Solid Earth Discuss.,
https://doi.org/10.5194/se-2019-53-AC1, 2019

Solid Earth
Discussions
Open Access
EGU

Interactive comment on "The acid-sulfate zone and the mineral alteration styles of the Roman Puteolis (Neapolitan area, Italy): clues on fluid fracturing progression at the Campi Flegrei volcano" *by* Monica Piochi et al.

Monica Piochi et al.

monica.piochi@ingv.it

Received and published: 17 July 2019

Here, we are responding to the comments of the reviewers, following the numbered notations sequence in their documents, and we upload the pdf with our annotations relative their marked points.

We have also been applied some editing that improves language. The analytical results in Table 1S and the list of references have been updated, considering the new done survey and the revision.

Printer-friendly version

Discussion paper

We are ready to upload the text revisited considering the whole indications by both reviewers. We are ready to upload the text revisited considering the all indications by both reviewers, as well as the implemented supplement and the two revisited figures.

Below, for each comment from Referees, our author's response, and author's changes in manuscript.

In the uploaded sections, I will include the pdf that I suppose can be useful to track our revisions.

Response to Pirajno Referee #2

Dear Dr. Pirajno, Thank you for your suggestions and some language editing that surely improve our manuscript. We accept all your indications through the text and we have applied related changes. The only exceptions concern with the terms "realm" and "vessels". We prefer "realm" with respect to "domain" or "settings", being the first too common and general, and the second confusingly with the (already used) geological/volcanological structural settings. The term "vessel" is, in our opinion, more adequate to give the idea of our conceptual model. Below replies to most important annotations in the pdf. Odd words (SSt, ASA, Stuff): we use acronyms that are explicated in captions of Fig. 1d,e. Therefore, we have edited the sentences. CH-line 16 of section 2.2 (pag 4): Selection of sampling sites (herein after referred using the acronyms in Fig. 1d,e).... CH-caption of Figure 1: (c) new pool (referred as New P) at Solfatara on September 2017. (d) the Solfatara crater with sampling sites, notably the Bocca Grande fumarole (referred as BG) and La Fangaia mud pool, and the old thermal baths (referred as Sst) as well". (e) the Pisciarelli sampling sites, notably Geiser vent and mud pool (referred as G and L3, respectively), the later delineated by shaded lines defining the observed widening variations. CH-Line 10 on pag 4: Sampling was conducted within the Solfatara crater and in the Pisciarelli and Cinofilo areas (Fig. 1a,d,e) with additional sites compared to Piochi et al. (2015); the crater floor, except the pool, was intentionally avoided because of the reworking in historical time (Photo-Jones et

Printer-friendly version

Discussion paper

al., 2016) and the possible anthropogenic contamination. CH-Lines 23-24 on pag 5: Na and NH4 sulphates induce the pale orange painting on efflorescences and encrustations, and generally of soils. CH-line 5 pag 8: Environmental realms: stationary phenomena and runoff processes In order to explain the meaning of terms realms and "stationary" we have modified the entire line 10 of section 4.1 on pag. 8: CH-Lines 9-12 pag 8: "However, the various sites further display reproducible rock geochemistry and stable isotope compositions at the timescale of survey; they can considered reference points for future investigations. Based on the presented dataset, we propose the existence of major realms, in which some (minor/peculiar) mineral phases can appear or disappear, in response to changing physical-chemical conditions mainly associated to weather circumstances, mostly humidity and water abundance. The realms are the geographical zones discriminated by their dominant and repetitive mineralogy, rock chemistry, and isotopic compositions, and characterized by temperature variations in a narrow range. Such a constancy is revealed when comparing results reported by Sicardi (1959) (see Geological setting at 2.1 section) with the present results, corroborating the existence of "stationary" realms that are presented in the following. The only exception is the mud pool in the crater. " CH-Lines 19-20 pag 9: Aerosol particles from inside and nearby the Solfatara crater that bear NH4+ (and Cl-, possibly in the form of NH4Cl) as major ion (Mather et al., 2004), as well as the NH4Cl inside the BG and BN orange-yellow encrustations (Fig. 3h,i), furthermore... CH-Line 6 on pag 10: 4.2 Classification of alteration and genetic environments: the contradictory data CH-Line 5 on pag 11: ...(ii) δ34S of sulfides (supergene) or (iii)... CH-Figure 1: It includes the Campi Flegrei location into an enlarged inset. You are right. Done. CH-Figure 11: "Swampy" in place of "palustrine". We have applied several additional changes to improve English. We hope that the improvement will allow a positive evaluation for publication on SE. Best regards, Monica Piochi and co-Authors

Other changes: CH-Line 10 pag. 1. "This is the case for the ...." changed to "This is the case of the..." CH-Line 11 pag. 1. "...where the landscape of Puteolis is characterized by acid sulfate alteration ...." changed to "...where the landscape of Puteolis is

characterized by an acid sulfate alteration . . .” CH-Line 14 pag. 1. “. . .2012 and 2019 “ changed to“. . .2013 and 2019 . . .” CH-Line 16 pag. 1. “. . .Sulfate terrains have higher contents of Ti, Ba, Au, As, Hg and Tl relative to their parent substrate. . ..” CH-Line 20 pag. 1. “. . .The style of mineralization and the stable isotope geochemistry do produce complex and not completely consistent classifications and genetic information. . ..” changed to “. . .The style of mineralization and the stable isotope geochemistry do produce complex and not completely consistent classifications and genetic constraints. . ..” CH-Lines 4-7 pag. 2. Their peculiarity arises from the stringent interaction between inorganic (mineral assemblages and geochemistry) and organic (biota) substances under extreme ambient conditions (pH, temperature, salinity, oxygen deficiency, etc.) associated with endogenous degassing (i.e., H2O, CO2, CH4, H2S, SO2, HCl, HF, etc.) and hot water fluid circulation (hydrothermal/geothermal systems) on dormant volcanoes. CH-Line 5 pag. 5. “Where coexisting, alunogen fibres grow from the edges of alunites . . .” changed to “Where coexisting, alunogen fibres grow from the edges of alunite crystals . . .” CH-Line 8 pag. 5. . . .3e). Dendritic and/or sometimes bi-pyramidal crystallites (Figs 2a,3a,3c) are ubiquitous habits for native sulfur (typically. . .. CH-Lines 31-32 pag. 5. Realgar (detected at the EDS-BSEM and not listed in Table S1) and ammonium chloride (Fig. 3g,h) appears as peculiar precipitates at the Bocca Grande and Bocca Nuova sites (Fig. 1d). Accessory minerals include hematite, quartz, and, possibly, Fe-hydroxides and phlogopite. CH-Lines 24-25 pag. 6. The new pool at Solfatara characterizes for peculiar DRIFT-FTIR spectra in the OH-stretching region (Fig. S2e; note the inset) due the presence of kaolinite, of kaolinite, in addition to alunite, and minor (or occasional) S, feldspar, pyrite and amorphous phases. Specifically,. . . CH-Line 25 pag. 7. . ..), and/or native S in the CH-Line 13 pag. 8. “The Pisciarelli and Solfatara pools (Fig. 1d,e) are the two major and distinctly different realms. They displays persistent. . ..” changed to “The Pisciarelli and Solfatara pools (Fig. 1d,e) are the two major and distinct realms. They display persistent. . .” CH-Lines 21-22 pag 8. . ... whereas they are different at the Pisciarelli mud pool (Fig. 6a, inset). The DRIFT-FTIR spectra

CH-Line 27 pag. 8. ..., although only by a few degrees Celsius.... temperature values at the geyser-vent (Chiodini et al., 2016). CH-Line 8 pag.9. We suspect that those at the ASA, M. Olibano and SSt sampling sites along the slopes of the Solfatara crater (Fig. 1a,d) are ascribable to long-lived encrustations;... CH-Lines 7-8 pag. 10. "...1992) allow classification of alteration and the differentiation of genetic environments." changed to "...The stable isotope geochemistry of minerals supports an interpretation of steam-heated to supergene environments (Fig. 7)." CH-Line 29 pag. 10. "...The stable isotope geochemistry of minerals support an interpretation as steam-heated to supergene environment (Fig. 7)." changed to "...1992) allow classification of alteration and differentiation of genetic environments." CH-Lines 4-5 pag.12. Some realgar encrustations sampled at BG and BN also associate with ClNH4 (Table S1; Fig. 3h,i). CH-Line 18 pag.9. The NH4+ ions were... CH-Lines 6-7 pag.11. Actually, Campi Flegrei lacks of the occurrence of enargite and luzonite, both diagnostic for high-sulfidation environments, and instead shows minor occurrences of realgar (AsS) as well as cinnabar (HgS) (Tables 1,S1), and orpiment has been described (Russo et al., 2017). CH-Lines 8-9 pag.11. Significantly lower δ34S values (< 15 ‰ for alunite can derive from: (i) the light sulfur isotopic composition of H2S during boiling (steam-heated or low-sulfidation setting), (ii) δ34S of sulfides (supergene) or (iii) the bulk sulfur isotope composition of magmatic steam (Rye et al., 1992). CH-Line 19 pag. 13. ... paleo-conduit. Our mineralogical and isotopical results overlap with those in Valentino et al. (1999), favouring a stability in the hydrothermal dynamics over the past 20 years. The zone... CH-Lines 23-24 pag. 13. Based on presently available data, several key aspects await further investigations. In particular, a detailed .... Table S1 updated to last surveys (april 2019)

Please also note the supplement to this comment:
https://www.solid-earth-discuss.net/se-2019-53/se-2019-53-AC1-supplement.pdf

Interactive comment on Solid Earth Discuss., https://doi.org/10.5194/se-2019-53, 2019.

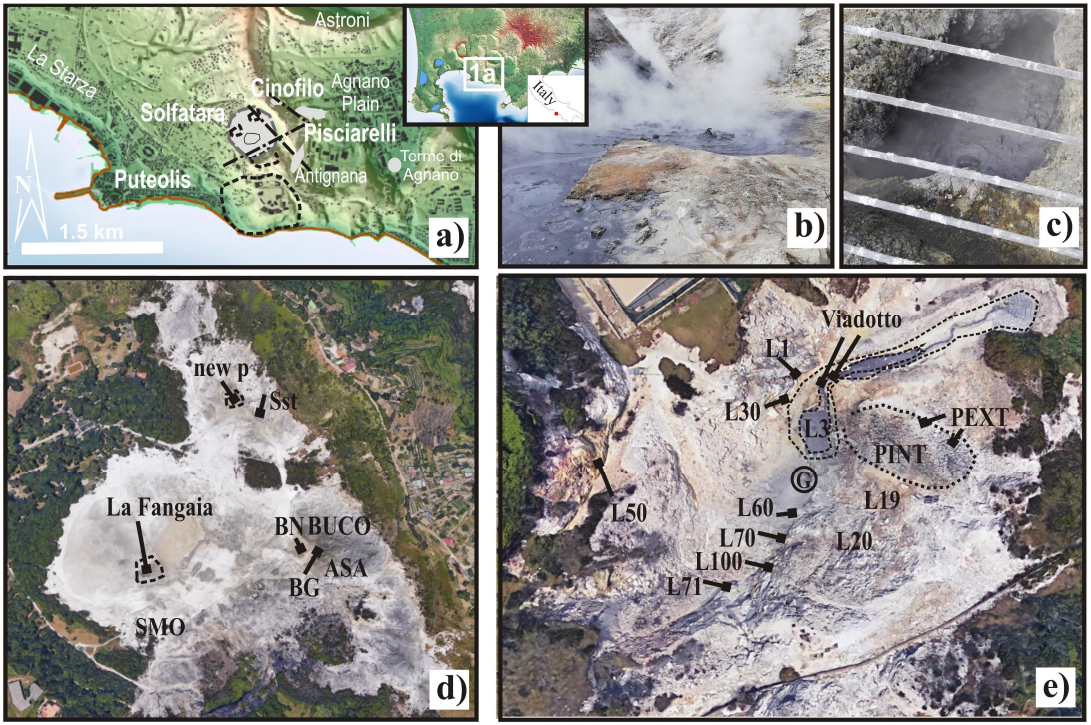

Fig. 1. revisited Fig 1 with inset

Printer-friendly version

Discussion paper

Solid Earth Discuss., https://doi.org/10.5194/se-2019-53
Manuscript under review for journal Solid Earth
Discussion started: 8 May 2019

The acid-sulfate zone and the mineral alteration styles of the Roman Puteolis (Neapolitan area, Italy): clues on fluid fracturing progression at the Campi Flegrei volcano.

Monica Piochi[1], Angela Mormone[1], Harald Strauss[2], Giuseppina Balassone[3]

[1]Osservatorio Vesuviano, Istituto Nazionale di Geofisica e Vulcanologia, Naples, I-80124, Italy
[2]Institut für Geologie und Paläontologie, Westfälische Wilhelms-Universität, Münster, 48149, Germany
[3]Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università Federico II, Naples, I-80134, Italy

Correspondence to: Monica Piochi (monica.piochi@ingv.it)

Abstract. Active fumarolic solfataric zones represent important structures of dormant volcanoes, but unlike emitted fluids, their mineralization are omitted in the usual monitoring activity. This is the case for the Campi Flegrei caldera in Italy, among the most hazardous and best-monitored explosive volcanoes in the World, where the landscape of Puteolis is characterized by acid sulfate alteration that is active at least since Roman time. This paper provides temperature, mineralogical, textural, compositional and stable isotope data for those solfataric terrains sampled at the crater and Pisciarelli slope of the Solfatara volcano between 2012 and 2019. Temperatures vary between 40 ° and 95 °C. Minerals include alunite with grain sizes generally larger than 20 μm, alunogen, native sulfur, well-ordered kaolinite, and, common at Pisciarelli, pyrite and NH_4-sulfates. Sulfate terrains have higher contents of Ti, Ba, Au, As Hg and Tl relative to their parent substrate. The Pisciarelli slope is anomalous in terms of the presence of NH_4. $\delta^{34}S$ values for sulfides and native S range between -3.00 and 0.49 ‰ and from -4.42 to 0.80 ‰, respectively. Sulfates show $\delta^{34}S$ and $\delta^{18}O$ values in the range of -3.35 to 3.80 ‰ and between 0.3 and 31.33 ‰, respectively. The style of mineralization and the stable isotope geochemistry do produce complex and not completely consistent classifications and genetic information. We merge our data with volcanological information, data from exploration drillings and geophysical results. With the conceptual model we suggest a series of shallow and deep aquifers interconnected like "communicating vessels" through a main fault system that downthrows Solfatara with respect to Pisciarelli. Fluid outflow from the different discrete aquifers hosted in sediments – and possibly bearing biological imprints – is the main dataset that allows determination of the steam-heated environment with a supergene settings superimposed. Supergene conditions and high-sulfidation relicts, together with the narrow sulfate alteration zone buried under the youngest volcanic deposits, point to the existence of a paleo-conduit. The data will contribute to monitor and evaluate the volcanic hazards.

Fig. 2. reply to annoted pdf

The acid-sulfate zone and the mineral alteration styles of the Roman Puteolis (Neapolitan area, Italy): clues on fluid fracturing progression at the Campi Flegrei volcano.

Monica Piochi[1], Angela Mormone[1], Harald Strauss[2], Giuseppina Balassone[3]

[1]Osservatorio Vesuviano, Istituto Nazionale di Geofisica e Vulcanologia, Naples, I-80124, Italy
[2]Institut für Geologie und Paläontologie, Westfälische Wilhelms-Universität, Münster, 48149, Germany
[3]Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università Federico II, Naples, I-80126, Italy

Correspondence to: Monica Piochi (monica.piochi@ingv.it)

Abstract. Active fumarolic solfataric zones represent important structures of dormant volcanoes, but unlike emitted fluids, their mineralization are omitted in the usual monitoring activity. This is the case of the Campi Flegrei caldera in Italy, among the most hazardous and best-monitored explosive volcanoes in the world, where the landscape of Puteolis is characterized by an acid sulfate alteration that is active at least since Roman time. This paper provides temperature, mineralogical, textural, compositional and stable isotope data for those solfataric terrains sampled at the crater and Pisciarelli slope of the Solfatara volcano between 2013 and 2019. Temperatures vary between 40 ° and 95 °C. Minerals include alunite with grain sizes generally larger than 20 µm, alunogen, native sulfur, well-ordered kaolinite, and, common at Pisciarelli, pyrite, illite and NH_4-sulfates. Sulfate terrains have higher contents of Ti, Ba, Au, As, Hg and Tl relative to their parent substrate. The Pisciarelli slope is anomalous in terms of the presence of NH_4. $\delta^{34}S$ values for sulfides and native S range between -3.00 and 0.49 ‰ and from -4.42 to 0.80 ‰, respectively. Sulfates show $\delta^{34}S$ and $\delta^{18}O$ values in the range of -3.35 to 3.80 ‰ and between 0.3 and 31.33 ‰, respectively. The style of mineralization and the stable isotope geochemistry do produce complex and not completely consistent classifications and genetic constraints. We merge our data with volcanological information, data from exploration drillings and geophysical results. With the conceptual model, we suggest a series of shallow and deep aquifers interconnected like "communicating vessels" through a main fault system that downthrows Solfatara with respect to Pisciarelli. Fluid outflow from the different discrete aquifers hosted in sediments – and possibly bearing organic imprints – is the main dataset that allows determination of the steam-heated environment with a supergene settings superimposed. Supergene conditions and high-sulfidation relicts, together with the narrow sulfate alteration zone buried under the youngest volcanic deposits, point to the existence of an evolving paleo-conduit. The data will contribute to monitor and evaluate the volcanic hazards.

1 Introduction

Active solfataric landscapes are among the most peculiar and fascinating environments on the Earth that may be considered as planetary analogues (e.g., White and Hedenquist, 1990; Rye et al., 1992; Lowe et al. 1993; Zillig et al., 1996; Ciniglia et al., 2005; Rye, 2005; Glamoclija et al., 2004; Sgavetti et al., 2008). Their peculiarity arises from the stringent interaction between inorganic (mineral assemblages and geochemistry) and organic (biota) substances under extreme ambient conditions (pH, temperature, salinity, oxygen deficiency, etc.) associated with endogenous degassing (i.e., H_2O, CO_2, CH_4, H_2S, SO_2, HCl, HF, etc.) and hot water fluid circulation (hydrothermal/geothermal systems) on dormant volcanoes. They allow investigating a variety of processes in the field of geology (i.e., magma and volcano dynamics), biology (i.e., physiological adaptation to environmental stresses and the origin of the life), medicine, astrology and archaeology (i.e., thermal bath and antibacterial applications), with possible future medical and biotechnological applications.

The Solfatara volcano (Campi Flegrei, CF, Italy; Fig. 1a) is perhaps the most famous and hazardous geothermal solfataric setting in the world (e.g., Rittmann, 1950; Rosi and Sbrana, 1987; De Vivo et al., 1989; Barberi et al., 1991; Piochi et al., 2014)

Fig. 3. complete revisited manuscript

Printer-friendly version

Discussion paper