equilibrium line. It is noteworthy to note, that, although out of equilibrium,

36 most fumaroles are located to the right of the 250 °C isoline, somehow corroborating what shown

37 in Fig. 14 for waters, that the geothermal potential of all volcanic areas (excluding the Alban Hills,

Roccamonfina and the Vulture volcanoes) is very high. There are gas samples from springs and mofettes, including those from the geothermal areas of Latium (*e.g.:* # 12, 20, 26, 32, etc) that, although far from the equilibrium line, cluster around the 200 °C isocontour line, and that this is, again, somehow paralleled with the 180 °C line of figure 20 for water samples.

12. Isodistribution maps of: Pco$_2$(*p*CO$_2$) in liquid phase, CO$_2$ concentration and δ^{13}C of CO$_2$ in gas phase, total He and R/Ra in gas phase

As mentioned, CO$_2$ is a gas of relevant presence in Central and Southern Italy, whose origin and occurrence has been studied by several authors (Chiodini e al., 1995; 2004; Minissale, 1991b; 2004 and references therein). At the top of figure 16 is shown the isodistribution map of this component (in % by vol.) in the gas emissions and/or in the gas phase associated with springs (both hot and cold), from which is evident that the Roman and the Neapolitan volcanic areas and the volcanic areas of Sicily (Etna and Iblean Mts.) have strong and wide CO$_2$ anomalies. Such CO$_2$ anomalies encompass the volcanic areas and certainly derive from the dissolution of the buried Mesozoic limestone (Panichi and Tongiorgi, 1976), being the isotopic composition of carbon often >-3.0 δ°/$_{\infty}$ PDB (Fig. 16, centre) clearly overlapping the anomalous areas of CO$_2$ concentration. The calculated Pco$_2$ in springs (Fig. 16, bottom), no matter if cold, warm or hot, again overlaps the same areas, a further evidence of the anomalous emission of CO$_2$ Italy as already reported in the literature (e.g. Rogie et al., 2001). Certainly, the presence of active hydrothermal systems makes a primary role in the degassing and lateral diffusion inside and expulsion outside the regional carbonate reservoir, with strong and focused emissions along faults. For example, the Mefite d'Ansanto mofette (# *108*) emits about 2,000 t/day of CO$_2$ to the atmosphere (Chiodini et al., 2010). Conversely, Fig. 16 (centre) shows also areas where the δ^{13}C of CO$_2$ is much lower (up to <-20.0 °/$_{\infty}$ PDB) than typical hydrothermal values (*e.g.:* in Calabria) as suggested also by the CO$_2$-δ^{13}C in CO$_2$ diagram of figure 11. The reason is that, in southern (and central) Italy, CO$_2$ may also form by the alteration of organic material embedded in Neogene sediments above the Mesozoic limestone (Marini and Chiodini, 1994; Minissale et al., 1997a) and/or because of depletion of carbon-13 in multiple step phases of precipitation and re-dissolution of calcite in veins or fracture during the motion from the hydrothermal systems to the surface (Minissale et al., 2002b). Figure 11 also suggests that there are several samples in the δ^{13}C range of CO$_2$ rising from the mantle (-8.0< δ^{13}C<-4.0; Rollison, 1993) whose values do not differ much from the ratio of atmospheric CO$_2$, as a result of equilibrium after long term Earth degassing. In this range there are several fumaroles from the quiescent volcanoes of Pantelleria Island (*e.g.:* # 228, 232) in the Sicily channel, and Ischia Island (*e.g.:* # 131) in the Neapolitan area, but most of all in the inactive Vulture volcano (*e.g.:* # 139) or the Logudoro basaltic area in northern Sardinia (# 236).

As regards the isodistribution map of the ^{3}He/^{4}He ratio, figure 17 (bottom) shows the very anomalous cases of Etna, Iblei Mts and Vulture volcanoes, characterized by strong "*intra-*

continent" mantle degassing. Indeed, the lavas produced by these volcanoes are quite primitive intraplate basalts. This list must include also the Pantelleria *rifting* volcano and the Aeolian Arc, both with abundant mantle degassing. On moving northwards in the Neapolitan and Roman volcanic areas, there is an increase in crustal contamination in the mantle-derived magma, as revealed by the increase of the $^{87}Sr/^{86}Sr$ ratio (Polyak et al., 1979), with a contemporary decrease of the $^3He/^4He$ ratio. The same correlation was later proposed by Tedesco (1997), Martelli et al. (2004) and Frezzotti et al. (2009) who suggested, generically, a northward increased assimilation and melting of crust into the Tyrrhenian mantle. The crustal material comes from subducted slabs rich in carbonate rocks from the Adriatic (Adria)-Ionian (African) plates .

By comparing the isodistribution map of total He in the gas phase (Fig. 17, top) with the respective $^3He/^4He$ ratios (Fig. 17, bottom), the results shown in the diagram of figure 13 are more clear from a territorial point of view. There is apparently more crustal radiogenic helium-4 on moving towards Calabria, but this is not supported neither by a similar decrease in the total CO_2 emission nor by a positive isotopic shift of $\delta^{13}C$ of carbon in CO_2. (Fig. 16). Being helium-4 decoupled (or diluted) by hydrothermal CO_2, it is difficult to ascertain if the decarbonation of limestone occurs in a subducted slab, as suggested by Minissale (1991b) and Frezzotti et al., (2009), or at a much shallower crustal depth, as originally proposed by Panichi and Tongiorgi (1976). What is relevant, from a geothermal point of view, is that the northern geothermal fields of Latium are located in areas where the $^3He/^4He$ ratio is always <1.5 Ra, but where also crustal helium-4 is apparently low, because of the dilution by hydrothermal CO_2. By putting these observation together it is possible to affirm that in the Latium area there is no transpressive fault that is deep enough to reach the mantle, or, if any, it is sealed. Furthermore, it is reasonable that the local crust is likely characterized by granitization at depth, like in northern Tuscany (Boccaletti et al., 1997), and that the anomalies of CO_2 are produced at shallow depth, inside the Mesozoic limestones.

13. Conclusive remarks

The strong dynamics of the mantle at the boundary between the African and the Eurasian continental plates, especially at the eastern and southern edges of the Tyrrhenian Sea, is characterized by: subduction, extension, active volcanism, strong heat flux and shallow Moho (Panza and Calcagnile, 1980). The concurrence of all these features make Southern Italy a perfect place for the presence of volcanoes, hydrothermal and geothermal systems. In fact, with the exclusion of the stable cratonic granitic area of Sardinia and the foreland territories of Puglia and southeast Sicily (Iblean platform, Fig. 3), several high enthalpy areas are known to be present. These areas coincide with the Latial volcanic districts (Roman Magmatic Province), active volcanoes around Naples (including Ischia Island and Phlegraean Fields) and with most of Sicilian volcanic islands (including those in the Channel of Sicily).

The contemporary presence of shallow magma chambers and of a regional high permeable carbonate reservoir surrounding them, the latter being in many places several km thick (Pescatore and Ortolani, 1973), is the ultimate reason for the presence of a large number of thermal springs (additional material, table 1) and of hydrothermal discharges including active and fossil travertine deposits. These occur both on-shore and off-shore, the latter especially in the southern border of the Tyrrhenian Sea (Lupton et al., 2011).

Boiling fumaroles, with gas emissions at atmospheric pressure, are present at Stromboli, Ischia, Vesuvius, Lipari and Pantelleria Islands; superheated fumaroles are present at Vulcano Island and occasionally also at Etna summit crater(s). A steam-saturated (T° = 160 °C) fumarole is permanently present at the Solfatara volcano in the Phlegraean Fields, 15 km north of Naples, which likely represents the surface expression of a shallow vapor-dominated system at the maximum enthalpic point (Cioni et al., 1984). These volcanic areas are evidently places of strong geothermal potential but, although deep hot wells have been drilled there at several places, a serious geothermal development plan has been achieved yet.

Some inactive and quiescent volcanoes, such as the Sabatini Mts (Cesano in Fig. 4) and Vulsini Mts volcaninc districts, and Alban Hills volcanoes (last eruption 35 ka ago; Fornaseri, 1985), located north and south of Rome, respectively, Roccamonfina (last eruption 50 ka; Radicati di Brozolo et al., 1988) or Vulture (140 ka; Capaldi et al., 1985) in the Apennines (Fig. 3), all have several CO_2 emission sites and cold natural sparkling mineral waters outpouring in their surroundings. In these places, geothermal exploration is still in its infancy, and it needs more investigations in the future, although deep temperature values from geothermometers in those areas are not promising. In fact, the two geothermometric diagrams shown in figure 14 and figure 15 for waters and gases, respectively, do not suggest any anomalous temperature for samples from these areas, nor of the occurrence of high enthalpy fluids at shallow depth.

If lower enthalpy fluids are considered, then the entire southern Italy including Sardinia (Logudoro volcanic area), with the only possible exclusion of Calabria, have high geothermal potential, as recently demonstrated for western Sicily (Montanari et al., 2017). In fact, although Mesozoic limestones are a preferential way for the infiltration of cold rain water through their outcrops, once in buried condition they allow a fast rise of fluids from convective systems residing deep into the often thick (several kilometres) Mesozoic platforms.

Conversely, limestones also act as reservoirs for CO_2 formed inside the hydrothermal systems. This gas can exsolve and expand laterally in those places where the carbonate reservoir is covered by impermeable material, even moving far away from the hydrothermal systems themselves. In these cases, CO_2 is favoured by the strong regional continuity of the Mesozoic limestone series and it may naturally dilute the crustal ^4He formed. Therefore, low values of the total He/CO_2 ratio in the gas phase, especially when associated to occurrence of "*regional*" thermal springs emerging at the feet of the regional limestone reservoir, can be a good indication of

hydrothermal systems nearby. This is certainly true for the Latium and Campania geothermal areas where low He/CO_2 ratios are quite common in gas emissions, but it is less valid for the Sicilian volcanic islands, including Pantelleria, as well as for Etna volcano if their magma chambers are not connected with the Mesozoic limestone where CO_2 may accumulate in huge quantities.

All Sicilian islands certainly have a high geothermal potential, partly already discovered, and most of them could produce geothermal power using small binary power plants, at least for the local consumption. Being the geothermal anomaly associated with those islands likely much larger than the islands themselves, exploration and exploitation of off-shore geothermal resources in the Tyrrhenian Sea and Sicily Channel, although not convenient at present, could be the target of future geothermal projects.

14. Acknowledgements

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16. Figure captions

Fig. 1 - Schematic illustration of a geothermal exploration program with proceeding phases. Credits for pictures and images: Map of geothermal resource of the United States (from Billy, 2009). Photo of the geological outcrop (New York State Museum). 3D geological model *(http://www.pdgm.com/products/skua-gocad/)* Geothermal field development (*http://www.thinkgeoenergy.com/nevada-geothermal-power-reports-on-progress-for-blue-mountain-plant/nevadageothermal_bluemountain_may19/).*

Fig. 2 - Illustrative geological cross section through a conventional geothermal system located along the Central Italy -Tyrrhenian margin, compared with Pco_2(pCO_2) values (expressed both in bar and log bar) in shallow groundwater. Following Doveri et al. (2010), three Pco_2 classes are taken as reference: *i)* highly anomalous, $Pco_2 > 0.18$ bar; *ii)* weakly anomalous, $0.078 < Pco_2 < 0.18$; *iii)* non-anomalous, $Pco_2 < 0.078$ bar.

Fig. 3 - Schematic geological map of Southern Italy showing main tectonic units and approximate location of thermal water and gas emissions.

Fig. 4 - Map of Latium region (east side), Abruzzi and Molise regions (west side) with location of thermal springs, some cold springs and gas emissions. The figure shows, with different colours, the type of main gas phase associated to the water, namely: CO_2-dominated in purple, N_2-dominated in blue, orange if CH_4-dominated.The map also shows outcrops of the regional Mesozoic carbonate reservoir and outcrops of Quaternay volcanics. In italics is the number referring to the gas phase data base.

Fig. 5 - Map of Campania, Puglia and Lucania regions, with location of natural thermal emissions. For the legend see figure 4.

Fig. 6 - Map of Calabria, Sicily and Sardinia regions, with location of natural thermal emissions. For the legend see figure 4.

Fig. 7 - Langelier-Ludwig (1942) diagram for the water samples investigated (mostly springs). Numbers refer to the file of water samples in additional material.

Fig. 8 - HCO_3-SO_4-Cl (left) and (Na+K)-Ca-Mg (right) ternary diagram for the water samples investigated. Numbers refer to the file of water samples in additional material.

Fig. 9 - δD-$\delta^{18}O$ (left) and δD-Cl (right) binary diagrams for the water samples investigated. Numbers refer to the file of water samples in additional material.

Fig. 10 - N_2-CO_2 diagram for the gas samples investigated. Numbers refer to the file of water samples in additional material.

Fig. 11 - Diagrams of CO_2 vs. $\delta^{13}C$ of carbon in CO_2 (top) and $\delta^{13}C$ of carbon in CO_2 gas phase vs. the $\delta^{13}C$ of carbon in dissolved inorganic carbon (D.I.C.) of the associated water phase (bottom), for the gas samples investigated. Numbers refer to the file of water samples in additional material.

1 **Fig. 12** - Plot of $\delta^{13}C$ of carbon in CO_2 gas phase vs. the $\delta^{13}C$ of carbon CH_4 (Giggenbach, 1982).

2 Numbers refer to the file of water samples in additional material.

3 **Fig. 13** - Plot of ^3He vs ^4He (left) and ^3He vs. R/Ra (right) for the gas samples investigated.

4 Numbers refer to the file of water samples in additional material.

5 **Fig**. **14** - K-Mg-Na ternary diagram (Giggenbach, 1988) for the water samples investigated.

6 Numbers refer to the file of water samples in additional material.

7 **Fig**. **15** - Plot of log(xH$_2$/xAr) vs. log(xCH$_4$/xCO$_2$) (Giggenbach, 1993) for the gas samples

8 investigated. See text.

9 **Fig. 16** - Isodistribution maps of: *i)* CO_2 concentration in the gas phase (top); *ii)* $\delta^{13}C$ of carbon in

10 CO_2 in the gas phase (middle); *iii)* calculated (Parkhurst D. and Appelo, 1999) pCO$_2$ [as -

11 log(pCO$_2$Pco$_2$)] in the water samples. Uncoloured areas of eastern and south-eastern Italy and

12 Sardinia island are due to insufficient concentration of CO_2 or low number of samples.

13 **Fig**. **17** - Isodistribution maps of: *i)* concentration of total helium in the gas phase (top); *ii)* $^3He/^4He$

14 (as R/Ra) ratio (bottom), prevalently measured in the free gas phase.

17. Table captions (additional material)

Table 1 - Chemical and isotopic analyses of thermal emissions in liquid phase of Southern Italy; ts= thermal spring; tsg=thermal spring with gas; sg=spring with gas; twg=thermal well with gas; wg=well with gas; mv=mud volcano; mo=mofette; fu=fumarole).

Table 2 - Chemical and isotopic analyses of gas emissions in gas phase of Southern Italy; ts= thermal spring; tsg=thermal spring with gas; sg=spring with gas; twg=thermal well with gas; wg=well with gas; mv=mud volcano; mo=mofette; fu=fumarole).
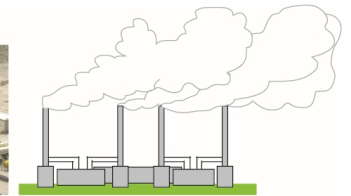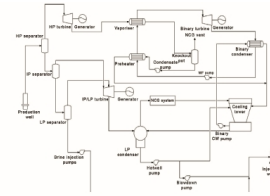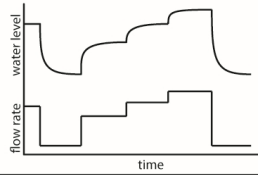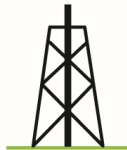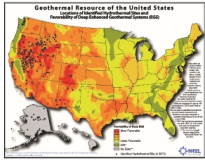
GEOTHERMAL FAVOURABILITY MAPPING → PRELIMINARY SURVEY → EXPLORATION & DRILLING → TEST DRILLING → PROJECT REVIEW & PLANNIG → FIELD DEVELOPMENT → POWER PLANT CONSTRUCTION / COMMISSIONING & OPERATION

P_{CO_2}

bar	log (bar)
1	0
0.18	-0.75
0.078	-1.75

HIGHLY ANOMALOUS

WEAKLY ANOMALOUS

NON-ANOMALOUS

areal extension
of the geothermal system

CO_2 soil
degassing

meters
(bsl) 0

CO_2 satured

groundwaters

1500

3000
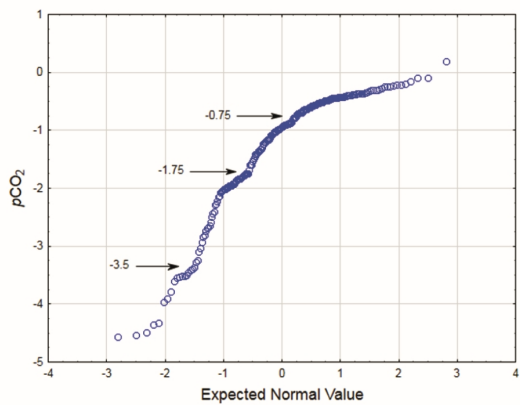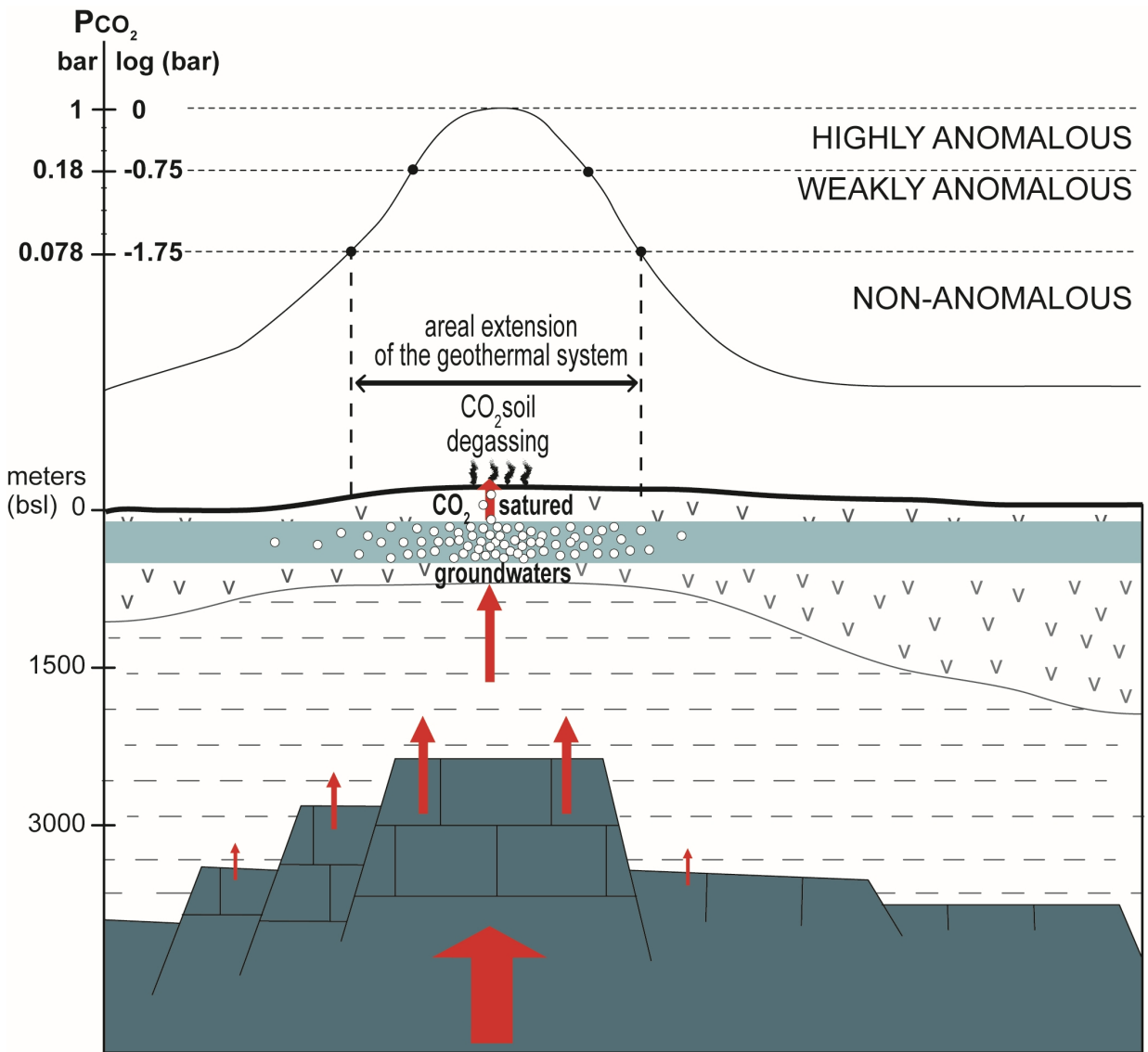
volcanic cover
clayish cover
} CAP-ROCK

carbonatic geothermal RESERVOIR

shallow aquifer

dissolved CO_2

CO_2-rich geothermal fluid
(the arrow size is proportional
to the degassing rate)

pCO_2

-0.75

-1.75

-3.5

Expected Normal Value

Fig. 3 - Schematic geological map of Southern Italy showing main tectonic units and approximate location of thermal water and gas emissions.
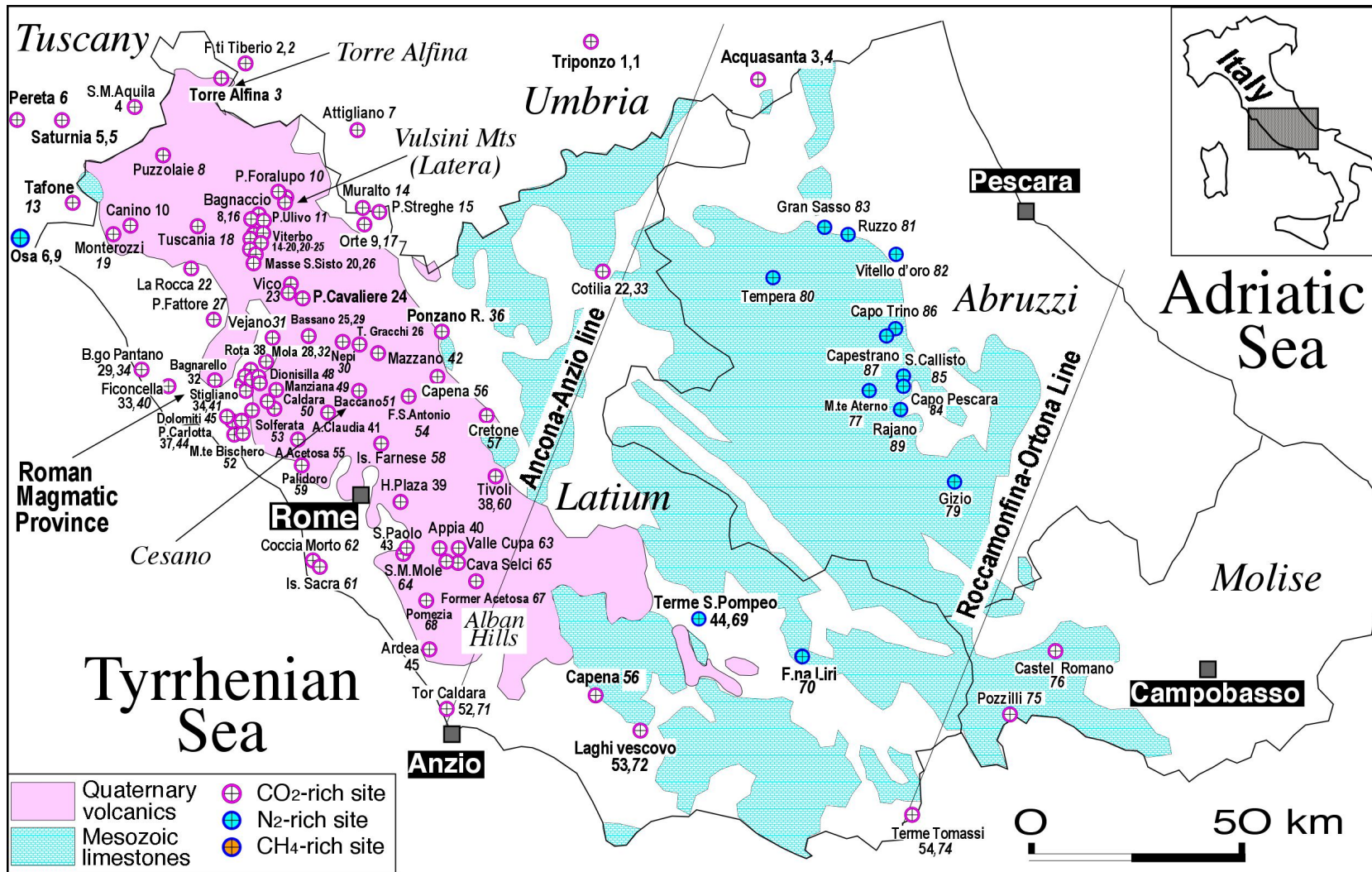
Fig. 4 - Map of Latium region (east side), Abruzzi and Molise regions (west side) with location of thermal springs, some cold springs and gas emissions. The figure shows, with different colours, the type of main gas phase associated to the water, namely: CO_2-dominated in purple, N_2-dominated in blue, orange if CH_4-dominated. The map also shows outcrops of the regional Mesozoic carbonate reservoir and outcrops of Quaternay volcanics. In italics is the number referring to the gas phase data base.
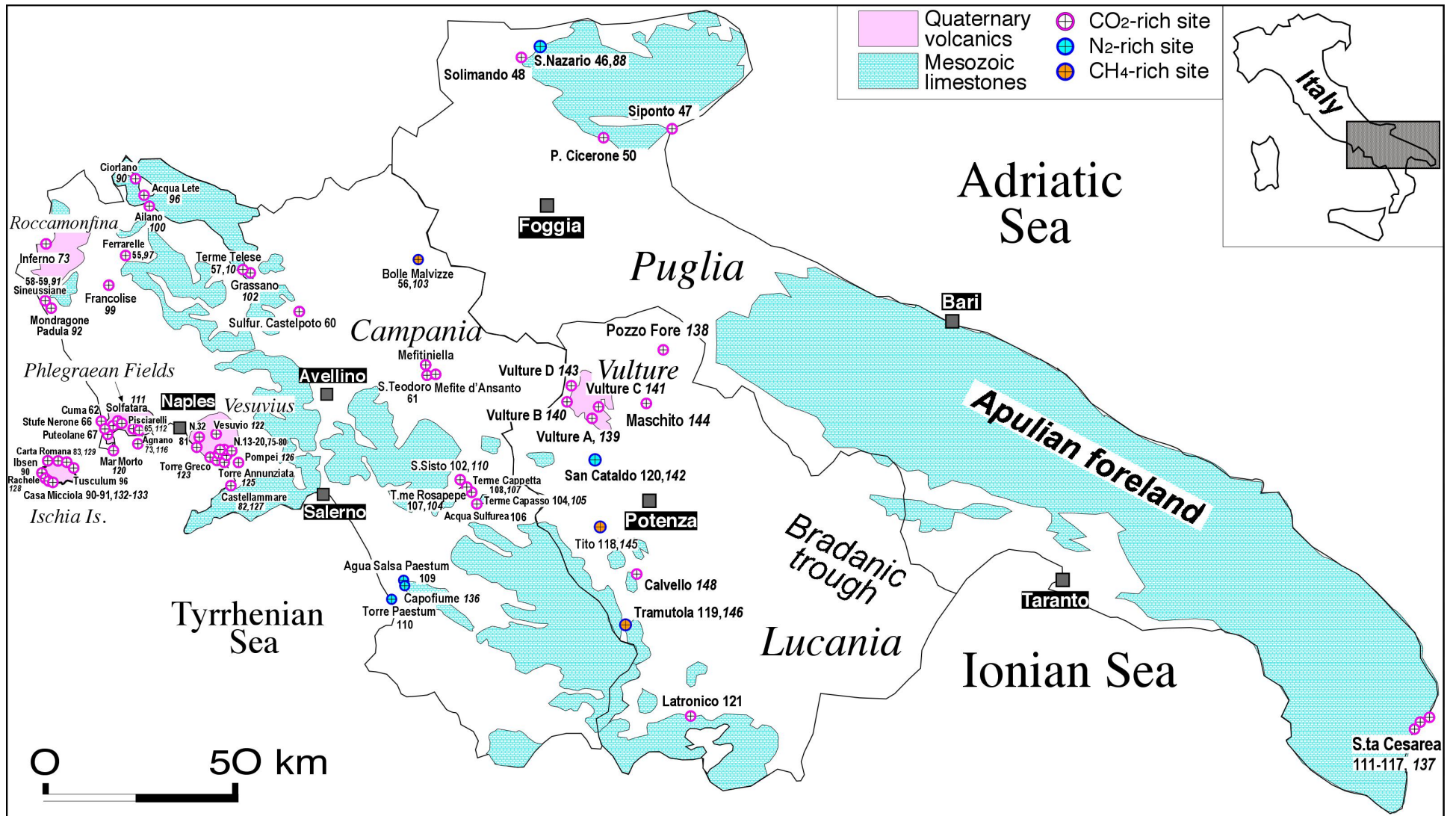
Quaternary volcanics
Mesozoic limestones
⊕ CO_2-rich site
⊕ N_2-rich site
⊕ CH_4-rich site

Italy

Adriatic Sea

S.Nazario 46,*88*
Solimando 48
Siponto 47
P. Cicerone 50

Ciorlano *90*
Acqua Lete *96*
Ailano *100*
Roccamonfina
Ferrarelle *55,97*
Inferno *73*
Terme Telese *57,10*
58-59,*91* Sineussiane
Francolise *99*
Grassano *102*
Mondragone Padula *92*
Sulfur. Castelpoto 60
Bolle Malvizze 56,*103*

Campania

Puglia

Bari

Foggia

Phlegraean Fields
Mefitiniella

Pozzo Fore *138*

Avellino
S.Teodoro Mefite d'Ansanto 61
Vulture D *143*
Vulture C *141*

Vulture

Naples *Vesuvius*
Cuma 62 Solfatara *111*
Stufe Nerone 66 Pisciarelli
Puteolane 67 *65,112* N.32 Vesuvio *122*
Agnano *81*
Carta Romana 83,*129* *73,116* N.13-20,*75-80*
Ibsen *90* Mar Morto Pompei *126*
Rachele *128* Torre Greco *123*
Casa Micciola 90-91,*132-133* Tusculum 96 *120* Torre Annunziata *125*
Ischia Is. Castellammare *82,127*

Vulture B *140*
Vulture A, *139*
Maschito *144*

S.Sisto 102,*110*
Terme Cappetta 108,*107*
T.me Rosapepe 107,*104* Terme Capasso 104,*105*
Acqua Sulfurea 106

San Cataldo 120,*142*

Potenza
Tito 118,*145*

Salerno

Agua Salsa Paestum 109
Capofiume *136*
Torre Paestum 110

Calvello *148*

Tramutola 119,*146*

Bradanic trough

Apulian foreland

Taranto

Tyrrhenian Sea

Lucania

Ionian Sea

Latronico 121

S.ta Cesarea 111-117, *137*

50 km

Fig. 5 - Map of Campania, Puglia and Lucania regions, with location of natural thermal emissions. For the legend see figure 4.

Fig. 6 - Map of Calabria, Sicily and Sardinia regions, with location of natural thermal emissions. For the legend see figure 4.
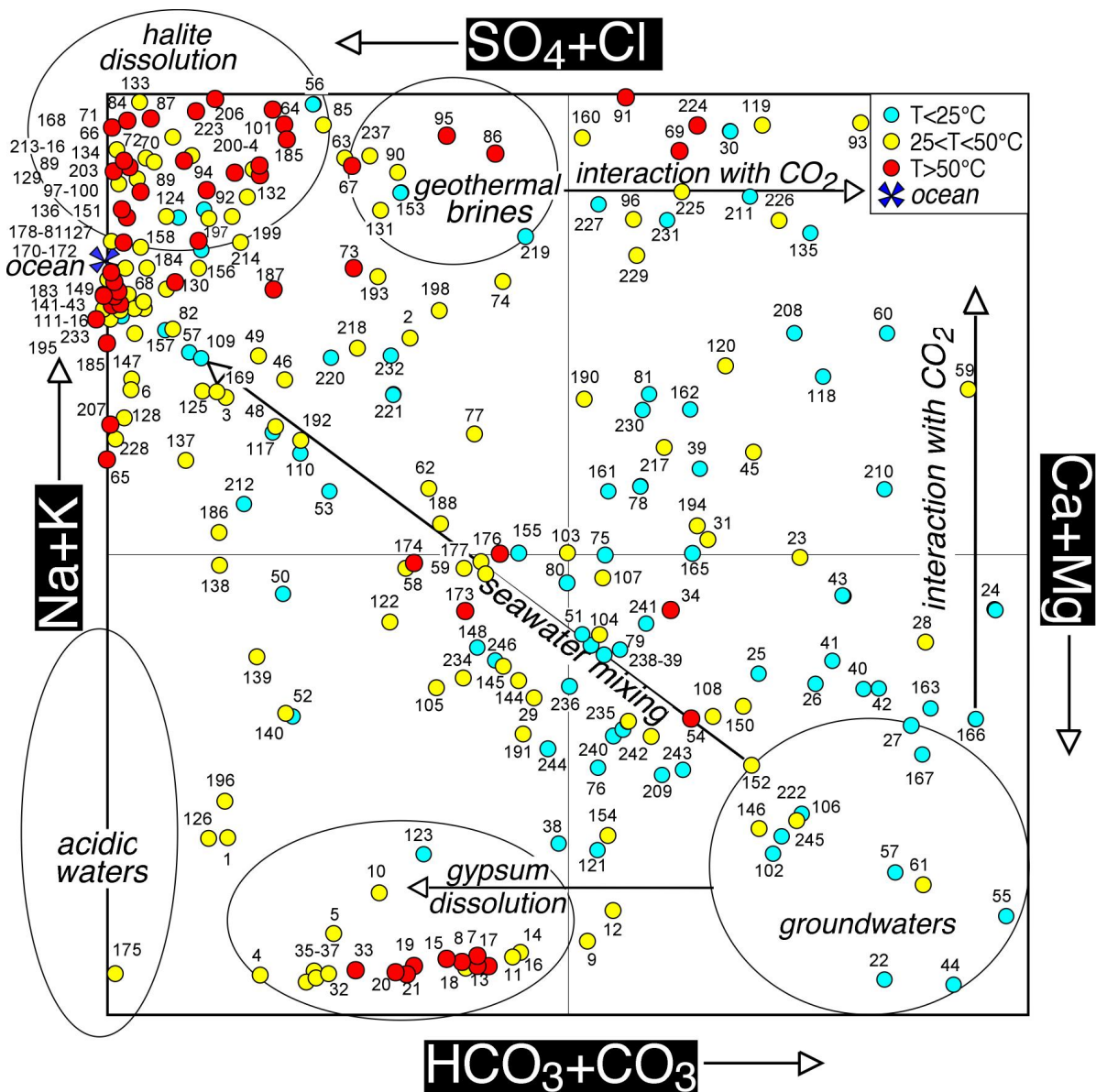
Fig. 7 - Langelier-Ludwig (1942) diagram for the water samples investigated (mostly springs). Numbers refer to the file of water samples in additional material.
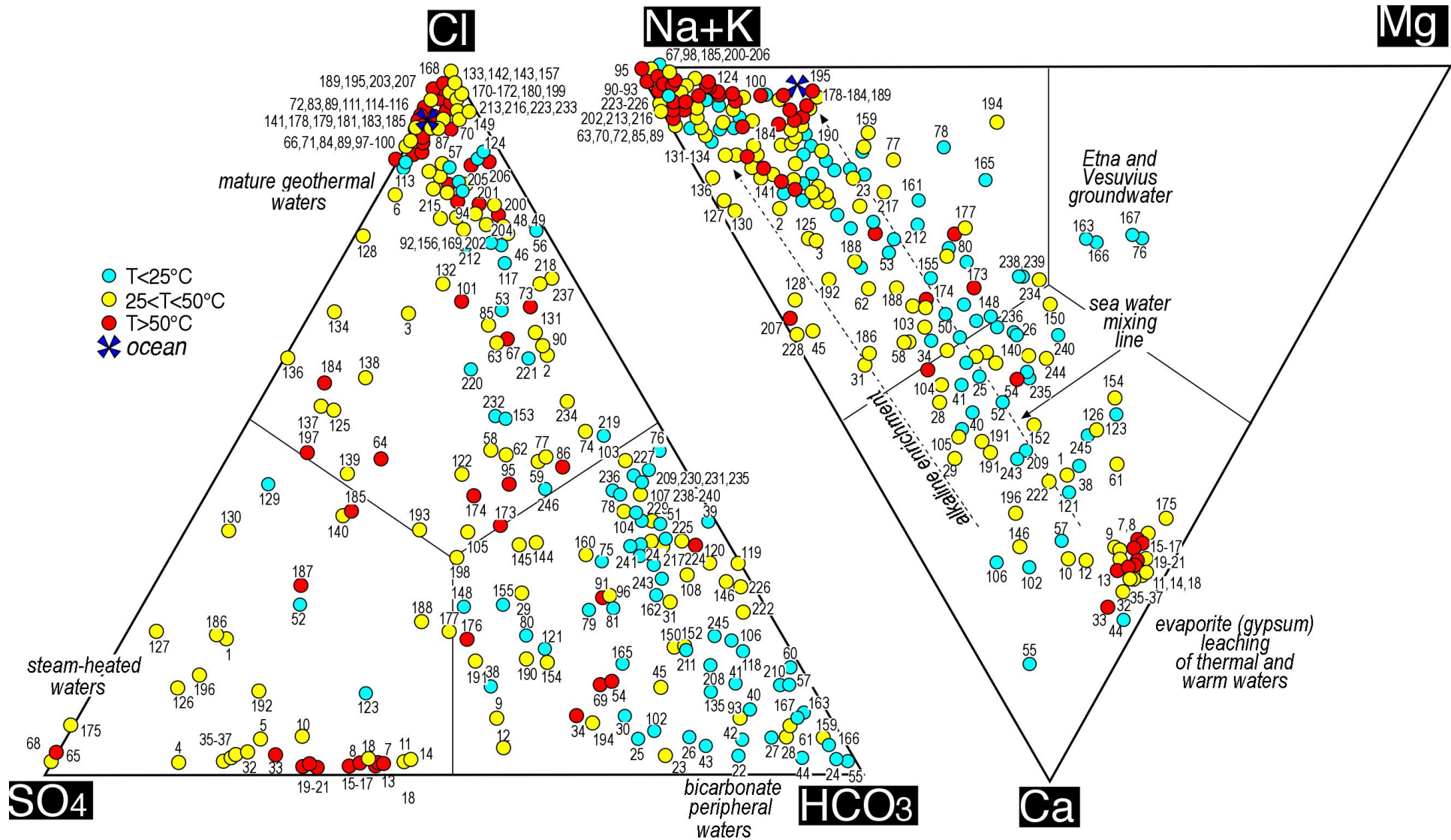
Fig. 8 - HCO₃-SO₄-Cl (left) and (Na+K)-Ca-Mg (right) ternary diagram for the water samples investigated. Numbers refer to the file of water samples in additional material
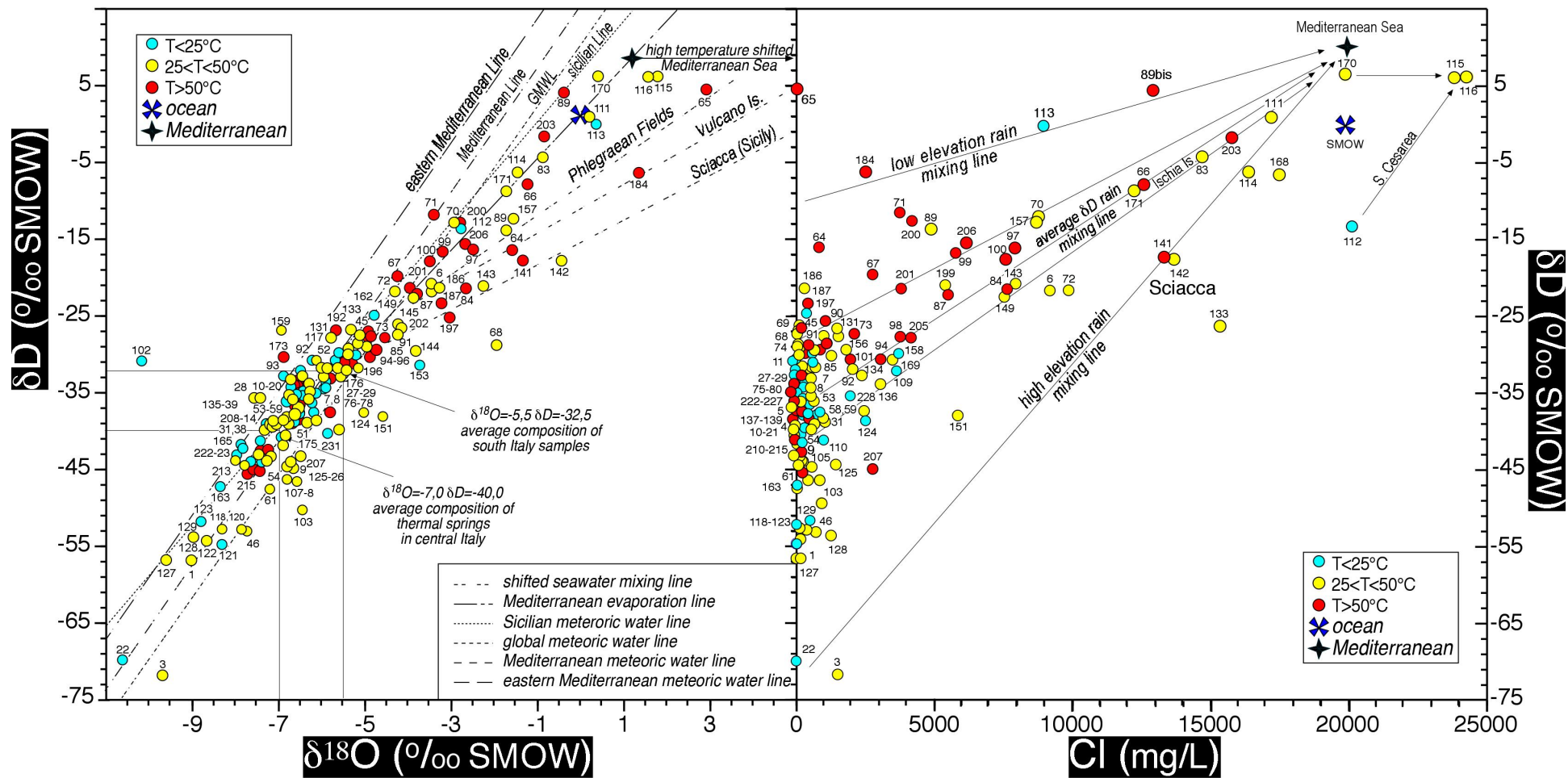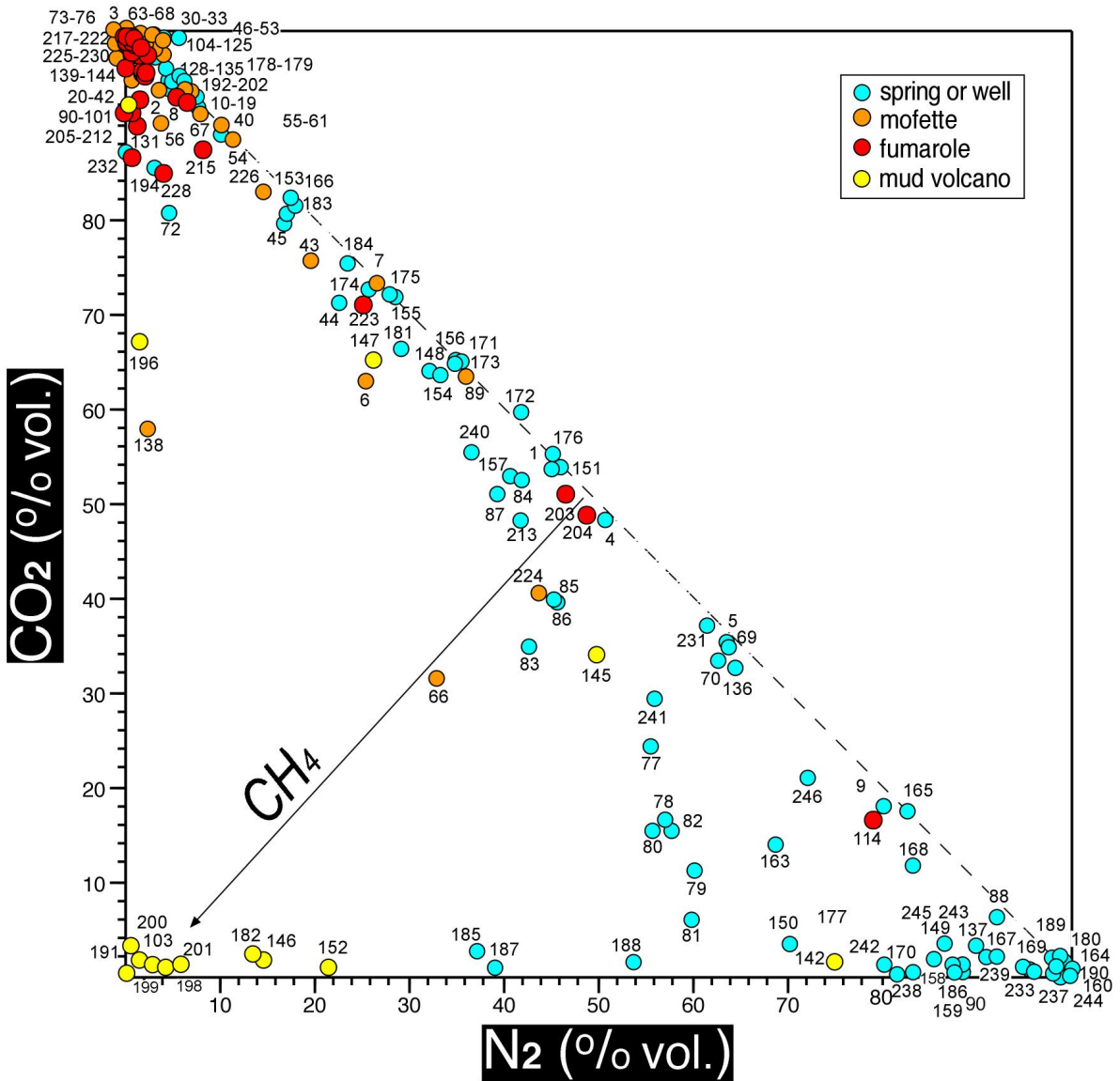
Fig. 9 - δD-δ^{18}O (left) and δD-Cl (right) binary diagrams for the water samples investigated. Numbers refer to the file of water samples in additional material.

Fig. 10 - N₂-CO₂ diagram for the gas samples investigated. Numbers refer to the file of water samples in additional material.

Fig. 11 - Diagrams of CO_2 vs. $\delta^{13}C$ of carbon in CO_2 (top) and $\delta^{13}C$ of carbon in CO_2 gas phase vs. the $\delta^{13}C$ of carbon in dissolved inorganic carbon (D.I.C.) of the associated water phase (bottom), for the gas samples investigated. Numbers refer to the file of water samples in additional material.

Fig. 12 - Plot of $\delta^{13}C$ of carbon in CO_2 gas phase vs. the $\delta^{13}C$ of carbon CH_4 (Giggenbach, 1982). Numbers refer to the file of water samples in additional material.
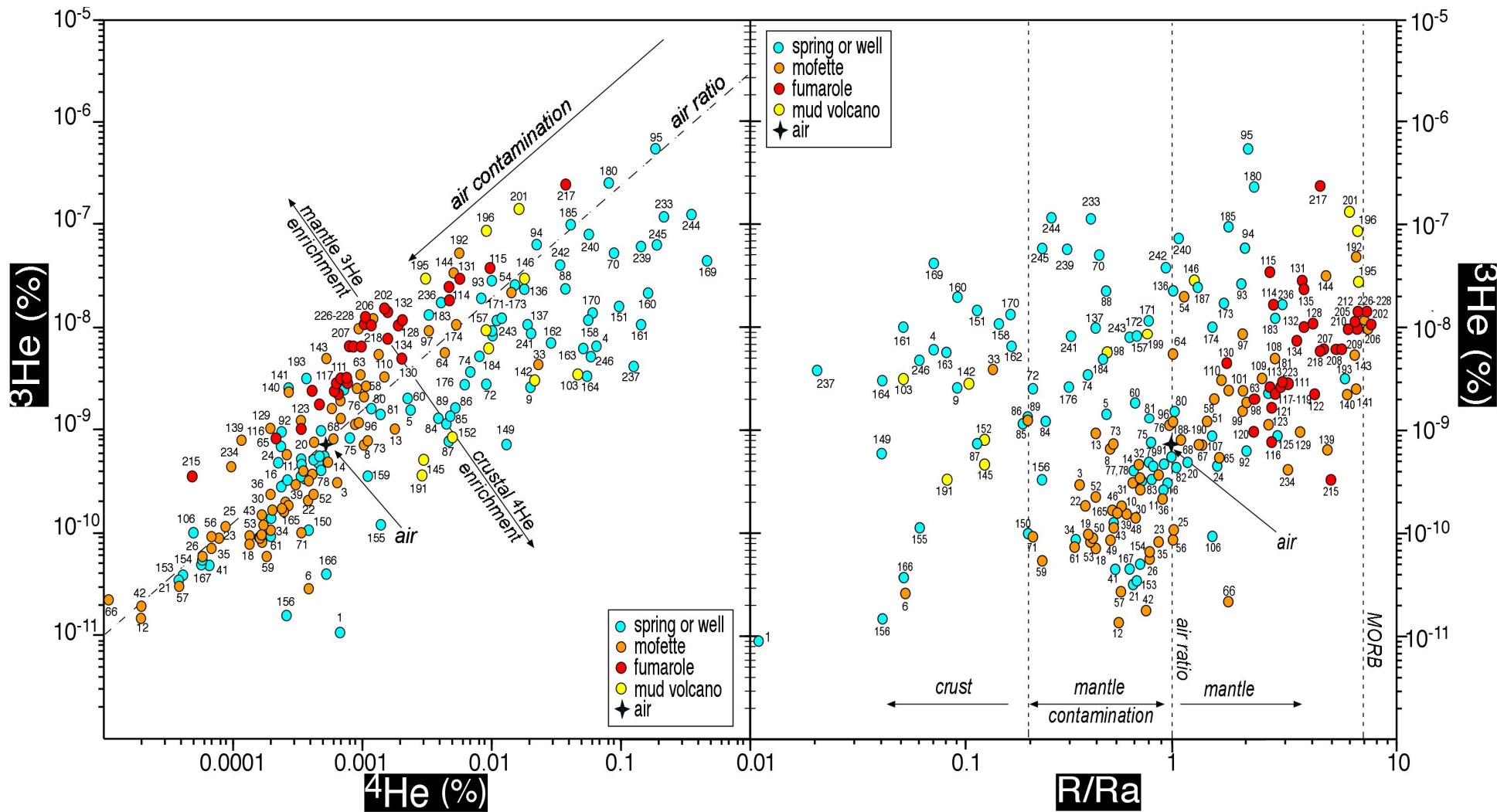
Fig. 13 - Plot of ^{3}He vs ^{4}He (left) and ^{3}He vs. R/Ra (right) for the gas samples investigated. Numbers refer to the file of water samples in additional material.
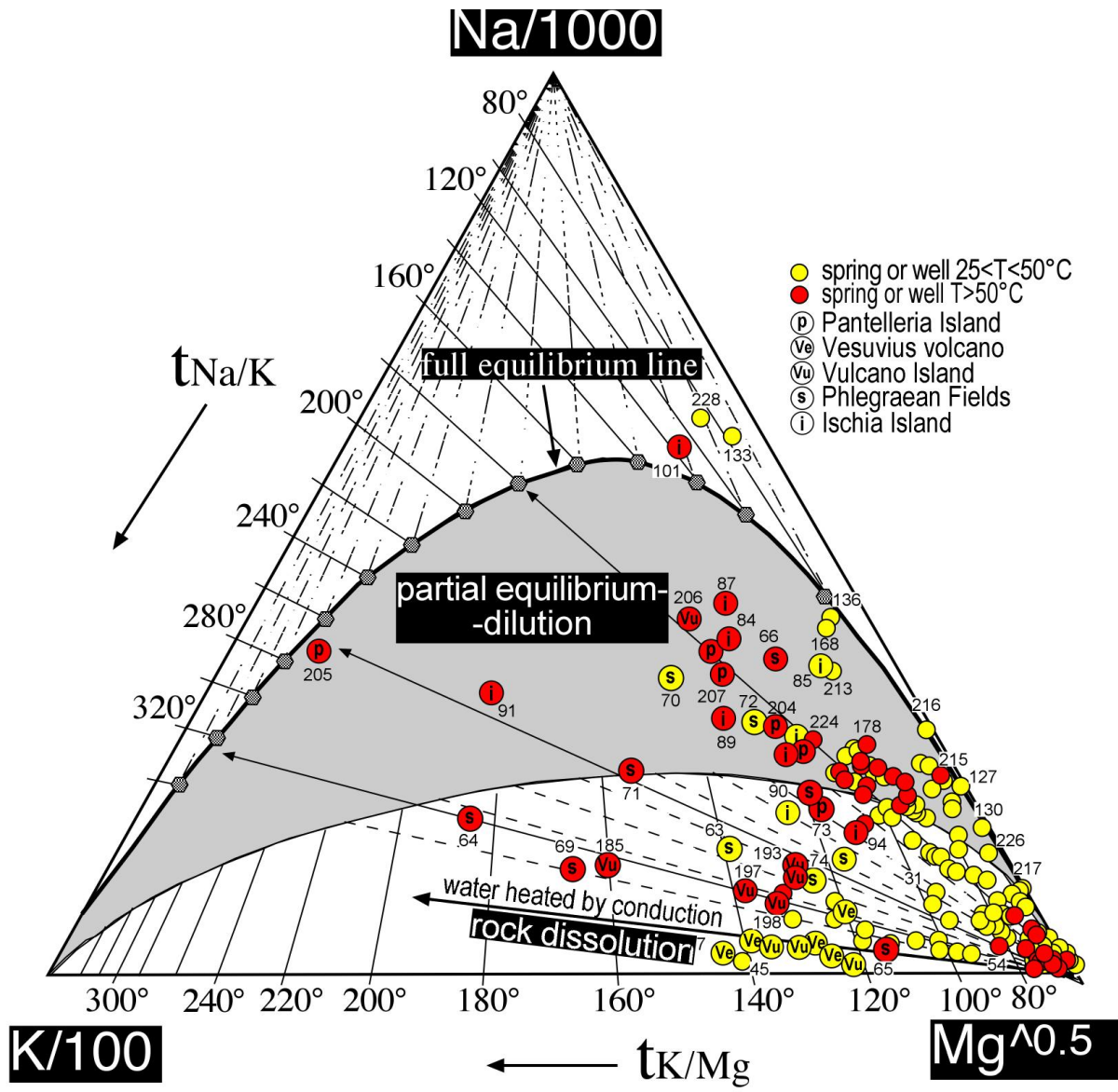
Fig. 14 - K-Mg-Na ternary diagram (Giggenbach, 1988) for the water samples investigated. Numbers refer to the file of water samples in additional material.
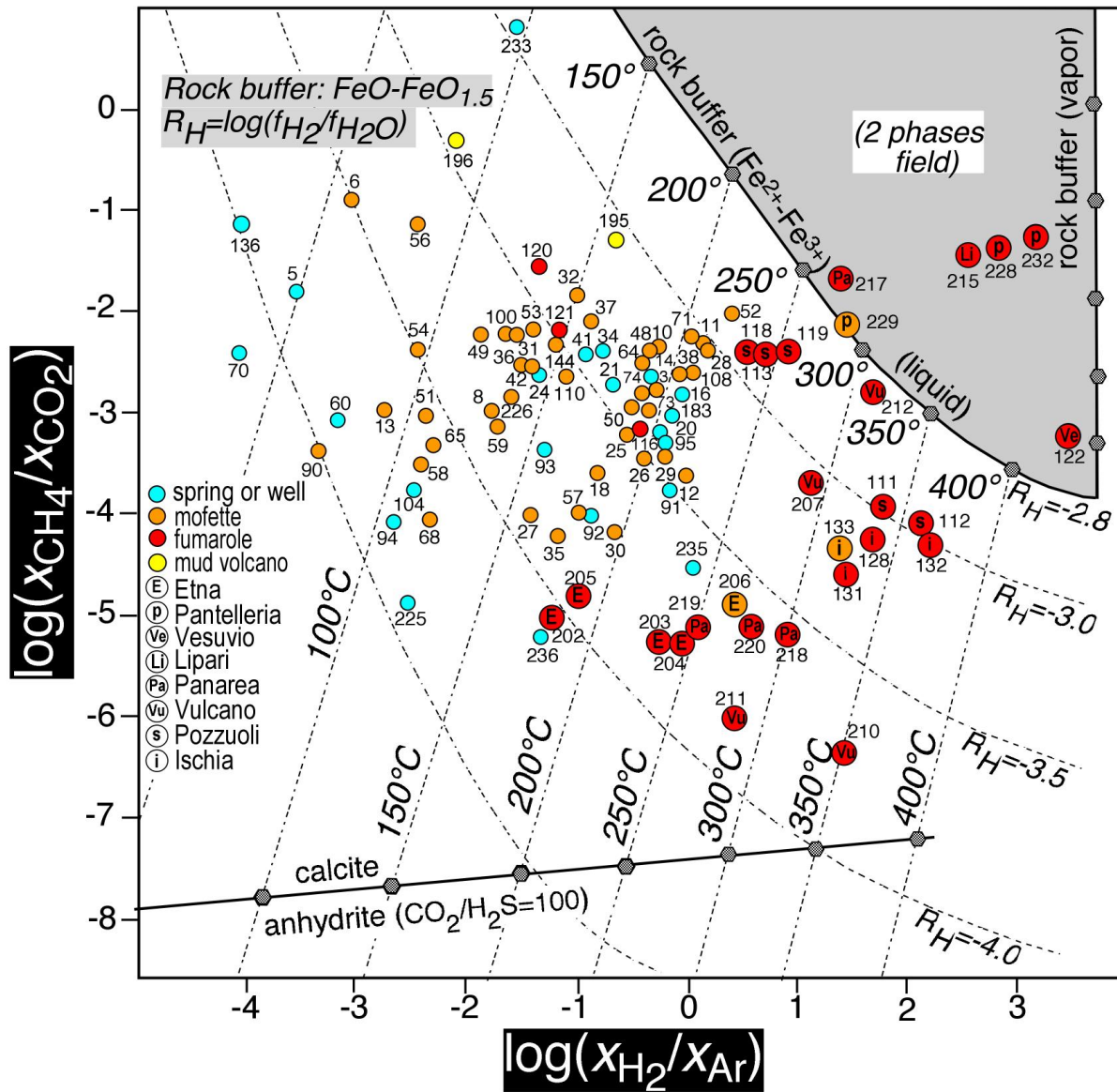
Fig. 15 - Plot of log(xH₂/xAr) vs. log(xCH₄/xCO₂) (Giggenbach, 1993) for the gas samples investigated. See text.
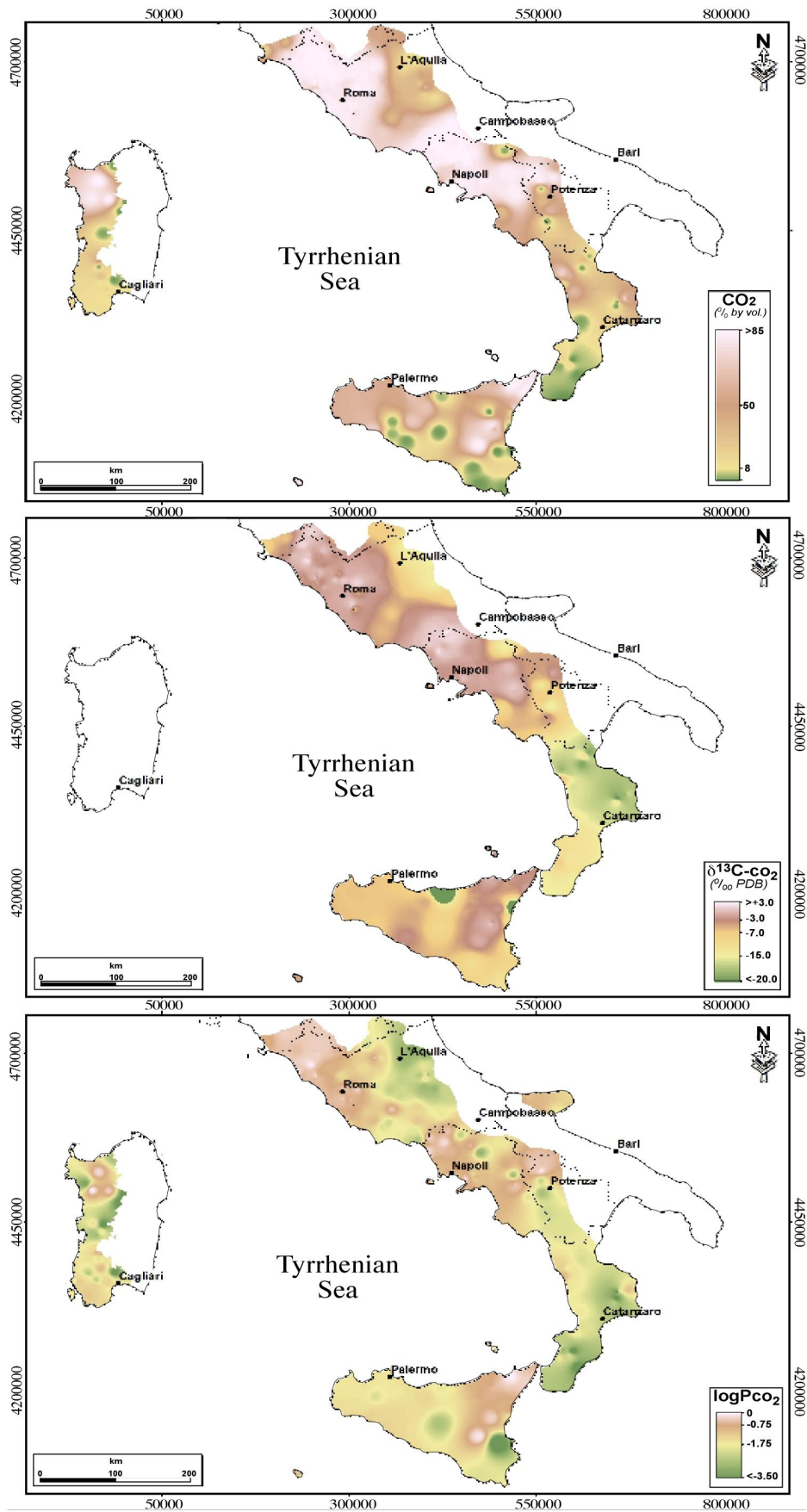
Fig. 16 - Isodistribution maps of: *i)* CO$_2$ concentration in the gas phase (top); *ii)* δ^{13}C of carbon in CO$_2$ in the gas phase (middle); *iii)* calculated (Parkhurst D. and Appelo, 1999) pCO$_2$ [as -log(pCO$_2$Pco$_2$)] in the water samples. Uncoloured areas of eastern and south-eastern Italy and Sardinia island are due to insufficient concentration of CO$_2$ or low number of samples.
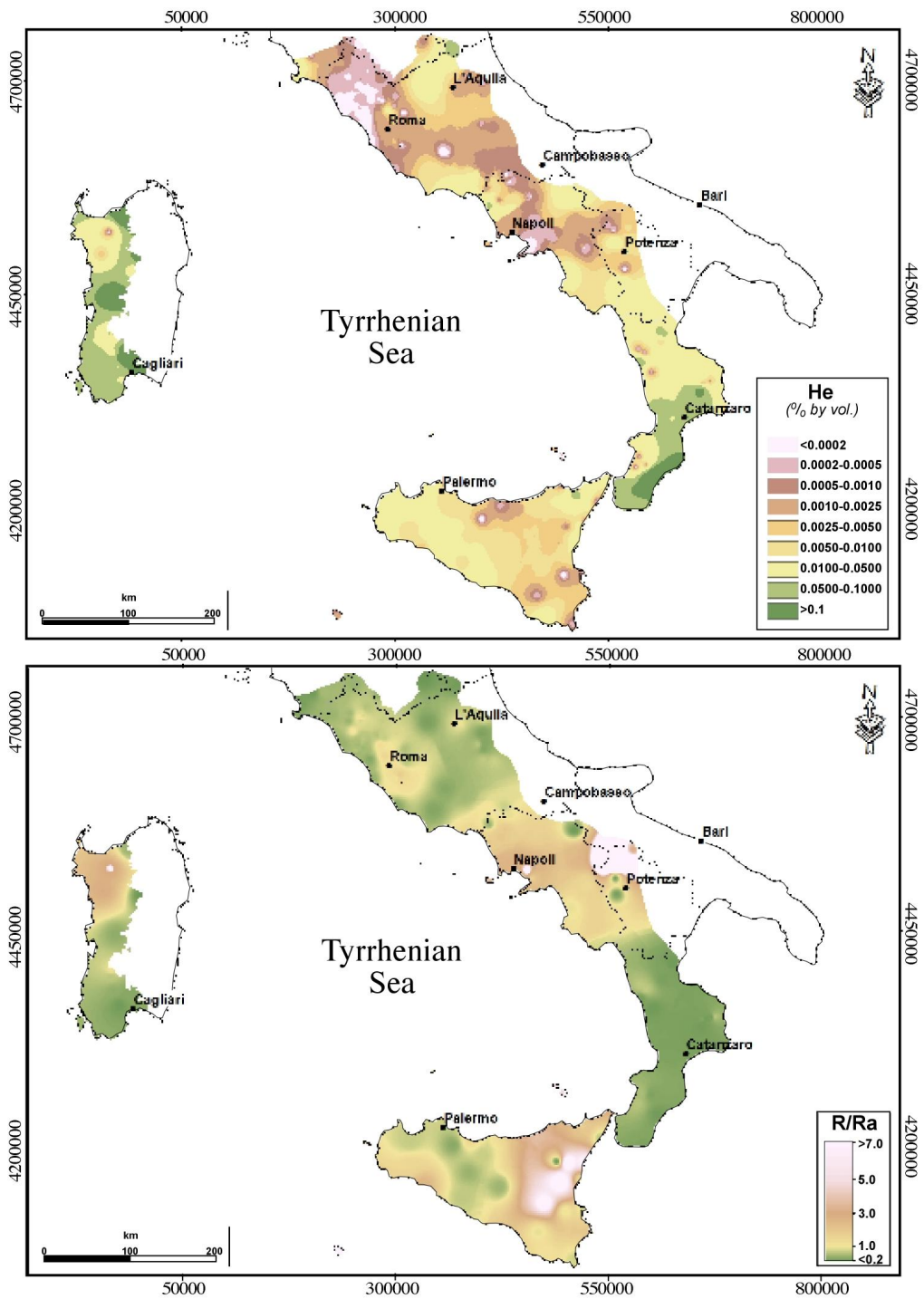
Fig. **17** - Isodistribution maps of: *i)* concentration of total helium in the gas phase (top); *ii)* ^{3}He/^{4}He (as R/Ra) ratio (bottom), prevalently measured in the free gas phase.