Revisiting the last major eruptions at Stromboli volcano: Inferences on the role of volatiles during magma storage and decompression

This is the author's manuscript

Original Citation:

Availability:
This version is available http://hdl.handle.net/2318/1566633 since 2019-01-07T11:21:44Z

Publisher:
Geological Society of London

Published version:
DOI:10.1144/SP410.3

Terms of use:
Open Access
Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)
This is an author version of the contribution published on:
Questa è la versione dell’autore dell’opera:

Revisiting the last major eruptions of Stromboli volcano: inferences on the role of volatiles during magma storage and decompression.


By

Cigolini C., Laiolo M., Coppola D. (2014)

The definitive version is available at:
La versione definitiva è disponibile alla URL:

http://dx.doi.org/10.1144/SP410.3
Revisiting the last major eruptions at Stromboli volcano: inferences on the role of volatiles during magma storage and decompression

Cigolini C.¹,², Laiolo M.¹, Coppola D.¹

¹ – Dipartimento di Scienze della Terra, Università di Torino, Via Valperga Caluso 35, 10125 Torino, Italy
² – NatRisk, Centro Interdipartimentale sui Rischi Naturali in Ambiente Montano e Collinare, Università degli Studi di Torino, Italy

Corresponding Author: Corrado Cigolini
Email: corrado.cigolini@unito.it; Phone: +39-011670-5107; Fax: +39-011670-5128

Abstract

Stromboli is a unique open conduit volcano and a natural laboratory to investigate how volatiles migrate and concentrate under dynamic conditions. Fluid phases are involved in magma decompression and pressurization, modulate Strombolian activity and rule magma rise and fragmentation processes. Here, we have revisited the available data on the last two major eruptions at Stromboli volcano and concentrated our analysis on the 2007 eruption. First, we further analysed petrological-geochemical data to assess equilibrium conditions by using standard thermobarometry; then we used a grid of selected reactions which involve solid-melt-fluid equilibria to better constrain the P-T regimes that adequately describe our system. Primitive hydrous basaltic melts, reported in literature, and preserved as melt inclusions in olivine (with 2.3-3.8 wt% of H₂O, and 890-1590 p.p.m. CO₂), are equilibrium with forsteritic olivine and a diopsidic clinopyroxene, at average pressures of 260 (±47) MPa for temperatures approaching 1170 (±17) °C, and calculated mole fraction of CO₂ within the melt) ranging from 0.60 to 0.76. Ca-rich or ultracalcic melts are regarded as a result of decompression along a steep adiabatic and/or isothermal curve. During this process the magma will crosscut the stability field of diopside and enter the liquidus field. The earlier crystallized diopside is destabilized and will react with the coexisting liquid phase leading to
the formation of ultracalcic melts. Ejected golden pumices (with 2-3 wt% H$_2$O), are in equilibrium with Ca-pyroxene, forsteritic olivine and anorthitic plagioclase at 150–220 MPa and temperatures of 1120-1150°C. Evolved melt inclusions (substantially degassed) in Fe-rich olivine (ca. Fo$_{70}$) of the scorias show average equilibration pressures of 78 (± 20) MPa, and temperatures 1138 (± 14) °C.

In summary, the higher $P$-$T$ regimes associated with the origin of primitive melt inclusions are representative of the base of the chamber, where the ferromagnesian phases may crystallise and cumulate. The magma with a bulk composition typical of the pumices is stored the middle and main part of the chamber (likely its axial sector) and these materials are erupted during paroxysmal, and more rarely, major explosions. Finally more evolved melts inclusions found in the olivine of the scorias are indicative of crystallisation within the conduit or its root-zone connected with the upper part of the chamber.

Pure extensional regimes and recent geophysical data suggest the existence of a prolate ellipsoidal magma chamber below Stromboli. To constrain its volume we estimated the magma volumes associated with SO$_2$ degassing (during the 2007 major eruption) by applying a refined petrological model that allowed us to estimate the magma fluxes in the subvolcanic region (i.e., the magma flux entering the degassing zone). The long term trend of this magma flux follows an overall exponential decay, typical of pressurised magmatic systems, and indicated that magma rise was accompanied and followed by a slow decompression. This trend was shown to be consistent release of elastic strain accumulated either by pressurisation of the rocks surrounding the magma reservoir, or by pressurisation of the magma itself, or both. By analyzing the reservoir elastic response during magma decompression, we found that the current Stromboli magma chamber volume may be adequately constrained within 1-2 km$^3$. 
Introduction

The role of volatiles is crucial in controlling petrogenetic and volcanic processes. Among these the most tangible are, for example, partial melting in the source region of primitive magmas, and the dynamics of fragmentation processes in magma chambers and volcanic conduits. Gaseous phases modulate magma transfer toward the surface and are involved in active degassing when magma batches are momentarily stored in the subvolcanic region before reaching the surface. Recent experimental progresses in igneous petrology and physical volcanology gave us the opportunity to refine solubility models to define degassing trajectories, and to better understand vesiculation processes. However, open conduit volcanoes are natural laboratories to investigate how volatiles migrate and concentrate under dynamic conditions. Fluid phases are involved in pressurising reservoirs, rule magma rise and wall-rock fracturing during dike injection that may lead to effusive-explosive eruptions at active volcanoes. A unique case to study these phenomena is Stromboli volcano located in the Tyrrhenian sea.

Stromboli is a composite stratovolcano with a persistent open-system activity used as a reference case by volcanologists to classify minor to intermediate volcanic eruptions (e.g. Newhall and Self, 1982). The role of fluids in modulating strombolian activity is fundamental since it is involved in the so called “gas puffing” when magma pulses reach the open vents. During these phases, the sudden outburst of gaseous phases induces minor explosions with the projection of scoria bombs, lapilli and ash that characterise the typically mild strombolian activity. In addition, more violent events, also known as “major explosions”, are triggered by portions of undegassed magma that reaches the upper part of the conduit and explosively releases the exsolving gases. However, more energetic paroxysmal explosions are strongly linked to fragmentation processes induced by a “nearly instantaneous” ascent of a fluid-saturated slug that migrates through the conduit and explosively expands in its upper part.
Stromboli rejuvenated the scientific interest with the onset of major eruptive cycle on December 28, 2002: lava effusion from summit vents was followed, on December 30, by a composite slump down the northern part of the cone, generating a tsunami that damaged part of the village and propagated to the north-eastern coast of Sicily. A multidisciplinary effort was coordinated by Italian Civil Defence authorities to mitigate volcanic risk and the potential effects of tsunami waves in the west-central Mediterranean region. This approach gave the scientific community the opportunity to carefully monitor the last effusive cycle (from February 27 to April 2, 2007) that culminated in the paroxysmal explosion of March 15, 2007.

In this review paper we integrate geophysical and petrological data to refine current models on the inner plumbing system of Stromboli volcano in the attempt to better decode the role of volatiles during magma storage and ascent. We will focus our analyses on available experimental petrologic data, melt inclusions and minerochemical data. We thermodynamically calculated mineral-melt-fluid equilibria on selected reactions to refine thermobarometry and magma compressibility during decompression. This will allow us, by means of geophysical models retrieved by analysing SO$_2$ emissions, to constrain magma chamber volumes for better interpreting the eruption dynamics.

**Fig. 1**

**Geological Setting**

Stromboli is the north-eastern island of the Aeolian Arc and has been built on a rather thin continental crust of the Calabrian arc (Fig. 1). This crustal unit extends westward beneath Lipari and Vulcano and then vanishes below Marsili submarine volcano. Fragments of this crust (quarzite, tonalite and diorite) were found as xenoliths in the older lavas of Stromboli (cf., Laiolo & Cigolini 2006; and references therein). The volcano is located onto the Stromboli-Panarea alignment: a NE-SW fault subsidiary of the Tindari-Leojanni fault that propagates NNW-SSE though Eastern Sicily below Etna volcano (Ventura et al., 1999; De Astis et al., 2003; Acocella et al., 2009). The Aeolian
Islands were built within the last 1.3 my (Gillot & Keller 1993). Lavas and tephra are essentially subduction-related calcalkaline, HK-calcalkaline, shoshonitic and potassic rocks. Subduction of the Ionian plate beneath the Calabrian Arc and was accompanied by a regional uplift (0.5-0.7 my), associated with crustal extension. Uplift within the forearc region was related to the rebound of the upper plate (Calabrian Arc and part of the Ionian lithosphere; e.g., Gvirtzman & Nur 2001). Current subduction is responsible of regional seismicity and volcanism (Fig. 1). A recent systematic analysis of teleseismic data by Pontevivo & Panza (2006) support the idea that the Moho below Stromboli is shallow, and located at about 15-17 km depth. These authors identified a low velocity layer ($v_s \sim 3.5 \text{ km}\cdot\text{sec}^{-1}$) at a depth of 15-32 km below the cone. However, the source region of Stromboli primitive melts is well deeper, since primitive magmas likely originate in the mantle wedge above the Benioff Zone (e.g. Peccerillo, 2001; Schiavi et al., 2012). Earthquake’s subduction-related hypocenters reach a depth of approximately 500 km and cluster at about 350-150 km below Stromboli (Fig. 1, see the INGV data bank ISIDe: Italian Seismological Instrumental and Parametric Data Base at http://iside.rm.ingv.it/iside/standard/result.jsp?rst=1&page=EVENTS).

Recently, D’Auria et al. (2006) have located, by means of broadband network operative at Stromboli, few seismic events at depths 4.5-6 km below the summit of the volcano. These hypocenters are positioned in the surroundings of the top of the magma reservoir.

**Stromboli volcano**

The cone of Stromboli is approximately 3 km high with the top reaching 924 m a.s.l. (above sea level). The typical Strombolian activity is characterised by the persistent moderate explosions with the ejection of scoriae, lapilli, ash and bombs from vents positioned at the summit of Sciara del Fuoco (a collapsed sector delimited by a horseshoe-shaped scarp opening north-westward, e.g. Tibaldi et al., 2009). The “mild” and persistent strombolian activity may be interrupted lava effusions, major explosions and paroxysms (Barberi et al., 1993; Bertagnini et al., 2011). A detailed study on the thermal regimes occurring at Stromboli, correlated with changes in volcanic activity
for over a decade, has been reported by Coppola et al. (2012). The material erupted during major and paroxysmal explosions consists of high vesicular lapilli and bombs, that are formed by the mingling of dark-coloured and crystal-rich scoria with golden-coloured crystal-poor pumice within a subvolcanic chamber (e.g., Francalanci et al., 1999; Métrich et al., 2001; 2005). The pumice contains olivine crystals that bear melt inclusions, likely representing the primitive shoshonitic Stromboli basalts. The April 5, 2003 and March 15, 2007 paroxysmal explosions occurred during both the last two effusive cycles. These explosions have been interpreted as a result of decompression induced by rapid magma discharge that triggered the ascent of a gas-rich deep-seated magma, leading to fragmentation of the pumiceous foam within the open conduit (Ripepe et al., 2005). According to Cigolini et al. (2008) this process follows the elastic rebound of the chamber walls that will squeeze up portions of the undegassed magma column (that, in turn, would instantaneously rise and cross-cut the depth where critical gas saturation occurs), leading to magma fragmentation with the ejection of the “primitive golden pumices”. The amount of lava discharged during both effusive cycles may be estimated to be around 1-1.3 x 10^7 m^3 (Calvari et al., 2005) and 0.7-1 x 10^7 m^3 (Neri & Lanzafame, 2009; Marsella et al., 2009; Calvari et al., 2010) (Fig. 2). Flank slumping onto Sciara del Fuoco occurred during several recent lava effusions (namely in 1879, 1916, 1919, 1930, 1944 and 1954, according to Barberi et al., 1993) and generated tsunamis waves in this sector of the Mediterranean.

**Fig. 2**

The cone of Stromboli is subdivided into five units (Hornig-Kjarsgaard et al. 1993; Keller et al., 1993; Francalanci et al., 1993) of calc-alkaline type and shoshonitic affinity: three of them refer to the older part of the volcano, known as Paleostromboli (110-35 ky). The Scari lavas and tephra (34 ± 3 ky in age) are basalts and shoshonite that overlay the Paleostromboli. The Vancori lavas
(shoshonitic basalts and trachytes, with ages 26 to 13 ky) lay on top of the above sequence. The *Neostromboli* unit (13-6 ka) is in the northern sector of the island (Fig. 1b) and consists of shoshonitic and potassic lavas. Recent *San Bartolo lavas*, erupted during roman times (Arrighi *et al.*, 2004; Speranza *et al.*, 2008), are high-K calc-alkaline basalts with abundant mafic and ultramafic mantle xenoliths, ascribed to the roots-zone of Stromboli plumbing system (Laiolo & Cigolini 2006). Current lavas and tephra are high-K calc-alkaline basalts and shoshonites (cf., Francalanci *et al.*, 2004; Landi *et al.*, 2009; Pompilio *et al.*, 2012).

Structurally, the architecture of the island is the result of summit collapses of caldera type that took place from 100 to 13 ky BP (e.g., Tibaldi *et al.*, 2009). The last one led to the formation of Sciara del Fuoco (Fig. 1b). Recently, Marsella *et al.* (2012) reconstructed the morphological evolution of the Sciara del Fuoco since 1868, and correlated it with the on-going volcanic activity. Summit vents were persistently (and are currently) located along a N40°E normal fault. This trend is also consistent with the main direction of dyking (e.g., Tibaldi *et al.*, 2003; Ripepe *et al.*, 2005).

The structure of the subvolcanic plumbing system has been recently discussed. According to several authors (Métrich *et al.*, 2001, 2005; 2010), Bertagnini *et al.* (2003), Francalanci *et al.* (2004) the plumbing system is represented by a lower main chamber (that contains the primitive undegassed low porphyritic magma, LP magma, normally ejected as golden pumices) connected to an upper subsidiary reservoir where the more evolved magma is momentarily stored (degassed high porphyritic magma, HP magma, erupted as lavas and/or scorias during effusive and mild strombolian activity). According to Cigolini *et al.* (2008) the geometry of the plumbing system is strongly controlled by the local structural setting and stress distribution, and is simply represented by a prolate ellipsoid connected, in the subvolcanic region, with the active conduit. In this view the primitive LP magma is confined within its lower part, whereas the HP magma is located in its upper portion. However, geophysical data support the occurrence of an ellipsoidal structure below Stromboli volcano (Bonaccorso *et al.*, 2008).
Analytical methods

Mineral phases and glasses of samples collected at Stromboli during 2006 and 2007 were analyzed at the Dipartimento di Scienze della Terra of the University of Torino with a SEM Cambridge Instruments Stereoscan 360 equipped with an EDS Energy 200 and a Pentafet detector (Oxford Instruments). Operating conditions were 15 kV accelerating voltage, and a beam current of 2.68 nA. Quantitative data (with spot sizes of 2 μm and 15 μm in diameter, for minerals and glasses respectively) were obtained and processed using the Microanalysis Suite Issue 12, INCA (Suite version 4.01). Analyses were corrected for background, drift, mass absorption and secondary fluorescence by using natural and synthetic standards. The relative errors are within 2% for most of major elements and may go up to 10% for minor elements (with concentrations < 1.00 wt %).

Bulk-rock compositions were acquired by inductively coupled plasma mass spectrometry (ICP-MS) analysis by ALS Chemex, Sevilla, Spain. Precision of analyzed major elements are better than ±0.2% for SiO₂, and ± 0.1% for the other oxides (with the exception of MnO and P₂O₅ which show errors of ca. ± 0.02%).

Background Petrology

We will briefly review the petrography of the lavas and the juvenile tephra erupted during 2002-2003 and 2007. The reader may refer to Landi et al. (2006; 2009), Cigolini et al. (2008), Métrich et al. (2001; 2005; 2010) and Bertagnini et al. (2003; 2008) for detailed descriptions.

Lavas and scorias erupted during the last two major eruptions (2002-2003 and 2007) are shoshonitic basalts with crystallinity up to 35-45% modal, consisting of diopsidic clinopyroxene (salite-augite), plagioclase and minor olivine on an interstitial glassy matrix (Fig. 3a; 3b). Groundmass microlites consist essentially of plagioclase and clinopyroxene. Scorias are slightly richer in SiO₂ and alkali when compared to the pumices ejected during both paroxysmal explosions.

Basaltic pumices have crystallinity <10% and consist of the above phases, with higher bulk MgO
(Mg# 0.55-0.60) and CaO contents, whereas K$_2$O is lower (2<wt %). Interstitial glass compositions are normally more evolved then those of the whole rock. *Melt inclusions* found within olivine crystals of the pumices are more primitive (with SiO$_2$ ranging between 45.6 and 49.4 wt % and Mg# ranging from 0.55 to 0.64). Some of these are richer in CaO and show lower alumina contents and are named *ultracalcic primitive melts*. These features have been ascribed by Pichavant *et al.* (2009) to crystal dissolution–reaction-mixing (DRM; cf., Danyushevsky *et al.*, 2004) of earlier fractionated clinopyroxene.

**Fig. 3**

Métrich *et al.* (2001; 2005; 2010) and Bertagnini *et al.* (2003; 2008), investigated in details primitive melt inclusions in olivine of the golden pumices. These contained 2-3.7 wt% H$_2$O and 700-1900 p.p.m. CO$_2$. They suggest the primitive gas-rich shoshonitic, or high-K basalt, is residing within the middle-lower part of the reservoir and during its ascent and storage, in a subsidiary chamber, undergoes decompression-driven crystallisation leading to the formation of a crystal-richer magma batch. The ejected materials of this kind are lapilli and scoria bombs produced during the typically “mild and persistent” Strombolian activity. However, the undegassed primitive magma is stored at deeper levels and is solely erupted during paroxysmal explosions with the ejection of the “golden pumices”. According to the cited authors, mingling and interactions of dark-coloured and crystal-rich scoria with golden-coloured crystal-poor pumice normally occur during major violent explosions (e.g., Francalanci *et al.* 1999; Métrich *et al.* 2001; 2005; Landi *et al.* 2004).

**Fig. 4 and Table 1**
In Fig. 4 we report a summary of petrochemical data onto the K₂O vs. SiO₂ diagram of Peccerillo & Taylor (1976) that shows the variability of the erupted materials. The selected analyses of the erupted products and melt inclusions are shown in Table 1.

Recently, Di Carlo et al. (2006) investigated phase relationships in melts of Stromboli golden pumices by selecting a sample named PST 9, that represents the less evolve pumice in the dataset. Experimental runs were carried out at temperatures of 1175-1050°C and pressures comprised between 400 to 50 MPa for variable H₂O contents (5.5-1.2 wt %) and oxygen fugacities (within 2 log units above the Ni-NiO buffer). According to their results a diopsidic pyroxene is a liquidus phase from 400 MPa to 150 MPa within the temperature range of 1175-1150°C. This phase is followed by olivine eventually crystallising with pyroxene and plagioclase, ± Fe-Ti oxide at lower P-T regimes. This is basically consistent with the cooling experiments of Conte et al. (2006) performed at 1 atm on somehow similar bulk compositions.

Di Carlo et al. (2006) experimentally confirmed that the magma type typical of the “golden pumices” is an undegassed melt that, undergoing decompression, did not extensively crystallise prior its ejection. Conversely, lava and scoria erupted during mild strombolian activity represent a degassed magma that underwent a larger degree of crystallisation at lower pressure regimes.

More recently, Pichavant et al. (2009) performed additional experiments on PST9 from Stromboli volcano under variable H₂O and CO₂ concentrations. Experimental fluids coexisting with primitive melts range from CO₂ rich (X_{H₂O} ~ 0.2) at 400 MPa to CO₂ poor (X_{H₂O} ~ 0.8) at 100 MPa. It was found that clinopyroxene is the liquidus phase in all high pressure experiments, either under hydrous or anhydrous conditions. In addition, at 0.1 MPa at temperatures of 1190 °C clinopyroxene and Mg-olivine appear together on the liquidus, being indicative of the onset of a cotectic relationship during decompression. The occurrence of this relationship was already established, for the assemblages of the golden pumices, by Cigolini et al. (2008) who found nearly constant olivine-
clinopyroxene $K_{D}^{\text{cpx}}$ values (based on the Fe$^{2+}$-Mg$^{2+}$ exchange) in the natural assemblages (ranging 0.5 ±0.06).

**Stromboli fluids**

It is generally accepted that melting processes at subduction zones are generally controlled by water and carbon dioxide concentrations (e.g. Wyllie, 1979; Yoder, 1969; Mysen & Boettcher, 1975a; 1975b). Indeed, these gases play a crucial role in most magmatic processes and their abundance has a direct influence on phase stabilities and crystal-melt-gas equilibria. In addition, gas exsolution during decompression substantially controls magma ascent and fragmentation processes. However, beside these, some other minor fluid phases play a considerable role as well. Among these, sulphur degassing is a key factor in decoding volcanic activity and magma dynamics in volcanic reservoirs.

A cross check between the S related petrologic method and plume SO$_2$ emissions is crucial for detecting magma recharge within the upper part of reservoirs, and to analyse eruption processes at active volcanoes.

Métrich et al. (2001; 2005; 2010) and Bertagnini et al. (2003) analysed sulphur, chlorine and fluorine within Stromboli glasses, including primitive melt inclusions. Sulphur concentrations found within the glasses of the “degassed” Stromboli scorias range from 170 to 250 p.p.m., whereas in primitive melt inclusions is comprised between 1200 and 2500 p.p.m.. Within the matrix glasses of porphyritic scorias, chlorine ranges from 1150 to 1270 p.p.m., while in the olivine-melt-inclusions is slightly higher, being comprised between 1500 and 2200 p.p.m.. Fluorine is rather variable: within scorias and pumices ranges from 780 to about 1050 p.p.m., whereas in primitive melt inclusions is somehow higher (960-1360 p.p.m.). Métrich et al. (2010) found that S is positively correlated with pressure, whereas Cl and F contents do not show appreciable variations with pressure changes. In particular, they suggested that SO$_2$ is released at pressures of about 170 MPa or lower. We will later discuss how sulphur degassing may give important information on magma volumes involved in recharge processes and magma chamber dynamics.
Stromboli fluids are also carefully monitored in volcano surveillance. Radon emissions (e.g., Cigolini et al., 2009; 2013; Laiolo et al., 2012) and CO$_2$ fluxes are automatically measured (Rizzo et al., 2009; Carapezza et al., 2009). Carbon dioxide SO$_2$ and H$_2$S are also continuously detected in the volcanic plume by means of a multigas analyzer (Aiuppa et al., 2005; 2009) and FTIR (La Spina et al., 2013). In addition, SO$_2$ is also carefully monitored by systematic COSPEC measurements (Burton et al., 2009). We will later consider some key issues that arise from the analyses of the collected SO$_2$ timeseries when compared to eruption discharge rates.

In this section, we prefer to briefly review gas compositions sampled at the summit of Stromboli. The data are few but quite significant. Following the early measurements of Tazieff and Tonani (1963), gases released at Stromboli summit fumaroles were analysed by Carapezza & Federico (2000) and by Finizola et al. (2003). Geothermometric estimates on the gases collected by Finizola et al. (2003), obtained by means of the CO$_2$-CH$_4$-CO geothermometer (Chiodini & Cioni 1989), give equilibration temperatures of 265-275°C. These temperatures are in good agreement with those obtained graphically on the diagram log(H$_2$O /H$_2$)+log(CO/CO$_2$) vs. 3log(CO/CO$_2$)+log (CO/CH$_4$) constructed by Chiodini & Marini (1998) that classify these fluids as superheated vapors. Thus, these gases have essentially an hydrothermal origin (with $X_{H_2O}$ approaching 0.90).

However, Martini et al. (1996) reported two gas compositions obtained on samples collected by M. Ripepe within a fracture located at the rim of the NE summit crater. These gases have definitely higher $X_{CO2}$ concentrations, ranging from 0.33 up to 0.73, and their sampling temperatures were 410 and 190°C. Noticeably, FTIR data reported by Burton et al. (2007) found that during the typical strombolian explosions $X_{CO2}$ fractions are normally 0.33, and $X_{H_2O}$ may be as high as 0.64. Conversely, during quiescent degassing (or gas puffing) the above reach 0.13 and 0.83, respectively (the rest, up to 1, being essentially SO$_2$ and HCl in equal proportions).
Equilibrium assemblages in primitive melts

Natural assemblages are complex systems. However, we may use experimental data and computer modelling (e.g., MELTS) to better constrain P-T-X variability. Both these approaches are based on the fact that equilibrium conditions are reached, and rule the evolution of the system. Unfortunately, the effects of volatile concentrations on phase stabilities are still inadequately known (such as the stability field of plagioclase and clinopyroxene in function of changing hydrous conditions, cf. Yoder, 1969; Kushiro, 1979; Métrich et al., 2001). In this section, we will analyse the available data on Stromboli to identify equilibrium assemblages by using standard consolidated methods, normally applied in igneous petrology.

We thus explored the equilibrium conditions of Stromboli primitive basalts by analyzing minerochemical data and melts compositions in terms of distribution coefficients.

Among these, we first consider the olivine-liquid distribution coefficient

\[
K_D^{ol-liq} = X_{Fe}^{ol} X_{Mg}^{liq} / X_{Mg}^{ol} X_{Fe}^{liq}
\]

According to Roeder & Emslie (1970), equilibrium conditions are satisfied for a value of 0.33 in this parameter. However, Kamenetsky et al. (1998) has suggested that this parameter may range from 0.27 to 0.29 in alkaline mafic magmas. According to Putirka (2008), the appropriate \( K_D^{ol-liq} \) values for basaltic magmas is 0.299 (±0.05). For Stromboli basalts, Métrich & Clocchiatti (1996) and Di Carlo et al. (2006) constrain the olivine-melt Mg-Fe distribution coefficient at 0.29 for equilibrium conditions. Thus a melt with a Mg-number (Mg#) of 0.58 (i.e., one of the more mafic within the melt inclusions) will be in equilibrium with an olivine Fo83. The latter authors suggest that the Mg-Fe partition coefficient, for clinopyroxene-liquid equilibrium

\[
K_D^{cpx-liq} = X_{Fe}^{cpx} X_{Mg}^{liq} / X_{Mg}^{cpx} X_{Fe}^{liq}
\]

is constrained to about 0.31 (±0.06) according to their experimental data. However, Putirka (2008) emphasised that the best estimate for this parameter is 0.28 (±0.08) over a wide range of magma compositions.

Concerning the plagioclase-melt equilibrium, we considered a Ca-Na exchange between the two phases, \( K_D^{pl-liq} = X_{Ab}^{pl} X_{NaAlO2.5}^{liq} X_{CaO}^{liq} / X_{NaAlO2.5}^{pl} X_{SiO2}^{liq} X_{NaO0.5}^{liq} \) accepting a value of 0.27 ±0.05 (cf. Putirka,
In Table 2 we report a selection of representative mineral phases of the erupted products that are compatible with their coexisting melts and satisfy the above partitions coefficients.

**Table 2**

An additional issue is plagioclase stability. First, petrography shows that plagioclase (locally euhedral) is an “ubiquitous” phase in all the erupted pumices. Second, Di Carlo et al. (2006) report a high-pressure run (at 400 MPa, 1100°C and 2.3 H₂O wt% ) of a pumiceous melt (PST9) where plagioclase crystallises. Five other experimental runs at the same temperature, lower pressure and lower H₂O contents define the plagioclase stability field. In the experimental works of Pichavant et al. (2009) plagioclase does not crystallise since they were performed at higher temperature (T>1150°C). However, starting from the same melt composition, Conte et al. (2006) found that plagioclase is a crystallising phase in their experiments at atmospheric pressure and temperature below the 1150°C. By testing the crystallisation Stromboli primitive basalts (including sample PST9) with the computer code MELTS (Ghiorso & Sack 1995), we found that clinopyroxene is liquidus phase above 250 MPa and 1175°C, whereas olivine becomes a liquidus phase together with clinopyroxene at lower pressure, and plagioclase would appear on the liquidus below 50 MPa for temperatures approaching 1100°C.

**Fig. 5**

In order to assess the role of plagioclase during the crystallisation of Stromboli primitive basalts we analyzed the data by means of Pearce element ratios (Pearce & Stanley, 1991). These can be used to constrain the fractionating mineral phases within a given magma (cf. Russell & Nicholls, 1988). We thus plotted the data (ours plus those in literature) on the (2Ca+3Na)/K vs. Si/K diagram (Fig. 5a). A slope approaching to 1 indicates a pair removal. In our case the calculated slope is 0.90 (with a
correlation coefficient of 0.85), thus suggesting the fractionation of both phases (clinopyroxene and plagioclase). Fig. 5b with (2Ca+Na)/K vs. Al/K indicates a higher proportion of clinopyroxene removal relative to plagioclase (0.60 to 0.40, respectively) (Fig. 5b). Finally, the 2Na/K vs. Al/K diagram allow us to estimate that an average plagioclase of composition of about An\textsubscript{82-76} was involved in the fractionation of Stromboli primitive basalts (Fig. 5c). Whereas a labradoritic plagioclase (An\textsubscript{67-62}) is involved in the crystallization of evolved melts. In both cases their values satisfy $K_{pl-liquid}$ constraints (0.23±0.01) and are consistent with the petrography of lavas and scoriaceous materials.

**Geothermometry and Geobarometry**

In this section we will first apply classical geothermometers and geobarometers to estimate the P-T regimes of Stromboli primitive melts. We will then refine our estimates by introducing a grid of selected reactions that will help us to further constrain equilibrium regimes for selected mineral-melt compositions. Finally, we synthesise our results and discuss them to better infer the extension of Stromboli magma reservoir.

First, the results obtained by systematically applying classical thermobarometers are reported in Table 3 (see the footnotes of this table relative uncertainties). Hydrous melt inclusions and bulk pumices with H\textsubscript{2}O contents comprised between 2-3 wt %, show equilibration temperatures for their liquids in the range of 1100-1220°C. Lower values are obtained by using the algorithm of Sisson & Grove (1993), being constrained to 1100-1160°C. With the exception of the results obtained by applying the Putirka (2008) liquid thermometer (leading to temperatures of 1145-1185°C), other geothermometers substantially overlap, in the range of approximately 1160-1220°C.

Olivine-liquid geothermometers only partly overlap. Higher temperatures are obtained by using the one proposed by Beattie (1993) leading to temperatures of 1150-1220°C. The results obtained by calculating the Sisson & Grove (1993) and Putirka (2008) geothermometers are basically consistent
at lower temperatures (1100 ± 30 °C), whereas in the higher temperature ranges lead to about 1150°C and 1190°C, respectively (Table 3).

Table 3

The geothermometers that use clinopyroxene-liquid equilibria are essentially those proposed by Putirka et al. (2003) and Putirka (2008; equations 32d, 33, 34), and practically overlap in the temperature range of 1110-1220°C (Table 3). Finally, the clinopyroxene-liquid barometers proposed by the latter author indentify rather variable equilibration pressures. Among these, the most coherent with previous estimates (Métrich et al., 2001; 2005; 2010; Bertagnini et al., 2003 and Cigolini et al., 2008) are those obtained by applying his equation (30) of Putirka (2008), leading to pressures of 170-360 MPa for the melt inclusions, and 210-290 MPa for the bulk pumices, respectively. Unfortunately, Putirka’s geobarometers show a good degree of uncertainty (see the footnote of Table 3), so we had to find more reliable geobarometers.

A grid of selected reactions

Thus, in order to minimize uncertainties related to the applications of the classical thermobarometers treated above, we used a grid of selected reactions which involve solid-melt equilibria to better constrain the P-T regimes that adequately describe our system. These are the following:

\[ \text{Mg}_2\text{SiO}_4 + \text{SiO}_2 = \text{Mg}_2\text{Si}_2\text{O}_6 \]  
\[ \text{Fo} \quad \text{liq} \quad \text{CEn} \]  

\[ \text{CaMgSi}_2\text{O}_6 = 1/2 \text{SiO}_2 + 1/2\text{Mg}_2\text{SiO}_4 + \text{CaSiO}_3 \]  
\[ \text{Di} \quad \text{liq} \quad \text{Fo (liq)} \quad \text{Wo (liq)} \]
17

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{Mg}_2\text{SiO}_4 + \text{SiO}_2 = 2\text{Mg}_2\text{Si}_2\text{O}_6 + \text{CaAl}_2\text{SiO}_6
\]

(3)

\[
\text{An} \quad \text{Fo} \quad \text{liq} \quad \text{CEn} \quad \text{CaTs}
\]

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 = \text{CaAl}_2\text{SiO}_6 + \text{SiO}_2
\]

(4)

\[
\text{An} \quad \text{CaTs} \quad \text{liq}
\]

Abbreviations below reaction components are: Fo – forsterite; CEn – clinoenstatite; Di – diopside; Wo – wollastonite; An – anorthite; CaTs – Ca-Tschermakite. Abbreviated mineral phases are solid, unless otherwise indicated (as liquid, liq).

Reactions (1) and (2) have been used to estimate P-T regimes for the coexistence of olivine and pyroxene, and to identify the upper stability field of diopsidic pyroxene in hydrous Stromboli basaltic melts. However, the use of melt components in thermodynamic calculations has the advantage of considering the water contents in the melt phase. In addition, reaction (3) is a rather efficient geobarometer (e.g., Laiolo and Cigolini 2006; Cigolini et al., 2008) in the stability field of bytownitic plagioclase and ferromagnesian phases consistent with the mineral assemblage found in Stromboli pumices. Finally, reaction (4) is typical of the low pressure assemblage where a labradoritic plagioclase is coexisting with augite and a differentiated groundmass melt under nearly anhydrous conditions (ca. 0.5 wt% H2O, cf. Stevenson & Blake 1998). Regarding this reaction, we will discuss the results of obtained in our previous study (Cigolini et al., 2008). The degree of oxidation of the melt has been retrieved, following Kress & Carmichael (1991), from the Ni-NiO buffer of Hübner & Sato (1970), appropriate for Stromboli magma (cf., Laiolo & Cigolini 2006), taking into account the effect of pressure (in the light of the data of Robie et al., 1979).

The Gibbs free energy for a generic i reaction is represented by

\[
\Delta G_{0}^{P,T} = \Delta G_{0}^{1,T} + RT \ln K_{i} + \int_{0}^{P} \Delta V dP
\]

(5)
where \( \Delta G_0^{1,T} \) is the Gibbs free energy for the reaction calculated at 1 bar and at the temperature of interest \( T \) by using the data of Berman (1988; cf. his Table 2, 3, and 4 p. 458-463) together with those of Richet et al. (1982) for amorphous silica, and those of Ghiorso & Sack (1995) for other melt components (Table A1, p. 209 of their work). A synopsis of used thermodynamic data is reported in Table A2 of Cigolini et al. (2008). \( R \) is the gas constant and \( K_i \) is the equilibrium constant for the \( i \) reaction considered, which may be calculated, knowing the chemical compositions of the analysed phases, from the appropriate solution models. The last term is the difference of the molar volumes of the reactants minus the products of the reaction integrated within the given pressure range. This can be solved numerically at given equilibrium conditions by using the cited data of Berman (1988), and those listed by Ghiorso & Sack (1995) for the melt components, that include thermal expansion and compressibility.

In the studied reactions, activities for olivine, pyroxene and plagioclase were calculated according to the solution models of Sack & Ghiorso (1989), Gasparik (1984; 1990) and Newton et al. (1980), respectively. Activities of melt components were obtained according to the regular solution model of Ghiorso & Sack (1995) and change with the water content in the melt phase. The solution of the above equation has been obtained numerically, by minimizing the free energy \( \Delta G_0^{p,T} \) (that goes to zero at equilibrium conditions) by fixing a given value of \( T \) and calculating \( P \) (or vice versa). The same procedure has been applied to the set of the above reactions. A summary for the equilibrium constants is given in Table 4. Melt compositions and mineral phases used in calculations are summarised in Table 1 and Table 2, respectively.

**Table 4**

The reference melt for reactions (1) and (2) are the selected melt inclusions found within the olivines of ejected pumices (reported by Métrich et al., 2001; 2005; 2010; and Bertagnini et al., 2003) and identified as a primitive Stromboli basalts. Reaction (3) defines equilibrium conditions of
the golden pumices (bulk composition). Reference data are given in Table 1, whereas the selected equilibrium mineral phases are summarized in Table 2.

In the APPENDIX we report the thermodynamic solutions for the for melt inclusions (Tables A1 and A2) and the bulk pumice (Table A3). The same data have been used to construct Figure 6.

**Fig. 6**

In particular, Stromboli primitive melts (Mg# 0.57 and CaO/Al₂O₃ 0.73) are in equilibrium with a Fo-rich olivine (Fo₈₄₋₈₀) and a diopsidic pyroxene (Wo₄₄₋₄₈ En₄₃₋₄₈ Fs₆₋₉) at temperatures of 1140-1170 °C and pressures of 260 (±60) and 440 (±70) MPa for water concentrations ranging 2-4 wt%, respectively. More realistic best solutions are those for water being comprised between 2-3 wt%, giving temperatures of 1150-1160 °C and pressures of **280-340 MPa**. Similar reasoning for the Ca-rich melts (Mg# 0.63 and CaO/Al₂O₃ 0.93) will give higher equilibration temperatures and lower pressures, with best solutions of 1160-1180 °C and pressures of 180 (±70) and 280 (±90) MPa with water contents of 2-3 wt%. The olivine in equilibrium with the ultracalcic melts are Fo₈₈₋₉₀. Finally, equilibration P-T regimes for the golden pumices, given by the coexistence of the above mineral phases and a bytownitic plagioclase (An₈₂₋₇₈) will constrain temperatures at 1120-1140 °C and pressures of 190 (±40) and 170 (±50) MPa for similar water contents (2-3 wt%).

Thermobarometric estimates for the upper part of the chamber were obtained by considering the equilibrium of phenocrystic rims with the coexisting groundmass melt (and the reader may refer to Cigolini *et al.*, 2008 for details). These data have been used, together with the above, to construct Fig. 7.

**Thermobarometry of Melt Inclusions**

Better constraining the P-T regimes of melts coexisting with volatiles is a key factor for decoding in-chamber magma dynamics (e.g., Witham, 2011a; Métrich *et al.*, 2011; Witham, 2011b).
In our earlier paper (Cigolini et al., 2008) we calculated mineral-melt equilibria for the melt inclusions reported by Métrich et al. (2001) according to the following reaction

\[ \text{Mg}_2\text{SiO}_4 = \text{Mg}_2\text{SiO}_4 \]  
\[ \text{Fo} \text{ (liq)} \]  

By summing up the above with reaction (2), we obtain the following:

\[ \text{CaMgSi}_2\text{O}_6 + \text{Mg}_2\text{SiO}_4 = \frac{1}{2} \text{SiO}_2 + \frac{3}{2}\text{Mg}_2\text{SiO}_4 + \text{CaSiO}_3 \]  
\[ \text{Di Fo liq Fo (liq) Wo (liq)} \]  

which is representative of the olivine-clinopyroxene cotectic relationship. According to Pichavant et al. (2009) such a relationship is critical for assessing equilibrium conditions in Stromboli basalt. We therefore extended our thermodynamic calculations by taking into account a more comprehensive data set (including the data of Bertagninì et al., 2003; Métrich et al., 2001; 2005; 2010). In Table 5 we report the selected melts together with the appropriate clinopyroxene compositions that satisfy the \( K^{\text{Cpx-liq}}_D \) requirements of Putirka (2008).

Table 5 and Table 6

In this section the notations \( X^m_{\text{H}_2\text{O}} \) and \( X^m_{\text{CO}_2} \) refer to the fractions of water and carbon dioxide in the binary mixture dissolved in the melt under saturation conditions (\( X^m=X^V \)); so that \( X^m_{\text{H}_2\text{O}} + X^m_{\text{CO}_2} = 1 \). The above equilibrium can be solved for \( P, T, X^m_{\text{H}_2\text{O}} \) and \( X^m_{\text{CO}_2} \) for the given fluid concentrations (in wt% as input data) by minimising the free energy of the above reaction and solving simultaneously the solubility equations of Dixon & Stolper (1995) and Dixon (1997). The insertion of the molar
heat of solution for H$_2$O in the melt (determined on albite melt by Silver & Stolper 1985) for polythermal calculations has been shown to be negligible with respect to free energy minimization. In other words, we are first solving thermodynamically the required thermodynamic conditions along a Clausius-Clapeyron equation representative of minerals-melt equilibrium. The solution is then found for the P-T conditions that satisfy the observed volatiles concentrations according to the model of Dixon for alkaline basalts (Dixon, 1997). We trust that this approach is more reliable because we are analyzing a three phase system (solids, melt and gas) that substantially improves the commonly used two phase solubility models (e.g., Newman & Lowenstern 2002; Papale et al., 2006).

In Table 6 we report the solutions for the above reaction for selected melts in equilibrium with the chosen clinopyroxene compositions. These data indicate that primitive melt inclusions are in equilibrium with ferromagnesian phases at pressures between 3.3 and 2 kbar and temperatures ranging from about 1150 to 1200°C (with average values of about 1170°C, and only one melt inclusion slightly above 1200°C). It is interesting to notice that calculated $X^m_{CO_2}$ values range from 0.6 to 0.76. These estimates are in good agreement with the previous ones obtained by the models of Newman & Lowenstern (2002) and Papale et al. (2006) models (e.g., Métrich et al., 2005; 2010; Bertagnini et al., 2003). However, similar calculations performed by mean of reaction (6) for the primitive melt inclusions lead to similar pressures but unrealistically higher temperatures (nearly 20-25°C higher, being incompatible with experimental data).

Notably, melt inclusions in scorias equilibrate with Fe-richer olivine (ca. Fo$_{70}$) and an augitic pyroxene at pressures of 60-100 MPa and temperatures ranging from 1120 to 1145°C (Table 7 and Table 8). However, calculated $X^m_{CO_2}$ are much higher (being comprised between 0.79 and 0.98) since the water contents of these melt inclusions are very low (and substantially they are indicative of a degassed magma). In this case also the thermodynamic solutions of reaction (6) give similar pressure ranges as well, but considerable higher temperatures (up to 60°C) which are definitely
unrealistic. Therefore a cotectic relationship defined by reaction (7) is by far more appropriate for identifying solid-melt-fluid equilibration regimes in Stromboli basalts.

**Table 7 and Table 8**

**Summary of Thermobarometry**

Our best estimates suggest primitive hydrous melts preserved as melt inclusions in olivine (with 2.3-3.8 wt% of H2O) are in equilibrium with forsteritic olivine and a diopsidic clinopyroxene at pressures of 200-340 MPa pressure and temperatures of 1150-1200°C. Average data of calculations on melt inclusions are 260 (±47) MPa and temperatures of 1170 (±17) °C. These regimes are representative of the base of the chamber, where the ferromagnesian phases may crystallise and cumulate (see Laiolo & Cigolini 2006; Cigolini et al., 2008). However, slightly more evolved melts, typical of the *golden pumices* (with 2-3 wt% H2O), are in equilibrium with Ca-pyroxene, forsteritic olivine and anorthitic plagioclase at 150–220 MPa and temperatures approaching 1120-1150°C. These materials likely represent the middle and main part of the chamber.

In turn, thermobarometric estimates for the upper part of the chamber were obtained by Cigolini *et al.* (2008) by considering the equilibrium of phenocrystic rims with coexisting groundmass melts (with Mg# of 0.20-0.25). The upper part of the chamber where the reservoir is connected with the conduit is confined at 140-120 MPa for temperatures approaching 1100°C (which is the measured effusion temperature for the lavas). Evolved melt inclusions in Fe-richer olivine (ca. Fo70) of the scorias show average equilibration pressures of 78 (±20) MPa, and temperatures 1138 (±14)°C, being indicative of crystallisation within the conduit or its root-zone that reaches the upper part of the chamber.

However, Stromboli magmas originate above the slab at an approximate depth of about 100 km (Schiavi *et al.*, 2012). From this depth melts will progressively migrate to upper levels and interact
with the ultramafic materials at depths of 34-24 km were temperatures reach 1200-1250°C (Cigolini \textit{et al.}, 2008). In this region, the magma is percolating through the wallrocks of the LVZ and may converge into a feeder dyke that crosscuts the Moho. On their way to the surface, basaltic magmas may decompress along a steep adiabatic and/or isothermal curve crosscutting the stability field of diopside thus entering the liquidus field and generating ultracalcic melt inclusions. To better visualize this process we compiled summary of the mineral stabilities in Stromboli basalts (Fig. 7) in the light of the previously cited experimental data and the above equilibria, together with those reported by Cigolini et al. (2008) for the low pressure assemblage. The possible decompressional $P$-$T$ path (at higher pressures) for explaining the origin of the ultracalcic melts is also plotted (upper path in Fig. 7). During decompression the magma path will cross the clinopyroxene stability field and enter the liquidus field. The earlier crystallized diopside is destabilized and will react with the melt leading to the formation of ultracalcic melts. Subsequent cooling associated with moderate decompression, and/or at nearly isobaric conditions, will lead to crystallization of the ferromagnesian phases again. This scenario is basically supporting the hypothesis of Pichavant \textit{et al.} (2009) that suggest that Ca-rich melts are related to crystal dissolution–reaction-mixing (DRM; cf., Danyushevsky \textit{et al.}, 2004) of earlier fractionated clinopyroxene.

\textbf{Fig. 7}

Once the magma has entered the chamber, it will be stored undergoing fractionation and degassing. Further decompression and cooling, accompanied by crystallisation of clinopyroxene followed by Fe-richer olivine and plagioclase, will lead the basaltic magmas typical of scorias and lavas (Fig. 7).

The most active part of the chamber is its axial sector, where the magma column, consisting of fresh magma of lower density and viscosity, will progressively migrate upward and degas before being erupted (cf., Cigolini et al., 2008).

\textbf{Geophysical constraints on magma chamber volumes: inference from SO$_2$ degassing}

\textbf{SO$_2$ flux and magma degassing rate}
Stromboli volcano is known for its remarkably steady state magma supply rates, as well as for the continuous degassing rates associated with magma rise within the shallow magmatic system (Allard et al., 1994). Recent SO\textsubscript{2} fluxes, representative of time-averaged sulphur emissions during strombolian activity, were estimated to be approximately 150-200 t day\textsuperscript{-1} (Burton et al., 2007; 2009). However, the February–April 2007 eruption was accompanied by an “exceptional” (above normal) degassing rate (Fig. 8) with mean SO\textsubscript{2} emissions of ca. 620 t day\textsuperscript{-1}, i.e. 3-4 times higher than those occurring during the typical strombolian activity (Burton et al. 2009). Although higher than normal, the volume of magma degassed during the 35 days of lava effusion (February-April 2007), estimated from the SO\textsubscript{2} flux (~2 x 10\textsuperscript{6} m\textsuperscript{3} dense rock equivalent, d.r.e., Burton et al., 2009) was drastically lower than the volume of erupted lava (~8 x 10\textsuperscript{6} m\textsuperscript{3} d.r.e.; Calvari et al., 2010, Marsella et al., 2009). Burton et al. (2009) suggested that such an unbalance could be reconciled by considering an unrealistically high vesicularity of the 2007 lavas (>60%) or, better, by the assuming that the most of the erupted magma volume (nearly 6 x 10\textsuperscript{6} m\textsuperscript{3}) was already degassed when it was erupted. Since, lava vesicularity at Stromboli is typically comprised between 16 and 32% (Fornaciai et al., 2009), the effusion of a large volume of degassed magma seems to be the case (due to the drainage of a shallow plumbing system where the magma undergoes degassing). This may explain the deficit in sulphur degassing observed during the February 2007 effusive eruption.

However, the long term record of sulphur output (Burton et al., 2009) reveals that high values of SO\textsubscript{2} flux persisted for several months after the ceasing of the effusive phase (see Fig. 8). In particular, the trend shown in Fig. 8 suggests that the period of anomalous degassing (February to October 2007) was characterised by an gradual decline of the SO\textsubscript{2} flux, which decreased to pre-eruptive levels (i.e 150 t day\textsuperscript{-1}; Burton et al., 2009) only in October 2007, about 200 days after the end of the lava effusion.

The sulphur output data shown in Fig. 8 allow us apply the petrologic method (cf., Palma et al., 2011) in order to estimate the magma degassing rate (\(Q_{\text{degas}}\)) of Stromboli during the period of anomalous degassing (i.e. February to October 2007). In fact, the magma degassing rates (in terms
of the volumetric flux of magma undergoing sulphur degassing; m³ s⁻¹) can be derived by the estimates of SO₂ flux (ϕSO₂) and by the measurements of sulphur concentration in melt inclusions (found within olivine phenocrysts) and in the interstitial glasses of the erupted materials (cf. Kazahaya et al., 1994; Gerlach et al., 1996). To retrieve the magma degassing rates (Qdegas), we may write this relationship as:

\[ Q_{\text{degas}} = 10^2 \frac{M_S \cdot \phi_{SO_2} \cdot 1}{M_{SO_2} \cdot \Delta S \cdot \rho_M} \]  

(8)

where \( M_S \) and \( M_{SO_2} \) (both in g/mol) are the molecular mass of sulphur and sulphur dioxide, respectively. The \( \phi_{SO_2} \) (kg/s) is the sulphur degassing rate and \( \Delta S \) (wt%) represents the total outgassed sulphur, calculated as \( \Delta S = S_m (1 - x_m) - S_{ig} (1 - x_{ig}) \), where \( S_m \) (wt%) and \( S_{ig} \) (wt%) are respectively the sulphur concentration in the melt inclusions and in the interstitial glass, and \( x_m \) and \( x_{ig} \) are, respectively, the crystals during the trapping of the melt inclusions (assumed to be zero) and the crystals content in the matrix, as fraction. Moreover, \( \rho_M \) represents the bulk density of the magma entering in the degassing zone. \( Q_{\text{degas}} \) was then calculated by taking into account a S content of 0.24 wt% and 0.04 wt% in the primitive magma and in the scoria interstitial glasses, respectively (cf. Bertagnini et al., 2003) and considering \( x_{ig} = 0.3 \) (being consistent with Stevenson & Blake, 1998).

It is generally accepted that at Stromboli volcano, the magma degassing rate (\( Q_{\text{degas}} \)) provides constraints for the magma supply rate (\( Q_m \)) or rather for the rate at which volatile-rich aphyric basalt (LP magma) enters in the shallow plumbing system where sulphur degassing takes place (Allard et al., 1994, 2008). Hence, the trend drawn by \( Q_{\text{degas}} \) (Fig. 8) can be regarded as the flux of magma rising from a deep portion of the plumbing system (hereby defined as \( R_{\text{deep}} \)), where the Low Porphyritic (LP) magma resides with little crystallisation and degassing, to a shallowest storage zone (defined as \( R_{\text{shallow}} \)) where gas-melt separation occurs, thus promoting the steady strombolian activity (Allard, 2008).
Thus, the magma supply (degassing) rate shown in Fig. 8 is likely representative of the LP magma flux that entered the degassing cell of Stromboli during and after the 2007 effusive eruption. As shown in Fig. 8 this magma flux see the contribution of two combined processes: (i) the constant supply of LP magma typical of the steady state regime of Stromboli ($Q_{in-steady}$) and (ii) the anomalous (in excess) supply of LP magma entered in the degassing zone during and after an effusive phase ($Q_{in-ex}$). Notably, the whole magma supply rate affected by degassing $Q_{degas}$ (being equal to $Q_{in-steady} + Q_{in-ex}$) describes a clear exponential trend (Fig. 8) that can be described by:

$$Q_{degas} = Q^0_{in-ex} \cdot \exp\left[\frac{-t}{\tau_{ex}}\right] Q_{in-steady}$$  \hspace{1cm} (9)

where $Q^0_{in-ex}$ is the initial excess of magma supply (i.e., related to the effusive phase) and $\tau$ is the calculated decay constant.

The coefficients retrieved from the best-fit regression indicates an initial $Q^0_{in-ex}$ of 0.73 m$^3$ s$^{-1}$, a decay constant ($\tau$) of 82.5 days and a steady magma supply ($Q_{in-steady}$) equal to 0.1 m$^3$ sec$^{-1}$, the latter being in good agreement with the typical magma degassing rate of Stromboli (Allard et al., 2008; Tamburello et al., 2012). It follows that the integration of the curve plotted in Fig. 8 provides the cumulative volume LP magma transferred from $R_{deep}$ to $R_{shallow}$ during the anomalous SO$_2$ flux (approximately 230 days). This volume is thus obtained by summing the volume of magma supplied at constant rate ($V_{in-steady} = Q_{in-steady} \times 230$ days $= \sim 2 \times 10^6$ m$^3$) and the volume of magma in excess, obtained by integrating $Q_{in-ex}$ ($V_{in-ex} = Q^0_{in-ex} \times \tau = \sim 5.2 \times 10^6$ m$^3$). As a whole these calculations brings the total volume of the LP magma that entered the shallow reservoir ($V_{in} = V_{in-ex} + V_{in-steady}$) to $\sim 7.2 \times 10^6$ m$^3$. This value is surprisingly similar to the volume erupted during the 35 days of effusion ($V_{erupt} \sim 8 \times 10^6$ m$^3$ d.r.e. between 27 February and 4 April 2007) and implies that $R_{shallow}$ was almost replenished in about 230 days. In addition it is remarkable to note that these results are in good agreement with the size of the degassing cell of Stromboli inferred by Allard et al. (2008; 12 (±3) x 10$^6$ m$^3$), as well as with the maximum residence time of magma in the
degassing cell (being around 215 days, as assessed from the ratios of short-lived radioactive daughters; Gauthier et al., 2000).

**Constraints on deep reservoir capacity and volume**

The fact that the long term trend of $Q_{in-ex}$ leads to an overall exponential decay is intriguing, since this relationship is typical of pressurised magmatic systems and generally characterise the magma discharge during some basaltic eruption (Wadge, 1981). In the case of Stromboli we explain this behaviour by suggesting that that the LP magma, rising and entering within $R_{shallow}$ was accompanied by a slow decompression of the deeper portion of the plumbing system of Stromboli ($R_{deep}$). This process was slower than the one associated to lava effusion (that, in turn, has been lasting for 32 days; Bonaccorso et al., 2008), and is indicative of the fact that deeper sector of the plumbing system exhibited a slow response to the pressure drop associated with lava effusion.

The exponential decline of $Q$ after a short waxing phase is generally ascribed to the release of elastic strain accumulated either by pressurisation of the rocks surrounding the magma reservoir, or by pressurisation of the magma, or both (Wadge, 1981, Stasiuk et al., 1993; Harris et al., 2000, Aki & Ferrazzini, 2001; Huppert & Woods, 2002). According to these models, if the elastic strain is the sole driving force of magma, at any time $t$, the volumetric flux $Q(t)$ is described by:

$$Q(t) = Q_0 \cdot \exp \left( \frac{t}{\tau} \right)$$  \hspace{1cm} (10)

where $Q_0$ is initial flux and $\tau$ is the time constant of the exponential decay. By analogy with a resistor-capacitor circuit, Aki & Ferrazzini (2001) proposed that the time constant $\tau$ can be simply expressed as:

$$\tau = R_c \cdot C$$  \hspace{1cm} (11)
where \( C \) is the capacity of the reservoir undergoing decompression (in \( \text{m}^3 \text{ Pa}^{-1} \)) and \( R_e \) is the resistance of the “channel” (dike or conduit) to the magmatic flux (in \( \text{Pa s m}^{-3} \)). Therefore, high reservoir’s capacity and/or high channel’s resistance will produce longer time constant and slower waning phases.

By assuming that the elastic strain is accumulated either by pressurisation of both the magma and the rocks surrounding the reservoir, the capacity \( C \) can be obtained, considering wall-rock and magma compressibility (cf., Mastin et al., 2008), as

\[
C = \frac{\rho_M}{\rho_e} \beta_R + \beta_M \frac{V_R}{R_e} \tag{12}
\]

where \( \rho_M, \rho_e \) are the densities of magma and erupted lava, respectively, \( \beta_M \) is the magma compressibility, \( \beta_R \) is the wall-rock compressibility and \( V_R \) is the reservoir volume undergoing strain release. On the other hand the initial effusion rate \( Q_0 \) is related to the channel (conduit) resistance \( R_e \) through the following Aki & Ferrazzini (2001):

\[
Q_0 = \frac{P_0}{R_e} \tag{13}
\]

where \( P_0 \) is the initial overpressure (in Pa). By integrating equation (9) it follows that a generic volume \((V_{out})\) transferred outside the chamber is given by

\[
V_{out} = Q_0 \tau, \tag{14}
\]

or alternatively by

\[
V_{out} = CP_0 \tag{15}
\]

In order to constrain the volume of the deep reservoir undergoing the strain realise, the anomalous (in excess) supply of LP magma entered in the degassing zone \((Q_{in-ex} = Q_{in-ex}^0 \times \exp(-t/\tau)\) can be analysed in the light of the above model. In particular, by determining the initial overpressure \((P_0)\),
magma compressibilities ($\beta_M$ and $\beta_R$) and densities ($\rho_M$ and $\rho_e$), the capacity ($C$) and volume ($V_R$) of the reservoir can be constrained throughout equations (10) to (15).

During the onset of 2007 eruption a near instantaneous pressure drop of about 4-6 MPa was transferred to the upper part of the reservoir that instantaneously decompressed (Calvari et al. 2011). At the same time, a large supply of CO$_2$-rich and SO$_2$-rich gas bubbles from the deep low porphyritic (LP) sector of the reservoir (Burton et al., 2009; Aiuppa et al., 2010a, b), has been invoked, as a consequence of depressurisation associated with lava drainage since the onset of the eruption (27 February 2007; Bonaccorso et al., 2008). Therefore, it is not unreasonable to assume that an initial overpressure $\geq$ 5 MPa affected the whole plumbing system of Stromboli during the beginning of the eruption. By setting $P_0 = 5 - 10$ MPa and by assuming that the magma volume entering in the degassing zone, was substantially the one removed outside the deeper reservoir ($V_{in-ex} \sim V_{out}$, recalling that is equal to $5.2 \times 10^6$ m$^3$), we estimated a capacity $C$ roughly comprised between 0.52 and 1.05 m$^3$ Pa$^{-1}$ (equation 15).

We than calculated the variation of compressibility of primitive melts by taking into account the variations in fluid contents during step-by-step decompression associated with bubble growth. Melt densities ($\rho_M$) were calculated according to Lange & Carmichael (1990), whereas the gas-mixture densities ($\rho_g$) were obtained by applying the Modified Redlich-Kwong (MRK) equation of Holloway (1977). The quantities of water and CO$_2$ (in wt%) released during decompression were obtained by applying the computer code VOLATILECALC of Newman & Lowenstern (2002). Thus, the magma bulk density ($\rho_M$) and compressibility ($\beta_M$) were calculated according to Huppert and Woods (2002, equations 5 and 6 of their work) that take into account crystallinity and the contribution of wall-rock compressibility ($\beta_R = 3 \times 10^{-11}$ Pa$^{-1}$). The latter parameter was retrieved (assuming a Poisson ratio of 0.25) from the rigidity calculated by D’Auria et al. (2006) for earthquakes located in the surrounding of the top of the magma reservoir (at 4.5-6 km depth). The selected melt for calculating the appropriate magma compressibility ($\beta_M$) is the average of the
analyses of melt inclusions reported in Table 5. Thus, given the magma pressure-dependent compressibility model shown in Fig. 9, we may consider that at 200 MPa (i.e., the main portion of the reservoir) the magma compressibility, $\beta_M$, reaches $4 \times 10^9$ Pa$^{-1}$, while the wall-rock compressibility, $\beta_R$, is almost one order of magnitude less. In Table A5 we report the isothermal decompression path together with the results of our calculations. Similarly, we may assume that during its transfer from the deep to the upper part of the chamber, the magma changed its density from $\rho_M = 2690$ kg m$^{-3}$ (unvesiculated magma) to $\rho_e = 2480$ kg m$^{-3}$ (erupted vesiculated magma). By using equation (12), for the above calculated reservoir capacity ($C = 0.52$ and 1.05 m$^3$ Pa$^{-1}$), we estimated the volume of the reservoir undergoing the elastic strain release ($V_R$): being comprised between 1 and 2 km$^3$, in good agreement with the lower volume estimates of Cigolini et al. (2008) for the Stromboli magma chamber.

Fig. 9

Discussion and conclusions

In this contribution we have revisited the data on the last two major eruptions at Stromboli volcano and concentrated our analysis on the 2007 eruption. Our main goal was to offer a comprehensive view of the problems connected with the interpretation of the onset and evolution of these events and how their analysis may contribute to better understand the inner dynamics of this complex volcanic system. We therefore focussed our research on how volatiles contents affect solid-melt equilibria and how they behave during magma storage and decompression. These processes have a direct link on the type of volcanic activity that is taking place at Stromboli. However, our effort was to reconcile the large amount of data collected on this volcano with a plausible picture that explains how this volcano works. The first part of this review paper was concentrated in revisiting mineral phase stabilities in Stromboli basalt and how these, together with volatiles, may affect magma
compressibility during progressive decompression. In this perspective, one of the open issue we attempted to unravel is the effective shape and extension of Stromboli magma chamber. In general, the geometry and dynamics of magma chambers are still debated issues (e.g., Bonafede et al., 1986; Dragoni & Magnanesi, 1989; Jellinek & De Paolo, 2003). Unfortunately, these authors essentially model magma chamber as spherical objects. In a recent contribution Zellmer & Annen (2008) discussed a full variety of plumbing systems, and attempted to correlate their geometry with magma transfer rates and magmatic differentiation processes. For instance, Stromboli is classified within the field of relatively small reservoirs found within extensional (or transtensional) settings, where the magma is stored for $10^3$ years at the most. However, in a recent paper Mastin et al. (2008) suggested a possible shape for Mount Saint Helen magma chamber that may be regarded as a prolate ellipsoid. Moreover, Gudmundsson (2006) discussed the possible shapes of magma chambers in relation to the structural setting of the region and indicates a prolate ellipsoid as a recurrent shape. In our specific case we are dealing with a rather unique case where seismic data indicate that the major structure underneath Stromboli is essentially a normal fault (the Stromboli-Panarea alignment) with a minor right-lateral strike-slip component SW of Panarea (e.g., Caccamo et al., 1996). According to Acocella et al. (2009) in the Stromboli area stress distribution approach pure extensional regimes, being consistent with the earlier works of Tibaldi (2001; 2004) and Tibaldi et al. (2003). Following Shaw (1980) and assuming that stress regimes are proportional to the geometry of the reservoir (whose vertical extension can inferred by fine thermobarometry), we may infer stress distribution and give more reliable estimates than those proposed earlier by Cigolini et al. (2008) for the Stromboli magma chamber volume. Another open issue is how the system pressurizes and what factors are involved in the development of this process. Allard et al. (2008) have shown that the eruption rate during mild and persistent Strombolian activity is at most 0.02 m$^3$/sec, whereas input flow rates at depth may be as high as 0.3-0.6 m$^3$/sec. This mechanism will progressively pressurize the “open” plumbing system until a critical threshold is reached and a major eruptive cycle begins. In this context strain rates at the chamber walls seems to be a critical
factor that need to be investigated in details and could be one of the goals for future research advancements.

In conclusion, current results can be summarised as follows:

i. The role of volatiles has been shown to be critical for identifying the equilibrium conditions of Stromboli magma during magma storage and decompression.

ii. Thermobarometric estimates indicate that Stromboli primitive hydrous basaltic melts (preserved as melt inclusions in olivine with 2-3.7 wt% H$_2$O) are in equilibrium with forsteritic olivine and diopside at pressures of 200-340 MPa pressure and temperatures of 1150-1200°C for $X_{CO_2}^m$ comprised between 0.6 and 0.76 (which is quite similar to the magmatic gas composition sampled at the crater rim). The higher pressure regimes are representative of the base of the chamber, where the ferromagnesian phases may crystallise and cumulate. A particular case is given by Ca-rich or ultracalcic melts that are regarded as a result of decompression along a steep adiabatic and/or isothermal curve. During this process the magma will crosscut the stability field of diopside and enter the liquidus field. The earlier crystallized diopside is destabilized and will react with the melt leading to the formation of ultracalcic melts. Pichavant et al. (2009) earlier discussed this possibility and we hereby explain how this process is occurring and quantify the P-T regimes associated with this dynamics.

iii. Ejected golden pumices (with 2-3 wt% H2O), are in equilibrium with Ca-pyroxene, forsteritic olivine and anorthitic plagioclase at 150–220 MPa and temperatures approaching 1120-1150°C. These materials likely represent the middle and main part of the chamber.

iv. Evolved melt inclusions in Fe-richer olivine (ca. Fo$_{70}$) of the scorias show average equilibration pressures of 78 (± 20) MPa, and temperatures 1138 (± 14)°C, being
indicative of crystallisation within the conduit or its root-zone that reaches the upper part
of the chamber.

v. The lower part of the chamber is located at 11-13 km below the summit whereas the upper
part of the chamber reaches 4.5-5 km below the summit itself;

vi. the magma chamber is substantially zoned and the undegassed magma is stored below the
latter depth (and may be ejected as pumice during paroxysmal explosions and, more rarely, major explosions);

vii. during its storage, within the upper part of the chamber and within the dike feeding the
summit craters, the magma undergoes progressive degassing, cooling and crystallisation.
These processes are involved in the genesis of lavas and scorias (that represent the
degassed magma reaching the surface).

viii. The Stromboli plumbing system consists of an ellipsoidal magma chamber of 1-2 km$^3$ in
volume, likely a prolate ellipsoid whose upper part is connected with the feeder dike.

ix. during major eruptions associated with lava effusions the dike feeding the summit vents is
substantially rejuvenated and the upper part of the chamber is progressively replenished by
the undegassed magma. During the 2007 eruption, the original magmastic equilibrium
was restored in about 230 days from the beginning of the effusive activity (as inferred by
our analysis on SO$_2$-derived magma fluxes).

Acknowledgements

The research was funded by the University of Torino - Fondazione Compagnia di San Paolo.
Additional funds were provided by MIUR and made available through the Cooperative Project
among the Departments of Earth Sciences of the University of Torino and the University of Firenze
(in the framework of the Devnet Project, funded by the Dipartimento della Protezione Civile, DPC).
We are indebted to M. Ripepe and M. Pichavant for the stimulating discussions. We also thank
Sébastien Jego and an anonymous reviewer for revising an earlier draft of the paper. Special
acknowledgements to INGV-Catania for making the SO$_2$ data available on the web. Additional funds for the improving our computing hardware were provided by Fondazione Cassa di Risparmio di Torino.

APPENDIX

We hereby report Table A1, A2 and A3 that summarizes the results of thermodynamic calculations regarding reactions (1) (2) and (3) that enabled us to construct Fig. 6.

Table A1, Table A2, Table A3

In Table A4 we summarize the list of symbols used in the equations discussed in the text.

Table A4

In Table A5 we report step-by-step calculations for the isothermal decompression of a primitive Stromboli basalt (cf., Fig. 9).

Table A5

References


Modern methods of igneous petrology: understanding magmatic processes. Reviews in Mineralogy and Geochemistry, 24, 25-59.


*Geochimica et Cosmochimica Acta, 60*(21), 4151-4160.


Sack, R.O. & Ghiorso, M.S. 1989. Importance of considerations of mixing properties in establishing an internally consistent thermodynamic database: thermochemistry of minerals in the system Mg$_2$SiO$_4$-Fe$_2$SiO$_4$-SiO$_2$. Contributions to Mineralogy and Petrology, 102, 41-68.


Figure Captions

**Fig. 1.** Sketch of the Aeolian Islands with the major tectonic units of the region (modified after De Astis *et al*., 2003; Ventura *et al*., 2013). (a) Stromboli is located on the Stromboli-Panarea alignment, a normal fault associated with pure extensional regimes (Acocella *et al*., 2009). Insets show the crust-mantle structure along a WNW-ESE cross section (cf. Pontevivo & Panza, 2006; Corazzato *et al*., 2008), and the summary of earthquake locations and magnitudes below the Aeolian arc. The earthquakes reported are included within a sector with 37°-40° latitude, and 12°-15° longitude, respectively (see text for details). LVZ: low velocity zone; (b) simplified geological map of Stromboli with major collapses and faults (modified after Hornig-Kjarsgaard *et al*., 1993; Tibaldi *et al*., 2009).

**Fig. 2.** Selected images of Stromboli volcano during and following the 2007 major eruption; (a) the 2007 lava field emplaced onto earlier lavas and debris of Sciara del Fuoco. Picture taken on August 3, 2007 during a helicopter survey; (b) view of the summit crater area where the typical strombolian activity was resumed on July 2, 2007. Summit vents are located on the N40°E graben-like fracture zone (red dashed line). Picture taken on August 3, 2007 during a helicopter survey.

**Fig. 3.** Microphotographs of the petrographic and textural features of Stromboli lavas, scorias and pumices erupted in 2002-2003; (a) scoria erupted on February 16, 2007 with euhedral phenocrysts of plagioclase, and clinopyroxene on a glassy matrix. Vesicles are also present (white). Scorias are
interpreted as “conduit assemblages”. Plane polarized light; b) microphotograph of lava erupted in March, 2007 during the last effusive event. Lava is phenocrysts-rich (around 40%) mainly represented by clinopyroxene and plagioclase, with the typical oscillatory zoning. Vesiculation is relatively high. Plane polarized light; c) Photomicrograph of a quenched “golden pumice” erupted during the paroxysmal explosion of March 15, 2007. Vesicularity is very high (~70%) with bubbles of variable size and low degree of cristallinity (<10%) with microliths of plagioclase, clinopyroxene and olivine (not visible at this scale). Plane polarized light.

**Fig. 4.** Low silica-moderate K₂O sector of the diagram of Peccerillo and Taylor (1976) with the plotting of the available data on the materials erupted at Stromboli; a) lavas and scorias, including matrix glasses. Grey fields refer to historical materials erupted from Stromboli volcano since 1906 (these data were summarized by Francalanci *et al.*, 2004; Pompilio *et al.*, 2012). The dark grey field show the glass composition of the 2002-2003 and 2007 erupted materials (data reported by Landi *et al.*, 2006; 2009); b) pumices erupted during paroxysmal and major explosions; melt inclusions are those reported by Métrich *et al.* (2001; 2005; 2010) Bertagnini *et al.* (2003). The grey field shows the bulk composition of the hystorical pumices reported by Pompilio *et al.* (2012).

**Fig. 5.** Pearce element ratio plots for Stromboli materials (including melt inclusions in olivines of the pumices); a) 2Ca+3Na/K versus Si/K diagram indicates fractionation of clinopyroxene and plagioclase; b) the diagram 2Ca+3Na/K versus Al/K indicates a lower proportion of plagioclase removal relative to pyroxene (0.40 to 0.60, respectively); c) Pearce element 2Na/K versus Al/K showing that fractionation of a bytownitic plagioclase (An₈₂-₇₆) has been effective in primitive melts (the regression line is y=0.276x+0.5312 with a correlation coefficient r=0.85); in more evolved melts the fractionating plagioclase is a labradorite (An₆₇-₆₂) (in this case the regression line is y=0.3576x+0.313 with a correlation coefficient r=0.74). Reference curves for fractionation of anorthite (An₁₀₀) and albite (An₀) are also reported for comparison.
Fig. 6. Thermobarometry of melt inclusions in olivine in primitive Stromboli basalts and pumices erupted at Stromboli. (a) P-T estimates for the equilibrium crystallization of primitive Stromboli basalts (preserved in melt inclusions). The graph summarizes the P-T grid obtained by solving thermodynamically reactions (1) and (2) indicated by the large numbers in parentheses. Smaller numbers are the water contents within the melt (wt% H₂O). Best solutions are outlined by rectangles (see text and Table A1). (b) P-T estimates for ultracalcic melt inclusions following the same procedure indicated above. Note that these melts equilibrate at moderately higher temperatures and slightly lower pressures than these reported above (Fig. 6b, Table A2). (c) P-T estimates for the crystallisation of the mineral phases of the pumices. In this case best estimates are obtained by solving thermodynamically reaction (2) and (3). See text and Table A3.

Fig. 7. Schematic sketch of phase stabilities for Stromboli primitive basalt and suggested P-T paths during decompression. Phase stabilities are consistent with previously discussed equilibria and the experimental data of Di Carlo et al. (2006), Pichavant et al., 2009. The stability field of the low pressure assemblage has been reconstructed following Cigolini et al. (2008) and the experimental work of Conte et al. (2006). Average primitive melt inclusions and ultracalcic melts are represented by white and grey squares, respectively (with their relative standard deviations, see Tables 5 and 6, see text). The average of evolved melt inclusions found in Fo₇₀ of the scorias are represented by a white circle (see Table 7 and 8). Line (a) represents the final decompression of the evolved Stromboli basalt erupted as scoria or lava; line (b) is the possible final P-T path associated with the ejection of pumices during paroxysmal explosions.

Fig. 8. Sulphur degassing rate (SO₂ flux - left axis) recorded between 27 February 2007 (the onset of the effusive activity) and 15 October 2007. This period was characterized by anomalous degassing rates, that exceeded average values recorded during the typical strombolian activity
(~100 ton/day). The SO$_2$ flux data are from INGV, available at


On the right axis, sulphur emissions were converted into volumetric flux of magma degassing ($Q_{\text{degas}}$), by using the petrologic method (see text for details). The trend obtained was fitted by using an “exponential + offset” equation (dashed line), where the offset component represents to the magma supply rate during the typical strombolian activity ($Q_{\text{in,steady}}$ – cf. bottom of the graph) and the exponential component represents to the “excess” of magma supply rate recorded during and after the 2007 effusive activity ($Q_{\text{in,ex}}$ – stippled field). The exponential trend retrieved for $Q_{\text{in,ex}}$ is ascribed to decompression from deep storage zone.

**Fig. 9.** Representative graphs that synthesize the isothermal decompression of a primitive Stromboli basalt (the selected melt is the average of melt inclusions reported in Table 5; see Appendix 5 for calculations). (a) Solubility of water and carbon dioxide as a function of pressure (for a temperature of 1170 °C) and (b) cumulative gas volume fraction during decompression calculated according to VOLATILECALC (Newman & Lowerstern 2002). (c) Variation of compressibility for the above primitive Stromboli basalt during decompression due to bubble growth and crystallization (see text for details).
**Fig. 1**

![Diagram](image1)

**Fig. 2**

![Diagram](image2)
Fig. 3

Fig. 4
Fig. 5

(a) 

(b) 

(c) 

$\text{Si/K} - (2\text{Ca}+3\text{Na})/K$

$\text{Al/K} - (2\text{Ca}+\text{Na})/K$

$\text{Al/K} - 2\text{Na}/K$

$\text{An}_{67-62}$

$\text{An}_{82-76}$

$\text{pl} + \text{cpx}$

$\text{pl}$

$\text{cpx}$

$\text{Ca-Rich Melt Inclusions}$

$X_{\text{cpx}} \sim 0.6$

$X_{\text{cpx}} \sim 0.4$
Fig. 6

Melt Inclusions

Ca-Rich MI

Pumices

Temperature (°C)
Pressure (MPa)
Fig. 7

**Phase stability at \( \approx 3 \text{ wt\% } H_2O \)**

- **Lavas & Scorias**
- **Melt Inclusions**
- **Ca-Rich MI**

- **Di**
- **Fo\(_{88-84}\) + Di**
- **An\(_{84-76}\) + Di**
- **An\(_{70-64}\) + Aug**
- **F0\(_{85-80}\)**
- **(a)**
- **(b)**

- *0.5 wt\% H\(_2\)O

Pressure (MPa) vs. Temperature (°C)
Fig. 8

\[ Q_{\text{degas}} = Q_{\text{in-ex}}^0 \exp \left(-t/\tau\right) + Q_{\text{in-steady}} \]

- \( Q_{\text{in-ex}}^0 = 0.73 \text{ m}^3\text{s}^{-1} \)
- \( \tau = 82.5 \text{ days} \)
- \( Q_{\text{in-steady}} = 0.1 \text{ m}^3\text{s}^{-1} \)
- \( r = 0.809 \)

SO₂ flux (tonn day⁻¹) vs. days since 27 Feb 2007.
Fig. 9

(a) H$_2$O dissolved in melt
(b) CO$_2$ dissolved in melt
(c) Magma Compressibility (Pa$^{-1}$)

Pressures: 0 to 250 MPa
Temperatures: T=1170°C

200 MPa line indicated on each graph.
Table A1. Summary of selected thermodynamic solutions of solid-liquid equilibria for melt inclusions in olivines of the pumices erupted during paroxysmal events. See text and Fig. 6 for details.

<table>
<thead>
<tr>
<th>Reaction (1)</th>
<th>Fo (sol) + SiO₂ = CEn</th>
<th>Hydrous melt with H₂O = 3 wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>a₉a</td>
<td>a₉CEn</td>
</tr>
<tr>
<td>1000</td>
<td>0.7785</td>
<td>0.5563</td>
</tr>
<tr>
<td>1100</td>
<td>0.7730</td>
<td>0.4857</td>
</tr>
<tr>
<td>1125</td>
<td>0.7717</td>
<td>0.4710</td>
</tr>
<tr>
<td>1150</td>
<td>0.7705</td>
<td>0.4572</td>
</tr>
<tr>
<td>1175</td>
<td>0.7693</td>
<td>0.4442</td>
</tr>
<tr>
<td>1200</td>
<td>0.7682</td>
<td>0.4320</td>
</tr>
<tr>
<td>1250</td>
<td>0.7661</td>
<td>0.4098</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Reaction (2)</th>
<th>Di = 1/2SiO₂(liq) + 1/2Ol(liq) + Wo(liq)</th>
<th>Hydrous melt with H₂O = 3 wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (MPa)</td>
<td>a₉Di</td>
<td>a₉Wo(liq)</td>
</tr>
<tr>
<td>10</td>
<td>0.8461</td>
<td>0.1082</td>
</tr>
<tr>
<td>100</td>
<td>0.8460</td>
<td>0.1086</td>
</tr>
<tr>
<td>200</td>
<td>0.8458</td>
<td>0.1090</td>
</tr>
<tr>
<td>300</td>
<td>0.8457</td>
<td>0.1094</td>
</tr>
<tr>
<td>400</td>
<td>0.8455</td>
<td>0.1093</td>
</tr>
<tr>
<td>600</td>
<td>0.8453</td>
<td>0.1104</td>
</tr>
<tr>
<td>800</td>
<td>0.8451</td>
<td>0.1111</td>
</tr>
</tbody>
</table>


The melt composition is the average melt inclusions in Table 1, clinine and clinopyroxene are analyses n. 1 and n. 14 in Table 2. Calculations are referred to an hydrous melt with 3 wt% H₂O.
Table A2. Summary of selected thermodynamic solutions of solid-liquid equilibria for Ultracalcic melt inclusions in olivines of the pumices erupted during paroxysmal events. See text and Fig. 6 for details.

<table>
<thead>
<tr>
<th>Reaction (1)</th>
<th>Fo (sol) + SiO₂ = CEn</th>
<th>Hydrous melt with H₂O = 3 wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>a_Fo</td>
<td>a_{CEn}</td>
</tr>
<tr>
<td>1000</td>
<td>0.8184</td>
<td>0.5336</td>
</tr>
<tr>
<td>1100</td>
<td>0.8152</td>
<td>0.4654</td>
</tr>
<tr>
<td>1125</td>
<td>0.8144</td>
<td>0.4512</td>
</tr>
<tr>
<td>1150</td>
<td>0.8137</td>
<td>0.4378</td>
</tr>
<tr>
<td>1175</td>
<td>0.8130</td>
<td>0.4253</td>
</tr>
<tr>
<td>1200</td>
<td>0.8123</td>
<td>0.4136</td>
</tr>
<tr>
<td>1250</td>
<td>0.8111</td>
<td>0.3922</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Reaction (2)</th>
<th>Di = 1/2SiO₂(liq) + 1/2Ol(liq) + Wo(liq)</th>
<th>Hydrous melt with H₂O = 3 wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (MPa)</td>
<td>a_Di</td>
<td>a_{Wo(liq)}</td>
</tr>
<tr>
<td>10</td>
<td>0.8485</td>
<td>0.1314</td>
</tr>
<tr>
<td>100</td>
<td>0.8454</td>
<td>0.1318</td>
</tr>
<tr>
<td>200</td>
<td>0.8482</td>
<td>0.1323</td>
</tr>
<tr>
<td>300</td>
<td>0.8481</td>
<td>0.1327</td>
</tr>
<tr>
<td>400</td>
<td>0.8480</td>
<td>0.1332</td>
</tr>
<tr>
<td>600</td>
<td>0.8478</td>
<td>0.1339</td>
</tr>
<tr>
<td>800</td>
<td>0.8476</td>
<td>0.1346</td>
</tr>
</tbody>
</table>


The melt composition is the average Ca-Rich Melt Inclusions in Table 1, olivine and clinopyroxene analyses n. 4 and n. 13 in Table 2. Calculations are referred to an hydrous melt with 3 wt% H₂O.
Table A3. Summary of selected thermodynamic solutions of solid-liquid equilibria for bulk rock pumices erupted during paroxysmal events. See text and Fig. 6 for details.

**Reaction (2)** Di = 1/2SiO₂(liq) + 1/2O(liq) + WO(liq)  
<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>a_Di</th>
<th>a_Wo(liq)</th>
<th>a_Fe(liq)</th>
<th>ΔG°₁,R (kJ)</th>
<th>log a_H₂O</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.8485</td>
<td>0.1084</td>
<td>0.0477</td>
<td>46.8573</td>
<td>-0.4987</td>
<td>1090</td>
</tr>
<tr>
<td>100</td>
<td>0.8484</td>
<td>0.1088</td>
<td>0.0479</td>
<td>46.2083</td>
<td>-0.4970</td>
<td>1106</td>
</tr>
<tr>
<td>200</td>
<td>0.8482</td>
<td>0.1092</td>
<td>0.0480</td>
<td>45.4956</td>
<td>-0.4972</td>
<td>1124</td>
</tr>
<tr>
<td>300</td>
<td>0.8481</td>
<td>0.1096</td>
<td>0.0481</td>
<td>44.7826</td>
<td>-0.4975</td>
<td>1141</td>
</tr>
<tr>
<td>400</td>
<td>0.8480</td>
<td>0.1099</td>
<td>0.0483</td>
<td>44.1000</td>
<td>-0.4977</td>
<td>1157</td>
</tr>
<tr>
<td>600</td>
<td>0.8478</td>
<td>0.1106</td>
<td>0.0485</td>
<td>42.7481</td>
<td>-0.4981</td>
<td>1187</td>
</tr>
<tr>
<td>800</td>
<td>0.8476</td>
<td>0.1112</td>
<td>0.0485</td>
<td>41.4424</td>
<td>-0.4985</td>
<td>1215</td>
</tr>
</tbody>
</table>


**Reaction (3)** An+2Fe₂O+SiO₂=2CEn+CaTs  
<table>
<thead>
<tr>
<th>T (°C)</th>
<th>a_An</th>
<th>a_Fe</th>
<th>a_CEn</th>
<th>a_CaTs</th>
<th>ΔG°₁,R (kJ)</th>
<th>log a_H₂O</th>
<th>P (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.7659</td>
<td>0.7785</td>
<td>0.5553</td>
<td>0.0465</td>
<td>31.0489</td>
<td>-0.4937</td>
<td>256</td>
</tr>
<tr>
<td>1100</td>
<td>0.7656</td>
<td>0.7730</td>
<td>0.4827</td>
<td>0.0458</td>
<td>34.3173</td>
<td>-0.4956</td>
<td>194</td>
</tr>
<tr>
<td>1125</td>
<td>0.7638</td>
<td>0.7717</td>
<td>0.4710</td>
<td>0.0457</td>
<td>35.1677</td>
<td>-0.4960</td>
<td>179</td>
</tr>
<tr>
<td>1150</td>
<td>0.7620</td>
<td>0.7705</td>
<td>0.4572</td>
<td>0.0455</td>
<td>36.0314</td>
<td>-0.4964</td>
<td>165</td>
</tr>
<tr>
<td>1175</td>
<td>0.7602</td>
<td>0.7693</td>
<td>0.4442</td>
<td>0.0454</td>
<td>36.9188</td>
<td>-0.4968</td>
<td>152</td>
</tr>
<tr>
<td>1200</td>
<td>0.7586</td>
<td>0.7682</td>
<td>0.4320</td>
<td>0.0453</td>
<td>37.7992</td>
<td>-0.4971</td>
<td>139</td>
</tr>
<tr>
<td>1250</td>
<td>0.7554</td>
<td>0.7661</td>
<td>0.4098</td>
<td>0.0450</td>
<td>39.6207</td>
<td>-0.4976</td>
<td>116</td>
</tr>
</tbody>
</table>


The melt composition is the average Recent Pumices reported in Table 1; olivine and clinopyroxene: analyses n. 1 and n. 14 in Table 2; plagioclase: analyses n. 20 in Table 2. Calculations refer to an hydrous melt (3 wt% H₂O).
Table A4. List of symbols for the physical parameters used in thermodynamic calculations and geophysical modeling. See text for details.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ(G_{\text{f}}^\circ)</td>
<td>kJ mol(^{-1})</td>
<td>Gibbs free energy at the (P) and (T) of interest</td>
</tr>
<tr>
<td>Δ(G_{\text{f}}^{1\text{bar}})</td>
<td>kJ mol(^{-1})</td>
<td>Gibbs free energy at 1 bar and (T) of interest</td>
</tr>
<tr>
<td>(R)</td>
<td>J mol(^{-1}) K(^{-1})</td>
<td>Gas constant</td>
</tr>
<tr>
<td>(K_i)</td>
<td>adim.</td>
<td>Equilibrium constant for a generic reaction (i)</td>
</tr>
<tr>
<td>Δ(V)</td>
<td>J bar(^{-1})</td>
<td>Difference of the molar volumes of the products minus those of the reactants opportune expanded and compressed at (P) and (T) of interest</td>
</tr>
<tr>
<td>(a_i)</td>
<td>adim.</td>
<td>activity of a generic phase (i) (calculated according to solution models, see text)</td>
</tr>
<tr>
<td>(\phi)</td>
<td></td>
<td>oxygen fugacity</td>
</tr>
<tr>
<td>(X_{\text{H}_2\text{O}}^m)</td>
<td>adim.</td>
<td>mole fraction of water in the melt</td>
</tr>
<tr>
<td>(X_{\text{CO}_2}^m)</td>
<td>adim.</td>
<td>mole fraction of CO(_2) in the melt</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Q_{\text{degas}})</td>
<td>m(^3) s(^{-1})</td>
<td>total magma degassing rate</td>
</tr>
<tr>
<td>(M_s)</td>
<td>g mol(^{-1})</td>
<td>sulphur molecular mass</td>
</tr>
<tr>
<td>(M_{\text{SO}_3})</td>
<td>g mol(^{-1})</td>
<td>sulphur dioxide molecular mass</td>
</tr>
<tr>
<td>(\phi)</td>
<td>kg s(^{-1})</td>
<td>sulphur degassing rate</td>
</tr>
<tr>
<td>(\rho_M)</td>
<td>kg m(^{-3})</td>
<td>density of the magma</td>
</tr>
<tr>
<td>(Q_{\text{in-steady}})</td>
<td>m(^3) s(^{-1})</td>
<td>magma input rate during steady state</td>
</tr>
<tr>
<td>(Q_{\text{in-ex}})</td>
<td>m(^3) s(^{-1})</td>
<td>magma input rate in excess</td>
</tr>
<tr>
<td>(V_{\text{in-steady}})</td>
<td>m(^3) x10(^{6})</td>
<td>magma volume entering in the degassing zone during steady state</td>
</tr>
<tr>
<td>(V_{\text{in-ex}})</td>
<td>m(^3) x10(^{6})</td>
<td>magma volume in excess entering in the degassing zone</td>
</tr>
<tr>
<td>(V_{\text{out}})</td>
<td>m(^3) x10(^{6})</td>
<td>generic volume transferred outside the chamber</td>
</tr>
<tr>
<td>(V_R)</td>
<td>m(^3) x10(^{6})</td>
<td>total volume of the reservoir</td>
</tr>
<tr>
<td>(t)</td>
<td>days</td>
<td>time since the beginning of eruption</td>
</tr>
<tr>
<td>(\tau)</td>
<td>days</td>
<td>time constant of the exponential decay</td>
</tr>
<tr>
<td>(C)</td>
<td>m(^3) Pa(^{-1})</td>
<td>capacity of the reservoir</td>
</tr>
<tr>
<td>(R_e)</td>
<td>Pa s m(^{-3}) x10(^{6})</td>
<td>resistance of the conduit</td>
</tr>
<tr>
<td>(\rho_e)</td>
<td>kg m(^{-3})</td>
<td>density of the erupted magma</td>
</tr>
<tr>
<td>(P_0)</td>
<td>Pa x10(^6)</td>
<td>initial overpressure</td>
</tr>
<tr>
<td>(\beta_R)</td>
<td>Pa(^{-1})</td>
<td>wallrock compressibility</td>
</tr>
<tr>
<td>(\beta_M)</td>
<td>Pa(^{-1})</td>
<td>magma compressibility</td>
</tr>
<tr>
<td>(\rho_l)</td>
<td>kg m(^{-3})</td>
<td>density of the liquidus</td>
</tr>
<tr>
<td>(\rho_g)</td>
<td>kg m(^{-3})</td>
<td>density of the gas mixture</td>
</tr>
</tbody>
</table>

\(^*\) SO\(_2\) values are from the Istituto Nazionale di Geofisica e Vulcanologia, INGV

http://www.pa.ingv.it/comunicati/Stromboli/comunicati_stromboli.php
### Table A5. Summary of the main physical parameters calculated for the isothermal decompression path of the Stromboli primitive melt

<table>
<thead>
<tr>
<th>Reference Melt Starting Conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>47.6</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.86</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>15.3</td>
</tr>
<tr>
<td>FeO$_2$</td>
<td>7.67</td>
</tr>
<tr>
<td>MnO</td>
<td>0.14</td>
</tr>
<tr>
<td>MgO</td>
<td>6.37</td>
</tr>
<tr>
<td>CaO</td>
<td>12.9</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>2.20</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.58</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.49</td>
</tr>
<tr>
<td>S</td>
<td>0.16</td>
</tr>
<tr>
<td>Cl</td>
<td>0.15</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>2.79</td>
</tr>
<tr>
<td>CO$_2$ (ppm)</td>
<td>1320</td>
</tr>
</tbody>
</table>

**Results**

<table>
<thead>
<tr>
<th>P* (MPa)</th>
<th>H$_2$O* (wt%)</th>
<th>CO$_2$* (ppm)</th>
<th>H$_2$O exs* (wt%)</th>
<th>CO$_2$ exs* (ppm)</th>
<th>H$_{gas}$ mixture (kg/m$^3$)</th>
<th>H$_{liquid}$ (kg/m$^3$)</th>
<th>H$_{melt}$ (kg/m$^3$)</th>
<th>Crystals Fraction</th>
<th>H$_M$ (Pa$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>233</td>
<td>2.69</td>
<td>1215</td>
<td>0.097</td>
<td>104</td>
<td>469</td>
<td>2691</td>
<td>0.010</td>
<td>2677</td>
<td>0</td>
</tr>
<tr>
<td>215</td>
<td>2.59</td>
<td>1111</td>
<td>0.199</td>
<td>208</td>
<td>444</td>
<td>2688</td>
<td>0.022</td>
<td>2659</td>
<td>0.1</td>
</tr>
<tr>
<td>206</td>
<td>2.54</td>
<td>1059</td>
<td>0.252</td>
<td>260</td>
<td>431</td>
<td>2687</td>
<td>0.029</td>
<td>2696</td>
<td>0.1</td>
</tr>
<tr>
<td>197</td>
<td>2.48</td>
<td>1007</td>
<td>0.308</td>
<td>312</td>
<td>417</td>
<td>2686</td>
<td>0.036</td>
<td>2684</td>
<td>0.1</td>
</tr>
<tr>
<td>178</td>
<td>2.37</td>
<td>903</td>
<td>0.423</td>
<td>416</td>
<td>388</td>
<td>2683</td>
<td>0.052</td>
<td>2658</td>
<td>0.1</td>
</tr>
<tr>
<td>159</td>
<td>2.24</td>
<td>799</td>
<td>0.546</td>
<td>520</td>
<td>357</td>
<td>2680</td>
<td>0.072</td>
<td>2634</td>
<td>0.2</td>
</tr>
<tr>
<td>140</td>
<td>2.11</td>
<td>695</td>
<td>0.679</td>
<td>624</td>
<td>322</td>
<td>2677</td>
<td>0.096</td>
<td>2592</td>
<td>0.2</td>
</tr>
<tr>
<td>120</td>
<td>1.97</td>
<td>591</td>
<td>0.824</td>
<td>728</td>
<td>285</td>
<td>2675</td>
<td>0.128</td>
<td>2565</td>
<td>0.3</td>
</tr>
<tr>
<td>109</td>
<td>1.89</td>
<td>539</td>
<td>0.903</td>
<td>780</td>
<td>265</td>
<td>2673</td>
<td>0.147</td>
<td>2530</td>
<td>0.3</td>
</tr>
<tr>
<td>100</td>
<td>1.80</td>
<td>487</td>
<td>0.986</td>
<td>832</td>
<td>245</td>
<td>2672</td>
<td>0.170</td>
<td>2489</td>
<td>0.3</td>
</tr>
<tr>
<td>79</td>
<td>1.62</td>
<td>383</td>
<td>1.169</td>
<td>936</td>
<td>201</td>
<td>2669</td>
<td>0.229</td>
<td>2377</td>
<td>0.3</td>
</tr>
<tr>
<td>58</td>
<td>1.41</td>
<td>279</td>
<td>1.383</td>
<td>1040</td>
<td>152</td>
<td>2665</td>
<td>0.317</td>
<td>2219</td>
<td>0.4</td>
</tr>
<tr>
<td>37</td>
<td>1.14</td>
<td>175</td>
<td>1.653</td>
<td>1144</td>
<td>100</td>
<td>2662</td>
<td>0.461</td>
<td>1888</td>
<td>0.4</td>
</tr>
<tr>
<td>15</td>
<td>0.76</td>
<td>71</td>
<td>2.034</td>
<td>1248</td>
<td>42</td>
<td>2659</td>
<td>0.716</td>
<td>1159</td>
<td>0.4</td>
</tr>
</tbody>
</table>

* - VOLATILECALC (Newman & Lowenstern, 2002); ** - Holloway (1977); † - Lange & Carmichael (1990); ‡ - Huppert & Woods (2002)

exs: exsolved gas concentration