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Secondary hydrothermal minerals in buried rocks at the Campi Flegrei caldera, Italy: a possible tool to understand the rock-physics and to assess the state of the volcanic system

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Abstract

The distribution of the alteration assemblages and the related physico-chemical changes induced in the rocks with depth, may provide useful information on the state of the system. Drillholes are the only way to define hydrothermal alteration depth-profiles in variable geological contexts. Deep drillings exploiting programs were conducted since the 1970's by the Agip-Enel Joint Venture in the Quaternary Campi Flegrei caldera (southern Italy), where a geothermal system has been active since at least historical times. New macroscopic and microscopic investigations were performed on selected samples made available by Agip in order to: 1) define the precursor lithology, 2) describe the relationships among texture, mineralogy and depth of the studied core samples and 3) examine the character of the secondary minerals and their distribution with depth and temperature. The new data are integrated with physical properties and elastic parameters of cored rocks, as well as structural information and field data, all available from the physical, seismological, geodetical and volcanological literature. The depth-related multi-parameters profiles provide evidence on the different behavior of the buried rocks beneath the Licola 1, Mofete and San Vito 1 areas, sited in three structurally different sectors of the caldera. The features of the hydrothermally altered rocks are a key to interpret the heterogeneities of the Campi Flegrei substratum, as deduced by velocity, attenuation and scattering P- and S- waves tomography. The time and space distribution of both the eruptive vents and the extruded magma volumes are consistent with the results of our analysis. Therefore, we interpret the observed Campi Flegrei geothermal system as a response to the distribution of volcanic activity in two structurally distinct sectors of the caldera. The central-eastern sector, where the San Vito 1 well was drilled, represents the preferential pathways for both gas escape and magma ascent at least since 8 kyrs, in contrast with the other sites of the caldera where eruptions occurred with minor frequency and magnitude.

Key words: Campi Flegrei; elastic proprieties; geothermal system; hydrothermal minerals; volcanism.

Introduction

Secondary (hydrothermal) mineral phases change the primary mineral assemblages and chemistry of rocks (e.g., Browne, 1978), as well as their physical features, and, in particular, their elastic behaviour (e.g., Zamora et al., 1994). In active volcanic areas, high-temperature, saline and deep-sourced fluids normally induce devitrification of volcanic glass, mineral phases dissolution and re-crystallization of new mineral phases in buried deposits (Browne, 1978). The main factors affecting these processes are i) fluids temperature and chemistry, and ii) the original rock type, porosity and permeability, in addition to the time interval of fluid circulation. Notably, all these factors strictly depend on the architecture of the volcanic system, especially the structural setting which determines the fluids pathways. Therefore, knowledge of the depth distribution of hydrothermal mineral phases, together with data on aquifer location and chemistry, is an important topic in studying a volcanic area and the behaviour of its associated geothermal system, constraining geophysical investigations, and, ultimately, providing information for the possible exploitation of geothermal energy and/or mineral systems (Browne and Ellis, 1970; Giggenbach, 1991; Pirajno, 1992; Barbier, 2002).

Areas of geothermal activity are common on Earth. In Italy, they are mostly associated to volcanic systems located along a NW-trending belt (Figure 1a) (Bertini et al., 2005). From North to South, we mention, for example, the Larderello (e.g., Batini et al., 2003) and the Latera caldera (e.g., Cavarretta et al., 1982) in Tuscany, the Campi Flegrei caldera (e.g., Guglielmetti, 1986; Rosi and Sbrana, 1987) and Ischia island (e.g., Sbrana et al., 2009) in Campania, Vulcano (e.g., Aubert et al., 2007) and Pantelleria (e.g., Gianelli and Grassi, 2001) islands, in Sicily. In particular, the active Campi Flegrei caldera (Figure 1b) hosts a geothermal system, which has been investigated for more that 40 years by drilling (Rosi et al., 1983; Guglielmetti, 1986; Agip, 1987; Rosi and Sbrana, 1987; De Vivo et al., 1989). Deep wells intersected the shallow crust (Figure 2) reaching depths ranging from 1600 m and 3000 m b.s.l. and showing a particularly interesting and complex geological setting. Notably, they evidenced the presence of high geothermal gradient and aquifers with temperature of > 350 °C and salinity of up to 20 wt% at depths of about 2700 m (Guglielemetti, 1986). Cored samples were the object of diverse studies (e.g., Agip, 1987; Rosi and Sbrana, 1987; De Vivo et al., 1989; Zamora et al., 1994; Caprarelli et al., 1997; Vanorio et al., 2002; Giberti et al., 2006; Vanorio et al., 2005) offering an accurate and detailed, albeit inhomogeneous and discontinuous, representation of the rock types and structure beneath the Campi Flegrei caldera, providing a powerful database for current and future research. In particular, Rosi et al. (1983), Rosi and Sbrana (1987), De Vivo et al. (1989) and Caprarelli et al. (1997) published on the following: i) the litho-stratigraphy, ii) the thermal gradient, iii) the distribution with depth of the main alteration mineral assemblages, and iv) the fossil temperature and salinity of fluid inclusions. Zamora et al. (1994), Vanorio et al. (2002) and Vanorio et al. (2005) determined some of the physical properties of core samples, mainly density and porosity and, in some cases permeability and P- and S-waves velocity. However, most recent literature focused on the

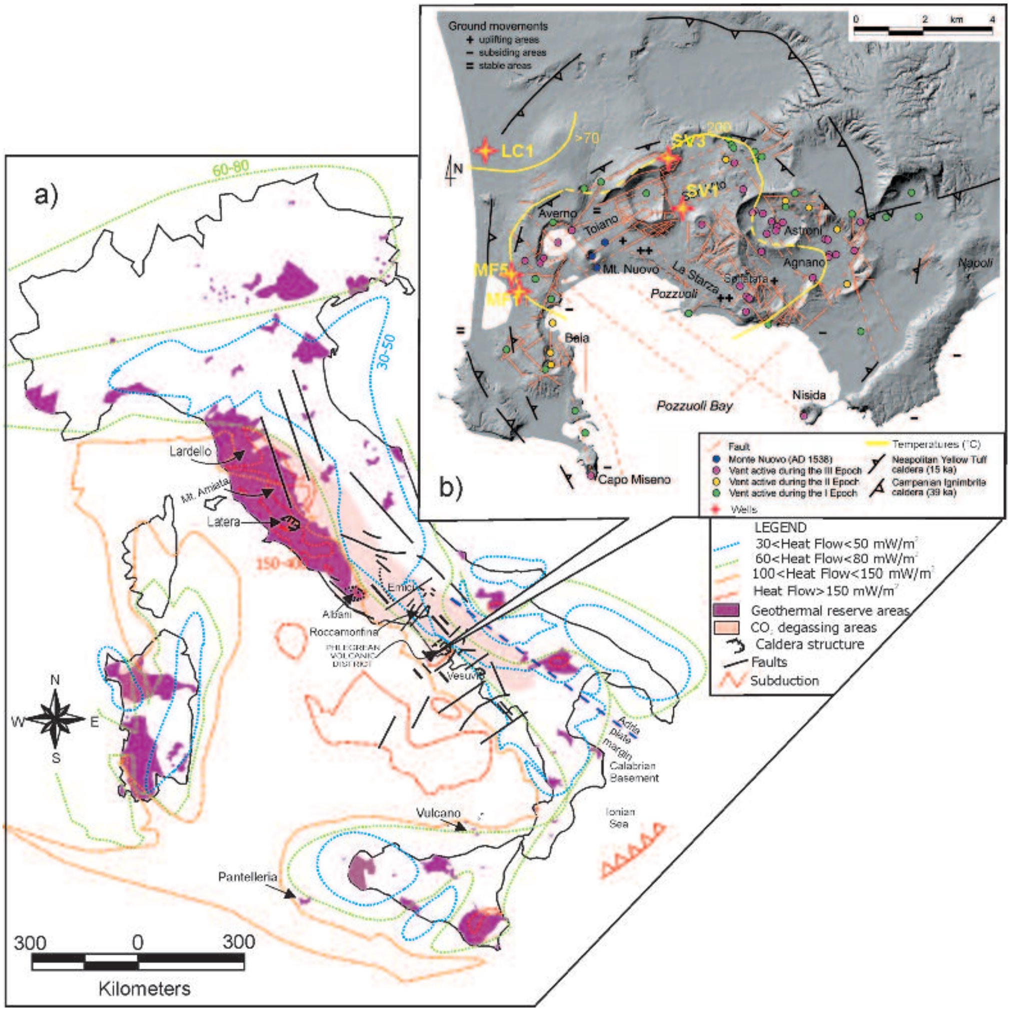

Figure 1. a) Geological sketch map of Italy showing the location of the main geothermal fields (modified from Carella et al., 1985 and Bertini et al., 2005), the CO_2 emission area (modified from Frezzotti et al., 2009), the distribution of the heat flux (mW/m^2; modified from Della Vedova et al., 1991), main tectonic trends and the Campi Flegrei site (modified from Acocella et al., 1999). b) Structural map of the Campi Flegrei caldera with the eruptive vent locations in the last 14.9 ka (from Di Renzo et al., 2011), distribution of the temperature > 100 °C at 1000 m b.s.l. (modified from Corrado et al., 1998), area of stability or ground movements (from Di Renzo et al., 2011) and the location of Agip's (1987) boreholes.

reconstruction of the history of the volcano and of its magmatic feeding system (e.g., Arienzo et al., 2010; Vilardo et al., 2010; Di Renzo et al., 2011; Mormone et al., 2011; and references therein). Other authors investigated the caldera's active geothermal system focussing on water tables and/or fumaroles emissions characteristics (Valentino et al., 1999; Chiodini et al., 2001;

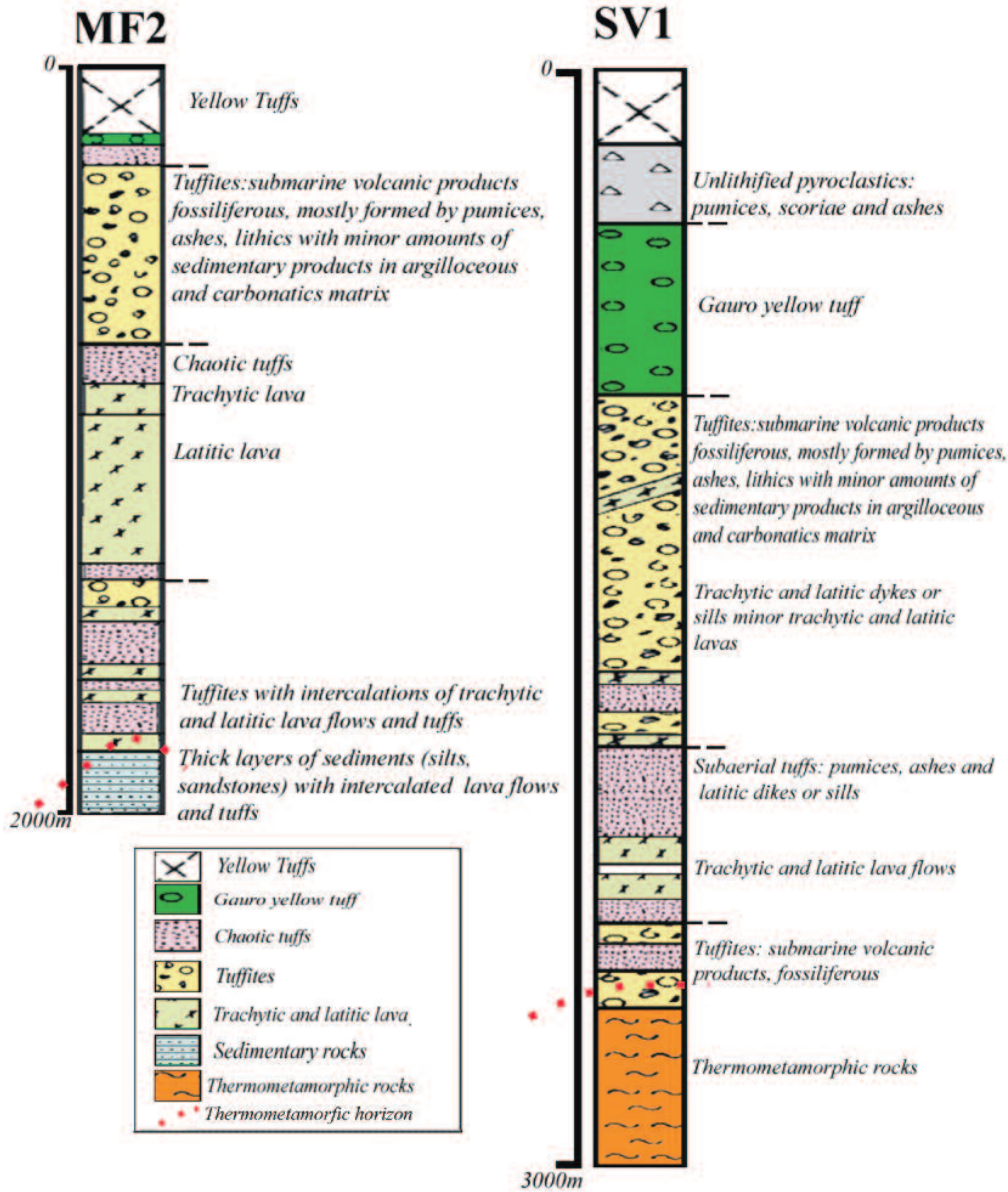

Figure 2. Representative well stratigraphy at the Mofete and San Vito 1 sites (from Rosi et al., 1983).

Valentino and Stanzione, 2004) or thermal and flux simulation modelling (Gaeta et al., 1998; De Lorenzo et al., 2001; Troiano et al., 2011 and references therein). Geophysical investigations allowed information on the main crustal structure (Zollo et al., 2008; Trasatti et al., 2011) through the use of velocity (Aster et al., 1989; Judenherc and Zollo, 2005; Battaglia et al., 2008), attenuation (De Lorenzo et al., 2007; De Siena et al., 2010) and scattering (Tramelli et al., 2006) seismic tomography.

This paper presents the results obtained from optical and electron microscopy on 22 core samples, drilled by Agip for geothermal energy research (AGIP, 1987). Our results were firstly integrated with those of the previously cited literature in order to augment our knowledge on the secondary mineralogy and its relationship with the original rock textures and depth distribution. Then, the integration of litho-stratigraphic, hydrothermal alteration distribution and temperature data with physical parameters and P- and S- wave velocities and Vp/Vs ratios by selected physical and seismological studies (Zamora et al., 1994; Tramelli et al., 2006; Battaglia et al., 2008; De Siena et al., 2010) allowed the reproduction of multi-parameters depth-related profiles (Figure 3). Finally, volcanological and structural data (Di Vito et al., 1999; Orsi et al., 2009; Vilardo et al., 2010; Di Renzo et al., 2011) and, in particular, the vents location and the volume of erupted magmas at Campi Flegrei in the past 14.9 ka, allow to present a model corroborating the idea that the caldera consists of two distinct sectors (Figure 4).

Geological and geophysical backgrounds

The Campi Flegrei caldera is a ~ 10 km diameter collapsed area. Its volcanism is older than 60 ka (Pappalardo et al., 1999) and caldera collapses occurred during two catastrophic eruptions at 39 ka (De Vivo et al., 2001) and 14.9 ka (Deino et al., 2004). At least 73 explosive eruptions took place within the caldera after the second collapse (Orsi et al., 2009; Di Renzo et al., 2011 and references therein). The last eruption formed the Monte Nuovo cone in 1538 A.D. (Rosi and Sbrana, 1987; Di Vito et al., 1999). The Campi Flegrei's rocks are generally trachytic to trachy-phonolitic in composition and mineralogically dominated by alkali (mostly potassic)-feldspars, plagioclase, Fe-oxides, apatite, diopside and biotite (e.g., Pappalardo et al., 2002 and references therein). Olivine phenocrysts are not common, leucite and sodalite are sporadically present and quartz is only found as xenocryst (Rosi and Sbrana, 1987). Least-evolved magmas were occasionally erupted during low-magnitude explosive events along regional faults (Di Renzo et al., 2011 and references therein). Chemical and mineralogical features of volcanic rocks derived from polybaric evolution processes in magmas stored within the crust (e.g., Pappalardo et al., 2002; Di Renzo et al., 2011; Mormone et al., 2011).

Based on the most recent research, the Campi Flegrei magmatic system consists of a deeper reservoir identified at about 7.5 km from large amplitude seismic reflection at the top of an extended melt-bearing rock formation (Zollo et al., 2008). Notably, this system coincides with the ~ 350 MPa entrapment pressures of melt inclusions within the host-olivine from the 18 ka Solchiaro 1 eruption products (Mormone et al., 2011). This suggests a long-lived deep magma reservoir beneath the Gulf of Pozzuoli (see Figure 1b). The chemical features of the melt-inclusions indicate a trachybasaltic composition and CO_2-dominated gaseous phases for the magma in this reservoir (Mormone et al., 2011). At shallower depth, less than 3 km, seismic data do not evidence magmatic bodies larger than 1 km^3 (Zollo et al., 2008). This contrasts with results from melt inclusions studies suggesting that magma storage frequently occurred in the pressure range 150-to-40 MPa before several explosive eruptions of the last 39 ka (Cecchetti

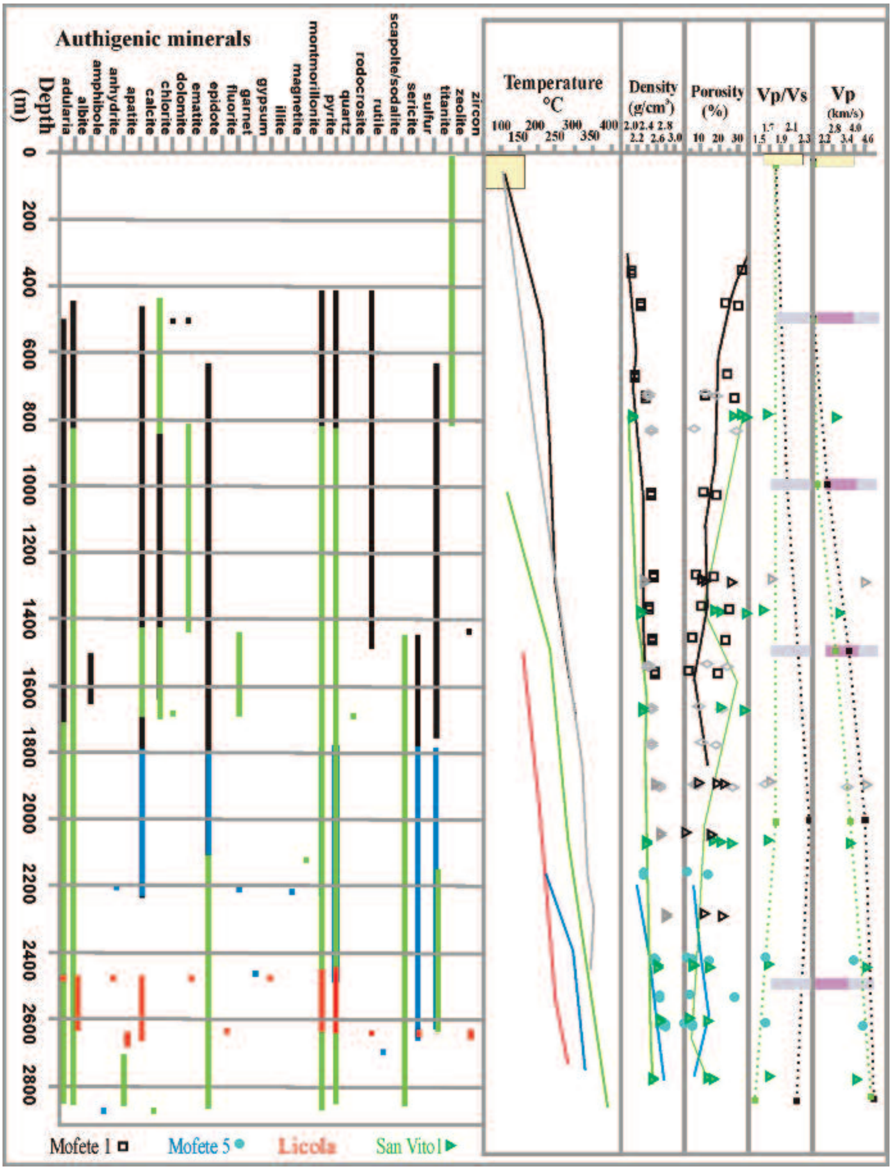

Figure 3. New data on the main hydrothermal mineral assemblage defined and observed (Figure 5) in rocks cored at the Mofete 1, Mofete 5, Vito 1 and Licola 1 wells. The last five column diagrams on the right show profiles of temperature, density, porosity, Vp, Vp/Vs as derived by literature (De Vivo et al., 1989; Zamora et al., 1994; Vanorio et al., 2002; Vanorio et al., 2005; Battaglia et al., 2008) data. For comparison and completeness, these columns also report data for San Vito 3 and Mofete 2 wells (open black triangles and open gray rhombus, respectively). Note: squares are Vp and Vp/Vs from active seismology; the yellow box indicates data on outcropping rocks, the pink boxes include elastic parameters measured on the outcropping rocks (tuffs and lavas, dark and bright pink colour, respectively) at room temperature and under indicate pressure (i.e., depth).

et al., 2003; Marianelli et al., 2006; Arienzo et al., 2010; Mormone et al., 2011). Besides, petrological studies (Di Renzo et al., 2011) corroborate the hypothesis that the Campi Flegrei magmatic system is formed by two reservoirs, the shallower of which, located at 6-4 km of depth, is discontinuous and characterized by small trachy-phonolitic magma pockets.

The deeper system is likely hosted by a Hercynian-type crust on the basis of xenoliths recovered in the least evolved magmas (Pappalardo et al., 2002); whereas the uppermost crust is not well-defined. In particular, the Miocene limestone and sandstone sequences that should be present as they constitute the nearby Apennine Chain and are revealed by seismic investigations in the majority of the Campanian Plain (Piochi et al., 2005 and references therein), have been not recovered beneath the caldera. Limestone xenoliths are not reported in the current literature. The stratigraphy of the uppermost 3000 meters has been directly defined thanks to drilling programs by Agip (1987) and synthesized in various papers (Rosi et al., 1983; Guglielmetti, 1986; Rosi and Sbrana, 1987; Caprarelli et al., 1997). We use the most representative one (Figure 2) from Rosi et al. (1983). These authors suggest various pumiceous, tufaceous, marine tuffites and lava flows overlying thermally metamorphosed rocks at > 2500 m b.s.l. Generally, thin further sandstone levels occur deep in the holes. According to the Authors, the sequence drilled in the San Vito plain mostly resulted by caldera filling phenomena. Furthermore, the thermal metamorphism was interpreted as due to the proximity of hot magma batches. Moreover, in contrast with the Mofete wells, for the San Vito 1 well Rosi et al. (1983) also show the presence of several intrusions deeper than 1500 (Figure 2).

Present fumaroles and thermal springs are the main evidence of the hydrothermalism that likely originated the well-developed alteration mineral zoning (Rosi et al., 1983; Rosi and Sbrana, 1987; Caprarelli et al., 1997; Guglielmetti, 1986). Fumaroles concentrate within and nearby the Solfatara crater where they are associated to at least 1500 tons/day of CO_2 emissions (Chiodini et al., 2001). Thermal springs are widespread in the caldera and are linked to shallow and locally discrete aquifers. The drilling programs carried out by Agip (1987) showed the presence of at least three main aquifers in the Mofete area (Guglielmetti, 1986), with the deepest at about 2300 m, showing the highest salinity. The chemical composition of thermal waters and fumaroles suggest that meteoric and sea water from the nearby Gulf of Pozzuoli (e.g., Cortecci et al., 1978; De Vivo et al., 1989) are the main sources of circulating fluids. Magmatic gases contribute to the composition of shallower fluids (e.g., Baldi et al., 1975; Bolognesi et al., 1986), also supply most of the carbon dioxide (e.g., Caliro et al., 2007) and are suspected to be the main engine for uplifting processes episodes (Todesco et al., 2010; Troiano et al., 2011). Ground deformation occurring continuously since Roman times is characterized by subsidence and uplift affecting the entire caldera depression. The main uplift episode preceded the Monte Nuovo eruption, whereas minor and intense episodes also occurred in 1969-72 and 1982-1984, determining a net vertical ground deformation along the Pozzuoli coast of 3.5 m. More than 16,000 earthquakes occurred in the Solfatara area during the 1982-84 unrest episode (Barberi et al., 1984; Aster et al., 1989; D'Auria et al., 2011).

Volcanological and structural data

The structural setting of the Campi Flegrei is the result of complex interactions between regional tectonics and volcanism (Figure 1b). Regional faults have strike mainly NW-SE and NE-SW (Rosi and Sbrana, 1987; Orsi et al., 1996). Faults and eruptive fissures within the youngest caldera show variable orientations (Di Vito et al., 1999; Vilardo et al., 2010; Di Vito et al., 2011): i) NW-SE and NE-SW trends on the central-eastern side, and, ii) NE-SW and N-S in the central-western side. Satellite images (Vilardo et al., 2010) show extensive deformation within the caldera and evidence that the maximum horizontal strain affects its central-eastern sector, where recent volcanism (3.8-4 ka), active degassing and seismicity are concentrated. These authors also note in the Pozzuoli centre, the presence of a high P-wave seismic attenuation and S-wave polarization oriented following the N-S direction (see Figure 1 in Vilardo et al., 2010).

We strongly support the Vilardo et al.'s model and, additionally, we highlight that 76% of the vents in the past 15 ka opened in the central-eastern sector of the caldera (Figure 1b). We also evidence that in the past 15 Ka about 4 km^3 of magma has been extruded in the central-eastern sector, whereas only 1 km^3 on the opposite side (Figure 4). Notably, the western sector was characterized by highly-evolved trachytic to trachyphonolitic magmas and low-intense explosive, phreato-magmatic eruptions. Conversely, the eastern sector was the site of plinian to strombolian, magmatic to phreatomagmatic events that produced rocks with variable evolution degree, from shoshonite to trachyphonolite.

On the basis of the above, Agip's wells were drilled in three different structural locations (Figure 1): 1) the Licola 1 well is external to the caldera depression, located nearby its north-western margin (Orsi et al., 1996), 2) the Mofete and San Vito 3 wells were drilled in the proximity of the structural margin of the Neapolitan Yellow Tuff caldera and 3) the San Vito 1 well is clearly within the caldera. In particular, the Mofete 1, 2, 5 wells are along the western caldera margin, dominated by N-S trending fault system; the San Vito 3 is in proximity of the NNW caldera boundary, where low-evolved magmas were erupted, likely along regional faults. Whereas, the San Vito 1 is in the eastern sector, characterized by recent intense and frequent volcanism. It is also the most proximal to the city of Pozzuoli, subject to the maximum uplift both during the last bradyseismic events (Orsi et al., 1999) and the long-term ground deformation of the caldera floor (Di Vito et al., 1999).

Seismological data

The knowledge of the very complex subsurface structure of the Phlegraean caldera derives from several geophysical analyses that were performed in this area. We are mainly interested on seismic wave velocities (Aster et al., 1989; Judenherc and Zollo, 2005; Battaglia et al., 2008), attenuation (De Lorenzo et al., 2001; De Siena et al., 2010) and scattering (Tramelli et al., 2006) tomographies that provide information about the elastic properties of the medium and are strictly related to the physical properties of the rocks. Most of the seismic investigations used the high number of seismic traces recorded during the 1982-1984 bradiseismic event. De Siena et al. (2010) analyzed these seismograms to define the attenuation properties of the travelled medium. Temperature, presence of fractures and type of fluid filling rock voids affect the seismic wave attenuation, calculated from the ratio of the peak strain energy stored in a volume, respect to the energy lost in each cycle. Tramelli et al. (2006) analyzed the codas of the same seismograms to define the scattering properties of the medium. These properties principally depend on the rock heterogeneities (mainly, fracture), the size of which can be determined from the frequency analysis in the coda waves. The scattering tomography is expressed in terms of relative scattering coefficient that can be interpreted as the mean free path of the seismic ray, i.e., the mean length that the seismic ray can travel before intercepting a scatterer. Finally, Battaglia et al. (2008) merged the passive seismic signals derived from > 15000 micro-earthquakes with

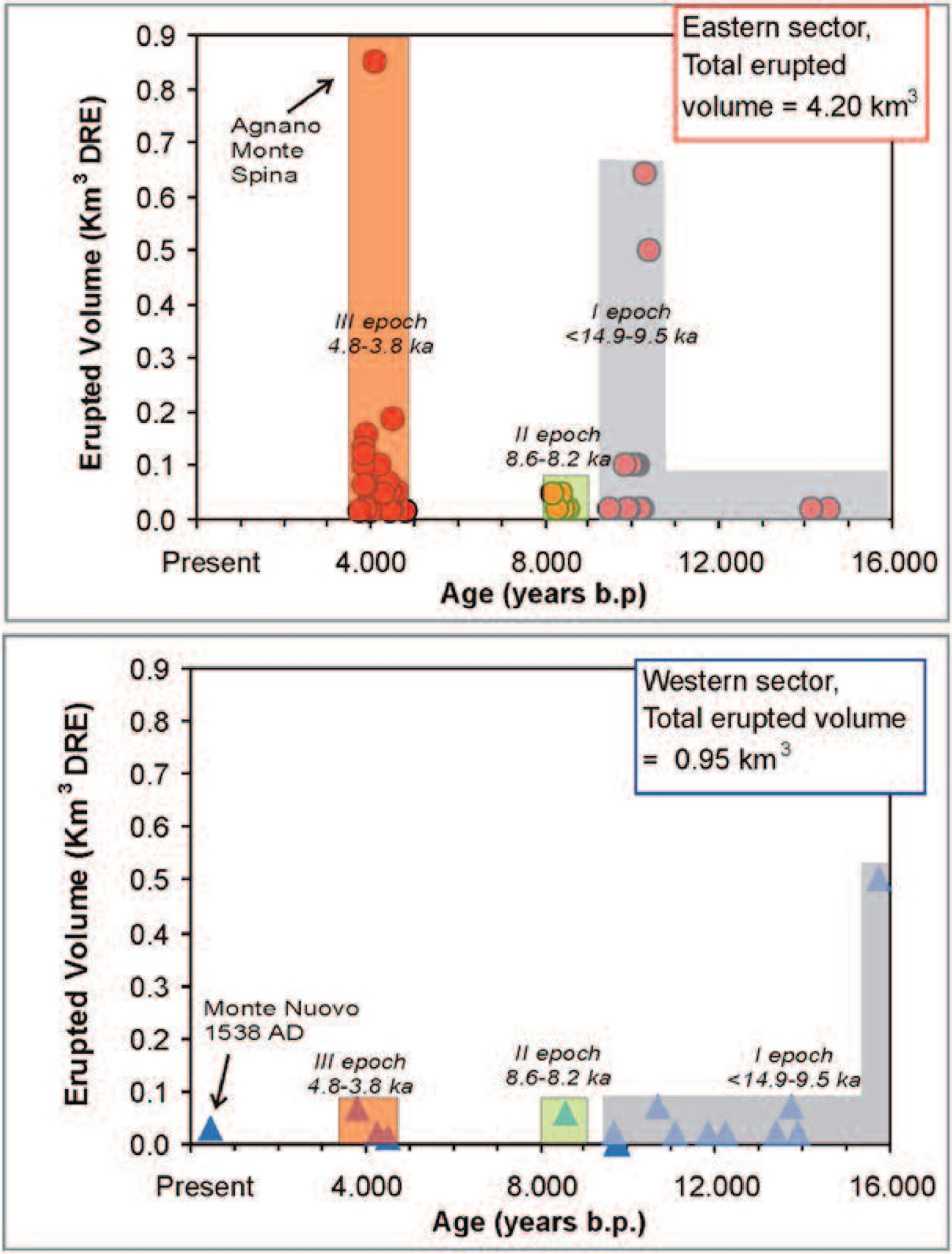

Figure 4. Volume (km^3 DRE) of products erupted through time in the past 14.9 ka in the two structurally and dynamically different sectors of the Campi Flegrei caldera. Shaded areas envelop the epochs of the volcanism, following Di Vito et al. (1999): I epoch between < 14.9 and 9.5 ka, III epoch between 8.6 and 8.2 ka, and III epoch between 4.8 and 3.8 ka, as indicated on the diagrams. Arrows indicate the highest magnitude and the last eruptions of Agnano Monte Spina and Monte Nuovo, respectively. See text for further details.

those from active seismology. These latter signals were produced by the 1528 shots of the 2001-SERAPIS experiment. The authors described the Vp and Vp/Vs ratio that characterize the medium in a volume of 18 x 18 x 9 km starting from 0.5 km a.s.l., with a node spacing of 0.5 km. Interestingly, the Vp/Vs values were long recognized as lithological indicators (Wang, 2000 and references therein). The results obtained by Battaglia et al. (2008) are represented in Figures 3 and 6.

An arc-like positive Vp values anomaly defines the southern caldera border, offshore, from Capo Miseno to Nisida (Battaglia et al., 2008). The measured Vp of 3.5-4 km/s is higher than the values of 2.5-3 km/s typically of the caldera filling sediments present at the centre of the Gulf. Here, a shallow (1-2 km depth) layer with high Vp/Vs ratio (2.3-2.7) overlies an area of anomalously low Vp/Vs ratio (1.2-1.4), between 3 and 4 km b.s.l. This low Vp/Vs volume almost attenuates P and S waves (De Siena et al., 2010) and, based on the distribution of the high seismic waves attenuation, likely extends in the Pozzuoli-Solfatara area. A further high attenuation rock volume, for both P and S waves, occurs beneath Pozzuoli, between 0 and -3 km, beneath the area between Mofete and Monte Nuovo, between -0.5 km and -2.5 km, and beneath Agnano, between -1 km and -3 km. The medium seems to be more homogeneous below -3 km. The on land caldera border is a highly heterogeneous volume, clearly identified by the scattering tomography (Tramelli et al., 2006). Scattering volumes also occur below the Solfatara crater and offshore of Baia. Based on the frequencies of scattering, the Authors suggest that the two volumes characterize for the fractures size, being larger offshore of Baia. This latter highly scattering structure clearly defines a NW-SE elongated shape in the Gulf of Pozzuoli and coincides with the western 1982-1984 seismogenetic volume (Orsi et al., 1999; D'Auria et al., 2011).

Petro-physics

Strategy and Methods

We focus on the Mofete 1, Mofete 5, San Vito 1 and Licola 1 wells, according to the structural position defined before: i.e., along the structural boundary, within the depression and outside of the caldera. We exclude from our analysis the rocks from the San Vito 3 well, which show both a comparable position and a transitional character, in term of stratigraphy and mineralogy, to the Mofete wells (Rosi et al., 1983; De Vivo et al; 1989; see also discussion and conclusions).

Core samples taken from variable depths in the Mofete 1, Mofete 5, San Vito 1 and Licola 1 wells, given directly by Agip were analyzed. Conventional 30 μm- thin sections of the selected samples were prepared and studied by using a petrographic microscope ZEISS Axioscop 40 equipped with reflection light (Istituto Nazionale di Geofisica e Vulcanologia, Napoli). Primary and, secondary (hydrothermal) mineral phases were identified and/or confirmed by using the SEM-EDS JEOL JSM 5310 electron microscopy installed at the Centro Interdipartimentale per analisi geomineralogiche (CISAG) – University "Federico II" of Napoli, Italy, equipped with energy dispersive system and operating at 15kV. Most useful for petrologic application was the acquisition of images from back scattered (BSEM) to establish the textural features and the minerals relationships. Clay minerals types are very difficult to determine, due the small crystal dimension and variability; therefore, their depth-distribution was also extrapolated from published data and not directly used in our analysis. Small grains, particularly when associated, pyrrhotite and pyrite may confused under the microscope and their distribution with depth requires X-ray diffractometric analyses.

Results

Our results are consistent with those already published in the literature showing a well-

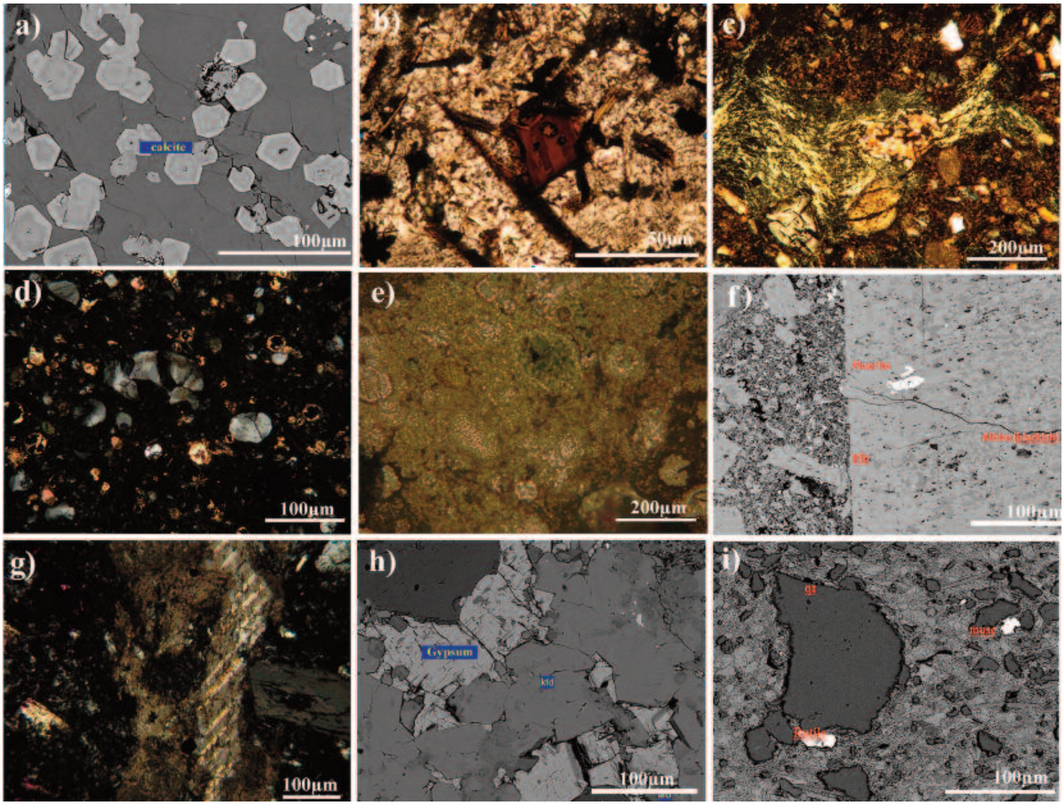

Figure 5. (a) Calcite grown in feldspar fractures. Back-scattered electron image (sample SV1 1713); (b) Amphibole and brown biotite flakes in the bulk matrix (sample SV3 2864); (c) Chlorite plates crystallized in fractures (sample MF1 402); (d) Rounded leucite grains diffused in the groundmass (sample MF1 1044); (e) Authigenic chlorite developed as plates in the cavities (sample MF1 1044); (f) Primary alkali feldspar with apatite and fluorite. Back-scattered electron image (sample MF1 617); (g) Calcite grown within rocks fractures (sample MF1 1714); (h) Gypsum crystals intergrown with primary alkali feldspar (sample MF5 2489); (i) Quartz grain associated with muscovite and rutile relict. Back-scattered electron image (sample LC1 2634).

developed and depth-dependent mineral alteration zoning related to the increasing-temperature of the hydrothermal system. However, our investigations further detail the mineralogical assemblage of core samples, evidencing some accessory minerals, and textural fabric of rocks not previously reported. Figure 3 shows the observed distribution of hydrothermal minerals in the San Vito 1, Mofete1, Mofete 5 and Licola 1 boreholes. This figure also reports selected physical parameters from seismological investigations (Battaglia et al., 2008) and laboratory measurements (De Vivo et al., 1989; Zamora et al., 1994). A detailed description of the obtained results is reported below for the three areas selected for this study including the San Vito 1, Mofete 1, Mofete 5 and Licola 1 deep drillings.

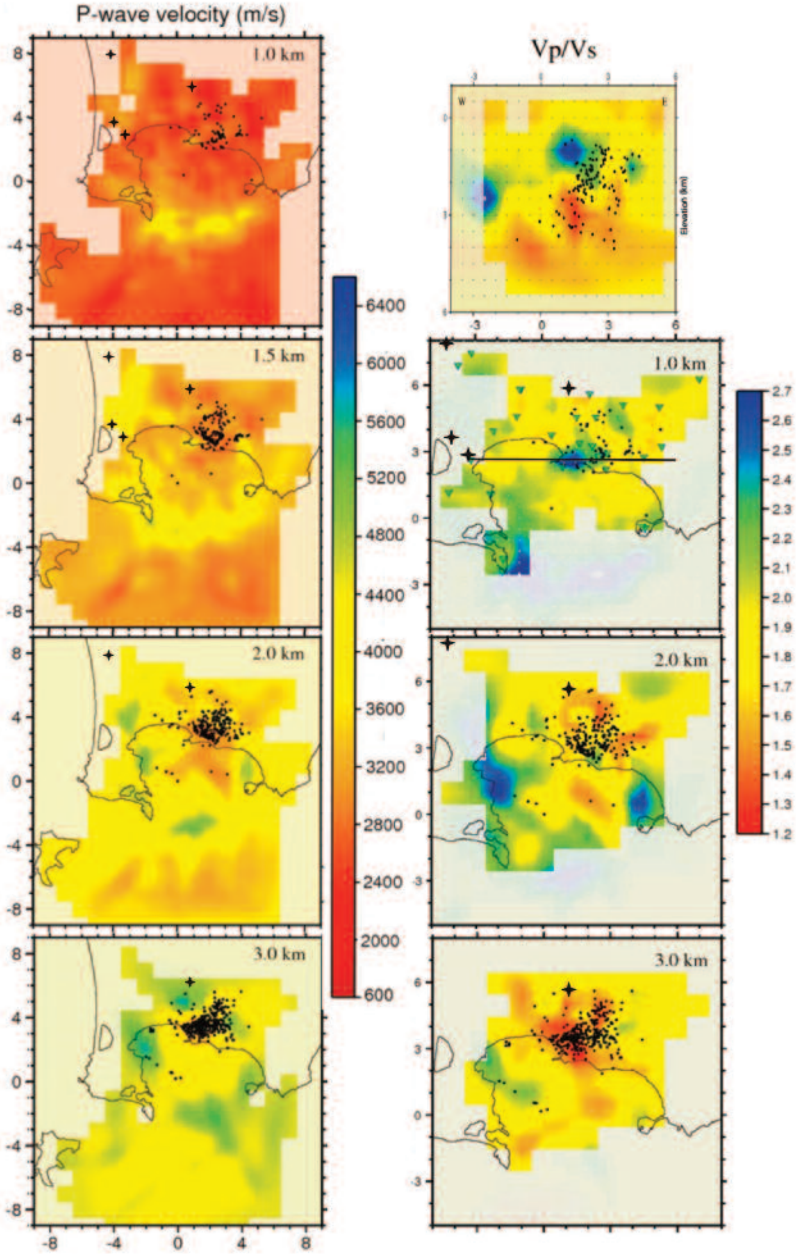

Figure 6. Horizontal and vertical section (top right) of the P-wave velocity model (left panels) and Vp/Vs ratio (right panels) modified from Battaglia et al. (2008). The wells described in the article are represented by the black crosses. The black line shown in the second right panel shows the location of the vertical section showed above. Black dots and green triangles indicate the earthquakes and stations, respectively, used for the tomography.

San Vito 1 well

Selected samples, listed according their depth from bottom to the top of the San Vito 1 borehole, have revealed the following features: at depths < 2130 m, rocks are represented by altered volcanic tuffs and volcaniclastic tuffites with a reddish or greenish ashy-to-sandy matrix. In this matrix we recognized plates of chloritized, elongate pumice fragments, variably crystallized, vesicular scoriae and poorly-vesicular lithic clasts, as well as loose crystals. The fine matrix is strongly altered to by clay minerals, very difficult to define. In some instances alteration is possibly represented by hematite or limonite, as testified by the brown-reddish colour in reflected light of some prismatic-fibrous minerals. Isolated broken plagioclase and green pyroxene are also present, together with biotite and magnetite in the microlite groundmass. Quartz and calcite are widespread, commonly filling voids. Pyrite occurs as isolated microcrysts and locally as aggregates in rock voids. At the shallowest depth (804 m), quartz (as tridimite) and zeolites were recognised also within rock voids. Other neogenic minerals that occur at shallower depths are: feldspar, hematite, adularia, clinopyroxene, dolomite, titanite, spinel, epidote. They occur from below 2130 m. Epidote crystals are observed in association with calcite at 1713 m (Figure 5a). EDS analyses also indicate the presence of rodocrosite and garnet.

Rocks intersected at greater depths, became more massive and micro-crystalline, with a homogenous texture and structure. At 2683 m the rock shows a fluidal-intersertal groundmass made of fine microlites mainly represented by plagioclase, alkali feldspar and biotite phenocrysts. Euhedral feldspars are generally observed in clusters (glomeroporphyritic texture), associated with quartz grain and a crystal with high interference colours, probably epidote. The opaques are represented by pyrite, pyirrhotite and magnetite mostly in the veins. At 2862 meters, lithologies appear to be re-crystallized or a hydrothermally altered sedimentary deposit. It consists of well-sorted grains of quartz and feldspars that mostly concentrate within voids. Chlorite is widespread and occurs in association with feldspar, pyroxene, epidote, hematite, sulphides. At depths of about 2864 m, rocks are either effusive or subvolcanic and characterized by elongated brown and squared black crystals in a white groundmass. Crystals have an isotropic and sub-idiomorphic structure and consist of nearly equigranular feldspar grains in the bulk mass, biotite (up to 15%), amphibole (like Fe-actinolite, up to 10%; Figure 5b), opaques (< 10%) and rare pyroxene. No glass has been identified. Feldspar is generally euhedral to subeuhedral plagioclase, includes abundant inclusions. Biotite occurs either as yellow-brown elongated and as tabular reddish-brown grains. Opaques minerals are mostly piryte and/or pyrrhotine and magnetite.

Mofete 1 and 5 wells

In the first 250 m, the Mofete 1 well intersected for yellow tuffs. Between 402 and 617 m, we have identified fossils-bearing volcanoclastic rocks. In particular, under the optical microscope these rocks are characterized by loose crystals reaching up to several mm in size and including plagioclase, pyroxene, biotite, rare magnetite, as well as fragments of pumice, scoria and lava. Pumices, scoriae and lavas fragments show variable degree of alteration, but in places maintaining their primary glassy and vesicular texture. The secondary paragenesis of these shallow pyroclastic deposits consists mainly of chlorite within fractures (Figure 5c) and calcite. Sulphides are generally rare (< 5% by area). Based on fossils evidence, the volcaniclastic tuffs were deposited between 79 and 200 m b.s.l. At 1044 metres, the cored rock consists of a mixture of greenish trachy-tephrite lava and tuff fragments with many Sr and Ba rich- leucite phenocrysts altered to analcyme (Figure 5d); the bulk matrix also includes plagioclase and pyroxene. Calcite and chlorite plats partially fill the different vacuoles (Figure 5e). Locally there are minute (< 10 μm in size) zircon, epidote and Cu-Fe sulphide grains as relict minerals. These mineral phases also occur in the rocks cored at 617 m where EDS analyses reveal the presence of titanite, quartz, epidote (allanite), fluorite apatite and albite (Figure 5f). At 1603 m the cored rock is a sandstone with intercalated siltstone laminae, showing quartz and feldspar grains as the main phenoclastic components. In its matrix, fibrosis crystals ascribable to the sericite group (muscovite) are diffuse. Pyrite is present in small amounts and is represented by minutes cubic crystals. Sometimes small euhedral horneblenda crystals appear. The matrix has a crystallized calcite vein, cutting through the entire core sample.

In the Mofete 5, tufaceous rocks occur at 1714 m. They are inhomogeneous and consist of an altered ash matrix with feldspars and calcite; the latter is the dominant mineral phase within fractures (Figure 5g), together with rare adularia and quartz. A crystalline aggregate consists of quartz and calcite, with the latter being more dominant. In places, within voids, a radial aggregate of a greenish mineral is probably chlorite. Pyrite is the dominant opaque mineral (> 5%). Between 2222 and 2225.8 m homogenous latite-trachitic lavas with a fluidal texture were recognized. We also identified feldspar and diopside as primary crystals. Calcite and chlorite dominate the neogenic (alteration) assemblage. Sulphides and apatite are also common, whereas other phases include quartz, sericite, titanite, magnetite, dolomite, epidote, garnet and adularia. The sample cored at 2489 m shows a re-crystallized microgranular groundmass that consists predominantly of quartz, alkali feldspars (adularia) and gypsum (Figure 5h). The pyroxenes are subeuhedral to anhedral and generally altered in the central part of the crystals. No calcite has been detected. Pyrite with corrosion margins, gypsum, and REE-rich phosphates also occur. At 2695 m an intrusive igneous or re-recrystallized rock has been recovered. Based on EDS investigations, the majority of phenocrysts comprises sodalite and/or scapolite associated with smaller crystals of clinopyroxene and titanite. Quartz is also present. Pyrite/pyrrhotite is present in large crystals with rounded margins (5-10%).

Licola 1 well

At a depth of 2634 m in the Licola 1 drillhole, arenaceous rocks with dark grey silt-to-sandstone interbeds is located between two lava flows. Under the microscope, these clastic rocks show similar secondary minerals namely: quartz and alkali-feldspars as the dominant phases, calcite plates (up to 5-10%), pyrite (< 5%) and widespread fibrous crystals (probably muscovite). EDS-BSEM investigations allowed us also to identify small (< 10 μm) crystals of rutile, zircon, titanite, Cu-Zn-Fe sulphides, in the part characterized by larger-sized crystals, and of apatite, ilmenite, zircon, K-feldspar, and biotite, in the finer matrix (Figure 5i). The two lava rocks are massive, strongly altered, porphyritic, uniform in texture and in primary and secondary paragenesis. The lava intersected at 2476 m consists of acicular feldspar arranged in radial and spherulitic textures. Calcite is widespread as minute grains and as cement in the rock voids. Locally we identified small quartz and opaque minerals; the latter are very few (< 1%) and are represented in order of abundance by pyrite/pyrrhotite and hematite. At 2637 metres, the lava rock has an intersertal-to-holocrystalline texture and is, possibly, a trachytic-latitic sub-volcanic intrusion. The phenocrysts are mainly plagioclase and alkali feldspar accompanied by minor pyroxene, with advanced sericite-type alteration. Other common secondary minerals include pseudo-rhombohedral crystals of calcite and chlorite. The latter occurs as small acicular crystals arranged in spherulitic clusters around the feldspars and calcite. Quartz occurs in association with calcite; with lesser garnet, apatite and scapolite. Sulphides and oxides occurs as exclusively small and disseminated grains of pyrite/pyrrhotite and magnetite/ ilmenite/titanite.

Discussion

The type and intensity of rock alteration and the distribution of secondary mineral phases at the Campi Flegrei caldera strongly depends on the depth of the cored rocks. Figure 3 shows the coherent variation with depth of both hydrothermal alteration and temperature increment. Low temperature minerals (argillic facies), such as zeolites and clay minerals, are in the upper sector of the investigated wells, gradually replaced by moderate temperature minerals, like quartz, calcite and pyrite, which, in turn, deeper in the wells give way to higher-temperature mineral assemblages, like epidote, actinolite and garnet (epidote-actinolite zone). The zeolitizzation process was detected at a depth range 90-800 m and, as shown by De Vivo et al. (1989); namely, 100-800 m in the San Vito 1 and Mofete 5 wells, respectively. The most frequent zeolite phases are phillipsite and chabazite, that generally characterize the welded outcropping tuffs, as reported by de Gennaro et al. (2000).

The temperature of zeolites crystallization is < 200 °C, as generally found in hydrothermal systems (Browne, 1978; Caprarelli, 1997; Schott, 2001; Gebreivot, 2010). This temperature is in agreement with those suggested by presence of clay minerals (Steiner, 1968; Kristmannsdottir, 1975; Elders et al., 1984; Harvey and Browne, 1991; Sener and Gevrek, 2000). These temperatures also coincide with the homogenization temperature measured on fluids inclusions by De Vivo et al. (1989). In particular, smectite is stable at 140 °C, and illite, above 220 °C in active systems (Browne, 1984). Chlorite forming microcrystalline aggregates or plats at the base of the profile (Figure 3), suggests temperatures of 220 °C (Kristmannsdottir, 1975). The argillic facies at greater depth, is replaced by minerals as epidote and calcite. Common minor phases are quartz, chlorite, alkali feldspar and albite. The top of this zone is also marked by a significant increase in pyrite, as tiny cubic crystals grown in fractures, vesicles and veins and widespread in the groundmass, in close association with quartz and calcite. Pyrite forms above 100 °C, is abundant in permeable zones (Reyes, 1990) and is a good indicator for aquifers (Reyes, 1990; Valentino and Stanzione, 2004). In our samples pyrite occurs from about the top to the bottom in San Vito 1 and Mofete 1 and 5 wells, so that the range of the temperatures is in perfect agreement with observations made on other geothermal systems (Browne and Ellis, 1970; Browne, 1978). At depths greater than 1000 m, we identified another highest-temperature mineralogical assemblage represented by epidote, garnet and actinolite. The first epidote occurrence was found at 617 m depth (Mofete 1) at temperature of the 250 °C (De Vivo et al., 1989), although more commonly also occurs at deeper levels, ≥ 1044 and 2130 m in Mofete 1 and San Vito 1 respectively, where the temperature was estimated at around 300-400 °C (De Vivo et al., 1989). Epidote is usually stable in many active geothermal system at temperatures above 200 °C (Browne and Ellis, 1970; Eldes et al., 1979; Cavarretta et al., 1982; Bird et al., 1984), where it generally replaces sodic plagioclase and clinopyroxene (Browne, 1978). Garnet and epidote grains are considered as indicator of high-temperature conditions, over 300 °C (Bird et al., 1984). Based on thin-section studies, it is found in rocks drilled at 1044 m in San Vito 1 and at 2222.5 m in Mofete 5. Garnet is usually not very common in the wells, as it is present only above 320 °C (Browne, 1978). In our samples, it is found as anhedral to subeuhedral crystals infilling vesicles together with quartz and epidote. Fluid inclusion homogenization temperatures indicated values ranging from 300 to 400 °C (De Vivo, 1989), in agreement with Browne (1978). The detected mineralogical association suggests hydrothermal temperatures higher in the Mofete area than in the San Vito 1 well. However, considering temperature measured in the wells and following De Vivo et al. (1989), the Mofete data record a "fossil" hydrothermal mineral assemblage suggestive of cooling of the system. Instead, the San Vito 1 area maintains equilibrium between the actual and the fossil system with temperatures of approximately 400 °C. Therefore, we can hypothesize a stable geothermal system with time in the San Vito 1 area. The San Vito 1 well, unlike at Mofete and Licola 1, typically shows a progressive disappearance of calcite. Moreover, here the garnet appears at a shallower depth with respect to the Mofete wells.

The degree of hydrothermal alteration with depth is related to rock density increase and corresponding porosity decrease (Figure 3). The variation of such features derives from the infilling rock pores by neogenic hydrothermal minerals, quite apart from rock compaction due to burial. Actually, the variable hydrothermal mineral assemblage, with the exception of quartz, is characterized by a density ≥ 2.5 g/cm^3 (Carmichael, 1982; Christensen, 1996), as measurements performed on cored samples (De Vivo et al., 1989; Zamora et al., 1994). In particular, the most widespread authigenic mineral is calcite (~ 2.71 g/cm^3), whereas opaques (> 5 g/cm^3) are the heaviest, hence denser. We calculated that a tuff may increase its density by about 0.3 g/cm^3 due to an amount of 25% of calcite grown in vesicles, fractures and/or been disseminated through the sample. A similar density increment is determined by widespread (10% by area) opaques in the samples. Finally, the re-crystallization of rocks induced by thermal-metamorphic processes causes the nearly complete loss of voids and the appearance of high density minerals typical of higher temperature, producing the highest density values (~ 2.5 g/cm^3) of the deeper drilled rocks. The associated porosity decreases down to $\sim$ 5%; with only some pyroclastics rocks showing higher values, up to 10-15%. Overall rock-physics patterns are comparable with those of sedimentary basins (Magara, 1980; Maxwell, 1964) and are in agreement with a volcanic caldera depression, filled by dominant pyroclastic deposits and affected by hydrothermal fluids circulation inducing changes on the rock properties.

Mineralogical features and physical parameters are compared with Vp and Vp/Vs values from laboratory determinations (Figure 3); in the last column the latter elastic parameters are also compared with those deriving from in-situ seismological experiments. Besides, the high resolution tomographic results do not resolve the entire caldera structure, with Mofete and San Vito areas lying close to the limit of data acquisition, whereas Licola is out of the resolved volume. Consequently some data were just extrapolated using the velocity stratification model employed for hypocenters location (Battaglia et al., 2008; Judenherc and Zollo, 2005). Furthermore, as stated before, the tomography resolution is > 500 m. Therefore, the comparison (Figure 3) is among different rock volumes, with tomographic data averaged over several hundred meters of traversed rocks (Battaglia et al., 2008; Tramelli et al., 2006; De Siena et al., 2010), which are much larger that the decimeter-sized samples measured in laboratory. This problem is overcome by using scattering and attenuation data that allow detection of rock heterogeneities.

The neogenic (hydrothermal) minerals, as well as the high-density and re-crystallized rocks, show waves velocities higher than those measured on the outcropping unaltered rocks. The P-wave velocities profiles, obtained at room pressure and temperature on the cored rocks, fit quite well those derived by active and passive seismology (Figures 3 and 6). Otherwise, the profiles of the Vp/Vs ratios, strictly related to lithology (Wang 2000, and references therein), measured on core samples and those derived from seismology, overlap only in the case of the San Vito 1 well (triangles versus dotted green line in Figure 3). In contrast, samples deeper than ~ 2000 m of the Mofete wells, show Vp/Vs ratios higher than those derived by seismology. They are also higher that those of the San Vito 1 well. This feature relates to Vs decrease in the buried deposits and likely suggest the presence of the water in rock voids. It is well established, that fluids do not sustain shear stress and decrease the Vs without any Vp variation; otherwise, the presence of gas-bearing rocks generally changes the rock compressibility with a Vp decrease (e.g., Vanorio et al., 2002).

The different behaviour as revealed by multi-parametric profiles of the structurally different San Vito 1 with respect to the Mofete area, can be interpreted in terms of volcanological and structural features. The significant different volumes of emitted magma and the higher percentage of active vents in the central-eastern with respect to the western (> 4 km^3 vs < 1 km^3, 76 vs 24%, respectively) sector, suggest that the central-eastern part of the caldera was the preferred pathway for magma ascent toward the surface. This hypothesis agrees with data on magma compositions that are more evolved in the western. As a whole, we infer more efficient magma fractionation processes in the western sector of the caldera possible due to longer residence time for the magmas at shallow depth. The occurrence of magmatic eruptions and the extrusion of relatively least-evolved magmas in the eastern part of the caldera could be favoured by the extensional setting as detected by satellite data (Vilardo et al., 2010). Furthermore, the fossil geothermal system and its cooling in the western sector, evidenced by disequilibria between the detected and mineralogically-derived temperatures, can be explained by minor volcanism and weak hydrothermal activity.

Conclusions

Fluid-rock interaction at the Campi Flegrei caldera has produced a suite of hydrothermal minerals that reflect the behavior of the reservoir(s) and, in turn, affect the elastic behavior of buried rocks. The distribution of the hydrothermal minerals with depths is also indicative of past variations of the fluids chemistry. In agreement with De Vivo et al. (1989), the temperature of the geothermal system decreased at the Mofete (as well at the San Vito 3) wells with time. The San Vito 1 well is, instead, characterized by high-temperature stability, as suggested by equilibrium between the secondary mineralogical assemblage and the detected on-site conditions. Furthermore, the Vp/Vs depth-profiles highlight the different behaviors of the medium beneath the Mofete and San Vito 1 areas. The San Vito 1 well is, interestingly, located within the area where magmas vented to the surface, at least in the last 8 ka. It is also the closest to the Solfatara crater, where more than 1500 tonnes/day of CO_2 are fluxed (Chiodini et al., 2001), and to the Pozzuoli-Solfatara area, characterized by intense volcano-tectonics (Di Vito et al., 1999), maximum ground deformation and detectable in present-day extension (Orsi et al., 1996; 1999; Vilardo et al., 2010). The scattering and velocity tomography (Judenherc and Zollo, 2005; Battaglia et al., 2008) confirmed the presence of a highly fractured medium below Solfatara. As a whole, the different subsurface conditions evidenced for the San Vito 1 area with respect to the Mofete (and San Vito 3) depends, in our opinion, on the volcanic system architecture and behaviour. In particular, the central-eastern part of the caldera is the preferential pathway for both the gas escape and fluid circulation (Caliro et al., 2007) as well as magma ascent to the surface.

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