Fourteen Years of Observations of the Hydrothermal System of Stromboli Volcano (Italy): Geochemical Features and Insights on the Volcanic Activity

Cinzia Federico[1], Salvatore Inguaggiato[1], Marcello Liotta[1], Andrea Luca Rizzo[2] and Fabio Vita[1]

[1]Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via Ugo La Malfa,153 - 90146 Palermo, Italy

[2]Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Milano, Via Alfonso Corti, 12 - 20133 Milano, Italy.

Corresponding author: Salvatore Inguaggiato (salvatore.inguaggiato@ingv.it)

Key Points:

- The composition of water and dissolved gases results from the mixing of meteoric and marine water and the input of volcanic gases
- ~~Variations are~~ due to the extent of mixing, the solubility-driven fractionation of dissolved gas species~~, the~~ volcanic activity
- The gas dissolved in the aquifer has a $^{3}He/^{4}He$ range of 3.-4.5 Ra, similar to that measured in olivines and pyroxenes.

Abstract

In active volcanoes, magmatic fluids rising toward the surface may interact with shallow waters, thereby ~~favoring the~~ form~~ation~~ of hydrothermal systems that~~, therefore, are supposed to~~ record variations ~~of the~~ magma~~tic~~ dynamics at depth. Here, we report on a dataset ~~on~~ the chemical and isotopic composition of thermal waters and dissolved gases from Stromboli Island (Aeolian Volcanic Arc, Southern Italy) that ~~globally~~ span fourteen years (2004-2018) of continuous observations.

We show that the shallow thermal aquifer of Stromboli results from variable mixing ~~proportions~~ between meteoric water, seawater~~,~~ and magmatic fluids~~;~~ ~~g~~as-water-rock interactions occur, which induce a large spectrum of variation~~s~~ in both water and gas chemistry. These processes ~~apparently~~ do not affect the 3He/4He of helium dissolved in thermal waters, which ~~has~~ a magmatic signature that varies in response to changes in magma~~tic dynamics~~ at depth. ~~By also considering previous investigations, we pointed out that,~~ in periods of more intense activity, the helium isotop~~es~~ approach~~ed~~ th~~e signature~~ of the gas emitted from the magma residing at 7-10 km depth.

We ~~ultimately~~ propose an interpretative model that reconstructs the complex processes occurring in the hydrothermal system, which is rooted below sea level and next to the main conduits.

~~We conclude by noting that the~~ investigation of hydrothermal waters ~~in~~ active volcanoes is a promising tool to examine magmatic fluids and their shallow circulation, as well as ~~for~~ evaluat~~ing~~ the state of activity of a volcano, ~~especially~~ when summit areas are inaccessible.

1 Introduction

Hydrothermal systems usually form in active volcanoes as a result of the condensation of a saline liquid phase upon decompression of H2O-rich fluids degassed from magma or by absorption of HCl-rich and SO_2-rich fluids in aquifers fed by meteoric or seawater and the contact of these acidic and hot fluids with the surrounding rocks (Webster and Manderville, 2007). The shallowest level of hydrothermal systems is often heated by the acidic vapor separated from deeper aquifers. Gas-water-rock interactions occur and trigger a set of chemical-physical processes and reactions that often lead to significant changes in the pristine composition of magmatic fluids. Hydrothermal systems can be found in many volcanoes on Earth, irrespective of the geodynamic setting of formation, as they form in open- or closed-conduit volcanoes, in subaerial or submarine conditions, and consist of one or two phases (liquid and/or vapor) developed into convective fluid cells (Chiodini et al., 1995, 2001, 2005; Osinski et al., 2001; Finizola et al., 2002; Caliro et al., 2004, 2007; Lupton et al., 2008; Antoine et al., 2009; Federico et al., 2010; Taran et al., 2017; Mauri et al., 2018; Rizzo et al., 2019). Hydrothermal systems dissipate much of the energy produced by the volcan~~o~~ and may display the first indications of impending crises (e.g., Chiodini et al., 2016). The nature and extent of hydrothermal systems (Revil and Linde, 2006; Finizola et al., 2009, Revil et al., 2011; Lénat et al., 2012; Mauri et al., 2018) influence the occurrence of hazards such as phreatic and phreatomagmatic explosions, and flank collapses (Lorenz and Kurszlaukis, 2007; Weinsten, 2007). ~~Similarly,~~ the geochemical characterization and monitoring of hydrothermal fluids are of great importance to constrain i) the composition, temperature, pressure, and redox conditions of the system, ii) the state of activity of the volcano, iii) the evolution of unrest, particularly in those

systems where access to high-temperature fumaroles is unsafe (Giggenbach, 1975; Chiodini et al., 1995, 2001, 2005; Caliro et al., 2004, 2007; Capasso et al., 1999; 2005; Inguaggiato et al., 2000, 2004, 2005, 2010; Lupton et al., 2008; Federico et al., 2010; Rizzo et al., 2015, 2019; Taran et al., 2017; Mauri et al., 2018). In many cases, the shallow fluids of meteoric or marine origin feeding the volcanic aquifers may modify the pristine signature of the deep fluids and the signals linked to volcanic activity. Understanding gas–water interaction processes, which modify the pristine physicochemical characteristics of fluids, sheds light on both the origin of the fluids and the degree of this interaction at depth. In recent years, the study of the volatiles dissolved in the thermal waters of several volcanic systems has provided useful ~~indications on~~ the origin of these fluids and the processes ~~able to~~ modify their chemical and isotope composition during their ~~pathway~~ toward the surface (Inguaggiato et al., 2000; 2005; 2010; Capasso et al., 2005; Paonita et al., 2016; Federico et al., 2017a).

Stromboli Island (Aeolian Volcanic Arc, Italy) is an open-conduit volcano characterized by persistent explosive activity, which makes the regular monitoring of fumarole gases in the crater area hazardous (Carapezza and Federico, 2000; Capasso et al., 2005; Rizzo et al., 2009). ~~Instead~~, the thermal aquifer identified at the base of the subaerial part of the edifice (Carapezza and Federico, 2000; Finizola et al., 2002, 2003, 2009; Capasso et al., 2005; Revil et al., 2011) represents a safe point of observation to acquire insights on the volcano-hydrothermal system.

Many geochemical studies on the thermal aquifer, which is ~~generally~~ accessible via privately drilled wells, have been carried out in the last two decades (Carapezza and Federico, 2000; Carapezza et al., 2004; Inguaggiato and Rizzo, 2004; Capasso et al., 2005; Liotta et al., 2006; Federico et al., 2008; Grassa et al., 2008; Rizzo et al., 2008, 2009, 2015; Madonia et al., 2021). These studies revealed i) the main composition of thermal waters and gases dissolved therein, ii) the influence of shallow marine and meteoric waters on the hydrothermal composition, iii) the presence and extent of gas-water-rock interaction processes, and iv) a magmatic signature concerning helium isotopes. These studies brought an invaluable understanding of fluid geochemistry at Stromboli, but most of them took place over short periods, often limited to single effusive eruptions.

In this work, we report on the chemical and isotopic composition of thermal waters and dissolved gases from Stromboli Island~~, which c~~over fourteen years of observations from 2004 to 2018. We characterize the hydrothermal system of Stromboli, highlighting the main processes occurring therein. The aim is to provide an interpretative framework ~~of~~ the variations in water and gas chemistry, which ~~takes into account~~ the ~~different~~ processes ~~related to~~ meteoric input, seawater contamination, gas-water-rock exchange~~s~~, and water mixing, before relating them to volcanological processes. We report on 8 thermal water wells located in the area of Stromboli village ~~for a total of~~ 112 sampling campaigns. We show that ~~the~~ magmatic fluids re-equilibrate at hydrothermal conditions and the gases collected in the monitored wells show variable relative contents of CO_2, He, and CH_4, the latter being of hydrothermal origin. The variable extent of rock-leaching and seawater/meteoric mixing modulate the chemistry and isotopic ratios of the shallow water. The dissolved gas shows a magmatic signature of $^3He/^4He$, comparable to that measured in olivine and pyroxene minerals (Martelli et al., 2014), whose temporal monitoring revealed systematic variations during ~~the recorded~~ effusive eruptions and ~~main~~ phases of ~~high~~ volcanic activity.

2 Study area

2.1 Volcanological background of Stromboli

Stromboli Island is an active volcano ~~belonging to~~ the Aeolian Archipelago (Italy), which is located in the southeastern Tyrrhenian Sea (Figure 1), and associated with the Quaternary subduction of the African plate below the European plate (e.g., Gasparini et al., 1982). Stromboli was built ~~up~~ on a 17 km-thick continental crust (Morelli et al., 1975; Panza et al., 2007) and is characterized by persistent explosive activity from the summit craters (usually every 10-20 min), known throughout the world as "Strombolian ~~A~~ctivity" (e.g., Rosi et al., 2000). This Strombolian activity is occasionally interrupted by lava effusions and/or violent explosions referred to as "major explosions" and "paroxysms", which eject large bombs and may occasionally cause hot avalanches, landslides~~,~~ and ~~ultimately also~~ tsunamis. In the last 35 years, four effusive eruptions occurred~~,~~ in 1985, 2002, 2007, and 2014 (Inguaggiato et al. 2018)~~,~~ in addition to many major explosions and lava overflows. Paroxysmal explosions were recorded in 2003, 2007, and two in 2019 (Andronico et al., 2021).

Stromboli erupts magmas belonging to four distinct series, i.e. calc-alkaline (CA), high potassium calc-alkaline (HKCA), shoshonitic (SHO), and potassic (KS) (e.g., Francalanci et al., 1988, 1989). All erupted magmas are mafic (SiO_2 < 55 %, MgO> 4%) and exhibit similar subduction-related patterns of trace elements (Francalanci et al., 1993, 2007; Tommasini et al., 2007). The geochemical signature of the primitive batches of the Stromboli magmatic series (CA, HKCA, SHO, KS) is attributed to the partial melting of a mantle wedge, made heterogeneous by the variable metasomatism by fluids released by the subducting slab (Tommasini et al., 2007; Schiavi et al., 2012). Moreover, crustal contamination likely occurred in the KS magmas (Ellam et al., 1989; Francalanci et al., 1993, 2004; Tommasini et al., 2007; Schiavi et al., 2012; Martelli et al., 2014).

The present-day activity of Stromboli belongs to the shoshonitic series and consists of two types of magmas: i) a high porphyritic (HP) volatile-poor magma, stored at 2-4 km depth bsl that undergoes slow but continuous degassing-induced crystallization and ii) a low porphyritic (LP) volatile-rich magma stored at 7-10 km depth bsl, refilled by CO_2-rich magmas rising from the mantle (e.g., Francalanci et al., 2004; Bertagnini et al., 2008; Métrich et al., 2010; 2021). The persistent Strombolian activity of the volcano is maintained in a steady state, driven by the continuous refilling of the shallow magmatic reservoir with deep volatile-rich magmas, together with almost continuous magma emission during ordinary activity (e.g., Landi et al., 2009; Métrich et al., 2010). Magmatic volatiles, which represent the engine of the explosive volcanic activity, are largely emitted from the summit craters during both quiescence and eruptive phases, but they also escape from the soil in the summit area and along the upper flanks of the edifice, and at the base of the cone, focused along tectonic lineaments (Carapezza and Federico, 2000; Finizola et al., 2006; Carapezza et al., 2009; Inguaggiato et al., 2019; 2020; 2021).

2.1 The Stromboli thermal aquifer

2.2.1 Hydrogeology

Previous hydrogeological studies (Revil et al. 2011; Madonia et al. 2021) described the characteristics of the aquifer in this sector of Stromboli. Based on electrical resistivity measurements, soil CO_2 concentrations, temperature, and self-potential measurements, Revil et al. (2011) provided insights regarding the position of shallow aquifers and the extension of the hydrothermal system. They found that ~~the~~ self-potential data reveal the position of an unconfined aquifer above the villages of Scari and San Vincenzo and provided an estimate of the depth of this aquifer. More recently, Madonia et al. (2021) indicated that there is a unique groundwater body in the form of a thin lens of fresh water~~,~~ floating above the infiltrating seawater and suggested the existence of a multi-level aquifer~~, according to the presence~~ of alternating lavas and pyroclastic deposits.

2.2.2 Chemistry of groundwater

The thermal waters were studied by Carapezza and Federico (2000), Carapezza et al. (2004), Capasso et al. (2005), and Grassa et al. (2008). The authors found that the chemical composition of thermal waters is the result of mixing in different proportions between seawater and meteoric water, heated by vapor ascending from depth, with limited interaction with the volcanic rocks. They reported temperatures in the range of 35–47°C, water table at depths of 5–20 m b.g.l., and a wide range of dissolved salt content ranging from 8,200 to 40,000 mg/L, as the result of variable fractions of seawater. The reported average pH values were in the range of 6.31 and 6.97. The chemical composition of both end-members is modified by the dissolution of a CO_2-rich gas phase and by leaching of the aquifer-hosting rocks. Liotta et al. (2006) also studied the chemical composition of the rainwater which is mainly controlled by the contribution of ~~the~~ marine aerosol near the coast, whereas it is strongly influenced by volcanic activity near the summit vents. The hydrogen and oxygen isotopic composition of rainfall shows seasonal variability and correlates with air temperature, while deuterium excess values show a positive correlation with altitude. The isotope composition of the meteoric recharge was retrieved from the mean annual volume-weighted values, being between -6.2 and -8.4‰ for $\delta^{18}O$ and between -35 and -45‰ for δD (versus the Vienna Standard Mean Ocean Water, V-SMOW) (Liotta et al. 2006).

2.2.3 Chemistry and carbon isotopes of dissolved gas

The chemical and isotope composition of ~~the~~ dissolved gas in the Stromboli shallow aquifer was discussed by Capasso et al. (2005) and Federico et al. (2008). The air-free composition of the dissolved gas is dominated by CO_2, with variable ~~contents~~ of He and CH_4. While the authors claim a magmatic origin for both CO_2 and He, the CH_4 contents were ascribed to a contribution of fluids from a hydrothermal system.

A wide compositional variability characterizes both the whole aquifer and each sampling site (Capasso et al., 2005; Federico et al., 2008). This variability was ascribed to the heterogeneity of volcanic deposits, made of alternating levels of pyroclastics of different grain sizes, porosity, and permeability, which host small water bodies variably contaminated by seawater and volcanic fluids. The variable enrichment in He and CH_4 compared to an original CO_2-dominated volcanic gas could be a consequence of modification of the gas during dissolution in the aquifer. Both vapor separation from a hydrothermal aquifer and dissolution in the shallow meteoric aquifer would promote the preferential partitioning of the less-soluble gas species into the vapor phase, namely He and CH_4 compared to CO_2, and also the isotope fractionation of gaseous CO_2 compared to dissolved carbon species (Capasso et al., 2005; Federico et al., 2008).

Some of the variability in the ~~observed data~~ was also ascribed to the changeable input of volcanic fluids over time. Carapezza et al. (2004) and Capasso et al. (2005) reported on significant variations in the chemical and isotopic composition of CO_2 in all the monitored thermal wells ~~by the time of~~ the effusive eruption that occurred in ~~the~~ 2002-2003 ~~period~~. Values of dissolved CO_2 as high as 75-220 cc/L at STP in March-July 2002 were measured six months before the onset of the eruption, which was shortly preceded by one order of magnitude increase in the soil CO_2 flux in the summit area (Inguaggiato et al., 2011). Moreover, before the 5 April 2003 paroxysm, Carapezza et al. (2004) and Rizzo et al. (2008) observed a marked decrease in the pH values of 0.1-0.5 pH units in the thermal water wells located in the Stromboli village, ascribed to the increased input of CO_2 in the shallow thermal aquifer.

Inguaggiato et al. (2017a,b) reported on variations in pCO_2 in two wells for a limited period, related to variations in soil CO_2 fluxes recorded both in Scari (~~str01,~~ Inguaggiato et al., 2017b) and at the summit of the volcano in the same period (Inguaggiato et al., 2017a).

2.2.4 Noble gases

Carapezza and Federico (2000) ~~were the first to~~ report on the noble gas composition (concentration of ^4He and ^{20}Ne, $^4He/^{20}Ne$ and $^3He/^4He$) of fluids from Stromboli in a fumarole located at Pizzo Sopra La Fossa (Figure 1), called SC5. This fumarole was monitored from 1992 to 1998 and showed $^3He/^4He$ values in the range of 2.71-3.55 R_a, indicating a clear magmatic signature. However, the gases showed a variable but significant air contamination, as suggested by $^4He/^{20}Ne$ between 1.0 and 3.2, implying an uncertainty in the corrected $^3He/^4He$ values. Carapezza and Federico (2000) evidenced that the $^3He/^4He$ values measured at SC5 were appreciably lower than those measured at Vulcano Island and Mt Etna, inferring a contribution of radiogenic crustal ^4He to the local fumarolic gas.

For the first time in 2002, Inguaggiato and Rizzo (2004) studied the noble gas composition of thermal waters from Stromboli within a methodological study aimed at developing and consolidating a technique to determine and monitor~~ing of~~ the isotope ratio of dissolved He in groundwater. Three wells were selected (Cusolito, Fulco, and Zurro; Figure 1) where water samples were collected. Helium concentrations were in the

range ~~of~~ 1.4–6.2·10^{-4} cc/L at STP, in the same order of magnitude as that measured by Carapezza and Federico (2000). Neon concentrations ranged between 3.5·10^{-5} and 1.6·10^{-4} cc/l at STP. The $^{4}He/^{20}Ne$ was 3.7–9.6. The $^{4}He/^{20}Ne$ corrected for air contamination (R_c/R_a) was in the range ~~of~~ 4.06–4.23 R_a.

Inguaggiato and Rizzo (2004) found $^{3}He/^{4}He$ values of 4.06–4.23 Ra in thermal waters sampled at the base of the subaerial volcanic edifice. To explain the lower isotopic signature of SC5, they argued that the water-rock interaction in a hydrothermal system recognized in the summit area by Finizola et al. (2002, 2003) could enhance the contribution of radiogenic ^{4}He from U and Th decay, thus decreasing the pristine $^{3}He/^{4}He$ in Pizzo Sopra La Fossa fumaroles. Finally, Inguaggiato and Rizzo (2004) highlighted that the study of dissolved gases in the thermal waters in Stromboli could be strategic for monitoring purposes, besides validating the technique for the determination of dissolved noble gases.

Between 2002 and 2014, Capasso et al. (2005) and Rizzo et al. (2009, 2015) reported on the first dataset of noble gas monitoring in thermal waters collected with a roughly monthly frequency. During that period of monitoring, i) an effusive eruption occurred at Stromboli in 2002-2003 as well as a paroxysmal explosion on 5 April 2003; ii) an effusive eruption occurred in February-April 2007, including a paroxysmal explosion that occurred on the 15th March, iii) an effusive eruption occurred in August-November 2014.

The above-reported studies on time series found that $^{3}He/^{4}He$ values ranged from 3.4 and 4.5 R_a, with slight or negligible differences among the wells, while the $^{4}He/^{20}Ne$ was in the range of 1-11. These values were comparable to those found by Inguaggiato and Rizzo (2004), except for the natural variability related to the persistent activity of Stromboli. In addition, Capasso et al. (2005) showed that the $^{3}He/^{4}He$ measured in the thermal waters were comparable to the unique value of 4.3 R_a found during the eruption in newly-formed fumaroles located close to the north-east crater (Finizola and Sortino, 2003; Finizola et al., 2002). ~~This evidence~~ further confirmed that the range of $^{3}He/^{4}He$ values found in thermal waters is representative of the magmatic signature and can be used for evaluating the state of activity of the volcano. In terms of application to volcano monitoring, Capasso et al. (2005) and Rizzo et al. (2009; 2015) showed that the temporal variations of $^{3}He/^{4}He$ occurred simultaneously in all the thermal water wells. Importantly, the highest $^{3}He/^{4}He$ values (4.50–4.56 R_a) were always measured during the eruptive phases~~. These high values~~ were interpreted as due to new input of undegassed LP-like magma and the transfer of its gas towards the surface. After the eruptive phases, ~~different pulses of magma input were hypothesized for a few weeks, as indicated by~~ relatively high $^{3}He/^{4}He$ values at all the sampling sites, suggest~~ing~~ ~~the~~ resumption of ~~the~~ Strombolian activity (Capasso et al., 2005; Rizzo et al., 2009; 2015).

Martelli et al. (2014) studied the elemental (He, Ne, and Ar) and isotopic (He and Ar) compositions of fluid inclusions hosted in olivine and clinopyroxene from lavas, pyroclastics, and cumulate xenoliths erupted by Stromboli in the last 60 ka. The authors found that most of the investigated samples exhibit a $^{3}He/^{4}He$ ratio in the range of 4.0–4.9 Ra, with only the minerals of the KS series showing lower isotopic values (≤3.5 Ra).

This variability was interpreted as due to a heterogeneous mantle source. In detail, the maximum $^{3}He/^{4}He$ ratio found in the LP fluid inclusions (i.e., 4.6 Ra) corresponds to the maximum ratio measured in the hydrothermal fluids (Capasso et al., 2005; Rizzo et al., 2009), suggesting that this value can be considered as a marker of the maximum contribution from the LP magma in surface gases.

3 Materials and Methods

3.1 Sampling and in situ measurements

Most of the sampling sites are wells located on the northeast side of Stromboli Island (Figure 1), drilled for private use. Limoneto and COA wells were drilled for purely scientific use aimed at groundwater monitoring. We will also report and discuss data relative to two samples of dripping water from a cave in the neighborhood of Fulco well (FCDW) that we consider representative of the infiltrating water of that area. The highest piezometric level (0.86 m asl) is measured in the COA well, the farthest from the coast, whereas in the other wells, closer to the coast, a piezometric level of around 0.5 m is measured, with a hydraulic gradient of 1.7 m km^{-1} at COA and 2.0 m km^{-1} at Limoneto. Groundwater monitoring was performed by using portable equipment, an electric submersible pump, or on-site plumbing when present. The chemical-physical parameters (pH, temperature, electrical conductivity, and Redox potential) were measured in the field using Orion Star A series instruments, equipped with Hamilton electrodes. At the beginning of each sampling activity, the pH-meter was calibrated using at least two buffers. Over the sampling period, the calibration of the pH-meter was verified between one sampling and another by a single-point calibration at pH 7. Calibration of the conductivity meter Orion Star A 122 was performed using the standard of a known concentration that is close to the expected range of conductivity of the water being sampled. The same sampling procedure was used over the entire study period. A submersible pump was placed approximately in the mid-portion of the water column in the wells and switched on for a sufficient duration (15-30 min) to purge the well of the stagnant water, before the sampling. During this stage, pH, electrical conductivity, and turbidity of the water were monitored in order to verify the achievement of adequate purging. Adequate purging is achieved when the pH and electrical conductivity of the water show constant values, and the turbidity has disappeared, resulting in water clarification. The condition of stability requires pH variations within 0.1 unit and conductivity variations within about 5%.

For the determination of dissolved major ions, water samples were filtered with 0.45 μm filters and stored in LD-PE (low-density polyethylene) bottles. The aliquots to be analyzed for cation content were also acidified to pH ≈ 2 with Suprapur(R) HNO_3. The alkalinity was determined by titration with HCl (0.1 N) on an untreated aliquot.

Water samples, used for dissolved gas and isotope determinations, were collected in serum bottles and sealed underwater with Teflon-faced rubber septa and aluminum seals, to minimize atmospheric contamination. Glass bottles were filled while avoiding

turbulent water flow, by keeping the pump flow rate low. In addition, silicon tubes were inserted directly down to the bottom of the serum bottle while it is immersed in a basin filled with the same water to be sampled (Liotta and Martelli, 2012). The bottles were sealed by crimping the Teflon-faced rubber septum using an aluminum seal.

3.2 Chemical and isotopic analyses

Major elements were analyzed in the laboratory of INGV-Palermo using ion chromatography systems (Dionex-Thermo ICS 1100) in suppressed mode, equipped with a column AS14A and a precolumn (AG14A) for anions (F^-, Cl^-, Br^-, and SO_4^{--}), and a column CS12A and precolumn CG12A for cations (Li^+, Na^+, K^+, Mg^{++}, and Ca^{++}). The columns work under a continuous flow of a carbonate–bicarbonate eluent for anions and a methanesulfonic acid eluent for cations. The precision and accuracy of the method are described in Prano and Liotta (2018) and are usually below 5%. During each analytical session, a certified material was analyzed to check the accuracy.

Dissolved gases were sampled and analyzed according to the method described by Capasso and Inguaggiato (1998), which is based on the equilibrium partition of gas species between a liquid and a gas phase after the introduction of a host gas (Ar) into the sample.

The analysis was performed in the INGV-Palermo laboratories using a gas chromatograph (Perkin Elmer Clarus 500) equipped with a double detector (a thermal conductivity detector [TCD] and a flame ionization detector [FID] with a methanizer) and Ar as the carrier gas. H_2, O_2, N_2, and CO_2 were measured using the TCD detector, while CH_4 and CO were determined using the FID detector coupled to the methanizer (Capasso and Inguaggiato, 1998). Standard mixtures ~~are~~ routinely analyzed before any analytical session, and the analytical precision was always better than 5%.

The isotope analyses were performed in the laboratories of INGV-Palermo.

~~A completely~~ automated procedure was used to determine the $\delta^{13}C$ of total dissolved inorganic C (TDIC) in water ($\delta^{13}C_{TDIC}$) (Capasso et al., 2005). C-isotope ratios ($^{13}C/^{12}C$) were measured using a mass spectrometer (Delta V Plus) connected online to the GasBench II system. The results were reported in δ‰ versus the V-PDB standard, with a precision better than ±0.1‰.

The analysis of He and Ne concentrations, $^3He/^4He$, and $^4He/^{20}Ne$ of the gases dissolved in thermal waters was performed in the laboratories of INGV-Palermo (Vita et al., 2023).

Noble gases were extracted from the water following ~~the~~ method developed by Inguaggiato and Rizzo (2004)~~. This method uses the same theoretical principle as~~ that proposed by Capasso and Inguaggiato (1998) for the study of gases dissolved in water, ~~but it was optimized for helium and neon isotopic measurements~~. ~~Therefore,~~ two ~~distinct~~ aliquots of water samples were sampled. After introducing the extracted gases in a system of ultra-high-vacuum purification lines, ^3He, ^4He, and ^{20}Ne and the $^4He/^{20}Ne$ ratios were determined by separately admitting He and Ne into a split flight tube mass spectrometer (GVI-Helix SFT, for He analysis) and a multi-collector mass spectrometer (Thermo-

Helix MC plus, for Ne analysis). He and Ne purification and separation were carried out based on standard purification procedures (Rizzo et al., 2015; 2016). $^{3}He/^{4}He$ ratio is expressed as R/R_a (R_a being the He isotope ratio of air and equal to $1.39 \cdot 10^{-6}$), and the analytical error is generally below 0.7%. The $^{3}He/^{4}He$ values were corrected for the atmospheric contamination based on the measured $^{4}He/^{20}Ne$ ratio, as follows:

$$R_c/R_a = \left[R_M/R_A \left(\frac{4He}{20Ne}\right)_M - \left(\frac{4He}{20Ne}\right)_A\right] / \left[\left(\frac{4He}{20Ne}\right)_M - \left(\frac{4He}{20Ne}\right)_A\right] \quad (1)$$

where subscripts M and A refer to measured and ASW theoretical values, respectively [$(4He/20Ne)_A$=0.285]. The corrected $^{3}He/^{4}He$ ratios reported in the text and Table 1 are expressed as R_c/R_a values.

4 Results

4.1 Chemistry of groundwater

The whole dataset covers the period 2004 – 2018 and includes data relati~~ve~~ to the wells ~~named~~ Fulco, Cusolito, Zurro, Limoneto, Ossidiana, Saibbo, COA, and Piscità ~~(~~All the data produced in this work have been archived in the EarthChem data repository~~,~~ Vita et al. 2023). We also report and discuss the geochemical data relative to two samples of dripping water from a cave in the neighborhood of Fulco well (FCDW, Fulco Cave Dripping Water) that we consider representative of the infiltrating water in that area. The water temperature is almost constant over time at each site (as previously observed by Grassa et al, 2008)~~:~~ mean values 35.8°C at Zurro, 41.5°C at Fulco, 40.1°C at Saibbo, 40.1°C at Limoneto, 41.9°C at COA, 42.8°C at Cusolito, 34.8°C at Ossidiana, and 32.7°C at Piscità. The pH values range between 5.72 and 7.43 and are systematically lower at COA, Saibbo, and Fulco sites, with average values of 6.33, 6.33, and 6.39, respectively. All the other sites exhibit higher average pH values: 6.70 at Cusolito, 6.75 at Limoneto, 6.93 at Ossidiana, 6.86 at Zurro, and 7.11 at Piscità. All the samples fall around the line representative of the Na/Cl ratio in seawater, between the FCDW sample and the Mediterranean seawater composition (Figure 2) (Grassa et al., 2008; Carapezza and Federico, 2000; Carapezza et al., 2004; Capasso et al., 2005). When taking into account the isotope composition of thermal waters, all the samples fall between the meteoric end-member and seawater (Figure 3).

4.2 Chemistry and carbon isotope~~s~~ of the dissolved gas

We present the dissolved gas composition and carbon isotope composition of dissolved carbon (Vita et al. 2023).

The ~~average composition of the~~ dissolved gas is dominated by CO_2 in all wells, ~~whose~~ contents range from 1.5 to 290 cc/L at STP. Nitrogen contents range from 3 to 23 cc/L at STP, whereas dissolved O_2 was always below the concentration of air-saturated water (7

cc/L at STP) with N_2/O_2 ratios much higher than in air-saturated water at STP (N_2/O_2 ~ 2). The CH_4 contents range from $1 \cdot 10^{-4}$ to $5 \cdot 10^{-2}$ cc/L at STP.

The triangular diagram of Figure 4 shows a wide variation in the relative proportions of He, CO_2, and CH_4 in the dissolved gas phase, in both the whole aquifer and each sampled well. In particular, Fulco and Ossidiana wells are characterized, on average, by the highest relative ~~contents~~ of CO_2, although some samples from both wells ~~point towards the~~ CH_4 ~~corner~~. The wells COA, Cusolito, and Zurro show a stronger enrichment in both He and CH_4, with few samples ~~pointing to the~~ CH_4 ~~corner~~. ~~Lastly,~~ Limoneto and Piscità are characterized by the most evident enrichment in He.

The Stromboli thermal aquifer is characterized by a wide range of CO_2 contents, observed even in wells located in a restricted area and, in some cases, in a given well over time. The high CO_2 contents in the aquifer are matched by correspondingly more positive values of the isotope composition of the dissolved CO_2 ($\delta^{13}C_{CO2}$, Vita et al., 2023), computed from the measured $\delta^{13}C_{TDC}$ (Vita et al., 2023). The pristine isotope composition of gaseous CO_2 is retrieved from the measured $\delta^{13}C_{TDC}$ by applying the fractionation factor between total dissolved carbon (TDC) and gaseous CO_2 ($\alpha_{TDC-CO_{2,g}}$), computed according to the weighted contribution of the enrichment factors ε between CO_2 and each dissolved carbon species, as described by Capasso et al. (2005) and Federico et al. (2008). As observed in the graph, the highest dissolved CO_2 contents, measured in Fulco well, are associated with values of $\delta^{13}C_{CO2}$ of about -1.5 ‰. The lowest CO_2 contents, characterized by relatively more negative $\delta^{13}C_{CO2}$ values, were measured in the wells Piscità and Zurro.

4.3 Chemistry of noble gases

Here, we integrate the existing data on He and Ne concentrations, $^4He/^{20}Ne$ and $^3He/^4He$ with new data that cover part of the inter-eruptive periods between 2004 and 2018 (Vita et al., 2023).

Helium concentrations are in the range of $9.2 \cdot 10^{-5}$–$2.3 \cdot 10^{-3}$ cc/L at STP (Figure 6), with the highest values measured in COA, Limoneto, and Piscità wells and the lowest in the Fulco well. Neon concentrations range between $4.2 \cdot 10^{-5}$ and $2.4 \cdot 10^{-4}$ cc/l at STP. The $^4He/^{20}Ne$ varies between 0.9 and 17.3 (Figures 6 and 7). In general, the R_c/R_a values do not show significant differences among the wells (Figure 7).

The $^3He/^4He$ corrected for air contamination (R_c/R_a) is in the range of 3.89–4.53 R_a (Figure 8). These ranges are in the same order of magnitude as those measured by Carapezza and Federico (2000), Inguaggiato and Rizzo (2004), Capasso et al. (2005), and Rizzo et al. (2009, 2015).

5 Discussion

~~The geochemical investigation carried out on the thermal aquifer of Stromboli Island helped improve our understanding of the processes affecting volcanic gases and the hydrological~~

~~system. This improved understanding has enhanced the potential for using fluid geochemistry for monitoring volcanic activity.~~
~~In the following discussion, we focus on:~~
~~- the processes controlling water chemistry, i.e. mixing between meteoric and marine water and gas-water-rock interaction;~~
~~- the effects of gas-water interaction on the composition of volcanic gases;~~
~~- the potentiality of helium isotopes measured in the shallow aquifer for tracking the variable input of early-degassed primitive fluids.~~

5.1 Processes controlling water chemistry

Each site shows chemical variability due to different mixing between ~~the~~ meteoric recharge and seawater. Fresh groundwater usually lies upon brackish waters, and fluctuations of the water table can occur in coastal sites as an effect of tides (Singaraja et al., 2018) and the seasonal variability of the meteoric recharge (Liotta et al., 2006). As a consequence, even if the sampling of thermal water is always carried out using the same protocol (pumping flux, depth of the pump, duration of pumping before collecting samples, etc.), samples from the same sites show temporal variability ~~of~~ their salinity~~. In addition, such variability has different extents~~ depending on the site features.

Among the elements that are enriched by the interaction with aquifer-hosting rocks (Capasso et al., 2005), K has the higher mobility since it does not precipitate as secondary phases, unlike Ca and Mg (e.g. calcite, Mg-calcite and gypsum), recognized in the hydrothermal alteration of the surface rocks (Finizola et al. 2002). Due to these characteristics, ~~it~~ offers the opportunity to evaluate the extent of water-rock interaction. In Figure 9, K is plotted versus Cl. All the samples exhibit a clear enrichment in K with respect to seawater. Samples from Fulco, Cusolito, Limoneto, Ossidiana, and Saibbo wells (with few exceptions probably due to direct seawater intrusion) fall ~~around an alignment~~ between Cusolito and FCDW. The alignment is indicative of a mixing process between a saline end-member (among the samples of Cusolito, EM3 in Figure 9) and the infiltrating water (FCDW and the poor saline samples from well Fulco, EM1 in Figure 9), being both enriched in K. This implies that ~~also the~~ shallow fresh waters interact with the host~~ing~~ rocks and leach K. Conversely, samples from Zurro well ~~show~~ mixing between a saline end-member with high Cl content (one sample from Piscità well, EM2 in Figure 9) and a shallow end-member (represented by poor saline samples from well COA, EM4 in Figure 9). Samples from COA well ~~show~~ mixing between a saline end-member (EM3) enriched in K and a shallow end-member (EM4 in Figure 9). For both Zurro and COA samples, the shallow end-member (EM4) does not show a clear K-enrichment and probably reflects the rainfall composition~~. This~~ suggest~~s~~ ~~a~~ fast infiltration of meteoric water and limited interaction with the hosting rocks.

The dissolution and hydration of magmatic CO_2 promote the chemical weathering of rocks. If ~~the~~ equilibrium is attained in the measured pH range, the carbonic acid dissociates as HCO_3^-. Total alkalinity is a measure of CO_2-water interaction and provides information about the paths through which CO_2 reaches the aquifer. In Figure 10 we show

that samples from Fulco, Cusolito, Limoneto, Ossidiana, and Saibbo define a negative relationship between Cl and total alkalinity. Since ~~the~~ freshwater floats on ~~the~~ saline ~~one~~, such a correlation implies that most of the CO_2 dissolved in water does not come from depth but is carried by infiltrating waters. The ~~huge amount~~ of CO_2 degassing from soils (Inguaggiato et al., 2019 and reference therein) as well as the identification of a low resistivity body in the summit area of the volcano (Revil et al., 2011 and references therein), are consistent with the idea that meteoric waters infiltrating ~~in~~ the summit area interact with CO_2 rising ~~from~~ fractures, favoring water-rock interaction and ~~the~~ increase of the total alkalinity. A fraction of the total dissolved carbon reaches the basal aquifer as dissolved CO_2. At the Zurro site, the freshwater end-member exhibits low ~~values of~~ total alkalinity, indicating ~~that~~ meteoric waters ~~infiltrate with limited interaction with~~ CO_2. Consequently, we observe a negative relationship between Cl and total alkalinity (Figure 10). At the COA site, samples display a large dispersion of ~~data~~ since the well is the most elevated (70 m a.s.l.) and deepest. As a consequence, ~~it~~ intercepts several lithological layers and receives different types of infiltrating waters ~~(~~with different CO_2 contents~~)~~.

The meteoric origin of fresh groundwater ~~was already~~ highlighted by Grassa et al. (2008) using water stable isotopes. ~~An update of the dataset~~ is ~~shown~~ in Figure 3. All the samples fall between the isotope composition of the Mediterranean seawater and the local meteoric end-member defined by Liotta et al. (2006).

5.2 ~~The g~~as/water interaction processes: dissolution-related gas fractionation

~~The integrated dataset presented in this paper confirms the outcomes reported by Capasso et al. (2005) and Federico et al. (2008) on the chemical and C isotope composition of the gas dissolved in the Stromboli shallow aquifer.~~

~~As shown in Figures 4 and 5,~~ the relative proportions of CO_2, CH_4 and He vary in the different sites and, in the same site, over time; moreover, the highest CO_2 contents also have a C-isotope signature close to -1.5 permil, which is in the range of values measured in the SC5 and Fossa fumaroles, in the summit area (Carapezza and Federico, 2000; Finizola et al., 2003; Capasso et al., 2005; Rizzo et al., 2009), as well as in fluid inclusions of olivine and clinopyroxene crystals separated from the San Bartolo ultramafic cumulates (Gennaro et al., 2017). The CO_2-poorer samples, namely Limoneto, Piscità, and Cusolito, ~~instead,~~ have more negative C-isotope composition and are enriched in both He and CH_4 by more than two orders of magnitude compared to ~~the~~ air-saturated water (ASW). Although the relationship shown in Figure 5, observed in other volcanic and non-volcanic aquifers (Chiodini et al., 2000; Federico et al., 2002; Ohsawa et al., 2002; Yamada et al., 2011), has generally been interpreted as ~~owing to the~~ mixing between volcanic CO_2-rich gases and soil CO_2-~~-~~poor gases with negative isotope composition~~,~~ typical of organic carbon~~,~~ other studies interpreted negative $\delta^{13}C$ values as due to fractionation of CO_2 during multistep dissolution in water (Simmons and Christenson, 1994 and references therein). ~~According to Capasso et al. (2005) and Federico et al. (2008),~~ the dataset presented here suggests that some portions of the aquifer are ~~reached~~ by a He-CH_4-rich gas phase, derived from a volcanic gas modified

during ~~the~~ interaction with a multilevel hydrothermal aquifer, where the gases could separate and dissolve from one level to another. The multilevel aquifer is probably hosted by the alternating levels of lavas and pyroclastics in the subsoil of the Scari area, as suggested by Madonia et al. (2021). During gas-water interaction, different gas species ~~would~~ fractionate according to their solubility in water~~. The fraction process is~~ described in Appendix 1.

The extent of Rayleigh~~'s~~ fractionation depends on the solubility of gases and the fraction of remaining gas (F) in equation 2 ~~(~~Appendix 1), which could be considered as a proxy for the relative mass rates of the CO_2-rich gas and the water with which it interacts. The larger the amount of gas interacting with a given volume of water in ~~the time unit~~, the smaller the relative amount of gas removed upon dissolution, and the fraction of residual gas F (eq. 1) would be slightly lower than 1. In this case, the dissolved gas composition would not be significantly different from the initial ~~one~~ and would represent the deep volcano-hydrothermal gas. The ~~CO_2-richest~~ samples from the Fulco well ~~plot in correspondence with~~ the highest values of F in Figure 4, which indicates that this well taps water levels entered by volcanic gases ~~poorly~~ modified by gas-water exchange~~s~~. ~~Indeed,~~ the area of Scari is considerably affected by the input of volcanic CO_2 (Inguaggiato et al., 2013; 2017) and some wells in this area, namely Fulco and Saibbo, have the highest dissolved CO_2 contents (290 and 180 cc/L at STP, respectively). On the contrary, in areas where the amount of gas interacting with the groundwater is lower, the extent of fractionation is larger, the fraction F of residual gas is significantly lower than 1, and the residual gas ~~would~~ be significantly different from the initial gas. In the Stromboli aquifer, this modified gas composition characterizes the most saline samples, with Cl contents as high as about 550 mmol/L, namely those collected in the well Piscità well and some samples from the well Limoneto well. Due to the significant contribution of seawater, these wells are characterized by relatively higher pH values (~~average values~~ from 6.7 to 7.1), and this plays a significant role in the fractionation process~~,~~ due to the ability of basic aquifers to trap CO_2.

In Figure 11, the groundwater He/CO_2 ratios are plotted versus the Cl contents, chosen as a proxy for seawater contribution.

The selected wells, namely COA, Limoneto, and Piscità, display variable Cl contents and, as ~~commented~~ in section 6.1, ~~they~~ result from ~~the~~ variable mixing between saline and meteoric-derived end members (~~namely from the mixing~~ between the end-members EM1 and EM2 and EM4 and EM3). The highest He/CO_2 values, measured in the most saline well ~~among them~~ (Piscità)~~, also~~ ~~correspond to~~ the lowest CO_2 and alkalinity contents (Figure 10) and the highest He contents, which implies a mechanism of helium enrichment in the saline aquifer in response ~~of~~ the lower solubility in water of He compared to CO_2 (e.g., Capasso et al., 2005; Sander, 2015 and references therein). As observed in Figure 4, these samples show the highest He/CO_2 ratios and correspond to values of the fraction F of residual gas lower than 0.01. This well taps water levels where the input of volcanic gases is probably minor and/or the effect of CO_2 trapping in the aquifer at depth is locally enhanced by higher contamination of seawater.

5.3 Variations of water chemistry and dissolved gases

~~In Figure 12, t~~he He/CO_2 and CH_4/CO_2 ratios measured in water samples are ~~plotted,~~ together with the theoretical curves derived from the processes of gas dissolution and mixing. As in Figure 4, the theoretical curves are plotted by assuming three different initial CH_4/CO_2 values, from $5{\cdot}10^{-5}$ to $2{\cdot}10^{-4}$, and He/CO_2 ratio of $2{\cdot}10^{-5}$. ~~The process of g~~as dissolution is ~~assumed to be~~ a ~~possible~~ cause of variable gas concentrations in the aquifer ~~because their effects are uneven in the whole basal aquifer~~. Moreover, as evidenced by water chemistry, ~~the~~ mixing between ~~water~~ end members of different salinity, and different gas contents, can add further variability~~,~~ in the different wells and in a single well over time. ~~We underline that s~~alinity and gas contents are sometimes related, as shown in Figure 11, which makes the processes of fractionation and mixing seldom indistinguishable.

~~On these grounds, by considering the end members identified in section 6.1 based on water chemistry, we tentatively~~ hypothesize various mixing trends which could account for the variability observed among the wells and in a single well over time (Figures 12 and 13). The composition of air-saturated meteoric water (MW) and air-saturated seawater (SW) are plotted for comparison.

~~By and large, as observed in Figure 13, the~~ CO_2 contents decrease ~~along with the increase of~~ Cl contents (Figure 13a), whereas CH4 and He increase ~~along~~ with Cl contents. Neither the air-saturated meteoric water (MW) nor the air-saturated seawater (SW) ~~do not represent a significant contribution~~ to the studied samples, which implies that a volcano-hydrothermal gas phase, variably enriched in CO2, CH4, or He, prevails over atmospheric gases, although the samples are meteoric or marine in origin. Samples from the Zurro and Cusolito wells display a fairly narrow range of Cl contents (except for some samples mixed with purely meteoric water), despite slightly variable CO_2, CH4 and He contents. These two wells, both in the Scari area, are characterized by rather high He/CO_2 values (Figure 12), which point ~~ot~~ a fractionation ~~upon~~ the preferential dissolution of CO_2. The~~ir~~ salinity ~~remai~~ns fairly homogeneous over time, so we could hypothesize the variable contribution of gas enriched in He upon dissolution and gas less fractionated and richer in CH_4 and CO_2, whereas the mixing of different water types should be negligible.

~~The m~~ixing between end members of different salinity, and different CO_2, He, and CH_4 contents is demonstrated for wells Limoneto, COA, SAIBBO, and Fulco, as evident in the graphs of Figure 13, and could be the origin of the variable composition detected in these wells. End member EM1 is meteoric in origin, rich in CO_2, and relatively poor in CH_4 and He; the gas has a CH_4/CO_2 ratio of around $2.5{\cdot}10^{-5}$ and a He/CO2 ratio of $2.4{\cdot}10^{-5}$, and is the less fractionated by dissolution in the shallow aquifer (curve 2 in Figure 12). End member EM4, meteoric in origin like EM1, has a CH_4-He-richer and CO_2 poorer composition, probably deriving from the fractionation after dissolution (curve 2 in Figure 12); EM3, prevalently of marine origin, lies on the same Rayleigh curve as EM4, at higher He and lower CO_2 contents, due to further fractionation. The mixing of EM1 and EM4 end members (representing the poorest saline samples from Fulco and COA) with EM3, already noted in Figure 9 to explain the composition of samples from

COA, is confirmed by the gas composition. The composition of some samples of COA ~~requires a~~ further contribution of CH_4, as evident in Figure 13b. ~~According to what is described so far,~~ the processes of fractionation upon dissolution and ~~the~~ mixing are closely related, and ~~probably~~ only when the water composition ~~does not vary it~~ would be possible to ~~ascertain~~ the variations exclusively related to ~~the~~ fractionation. While it is probable that ~~the~~ enrichment in He and, to some extent, CH_4 is related to gas fractionation during dissolution, apparently most effective in saline water bodies (see Figure 11), the temporal variations, at least in some cases, are ~~more~~ probably affected by the mixing between water bodies of different ~~Cl content~~ (and ~~different~~ gas composition), as in the case of Limoneto well (Figure 14). In other cases, the effects of mixing or fractionation upon dissolution are not clearly distinguishable and the scatter ~~of~~ the ~~measured~~ data compared to the ~~curves of~~ theoretical mixing ~~would~~ confirm the occurrence of both processes~~; nevertheless, we could provide some suggestions about the possible causes behind them~~.

The mixing between water bodies of different compositions is not surprising in a stratified aquifer, in a coastal area, where seawater-contaminated water levels lie below meteoric water levels and extend inland for tens or hundreds of meters. Additionally, the contribution of the magmatic-hydrothermal gas is uneven in the shallow aquifer and likely variable over time, thus increasing the spatial and temporal variability. In a single well, the dominance of one type of water or another can result from the variable meteoric input over time, from variations of the seawater level (Capasso et al., 2014), or modification of water circulation due to variations of crustal strain, as an effect of volcanic activity (Federico et al., 2017b and references therein). Additional information on the rainfall amount, the fluctuations of the sea level, and the water table elevation could ~~contribute to~~ shed~~ding~~ light on the effects of the different processes.

The fractionation of the volcanic gases upon dissolution ~~has to be~~ ascribed to the relative amount of gas and water in equilibrium in a given time unit and~~, lastly,~~ to the mass rate of the volcanic gas compared to the water yield. The mass rate of gas entering the shallower water levels is supposed to be different in the various wells and, accordingly, the extent of Rayleigh's fractionation. In particular, the wells Fulco, SAIBBO, and COA tap water levels interact with a larger amount of volcanic gas, probably drained by the structural lineaments recognized by Finizola et al. (2002). The wells Piscità, Cusolito, and Zurro tap portions of the aquifer ~~deeply~~ contaminated by hot seawater (modified by water-rock exchanges, as testified by the enrichment in K, Figure 9), interacting with lower amounts of volcanic gases~~, deeply~~ modified by the fractionation due to dissolution.

5.4 Chemistry of noble gases

As already highlighted and modeled in Section 6.2, the concentration (in cc/L at STP) of ^{4}He dissolved in thermal waters from different wells differs mostly in response to its preferential partitioning into the vapor phase compared to CO_2. Instead, ^{20}Ne concentration do~~es~~ not show the same ~~differences~~ among the wells, although ^{20}Ne and ^{4}He solubility in water is comparable (Sander, 2015). In detail, the concentration of ^{20}Ne

varies ~~in a range of values~~ that includes the theoretical value in air-saturated water and is comparable among the different wells, irrespective of the extent of the fractionation due to gas-water interaction. This indicates that the mixing between magmatic and atmospheric fluids ~~mostly~~ modulates the variability ~~of~~ ^{20}Ne concentration, further supporting the idea that hydrothermal vapor mixes with the shallower meteoric aquifer, variably contaminated by seawater (Capasso et al., 2005; Grassa et al., 2008 and this work). Consequently, ~~the~~ atmospheric ~~neon~~ ~~completely~~ masks that of magmatic origin, which we expect to have a concentration of 2-3 orders of magnitude lower. ~~Following this evidence, we~~ argue that ^{20}Ne cannot be use~~ful~~ to evaluate the extent of gas-water interaction in the different wells and, more importantly, that the variability of ^{4}He/^{20}Ne is mostly modulated by the variability ~~of~~ ^{4}He concentration, as can be visualized in Figure 6. ~~Indeed,~~ Limoneto and Piscità wells that show the highest enrichment in ^{4}He also display the highest ^{4}He/^{20}Ne values (Figure 6)~~. This~~ could ~~theoretically affect~~ the correction of atmospheric contamination, which is based on the ^{4}He/^{20}Ne ratios. Nevertheless, considering that ^{4}He/^{20}Ne values are generally at least one order of magnitude higher than in ASW (^{4}He/^{20}Ne =0.285) even in those wells less modified by the fractionation due to gas-water interaction, we point out that the R_c/R_a corrected values generally differ from measured R/ R_a values of less than 0.2 R_a, leading us to consider the correction we applied ~~as~~ reliable. Some exceptions ~~regard~~ a few samples ~~of~~ the Cusolito, Fulco, and Zurro wells sampled during 2004-2008 that showed among the lowest ^{4}He content and ^{4}He/^{20}Ne next to or below 1, which probably led to an uncertainty in the correction of ^{3}He/^{4}He and an underestimation of R_c/R_a values.

5.4.1 Statistical evaluation of ^{3}He/^{4}He ratios in the thermal aquifer

The regular monitoring of ^{3}He/^{4}He at Stromboli allows a statistical evaluation of the dataset. Because ^{3}He/^{4}He ratios are not fractionated by gas-water interaction in the hydrothermal aquifer, they preserve their original signature and are thus used within the INGV-Palermo monitoring protocol. ~~For these reasons, we focus our statistical evaluation on this tracer.~~ We already noted that there is no difference in the ^{3}He/^{4}He signature among the various wells, therefore our discussion concerns the whole dataset. Considering the discrete sampling of the seven thermal wells, a total of 511 measurements of ^{3}He/^{4}He were carried out during 2004-2018. The He isotopic ratios vary between 3.74 and 4.56 R_a with a mean±standard deviation of 4.24 ± 0.13 R_a. In terms of frequency, 63 measurements fall below 4.1 R_a, equivalent to 12% of the dataset, 398 between 4.1 and 4.4 R_a, equivalent to 78%, and 50 above 4.4 R_a, equivalent to 10% (Figure 15). Considering that i) magma replenishments by poorly degassed melts are characterized by increasing ^{3}He/^{4}He values (Capasso et al., 2005; Rizzo et al., 2009, 2015; Martelli et al., 2014), ii) the maximum values measured in phenocrysts of LP magma are about 4.6 R_a (Martelli et al., 2014), and iii) the highest ^{3}He/^{4}He values (4.50-4.56 R_a) were always measured during eruptive phases characterized by weeks to months of lava effusion (Rizzo et al., 2009, 2015; Martelli et al., 2014), we conclude that ^{3}He/^{4}He values exceeding 4.4 R_a represent phases of dominant degassing of the LP magma, able to potentially feed high magmatic activity.

5.4.2 Variations of ^{3}He/^{4}He ratios in relation to volcanic activity

~~We now evaluate the temporal variations of $^3He/^4He$ ratios (R_c/R_a units) in relation to the volcanic activity during 2004-2018 (Figure 8).~~ To the best of our knowledge, this is the first time that a data set of fourteen years of regular measurements of $^3He/^4He$ is presented and discussed in a single volcanic system, offering a unique opportunity to better comprehend the short- and long-term evolution of the magmatic activity of Stromboli.

As highlighted in the previous studies by Capasso et al. (2005) and Rizzo et al. (2008, 2009, 2015), the sampled wells have a comparable range of R_c/R_a values (3.7-4.5 R_a) and temporal variations of $^3He/^4He$ that occurred almost simultaneously (Figure 8). This is confirmed for the periods of monitoring 2004-2005, 2008-2009, and 2015-2018 that are presented in this study for the first time, supporting the idea that the magmatic fluids dissolving in the hydrothermal aquifer have a common source. However, an important difference in R_c/R_a values can be observed between 2002-2007 and 2008-2018: during 2002-2007, the range of $^3He/^4He$ varied between 3.7 and 4.5 R_a with a mean ± standard deviation of 4.19 ± 0.13 R_a, whereas during 2008-2018 it moves from 4.2 to 4.6 R_a with a mean of 4.34 ± 0.08 R_a (Figure 8). The entire period of monitoring (2002-2018) has a mean $^3He/^4He$ of 4.24 ± 0.13 R_a. In detail, since 2008 onwards we have not measured $^3He/^4He$ lower than 4.2 R_a (except one sample from COA), in contrast to what was observed from 2001 to 2007, and there is a reduced variability in the $^3He/^4He$ ratios of each well (Figure 8). However, the highest R_c/R_a values never exceeded 4.6 R_a during 2002-2018. We suggest that the differences between the two periods could ~~depend on~~ a modification of the degassing path and the magmatic activity of the volcano (Calvari et al., 2014), which could have ~~been~~ favored ~~by~~ an enhanced contribution of the ^3He-rich LP melt.

During 2004-2014, R_c/R_a values ≥ 4.4 were measured during and/or in the proximity of the effusive eruptions of 2007, and 2014, and in periods of an increased occurrence of major explosions (Bevilacqua et al., 2020), as in 2017-2018. These values approached the maximum $^3He/^4He$ (i.e., 4.6 R_a) measured by Martelli et al. (2014) in fluid inclusions hosted in olivine and clinopyroxene from LP volatile-rich pumices. These high R_c/R_a values were interpreted as due to the enhanced contribution of gas from a new batch of LP magma which prevails over the degassing of the residing HP magma. Therefore, the temporal variations of the $^3He/^4He$ ratio can be explained as a mixing of volatiles persistently emitted from LP magma ($^3He/^4He$ ratio≥4.6 R_a) with those degassed from batches of magma resident in the shallow portions of the plumbing system up to the HP reservoir (~ 2 km below the sea level; e.g., Métrich et al., 2010, 2021 and references therein). This model was already proposed to explain the variability in the composition of plume gases emitted from the craters (Aiuppa et al., 2010). In addition, we recall that the continuous refilling of the shallow magma body by deep volatile-rich magmas, together with the continuous magma emission, ~~determines~~ the steady state of the Stromboli plumbing system (e.g., Landi et al., 2009; Métrich et al., 2010). The shallow batches of magma would reasonably have a $^3He/^4He$ signature (not yet constrained) lower than LP magma. This signature would result from the

addition of radiogenic ^{4}He, produced from U and Th contained in differentiated rocks in contact with the magma, to the residual helium dissolved at low concentrations in the extensively degassed melts. We cannot exclude that part of this shallow contamination occurs within the hydrothermal system. The temporal variations as well as the absolute values of ^{3}He/^{4}He measured in the fluids resulting from the hypothesized mixing and last dissolving in the hydrothermal aquifer of Stromboli, would largely be ~~mostly~~ regulated by the mass rate of volatiles degassed from the LP magma, which depends on the magma dynamics at depth. Further studies aimed at better constraining the ^{3}He/^{4}He signature of magmas residing in the shallowest portions of the plumbing system and feeding ordinary activity of Stromboli (i.e., HP magma), as well as the path and depth of helium degassing from the mantle, would enable quantitative refinement of this interpretative model.

~~Having updated the period of monitoring to June 2018, we can better detail the evolution after the 2014 eruption (Figure 8). The data series presented by Rizzo et al. (2015) stopped on 24 November 2014, when ^{3}He/^{4}He values were still high (Figure 7). After then and~~ until April 2016, the Rc/Ra values remained high (~4.4 R_a) while the resumption of Strombolian activity was ongoing. After April 2016, the ^{3}He/^{4}He decreased to average values, ~~which represent~~ almost 80% of the dataset (Figure 17). Since September 2017, ~~a new~~ increase of ^{3}He/^{4}He ratios was observed with values as high as 4.5 R_a at the end of November 2017 (Figure 8). After this peak, R_c/R_a values varied around medium-to-medium-high values until June 2018. We highlight that during 2017-2018, the activity at Stromboli was characterized by an increase in the rate of occurrence of Strombolian explosions as well as by the occurrence of several explosions of major intensity and lava overflows (Giudicepietro et al., 2019). During the same period, Inguaggiato et al. (2019) reported a progressive increase of CO_2 degassing from the soil in the summit area, further supporting the idea that the level of activity of Stromboli was increasing again in that period.

We argue that the increases in the ^{3}He/^{4}He ratios recorded in 2017-2018 can be explained as a variable replenishment of the deep (>7-10 km) portions of the plumbing system by the LP magma. It is reasonable to suppose that this replenishment progressively pressurized the main zone of storage of LP magma up to critical conditions.

5.5 Input of volcanic fluids in the shallow aquifer: an interpretative model

~~As discussed so far, the interaction of volcanic-hydrothermal fluids with the shallow basal aquifer in Stromboli produces a complex scenario. In the area of Scari, magmatic fluids, emitted throughout the shallow conduit system, permeate along discontinuities, condense in shallower and colder portions of the volcanic edifice, and undergo chemical and physical modifications, in response to non-magmatic temperature and redox conditions. The development of hydrothermal systems is hypothesized or indirectly observed in many volcanic systems worldwide and, specifically, in volcanic islands~~

~~(Fournier, 1999; Hedenquist and Lowenstern, 1994; Valsami-Jones et al., 2005; Aizawa et al., 2009; Villasante-Marcos et al., 2014).~~

~~The investigations performed by Revil et al. (2011) gave evidence of a~~ conductive zone in the central portion of the volcanic edifice, interpreted as the main hydrothermal system, and an adventive hydrothermal circulation downward E and NE, in the area of Scari. The boundary between hydrothermal water and groundwater was estimated at about 100+/- 60 m asl, while the intrusion of the seawater was assumed to be as low as -3 km in depth (figure 16).

~~According to Revil et al. (2011~~), the main hydrothermal system is localized in the central part of the volcanic edifice up to the area of Pizzo, has a deep root, and releases the hydrothermal fluids circulating in the area of Stromboli village. In the summit area of Pizzo, then, we should expect the strongest magmatic signature of $^3He/^4He$. Instead, the highest ratios are measured in the thermal water wells of Stromboli village, while fumarole gases located at Pizzo Sopra La Fossa (SC5) display $^3He/^4He$ values about 1 unit Ra lower than those measured in the basal aquifer (Carapezza and Federico, 2000; Capasso et al., 2005, Rizzo et al., 2009). Therefore, we argue that magmatic fluids degassed from melts at depth, first dissolve in a hydrothermal system localized below the sea level and close to the main conduits, and then ascend to the summit area, where the leaching of old and differentiated rocks provides radiogenic ^4He, deriving from the decay of U and Th, and thus decreases the $^3He/^4He$ of Pizzo Sopra La Fossa fumaroles.

There is geochemical evidence that the unconfined meteoric aquifer is variably contaminated by seawater, which infiltrates deep inside the volcanic edifice and is overlaid by the meteoric water. The saline water tapped by some of the wells (namely Piscità, Zurro, and Cusolito), albeit marine in origin, is deeply modified by the input of thermal fluids and by water-rock interaction. This confirms that the hydrothermal circulation is certainly rooted within the volcanic edifice below the seawater level.

The composition of the dissolved gas marks some peculiarities among the different water levels tapped by the studied wells. As observed in the Piscità well, the CO_2-poor and CH_4-He-rich composition, together with a temperature higher than 30°C, would be compatible with the interaction with hot volcanic fluids, whose composition is modified by the removal of CO_2 in deeper and, probably, saline water levels, promoted by a relatively low gas flux, according to a mechanism of Rayleigh's fractionation, as described in section 6.2. The contribution of CH_4 observed in all the monitored wells is probably derived from the boiling of a typical hydrothermal system. In some cases, (either in seawater-derived samples such as Zurro and Cusolito or meteoric-derived samples, such as COA and Limoneto), the hydrothermal gas undergoes further fractionation during its traveling toward the shallower levels of the aquifer. The monitored wells show variations in water chemistry, due to variable mixing of the meteoric/saline water, paralleled by different CO_2-He and CH_4 contents. The compositional variability of the groundwater leads to difficulty in ascertaining the variable contribution over time of gas of different origins (hydrothermal or prevalently magmatic), possibly modified by dissolution. Probably, variations in gas composition not paralleled by variations in water composition could be ascribed to a variable input of

magmatic or hydrothermal gases, to variation in their composition, and/or to Rayleigh's type fractionation, whereas variations in water chemistry point to the mixing between waters, different in both chemistry and gas contents.

6 Conclusions

The long-term monitoring of the Stromboli basal aquifer allowed the development of a comprehensive framework of the interactions among magmatic-hydrothermal fluids and shallow water. The complexity related to the presence of meteoric water, extensively contaminated by seawater and modified by water-rock exchanges, the reactivity of ~~(most)~~ the volcanic gas species, and their different solubility in water, requires some caution when interpreting ~~of~~ the observed variations in both water and gas chemistry. The monitored wells tap water levels that are variably contaminated by seawater and CH_4-rich hydrothermal fluids and are characterized by different CO_2 and He contents. Besides the mixing of different water types, the gas composition ~~is expected to vary~~ as an effect of i) the different solubility in water of gas species and the variable input of gas over time, which primarily controls the extent of the gas fractionation in water; ii) different contributions of magmatic and hydrothermal gases. ~~We suggest that r~~ainfall ~~amounts~~, fluctuations of the seawater level and the water table head in the wells must be routinely monitored, to determine the hydrological causes of the variations in water chemistry.

The long-term monitoring of helium isotopes in thermal waters has demonstrated that i) thermal waters have dissolved helium with a magmatic signature that varies in response to medium- to long-term changes in magmatic dynamics at depth and represents a safe method for monitoring the activity of the volcano; ii) low to ordinary activity is generally characterized by $^3He/^4He$ values below 4.4 Ra, whereas $^3He/^4He$ values greater than 4.4 Ra probably derive from a higher contribution of gas emitted from the LP magma, which may prelude an increase in the eruptive activity.

Acknowledgments

The authors wish to thank their colleagues at the Istituto Nazionale di Geofisica e Vulcanologia of Palermo for their contribution in collecting samples and analyzing data. All the chemical and isotopic data were produced in the Geochemical Laboratories of INGV Palermo. This research was funded by the INGV-DPCN (Italian National Institute of Geophysics and Volcanology-Italian National Department for Civil Protection) volcanic surveillance program of Stromboli volcano. ObFu 0304.010.

Data Availability Statement

All the data produced in this work are publicly available in the Earthchem data repository (Vita et al., 2023).

References

Aiuppa, A., Bertagnini, A., Métrich, N., Moretti, R., Di Muro, A., Liuzzo, M., Tamburello, G., (2010), A model of degassing for Stromboli volcano, 10.1016/j.epsl.2010.03.040, *Earth Planet. Sci. Lett*. *295*, 95-204.

Aizawa, K., Ogawa, Y., & Ishido, T. (2009), Groundwater flow and hydrothermal systems within volcanic edifices: Delineation by electric self-potential and magnetotellurics, *Journal of Geophysical Research: Solid Earth, 114*(B1). https://doi.org/10.1029/2008JB005910.

Albarède F. (1995), Introduction to geochemical modeling. Cambridge University Press, Cambridge

Andronico, D., Del Bello, E., D'Oriano, C., Landi, P., Pardini, F., Scarlato, P., ... & Valentini, F. (2021), Uncovering the eruptive patterns of the 2019 double paroxysm eruption crisis of Stromboli volcano, *Nature Communications, 12*(1), 4213.

Antoine, R., Baratoux, D., Rabinowicz, M., Fontaine, F., Bachelery, P., Staudacher, T., Saracco, G., Finizola, A., 2009, Thermal infrared image analysis of a quiescent cone on Piton de la Fournaise volcano: evidence of convective air flow within an unconsolidated soil, *J. Volcanol. Geotherm. Res. 183,* 228–244.

Bertagnini, A., Métrich, N., Francalanci, L., Landi, P., Tommasini, S., Conticelli, S. (2008). Volcanology and magma geochemistry of the present-day activity: constraints on the feeding system. In: Calvari, S., Inguaggiato, S., Puglisi, G., Ripepe, M., Rosi, M. (Eds.), Learning from Stromboli. Geophysical Monograph 182. American Geophysical Union, pp. 19–38.

Bevilacqua, A., Bertagnini, A., Pompilio, M., Landi, P., Del Carlo, P., Di Roberto, A., ... & Neri, A. (2020), Major explosions and paroxysms at Stromboli (Italy): A new historical catalog and temporal models of occurrence with uncertainty quantification*, Scientific reports, 10*(1), 17357.

Caliro, S., Caracausi, A., Chiodini., G., Ditta., M., Italiano, F., Longo, M., Minopoli., C., Nuccio, P.M., Paonita, A., Rizzo, A. (2004), Evidence of a recent input of magmatic gases into the quiescent volcanic edifice of Panarea, Aeolian Islands, Italy, *Geophys. Res. Lett. 31*, L07619.

Caliro S., Chiodini G., Moretti R., Avino R., Granieri D., Russo M. and Fiebig J. (2007), The origin of the fumaroles of La Solfatara (Campi Flegrei, South Italy), *Geochim. Cosmochim. Acta 71*, 3040–3055. http://dx.doi.org/10.1016/j.gca.2007.04.007.

Calvari, S., et al. (2014), Major eruptive style changes induced by structural modifications of a shallow conduit system: The 2007–2012 Stromboli case, *Bull. Volcanol*., doi:10.1007/s00445-014-0841-7.

Capasso, G. and Inguaggiato, S. (1998), A simple method for the determination of dissolved gases in natural waters: An application to thermal waters from Vulcano island, *Applied Geochem., 13*, 631-642.

Capasso, G., Favara, R., Francofonte, S., & Inguaggiato, S. (1999), Chemical and isotopic variations in fumarolic discharge and thermal waters at Vulcano Island (Aeolian Islands, Italy) during 1996: evidence of resumed volcanic activity, *Journal of volcanology and geothermal research, 88*(3), 167-175.

Capasso G., Carapezza M. L., Federico C., Inguaggiato S. and Rizzo A. (2005), Geochemical monitoring of the 2002–2003 eruption at Stromboli volcano (Italy): precursory changes in the carbon and helium isotopic composition of fumarole gases and thermal waters, *Bull. Volcanol. 68,* 118–134.

Capasso, G., Federico, C., Madonia, P., & Paonita, A. (2014), Response of the shallow aquifer of the volcano-hydrothermal system during the recent crises at Vulcano Island (Aeolian Archipelago, Italy), . *Volcanol. Geotherm. Res., 273*, 70-80.

Carapezza M. L. and Federico C. (2000), The contribution of fluid geochemistry to the volcano monitoring of Stromboli, *J. Volcanol. Geotherm. Res. 95*, 227–245.

Carapezza, M. L., Inguaggiato, S., Brusca, L., and Longo, M. (2004), Geochemical precursors of the activity of an open-conduit volcano: The Stromboli 2002-2003 eruptive events, *Geoph. Res. Letters, 31*, L07620.

Carapezza, M.L., Ricci, T., Ranaldi, M. & Tarchini, L. (2009), Active degassing structures of Stromboli and variations in diffuse CO2 output related to the volcanic activity, *J. Volc. Geotherm. Res., 182*, 231–245.

Chiodini G., Cioni R., Marini L., and Panichi C. (1995), Origin of the fumarolic fluids of Vulcano Island, Italy, and implications for volcanic surveillance, *Bull. Volcanol. 57*, 99–110.

Chiodini, G., Frondini, F., Cardellini, C., Parello, F., & Peruzzi, L. (2000), Rate of diffuse carbon dioxide Earth degassing estimated from carbon balance of regional aquifers: The case of central Apennine, Italy, *Journal of Geophysical Research: Solid Earth, 105*(B4), 8423-8434.

Chiodini, G., Marini, L., and Russo, M. (2001), Geochemical evidence for the existence of high temperature brines at Vesuvio volcano, Italy, *Geochem. Cosm. Acta 65*, 2129–2147.

Chiodini, G., Granieri, D., Avino, R., Caliro, S., Costa, A., Werner, C. (2005), Carbon dioxide diffuse degassing and estimation of heat release from volcanic and hydrothermal systems, *J. Geophys. Res. 110*, B08204. http://dx.doi.org/10.1029/2004JB003542.

Chiodini, G., Paonita, A., Aiuppa, A. et al. 2016, Magmas near the critical degassing pressure drive volcanic unrest towards a critical state. Nat Commun 7, 13712. https://doi.org/10.1038/ncomms13712

Deines P, Langmuir D, Harmon RS (1974) Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate groundwaters. Geochim Cosmochim Acta 38:1147–1164

Ellam, R.M., Hawkesworth, C.J., Menzies, M.A., Rogers, N.W., 1989. The volcanism of southern Italy: role of subduction and relationship between potassic and sodic alkaline magmatism. J. Geophys. Res. 94, 4589–4601.

Federico, C., Aiuppa, A., Allard, P., Bellomo, S., Jean-Baptiste, P., Parello, F., & Valenza, M. (2002). Magma-derived gas influx and water-rock interactions in the volcanic aquifer of Mt. Vesuvius, Italy. Geochimica et Cosmochimica Acta, 66(6), 963-981.

Federico, C., Brusca, L., Carapezza, M. L., Cigolini, C., Inguaggiato, S., Rizzo, A., & Rouwet, D. (2008). Geochemical prediction of the 2002-2003 Stromboli eruption from variations in CO2 and Rn emissions and in helium and carbon isotopes. In: Learning from Stromboli and its 2002-03 eruptive crisis. AGU, 2008 Washington DC American Geophysical Union Geophysical Monograph Series, 182, 117-128.

Federico, C., Capasso, G., Paonita, A., Favara, R. (2010) Effects of steam-heating processes on a stratified volcanic aquifer: Stable isotopes and dissolved gases in thermal waters of Vulcano Island (Aeolian archipelago). Journal of Volcanology and Geothermal Research, 192, 178-190.

Federico C., Inguaggiato, S., Chacón, Z., Londoño, JM., Gil, E., Alzate, D. (2017a) Vapour discharges on Nevado del Ruiz during the recent activity: Clues on the composition of the deep hydrothermal system and its effects on thermal springs - Journal of Volcanology and Geothermal Research, 2017; https://doi.org/10.1016/j.jvolgeores.2017.04.007

Federico, C., Longo, M., D'Alessandro, W., Bellomo, S., Bonfanti, P., & Brusca, L. (2017b). Hydrological versus volcanic processes affecting fluid circulation at Mt. Etna: inferences from 10 years of observations at the volcanic aquifer. Chemical Geology, 452, 71-84.

Finizola A., Sortino F., Lénat J.-F. and Valenza M. (2002) Fluid circulation at Stromboli volcano (Aeolian Islands, Italy) from self-potential and CO2 surveys. J. Volcanol. Geotherm. Res. 116, 1–18.

Finizola A, Sortino F (2003) Preliminary model of fluid circulation at Stromboli volcano inferred by water and gas geochemistry. ICGG7-A-00108, 22-26 September 2003 Freiberg, Germany

Finizola, A., Sortino, F., Lénat, J. F., Aubert, M., Ripepe, M., & Valenza, M. (2003). The summit hydrothermal system of Stromboli. New insights from self-potential, temperature, CO 2 and fumarolic fluid measurements, with structural and monitoring implications. Bulletin of Volcanology, 65, 486-504.

Finizola, A., Revil, A., Rizzo, E., Piscitelli, S., Ricci, T., Morin, J., Angeletti, B., Mocochain, L., Sortino, F., 2006. Hydrogeological insights at Stromboli volcano (Italy) from geoelectrical, temperature, and CO2 soil degassing investigations. Geophys. Res. Lett. 33, L17304. doi:10.1029/2006GL026842

Finizola, A., Aubert, M., Revil, A., Schutze, C., Sortino, F. (2009). Importance of structural history in the summit area of Stromboli during the 2002–2003 eruptive crisis inferred from temperature, soil CO2, self-potential, and electrical resistivity tomography. Journal of Volcanology and Geothermal Research, 183, 213-227.

Finizola, A., Ricci, T., Deiana, R., Cabusson, S. B., Rossi, M., Praticelli, N., ... & Lelli, M. (2010). Adventive hydrothermal circulation on Stromboli volcano (Aeolian Islands, Italy)

revealed by geophysical and geochemical approaches: implications for general fluid flow models on volcanoes. Journal of Volcanology and Geothermal Research, 196(1-2), 111-119.

Fournier, R. O. (1999), Hydrothermal processes related to movement of fluid from plastic into brittle rock in the magmatic-epithermal environment, Econ. Geol., 94, 1193–1211.

Francalanci, L., Manetti, P., Peccerillo, A., Keller, J., 1993. Magmatological evolution of the Stromboli volcano (Aeolian Arc, Italy): inferences from major and trace element and Sr-isotopic composition of lavas and pyroclastic rocks. Acta Vulcanol. 3, 127–151.

Francalanci, L., Tommasini, S., Conticelli, S., 2004. The volcanic activity of Stromboli in the 1906–1998 period: mineralogical, geochemical and isotope data relevant to the understanding of Strombolian activity. J. Volcanol. Geotherm. Res. 131, 179–211.

Francalanci, L., Avanzinelli, R., Tommasini, S., Heuman, A., 2007. Awest–east geochemical and isotopic traverse along the volcanism of the Aeolian Island arc, southern Tyrrhenian Sea, Italy: inferences on mantle source processes. In: Beccaluva, L., Bianchini, G.,Wilson, M. (Eds.), Cenozoic Volcanism in the Mediterranean Area. Geological Society of America, Denver, U.S.A., pp. 235–263.

Gasparini, C., G. Iannaccone, P. Scandone, and R. Scarpa (1982), Seismotectonics of the Calabrian Arc, Tectonophysics, 84, 267–286.

Gat, J. R., and I. Carmi (1970), Evolution of the isotopic composition of atmospheric waters in the Mediterranean Sea area, J. Geophys. Res., 75, 3039–3048, doi:10.1029/JC075i015p03039.

Gat J. R., Shemesh A., Tziperman E., Hecht A., Georgopoulos D. and Basturk O. (1996) The stable isotope composition of waters of the eastern Mediterranean Sea. J. Geophys. Res. Ocean. 101, 6441–6451.

Gennaro, M. E., F. Grassa, M. Martelli, A. Renzulli, and A. L. Rizzo (2017). Carbon isotope composition of CO2-rich inclusions in cumulate-forming mantle minerals from Stromboli volcano (Italy). J. Volcanol. Geotherm. Res., 1–9, http://dx.doi.org/10.1016/j.jvolgeores.2017.04.001

Giggenbach, W.F. (1975). A simple method for the collection and analysis of volcanic gas samples, Bull. Volcanol. 39, 132–145.

Giudicepietro, F., Calvari, S., Alparone, S., Bianco, F., Bonaccorso, A., Bruno, V., Caputo, T., Cristaldi, A., D'Auria, L., De Cesare, W., Di Lieto, B., Esposito, A.M., Gambino, S., Inguaggiato, S., Macedonio, G., Martini, M., Mattia, M., Orazi, M., Paonita, A., Peluso, R., Privitera, E., Romano, P., Scarpato, G., Tramelli, A., Vita, F. (2019). Integration of Ground-Based Remote-Sensing and In Situ Multidisciplinary Monitoring Data to Analyze the Eruptive Activity of Stromboli Volcano in 2017–2018. Remote Sens. 2019, 11, 1813; doi:10.3390/rs11151813

Grassa, F., Inguaggiato, S., Liotta, M. (2008), Fluids geochemistry of Stromboli. In "The Stromboli Volcano – An Integrated study of the 2002-2003 Eruption" AGU Geophysical monograph" 182, 49-63.

Hedenquist, J. W., and J. B. Lowenstern (1994), The role of magmas in the formation of hydrothermal ore deposits, Nature, 370, 519–527, doi:10.1038/370519a0.

Inguaggiato, S., Pecoraino, G., and D'Amore, F., 2000, Chemical and isotopical characterization of fluid manifestations of Ischia Island (Italy).: J.Volcanol.Geoth.Res., v. 99, p. 151-178.

Inguaggiato, S. and Rizzo, A., 2004, Dissolved helium isotope ratios in ground-waters: a new technique based on gas-water re-equilibration and its application to Stromboli volcanic system: Applied Geochem., v. 19, p. 665-673.

Inguaggiato, S., Martin-Del Pozzo, A. L., Aguayo, A., Capasso, G., and Favara, R., 2005, Isotopic, chemical and dissolved gas constraints on spring water from Popocatepetl (Mexico): evidence of gas-water interaction magmatic component and shallow fluids: J.Volcanol.Geoth.Res., v. 141, p. 91-108.

Inguaggiato, S; Hidalgo S.; Beate B; and Bourquin J. (2010) Geochemical and isotopic characterization of volcanic and geothermal fluids discharged from the Ecuadorian volcanic arc GEOFLUIDS 10, 525–541- 2010

Inguaggiato S, Vita F, Rouwet D, Bobrowski N, Morici S, Sollami A (2011)- Geochemical evidence of the renewal of volcanic activity inferred from CO2 soil and SO2 plume fluxes: the 2007 Stromboli eruption (Italy) Bullettin of Volcanology 2011, Vol 73, Number 4, Pages 443-456

Inguaggiato S., M.P. Jacome Paz, A. Mazot, H. Delgado Granados, C. Inguaggiato, F. Vita (2013) CO2 output discharged from Stromboli Island (Italy). Chemical Geology (2013) http://dx.doi.org/10.1016/j.chemgeo.2012.10.008

Inguaggiato, S., Vita, F., Cangemi, M., Mazot, A., Sollami, A., Calderone, L., ... & Paz, M. P. J. (2017a). Stromboli volcanic activity variations inferred from observations of fluid geochemistry: 16 years of continuous monitoring of soil CO2 fluxes (2000–2015). Chemical Geology, 469, 69-84.

Inguaggiato, C., Vita, F., Diliberto, I. S., & Calderone, L. (2017b). The role of the aquifer in soil CO2 degassing in volcanic peripheral areas: A case study of Stromboli Island (Italy). Chemical Geology, 469, 110-116.

Inguaggiato, S.; Diliberto, I.S.; Federico, C.; Paonita, A.; Vita, F. (2017). Review of the evolution of geochemical monitoring, networks and methodologies applied to the volcanoes of the Aeolian Arc (Italy). Earth-Sci. Rev. 2018, 176, 241–276 10.1016/j.earscirev.2017.09.006

Inguaggiato S., Vita F., Cangemi M. and Calderone L. (2019) Increasing Summit Degassing at the Stromboli Volcano and Relationships with Volcanic Activity (2016–2018). Geosciences 9, 176.

Inguaggiato, S.; Vita, F.; Cangemi, M.; Calderone, L. Changes in CO2 Soil Degassing Style as a Possible Precursor to Volcanic Activity: The 2019 Case of Stromboli Paroxysmal Eruptions. Appl. Sci. 2020, 10, 4757

Inguaggiato, S.; Vita, F.; Cangemi, M.; Inguaggiato, C.; Calderone, L. (2021) The Monitoring of CO2 Soil Degassing as Indicator of Increasing Volcanic Activity: The Paroxysmal Activity at Stromboli Volcano in 2019–2021. Geosciences 2021, 11, 169. https://doi.org/10.3390/geosciences11040169

Lages, J., Rizzo, A.L., Aiuppa, A., Robidoux, P., Aguilar, R., Apaza, F., Masias, P. (2021) Crustal controls on light noble gas isotope variability along the Andean Volcanic Arc. Geochem. Persp. Let. 19, 45–49| doi: 10.7185/geochemlet.2134

Landi, P., Corsaro, R. A., Francalanci, L., Civetta, L., Miraglia, L. Pompilio, Tesoro, R., 2009. Magma dynamics during the 2007 Stromboli eruption (Aeolian islands, Italy). Mineralogy, geochemistry and isotope data. J. Volcanol. Geother. Res. 182, 255-268.

Lénat, J.F., Bachélery, P., Peltier, A., (2012). The interplay between collapse structures, hydrothermal systems, andmagma intrusions: the case of the central area of Piton de la Fournaise volcano. Bull. Volcanol. 74, 407–421. https://doi.org/10.1007/s00445-011-0535-3.

Liotta M., Brusca L., Grassa F., Inguaggiato S., Longo M. and Madonia P. (2006) Geochemistry of rainfall at Stromboli volcano (Aeolian Islands): Isotopic composition and plume-rain interaction. Geochem. Geophys. Geosyst. 7.

Lorenz, V. & Kurszlaukis, S., 2007. Root zone processes in the phreatomagmatic pipe emplacement model and consequences for the evolution of maar-diatreme volcanoes, J. Volc. Geotherm. Res., 159(1–3), 4–32.

Lupton, J., M. Lilley, D. Butterfield, L. Evans, R. Embley, G. Massoth, B. Christenson, K.-I. Nakamura, and M. Schmidt (2008), Venting of a separate CO2-rich gas phase from submarine arc volcanoes: Examples from the Mariana and Tonga-Kermadec arcs, J. Geophys. Res., 113, B08S12, doi:10.1029/2007JB005467.

Madonia, P.; Campilongo, G.; Cangemi, M.; Carapezza, M.L.; Inguaggiato, S.; Ranaldi, M.; Vita, F. Hydrogeological and Geochemical Characteristics of the Coastal Aquifer of Stromboli Volcanic Island (Italy). Water 2021, 13, 417. https://doi.org/10.3390/w13040417

Martelli, M., A.L., Rizzo, A., Renzulli, F., Ridolfi, I., Arienzo, A., Rosciglione (2014) Noble-gas signature of magmas from a heterogeneous mantle wedge: The case of Stromboli volcano (Aeolian Islands, Italy). Chem. Geol. 368, 39-53.

Mauri, G., Saracco, G., Labazuy, P., Williams-Jones, G. (2018). Correlating hydrothermal system dynamics and eruptive activity – A case-study of Piton de la Fournaise volcano, La Réunion. J. Volcanol. Geother. Res. 363, 23-39.

Métrich, N., Bertagnini, A., Di Muro, A., 2010. Conditions of magma storage, degassing and ascent at Stromboli: new insights into the volcano plumbing system with inferences on the eruptive dynamics. J. Petrol. 51, 603–626. doi: 10.1093-petrology-egp083.

Métrich N, Bertagnini A and Pistolesi M (2021) Paroxysms at Stromboli Volcano (Italy): Source, Genesis and Dynamics. Front. Earth Sci. 9:593339. doi: 10.3389/feart.2021.593339

Morelli, C., Giese, P., Cassinis, R., Colombi, B., Guerra, I., Luongo, G., Scarascia, S., Schutte, K.G., 1975. Crustal structure of Southern Italy. A seismic refraction profile between Puglia–Calabria–Sicily. Boll. Geofis. Teor. Appl. 18, 183–210.

Ohsawa, S., Kazahaya, K., Yasuhara, M., Kono, T., Kitaoka, K., Yusa, Y., & Yamaguchi, K. (2002). Escape of volcanic gas into shallow groundwater systems at Unzen Volcano (Japan): evidence from chemical and stable carbon isotope compositions of dissolved inorganic carbon. Limnology, 3(3), 0169-0173.

Osinski, G.R., Spray, J.G., Lee, P., 2001. Impact-induced hydrothermal activity within the Haughton impact structure, arctic Canada: generation of a transient, warm, wet oasis. Meteorit. Planet. Sci. 36 (5), 731–745.

Panza, G.F., Peccerillo, A., Aoudia, A., Farina, B., 2007. Geophysical and petrological modelling of the structure and composition of the crust and upper mantle in complex geodynamic settings: the Tyrrhenian Sea and surroundings. Earth Sci. Rev. 80, 1–46.

Paonita, A., M. Longo, S. Bellomo,W. D'Alessandro, L. Brusca (2016). Dissolved inert gases (He, Ne and N2) as markers of groundwater flow and degassing areas at Mt Etna volcano (Italy) Chemical Geology 443, 10–21 doi: 0.1016/j.chemgeo.2016.09.018

Prano, V. Liotta M. (2018), Precisione e accuratezza nella determinazione dei costituenti maggiori in soluzione acquosa mediante cromatografia ionica: stime per i cromatografi Dionex ICS-1100 utilizzati presso la Sezione INGV di Palermo. INGV Technical Reports https://doi.org/10.13127/rpt/390

Revil, A., Linde, N., 2006. Chemico-electromechanical coupling in microporous media. J. Colloid Interface Sci. 302, 682–694. doi:10.1016/j.jcis.2006.06.051.

Revil, A., Finizola, A., Ricci, T., Delcher, E., Peltier, A., Barde-Cabusson, S., ... & Tsang Hin Sun, E. (2011). Hydrogeology of Stromboli volcano, Aeolian Islands (Italy) from the interpretation of resistivity tomograms, self-potential, soil temperature and soil CO2 concentration measurements. Geophysical Journal International, 186(3), 1078-1094.

Rizzo, A., Aiuppa, A., Capasso, G., Grassa, F., Inguaggiato, S., Longo, M., & Carapezza, M. L. (2008). The 5 April 2003 paroxysm at Stromboli: A review of geochemical observations. In Learning from Stromboli and its 2002-03 eruptive crisis. American Geophysical Union. Washington DC American Geophysical Union Geophysical Monograph Series, 182, 347-358.

Rizzo A., Grassa F., Inguaggiato S., Liotta M., Longo M., Madonia P., Brusca L., Capasso G., Morici S., Rouwet D. and Vita F. (2009) Geochemical evaluation of observed changes in volcanic activity during the 2007 eruption at Stromboli (Italy). J. Volcanol. Geotherm. Res. 182.

Rizzo A L, Federico C, Inguaggiato S, Sollami A, Tantillo M, Vita F, Bellomo S, Longo M, Grassa G, Liuzzo M (2015). The 2014 effusive eruption at Stromboli volcano (Italy): Inferences from soil CO2 flux and He-3/He-4 ratio in thermal waters. GEOPHYSICAL RESEARCH LETTERS, vol. 42, p. 2235-2243, ISSN: 0094-8276, doi: 10.1002/2014GL062955

Rizzo A. L., Caracausi A., Chavagnac V., Nomikou P., Polymenakou P., Mandalakis M., Kotoulas G., Magoulas A., Castillo A., Lampridou D. 2016a, Kolumbo submarine volcano (Greece): An active window into the Aegean subduction system. Sci. Rep. 6, 28013; doi: 10.1038/srep28013

Rizzo AL, Caracausi A, Chavagnac V, Nomikou P, Polymenakou PN, Mandalakis M, Kotoulas G, Magoulas A, Castillo A, Lampridou D, Marusczak N and Sonke JE (2019) Geochemistry of

CO2-Rich Gases Venting From Submarine Volcanism: The Case of Kolumbo (Hellenic Volcanic Arc, Greece). Front. Earth Sci. 7:60. doi: 10.3389/feart.2019.00060

Rizzo A.L., Robidoux P., Aiuppa A., Di Piazza A. (2022). 3He/4He signature of magmatic fluids from Telica (Nicaragua) and Baru (Panama) volcanoes, Central American Volcanic Arc. Appl. Sci., 12, 4241. https://doi.org/10.3390/app12094241

Robidoux, P., Rizzo, A., Aguilera, F., Aiuppa, A., Artale, M., Liuzzo, M., Nazzari, M., Zummo, F. (2020). Petrological and noble gas features of Lascar and Lastarria volcanoes (Chile): Inferences on plumbing systems and mantle characteristics. LITHOS, ISSN: 0024-4937, doi: 10.1016/j.lithos.2020.105615

Rosi, M., A. Bertagnini, and P. Landi (2000), Onset of the persistent activity at Stromboli volcano (Italy), Bull. Volcanol., 62, 294–300.

Sander, R. (2015). Compilation of Henry's law constants (version 4.0) for water as solvent. Atmos. Chem. Phys., 15, 4399–4981.

Schiavi, F., Kobayashi, K., Nakamura, E., Tiepolo, M., Vannucci, R., 2012. Trace element and Pb–B–Li isotope systematics of olivine-hosted melt inclusions: insights into source metasomatism beneath Stromboli (southern Italy). Contrib. Mineral. Petrol. 163, 1011–1031.

Simmons, S. F., & Christenson, B. W. (1994). Origins of calcite in a boiling geothermal system. American journal of science, 294(3), 361-400.

Singaraja C., Chidambaram S. and Jacob N. (2018) A study on the influence of tides on the water table conditions of the shallow coastal aquifers. Appl. Water Sci. 8, 11.

Taran, Y., Kalacheva, E., Inguaggiato, S., Cardellini, C., Karpov, G. (2017). Hydrothermal systems of the Karymsky Volcanic Centre, Kamchatka: Geochemistry, time evolution and solute fluxes. J. Volcanol. Geotherm. Res. 346, 28-39.

Tommasini, S., Heumann, A., Avanzinelli, R., Francalanci, L., 2007. The fate of high-angle dipping slabs in the subduction factory: an integrated trace element and radiogenic isotope (U, Th, Sr, Nd, Pb) study of Stromboli volcano, Aeolian Arc, Italy. J. Petrol. 48:2407–2430. http://dx.doi.org/10.1093/petrology/egm066.

Valsami-Jones, E., Baltatzis, E., Bailey, E. H., Boyce, A. J., Alexander, J. L., Magganas, A., ... & Ragnarsdottir, K. V. (2005). The geochemistry of fluids from an active shallow submarine hydrothermal system: Milos island, Hellenic Volcanic Arc. Journal of Volcanology and Geothermal Research, 148(1-2), 130-151.

Villasante-Marcos, V., Finizola, A., Abella, R., Barde-Cabusson, S., Blanco, M. J., Brenes, B., ... & Trigo, P. (2014). Hydrothermal system of Central Tenerife volcanic complex, Canary Islands (Spain), inferred from self-potential measurements. Journal of volcanology and geothermal research, 272, 59-77.

Vita, F., Inguaggiato, S., Capasso, G., Liotta, M., Rizzo, A. L., 2023. Chemical-physical parameters, major, and minor elements composition of thermal waters from 8 wells in the Stromboli aquifer (Italy), Version 1.0 [Dataset]. Interdisciplinary Earth Data Alliance (IEDA). https://doi.org/10.26022/IEDA/112932.

Weinstein, Y., 2007. A transition from strombolian to phreatomagmatic activity induced by a lava flow damming water in a valley, J. Volc. Geotherm. Res, 159(1–3), 267–284.

Yamada, M., Ohsawa, S., Kazahaya, K., Yasuhara, M., Takahashi, H., Amita, K., ... & Yoshikawa, S. (2011), Mixing of magmatic CO2 into volcano groundwater flow at Aso volcano assessed combining carbon and water stable isotopes, *Journal of Geochemical Exploration, 108(1)*, 81-87.

Figure 1. Location of sampling points and main regional faults N41°; N64° (Finizola et al., 2002). The map reference system is ETRS89/UTM 33 N. The red square marks the position of Stromboli Island in Southern Italy.

Figure 2. Well data plotted on a chlorine (Cl) - sodium (Na) diagram. The mean amount-weighted composition of rainwater (Liotta et al. 2006) and dripping water from a cave in the neighborhood of Fulco well are also plotted.

Figure 3. Diagram showing δD versus $\delta^{18}O$ in the groundwater of Stromboli. The grey area defines the composition of the meteoric recharge (Liotta et al., 2006). The dashed lines are the Global Meteoric Water Line (GMWL) and the Eastern Mediterranean Meteoric Water Line (EMMWL) (Gat and Carmi, 1970). Dripping water at Fulco cave (FCDW) is also plotted as well as the Mediterranean seawater (SW) (Gat et al., 1996).

Figure 4. Relative contents of He, CH_4, and CO_2 (cc/L at STP). Curves 1, 2, and 3 represent the modeled composition of the dissolved gas, obtained by partial dissolution, in a shallow aquifer at 40°C, of a gas having initial CH_4/CO_2 ratios of $5\cdot10^{-5}$, $1\cdot10^{-4}$ and $2\cdot10^{-4}$ respectively, and $He/CO_2= 2.4\cdot10^{-5}$, hypothesized to be separated from an underlying boiling aquifer. The crosses on the red curves refer to different fractions of residual gas after dissolution (F_2 in equation 2, see Appendix 1).

Figure 5. $\delta^{13}C_{CO2}$ versus dissolved CO_2. Values of $\delta^{13}C_{CO2}$ are computed from measured $\delta^{13}C_{TDC}$ (method given in the text).

Figure 6. $^4He/^{20}Ne$ vs ^4He cc/L at STP in the thermal wells of Stromboli. Air Saturated Water (ASW) with $^4He/^{20}Ne$ =0.285 and ^4He =$4.55\cdot10^{-5}$ cc/L at STP is plotted for comparison.

Figure 7. $^4He/^{20}Ne$ vs $^3He/^4He$ expressed as R/Ra. The two curves indicate mixing lines between an atmospheric component with $^4He/^{20}Ne$ =0.318 and R/Ra=1 and two possible magmatic end members with $^4He/^{20}Ne$ =100, as observed in other analogous investigations (e.g., Rizzo et al., 2015, 2022; Robidoux et al., 2020; Lages et al., 2021), and 3.8-4.6 Ra that includes all the data variability observed in 2004-2018. The rectangle reports the maximum range of values measured in fluid inclusions from LP magma minerals (Martelli et al., 2014).

Figure 8. Time series of Rc/Ra values measured in gases dissolved in the thermal waters of Stromboli. Red bars indicate the periods of lava effusion, the red symbol the paroxysmal explosion occurred on the 15 of March, 2007.

Figure 9. Stromboli groundwater samples displayed on a plot of Cl against K. All the samples show enrichment in K compared to the seawater ratio. The mean amount-weighted composition of rainwater (Liotta et al. 2006) and dripping water (FCDW) from a cave in the neighborhood of Fulco well are also plotted.

Figure 10. Stromboli groundwater samples displayed on a plot of Cl against total alkalinity. With the exception of Zurro and COA, samples exhibit a negative relationship between Cl and total alkalinity (see text for details).

Figure 11. Chlorine versus dissolved He/CO_2 ratios in the wells COA, Limoneto, and Piscità. Symbols as in Figure 2.

Figure 12. Scatter plot of CH_4/CO_2 versus He/CO_2 ratios measured in well waters. Gas concentrations are expressed as cc/L at STP. Curves 1, 2, and 3 represent the modeled composition of the dissolved gas, obtained by partial dissolution, in a shallow aquifer at 40°C, of a gas having initial CH_4/CO_2 ratios of $5\cdot10^{-5}$, 1·10-4 and $2\cdot10^{-4}$ respectively, and He/CO_2= $2.4\cdot10^{-5}$, hypothesized to be separated from an underlying boiling aquifer. The crosses on the red curves refer to different fractions of residual gas after dissolution (F2 in equation 2, Appendix 1). Colored lines represent the mixing between different end members (green crosses), marine or meteoric in origin, characterized by different gas compositions. The composition of air-saturated water (MW) and seawater (SW) at 15°C is plotted for comparison (ASW: CO_2=0.38 cc/L, He=$4.5\cdot10^{-5}$ cc/L, CH_4= $7.8\cdot10^{-5}$ cc/L at STP; ASSW: CO_2=0.32 cc/L, He=$3.8\cdot10^{-5}$ cc/L, CH_4= $5.9\cdot10^{-5}$ cc/L at STP; Liotta and Martelli, 2012).

Figure 13. a) Scatter plot of Cl versus CO_2 contents measured in well waters. Colored lines represent the mixing between different end members, marine or meteoric in origin, characterized by different CO2 contents. The composition of air-saturated water (MW) and seawater (SW) is plotted for comparison; b) scatter plot of Cl versus CH4 contents measured in well waters. Green lines represent the mixing between different end members, marine or meteoric in origin, characterized by different CH_4 contents; c) scatter plot of Cl versus He contents measured in well waters. Green lines represent the mixing between different end members, marine or meteoric in origin, characterized by different He contents.

Figure 14. Time trends of He (left axis) and Cl (right axis) in well Limoneto.

Figure 15. Frequency and cumulative frequency distribution of $^3He/^4He$ in Stromboli thermal wells, based on 511 measurements carried out between 2004 and 2018. Considering the analysis of the frequency of occurrence of Rc/Ra values over 14 years of monitoring and taking into account the maximum value measured in fluid inclusions of LP minerals (Martelli et al., 2014), the variability of Rc/Ra values is reported as a function of variable extents of mixing between fluids degassed from an LP magma, having ratios as high as 4.6 Ra, and those from an HP magma, supposed to have the lowest Rc/Ra values recorded in the time series.

Figure 16. Interpretative model of the shallow thermal aquifer obtained by merging the outcomes of Finizola et al. (2010), Revil et al. (2011), Madonia et al. (2021) and the elaborations of the present work.

Appendix 1

Chemical fractionation of gas as an effect of dissolution

The chemical fractionation upon dissolution can be reliably modeled by a Rayleigh's type process, according to the equation (Albarède, 1995; Capasso et al., 2005):

$$\left(\frac{[G_1]}{[G_2]}\right)_{liq} = \frac{K_{H,2}}{K_{H,1}} \cdot \left(\frac{[G_1]}{[G_2]}\right)_{gas,i} \cdot F_2^{\left(\frac{K_{H,2}}{K_{H,1}}-1\right)} \qquad (1)$$

where G1 and G2 are two gas species, the subscripts liq and gas, i refer to the liquid and the initial gas phase, respectively; F2 is the residual fraction of the gas species 2, KH is Henry's constants of the two gas species.

In the following, we compute the evolution of He/CO2 and CH_4/CO_2 ratios according to eq. 1, by assuming He and CH_4 as species 1, and CO_2 as species 2, respectively. In Figure 4, the theoretical composition of the dissolved gas, after the removal of an increasing amount of gas upon dissolution in water, is plotted. The initial gas compositions (i.e. $\left(\frac{[G_1]}{[G_2]}\right)_{gas,i}$) in equation 1 are selected to best fit the observed data. The different curves refer to three different initial CH_4/CO_2 ratios.

The Henry's constants were computed at 40°C, and their values are 144000 and 50560 bar mol mol^{-1}, for He and CH_4, respectively. The Kh computed for CO_2 (2263 bar mol mol^{-1} at 40°C) is reduced by the effect of CO_2 hydration, which depends also on pH and on the dissociation of carbonic acid (see Capasso et al., 2005). The used value is 1440 bar mol mol^{-1}, computed at pH = 6 and 40°C.

As explained by Capasso et al. (2005), the retrieved initial He/CO_2 ratios ($2\cdot10^{-5}$) are higher than those measured on average in a fumarole sampled in the Pizzo area (SC5; Capasso et al., 2005) and measured in fluid inclusions (Gennaro et al., 2017) (He/CO_2 ratio ranging from $3\cdot10^{-6}$ to 10^{-5}), and this implies a probable enrichment in He during the vapor separation from an underlying biphase aquifer, and particularly for a small fraction of separated gas. The modeled initial CH_4/CO_2 contents span from $5\cdot10^{-5}$ to $2\cdot10^{-4}$ and are higher than those measured in the SC5 fumarole (Carapezza and Federico, 2000; Capasso et al., 2005), suggesting a variable CH_4 production in different portions of the hydrothermal aquifer or different periods, besides an additional enrichment after vapor separation.

Madonia et al. (2021) suggested the existence of a stratified (multilevel) hydrothermal aquifer, with temperatures that could be progressively higher, in the deeper and inner parts of the island. The hypothesized fractionation upon dissolution in the shallow aquifer would produce a progressive enrichment in He and CH_4 and depletion of CO_2, toward a gas composition, which in the studied aquifer is characterized by He contents as high as $2.5\cdot10^{-3}$ cc/L at STP and CO_2 contents as low as 10 cc/L at STP.