The acidic waters in Italy: a brief overview

Le acque acide in Italia: una breve panoramica

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Riassunto: Lo scopo di questo lavoro è quello di fornire una breve panoramica relativa alla geochimica delle acque acide italiane, sia in base alla letteratura esistente che a dati originali. Le acque acide, in Italia come in altre zone del mondo, sono relativamente comuni e associate a vari contesti geologici. A causa delle loro peculiari caratteristiche chimiche, queste acque possono costituire un serio pericolo per gli ecosistemi naturali. Lungo la catena Appenninica, i settori occidentali (interni) della Penisola Italiana sono caratterizzati da un'anomalia del gradiente geotermico che perlopiù coincide con le aree interessate da magmatismo Neogenico-Quaternario ed attuale. Questo spiega la presenza di (i) emissioni di gas e acque termali ricche in CO_2 e, subordinatamente, H_2S, (ii) campi geotermici (es. Larderello e Monte Amiata) e (iii) giacimenti minerari (es. giacimenti a ferro e solfuri misti dell'Isola d'Elba e Colline Metallifere). Le acque acide (a pH ≤5) legate ad aree vulcano-geotermiche sono caratterizzate rispettivamente da temperature all'emergenza mediamente comprese fra 10 e 96 °C e da salinità che vanno da <1 a circa 30 g/L e, in genere, mostrano composizioni chimiche appartenenti alle facies Ca-SO_4, NH_4-SO_4 or Na-Cl. Solitamente, questi fluidi sono associati a "polle gorgoglianti" in virtù dell'interazione di gas di origine profonda con acquiferi superficiali e/o acque meteoriche. Queste acque sono arricchite in metalli pesanti e metalloidi. Valori di concentrazione particolarmente elevati di tali elementi si registrano anche in acque acide di miniera (appartenenti alla categoria delle Acid Mine Drainage l.s. e Acid Rock Drainage), emesse in corrispondenza di distretti minerari oramai in abbandono, prevalentemente situati in Sardegna (non inclusi nel presente lavoro), Toscana ed Alpi nord-occidentali. I valori di pH raggiungono valori sino a 2.08 con concentrazioni variabili di solidi disciolti totali. Da un punto di vista composizionale, le facies dominanti sono Na-SO_4, Ca(Mg)-SO_4 o Mg(Ca)-SO_4, dovute principalmente a processi ossidativi a carico di solfuri polimetallici.

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Abstract: *The present study is aimed at providing a brief overview of the Italian acidic waters based on literature and unpublished data. Acidic waters in Italy, as elsewhere, are relatively common and associated with extremely variable geological settings. Owing to their peculiar features, these waters may seriously affect the environment and the ecosystems.*
Along the Apennine belt, the western and inner sectors of the Italian peninsula record an anomalous geothermal gradient, mostly overlapping with the Neogene-to-present magmatism, that explains the presence of a huge amount of $CO_2(H_2S)$-rich gas and thermal water discharges, geothermal fields (e.g. Larderello and Mt. Amiata) and ore deposits (e.g. Fe- and polymetallic sulfides, e.g. Elba Island and Colline Metallifere). Acidic waters (pH ≤5) from volcanic and geothermal areas show outlet temperatures and Total Dissolved Solids (TDS) from 10 to 96 °C and

<1 to ≈30 g/L, respectively, with a chemical composition usually belonging to the Ca-SO₄, NH₄-SO₄ or Na-Cl facies. Frequently, they are related to bubbling and boiling pools due to the interaction between deep-sourced gases and shallow aquifers or meteoric waters. Concentrations of heavy metals and metalloids are in most cases high. Extremely high contents of metals are also recorded for those acidic waters that characterize the main Italian mining districts, mostly located in Sardinia (not included in the present study), Tuscany and NW Alps, where they are related to Acid Mine Drainage l.s. or Acid Rock Drainage. The pH values are as low as 2.08, with variable TDS concentrations. Compositionally, they are Na-SO₄, Ca(Mg)-SO₄, and/or Mg(Ca)-SO₄ waters, prevalently due to oxidative processes affecting polymetallic sulfides.

Introduction

Although quite widespread worldwide, low pH acidic waters represent a peculiar category of geo-fluids, since they are commonly found in correspondence of tectonically active areas, where their occurrence is thought to be mainly associated with the presence of volcano-hydrothermal systems (e.g. Giggenbach et al. 1990; Hedenquist and Aoki 1991; Marini et al. 2003a; Bienowski et al. 2005; Nordstrom et al. 2009). However, acidic waters are also commonly encountered in dismissed or active structures (e.g. wells and/or tunnels) related to mining districts (Nordstrom and Alpers 1999a-b; Nordstrom 2011) and known as Acid Mine Drainage (AMD), although ore exploitation processes do not necessarily imply the formation of strongly acidic waters (Nordstrom and Alpers 1999 a-b).

Low pH-waters are also considered powerful and predictive tracers for geothermal prospection purposes of unexplored areas, especially when occurring in flat plains with apparently no significant hydrothermal emergences at the surface (Minissale et al. 2013; Minissale 2018).

A more or less remarkable acidification of groundwater can be regarded as a useful seismic precursor to be carefully evaluated along with other hydrogeological (e.g. flow rates) and chemical-physical parameters (such as temperature, Eh, salinity, concentrations of dissolved metals and chemical-isotopic characteristics of the associated gaseous compounds), in the framework of routine monitoring (e.g. Federico et al. 2004; Barberio et al. 2017; Pierotti et al. 2017). Eventually, naturally or anthropogenic-derived acidic fluids can act a strong environmental impact (e.g. Feasby et al. 1991; Nordstrom 2011).

The Italian peninsula is characterized by the occurrence of volcanic-geothermal systems, which host a large variety of hydrothermal manifestations (e.g. Minissale et al. 2004 and references therein), often associated with epithermal ore deposits (e.g. Lattanzi 1999; Tanelli et al. 2001).

The intent of this study is to summarize the most significant geochemical features of the acidic waters discharging from the main Italian volcanic-geothermal and mining areas, with the exception of those occurring in the dismissed mining districts from Sardinia, for which the reader can refer to some

recently published papers (e.g. Lattanzi 1999; Frau 2000; Cidu et al. 2012 and references therein). Consequently, fifteen representative water samples (Fig. 1), related to different areas of Italy, were considered. It is to mention this brief overview does not want to be exhaustive of all the Italian acidic waters since the main aims of this paper are to highlight the importance of these fluids in terms of geochemical processes involved in their formation and their potential environmental impact

Geological and geothermal outlines of the study areas

In the following paragraphs, an overall description of the main geological-geothermal features of different selected areas, whose location is reported in Fig. 1, is provided.

The Larderello-Travale geothermal field

The Larderello-Travale field, located in the inner portion of the Apenninic orogenic belt, is the largest and most important geothermal system in Italy and one of a few superheated geothermal systems in the world, together with "The Geysers" in California (e.g. Romagnoli et al. 2010).

Fig. 1 - Satellite image map of Italy where the location of the selected 15 samples is reported. Symbol Legend: acid mine drainage (green circles), cold bubbling pools or cold gas-charged spring waters (cyan circles), thermal springs/bubbling pools (fuchsia diamonds), steam-heated pools/steam-vents (red triangles).

Fig. 1 - La figura mostra una carta schematica dell'Italia (immagine satellitare) in cui vengono riportate le 15 differenti ubicazioni dei campioni. Legenda: drenaggio acido di miniera (cerchietti verdi), polle gorgoglianti e acque fredde ricche in gas (cerchietti azzurri), sorgenti termali e bubbling pools (rombi fucsia), steam-heated pools/ steam-vents (triangoli rossi).

The area is affected by (i) an anomalous heat flow (more than 1,000 mW/m^2) (Baldi et al. 1995), (ii) a thermal gradient up to 300 °C/km and (iii) the occurrence of thermal springs, acidic and boiling steam-heated pools, mud pools (namely "lagoni") and steam vents (Duchi et al. 1986, 1992), related to the emplacement, during the Mio-Pliocene post-orogenic magmatism, of granitic stocks (3.8 - 1.3 Ma; Villa and Puxeddu 1994; Gianelli and Laurenzi 2001; Dini et al. 2004, 2005) at depth between 3 and 8 km (K-horizon bright spot; Batini et al. 2003, and references therein).

The Larderello-Travale geothermal field is mainly fed by meteoric waters, even though a mixture of thermo-metamorphic and magmatic fluids was also recognized in the reservoir fluids (Minissale 1991b; D'Amore and Bolognesi 1994). This system consists of two different geothermal reservoirs: i) a shallow aquifer (500-1500 m), hosted in the Mesozoic carbonate-evaporite rocks, characterized by temperature (T) and pressure of 220-260 °C and of 30-60 bars, respectively, and ii) a deep aquifer (> 3,000 m) within the Paleozoic metamorphic rocks, with temperature of 300-350 °C and pressure up to 40-70 bars (Barelli et al. 1995c; Bertani et al. 2005). According to Bertani et al. (2016) the current installed capacity in Larderello-Travale field is about 800 MW.

The Mt. Amiata geothermal field and mining district

The area (about 50 km south of Siena) is affected by an anomalous geothermal gradient (ranging from 300 up to 400 °C/km; e.g. Burgassi et al. 1970; Calamai et al. 1970) and high heat fluxes (up to 600 mW/m^2; Baldi et al. 1995), being these features intimately linked to the presence of the Quaternary Mt. Amiata volcano-plutonic system (Gianelli et al. 1988). Here, at depth, a high-enthalpy water-dominated geothermal field is hosted. According to Barelli et al. (2010), the hydrothermal system consists of: i) a shallow reservoir located in the Mesozoic carbonate-evaporite formations at depth of ~1,000 m b.g.l., with temperatures between 150 and ~230 °C and ii) a deeper reservoir, hosted within the metamorphic basement (~3,000 meters b.g.l.), with T ranging from 300 to 360 °C and hydrostatic pressures around 200-250 bars (Batini et al. 2003). As in the Larderello-Travale area, ENEL Green Power Ltd. (The National Italian Electricity Board) operates the geothermoelectric power generation, with an installed capacity of 121 MW (Bertani et al. 2016).

In the past, the Mt. Amiata area was also known for being the fourth most important mercury mining district worldwide, where Sb-Hg ores (e.g. Tanelli 1983; Dini et al. 2005) were exploited since the mid-'800s until 1977, mostly in the Abbadia San Salvatore mining area. In the last decades, several works focused on the environmental issues related to the past mining activities in the area (for further information the reader may refer to, e.g. Rimondi et al. 2012; 2014; 2015; Vaselli et al. 2013; 2015; 2017; Chiarantini et al. 2017 and references therein), clearly demonstrating the impact on the local ecosystems.

Currently, several hydrothermal features, such as diffuse and intense punctual degassing (e.g. bubbling pools), still occur all around the extinct volcano edifice (Frondini et al. 2009; Tassi et al. 2009). At places, huge volumes of $CO_2(H_2S)$-rich gas are similarly discharged in correspondence to dismissed mining structures (e.g. wells and borehole), such as that named "Acqua Passante" and "Ermeta" (Nisi et al. 2014), close to the Abbadia San Salvatore mining area.

Viterbo area (Vicano-Cimino Volcanic District, VCVD)

Among the most important volcanic centers of Latium region (central Italy), the Cimino Complex (age 1.35 to 0.94 Ma; Nicoletti 1969) is made up of a sequence of rhyodacitic domes, ignimbrites and olivine-latitic lavas (Cimarelli and De Rita 2006), whereas the younger Vicano Complex (0.42-0.09 Ma; Laurenzi and Villa 1987) mainly consists of leucitites, phono-tephrites and leucite-phonolites (Perini et al. 2000). The area is part of a Tuscan-Roman thermally anomalous province, where the past volcanism and the current thermal emissions are structurally controlled by high-angle NE-striking faults under a prevailing extensional regime (Minissale et al. 2004). The VCVD area was extensively investigated in the past (mid-'50s) by the principal national Italian drilling companies (e.g. ENI-AGIP and Enel Ltd.) for the assessment of geothermal resources (Cinti et al. 2014 and references therein). According to exploratory data, T to up to 218 °C were encountered during the drilling operations of the 2,153 m deep Cimino 1 well, which are in good agreement with the geo-thermometric results obtained by Cinti et al. (2014), showing evidence of deep equilibration for the reservoir fluids at temperatures slightly lower than 200 °C.

Solfatara crater and Pisciarelli vent (Campi Flegrei)

Solfatara crater is a tuff cone (4 ka; Rosi and Sbrana 1987) pertaining to the 12 km-wide Campi Flegrei caldera, whose origin is directly related to two main eruptive stages: (i) Campanian Ignimbrite (39 ka; De Vivo et al. 2001) and (ii) the Neapolitan Yellow Tuff (14.9 ka; Deino et al. 2004), respectively. The area is characterized by a strong hydrothermal activity resulting in the occurrence of thermal springs, steam-heated pools and fumaroles with temperature up to 150-160 °C (e.g. Chiodini et al. 2011; Valentino and Stanzione, 2003, 2004; Vaselli et al. 2011; Venturi et al. 2017).

The multilayered system consists of two main saline reservoirs: i) a shallower one (<2,000 m depth), mainly fed by meteoric waters with minor contributions from seawater and ii) a hyper-saline deeper one (>2,000 m depth), that shows evidence of deep fluids input (Caprarelli et al. 1997) from a heating magma chamber, likely in correspondence to the top of the Mesozoic carbonate substratum (ca. 5 km depth; Rosi et al. 1983; Rosi and Sbrana 1987; Scandone et al. 1991). Hot fluids with T between 250 and 420 °C, respectively, were encountered by exploratory drillings (Guglielminetti 1986) whilst pressure values up to 250 bars were computed (Caliro et al. 2007). The volcanic apparatus is affected by intense degassing, both diffuse and punctual, yielding a daily CO_2 output ranging from 1,116 ± 138 to 1,524 ± 164 t/d (Cardellini et al. 2017). During the last 2,200 years, Campi

Flegrei were also affected by strong bradyseismic (vertical ground displacements) events, such as that occurring in 1982-1984 (Barberi et al. 1984; Chiodini et al. 2003), when the ground lifted up more than 2 m downtown Pozzuoli. Since then, the volcanic surveillance was intensified and currently, geochemical, ground deformation and geophysical monitoring activities to constrain and forecast the dynamics of the new unrest phase (Chiodini et al. 2017b, and references therein) are carried out.

Three mud pools discharging acidic fluids occur in the central portion of La Solfatara (Tassi et al. 2016 and references therein), although the most impressive and spectacular hydrothermal occurrence in the Campi Flegrei is represented by the Pisciarelli steam-vent, which is associated with acidic pools. This steam-jet was affected by several fluctuations over the last few years, as documented by Chiodini et al. (2017).

Vulcano (Eolie Islands)

Vulcano Island is the southernmost of the Aeolian Islands and its genesis is related to an arc-subduction volcanism (Keller 1980; Beccaluva et al. 1985; De Astis 1995). The structure of the island consists of a sequential superimposition of different calderas such as those of Piano and La Fossa, which are the most important over a period ranging from 120 Ka up until the present time (e.g. De Astis et al. 1997). Compositionally, the volcanic rocks include calc-alkaline, high-K calc-alkaline, shoshonitic and potassic series (Keller 1980; Francalanci et al. 1989; 1993; Fulignati et al. 1998). After the last eruption (1888-90; e.g. De Astis et al. 1997), intense fumarolic activity is prevalently displayed in correspondence to La Fossa crater. The gas emissions currently show outlet temperatures up to 400 °C with a dry gas fraction dominated by CO2 and relatively high concentrations of SO_2, H_2S, HCl and HF (e.g. Capasso et al. 1997, 1999; Inguaggiato et al. 2012). During the last decades, compositional variations of the fumarolic discharges were recorded and initially attributed to a volcanic unrest in the late eighties-early nineties, because of a sudden increase of the outlet temperatures of the fumarolic discharges from about 300 °C in 1987 (Barberi et al. 1991) to up to 690 °C in 1993 (Chiodini et al. 1995). A low-temperature fumarolic field is located at Baia di Levante and shows typical hydrothermal features, being characterized by H_2O, CO_2 and H_2S with relatively high CH_4 contents (e.g. Capaccioni et al. 2001), likely due to interaction processes between deep sourced fluids and a shallow boiling aquifer (Capasso et al. 1997, 2001; Chiodini et al. 1995).

According to geothermal exploratory wells (Vulcano1, Porto1, Vu2bis), drilled in the '50s at Baia di Levante (AGIP-Sommaruga 1984), the Vulcano geothermal system consists of three aquifers: i) shallow cold (≈10 m thick), ii) intermediate (100 m deep) and iii) deep (~ 200 °C at > 200 m depth).

Panarea Island

Panarea Island is part of a stratovolcano (20 km long × 2,000 m high) (Gabbianelli et al. 1993; Gamberi et al. 1997) related to a subduction arc-magmatism of the Peloritanian

arc, started at 400 Ky (Gabbianelli et al. 1990). The volcanic complex includes both the main island of Panarea (dated 100-150 Ky and formed by the superimposition of several dacitic domes) and other islets and reefs (Basiluzzo (50 Ky), Dattilo, Bottaro, Lisca Bianca, Lisca Nera, and Panarelli) that are emerging around a submarine fumarolic field. These reefs consist of K calc-alkaline dacite and porphyritic basaltic-andesite lavas (Calanchi et al. 1999). The main fumarolic field of this volcanic complex is nested in a 1 km-wide depression, located 2 km off the eastern coast of Panarea, where the maximum seafloor depth is at about 30 m. Fluids are discharging in correspondence to numerous vents along a NNE and NW-SE trending fracture zone (Lanzafame and Rossi 1984). In November 2002, the system was affected by a sudden and violent paroxysmal gas burst (Caliro et al. 2004; Capaccioni et al. 2005, 2007; Tassi et al. 2009).

The Tuscan and Ligurian mining districts (Alpi Apuane, Campiano-Colline Metallifere, Rio Marina - Elba Island, Libiola mine – Genoa, Liguria)

The whole Tuscan area has always represented a "hot-spot" for mining and metallurgic industries since the Neolithic Age when Cu and, thereafter, Fe, Mn, Sn, Pb, Sb, Ag, Hg-bearing minerals were extracted from around 2,500 to 800 years BC (Cipriani and Tanelli 1983). The presence of large volumes of ore deposits in Tuscany is thought to be associated with the Mio-Pleistocene anatectic magmatism and occurred in the inner (western) sector of this region, namely Colline Metallifere (Tanelli 1983, 2001 and references therein). The ore bodies are frequently hosted within the Mesozoic carbonate-evaporite sequences (e.g. within the Calcare Cavernoso formation) and secondarily, in the upper levels of the Paleozoic basement (e.g. Verrucano s.s) (Tanelli 1977, 1983). Tectonically-driven hydrothermal processes likely leached and mobilized heavy metals and metalloids from the Paleozoic phyllites, leading, for example, to the emplacement of Hg-(Sb) epithermal ores in the Mt. Amiata area (Tanelli 1983).

Different types of poly-metallic ore deposits are found in the Colline Metallifere, as well as the Apuan Alps and Elba Is. Among these, pyrite-barite-Fe oxides (hematite and magnetite) stratabounds of epigenetic-sedimentary origin, Cu-Zn-Pb volcano-sedimentary ores and Cu-Pb-Zn(Ag) skarn mineralizations (e.g. in Campiglia Marittima area) are noteworthy to be mentioned (Tanelli 1977, 1983). Some of the main Tuscan mining districts, in particular those from the Apuan Alps, Colline Metallifere and Rio Marina (Elba Island), were investigated in the last decade in the framework of studies (e.g. Servida et al., 2009 and Raco et al., 2012 and references therein) aimed at evaluating and minimizing the environmental impact possibly induced by the presence of abandoned mine wastes and AMD waters flowing out from these sites.

The Libiola mine, located in the hinterland of Genoa (Liguria), along the Gromolo River, was an important pyrite-chalcopyrite-sphalerite mining district, already known from the Bronze Age and economically exploited starting from the

17th century. The mineralization was prevalently associated with the outcropping ophiolitic lithologies, pertaining to the Ligurian Units l.s. (e.g. pillow basalt breccias, gabbros, serpentinites, cherts and limestones), being concentrated at the tectonic contact between the brecciated basalts and the overlying serpentinites (Marini et al. 2003b; Dinelli et al. 2001 and references therein). Mining activity ended in 1965 and recently the presence of mine wastes and low-pH waters was assessed (e.g. Dinelli et al. 2001; Marini et al. 2003b and references therein).

Geochemical features

The geochemical features of selected acidic waters (15), related to the already mentioned areas, are listed in Table 1 (see next page) while their sampling location is reported in Fig.1.

Water samples include cold springs charged with a CO_2-(H_2S)-dominated free-gas phase (i.e. samples # 1, 2, 3, 4, 6 are hypothermal springs (# 2) or bubbling gas pools), hot boiling steam-heated pools from geothermal systems ("putizze", e.g. # 5) or volcanic-hydrothermal systems and associated with powerful jet steam-vents (e.g. # 7). Sample # 8 (i.e. Pozzo Vasca at Vulcano) is related to a steam-heated pool, whose fluids are supplied by a nearby dismissed geothermal exploratory well. Sample # 9 is from the submarine fumarolic field of Panarea, affected by continuous degassing and intermittent burst events over the last two decades. Samples # 10 and 14 (Elba), 11 (Apuan Alps), 12 (Mt. Amiata), 13 (Campiano area, Colline Metallifere) and 15 (Libiola) are acidic waters pertaining to the category of AMD, according to the definition proposed by Nordstrom and Alpers (1999), and are related to different abandoned mining districts from Tuscany and Liguria.

Temperatures are extremely variable (from 8.0 °C: # 12 to 133 °C: # 9) as well as the pH (from 1.30: # 6 to 5.79: # 2) and electrical conductivity (342 µS/cm: # 1 to 9,470 µS/cm: # 14) values. The TDS vs. pH diagram allows to recognize at least 3 different groups of acidic waters (Fig. 2). Most samples from geothermal and mining areas plot in a range of TDS values from about 5,000 to 15,000 mg/L and are characterized by pH < 4. The strongly acidic waters represent sometimes also the most saline ones (pH = 1.3 and TDS values up to 59,700 mg/L; sample # 6). Sample # 1 and 2 are instead the most diluted waters (Fig. 2) and are related to the Mt. Amiata area, being their emergence within the lower portion of the cold and shallow "volcanic" aquifer hosted in the Quaternary volcanics (mainly trachytes) of this extinct volcano (Doveri et al. 2012). The oxidation-reduction potential of the considered waters, expressed as Eh, displays variations ranging between 70 (# 8) and 713 (# 3; Tab. 1) mV.

The water chemistry is dominated by sulfate, which is the main species among the anionic solutes (Tab.1 and Fig. 3a), with concentrations up to 46,500 mg/L (sample # 6), followed by Cl- (up to 28,000 mg/L: # 9). Conversely, HCO_3^- is practically absent in all the waters as a consequence of their low-pH values, except for sample # 2 (32 mg/L), which has a pH of 5.79 and therefore it has to be regarded as weakly acidic. The main cationic species are represented by Ca^{2+}, ranging between 9 mg/L (# 1) and 2,740 mg/L (# 9), and Na^+, with contents up to 13,000 mg/L (# 9). Magnesium is up to 1,153 mg/L (# 14) whereas K^+ and NH_4^+ are from 0.21 (#15) and 810 mg/L (# 6) and up to 900 mg/L (# 5), respectively. The highest contents of F- and Br- are recorded in samples # 14 (60.6 mg/L) and # 9 (105 mg/L), whereas SiO_2 is up to 330
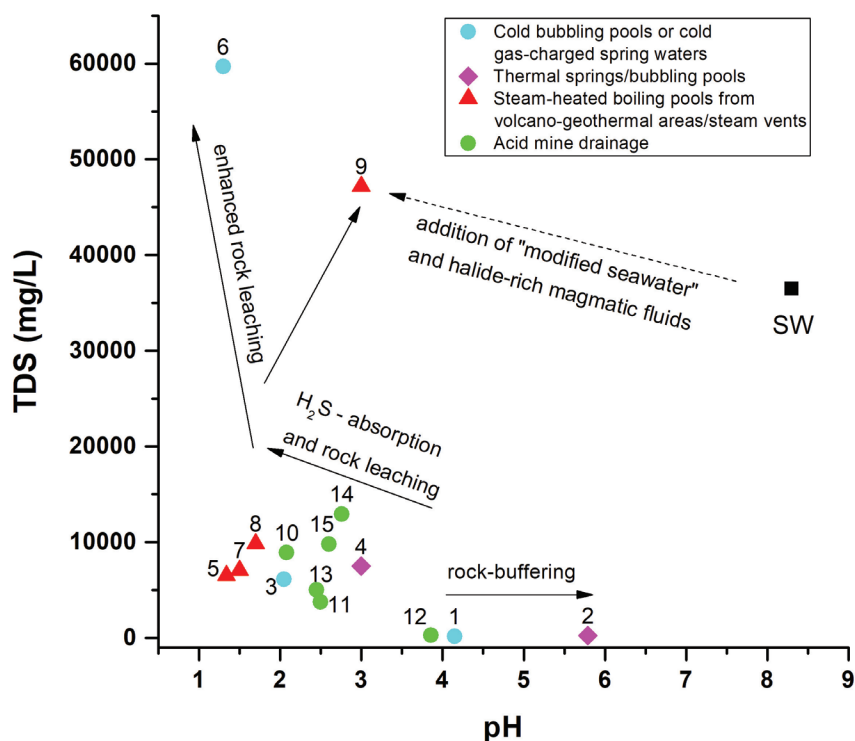

Fig. 2 - pH vs. TDS (mg/L) binary diagram of the selected water samples. The seawater field is also reported (Nordstrom et al. 1979).

Fig. 2 - Diagramma binario pH vs. TDS relativo alle acque selezionate. Viene anche riportato il campo relativo all'acqua di mare (Nordstrom et al. 1979).

Tab. 1 - *Temperature (in °C), electrical conductivity (in µS/cm), Eh (in mV) and concentration of the main, minor and trace constituents (in mg/L) of selected water samples. TDS values (in mg/L) were computed only on species available from literature. The geographic coordinates are in Gauss-Boaga, Roma Monte Mario 1. Legend: bp= bubbling pools; csg=cold springs with gas; tsg= thermal springs with gas; gp= gas pools; shp=steam-heated pools; AMD = acid mine drainage; sv= submarine vent; mine well; na=not analyzed; *=Fetot and Altot concentrations from MAC-GEO project. A column showing the reference source of the data is also provided. Data are from Minissale et al. (1997), Pierotti et al. (2017), Tassi et al. (unpublished), Duchi and Minissale (1992), Cinti et al. (2014), Valentino and Stanzione (2004), Aiuppa et al. (2000), Tassi et al. (2009), Servida et al. (2009), Raco et al. (2012), Dinelli et al. (2001). The analytical methods are those reported by Tassi et al. (2009), where the superscript numbers are corresponding to the water samples' IDs.*

Tab. 1 - La tabella riporta i valori di concentrazione per i costituenti maggiori, minori ed in tracce disciolti nelle acque prese in esame. La temperatura è espressa in gradi Celsius, l'elettroconducibilità in µS/cm e l'Eh in mV. I valori di TDS e SiO$_2$ sono espressi in mg/L. I valori della TDS sono stati ricalcolati sulla base delle specie chimiche reperibili in letteratura. Nella tabella è presentata anche una colonna che fornisce la letteratura di riferimento relativa ai dati riportati. Sono riportate le coordinate geografiche in Gauss-Boaga, Roma Monte Mario 1. Legenda: bp= polle gorgoglianti; csg= sorgenti fredde ricche in gas; tsg= sorgenti termali con gas libero; gp= gas pools; shp=steam-heated pools; amd= drenaggio acido di miniera; sv= vent sottomarino; mw=pozzi minerari; na=non analizzato; *=le concentrazioni di Fetot e Altot sono riprese dai dati del progetto MAC-GEO . E' stata inclusa anche una colonna che riporta la bibliografia di riferimento adottata. I dati sono tratti da Minissale et al. (1997), Pierotti et al. (2017), Tassi et al. (unpublished), Duchi e Minissale (1992), Cinti et al. (2014), Valentino e Stanzione (2004), Aiuppa et al. (2000), Tassi et al. (2009), Servida et al. (2009), Raco et al. (2012), Dinelli et al. (2001). I metodi analitici sono quelli riportati in Tassi et al. (2009).

ID	Name	X_GBX	Y_GB	Type	T (°C)	pH	CND	Eh	TDS	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	NH$_4^+$
1	Acquapassante - Amiata	1716542	4752544	csg	11	3.96	342	452	168	9	2.5	5.1	5.3	0.06
2	Fonte Bagnore- Amiata	1709666	4746969	tsg	21	5.79	379	319	235	28	8.3	21	16	0.04
3	Acquapuzzola Pienza	1717760	4771675	gp	11	2.05	5820	713	6140	581	143	98	15	<0.1
4	Vasca Sant'Albino	1728146	4772785	bp	26	3.00	6600	480	7492	454	160	103	31	na
5	Lagoni Rossi 4 (Larderello)	1645230	4780455	shp	94	1.34	na	na	6531	190	22	4.36	12	900
6	Solforata Marta	243698	4695095	bp	18	1.30	na	320	59700	1990	510	380	810	na
7	Pisciarelli 7 (La Solfatara)	1934102	4532572	shp	90	1.50	9415	na	7050	89	20	12	56	858
8	Pozzo Vasca (Vulcano Is.)	2020515	4268834	shp	87	1.70	na	70	9872	266	245	1776	191	na
9	Panarea (Bottaro)	2032023	4294216	sv	133	3.00	na	na	47200	2740	1000	13000	690	3.3
10	Rio Marina - Valle di Giove	1616190	4742462	amd	na	2.08	7540	592	8921	137	484	6.4	1.8	na
11	CRAP 2 (Stazzema mine)	1603267	4869594	amd	13	2.50	9450	na	3779	207	88	7.6	0.58	0.40
12	CR4 (Galleria VII)	1718482	4751481	amd	8	3.86	3780	75	305	42	6.4	7.9	3.9	0.18
13	CR 20 (Pozzo Serpieri)	1665593	4773845	mw	20	2.45	5230	363	5027	202	95	9.4	4.4	0.47
14	CR35 -Elba Is.	1616394	4741578	amd	30.5	2.76	9470	412	12945	245	1153	37	7.7	0.17
15	Libiola mine	1535849	4905871	amd	na	2.60	8000	590	9808	149	1080	41	0.21	na

mg/L (# 7). The trace metals are mainly represented by Fe$_{tot}$ and Al$_{tot}$, whose concentrations range between 0.02 (# 1) and 4,080 mg/L (# 6) and between 0.003 (# 2) and 5,220 (# 6) mg/L, respectively.

According to the square (Fig. 3a) and triangular cationic diagrams (Fig. 3b), most waters can be ascribed to (i) a prevailing Ca(Mg)-SO$_4$ and/or (Fe+Al)-SO$_4$ and/or Mg(Ca)-SO$_4$ geochemical facies, particularly for those fluids related to both cold and thermal springs (including those related to bubbling pools; e.g. samples # 1, 2, 3, 4, 6) and those occurring in the mining areas (e.g. # 10, 11, 12, 13, 14, 15), ii) an alkaline Na-NH$_4$-SO$_4$ facies for those waters collected in correspondence to acidic steam-heated pools/steam vents (i.e. samples # 5, 7, 8) and iii) a Na-Cl facies from the submarine vent (# 9).

Origin of the acidic waters

Some authors, e.g. Guo et al. (2014), argued that some fundamental conditions are absolutely crucial to allow the presence of acidic thermal springs in hydrothermal areas, especially for those low-pH waters that show a direct input of magmatic fluids. A few main requirements were highlighted, as follows: (i) relatively shallow depth of the magma heating bodies; (ii) presence of a sufficient burden of volatiles of deep magmatic origin; (iii) absence of permeability barriers l.s. between the shallow and deep levels of the reservoir; (iv) proper angle of steepness of those vertically extended faults reaching the reservoir at depth.

In Italy, low-pH fluids are instead relatively common in both volcanic and hydrothermal systems and their peripheral areas, whose features depend on: the local geological-structural

Tab. 1 - Temperature (in °C), electrical conductivity (in µS/cm), Eh (in mV) and concentration of the main, minor and trace constituents (in mg/L) of selected water samples. TDS values (in mg/L) were computed only on species available from literature. The geographic coordinates are in Gauss-Boaga, Roma Monte Mario 1. Legend: bp= bubbling pools; csg=cold springs with gas; tsg= thermal springs with gas; gp= gas pools; shp=steam-heated pools; AMD = acid mine drainage; sv= submarine vent; mine well; na=not analyzed; *=Fetot and Altot concentrations from MAC-GEO project. A column showing the reference source of the data is also provided. Data are from Minissale et al. (1997), Pierotti et al. (2017), Tassi et al. (unpublished), Duchi and Minissale (1992), Cinti et al. (2014), Valentino and Stanzione (2004), Aiuppa et al. (2000), Tassi et al. (2009), Servida et al. (2009), Raco et al. (2012), Dinelli et al. (2001). The analytical methods are those reported by Tassi et al. (2009), where the superscript numbers are corresponding to the water samples' IDs.

Tab. 1 - La tabella riporta i valori di concentrazione per i costituenti maggiori, minori ed in tracce disciolti nelle acque prese in esame. La temperatura è espressa in gradi Celsius, l'elettroconducibilità in µS/cm e l'Eh in mV. I valori di TDS e SiO$_2$ sono espressi in mg/L. I valori della TDS sono stati ricalcolati sulla base delle specie chimiche reperibili in letteratura. Nella tabella è presentata anche una colonna che fornisce la letteratura di riferimento relativa ai dati riportati. Sono riportate le coordinate geografiche in Gauss-Boaga, Roma Monte Mario 1. Legenda: bp= polle gorgoglianti; csg= sorgenti fredde ricche in gas; tsg= sorgenti termali con gas libero; gp= gas pools; shp=steam-heated pools; amd= drenaggio acido di miniera; sv= vent sottomarino; mw=pozzi minerari; na=non analizzato; *=le concentrazioni di Fetot e Altot sono riprese dai dati del progetto MAC-GEO . E' stata inclusa anche una colonna che riporta la bibliografia di riferimento adottata. I dati sono tratti da Minissale et al. (1997), Pierotti et al. (2017), Tassi et al. (unpublished), Duchi e Minissale (1992), Cinti et al. (2014), Valentino e Stanzione (2004), Aiuppa et al. (2000), Tassi et al. (2009), Servida et al. (2009), Raco et al. (2012), Dinelli et al. (2001). I metodi analitici sono quelli riportati in Tassi et al. (2009).

ID	Name	HCO$_3^-$	(SO$_4$)$^{2-}$	Cl$^-$	F$^-$	Br$^-$	(NO$_3$)	SiO$_2$	Fe	Al	References
1	Acquapassante - Amiata	5.5	164	6	na	na	0.2	51	0.02*	12*	Minissale et al. 1997a
2	Fonte Bagnore- Amiata	32	106	16	na	na	9.8	90	<10*	0.003*	Minissale et al. 1997a
3	Acquapuzzola Pienza	abs	4680	74	na	na	na	109	390	44	Minissale et al. 1997a
4	Vasca Sant'Albino	abs	6600	138	6.20	0.12	0.5	na	na	na	Tassi et al. (unpub.)
5	Lagoni Rossi 4 (Larderello)	abs	5280	21	na	na	na	102	na	na	Duchi & Minissale 1992
6	Solforata Marta	abs	46500	62	4.70	<0.01	<0.01	na	4080	5220	Cinti et al. 2014
7	Pisciarelli 7 (La Solfatara)	abs	3300	7	1.40	na	na	330	129	54	Valentino & Stanzione 2004
8	Pozzo Vasca (Vulcano Is.)	abs	4200	2680	8.00	na	na	na	507	<10	Aiuppa et al. 2000
9	Panarea (Bottaro)	abs	1500	28000	17.40	105	6.9	136	na	na	Tassi et al. 2009
10	Rio Marina - Valle di Giove	abs	7370	18	na	na	0.7	na	903	na	Servida et al. 2009
11	CRAP 2 (Stazzema mine)	abs	2668	16	<0.01	na	<0.5	22	750	19	Raco et al. 2012
12	CR4 (Galleria VII)	abs	176	13	0.13	na	<0.5	48	3.27	5	Raco et al. 2012
13	CR 20 (Pozzo Serpieri)	abs	3638	13	<0.01	na	<0.5	80	808.06	177	Raco et al. 2012
14	CR35 -Elba Is.	abs	10098	54	60.6	na	<0.5	96	675	517	Raco et al. 2012
15	Libiola mine	abs	7000	533	na	na	na	na	775	230	Dinelli et al. 2001

setting, the composition of the outcropping magmatic rocks and the host-rock reservoirs.

Cold and thermal acidic waters

The chemistry of samples # 1 and 2, pertaining to a geochemical facies ranging from Ca(Na)-SO$_4$ and Ca(Mg)-SO$_4$ to Fe+Al(Ca,Mg)-SO$_4$, seems to be governed by prevailing water-rock interaction processes involving the volcanic rocks and locally meteoric-fed groundwater, affected by a significant influx of a deep sourced (CO$_2$-(H$_2$S)-dominated) gas phase (e.g. δ^{13}C-TDIC = -7.76 ‰ vs. V-PDB in # 2; Frondini et al. 2009; Tassi et al. 2009; Pierotti et al. 2016, 2017). In particular, a more pronounced rock-buffer resulting in slightly higher pH values (Fig. 2) could be hypothesized for the weakly acidic Bagnore hypothermal water (# 2), likely due to faster kinetics

also linked to a relatively warmer temperature of this water with respect to sample # 1. Water samples (e.g. springs and bubbling pools) emerging in the Tuscan-Roman magmatic province generally have a strong structural control, being located along the main NE-SW trending trans-tensional tectonic lineaments (Pandeli et al. 2005; Brogi et al. 2010). These structures are indeed preferential pathways for the migration of large amounts of a CO$_2$-dominated gas phase that interacts with surficial aquifers. The source of this gas phase was hypothesized to be of crustal origin, released during the subduction of the Adria Plate (Martelli et al. 2004; Frondini et al. 2009) and related to thermo-metamorphic decarbonation processes with an additional contribution from a "metasomatized mantle" (e.g. average values of δ^{13}C-CO$_2$ = -3.8 ‰ vs. V-PDB; ^{3}He/^{4}He =0.214; δ^{15}N/^{14}N = 5.42 ‰

a)

b)
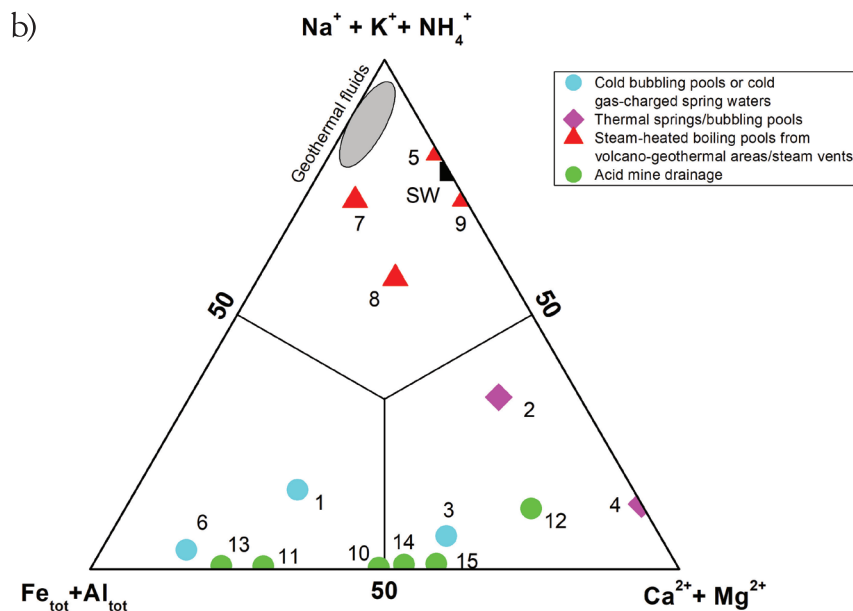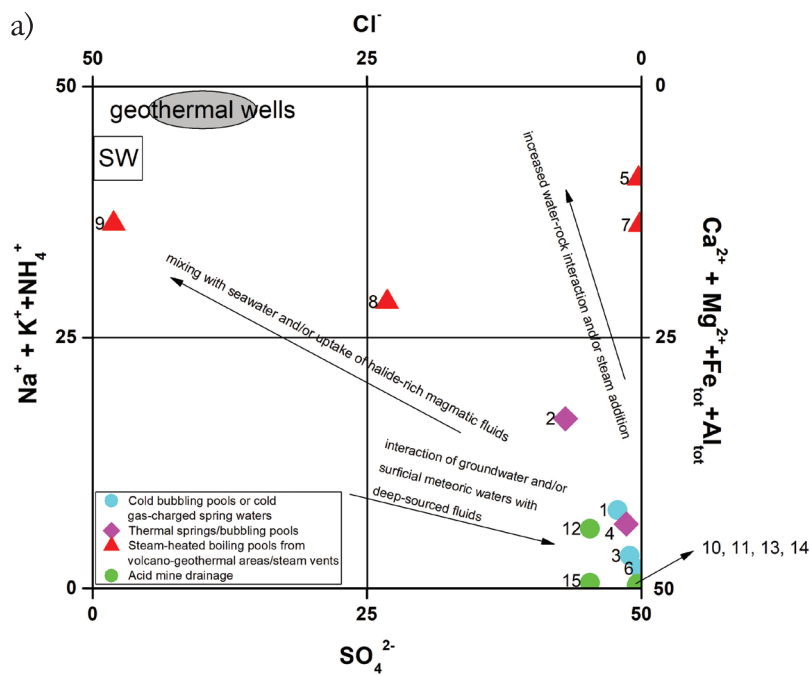
and $^{40}Ar/^{36}Ar$ = from 295 to >328; Minissale et al. 1997a, Minissale, 2004). This is also consistent with the isotopic data reported by Cinti et al. (2014) for the $\delta^{34}S$-$H_2S(g)$ values (+9.3 to +11.4 ‰, vs. V-CDT), clearly pointing out a hydrothermal origin for H_2S, formed via thermochemical reduction (at T < 200 °C) of buried Triassic carbonate-evaporite sequences (e.g. mainly anhydrites) hosting the geothermal aquifers in the area.

An additional supergenic oxidation of hydrogen sulfides is also likely. The oxidation is triggered by prevailing oxidizing conditions (e.g. Eh values are up to 713 mV: sample # 3; Table 1) and/or Fe(II)-Fe(III) redox reactions, involving Fe-hydroxides of the rock matrix and leading to a complete conversion of $H_2S(g)$ to $SO_4^{2-}(liq)$, as confirmed by the

$\delta^{34}S$-SO_4 values (-6.9 to - 5.9 ‰ vs. V-CDT of sample # 2; Pierotti et al. 2016), and shown in Fig. 4a. This process is possibly responsible for the SO_4^-enrichment showed by the bubbling pools in the Mt. Amiata area and northern Latium (Frondini et al. 2009).

Whenever a non-negligible amount of Ca-bearing minerals (e.g. plagioclase) or volcanic glass is supplied by the geological substratum, on which an emission is emplaced, the pH decrease, due to the interaction with the acidic gases, can weakly be buffered (Fig. 2; Pierotti et al. 2016). Alternatively, the interaction with turbiditic-siliciclastic sedimentary units l.s. (e.g. Ca(Na)-HCO$_3$ or Na(Ca)-HCO$_3$ *"acque acetose"* springs reported by Cinti et al. 2014) can be invoked. Otherwise, strongly acidic values down to 2.05 are easily reached, e.g.

samples # 3, 4 (Table 1), producing Ca(Fe)-SO$_4$ and/or (Fe+Al)(Ca,Mg)-SO$_4$ compositions (e.g. # 6), these waters being also strongly enriched in dissolved metals due to the particularly low pH (1.3).

Steam-heated pools

Samples # 5, 7 and 8, from the westernmost portion of the Larderello geothermal area, Solfatara crater and Vulcano Is., respectively, can be grouped together as they are represented by those acidic and sulfate-bearing emissions, normally defined as "steam-heated" pools (Giggenbach 1988), typical of high-temperature systems. Fluids from these hot boiling pools (e.g. T up to 94 °C, # 5) show relatively high TDS (e.g. 9,872 mg/L in sample # 8) and very low pH values (e.g. 1.34 in # 5; Fig. 2). The composition is dominated by the presence of high amounts of both SO$_4^{2-}$ (up to 5,280 mg/L, in # 5) and NH$_4^+$ (e.g. 900 mg/L in # 5), respectively (Table 1; Fig.3 a-b). Differently from the deep, neutral-

chloride geothermal brines that are preferentially enriched in Li and B (Duchi and Minissale 1992), the chemistry of these fluids reveals the occurrence of continuous interactions between a shallow aquifer fed by local meteoric waters (e.g. δ^{18}O = + 3.8 ± 1.3 ‰ vs. V-SMOW and δ^{2}H =+6.5 ± 2.2‰ vs. V-SMOW; Valentino et al. 1999) and an uprising hydrothermal/magmatic and ammonia-bearing steam phase. The gas phase is dominated by CO$_2$ and H$_2$S: 92.84 % and 5.62 %, respectively, in # 5 (Duchi and Minissale, 1992) and 99.13% and 0.44 %, respectively, in # 7 (Capaccioni et al. 1993), the latter characterized by sulfur of magmatic origin (δ^{34}S = -0.1 ‰ Valentino et al., 1999).

Moreover, whilst the most acidic magmatic compounds (e.g. SO2, HCl) suffer "gas scrubbing" processes at deeper levels within a so-called "primary neutralization zone" (Giggenbach, 1988), usually characterized by δ^{18}O-shifted geothermal brines (D'Amore and Bolognesi 1994), the H$_2$S-rich separated steam phase is instead affected by condensation at shallow depth (Figs. 3a,b and 4a).
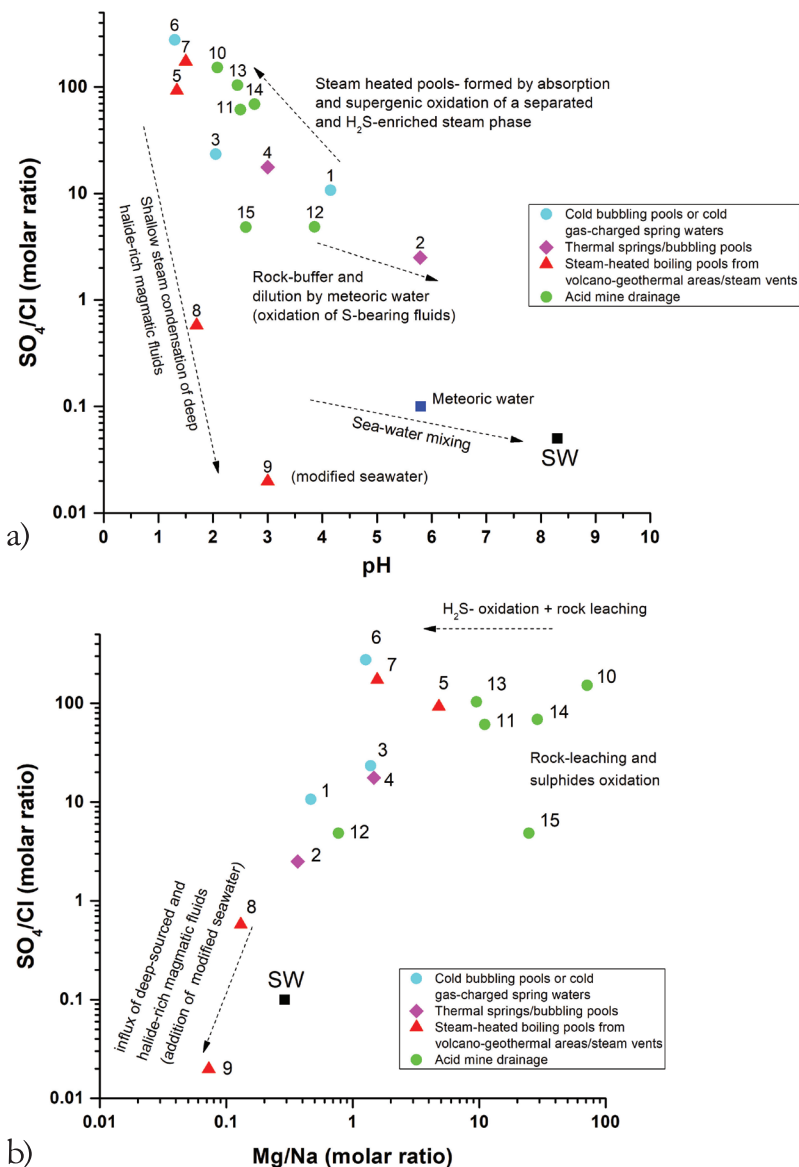
Fig. 4 - a) pH vs. SO$_4^{2-}$/Cl (expressed as molar ratios). b) Mg^{2+}/Na$^+$ vs. SO$_4^{2-}$/Cl$^-$ (expressed as molar ratios) binary diagrams for the considered waters. The meteoric (Gambardella et al. 2005) and sea (SW; Nordstrom et al. 1979) water fields are also reported.

Fig. 4 - Grafici binari: a) pH vs. SO$_4^{2-}$/Cl$^-$ espresso come rapporto molare) e b) Mg^{2+}/Na$^+$ vs. SO$_4^{2-}$/Cl$^-$ (espressi come rapporti molari) per le acque considerate. Vengono riportati i campi di pertinenza dei fluidi geotermici (Minissale et al. 1997a) e dell'acqua di mare (SW; Nordstrom et al. 1979).

According to Valentino and Stanzione (2004), H_2S is then converted to SO_4 by a multi-step supergenic oxidation process, as further supported by the isotopic values of the Pisciarelli steam and waters (e.g. $\delta^{34}S$ = - 1.3 ± 0.3 ‰ vs. V-CDT; Valentino et al. 1999). In addition, a minor contribution to the oxidation of S-bearing compounds from microbial communities (e.g. Sulfobacillus) living in close proximity to pool rims and/or fumarolic orifices of Solfatara crater (Crognale et al. 2018) seems to be likely.

When this process occurs in a carbonate-depleted environment (e.g. Neogene covers as at # 5 sampling site and/or on silicified escarpments of the fumarolic fields from Larderello) or in hydrothermalized substratum (e.g. at Solfatara and Pisciarelli, # 7), the pH values are not efficiently buffered, also due to the strong gas fluxes (Cardellini et al. 2017; Chiodini et al. 2017).

In such conditions, a neo-formation mineral assemblage, typical of an "argillic" hydrothermal-alteration facies, is found, prevalently consisting of alunite, opal, halotrichite, letovicite, alunogen, tschermigite and native sulfur. On one hand, the formation of Mg-bearing clays and kaolinite is prevented by the increase of cations concentration (increased Mg solubility) and on the other hand, by the Na, K removal from the solution (Valentino et al. 1999; Valentino and Stanzione, 2003; 2004), as confirmed by their relatively high $SO_{42.}/Cl^-$ and Mg^{2+}/Na^+ molar ratios (Fig. 4b).

Conversely, at the sampling site # 8 (Pozzo Vasca) in the area of Baia di Levante-Vulcano Porto (Vulcano Is.), a similar paragenesis was encountered on both surface and drilling cores from exploratory drillings (Capaccioni et al. 1995, 2001; Fulignati et al. 1996), with the only exception of the abundant occurrence of kaolinite, associated with native sulfur and smectite. The argillic facies of hydrothermal origin occurring at this site is the result of strong rock-leaching. The sulfate composition is likely due to the oxidation of H_2S, which could also be generated by alkaline hydrolysis of iron sulfides from the shallow aquifers (e.g. marcasite and pyrrhotite; Capaccioni et al. 2001).

An enhanced absorption of halide-rich fluids of magmatic origin was hypothesized (Capasso et al. 2001) for this sample (Fig.4a-b), although a strong but temporally intermittent contribution of the local seawater to the chemistry of this hot shallow aquifer cannot be ruled out (Aiuppa et al. 2000; Capasso et al. 2001). A more or less direct steam condensation process was therefore envisaged by Aiuppa et al. (2000) and Capasso et al. (2001) for the shallow groundwater body beneath the Baia di Levante plain; this might indeed represent a kind of "outflow" zone for volcanic condensates from the surficial hydrothermal system of La Fossa volcanic edifice.

The Panarea submarine fumarolic field underwent a period of volcanic crisis, namely the "gas burst", which occurred in November 2002, when a strong increase of Cl- in waters was simultaneously accompanied by a sharp decrease of the pH values, the latter likely due to a deep magmatic end-member input of HCl-bearing fluids. Sample # 9 collected in 2006 from the submarine vents of Panarea Is. represents a high-temperature (133 °C, Table 1; Tassi et al. 2009) volcanic end-member. According to the high concentrations of Cl- and Ca^{2+} (28,000 and 2,740 mg/L, respectively; Table 1) and those of B (177 mg/L: Tassi et al. 2009), the Na/Cl ratios up to 2.5 and the low Mg^{2+}/Na^+ and SO_4^{2-}/Cl^- molar ratios (Fig. 4b), the presence of an ongoing mixing process between a Ca^{2+}-rich deep end-member and a local "concentrated" seawater (by boiling and vapor loss) was suggested by Tassi et al. (2009). This is also consistent with a solution oversaturated in $CaSO_4$, particularly at the interface between the shallow SO_4^{2-}-rich seawater end-member and the Ca-rich deep one, where a consequent precipitation of anhydrite is favored. The low pH values further confirm an exhausted buffering capacity by the host rocks, all converted in hydrothermal mineral phases and amorphous silica (Tassi et al. 2009), consistent with the highest concentration of SiO2 (136 mg/L; Table 1) measured in this sample.

During subsequent geochemical surveys, carried out after the 2002 gas blast, the system appeared to be affected by different events of deep degassing, never reaching a steady-state; currently a "normal" hydrothermal activity is reported (Tassi F., unpublished data).

Differently from the already mentioned active volcanic areas, to the best of our knowledge, acidic waters of geothermal origin with pH < 4 are apparently absent in other systems from the Neapolitan area, such as Vesuvio and Ischia, although a structural control, operated by regional tectonics, on the types and chemistry of the emissions was assessed (Federico et al. 2004; Di Napoli et al. 2009). Although the presence of some steam-heated waters (weakly acidic, pH around 5.5) from a shallow thermal aquifer at Ischia was reported, the lack of strongly acidic fluids is likely to be ascribed to a greater influence from the local seawater, which is able to efficiently mix with and buffer the deep-sourced thermal fluids (Di Napoli et al. 2009). The isotopic data from these weakly acidic hydrothermal waters clearly point out the contribution by local seawater ($\delta^{18}O$ = 0.54 ‰ vs. V-SMOW and δ^2H = 2 ‰ vs. V-SMOW; Di Napoli et. 2009).

Mine Waters

The definition of "acidic waters" was provided by Nordstrom and Alpers (1999a), who classified as belonging to this category all those low-pH fluids from mining areas usually showing pH values in a range comprised between -3.5 and 5 and enriched in sulfate, iron and aluminum with TDS grazing values of around 200 g/L (Nordstrom and Alpers 1999b).

The main process recognized to be responsible for AMD is the oxidative dissolution of sulfides (e.g. pyrite and pyrrhotite; e.g. Blowes et al. 2003 and references therein). Physicochemical factors (e.g. O_2, pH, Eh) and the presence/absence of bacteria and archea (e.g. Acidithiobacillus ferrooxidans) may accelerate the conversion of Fe^{2+} to Fe^{3+} and that of S^{2-} to SO_4^{2-} (e.g. Nordstrom and Southam 1997; Nordstrom 2011b). Fe^{+3} is a strong oxidant that has the capability to release H^+ to the solution with a ratio of 16:1 moles for each available mole of pyrite.

The acidic waters listed in Table 1 and related to different Italian mining districts pertain to three main chemical facies (Fig. 3): (i) Ca(Mg)-SO$_4$ (sample # 12); (ii) Mg(Fe+Al)-SO$_4$ (# 14,15) and (iii) Fe+Al(Ca,Mg)-SO$_4$ (# 10,11, 13). These are cold and strongly acidic waters, characterized by pH values as low as 2.08 (# 10) and electrical conductivity up to 9,470 µS/cm (sample # 14) (Table 1 and Fig. 2). The high concentrations of sulfate (10,098 mg/L in # 14) likely refer to dissolution processes of polymetallic sulfides. The SO$_4^{2-}$/Cl$^-$ and Mg^{2+}/Na$^+$ molar ratios as well as the Fe$_{tot}$ and (Fe$_{tot}$+Al$_{tot}$) contents (Table 1; Figs. 3 and 4b), the latter particularly high for samples # 10, 13, 14 and 15, are reflecting water-rock interactions involving Mg^{2+}-, Fe$^-$ and Al-rich lithologies. This is consistent with the geological setting, affected by the occurrence of large outcrops of mineralized ophiolitic units (e.g. mineralized serpentinites, gabbros and basalts; Dinelli et al. 2001; Raco et al. 2012). An additional contribution to the Al concentrations from meta-siliciclastic rocks of the Verrucano group s.l. for sample # 14 is likely (Servida et al. 2009), consistent with a general oversaturation of these waters in insoluble Al-bearing sulfate species (Raco et al. 2012). Therefore, also according to the findings of Raco et al. (2012), it is possible to state that processes involving the degradation of mine wastes and oxidation of polymetallic sulfides (e.g. oxidative dissolution) are to be regarded as the main source of the AMD fluids reported in this work.

Environmental impacts of the acidic water

Acidic waters related to geothermal environments rarely impact the surrounding population, because of their limited areal extension. Contrarily, some other studies dealing with the geochemical characterization of the main decommissioned mining districts from central-northern Italy (e.g. Dinelli et al. 2001; Marini et al. 2003b; Servida et al. 2009; Raco et al. 2012) pointed out some outstanding issues: (i) the existence of environmental threats represented by the almost complete neglect of certain mining areas; (ii) a consequent lack of a prompt and continuous monitoring process after their closure; (iii) the costs related to their remediation and (iv) the difficulty in providing always straightforward and effective solutions to the problems.

The above-mentioned geochemical surveys indeed evidenced the potential hazard due to the presence of abandoned mine spoils and tailings (e.g. Dinelli et al. 2001; Marini et al. 2003b; Servida et al. 2009; Raco et al. 2012) having a positive and possibly long-lasting NAPP (Net Acid Producing Potential; Servida et al. 2009). Additionally, strongly acidic drainage waters, that are formed by the interaction of meteoric waters with the exposed mine wastes, may also be able to flow out from the source site (e.g. from mining boreholes, wells, tunnels), likely posing serious concerns about the integrity of the local eco-systems (Dinelli et al. 2001; Marini et al. 2003b for the Libiola-Gromolo River case study; Raco et al. 2012, for Merse River).

Fortunately, despite all the assessments confirming the local occurrence of pollution, a real and so-called "environmental disaster" on a larger scale is unlikely (Dinelli et al. 2001; Marini et al. 2003b; Raco et al. 2012). This important result was achieved mainly by a correct employment of some of those biotic "active" and/or abiotic "passive" remediation technologies proposed by Johnson and Hallberg (2005).

Nevertheless, even though such interesting solutions such as the use of chemically reactive cartridges (e.g. those designed by Raco et al. 2012) were suggested by some authors to solve environmental issues, several dismissed and polluted mining districts in Italy, not mentioned in this work, are still waiting for remediation activities to be undertaken.

Concluding Remarks

This work was aimed at summarizing the results obtained by different authors on the main processes leading to the formation of acidic waters in Italy. The 15 selected samples, chosen as representative, were related to both volcanic-geothermal areas, from North to South: Larderello and Mt. Amiata geothermal fields, Vicano-Cimino Complexes, Solfatara crater (Campi Flegrei), Vulcano and Panarea Is. (Aeolian Islands) and mining districts: Libiola mine (Liguria), Stazzema (Apuan Alps), Colline Metallifere and Elba Island (Tuscany).

According to the geochemical features of the acidic waters considered in this study, two different processes were recognized as dominant, as follows:

i. a dominant supergenic abiotic and/or biotic oxidation of gaseous sulfur species (e.g. mainly H$_2$S of hydrothermal origin) in hydrothermal and volcanic environments;

ii. an oxidative dissolution of polymetallic sulfides, via predominantly abiotic redox processes in all the mentioned mining districts.

Different studies pinpointed the importance of: a) monitoring activities to control groundwater quality (e.g. in peripheral portions of geothermal systems) or alternatively b) responsible and scientifically-based management actions for those dismissed mining sites after their industrial closure, in order to avoid exaggerate remediation-related expenses.

The same authors highlighted the presence of polluted areas around the former mining areas, even though no hazard for the population was currently detected. Moreover, physically and chemically-based remediation technologies were successfully applied in different sites (REF!!), in order to minimize the related environmental impacts.

Nevertheless, despite the likely harmful potential of acidic waters to the environment, their composition and geochemical processes (still poorly constrained) are 'fascinating and intriguing', suggesting that future studies are expected to be carried out along with a compilation of database where the Italian acidic fluids are to be listed.

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