Low-pH waters discharging from submarine vents at Panarea Island (Aeolian Islands, southern Italy) after the 2002 gas blast: origin of hydrothermal fluids and implications for volcanic surveillance.

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Abstract

A geochemical survey of thermal waters collected from submarine vents at Panarea Island (Aeolian Islands, southern Italy) was carried out from December 2002 to March 2007, in order to investigate i) the geochemical processes controlling the chemical composition of the hydrothermal fluids and ii) the possible relations between the chemical features of the hydrothermal reservoir and the activity of the magmatic system. Compositional data of the thermal water samples were integrated in a hydrological conceptual model, which describes the formation of the vent fluid by mixing of seawater, seawater concentrated by boiling, and a deep, highly-saline end-member, whose composition is regulated by water-rock interactions at relatively high temperature and shows clear clues of magmatic-related inputs. The chemical composition of concentrated seawater was assumed to be represented by that of the water sample having the highest Mg content. The composition of the deep end-member was instead calculated by extrapolation assuming a zero-Mg end-member. The Na–K–Ca geothermometer, when applied to the thermal end-member composition, indicated an equilibrium temperature of
approximately 300 °C, a temperature in agreement with the results obtained by gas-
geothermometry.

*Keywords: low-pH waters; shallow submarine hydrothermal springs; Panarea Island*

1. Introduction

On a global scale submarine thermal fluid discharges occur in several tectonic settings and
are thought to significantly affect the composition of seawater and marine sediments (Thompson,
1983; Von Damm, 1990), particularly in the Mediterranean Sea, where coastal seawater is poorly
flushed with respect to that of the oceans. Relatively few marine shallow-water hydrothermal
systems have been previously studied in terms of fluid geochemistry characterization and
thermo-chemical processes. Examples include sites widely differing in terms of tectonic setting,
e.g. areas around Ambitle and Lihir Islands, Papua New Guinea (Pichler and Dix, 1996; Pichler
et al., 1999), Galapagos Islands, Ecuador (Edmond et al., 1979), White Point in Palos Verdes,
California (Stein, 1984), Krakemaya Bay in the Kuriles (Taran et al., 1993), Kodakara-Jima
Island, Japan (Hoaki et al., 1995), Vulcano Island, Italy (Sedwick and Stüben, 1996), Milos,
Greece (Cronan and Varnavas, 1993; Dando et al., 1995; Botz et al., 1996; Fitzsimons et al.,
1997), and Punta Mita near Puerto Vallarta in Central Mexico (Prol-Ledesma et al., 2002; Taran
et al., 2002). Hydrothermal emissions in marine environments are commonly found in
association with volcanic islands, seamounts and in areas of active tectonics, where fault and
fissure systems allow the release of deep-originated hydrothermal fluids (e.g. Vidal et al., 1978;
Von Damm et al., 1985; Butterfield et al., 1990; De Lange et al., 1990; Barragán et al., 2001) and
typically discharge warm-to-hot, acidic, highly reducing, metal-rich fluids.
The occurrence of submarine hydrothermal exhalative activity off-shore 3 km east of Panarea Island was probably known since the Roman age (e.g. De Dolomieu; 1783; Mercalli, 1883), although systematic geochemical studies of these hydrothermal discharges have been carried out only in the last decades (e.g. Gabbianelli et al., 1990; Italiano and Nuccio, 1991; Calanchi et al., 1995).

On the 3rd of November 2002 an impressive “gas burst” (consisting of emissions of a mixture of gas mainly composed of CO$_2$, fine-grained suspended sediments and colloidal sulfur released from the sea floor at a depth of 10-15 m) led to the formation of a crater-like depression about 20x14 m wide and 10 m deep (Fig. 1b) (Chiodini et al., 2003; Capaccioni et al., 2005, 2007; Caracausi et al., 2005). Similar emissions had occurred in this area in historical times, i.e. in 126 B.C. (e.g. De Dolomieu, 1783; D’Austria, 1895; Dumas, 1860). The presence of SO$_2$, HF and HCl, and the relatively high $^{3}$He/$^{4}$He ratios (up to 4.6 R/Ra) in the fluids discharged in the two months immediately following the most recent event, have suggested the occurrence of significant contribution of fluids from a magmatic-related source (Capaccioni et al., 2005, 2007). This event highlighted the unexpected renewal of volcanic activity at Panarea Island, which until November 2002 was considered an extinct volcano (e.g. Gabbianelli et al., 1990; Calanchi et al., 2002). Interestingly, the November 2002 gas burst episode occurred near the end of a prolonged seismotectonic paroxysmal period in southern Italy, as testified by: $i$) the occurrence (on the 6th of September 2002) of a strong earthquake (M = 5.6) in the southern Tyrrhenian Sea, with an epicenter offshore of Palermo between the Eolian Arc and Ustica Island, $ii$) the onset (on the 27th of October 2002) of the strongest Mount Etna eruption in the last decades (Neri et al., 2005) and $iii$) the onset (on the 28th of December 2002) of the strongest Stromboli eruption since 1930, with lava-flows and explosive activity lasting through May, 2003 (e.g. De Astis et al., 2003). Detailed geochemical and bathymetric studies carried out after the degassing (e.g. Anzidei et al., 2005;
showed that this area is marked by tens of \( \text{CO}_2\text{(H}_2\text{S}) \)-rich submarine fumaroles and several low-pH hydrothermal emissions, with maximum temperature up to 130 °C.

The present study highlights the physical-chemical processes that control the composition of these submarine hydrothermal springs in order to i) construct a conceptual geochemical model of the circulation pattern of thermal fluids and ii) provide useful insights into the relations of the deep-originated fluids with the magmatic system of Panarea Island for volcano monitoring purposes.

### 2. Geological and volcanological setting

Panarea is the smallest (3.3 km\(^2\)) of the Aeolian Islands (southern Tyrrhenian Sea), although it represents the emergent part of a wide stratovolcano more than 2,000 m high and 20 km long (Gabbianelli et al., 1993; Gamberi et al., 1997). The Aeolian archipelago is a ring-shaped volcanic arc, composed of 7 islands and 10 seamounts, associated with the Peloritanian-Calabrian orogenic belt (e.g. Boccaletti and Manetti, 1978; Beccaluva et al., 1982; 1985; Gabbianelli et al., 1990). The subduction-related volcanic activity, which started during the Quaternary (400 ka), is still presently active (Calanchi et al., 2002) and magma compositions range from calc-alkaline to shoshonite. The Panarea volcanic complex consists of at least three separated portions: 1) the main Panarea Island, showing a complex morphology resulting from the subaerial emplacement of several dacitic domes between 150 and 100 ka; 2) the endogenous dome of Basiluzzo (3 km NE of Panarea Island), dated at 50 ka; and 3) the submarine fumarolic field, located about 2.5 km E of Panarea Island, surrounded by five emerging reefs (Dattilo, Bottaro, Lisca Bianca, Panarelli and Lisca Nera). The emerging reefs are arranged along a circular rim of about 1 km in diameter and are characterized by a maximum sea depth of 30 m.
According to Calanchi et al. (1999), the reefs are made of high potassium calc-alkaline dacite and porphyritic basaltic-andesite lavas. The Panarelli reef has been dated at 130 ka (Calanchi et al., 2002). The seafloor of the inner shallow sea, partly covered by *Posidonia* mats, consists of loosely- to partly-consolidated Holocene sands and conglomerates that are mainly derived from the erosion of the emerging islets. The resulting debris fan lies on porphyritic basaltic-andesite lavas, that, along with the emerging reefs, represent the remnants of undated lava domes (Calanchi et al., 1999). The spatial distribution of fumarolic vents appears to be controlled by NNE and NW oriented fault systems, which align with the dominant regional tectonic lineaments of the Aeolian Islands (Gasparini et al., 1982; Lanzafame and Rossi, 1984). The discharging fluids are the surficial expression of a marine shallow-water hydrothermal system (e.g. Gabbianelli et al., 1990; Italiano and Nuccio, 1991; Calanchi et al., 1995), whose composition was modified during the 2002 gas blast by inputs of magmatic-related fluids (Capaccioni et al., 2005, 2007). The pre-2002 conditions were more or less restored after few months (Capaccioni et al., 2005).

3. The November 2002 gas burst and evolution of the submarine fumarolic field of Panarea Island

The gas exhalations of the Panarea submarine fumarolic field before the November 2002 degassing event were dominated by CO₂ and H₂S, with relatively low amounts of atmospheric species, CH₄, H₂, and traces of CO and light unsaturated hydrocarbons (Italiano and Nuccio, 1991; Calanchi et al., 1995). The activity of this marine shallow-water hydrothermal system was considered almost static and interpreted as the waning activity of a still cooling and extinct volcano. However, on the basis of the chemical and helium isotopic compositions of the fluids discharged in the months immediately following the burst, the 2002 gas burst was interpreted as
the result of a sudden and local fluid input from the deep magmatic system (Caliro, et al., 2004; Capaccioni et al., 2005, 2007). This argued for reevaluation of the stage of activity of the Panarea volcanic system. By May 2003, the hydrothermal conditions dominating the fluid reservoir prior to the degassing event were completely restored, as testified by: i) the significant decrease of the flux of the submarine emissions, allowing the progressive sediment in-filling of the crater-shaped depression in the seafloor, which formed after the main gas explosion; ii) the almost complete disappearance of the magmatic chemical markers; and iii) the decrease of the helium isotopic ratio to pre-eruption values. This rapid evolution has suggested that the November 2002 gas burst was probably triggered by a limited volume of deep-originated gas passing through the relatively shallow hydrothermal system that potentially acted as a transient gas-vapour accumulation chamber (Capaccioni et al., 2007).

4. Field and laboratory analytical procedures

Water samples were collected from six different sites (Fig. 1b) with a 200 mL syringe connected to a steel hose inserted into the vents and then transferred into glass tubes tapped with Thorion valves (Giggenbach, 1975). We adopted this sampling method to minimize potential seawater contamination and to prevent CaCO$_3$ precipitation related to the depressurization of the water sample when reaching the sea surface. To follow the temporal evolution of the system, 29 water samples at Pa5 and Pa6 (Fig. 1b) were collected from December 2002 to March 2007. Fluid temperature was measured in situ by inserting a mercury thermometer into the vents through a 2 m long metal duct, while pH was measured at the surface after collecting the water sample at depth. Alkalinity (titration with 0.01N HCl), B (Azometina-H method; Bencini, 1985), NH$_4$ (molecular spectrophotometry), SiO$_2$ (colorimetry), the main anions (SO$_4^{2-}$, Cl$^-$, Br$^-$, F$^-$ and NO$_3^-$ with a Dionex DX100 ion chromatograph) and main cations (Ca, Mg, Na, K and Li with a
Perkin-Elmer AAnalyst 100) for water samples # 1-6 (Table 1) were determined at the
Laboratories of Fluid Geochemistry of CNR – Institute of Geosciences and Earth Resources
(IGG) and Department of Earth Sciences of Florence (Italy). The main composition (Ca, Mg, Na,
K, Cl$, SO$_4^{2-}$) of the waters of the two temporal series (samples # 7-35; Table 2) were performed
with a Dionex DX500 ion chromatograph at the Laboratory of Fluid Geochemistry of the
National Institute of Geophysics and Volcanology (INGV) of Rome (Italy). Analytical methods
and precisions are summarized in Table 3. The quality of each analysis was checked by
calculating the analytical error according to: $\frac{\sum \text{anions} - \sum \text{cations}}{\sum \text{anions} + \sum \text{cations}} \times 100$ (all concentrations in meq/L). Analytical error was always less than 3%.

5. Description of the thermal fluids discharges

The submarine fumarolic field at Panarea Island lies on the top of a shallow rise (8-40 m deep) and covers an area of the 2.3 km$^2$. The site is surrounded by strongly hydrothermally altered Panarelli, Lisca Bianca, Bottaro, Lisca Nera and Dattilo reefs (Fig. 1a, b). Hydrothermal fluid emissions are commonly found in association with dykes composed of highly silicitized mineralogical assemblages and polymetallic sulphides, suggesting that local fault systems control the location of the main hydrothermal vents (Anzidei et al., 2005).

The hydrothermal emissions investigated here are the only sites emitting a warm-to-hot liquid phase, and were detected by SCUBA divers during the 40 sampling campaigns carried out between November 2002 and March 2007. Presently, the majority of the fumarolic emissions discharge only gas phases. At sites Pa1, Pa2 and Pa3 hydrothermal fluids discharge from fissures and/or small holes ($\phi < 50$ cm) in the seafloor, at depths between 19 and 24 m. Vent Pa4, the deepest sampled site at 32.5 m, was characterized by an impressive flow rate of hot water and gases seeping from a cavern (about 2x1.5 m wide) with walls that are entirely covered by
yellowish sulphur deposits (Fig. 1b; Table 1). Site Pa5 (23 m deep, Tables 1 and 2), the so-called “Black Smoke” due to the black colour of the fluids emitted in the period 2002-2005 and the thick black encrustations characterizing the vent, is located almost at the centre of a sub-circular depression (φ ~ 40 m, 2 m deep) with a flat bottom of fine-grained sand. Site Pa5 clearly resembles the morphological features of the depression created at the site of the main gas explosion of November 2002 (Fig. 1b). Finally, site Pa6, a high-flux emission (up to ~ 0.1 m³/min) that mainly discharges a gas phase with minor amounts of hot water from a small fissure in the unconsolidated rocky seafloor, is the shallowest sampled vent (8 m deep; Table 1). Vent Pa6 likely originated after the November 2002 degassing event, as reported by local SCUBA divers, who had never observed that hydrothermal emission before.

6. Results and discussion

6.1 Geochemistry of waters

The discharge temperatures, pH, TDS (total dissolved solids) values and the chemical composition for water samples from the Panarea marine shallow-water hydrothermal system are given in Table 1. Chemical data for the two time series at sites Pa5 and Pa6 are reported in Table 2. The hydrothermal springs are characterized by discharge temperatures ranging from 46° to 135 °C and pH values varying between 2.6 and 6.0. Although TDS concentrations (up to 54,500 mg/L; Table 2) are significantly higher than that of local seawater (36,100 mg/L; Table 1), the hydrothermal springs have a seawater-like Na-Cl composition. The minor constituents B, SiO₂, F⁻, Li and NH₄ are particularly high (up to 177, 136, 17.4, 7.5 and 3.3 mg/L, respectively), exceeding those of local seawater by more than one order of magnitude, while Br⁻ concentrations (up to 105 mg/L) show only a relatively low enrichment (up to ~ 60%) with respect to that of seawater. The distribution of data points in the Cl⁻ vs. outlet temperatures (Fig. 2a) and Cl⁻ vs. pH (Fig. 2b) diagrams suggests, at first approximation, that water chemistry is governed by a
mixing process between seawater and a hot, low-pH and Cl\textsuperscript{-}-rich end-member. The distribution of data points in the Na vs. Cl\textsuperscript{-} diagram (Fig. 3) indicates the existence of at least two distinct mixing trends. Trend A (Fig. 3) relates to local seawater to “concentrated seawater” (the latter having Cl\textsuperscript{-} concentrations up to about 25,000 mg/L but closely maintaining the original solute composition, i.e. Na/Cl\textsuperscript{-} ratios similar to that of seawater, possible due to vapour loss). Trend B (Fig. 3) refers to “concentrated seawater” that interacts with a Cl\textsuperscript{-}-rich hyper-saline end-member, including thermal waters with Cl\textsuperscript{-} concentrations >25,000 mg/L, which show Cl\textsuperscript{-}/Na ratios (~2.4) significantly exceeding that of seawater (~1.8). Therefore, the spatial and temporal variability of the chemical composition of the marine shallow-water hydrothermal system of the Panarea volcanic complex seems to be controlled by three different end-members: 1) a chemically modified, hot, highly-saline end-member, which, according to the compositional features of the associated gas phase (Capaccioni et al., 2007) and the high concentrations of B (Table 1) that is typically mobilized by high-temperature steam (e.g. Giggenbach, 1991; Martini, 1996), represents a magmatic-related source; 2) a shallow end-member represented by “concentrated seawater” with relatively high salinity that is likely related to boiling of seawater (Dando et al., 1999) heated by the ascending hot gases; and 3) local seawater, whose presence may be ascribed, at least partly, to contamination during sample collection.

The (Na+K)-Ca-Mg ternary diagram (Fig. 4) shows that the water samples plot along a line that seems to point toward an end-member with very low Mg concentrations. Several authors have demonstrated that Mg can easily be removed from seawater heated by interaction with hot rocks and hydrothermal fluids (e.g. Bischoff and Seyfried, 1978; Seyfried and Mottl, 1982; Thornton and Seyfried, 1987; Scott, 1997). This explains the extremely low Mg concentration in hydrothermal systems (Giggenbach, 1988). Since the Mg concentrations of the Panarea submarine hydrothermal springs can almost be entirely ascribed to seawater and seawater-related
contributions, the composition of sample # 33 (vent Pa6 collected on the 21st of September, 2006; Table 2) may be considered to closely resemble that of “concentrated seawater”. This sample is indeed characterized by the highest Mg concentration (1,800 mg/L, Table 1) still maintaining the typical Cl/Na seawater ratio. This sample separates the two different mixing trends shown in Fig. 3. Accordingly, the composition of the main constituents of the deep end-member can be estimated by extrapolation of Mg=0 using a linear regression of the composition of sample # 33 (the shallow end-member) and those of samples # 7 and 8 (vent Pa5 collected on the 6th of March and 3rd of June, 2003, respectively; Table 2). Samples # 7 and 8, having Cl concentrations exceeding 32,000 mg/L (Table 2), Cl/Na ratios greater than 2.3, and the lowest Mg concentrations (<750 mg/L; Table 2), can be regarded as the closest samples to the deep end-member (Fig. 5a-d). The resulting estimates for Cl, Na, Ca and K concentrations of the deep end-member are reported in the last row of Table 1. The scatter of data points about the two main mixing trends (Fig. 5a-d) may be due, at least partly, to phase separation induced by boiling of seawater (Von Damm et al., 2003 and references therein). The results of phase separation on the chemical composition of the hydrothermal emissions are difficult to discern since the emissions are likely overprinted by mixing and gas-water-rock interaction processes. Carbonate species were excluded for the calculation of the deep end-member composition, which, as suggested by the distribution of samples on Fig. 2b, should have a very low pH (likely <3). Among the major water components, SO$_4^{2-}$ is the only one that seems to show a positive correlation with Mg, especially if only the composition of the Pa5 vent is considered (Fig. 6). This suggests that, like Mg, SO$_4^{2-}$ is strongly depleted in the deep end-member. Conversely, higher SO$_4^{2-}$ concentrations indicate a larger contribution by shallow seawater-related end-members. Actually, at highly reducing conditions, like those commonly dominating hydrothermal systems (e.g. Giggenbach, 1980; 1987), sulphur is mainly present in the liquid phase as HS$^-$ and H$_2$S$_{aq}$. Nevertheless, CaSO$_4$
precipitation from the uprising fluids, and associated decrease of \(\text{SO}_4^{2-}\) concentrations in the fluids, may also occur, at least at the interface between the high-\(\text{SO}_4^{2-}\) shallow waters and the Ca-enriched deep fluids. This is also indicated by the anhydrite SI (Saturation Index) values, which vary from -0.57 (vent Pa1; Table 1) to 2.72 (Tables 1 and 2). The Saturation Index values (expressed as \(\log(a[\text{Ca}]^*a[\text{SO}_4^{2-}]/\text{Ksp})\); Ksp: solubility constant of anhydrite) were calculated with the Phreeqc 2.13 software package (Parkhurst and Appelo, 1999) using the specific ion-interaction equations of Pitzer that is commonly adopted to calculate activity coefficients for highly-saline (up to 5 molality of NaCl), high-temperature (up to 250 °C) fluids (e.g. Li and Duan, 2007). The estimated low pH (<3) and the high Ca concentration (7,900 mg/L; Table 1) of the deep end-member indicate an almost exhausted buffering capacity of the host rock due to a total dissolution of \(\text{CaCO}_3\) and a complete conversion of rock silicates into hydrothermal mineral phases and amorphous silica. High Ca contents can also account, at least partly, for the almost complete disappearance of \(\text{SO}_4^{2-}\) ions related to anhydrite precipitation.

Summarizing, the chemical features of the Panarea submarine hydrothermal fluid discharges seem to depend on three main processes: 1) phase separation related to seawater boiling at the contact with hydrothermal fluids and hot rock, 2) mixing of seawater, concentrated seawater and deep-originated fluids and 3) precipitation of mineral phases.

6.2 Geothermometry

Mixing processes and lack of thermodynamic equilibrium generally pose difficulties for estimating temperatures under reservoir conditions using chemical geothermometers based on cationic concentrations (Giggenbach, 1988). As suggested by some authors (e.g. Kharaka and Mariner, 1989; Prol-Ledesma et al., 2004), the best temperature estimation of deep fluid reservoirs for highly-saline waters can be obtained using geothermometers that do not include
Mg in their equations, i.e. the Na-Li and Na-K geothermometers (Fouillac and Michard, 1981; Giggenbach, 1988). The equilibrium temperatures provided by the Na-K geothermometer range between 150° and 260 °C, suggesting that the composition of discharged waters was not related to chemical equilibrium. This is likely due to the previously hypothesized mixing of the deep fluid with the relatively shallow end-members (seawater and concentrated seawater). The application of the SiO$_2$ geothermometer, using a formula for quartz solubility as a function of temperature (Ellis and Mahon, 1977), provides relatively low equilibrium temperatures (<155 °C), likely due to the mixing process of the hydrothermal fluids with cold seawater (Fournier, 1991). By applying the Na-K geothermometer to the calculated compositional data of the deep thermal end-member (Table 1), an equilibrium temperature of 300 °C is obtained. This temperature is in agreement with those estimated for this hydrothermal system on the basis of gas equilibrium in the H$_2$O-CO$_2$-H$_2$-CO-CH$_4$-O$_2$ system (Caracausi et al., 2005).

6.3 Temporal evolution

The discontinuous monitoring of the main chemical constituents carried out at vents Pa5 and Pa6 since March 2003 and December 2002, respectively (Table 2), provides significant insights into the temporal evolution of the Panarea marine shallow-water hydrothermal system. The two selected emissions show strong synchronous compositional variations (Fig. 7a-f) that can be explained by changes of the fluid inputs at various degrees. Chloride, Na, Ca and K contents have significantly decreased after September 2003 (Fig. 7a-d), whereas those of SO$_4^{2-}$ and Mg show contemporaneous strong increases (Fig. 7e-f). These temporal patterns are likely related to a general decrease, after the November 2002 gas burst, of the contribution of the deep end-member to the submarine hydrothermal emissions. This is in agreement with the evolution of the volcano-hydrothermal system between November 2002 and June 2004, on the basis of 1)
the diminishing presence of acidic gases in the fumarolic discharges, 2) the decrease of the gas flux from the main emission sites of the November 2002 event (Caliro et al., 2004; Caracausi et al., 2005; Capaccioni et al., 2007), and 3) the morphological evolution of the discharging vents (Caramanna et al., 2004). The compositional variations recorded at vent Pa6 are less extreme than those observed at vent Pa5 possibly because the latter, whose discharge temperature is the highest among those measured in the area (up to 135 °C, Table 2), closely represents the deep feeding system, and, consequently, is more sensitive to dilution by surrounding waters.

It is worthwhile to mention that at the end of 2006 the compositional temporal trend seems to indicate a new increase of the contribution of the deep end-member (Fig. 7a-f), suggesting that this volcanic system is far from the attainment of a steady-state condition.

7. Conclusions

The fumarolic field located 3 km E of Panarea Island represents the surficial expression of a medium-to-high enthalpy marine shallow-water hydrothermal system. The chemical composition of hydrothermal springs emerging from the seafloor changes both in time and space. The thermal waters are derived from seawater-related fluid sources that are chemically modified by complex gas-water-rock interactions. The main process responsible for the observed compositional variability is mixing, at different degrees, among at least three superimposed end-members: i) local, almost un-modified seawater, added to the emerging thermal waters from very shallow levels, likely within the unconsolidated sediments of the sea bottom, and, at least partly, during sampling procedure; ii) concentrated seawater or seawater affected by boiling due to heat rising from the deep system that significantly increases salinity; iii) chemically modified seawater, having low pH and strong Cl-excess with respect to seawater, with an origin that is likely due to hot, acidic, HCl-bearing fluids from depth. The calculated physical-chemical
parameters characterizing the deep end-member (T ~ 300 °C, pH <3), in the presence of particularly high convective heat flux from depth, do not allow complete absorption of highly acidic gas species (i.e. HCl, HF and SO\textsubscript{2}) (Capaccioni et al., 2005 and 2007). This explains the chemical evolution of the marine shallow-water hydrothermal system: in the two months immediately following the November 2002 gas burst the fluids were found to be rich in magmatic-related compounds (Capaccioni et al., 2005 and 2007), while in the periods characterized by normal degassing activity, i.e. prior to November 2002 and after December 2002, the fluids had typical CO\textsubscript{2}(H\textsubscript{2}S)-dominated hydrothermal compositions (Italiano and Nuccio, 1991; Calanchi et al., 1995). Accordingly, the November 2002 gas burst can be interpreted as the result of a particularly rapid increase in convective heat flux from the deep, active magmatic system. This generated a separate, acid-bearing gas phase that largely exceeded the hydrostatic pressure and thus was able to intrude the shallower aquifers without significant interactions with seawater (Capaccioni et al., 2005 and 2007).

The chemical reactions in the liquid phase coupled with those in the gas phase released at the seafloor offshore Panarea Island reveal that this portion of the Tyrrhenian Sea is affected by an on-going process that involves the presence of a hydrothermal/magmatic system. Accordingly, the chemical composition of the hydrothermal discharges may vary as the deep- and shallow-related systems are affected by variations in permeability, induced by seismic events and/or self-sealing-related fluid overpressures, which can trigger new blast events. Therefore, the physical-chemical parameters of the hydrothermal discharges that are strongly related to the contribution of the deep end-member (i.e. Cl\textsuperscript{-} concentration, discharge temperature, pH) may be regarded as useful precursors to forecast future eruptive/explosive events. This suggests that a periodical monitoring of the main physical-chemical features of the thermal waters and the associated gas phase emitted into the seawater from the main hydrothermal vents (i.e. Pa5), is
highly recommended. Monitoring is warranted as the area is frequented by thousands of summer tourists.

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**Table captions**

Table 1. Outlet temperatures (°C), pH, total dissolved solids values, Saturation Index (SI) of CaSO$_4$ and chemical composition of the submarine thermal water discharges at Panarea Island. The measured chemical composition of local seawater (mean composition of 5 seawater samples collected in 2006 and 2007) and the estimated chemical composition of the hydrothermal end-member are also reported; n.c: not calculated; n.d.: not determined. Ion contents are in mg/L.

Table 2. Chemical composition, Saturation Index (SI) of CaSO$_4$ and TDS values of submarine thermal water discharges (samples # 5 and 6) collected offshore Panarea Island during the period December 2002 – March 2007; n.d.: not determined. Ion contents are in mg/L.
Table 3. Analytical methods and precisions for main and minor element/species; FAAS: Flame atomic absorption spectrophotometry.

**Figure captions**

Fig. 1a-b. Map of a) Panarea Island and b) submarine fumarolic field with the location of thermal fluid discharges.

Fig. 2a-b. Cl$^-$ (in mg/L) vs. outlet temperature (in °C) (a) and pH (b) binary diagrams of the thermal springs from the submarine fumarolic field of Panarea Island. Symbols are: vents Pa1 to Pa4, open square; vent Pa5, open circle; vent Pa6: open triangle.

Fig. 3. Na vs. Cl$^-$ (in mg/L) binary diagram for the water samples from the submarine fumarolic field of Panarea Island. Symbols as in Fig. 2. Sample # 33 from Table 2 is shown.

Fig. 4. (Na+K)/10-Ca-Mg ternary diagram for the water samples from the submarine fumarolic field of Panarea Island. Symbols as in Fig. 2.

Fig. 5a-d. Mg vs. Cl$^-$ (a), Na (b), Ca (c), K (d) binary diagrams for the water samples from the submarine fumarolic field of Panarea Island. Ion contents are in mg/L. Symbols as in Fig. 2.

Fig. 6. Mg vs. SO$_4^{2-}$ (in mg/L) binary diagrams for the water samples from the submarine fumarolic field of Panarea Island. Symbols as in Fig. 2.

Fig. 7a-f. Temporal evolution of Cl$^-$ (a), Na (b), Ca (c), K (d), SO$_4^{2-}$ (e) and Mg (f) contents for vents Pa5 and Pa6. Ion contents are in mg/L.