ISOTOPE GEOCHEMISTRY OF RAINFALL, THERMAL AND NON-THERMAL WATERS FROM THE MT. AMIATA AREA (NORTHERN-CENTRAL ITALY)

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INTRODUCTION AND AIMS OF THE WORK

The Mt. Amiata geothermal area (southern Tuscany), where thermal waters and gas emissions are widely distributed and associated with the presence of geothermal fluids, was thoroughly investigated starting from the second half of the last century from different perspectives both geochemical, structural and hydrogeological. A relatively small area, occupied by the homonymous volcanic edifice, hosts valuable resources, the latter being mainly represented by both the largest reservoir of drinkable freshwater of the southern Tuscany (estimated volume: ≈ 1.4 km^3; Barazzuoli *et al.*, 1995) and the second most important geothermal field exploited in Italy.

Some concerns about possible interactions between the cold freshwater resource and the deep thermal fluids had arisen in the past, on the basis of the conceptual models proposed by Calamai *et al.* (1970) and Pizzi (1998). These authors suggested a deep infiltration mechanism, likely taking place from the most elevated areas towards the deep systems throughout the relict volcanic conduits of the Mt. Amiata silicic complex.

More recently, Delcroix *et al.* (2006), Borgia *et al.* (2014) and Mazzoldi *et al.* (2015) hypothesized that geothermal exploitation may somehow jeopardize the freshwater resource in terms of both quality and abundance. Consequently, the regional administration appointed other researchers to prepare environmental reports. The aims were to clarify the contradictions between the two interpretations since that of Borgia *et al.* (2014) posed anxiety and doubts to the local inhabitants, who were also increasingly worried about new perspectives of further geothermal explorations in the area. According to the results of one of these multidisciplinary studies (Barazzuoli *et al.*, 2008; Barazzuoli *et al.*, 2015), clear signs of environmental impact were apparently not detected.

The main purposes of this work, aimed at providing additional clues and insights to the formerly presented topics, were to: *i*) build up the first Local Meteoric Water Line (LMWL), by analyzing the oxygen and hydrogen isotopes of rainwater through a designed pluviometric network from the summit to the foothill; *ii*) better characterize the shallower hydrogeological environments related to both the cold homonymous volcanic and regional-carbonate aquifers by computing the average infiltration/recharge altitudes of the main springs; *iii*) define the hydrogeological dynamics and determine the radiometric age of the circulating waters; *iv*) verify the possible influence of the climate change in the area and the co-related response of the shallow groundwater bodies, through the last decade; *v*) understand the chemical isotopic relationships among different fluid end-members in both aqueous and gaseous phases as well as their filtration and/or migration with respect to the geological structures; *vi*) explore the overall water quality of the spring waters, mainly on the basis of inorganic chemistry, in the framework of a cooperation with the local water provider (Acquedotto del Fiora Ltd.).

MATERIALS AND METHODS

Eight passive rain gauge stations, placed at fixed elevation levels over the study area, were installed to collect rain water samples and record measurements of the rainfall levels (Fig. 1a). Simultaneous checking of the meteorological parameters was carried out by consulting the on-line archives from the Regional Hydrological Service (SIR: http://www.sir.toscana.it/ricerca-dati). More than 128 rain water samples were retrieved, which also included unpublished data from CNR-IGG of Pisa; 128 of them were analyzed for the stable isotopic composition. Additionally, 6 rainfall samples were collected during the year 2011 and 7 in 2018 to be analyzed for tritium activity. Spring water samples (126) with different chemical composition (emerging from both the volcanic and regional carbonate aquifers) were collected and analyzed for main, minor, trace and isotope chemistry (124 for stable water isotopes and 15 for tritium) (Fig. 1b).

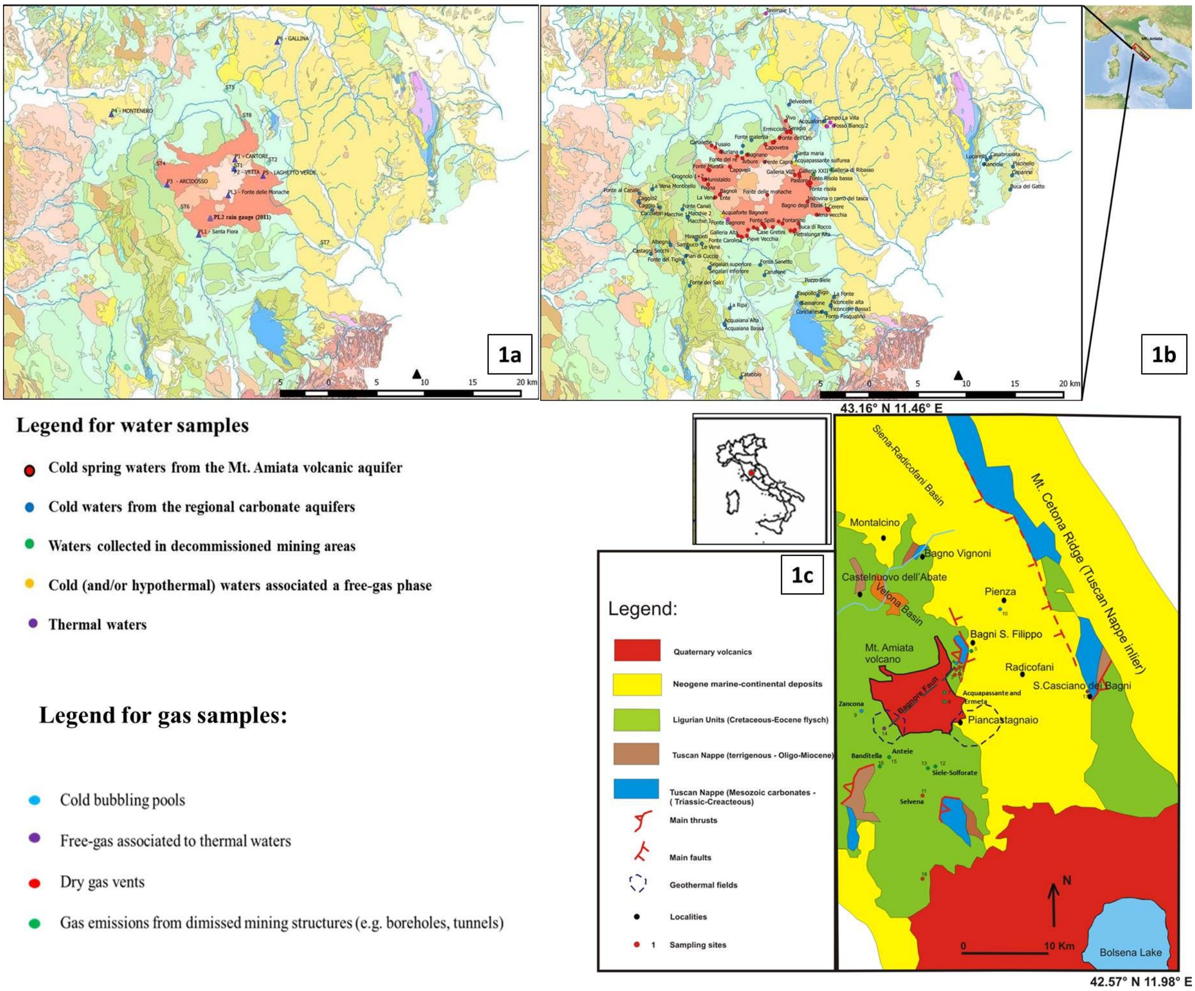

Fig. 1 - a) Geological map of Mt. Amiata and location of the rain gauge stations used for this project and the automatic pluviometric stations pertaining to the SIR's monitoring network. The position of PL2 rain gauge, which was only used in 2011, is also reported; b) location of the spring sampling sites and c) location of the gas emission sampling sites.

A sampling campaign was also conducted to collect gas samples from the main gas emissions in the surroundings of the Mt. Amiata volcano (included some dismissed mining areas affected by both diffuse and punctual degassing). Eighteen samples were analyzed to obtain information on parameters that had never been thoroughly investigated before (Fig. 1c). Particularly, due to their highly impacting potential on both the air quality and human health, it was paid great attention in providing an updated census of the natural punctual and/or diffuse emissions in the area. For this purpose, a detailed study was carried out by noble gas (NG) isotopic tracers to understand whether the geological structures were affecting and/or favoring the gas release mechanisms to the surface.

This constitutes the very first work, performed in the area, which is involving a full scan of NG nuclides, from the lighter He (helium) to the heavier Xe (xenon).

ISOTOPIC FEATURES ON RAINFALL AND SPRING WATERS FROM THE MT. AMIATA GEOTHERMAL AREA

According to the aims of this work, reported in the introduction, the main achievements obtained for both liquid and gaseous matrices can be summarized as follows:

i) the LMWL was computed and resulted to be similar to that calculated for Central Italy (Longinelli & Selmo, 2003), being defined by the following equation: $\delta D = 7.042 * \delta^{18}O + 5.88$ (Fig. 2);

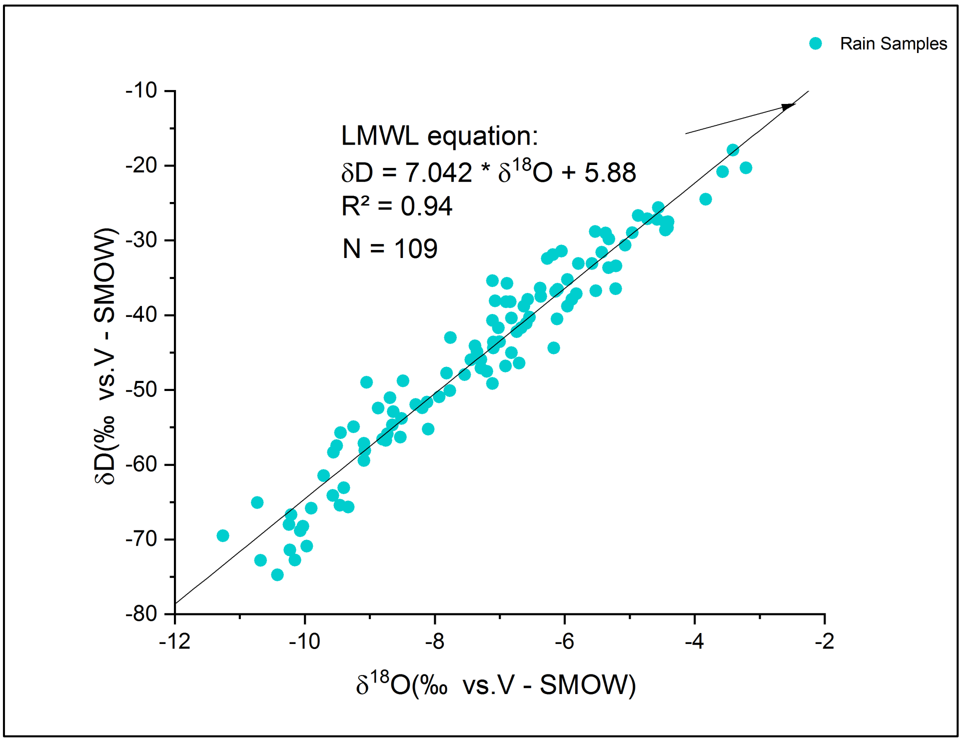

Fig. 2 - The novel LMWL-A for the Mt. Amiata region, obtained from 109 out of 128 rain samples collected over the area during two distinct hydrological surveys (2011 and 2017/2018).

ii) based on a vertical isotopic gradient, being for oxygen set around -0.19‰/100 m, the average recharge altitudes for spring waters from the Mt. Amiata aquifer were computed in about 1200 m a.s.l. and around 1000 m a.s.l. for waters from the regional aquifer, respectively;

iii) the Mt. Amiata aquifer responds with a lag-time of a few months to relevant inputs of meteoric recharge, as already reported by Doveri *et al.* (2012). The study of different selected springs evidenced that the aquifer was likely characterized by at least three different circulation patterns. Nevertheless, tritium data did not completely validate this hypothesis as a likely consequence of both a still lacking suitable circulation model and the low activity measured in spring waters that resulted to be very close to the current atmospheric signature, the latter ascribable to a sort of "isotopic background noise". However, tritium revealed to be useful in air masses trajectories tracking as well as stable isotopes signature in highlighting different hydrogeological circuits, the latter in good agreement with previous studies (Doveri *et al.*, 2013).The average radiometric age of the different waters resulted to be quite homogenous, being in the range of <10 and up to >15 years for cold spring waters emerging from the shallow volcanic aquifer, whilst a deep hydrothermal circulation, related to those fluids from Bagni San Filippo-Bollore, Bagno Vignoni and Saturnia was found to be >40 and up to 70 years old, the latter being intimately linked to the buried geothermal systems.

iv) water samples collected during the year 2017/2018 from the shallow volcanic aquifer showed to be isotopically heavier with respect to those from previous sampling campaigns carried out in 2011 and consistent with heavier rainfall isotopic signatures, thus likely suggesting a response of this groundwater body to the changing climate regime (Fig. 3), as already pointed out by preliminary data acquired during the very first stage of this research project (Magi *et al.* 2019).

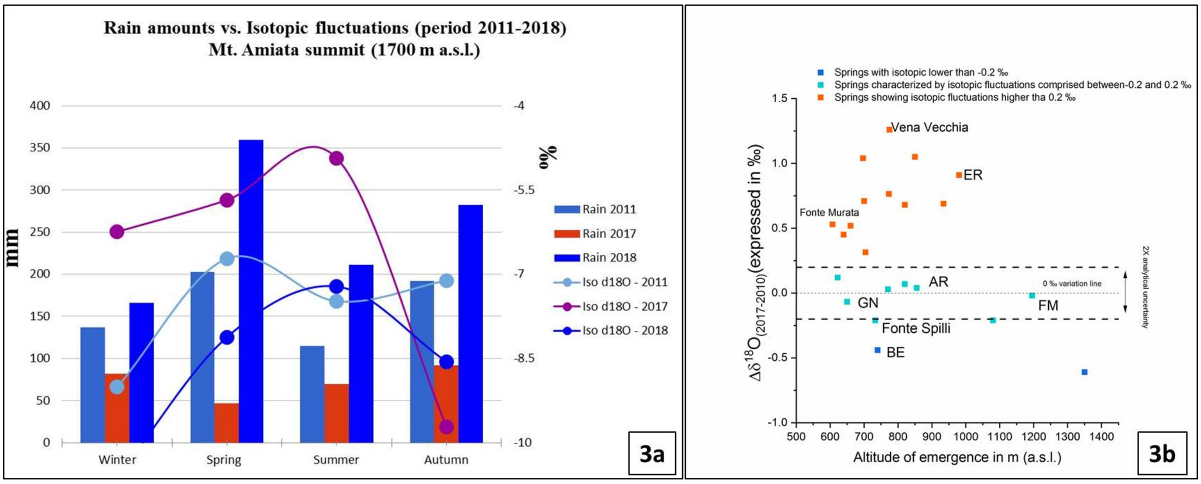

Fig. 3 - a) Comparison on a seasonal base of the main hydrologic parameters: average rainfall and weighted isotopic ($\delta^{18}O$) composition of rain at the Mt. Amiata summit in 2011, 2017, and 2018; b) Binary diagram of $\Delta\delta^{18}O = \delta^{18}O$ (2017) - $\delta^{18}O$ (2010) *vs.* 22 springs from Mt. Amiata arranged according to increasing altitude of discharge (see Fig. 1b for their location). The diagram highlights fluctuations of the isotopic composition for these spring waters over the last decade.

FLUID GEOCHEMISTRY

Geochemical features of the spring waters

During the geochemical survey, water samples pertaining to different chemical facies were collected. According to the square water classification diagram (Fig. 4), the following facies were recognized: *i*) **Group A**: Ca(Na)-HCO_3 and Na(Ca)-HCO_3 cold waters from the Mt. Amiata shallow volcanic aquifer characterized by low TDS values (<200 mg/L) and (Na+K)/(Ca+Mg), (HCO_3/Cl+SO_4) ≅ 1; *ii*) **Group B**: cold Ca(Mg)-HCO_3 waters showing 200<TDS<400 mg/L, emerging from the regional carbonate aquifer; *iii*) **Group C**: Ca-SO_4 thermal waters with TDS between >2,000 and up to 4,600 mg/L; *iv*) **Group D**: Ca-SO_4 acidic waters with an associated free gas-phase. The Na-HCO_3 waters were only represented by one sample (Pozzo Siele). An additional compositional end-member, represented by Na-Cl waters, is related to the geothermal fluids exploited from the Mt. Amiata geothermal wells (Minissale *et al.*, 1997). This grouping is in agreement with that reported by Frondini *et al.* (2009).

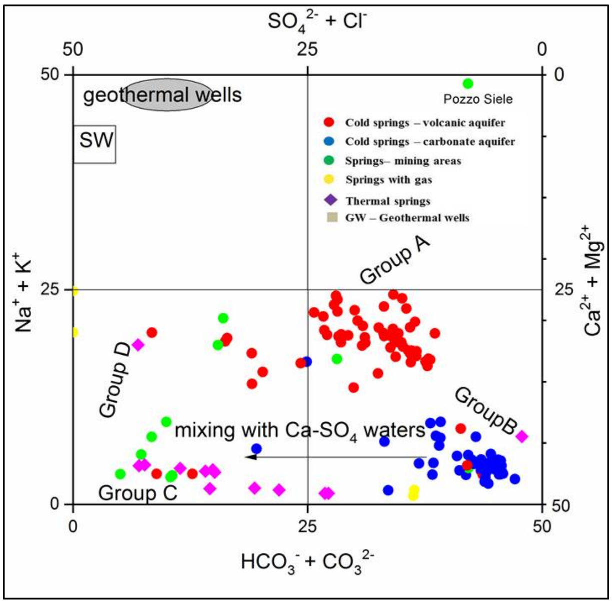

Fig. 4 - Langelier-Ludwig (1942) square diagram showing the analyzed water samples.

The Mt. Amiata cold and thermal water discharges are of meteoric origin and interact with different lithologies, depending on the area of infiltration (siliciclastic and/or carbonate or volcanic rocks). Locally, *i.e.* in both Bagni San Filippo/Bagno Vignoni and Saturnia areas, secondary processes likely ascribable to interactions with an uprising steam phase (separated from the geothermal brine) can be reported, as suggested by water geochemistry (*i.e.*, higher chloride, boron and ammonium concentrations).

Water Quality

The inorganic solutes (including a large set of heavy metals) were generally lower than the required limits of the Italian law and, therefore the water quality of the springs, utilized by the local water management company for supplying drinkable water is to be regarded as good.

Chemical-isotopic characteristics and origin of the Mt. Amiata natural gases

A statistical summary of the isotopic composition of the gases collected in the study area is reported in Table 1.

Table 1 - Statistical parameters of selected isotopic ratios from the Mt. Amiata gas emissions.

Parameter (ratios)	N° obs	Min.	Max.	Average	Med.	St. Dev.	25th percentile	75th percentile
$CO_2/^{3}He$	18	6.23E+08	6.46E+09	1.87E+09	1.78E+09	1.27E+09	1.10E+09	2.34E+09
$^{20}Ne/^{22}Ne$	18	9.776	9.897	9.822	9.819	2.88E-02	9.80	9.84
$^{21}Ne/^{22}Ne$	18	0.029	0.029	0.029	0.029	1.29E-04	0.03	0.03
$^{20}Ne/^{36}Ar$	18	0.120	0.674	0.441	0.463	1.72E-01	0.32	0.61
$^{84}Kr/^{36}Ar$	18	0.002	0.048	0.022	0.0218	1.27E-02	0.01	0.03
$^{132}Xe/^{84}Kr$	18	0.019	0.518	0.093	0.046	1.16E-01	0.04	0.08
$^{4}He/^{21}Ne*$	18	-4.71	253.49	61.31	26.51	7.68E+01	7.33	103.60
$^{4}He/^{40}Ar*$	18	-183.30	35.74	-6.17	3.02	4.38E+01	-0.40	5.44
N_2/Ar	18	56.79	613	190	107	158.58	79.59	307.25
He/Ne	18	0.32	2701	348	47	732	13	199
$^{40}Ar/^{36}Ar$	18	295	477.59	323	301	53.33	295.89	315.00
R_C/R_A	18	0.09	1.06	0.34	0.31	0.25	0.12	0.52
$\delta^{13}C-CO_2$	18	-7.05	0.08	-4	-3.59	1.77	-4.92	-2.76

The gas samples showed CO_2 concentrations up to over 98% by vol. (#6 the "Hole", close to the Bagni San Filippo area), followed by N_2 (as high as 5.2%) and CH_4 (up to 13.7 %). Some gases, especially those emitted by dry gas vents, were displaying quite a strong N_2 excess, supported by measured N_2/Ar ratios (up to 613) (Fig. 5). This feature was then combined with ≅ $\delta^{13}C-CO_2$ usually ranging between -4.5 and -2.5‰ (V-PDB), along with the $^{40}Ar/^{36}Ar$ ratio up to 478 and He isotopes (as R/Ra) from 0.1 to <0.6. Therefore, the analytical outcomes on these genetic parameters allowed to hypothesize that these huge amounts (several hundreds of tons) of CO_2-dominated gases, daily emitted by Mt. Amiata geothermal system, should have a likely primary crustal-thermo-metamorphic origin to which small variable contributions of metasomatically enriched-mantle CO_2 (apparently ranging from 1 to 5%) might be added. The release of CO_2 at relatively shallow crustal levels is indeed consistent with the occurrence of thermo-metamorphic mineral assemblage of pneumatolytic-like environment including wollastonite, diopside, epidote and K-feldspar along with the presence of a poikiloblastic datolite. These mineral phases replaced the primary paragenesis related to the carbonatic quartz-phyllite basement rocks, as also observed in samples cored at depths >3000 m, from deep geothermal boreholes at Piancastagnaio (Gianelli *et al.*, 1988). Thermo-metamorphic conditions, affecting the Palaeozoic host-rocks, should likely be encountered even today at the outer interface of the buried pluton, namely "carapace" (at 5-7 km of depth), the latter corresponding to the so-called K-horizon and characterized by the presence of geo-pressurized fluids and brittle-ductile rheological transition (Gianelli *et al.*, 1988 and references therein).

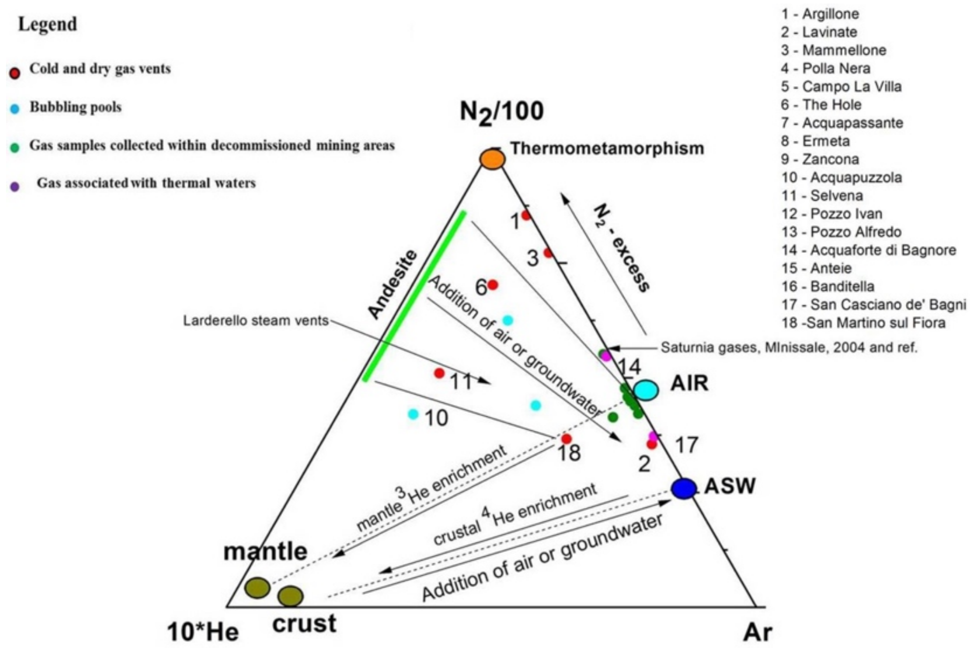

Fig. 5 - Ternary Ar-N_2/100-10*He plot for the Mt. Amiata gases. The reference fields for AIR, ASW, thermo-metamorphic processes and mantle/crust values are also reported.

In this framework, simultaneous N_2 release from micas-bearing Palaeozoic basement rocks (such as phyllites, michaschists, gneisses) can be triggered, coherently with the findings of Honma & Itihara (1981) and Mingram & Brauer (2001) and evidenced by Minissale *et al.* (1997). This interpretation is in good agreement with published N_2 isotopic data, generally showing a typical signature around 4.5 - 5.0‰ (*vs.* AIR-NBS; Minissale *et al.* 1997) in the area. This points to a more dominant crustal source for the analyzed gases. Being some of the analyzed samples (*e.g.* Selvena) characterized by relatively anomalous contents of both hydrogen and methane (up to 2.6 and 13.7% by vol., respectively), some considerations, related to possible geochemical causes, can be proposed. Both hydrogen and methane could be generated by multiple processes, mainly involving thermogenic and biogenic sources. In fact, according to Seewald (1996), Cabassi *et al.* (2019), Fiebig *et al.* (2019), Venturi *et al.* (2019), the redox conditions, as well as the microbial activity and the availability of rock-buffer/catalysts, play a key-role in governing the distribution of hydrogen and short-chain alkanes and/or alkenes (*i.e.*, through redox-dependent processes such as Fisher-Tropsch-like).

Nevertheless, as far as the Mt. Amiata geothermal area is concerned, it was demonstrated that H_2 along with CO_2, CO, CH_4 and other aliphatic-aromatic compounds can be produced under hydrothermal conditions by Mg-siderite decomposition, occurring at temperatures of about 300°C, whenever Palaeozoic basement phyllites are suffering thermo-metamorphic processes (Orlando *et al.*, 2010). Additional and shallower sources of both CH_4 and H_2 could be ascribed to either abiogenic methanation, likely involving serpentinized rocks, or mineralization of organic matter. Moreover, artificial H_2 addition through the corrosion of casing tubes triggered by acidic gases should be invoked (Tassi *et al.*, 2009; Nisi *et al.*, 2014). These interpretations are consistent with the already presented hypothesis related to a still ongoing process of thermo-metamorphic decarbonation beneath the Mt. Amiata geothermal area, as well as with the carbon isotopic data on CH_4 (around -28‰ V-PDB, Minissale *et al.*, 1997). Even geothermometric estimates, the latter performed by applying the log(XH_2/XAr) *vs.* log(CH_4/CO_2) geothermometer (Giggenbach, 1993), seem to suggest that the studied gas emissions are intimately linked to the onset of steam and gas separation from a parent geothermal fluid occurring at depth, where temperatures up to 300°C should be experienced, as also confirmed by geothermal-wellbore logging. Furthermore, as already mentioned, a minor input from a secondary "metasomatic-like" mantle end-member, typical of the central-Italy sector (*e.g.*, Tedesco *et al.*, 1997) was observed and resulted to be progressively increasing towards the distal and southernmost areas. Additionally, gas migration far from the Mt. Amiata volcano along the Plio-Pleistocene transfer faults was hypothesized, in accordance with speculations performed on NG isotope data, the latter mainly based on the specific use of powerful indicators, such as $^4He/^{40}Ar^*$ and $^{21}Ne^*/^{40}Ar^*$ ratios. Concerning the flowrate features of the natural gas vents, the daily emitted amounts of CO_2 appeared to be somewhat underestimated, at least for the punctual degassing sites. New estimates should be provided, also taking in consideration their likely harmful potential for the local populations.

CONCLUSIONS

The present work has dealt with shallow and deep-seated (with the exception of the geothermal wells to which we did not have the access) fluid geochemistry, evidencing the complexity of the geological, structural and hydrogeochemical system of the Mt. Amiata volcano. Even though the connections between the shallow and deep aquifers are not still fully understood, a partial hydraulic continuity cannot be excluded. This implies that more efforts are to be done to better constrain the Mt. Amiata system as a whole.

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