Hydrothermal alteration of surficial rocks at Solfatara (Campi Flegrei): Petrophysical properties and implications for phreatic eruption processes

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A B S T R A C T

Solfatara crater is located within the Campi Flegrei caldera to the west of Naples (Italy). It is one of the largest fumarolic manifestations known, and the rocks hosting the hydrothermal system are affected by intense hydrothermal alteration. Alteration can result in changes of degassing behavior, and in the formation of a cap rock thereby increasing the probability of phreatic eruptions. Here, we investigate the effects of alunitic (solfataric) alteration on the mineralogy, the physical properties (porosity, density, permeability) and the mechanical properties (strength) of the rocks involved, as well as its influence on fragmentation and ejection behavior. Our results show that the pristine mineralogy of deposits from the vicinity of the Solfatara cryptodome and from Pisciarelli is almost completely replaced by amorphous silica and alunite. The differences in the degree of alteration among the samples series are reﬂected in the investigated properties and behavior as well as in the analysis of the experimentally generated particles. Alunitic alteration increases porosity and permeability, whereas it reduces density, elastic wave velocity and strength leading to higher fragmentation and ejection speeds for the sample series examined in this study. Our results also show that alteration results in the generation of a high fraction of fines (particle sizes < 10 μm) during fragmentation, mainly composed of alunite crystals. Due to their potential for inducing chronic disease, dispersion of such material should represent a serious health hazard on a local scale and the evaluation of precautions should be considered.

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1. Introduction

Alteration is a common feature observed in volcanic environments. It comprises a complex series of processes involving chemical, mineralogical and textural as well as rock physical (porosity, density, permeability, elastic wave velocity) (Pola et al., 2012) and rock mechanical (e.g. strength) changes due to rock–fluid interaction (Pirajno, 2009; Pola et al., 2014; Wyering et al., 2014). Hydrothermal alteration induced by hot acidic ﬂuids may lead to dissolution and precipitation of minerals and thereby drive the affected rocks to new mineralogical parageneses (Pirajno, 2009; Wyering et al., 2014). The main factors controlling hydrothermal alteration are temperature, pressure, rock type, permeability, ﬂuid composition and event duration (Browne, 1978; Robb, 2005). The effects of hydrothermal alteration on rock physical and as a consequence on rock mechanical properties have been investigated in several studies (Pola et al., 2012, 2014; Mormone et al., 2011, 2015; Wyering et al., 2014; Heap et al., 2014, 2015; Mayer et al., 2015; Carlino et al., 2016). Recent studies have investigated the effects of alteration and mineral precipitation on outgassing, and on the potential for the development of a low-permeability cap rock causing the pressurization of the system (Edmonds et al., 2003; Christenson et al., 2007; Mayer et al., 2015; Vignaroli et al., 2015). Such processes may lead to explosive events such as hydrothermal or phreatic eruptions (Browne and Lawless, 2001; Christenson et al., 2007, 2010; Vignaroli et al., 2015).

Upper regions of hydrothermal systems may also be characterized by steam-heated fumarolic alteration due to the presence of acidic sulfate-rich ﬂuids (Rye, 2005; Hedenquist et al., 2000). These ﬂuids cause leaching of the host rocks, resulting in an increase in both rock porosity and permeability. Eventually they may generate the development of vuggy silica and facilitate thereby faster gas escape in the shallow zone (Ellis and Mahon, 1964; Hedenquist and Lowenstern, 1994; Boyce et al., 2007; John et al., 2008; Scher et al., 2013; PIOCHI et al., 2015). Lateral to the degassing vents, the ﬂuids undergo progressive neutralization forming a sequence of alteration facies from silicic to advanced argillic to intermediate argillic (Fulignati et al., 1998). Campi Flegrei (CF) caldera (Fig. 1) hosts a large, complex hydrothermal system active (at least) since historic times (Mormone et al., 2011) which is
characterized by periods of ground uplift (bradyseism) accompanied by seismic events. At depth it can be assumed that magmatic gases mix with hydrothermal liquids and form a rising gas plume (Caliro et al., 2014). At the top of the rising plume, a single phase gas zone at shallow depth (300–100 m) develops (Caliro et al., 2007), where fluid circulation and fluid-induced alteration of the host rock are believed to influence pressurization events (Bruno et al., 2007). Permeability decreases due to the alteration process, could however cause pressurization and, in turn, result in hydrothermal explosions at depths of a few hundred meters.

The likelihood of phreatic eruptions at shallow depth was analyzed by Italiano et al. (1984) who constructed a thermodynamic model based on the gas emission rates at Solfatara. A similar scenario was recently reconstructed by Isaia et al. (2015) on the base of stratigraphic field analysis of ejected material. Their study indicates a multiphase eruptive evolution of the Solfatara crater derived from an early phreatic phase excavating the pre-eruptive strata, followed by phreatomagmatic events. Deposits of phreatic eruptions generally contain non-juvenile ejecta and are typically poorly sorted and matrix-supported. Phreatomagmatic eruptions are generated by the interaction of magma and external water and usually produce surge and fall deposits characterized by host rock fragments and juvenile material (Heiken and Wohletz, 1985; Browne and Lawless, 2001). Alteration could however also enhance permeability, thereby hindering the pressurization in the subsurface and, in turn, reducing the risk of an eruption. A recent mineralogical and isotope study by Piochi et al. (2015) concluded that the CF caldera represents a low sulfidation system grading in its most active centers (Solfatara–Pisciarelli) into the high sulfidation regime. They additionally proposed, that the increasing CO₂-degassing-surface area results from fracturing of the surficial rocks with major leaching of gas favoring increased outgassing.

The aim of this study is to investigate the influence of hydrothermal alteration on rocks, outcropping at the sites of the main hydrothermal activity of CF caldera (Solfatara and Pisciarelli area; Fig. 2). Samples have been collected and geochemically and mineralogically investigated in particular with respect to their degree of alteration. The effects of alteration on rock physical and mechanical properties have been measured and experimentally determined. This analysis included rapid decompression experiments at elevated temperatures to simulate possible phreatic eruption conditions whereby eruptive processes of this type of event and the fragmentation behavior of the involved rocks were studied. We present for the first time fragmentation experiments in the presence of steam expansion and compare them with control experiments driven by pure argon gas expansion in order to best mimic the possible conditions at the investigated sites. Additionally, the size of experimentally-generated particles, as well as the amount and composition of fine particles have been analyzed and evaluated.

2. Geological setting

Campi Flegrei is a densely-inhabited area located west of Naples characterized by an active resurgent caldera system (e.g. Vitale and Isaia, 2014 and reference therein). Since the second major caldera collapse formed the Neapolitan Yellow tuff ~15 ka ago, an intense volcanic
activity has produced more than 70 explosive eruptions, separated by rest periods of variable duration (e.g. Di Vito et al., 1999; Orsi et al., 2004; Isaia et al., 2009). These eruptions were predominantly phreatomagmatic with minor magmatic events occurring along the structural boundaries of the caldera as well as along faults inside the caldera, producing several tuff cones and tuff rings (Di Vito et al., 1999; Orsi et al., 2004; Costa et al., 2009; Smith et al., 2011). The most violent among them was produced following an intra-caldera collapse (e.g. Agnano–Monte Spina, AMS; de Vita et al., 1999; Di Vito et al., 2011; Isaia et al., 2004, 2015). A historic eruption formed the Monte Nuovo tuff cone (1538; Guidoboni and Ciuccarelli, 2011). The volcanism has also included phreatic events and the formation of maar–diatreme structures (Lorenz, 1986; White and Ross, 2011), as recently postulated for the Solfatara crater (Isaia et al., 2015). Solfatara volcano is part of a cluster of vents within less than 2 km², located at the southwestern rim of the AMS caldera (Fig. 1) (Isaia et al., 2009). The reactivated volcanic activity started after the AMS Plinian eruption (~4.5 ka; Smith et al., 2011) after a refilling of the reservoir at a depth of less than 3 km and generated vents in the central area of the caldera including Solfatara crater (Isaia et al., 2009). Solfatara crater developed during a maar–diatreme evolution 4200 yr B.P. and presently hosts very intense hydrothermal and fumarolic activity both occurring within the crater as well as on the eastern flanks toward Via Antiniana and the Pisciarelli area. The latter has exhibited a significant increase in degassing activity over the past 10 years marked by i) a widening of the hydrothermal area, ii) an increase in temperature and gas emissions and iii) the formation of new vents (Chiodini et al., 2012, 2015; Troiano et al., 2014; Isaia et al., 2015). The majority of the wall rocks affected by alteration at both sites are parts of the pre-AMS and AMS volcanic deposits (Isaia et al., 2009, 2015).

2.1. Hydrothermal system

The level of historical knowledge surrounding the history of the CF hydrothermal system is unsatisfactory. Currently the Solfatara area, including Pisciarelli and Via Antiniana, is the hydrothermally most active part of one of the largest fumarolic manifestations worldwide. It consists of a) a deeper-seated mixing zone and b) a shallow zone; interacting with each other (Caliro et al., 2007).

Changes within the deeper-seated hydrothermal system have been caused by repeated injections of magmatic fluids in the past (Chiodini et al., 2012), where mixing with liquids of meteoric origin occurred (Caliro et al., 2014). These injections led to the pressurization of the system resulting in periods of ground uplift (Orsi et al., 1999; Vilaro et al., 2010) and accompanied by increased seismicity (Orsi et al., 1999; D’Auria et al., 2011). The magmatic fluids appear to derive from two sources: (1) a deep stable magma chamber at approximately 8 km depth, which has fed volcanism over the last several thousand years (Mangiagapra et al., 2008; Arienzo et al., 2010) and (2) a shallower magma reservoir, intruded at approximately 4 km depth during the unrest episode occurring from 1982 to 1984 (Moretti et al., 2013, and references therein). The mixing of these fluids occurs at high temperature (>350 °C) at the deeper part of the hydrothermal system (2.0–2.5 km), from which the rise of a plume (gas and liquid) to shallow depths is largely controlled by a volcano-tectonic system of a complex collapsed maar–diatreme structures (Isaia et al., 2015). According to Caliro et al. (2007) a single-phase gas zone exists at shallow depth (100–300 m). But recent electrical resistivity tomography studies have revealed the existence of a two-phase system represented by liquid- and gas-dominated zones in the subsurface of Fangia mud pool and the fumaroles of Bocca Grande (BG) and Bocca Nuova (BN) (Fig. 2), respectively (Byrdina et al., 2014).

The thermal energy release associated with the surficial gas emissions represents a major proportion of the energy balance of the CF caldera (Cardellini et al., 2003; Chiodini et al., 2001, 2011). The fumarole temperatures measured at the surface range up to 165 °C and 160 °C for BG and BN, respectively and up to ~115 °C for Pisciarelli (Valentino et al., 1999; Chiodini et al., 2015). The main components of the fumarolic effluents are H₂O and CO₂, followed by H₂S, H₂, N₂ and CH₄ (Caliro et al., 2007). Due to the buffering of magmatic fluids by the large hydrothermal system, components like SO₂, HCl and HF are not detected at the surface (Chiodini et al., 2001; Moretti et al., 2013). The substantial release of CO₂ by both fumarolic and diffuse degassing within the Solfatara–Pisciarelli area is anomalously high (>2000 ton d⁻¹), and is

Fig. 2. Google Earth™ image of Solfatara crater and Pisciarelli fumarole. Insets show the details of the sampling locations.
typical of volcanoes in eruptive phases (Caliro et al., 2014, and references therein).

2.2. Hydrothermal alteration

2.2.1. Deep system

In the geothermal exploration program of the Agip–Enel Joint Venture several deep drillings (e.g. San Vito 1) have been conducted in the Campi Flegrei caldera since the 1970s. These were located beyond the high-outgassing zone investigated in this study (Agip, 1987). Drill log information was used to analyze the fluid–rock interaction at depth (~2800 m) that has produced a suite of hydrothermal alteration minerals leading to increasing rock density and a corresponding decrease in porosity (Mormone et al., 2011) as well as an increase in shear and tensile strengths of the rocks (Vanorio and Kanitpanyacharoen, 2015). The formation of argillic phases, especially in the shallow alteration zones of these drillings and accompanied by a decrease in rock permeability, favors the interpretation of the creation of a cap rock within the hydrothermal system (Todesco et al., 2003; Bruno et al., 2007). Rock samples from the drill cores obtained during the Campi Flegrei Deep Drilling Project (CFDDP), located in the eastern sector of the caldera, have been investigated recently (De Natale and Troise, 2011). Drill log analysis has shown a hydrothermal alteration-induced rock mineralization leading to the filling of voids and veins (Mormone et al., 2015) and a reduction of rock permeability (Carlino et al., 2016). In general, the mineralogy detected in these drill holes is characteristic for a neutral-pH, low-sulfidation system (Piochi et al., 2015).

2.2.2. Surficial system

Steam-heated environments, in the upper portions of hydrothermal systems, in which sulfuric acid is created at or above the water table by the oxidation of H₂S (H₂S + 2O₂ = H₂SO₄), lead to an advanced argillic alteration (Rye, 2005). This type of alteration is characterized by acidic fluids and the formation of amorphous silica and alunite (Pirajno, 2009) which is a very common feature in surficial regions of high-sulfidation epithermal systems, often referred to as solfataric alteration (Bishop et al., 2007). In the presence of abundant sulfate ions and Al-rich protoliths, alunite forms veins, lenticular bodies and may even replace entire rock masses (Pirajno, 2009). The formation of alunite from K-feldspar follows the reaction:

\[ 3\text{K}(\text{AlSi}_3\text{O}_8) + 3\text{H}_2\text{SO}_4 \Rightarrow \text{KAl}_3(\text{OH})_6(\text{SO}_4)_2 + 9\text{SiO}_2 + \text{K}_2(\text{SO}_4)_2 \]

(Höller, 1967). During the transition from K-feldspar to alunite, SiO₂ is released (Hedenquist et al., 2000) which, together with the residual SiO₂, caused by the extreme leaching of the alkali cations by acidic fluids (pH 1.3–2.5) at high temperature, may lead to the formation of vuggy silica (Bruno et al., 2007; Boyce et al., 2007). As a result, the K-feldspar and maﬁc silicate phases within the trachytic host rocks are completely altered (Pirajno, 2009) and volcanic glass dissolves (Hedenquist et al., 2000, Boyce et al., 2007).

The Solfatara–Pisciarelli area is characterized by the surficial formation of alunite and amorphous silica (De Gennaro et al., 2000; Bruno et al., 2007; Pinto et al., 2007). A recent study based on SEM and isotope analysis conﬁrms the genesis of alunite at Solfatara and Pisciarelli via hydrolysis of K-feldspar (Piochi et al., 2015). In contrast, the low pH of fluids hinders the formation of kaolinite (Zimbelman et al., 2005) at Pisciarelli (Valentino et al., 1999) and at the highly degassing vents at Solfatara (Bruno et al., 2007). Due to the lack of wells in the proximity of Solfatara crater, a detailed distribution of hydrothermal alteration minerals in the subsurface is not yet possible (Bruno et al., 2007). Piochi et al. (2015) have developed a conceptual model of the Campi Flegrei hydrothermal system, based mainly on geochemical and mineralogical data as well as on input from drilling studies. They propose an acid sulfate environment along the SW–NE section from Solfatara crater to the Pisciarelli area at shallow depth of a few hundred meters and high-sulfidation zones associated to the hydrothermal vents of Solfatara and Pisciarelli. Previous studies examined the effects of surficial alteration on rocks from the Solfatara crater walls (lavas and pyroclastic rocks) as well as by investigating rock physical and rock mechanical properties (Pola et al., 2012, 2014). Those results indicate that in the shallow part of the hydrothermal system, an increasing degree of alteration leads to 1) an increase in porosity, 2) a decrease of elastic wave velocities, and 3) a decrease in tensile and compressive strengths.

3. Material investigated

In order to investigate the influence of hydrothermal alteration on rock properties, and as a consequence to infer implications for possible phreatic eruptive processes, two areas of intense hydrothermal activity (Solfatara crater and Pisciarelli area) were chosen as sampling sites (Figs. 2, 3). Rock samples from AMS and pre-AMS lithostratigraphic units, exhibiting variable degrees of alteration have been collected (Fig. 4). These sequences represent the oldest rocks exposed in the Solfatara–Pisciarelli area (Fig. 3) and consist of pyroclastic fallout, coarse to fine-ash beds, and pyroclastic density current deposits (Isaia et al., 2015). Post-depositional processes and alteration have led to the consolidation and compaction of the deposits, which have been transformed thereby from loose deposits to solid rocks. The sampled blocks represented individual layers of a multi-layer sequence. Therefore

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![Fig. 3. Geological cross-section (2 × vertical exaggeration) of the study area showing stratigraphic units, shallow fluid flow and sampling locations. Modified after Isaia et al. (2015).](image-url)
an oriented collection in the field and a coring perpendicular to the layering in the lab was possible. Samples were selected based on observable differences in macroscopic texture, color and particle size after the removal of surficial encrustations and weathering effects. Two blocks from the vicinity of the Solfatara cryptodome were collected (Fig. 2; see also Isaia et al., 2015): one block of a pyroclastic current deposit comprising a lesser altered core (S1) and a more altered rim (S2), and a heavily altered block from a second current deposit (S3) (Fig. 4). Within the Pisciarelli, three blocks from a several meter-thick consolidated ash fall sequence were collected (P1, P2, P3) (Fig. 4).

4. Methods

4.1. Mineralogical and geochemical characterization

Mineralogical and geochemical analyses were conducted by optical microscopy as well as by wavelength dispersive X-ray fluorescence (WD-XRF) and X-ray powder diffraction (XRD). To further investigate the intensely-altered samples, electron probe micro analysis using an energy-dispersive system (EPMA-EDS) was employed.

XRD analysis was conducted using a General Electric XRD 3003 TT diffractometer (CuKα, graphite monochromator, step-scan 0.0013° 2θ increments per second, counting time 100 s per increment, 30 mA, 40 kV) at the Ludwig-Maximilians-Universität München. For this analysis, samples were disaggregated and ground for 8 min with 10 ml of isopropl alcohol in a McCrone Micronising Mill using agate cylinder elements. Phase identification was made with the interface Rayflex ANALYZE (Putz and Brandenburg, 2003). The whole rock element compositions were determined by WD-XRF analysis (Philips, MagiX Pro) at the LMU. Major and minor elements were measured using glass beads prepared by fusion of 1 g sample and 9 g SPECTROMELT A12 (66% di-lithium tetraborate, 34% lithium metaborate) in a Panalytical Egon 2 furnace fusion system. SO₃ was measured by XRF of powder tablets. Therefore 8 g of the sample powder was mixed with 2 g of Merck Hoechst wax C micropowder (C₃₈H₇₆N₂O₂), homogenized and pressed with P = 15 bar for > 1 min. Additional geochemical information was attained by a Cameca SX 100 (EMPA) equipped with a Bruker AXS XFlash Detector 3001 at the LMU. Chemical composition based on the results obtained by WD-XRF analysis allowed determination of the Chemical Index of Alteration (CIA) which is one of many indices proposed in literature to characterize the alteration degree of different rocks (Pola et al., 2012, 2014; and references therein). The index, based on the weight percentage ratios of major elements, is applied to correlate the degradation trend exhibited by rock physical and mechanical properties.

\[ \text{CIA} = \frac{(A\text{L}_2\text{O}_3) \times 100 \times (A\text{L}_2\text{O}_3 + C\text{aO} + N\text{a}_2\text{O} + K\text{2O})^{-1/2}}{ \text{CIA} = \frac{(A\text{L}_2\text{O}_3) \times 100 \times (A\text{L}_2\text{O}_3 + C\text{aO} + N\text{a}_2\text{O} + K\text{2O})^{-1/2}}{Nesbitt and Young, 1982} \]

4.2. Rock physical properties

Cylinders of all blocks sampled were cored for the determination of rock physical properties. Bulk density, matrix density, and connected porosity of dry (oven-dried at 65 °C for 24 h), cored cylinders were measured using a helium pycnometer (Ultrapyc 1200e®, Quantachrome, USA) at the Ludwig-Maximilians-Universität München. A portable air permeameter was used to measure the permeability of samples in the field (New England Research, TinyPerm III). This handheld device calculates the Darcian permeability based on the monitored response function of the transient vacuum at the interface between the nozzle and the rock during the evacuation of air from the rock (Possemiers et al., 2012; Vignaroli et al., 2015; Fargeaharson et al., 2015). Additionally, gas permeability measurements of selected cylindrical samples (40 mm length; 20 mm diameter) were conducted under a confining pressure of 1.0 MPa at the École et observatoire des sciences de la Terre (EOST) - Université de Strasbourg. Further, benchtop P-wave velocity of dry, cylindrical samples (60 mm length; 25 mm diameter) was determined at the Ludwig-Maximilians-Universität München.

4.3. Ultrasonic wave velocity and strength tests

Experiments to determine the rock mechanical properties were performed on dry and saturated (i.e., complete, vacuum-saturation of samples with distilled water) samples. P wave velocities were measured along the long axis of the cylindrical samples which were later used for the strength tests. The unconfined compressive strength (UCS) experiments (i.e., \( \sigma_1 > \sigma_2 = \sigma_3 \); \( \sigma_2 = \sigma_3 = 0 \)) as well as the indirect tensile strength (ITS) experiments of this study were performed at the Technische Universität München, on all sample types under a constant strain rate of \( 3.3 \times 10^{-4} \text{ s}^{-1} \) and a constant deformation rate of 0.03 kN s⁻¹ respectively. Axial strain and stress were continuously monitored during deformation, by displacement transducers and by a load cell, until failure. Samples for UCS tests were cored with a diameter of 25 mm and with their end-faces ground flat and parallel to a nominal length of 50 mm (length–diameter-ratio of 2:1). For the ITS tests the same sample preparation was applied however the nominal length was shortened to 25 mm ensuring a length–diameter-ratio of 1:1. The load applied to the standing sample disk, perpendicular to the coring orientation was transmitted by a hardwood fiber stripe above and below the sample along the entire sample length.

4.4. Fragmentation experiments

Use of a shock-tube apparatus (Alidibirov and Dingwell, 1996a, b; Martel et al., 2000; Spieler et al., 2003, 2004 Kueppers et al., 2006; Scheu et al., 2006, 2008; Mueller et al., 2005, 2008; Richard et al., 2013; Rager et al., 2013, Mayer et al., 2015) yielded the determination the fragmentation threshold, as well as the fragmentation- and particle ejection-speeds of all samples. The experimental procedures and details are described in the Appendix. In its present configuration this device permits the accurate control of temperature, gas overpressure and decompression rate in order to best represent variable volcanic and
hydrothermal conditions (Mayer et al., 2015). The stainless steel low-pressure tank (l = 3.0 m; d = 0.4 m) at ambient pressure and temperature to collect the experimentally generated particles is located above a high-temperature steel autoclave in which the sample is mounted (Fig. 5A). First, fragmentation threshold experiments on dry samples at room temperature, determined by rapid decompression of argon gas, were performed on all samples series. A further series of experiments was conducted in order to determine the fragmentation speed, as well as the ejection speed of the gas-particle mixture front in the presence of steam expansion (phreatic experiments) at a target temperature of 260 °C and hence a dwell pressure of 4 MPa. These conditions are close to those indicated by gas geoindicators (Chiudini et al., 2003) and also in the range of conditions independently simulated by a physical numerical approach (Todesco et al., 2003) for the single-phase gas zone in the shallow part of the hydrothermal system. Water vapor is the main component of the degassing fluids at Solfatara and Pisciarelli (Caliro et al., 2007).

An additional series of control experiments in which fragmentation and ejection speed were initiated solely by argon gas expansion (at identical pressure and temperature conditions) was performed. The pressure–volume–temperature properties of argon gas are very similar to those of CO₂, which is the second largest contributor to the fumarolic fluids at Solfatara and Pisciarelli (Caliro et al., 2007). For the latter experiments, the dry samples were inserted in the high-temperature steel autoclave in which the sample is mounted (Fig. 5A). This enabled to obtain the targeted overpressure solely by the expansion of liquid water to steam. Temperature and pressure within the system rose along the boiling curve of water (Fig. 5B) until targeted dwell conditions of 4 MPa at 260 °C were reached after a heating time of 60 min. Before triggering the fragmentation an equilibration time of 10 min was occupied. Throughout all experiments, pressure and temperature in the system were monitored at rates of 1000 Hz and 2 Hz, respectively. For this a sensor pair consisting of a dynamic pressure sensor and a thermocouple was located at the bottom of the sample, whereas a second pair sits at the upper end of the autoclave, 225 mm above the sample (Fig. 5A). The low-pressure tank and the autoclave are separated by a set of two diaphragms that allow triggering of decompression by a controlled failure of the uppermost diaphragm (Mayer et al., 2015). The decompressing, expanding fluid fragments the sample brittlely in a layer-by-layer fashion (Alidibirov and Dingwell, 2000; Fowler et al., 2010) and the particles are ejected into and stored in the collector tank (Mayer et al., 2015). Evaluation of the travel time of the rarefaction wave from the upper pressure sensor to the top of the sample and analyzing the pressure decay monitored by the dynamic pressure transducers, provided a quantification of the fragmentation speed, according to the procedures developed by Schue et al. (2006). For each experiment the ejection of the gas-particle mixture was recorded by a high-speed camera (Phantom V710®, Vision Research, USA) at 10,000 frames per second through a transparent Plexiglas at an area (h = 21.0 cm, w = 12.5 cm) at the base of the collector tank, just above the diaphragms (Fig. 5A). Analysis of the footage by tracking of fragmented particles allowed measurements of their ejection velocities.

4.5. Analysis of experimentally generated particles

In order to investigate the experimentally-generated particles, fragmented sample material of each experiment was collected from the low-pressure tank. Particle size distribution (PSD) analyses of the fragments were carried out by dry-sieving of coarse particles (≥63 μm). Based on PSD data the geometric mean particle size for each sample series was calculated (Folk and Ward, 1957). Laser refraction techniques, using a Coulter LS230 (measuring range 0.375–2000 μm, wave length 750 μm) were applied for the PSD analysis of the fine fraction (<63 μm). Further, the size range and composition of fine particles (<63 μm) from selected samples were investigated by scanning electron microscope equipped with an energy-dispersive system (SEM–EDS) at the LMU using a Bruker AXS DSM 960 A. Additional WD–XRF analysis allowed to quantify the mineralogical composition of the fine fraction (<63 μm), generated during phreatic experiments.

5. Results

5.1. Mineralogy of hydrothermally altered samples and CIA

The mineralogy of the investigated rocks subjected to intense surficial solfatara alteration consists mainly of i) amorphous silica and ii) alunite. In addition, the Solfatara (S) samples S1 and S2 contain remnants of pristine sanidines. Amorphous silica occurs as pseudomorphs after primary minerals or mineral fragments such as amphibole, pyroxene and feldspar (30–500 μm) indicated by euhedral crystal habits and preserved growth zonations (Fig. 6A–D) and as silicified accretionary lapilli (100–600 μm) (Fig. 6E–F). EPMA–EDS analysis reveals that locally core
zones of crystals are not yet completely replaced by amorphous silica (Fig. 6G). XRD whole rock analysis indicates opal-A as the main amorphous silica phase (Fig. 6H) (Rogers et al., 2004; Lynne et al., 2005) whereas volcanic glass may also occur, however probably only as minor amount. Alunite (5–10 μm) occurs as i) replacement of matrix (Fig. 6D, F), ii) alteration rims around silica pseudomorphs, and around silicified accretionary lapilli (Fig. 6B, F), and iii) single crystals enclosed within these pseudomorphs and silicified accretionary lapilli (Fig. 6D, F) but also along fractures of primary minerals replacing sanidine (Fig. 6I). XRD and WD-XRF analyses suggest that the alteration affecting the block of samples S1 and S2 led to the formation of amorphous silica and a substantial amount of alunite (increasing from S1 to S2) whereas leaching occurred as the dominant process for S3 resulting in only minor amounts of alunite. Pisciarelli (P) samples showed a more homogeneous mineralogy caused by the alteration effects, which resulted in both leaching and alunite formation. WD-XRF analysis supports a slightly higher amount of alunite in P2 compared to P1 and P3. The CIA, based on the WD-XRF analysis (Table 1), nevertheless increases from S1 (67.8) to S2 (74.4) and S3 (79.8) and from P1 (73.7) to P2 (75.8) and P3 (77.8) respectively.

5.2. Bulk density, connected porosity and gas permeability

Fig. 7 illustrates the relation of the CIA and the rock physical properties obtained for dry samples at room temperature. The density decreases with increasing degree of alteration from 2.44 to 2.21 and from 2.45 to 2.36 for S and P samples (Fig. 7A). By contrast, connected porosity (Fig. 7B) and gas permeability (Fig. 7C) increase from 26.6 to 15 m² for S samples as well as 15 m² for P samples, respectively.

5.3. Elastic wave velocity, UCS and ITS

The relationship between rock mechanical properties and the connected porosity is shown in Fig. 8 and summarized in Table 3. P-wave velocities of dry and water saturated samples decrease with increasing connected porosity from 2.5 to 0.6 km/s and 4.0 to 0.8 km/s (Fig. 8A). As a further consequence, the UCS (Fig. 8B) as well as the ITS (Fig. 8C) of dry samples decreases from 34.8 to 5.5 MPa and from 4.4 to 0.6 MPa. Water-saturated samples exhibit both lower UCS and ITS values ranging between 33.5 and 4.0 MPa and between 3.7 and 0.5 MPa, respectively.

5.4. Fragmentation threshold, speed and ejection speed of the particle front

Experiments to determine the fragmentation threshold have been repeated three times in order to account for sample heterogeneities. Investigated samples fully fragment during decompression at initial pressures ranging from 4.2 to 2.0 MPa (Fig. 9; Table 3). The results follow the trend defined in previous studies (e.g., Mayer et al., 2015 and references therein) and plot slightly below the fragmentation criterion of Koyaguchi et al. (2008) derived from experiments with pristine volcanic rocks. Fragmentation and ejection speed of particles front in the presence of dry argon gas and stream expansion at 260 °C and at an initial pressure of 4 MPa are summarized in Table 3 and displayed in Fig. 10. Both values were obtained in a single experiment that was again repeated three times to account for sample heterogeneities. The fragmentation velocities (Fig. 10A) obtained in the phreatic experiments generally rise with increasing porosity and range between 15.2 and 45.0 m/s (S) as well as between 26.2 and 34.9 m/s (P). Fragmentation speeds resulting from pure argon gas expansion (control experiments) follow a similar trend but exhibit lower speeds ranging between 10.6 and 34.9 m/s (S) and between 16.4 and 27.2 m/s (P). The ejection speed of the particle front obtained by high-speed video analysis reveals a similar dependence (Fig. 10B). Particle ejection velocities in the presence of steam expansion (phreatic experiments) ranging from 74.5 to 174.3 m/s (S) and from 111.0 to 139.1 m/s (P) are higher than those attained in the control experiments extending from 52.9 to 158.9 m/s (S) and from 91.4 to 121.8 m/s (P).

5.5. Size and compositional analysis of experimentally generated fragments

Particles generated during fragmentation have been recollected and the PSD of the coarse (≥63 μm) and fine (<63 μm) fraction was determined. Fig. 11 shows the cumulative curve of the weight fractions for phreatic (Fig. 11A, B) and control experiments (Fig. 11C, D) in which every individual line represents the entirety of particles collected from three experiments. The geometric mean particle size (Folk and Ward, 1957) of S fragments decreases in the phreatic experiments from S1 (2412 μm) to S2 (2217 μm) and S3 (1696 μm) and is smaller than the mean particle size generated in the control experiments, which decrease from S1 (3948 μm) to S2 (2985 μm) and S3 (2301 μm).

PSD of P samples after the phreatic experiments shows P1 containing a higher amount of fines and smaller amount of coarse particles.
when compared to P2. The mean particle diameter of P1 (564 μm) is slightly higher than P2 (550 μm). P3 differs significantly with a mean particle diameter of 208 μm and a PSD shifted toward a high amount of fines. The size analysis of P samples after the control experiments shows bigger mean particle sizes than in the phreatic experiments, of which the size analysis of P samples after the control experiments in comparison to those generated in the phreatic experiments. Results show only minor amounts (0.3–0.5%) of fines for S samples in control experiments and slightly increased amounts (0.5–0.9) in the phreatic experiments. In contrast P samples fragmented during argon gas expansion produced 1.1–2.3% of fines, whereas steam expansion led to an increased amount of very fines compared to S3 whereas P samples show a gradual trend toward more very fines from P1 to P3 and P2. SEM images of P1, P2 and S2 samples are characterized by amorphous silica particles with different amounts of alunite crystal growth on the surface. In contrast S3 shows only minor amounts of alunites, but instead typical “vuggy silica” features of the particles.

6. Discussion

According to the above, surficial solfataric alteration has significant effects on the mineralogy of rocks and led to dramatic changes of their physical properties — a trend confirmed by an increasing CIA. The increase in porosity due to acidic leaching in combination with the replacement of pristine mineralogy by alunite has a first order control on the mechanical properties, on the fragmentation behavior of...
investigated rock samples and on the production of fines during fragmentation initiated in rapid decompression experiments.

6.1. Mineralogy, rock physical and mechanical properties

The mineralogy determined in this study derives from a complex interaction of alunite and amorphous silica formation. It is most likely generated by the repetition of alteration processes with spatial and temporal variability depending on temperature, pH and fluid composition (Zimbelman et al., 2005). A dominant process can hardly be identified as alunite is enclosed in amorphous silica and vice versa. Acidic leaching of the rocks caused the decrease and almost entire removal of mobile elements (Ca, Na, Mg) and led to relatively high amounts of residual silica. However, the formation of alunite has prevented the removal of aluminum and potassium (Table 1). The CIA values obtained for the investigated rocks confirm the alteration trend found by optical microscopy and also correlate well with those determined by Pola et al. (2012) for altered pyroclastic rocks. The mineralogy of surficial encrustations and efflorescences on rocks from Solfatara and Pisciarelli determined by Piochi et al. (2015) differ from the results of this study. Within the internal rock structure, leaching and thus formation of amorphous silica is one of the main processes. This appears not to be evident at the rock surface. The formation of native sulfur and other sulfates (e.g. alunogen, pickeringite, potassium alum; Piochi et al., 2015) seems to occur solely on the rock surfaces. Fulignati et al. (1998) suggested supergene origin of sulfates (e.g. gypsum) due to the circulation of surface rainwater fluids in their study investigating hydrothermal alteration at Vulcano (Aeolian Islands, Italy). Although these two studies did not focus on effects of alteration on rock physical properties, their results nevertheless highlight the high variability in alteration minerals on a small scale. The alteration processes observed in this study cause a general decrease in sample density, an increase in connected porosity and as a consequence a higher gas permeability of the investigated rocks. Hence these effects lead to lower elastic wave

Table 3

<table>
<thead>
<tr>
<th>Sample series</th>
<th>Connected porosity (mean) (%)</th>
<th>Vp dry (mean) (km/s)</th>
<th>Vp saturated (mean) (km/s)</th>
<th>UCS dry (mean) (MPa)</th>
<th>UCS saturated (mean) (MPa)</th>
<th>ITS dry (mean) (MPa)</th>
<th>ITS saturated (mean) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>26.6</td>
<td>2.5</td>
<td>4.0</td>
<td>34.8</td>
<td>33.5</td>
<td>4.4</td>
<td>3.7</td>
</tr>
<tr>
<td>S2</td>
<td>38.4</td>
<td>2.0</td>
<td>3.4</td>
<td>20.3</td>
<td>16.8</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>S3</td>
<td>61.3</td>
<td>0.6</td>
<td>0.8</td>
<td>5.5</td>
<td>4.5</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>P1</td>
<td>35.0</td>
<td>1.9</td>
<td>2.5</td>
<td>17.0</td>
<td>10.2</td>
<td>2.1</td>
<td>1.6</td>
</tr>
<tr>
<td>P2</td>
<td>40.0</td>
<td>1.4</td>
<td>2.1</td>
<td>11.3</td>
<td>9.7</td>
<td>1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>P3</td>
<td>48.5</td>
<td>0.9</td>
<td>1.6</td>
<td>6.3</td>
<td>4.0</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Fig. 9. Fragmentation threshold of investigated samples at 20 °C during rapid decompression experiments. Fragmentation threshold for several rocks obtained in other studies is also compiled. The dashed line corresponds to the fragmentation criterion proposed by Koyaguchi et al. (2008). Samples with a higher porosity fragment at a lower initial pore pressure. Altered samples of this study confirm the criterion plotting slightly below the dashed lines.

Fig. 10. Fragmentation and ejection speed of particle front obtained by rapid decompression experiments at 260 °C and 4 MPa initial pressures. (A) Fragmentation speeds within sample series (S, P) increase with porosity and in the presence of steam expansion. (B) Ejection speed of the particle front in the presence of argon gas and steam expansion. The ejection speed values correspond to the average of the velocities of several particles (>5) traveling at the front of the gas-particle mixture. The velocity of ejected particles increases with porosity and in the presence of steam expansion. (Note: Plotted values represent the average of three experiments; error bars indicate the range of porosity and of obtained speeds).
velocities as well as lower uniaxial compressive and indirect tensile strengths (Fig. 8). The obtained results are in agreement with the mechanical properties of altered pyroclastic rocks investigated by Pola et al. (2014). The samples mainly consist of silicified components within a matrix replaced by abundant alunite crystals with sizes of few microns in sizes (Fig. 6). This hydrolytic alteration causing the dissolution of silicate minerals leads to a decrease in bulk rock density by removal of cations and silica in solution, destroying the primary rock fabric (Vikre and Henry, 2011).

Density reduction and alteration in combination with the development of the resulting fine-grained microstructure impart weak bonding forces to the rock, exhibited by low values of P wave velocity, tensile and compressive strength. Water saturation of samples increases the ultrasonic wave velocities (as P wave velocity is higher in water than in air) (Heap et al., 2014) and additionally decreases the strength values due to the weakening effect of water (Baud et al., 2000). Our results therefore confirm the findings of previous studies on different hydrothermally altered volcanic rocks (Arıkan et al., 2007; del Potro and Hürlimann, 2009; Pola et al., 2012).

6.2. Fragmentation behavior

The fragmentation threshold of investigated samples decreases with increasing degree of alteration as a consequence of the increased porosity. Alteration and the fine-grained microstructure cause a weaker cementation of samples when compared to unaltered tuffs (e.g. NYT, Montanaro, pers. comm.). This leads to fragmentation below the threshold defined by Koyaguchi et al. (2008). These results are in agreement with the fragmentation threshold of hydrothermally-altered ash tuffs (Mayer et al., 2015), which also plot slightly below the fragmentation criterion (Fig. 9). Rock physical and mechanical properties as well as the initial overpressure and the type of fluid within the pores have a first order control on the fragmentation and ejection speed of the sample (Mayer et al., 2015 and references therein). The analysis of fragmentation experiments reveals that fragmentation and ejection speed generally increase with increasing porosity. The amount of pressurized fluid stored within the sample and causing the fragmentation and ejection of particles during rapid decompression is controlled by the connected porosity (Scheu et al., 2006; Mayer et al., 2015). Further, steam...
expansion leads to slightly higher fragmentation and ejection speed than expansion of argon gas. This highlights the influence of the fluid type and especially the expansion coefficient on the processes. Water vapor at 4 MPa and 260 °C has a 1.2-fold larger volume increase during the isothermal expansion to ambient pressure compared with pure argon gas expansion. As a result, the fragmentation and ejection speeds are somewhat higher in the phreatic experiments as the processes involved are more energetic (Wohletz, 1983). Our results are in agreement with previous studies determining the fragmentation speed of pristine samples at an initial argon gas overpressure of 4 MPa (Spieler et al., 2004; Richard et al., 2013). In those studies, samples with a connected porosity of 48.0% and 59.8% fragmented at 14 and 22 m/s, respectively, lower than the fragmentation speeds of heavily altered samples of this study with similar porosities (P3, S3). This indicates a weaker strength of altered samples resulting in a faster fragmentation when compared to unaltered samples.

Under constant initial conditions, the ejection velocity of the gas-particle mixture increases with increasing porosity but also with increasing fragmentation velocity. In addition, the ejection speed is higher than the fragmentation velocity. These results confirm the findings of previous studies (Alatorre-Ibargüengoitia et al., 2011; Mayer et al., 2015). As the alteration lowers the strength of the rock, a lower amount of energy is consumed by fragmentation and, as a consequence, more energy is available for acceleration and ejection of the fragments resulting in a higher ejection speed.

Further, the degree of alteration showed an influence on the particle size distribution of experimentally generated particles — this effect is mainly due to the increase in porosity. Samples with higher porosities contain a higher gas volume resulting in higher fragmentation energy (Rueppers et al., 2006). Therefore, our results might support the statement that the fragmentation of altered samples may lead to a decreased mean fragment diameter and produce an increased amount of fine particles. Such high proportions of fine (<10 μm) and very fine (<4 μm) particles, which lie in the “thoracic” and respirable fraction, constitute a severe hazard due to the potential for causing acute and chronic respiratory diseases (Horwell and Baxter, 2006; Horwell, 2007). Extremely fine ash was also reported to have generated during the August 6, 2012 hydrothermal eruption of Upper Te Maari, New Zealand (Breard et al., 2014; Lube et al., 2014). PSD analysis further revealed however that the production of fines is not only controlled by porosity. The samples investigated exhibit different productions of fines depending on the type of fluid (steam vs. argon gas), which is transmitting the energy deriving from decompression for fragmentation of the rock. The complex microstructure (distribution of alunite within the sample, size of amorphous silica particles) of these heavily altered, fine-grained surge deposits seems to have a control on the fragmentation process. The phreatic experiments with P samples in particular generated abundant fines (Fig. 12A). WD-XRF analysis revealed that the fraction <63 μm experienced a decrease in silica (Fig. 12B) resulting in an increased amount of alunite. These findings are in good agreement with the PSD (<63 μm) obtained by laser refraction analysis and with SEM–EDS analysis. Smallest particles generally characterized by a rhombohedral morphology are predominantly alunites (Fig. 13). They appear as small clusters precipitated on the surface of amorphous silica clasts (Fig. 13). Very few amorphous silica particles of P samples contain surfaces that are “alunite-free” consistent with the proposal that fragmentation within the samples initiates at the contact between alunites. A higher fraction of alunite and a more homogeneous distribution among the amorphous silica particles would thereby favor a higher fraction of finer fragments. In particular, the interaction of steam and a homogeneous alunite distribution appears to enhance very efficient fragmentation.

7. Summary and conclusions

We have investigated the effects of surficial solfataric alteration on mineralogy, rock physical and mechanical properties and as a consequence on the fragmentation and ejection behavior of samples from most active hydrothermal CF sites of Solfatara and Pisciarelli. The PSD and composition of selected fine-grained particle fractions was also analyzed. Rapid decompression experiments were designed to compare phreatic conditions (steam expansion) with dry argon gas expansion at initial conditions of 260 °C and 4 MPa in order to evaluate the influence of different fluids. For quantification of sample’s degree of alteration we applied a chemical index (CIA) and compared this index to...
the experimentally obtained properties. The main observations and conclusions are:

1. Alteration by sulfuric acid causes leaching of the rocks and thereby the formation of amorphous silica (mainly opal-A) as well as the formation of alunite as a replacement of crystals and groundmass.
2. The investigated rocks do not contain any clay minerals due to the high acidity of the fluids involved.
3. The alteration weakens the rocks, increases porosity and permeability and leads to a lower fragmentation threshold.
4. Fragmentation and ejection speed of samples increase with increasing porosity and with a higher degree of alteration respectively. Both velocities are slightly enhanced in the presence of steam expansion.
5. The microstructure of the samples has an influence on the rock mechanical properties, on the fragmentation behavior and on the production of fine particles.
6. Fragmentation of fine-grained ash fall deposits (P samples) affected by solfataric alteration produces a significant amount of fines containing a considerable proportion of very fines (<10 μm).
7. Due to their potential to instigate chronic diseases, dispersion of such material would represent a serious health hazard on a local scale.

In summary our results have shown that solfataric alteration in the upper regions of hydrothermal systems is increasing the permeability of surficial rocks. A conceptual model for the formation of near surface high-sulfidation alteration is illustrated in Fig. 14. Depending on pH, fluid temperature and composition, a sequence of different zones develops with increasing distance to the main fumarolic conduits. The most acidic core is characterized by a halo of amorphous silica, the residual phase after the mobilization of all other elements. The depletion in \( \text{Al}_2\text{O}_3 \) within this silicic alteration zone is significant for conditions with \( \text{pH} < 2 \) (Stoffregen, 1987). Laterally the progressive neutralization of fluids by reaction with the rocks generates a domain with \( \text{pH} > 2 \). This in turn results in much less depletion due to the immobility of aluminum and thereby the formation of alunite (Fulignati et al., 1998). A further neutralization of the fluids favors the formation of kaolinite at lower acidity (4 < \( \text{pH} < 6 \) ) in an intermediate argillic alteration regime (Boyce et al., 2007). Rock permeability as well as the degree of alteration increases toward the center of the hydrothermal activity, in agreement with the study by Piochi et al. (2015). As a consequence, this should reduce the risk of pressurization within the shallow subsurface. Alteration at greater depth (Mormone et al., 2011) and its effect on the permeability by argillic alteration and by vein and pore filling precipitation might be a process of higher importance concerning volcanic unrest. But still the risk of surficial phreatic events can’t be excluded. Pressurization can also be caused by an increased fluid supply deriving from the hydrothermal system, which could in turn exceed the outgassing capacities and result in a phreatic eruption.

Our study investigated the processes of such an event and highlights the effects on the rocks present at the main hydrothermal sites of Campi Flegrei. Further, rocks dominated by secondary precipitated alunite and amorphous silica produce an increased fraction of very fine particles during fragmentation. Ash particles in this size range and especially those possessing silica- and alumina-rich compositions constitute a high potential for respiratory diseases and their dispersion would represent a serious health hazard on a local scale. The mineralogy of host rocks should therefore be considered for modeling of eruptions in hydrothermally active sites and taken into account for hazard assessment.

**Fig. 14.** Conceptual model for the formation of near surface high-sulfidation alteration. pH, fluid temperature and composition control the development of alteration zones with increasing distance to the main fumarolic conduit. A highly permeable, acidic core characterized by amorphous silica is laterally replaced by a zone of alunite and amorphous silica. Successive neutralization of the fluids promotes the formation of kaolinite. Rock permeability as well as the degree of alteration increase toward the center of the hydrothermal activity. Modified after Robb (2005).


