

Massive submarine gas output during the volcanic unrest off Panarea Island (Aeolian arc, Italy): Inferences for explosive conditions

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(Received April 7, 2004; Accepted June 20, 2005)

The possibility of understanding natural processes leading to explosive events in volcanic systems provides advantages for a better management of possible volcanic crises. On account of the possibility of the occurrence of other phenomena, such as tsunamis, the explosions driven by submarine volcanic systems are of particular interest, although little investigated. The recent sudden increase in the degassing activity of the submarine geothermal system of Panarea Island (Aeolian arc), has allowed us to better understand the way in which the quiet degassing activity of a submarine hydrothermal system may develop if new magma or magmatic gases feed it. We focused our investigations on the crater-shaped area where the volcanic crisis started, with the aim of evaluating whether the crater was formed by an explosive event or by sediment erosion due to the intense gas flow rate. The calculated energetic conditions, coupled with the computed physicochemical state of the fluids at the level of the deep reservoir, provided the theoretical boundary conditions of the occurred event, while suggesting that a low-energy explosion was responsible for producing the crater at the sea bottom.

Keywords: hydrothermal system, explosion, submarine vents

INTRODUCTION

Large changes in the geochemical features and in the rate of release of the fluids outgassed from hydrothermal systems can occur as a response to magmatic inputs or tectonic activity. In the case of sudden energetic variations of the deep hydrothermal system, the capability of the system to discharge huge amounts of fluids through the pathways in fractured rocks becomes a key condition in determining whether the gas emissions will simply increase their flow rate or if, instead, they will become explosive. The balance between local rock permeability and the mass of the available fluids, determines the possibility of a natural system to move toward explosive conditions. Low permeability, coupled with a high contribution of fluids, could in fact cause either vapor or gas accumulation and an abrupt release by explosive episodes. In contrast, an increased input of magmatic fluids into a hydrothermal system, can hardly cause an explosion when highly permeable pathways already exist or are determined by the local tectonic activity. Obviously, a number of hazards are related to explosive degassing. In submarine vents, explosive episodes can cause massive releases of toxic gases and anomalous waves that create dangerous scenarios for the inhabitants of nearby land masses. An episode of sudden and massive gas release recently

occurred off Panarea Island (Aeolian arc, Italy) where the already known submarine degassing activity suddenly increased without any geophysical precursory signal. The modifications that occurred at the local hydrothermal system produced five large areas of “bubbling sea water” near the islets of Bottaro and Lisca Bianca (Figs. 1a and b). In the main vent, close to Bottaro rock, a crater several meters wide, was formed at the sea bottom, strengthening the hypothesis that the onset of the outgassing event was explosive. The involved area is densely populated during the tourist season, above all in summer. Because of the possible implications in Civil Defense, it would be of extreme importance to establish whether or not explosive outgassing really did form the Bottaro crater, or if, instead, its existence is merely to be referred to the erosion of sediments by the flowing gases.

The aim of this work is to model explosive events caused by the abrupt expansion of CO₂ and steam, while taking into account possible condensation processes. In the case of the Panarea event, constraints on the expansion process can be achieved by ascertaining the physicochemical conditions of the hydrothermal fluids and the size of the produced crater. A comparison between the measured gas output and the required amounts of gas or vapor computed by the models, highlights the explosive character of the gas release. Some outcomes regarding the maximum expected explosive event, occurring with a similar mechanism, can be inferred on the basis of a few reasonable assumptions.

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1986; Italiano and Nuccio, 1991). These showed that the degassing activity was spread over a 4 km²-wide area, and that the main gas vents were approximately located in the central portion. It is worth while noting that the highest gas flux from one single vent was measured to be 9·10³ moles CO₂ per day. According to previous studies (Italiano and Nuccio, 1991; Calanchi *et al.*, 1995) the degassing activity is fed by an underlying geothermal system, that supplies both vapor and thermal waters. The energy source of the deep geothermal system was hypothesized as being a cooling magma having an estimated volume of 1 km³.

After the sudden variation in the degassing activity, new studies were developed in the area, and Caracausi *et al.* (2005) modeled both the geochemical processes and the physico-chemical conditions of the volcano-geothermal system in the new energetic conditions. Here we shortly summarize their results. Gas geothermometry in the CO₂-CH₄-CO-H₂ gaseous system, performed after the onset of the crisis, has suggested that the deep geothermal system is characterized by a 12 mol% CO₂ vapour, which coexists with an aqueous solution at temperatures up to 350°C and 16 MPa. The rising vapour probably undergoes variable condensation when moving through shallow levels. Based on a dissolution model of volcanic gases in water, the rising geothermal vapor interacts with air saturated sea waters at low depths, dissolving 30–40% CO₂ and even more H₂S, modifying the pH of the aqueous solution and stripping the dissolved atmospheric volatile. Thermal water also interacts with country rocks and extensively mixes with sea water.

Measurements of the gas output (3–4 × 10⁵ mol/day) from the entire submarine degassing system have been performed by Italiano and Nuccio (1991) since the 1980s. Caliro *et al.* (2004) reported new data obtained after the onset of the crisis, which highlighted an increase in the degassing rates by almost two orders of magnitude (about 1.8 × 10⁷ mol/day on November 13th).

In accordance to Caliro *et al.* (2004) and Caracausi *et al.* (2005), a new magmatic input would have caused the last episode of volcanic unrest, supplying a much intense feeding of magmatic fluids to the deep geothermal reservoir. As a consequence, geothermal P and T conditions increased as well as the extent of vaporization, causing the huge outgassing observed at the surface.

At the onset of the crisis (November 3rd, 2002), the main degassing emission near Bottaro islet was so intense that it was impossible to carry out any direct measurements at the emission point. Since the “flux” (Φ) of a physical quantity is expressed as the amount of gas moles (N) flowing across a given area (A) per unit of time (t):

$$\Phi = Nt^{-1}A^{-1} \quad (1)$$

it can be converted into “output” (Φ·A) when the crossing area is known. Being Φ·A = v·A, where v is velocity of the flowing fluid, it was possible to estimate the gas output by examining an underwater movie filmed at the early stage of the degassing activity. With this aim, we assessed the rising rate of the gases by comparing the rising rate of the bubbles with respect to reference segments having known measured lengths. By playing the film frame by frame, the gas-puffs were followed up to a few tenths of a centimeter from the exhaling surface, so as to maximize the gas/liquid ratio of the bubble/sea water mixture. This also allowed us to take into consideration only the ascending column of gas-puffs, before it spread out into a lot of slower small bubbles. The estimation of the rising rates at progressively greater distances from the bottom in fact resulted in decreasing values. The rate of ascent was calculated at several points of the gas emission and the average value multiplied by the exhalative area measured at the onset of the crisis. The obtained value (1.3 × 10⁸ mol/day) highlights that the gas output from Bottaro crater was about one order of magnitude higher than that measured two weeks later.

THE EXPLOSIVE EVENT

The massive and sudden output of hydrothermal fluids, which occurred near the islet of Bottaro, formed a depression 20 by 8 meters wide and 7 meters deep. In the hypothesis that this crater was caused by an explosive event, the required energy was performed by the abrupt expansion of a gas phase. The first step towards the understanding of the process is that of assessing the total amount of energy involved in forming the crater at the beginning of the crisis. By developing reliable and adequately constrained models of explosive gas expansion, we will be able to calculate the amount of gas required to perform this work and compare it with the gas output supplied by the system.

Energy involved in forming the Bottaro crater

As can be seen along the wall-rocks of the crater, the sediments involved in the explosive event are sands of variable grain size that are very poorly cemented by fine material. Levels of conglomeratic and more cemented materials are inserted, however the rock as a whole results as being poorly consolidated. At a first approximation, we can consider the energy of the crater formation as matching that required to lift the rock volume originally filling the crater. With “h” as the depth from the sea bottom to the crater bottom, the energy is calculated as the vertical shift of the involved rock times “h”. In order to calculate the volume of sediment, the geometry of the crater was assumed as being that of a regular solid hav-

ing an elliptic basis (20 and 8 are the axes), 7 meters high. The calculated work (w_c) is given by:

$$w_c = \rho g V h \quad (2)$$

where ρ is the density of the local sediments ($2.2 \times 10^3 \text{ kg/m}^3$; Schön, 1996), g is the gravity acceleration and V is the volume lifted, so the computed energy is $1.3 \times 10^8 \text{ J}$.

Modelling the explosion

In order to abruptly expand and generate an explosion, hydrothermal vapor must rise towards shallower levels while maintaining pressure higher than that caused by the hydrostatic gradient. The over-pressurization that can be reached depends on the rising rate of the vapor compared to: a) its capability of expanding throughout the fracture network that forms the ascending conduits and b) cooling during rising. At shallow levels, the wall rocks are not able to contain the over-pressurization of the vapour, which has then achieved the required conditions for exploding. The explosive expansion occurs in a very short time, and prevents any loss or gain of conductive heat from the wall rocks, thus the process can reliably be modelled as an adiabatic one.

In our hypothesis, such a condition was obtained at a depth corresponding to the crater bottom, which became the explosion centre (hereafter defined as E.C.). It is located at a depth of about 14 m from sea level and 7 m beneath the sea bottom, and is under a pressure between 0.15 and 0.2 MPa (hydraulic pressure or slightly more). We do not know the pressure of the vapour at the E.C. before the explosion (hereafter defined initial pressure, P_i).

We may suppose that the hydrothermal vapour reaches the E.C. in two different conditions: the ascent of a monophasic fluid (only vapour) at the P and T conditions of the geothermal reservoir (16 MPa and 350°C) (squared mark, Fig. 2) or the ascent of the coexisting gas and liquid at lower T-P conditions to the respect of the hydrothermal system. For both of above mentioned initial conditions, the subsequent adiabatic expansion down to the final pressure (the hydrostatic load at the depth of the E.C., namely 0.2 MPa) causes steam condensation throughout the entire process along the liquid-vapour equilibrium (case 1, grey line, Fig. 2). The final pressure also constrains the final temperature, namely that of the coexisting liquid and vapour at P_f (about 113°C ; mark "a" on Fig. 2). Clearly, higher P_i can give rise to greater expansion works.

Another possible condition (case 2) concerns the vapour rising isothermally but losing pressure (black vertical arrow, Fig. 2); it would reach the E.C. at a lower pressure and would expand without condensation, at least not

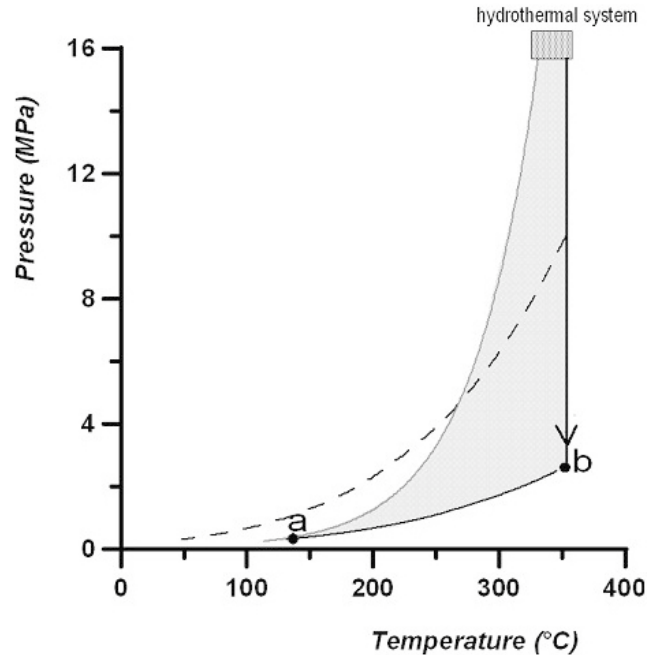


Fig. 2. Pressure versus temperature graph modeling various expansion processes of the thermal fluids at the E.C. The squared mark displays the highest P-T conditions (namely the equilibrium conditions estimated by geothermometric considerations for the deep hydrothermal system). As reported in the text the grey line refers to the liquid/vapour equilibrium curve; the black line from "b" to "a" represents pressure drop after isothermal expansion (vertical black arrow) of the rising steam, while the dashed line refers to CO_2 adiabatic expansion. See text for details.

during the early stages of the expansion process. From any point of the isothermal expansion curve the steam may start to expand adiabatically (e.g., black line from "b" to "a" marks, Fig. 2) and start to condense only when the liquid vapour equilibrium curve is intercepted (point "a" Fig. 2).

Due to the low CO_2 concentration in the pristine hydrothermal fluids, any-one of the above two cases can roughly be treated like steam expansion, even when partial condensation takes place during explosive expansion.

As another boundary case (case 3), we can assume that steam totally condensates at depth and CO_2 becomes the main component of the thermal gas. In this case, the explosion from the E.C. is caused by over-pressurized CO_2 that expands adiabatically (dashed line, Fig. 2).

The discussed cases can be resumed in the following boundary conditions to be modelled.

CO_2 and steam adiabatic expansion

The equation that models the molar work performed by an adiabatic gas expansion is (Atkins, 1986), w :

$$w = C_v T_f (P_i/P_f)^{R/C_p} \{ (P_i/P_f)^{(\gamma-1)/\gamma} - 1 \} \quad (3)$$

where C_v and C_p represent thermal capacities at constant pressure and constant volume respectively (Perry, 1984); γ is the ratio between C_p and C_v and R is the gas constant; T_f is the final temperature of the expansion. P_i and P_f have already been defined. The total work performed in those conditions (cases 2 and 3) is drawn out by:

$$w_{tot} = N \cdot w \quad (4)$$

where N is the total number of gas moles involved in the explosion. It is worth while noting that w_{tot} is equal to the previously computed energy in Eq. (1), thus Eq. (2) allows us to compute the number of moles involved in the expansion process.

Steam adiabatic expansion with condensation

Contrary to the previous case, the adiabatic steam expansion with condensation (case 1 in the above paragraph) must take into account the thermal contribution linked to the moles of steam converted into a liquid state. The conservation of energy requires that the variation of the internal energy of the gas phase (dU) is the sum of the expansion work ($-pdV$) plus the heat produced by steam condensation (Q_{lat}):

$$dU = -pdV + Q_{lat}$$

By using molar quantities (i.e., molar volume v and molar internal energy u) and the definition of thermal capacity at constant volume ($c_v = du/dT$), the equation can be written in the form:

$$n_g c_v dT = -n_g p dv + n_w \Delta H_{lat} \quad (5)$$

where n_g indicates the number of steam moles, n_w the condensing steam moles and ΔH_{lat} the heat of condensation (Haar *et al.*, 1984). For a closed system containing N moles of water and undergoing condensation by adiabatic expansion, n_g varies throughout the entire process because steam moles are continuously condensed. For the purpose of practical calculation, we consider that the number of condensing moles during an infinitesimal depressurization is small enough to assume n_g as a constant. For this infinitesimal step, a simple mass balance can then be written between the total number of steam moles and the residual ones after condensation:

$$N = n_g + n_w \quad (6)$$

The relationship between P , T and v of steam during the condensation process is constrained by the coexistence of liquid and vapour phases at equilibrium (Lide, 1998).

So, by fixing a step of depressurization and the total moles N , the corresponding temperature and volume variations are known, and n_g and n_w can accordingly be calculated by coupling Eqs. (4) and (5). The calculated n_g value can be used as the total number of steam moles for a subsequent depressurization step. On this basis, the whole expansion process (from P_i to P_f) can be considered as a sum of infinitesimal depressurization steps and accordingly modelled by the above equations.

The term $n_g p dv$ in Eq. (4) gives the expansion work performed by steam at each infinitesimal step of pressure drop, thus the total work performed by steam moles expanding from P_i to P_f is easily computed. On the condition that the calculated total work must be equal to the work in Eq. (1), the total number of moles involved in the formation of the crater can be calculated.

The steam's thermal capacity c_v (Haar *et al.*, 1984), and the P - T - v values for liquid-vapor equilibrium were interpolated by empirical functions used for the integration of Eq. (4). A pressure step of 0.1 MPa was considered for any simulated expansion, after testing that the smaller pressure step does not affect our calculation.

RESULTS AND DISCUSSION

The T - P gas conditions at the beginning of the adiabatic expansion have been computed using the above described calculations. Figure 2 displays these results, as well as showing the liquid-vapor boundary line that constrains gas expansion and steam condensation.

In order to depict a range of possible initial conditions of the vapor at the E.C., we fixed the extreme conditions by selecting the highest pressure and temperature estimated for the hydrothermal system by the application of gas geothermometric considerations (Caracausi *et al.*, 2005). As previously stated, the hydrothermal vapor isothermally and isobarically (350°C, 16 MPa) rises to the E.C., expands adiabatically and undergoes condensation, thus it moves along the liquid-vapor line and cools down to about 113°C (the temperature of vapor coexisting with liquid at the final pressure of expansion). Vapor can cool and condense before reaching the E.C., with the initial conditions equally moving along the liquid-vapor equilibrium line (Fig. 2).

Alternatively, the hydrothermal vapor could also rise isothermally to 350°C, while reaching the E.C. at lower pressure than 16 MPa. In such a case, the crossing point of the 350°C isotherm-curve with the adiabatic vapor expansion curve, occurs at 2.5 MPa (mark b, Fig. 2), thereby achieving special significance: such an initial pressure causes vapor to expand adiabatically without condensing, whereas lower initial pressures of expansion would give superheated vapors at the sea bottom (never detected). Vapor at a pressure higher than 2.5 MPa in the

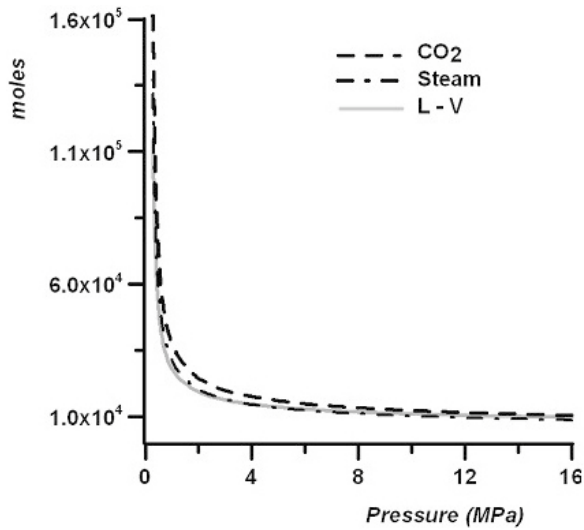


Fig. 3. Calculated mass of fluids (expressed as number of moles) able to produce the minimum of energy to form the “crater” as a function of possible P_i at the E.C. L-V = liquid-vapour equilibrium curve.

E.C. moves along an adiabatic line when expanding, until it reaches the liquid-vapor line. There condensation starts and the vapor follows the two-phase boundary. Based on these constraints, we highlighted an area defining the possible starting conditions of vapor expansion in the E.C. (shaded area, Fig. 2). Indeed, any point in such an area is a possible starting condition of vapor expansion. In the case of CO_2 expansion, the process is constrained by the final pressure (0.2 MPa) and final temperature, the latter being the emission temperature of the underwater vents (around 20°C). The possible initial T-P pairs are defined by the curve in Fig. 2, and the highest P-T conditions are given by the crossing of such a curve with the 350°C isotherm.

Figure 3 displays the amount of vapor (in moles) required to form the Bottaro crater, based on the discussed expansion models and boundary conditions. As can be seen, all the curves show that an almost constant number of moles is able to form the crater when the initial pressure of expansion is higher than 2 MPa. Instead, the required number of moles grows exponentially when pressure is below such a value. Moreover, similar required amounts of gas have been computed for both CO_2 and vapor, whereas a number of moles about 20% lower has been computed to perform the work when steam undergoes condensation throughout the expansion process (Eqs. (3) and (4)).

The computed amount of gas involved in the crater formation (N) has to be compared with the amount of gas that the system can supply. In fact, by inserting the N value into Eq. (1), where the gas output ($\Phi \cdot A$) is known

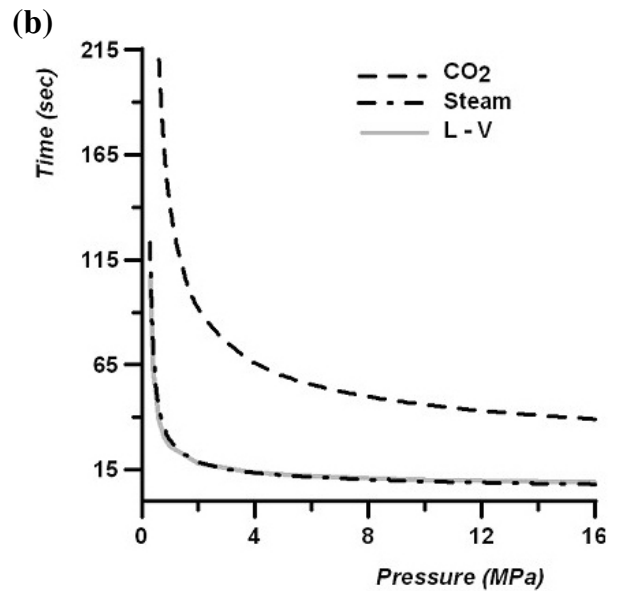
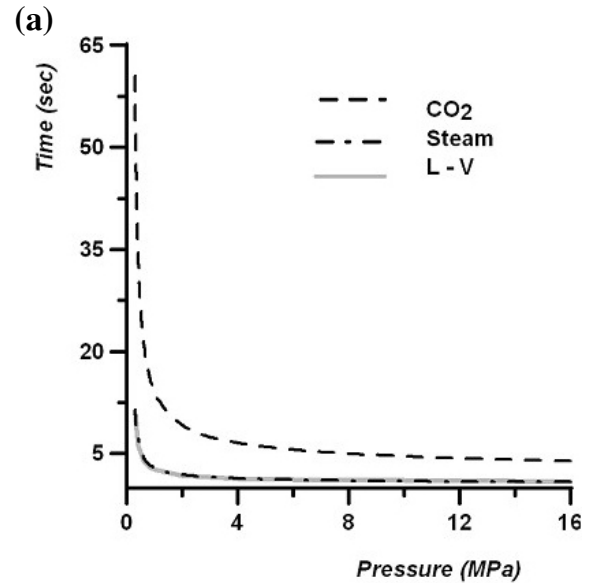


Fig. 4. Estimated time intervals occurring to release the volume of the expanding gas. (see text) (a) based on the gas output measured two weeks after the crisis onset and (b) at the onset of the crisis. The very short times underline the explosive origin for the submarine “crater”. L-V = liquid-vapour equilibrium curve.

by measurement (see Section “The Volcanic System of Panarea and Its Recent Crises”), we compute the time interval needed to discharge the amount of gas required to form the crater. Calculating the time for case 3 involving CO_2 allows us to directly use the measured CO_2 output, whereas the vapor output to be used for cases 1 and 2

must be scaled to CO₂ output through the mentioned H₂O/CO₂ ratio of hydrothermal gases.

The result of this calculation shows that some tenths of a second (or some minutes in the case of CO₂ expansion) are needed to achieve the required number of gas moles when considering the gas output measured two weeks after the onset of the crisis (Fig. 4a). That means that it only took a very short time for this massive emission to form the crater and highlights the explosive character of the outgassing event at Bottaro. These results become more and more striking when the output estimated at the onset of the crisis is considered (Fig. 4b): a few seconds (tenths of a second in the case of CO₂ expansion) are enough to form a Bottaro-like crater when such high amounts of vapor are outgassed from the sea bottom, thus the creation of the crater can indeed be considered explosive.

Even considering the gas output values measured some months after the onset of the crisis, when the emissions were much less intense, it took several minutes to achieve the required amount of gas. This outlines that significant gas accumulation at shallow levels is not necessary to produce a similar crater. Therefore, at the present state of activity, we cannot expect to observe important variations in the gas output of the submarine emissions or in the geophysical signals (deformation, seismicity) before the onset of a possible new crisis. For similar reasons, long periods of accumulation would not be necessary even considering the emission rates measured some years before the crisis. Assuming that such values did not greatly change right before the unrest (no anomaly was observed by fishermen the day before), our result is somewhat in agreement with the lack of seismic precursors preceding the Panarea crisis. Indeed, in an open, widely fractured outgassing system like the submarine exhalative field of Panarea, it would appear reasonable to assume that the accumulation of gases at shallow depth cannot easily occur. In accordance with Caracausi *et al.* (2005), the system fortunately seems to have a high capability of transferring fluids towards the surface. On the other hand, intensive geochemical parameters representative of the physico-chemical conditions in the feeding magmatic and/or geothermal system, may undergo appreciable modifications, outlining a possible evolution towards an unsteady state.

Maximum expected event

An interesting question in terms of both volcanological and Civil Defense implications concerns what could be the most violent expected event occurring in the area caused by a similar mechanism. We have already ascertained that the most energetic process involves condensation, and it goes without saying that the highest gas amounts involved in the explosive event of Bottaro cor-

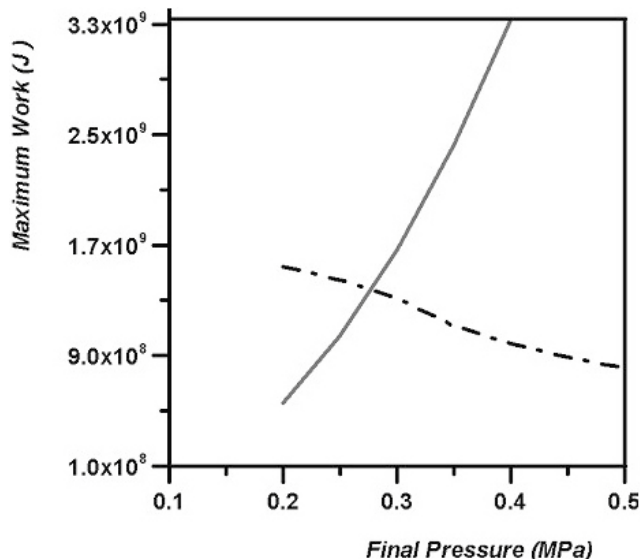


Fig. 5. Estimated maximum work as function of growing final pressure of adiabatic gas expansion (namely, increasing depth of E.C., dash-dot line). The grey line shows the work to lift a rock volume having the same area of Bottaro crater by a height equal to its depth.

respond to the lowest initial gas pressures at E.C. (namely, the pressure to which the hydrothermal vapor arrived at the E.C.). In order to assess the greatest possible number of moles, we constrained a minimal overpressure needed at the E.C. to break local sediments. We do not know the mechanical parameters of these latter, however overpressures around 0.1 MPa (then initial pressure of 0.3 MPa) are required to break the material by shear and start the explosion when considering silt and unconsolidated sands (Schön, 1996). The estimated number of moles calculated in this manner can be defined as being those capable of forming the Bottaro crater when the gas phase reached the E.C. ($P_f = 0.2$ MPa) at initial pressure and temperature of 0.3 MPa and 130°C respectively (the latter is constrained by water-steam coexistence). We may reason on what it would occur if the so estimated utmost gas amount rose isothermally and isobarically (350°C and 16 MPa) at the E.C., since such conditions would be more probable in an already heated system as nowadays is the venting system off Panarea island. The so-obtained work would be 10 folds higher than that which formed the Bottaro crater (Fig. 5). At fixed depth (P_f at E.C.), the potential area of the crater would be about 10^3 m² wide.

On the other hand, the higher available energy could cause deeper E.C. and a related wider crater, thus we computed the work to move a larger volume having an area similar to that of the Bottaro crater. Figure 5 displays this

work computed as a function of the final pressure. Likewise, we calculated the expansion work performed by the highest possible number of moles as a function of the final pressure at the E.C. (clearly, depth and final pressure are related by the hydrostatic gradient). The crossing point between the two curves gives the gas expansion work and depth of the probable E.C. As a result, we have roughly estimated a range of possible conditions for the maximum explosive event that may be expected in the area, in terms of involved energy and depth of the E.C. The estimated energy was in the order of 10^9 J, about 10 times higher than the Bottaro event. However, it remains less energetic by some orders of magnitude with respect to typical tsunami (e.g., about 10^{12} J estimated for both the September 1954 tsunami in Alboran Sea and the October 1966 tsunami at the Perù Coasts; Soloviev *et al.*, 2000; Paras-Carayannis, 1968). Thus, submarine gas explosions involving the estimated amount of volatiles would not be able of causing tsunamis. However, such a hazard has to be taken into serious consideration if any unrest of the volcanic activity involves an amount of volatiles two orders of magnitude higher than that estimated for the last volcanic crisis of Panarea. Of course the tsunami hazard would be considered in case of phreato-magmatic explosions when a more direct magma involvement allows energy release in the order of 10^{17} – 10^{18} J (Gorshkov, 1959; Nakamura, 1965)

CONCLUDING REMARKS

A large underwater crater was observed near the Bottaro islet after the massive and abrupt gas release that occurred on November 3rd, 2002 at the sea bottom. The genesis of this crater was a subject of debate, due to their volcanologic and Civil Defense implications since erosion by flowing gases with high emission rates or explosive gas expansion have deeply different impacts. Here we proposed the theoretical approach to solve this problem.

We performed several calculations of CO_2 and steam expansion, with boundary conditions deriving from the physico-chemical state of the Panarea geothermal system, the emission temperature and the energy involved in forming the crater. When compared to the gas output measurements, the results clearly displayed that the observed crater was caused by a dramatic and abrupt gas expansion, typical of low-energy explosive events. As a consequence, no gas accumulation occurred at depth, thereby highlighting the system's considerable capability of releasing thermal fluids and preventing significant overpressure. We therefore cannot expect important precursors such as increasing seismicity and ground deformation, or gradual growth of the gas output. Instead, we suggest that intensive geochemical parameters (i.e.,

chemical and isotopic compositions) should highlight variations in the physico-chemical conditions of the feeding hydrothermal system, which in fact represents the true engine of degassing crises.

A range of possible initial conditions of the explosion were also defined, providing information on the rising modalities of hydrothermal fluids. By considering the most critical conditions and the highest possible amounts of expanding gas, we constrained the maximum expected event assuming that the outgassing rate would be similar to that of the last crisis. The resulting energy was one order of magnitude higher than that which formed the Bottaro crater: energy that would be able to move ten times the amount of sediment volume. Even in these conditions, the energy involved is much lower than that typical of tsunami waves, and this allows us to reasonably exclude such an event. Nevertheless, risks for fishers, divers and boat tourists, who spend time in the area, are relevant, as are gas hazards. Finally, since the unrest of the degassing activity was probably related to a deep injection of hot fluids from a deep massive magmatic intrusion, we cannot exclude future more energetic episodes due to more intense gas releases or a more direct involvement of magma.

Acknowledgments—We wish to thank Dr. E. Faber whose comments and suggestions improved the earlier version of the manuscript. Mrs. Penny Dyer is thanked for revising the English and Mr. Giuseppe Donato for providing the video used to estimate the rising velocity of the gases. The paper was supported by funds from Civil Protection.

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