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Solid Earth Discussions

# *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.

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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.



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 Anonymous Referee #1

Dear Reviewer,

thank you for your work. We have greatly appreciated your comments and indications. We are also gratified in reading that the new data might extend to other similar sites and that our work can be considered interesting and suitable for publication on SE.

We are here interested to address the weaknesses that may affect results and discussions in our manuscript. Therefore, we are responding to your comments, following your adopting numbered notation structure and we upload the pdf with our annotations relative to marked points.

Before our reply to the specific comments, we underlie (and this is in agreement with your statements) that the presented mineralogical assemblages essentially derive from XRDP data (as stated in the caption of Table 1). Note also that by accepting your indications, we have inserted representative XRDP spectra in the supplementary materials, and we applied some changes throughout the text in order to avoid the possible weaknesses addressed in your points 1 to 6. Also, we underlie that our manuscript has the aim to unravel the active setting of the Campi Flegrei caldera through information uncommon in the current published researches; mineralogy is used with this aim and details of minerals (particularly of clays) are not the specific focus of this study. Certainly, the clays merit attentions and we absolutely agree with you in considering that

these phases should bear interesting (and additional) information. However, the clays are present in relative low abundance in our samples and the study on clays need specific sample preparation and additional techniques that are beyond our purposes and are not considered in this context. Therefore, we reply to your specific annotations by using the available information on clays that we consider essential/useful in the study frame; the information implements the discussion and further corroborates our conclusions. To note, we have moved the figure with FT-IR spectra in the supplement. In our opinion, this is more adequate considering your comments, the study aim and the manuscript structure. The new figure 4 illustrates the kaolinite plates at the SEM.

Below, our reply (R with your point letter/number in bold) to your general (a, b) points and the underlined numbered points. Within each reply there are listed the changes we applied to the text with reference to lines and pages (CH line and pag). We have used the number of lines of the submitted text.

a. the section 4.1 is not actually discussion but presentation of some data. For instance, the term realm should be replaced by assemblage. Ra. We are not in agreement here; this is the definition of the realms that can be used as reference points to future investigations. See our reply R7, below and in the pdf.

b. Rb. We have changed FTIR peaks into bands. CH-Line 5 pag. 6 CH -Line 10 pag 6 CH -Line 15 pag 6, two words CH -Line 25 pag 6, two words

1. The FTIR technique is not appropriate for detailed studies in multimineralic samples because of band overlapping. There are too many oversimplified assumptions which are not justified by the data. R1. You are right here, in principle, but a) our study essentially bases on mineralogical results that come from XRD analyses (see also the following point 4) and b) the literature reports several infrared studies in which bands of specific minerals can be detected in mixtures (e.g., Nayak and Singh, 2007; Madejova et al., 2002). The USGS also reports FT-IR spectra (https://www.usgs.gov/labs/speclab/capabilities/spectral-library) for mineral mixtures and we are showing that a similar



first analytical set can be produced in mixtures for the Campi Flegrei. Madejova et al. verified that infrared spectroscopy is suitable for detecting small amounts of kaolinite in smectite-rich samples, and amounts of smectite in kaolinite-rich samples. Our data also testify that the FT-IR coupled with XRD allows some information to be detected, although very details on structure require mineral separation. For example, the alunite and kaolinite have not overlapping bands in the OH-region and here the kaolinite has bands that furnish useful clues. The FT-IR allows us to check for eventual organic groups in samples corroborating the whole-rock geochemistry. In substance, some samples have restituted FT-IR spectra that are reproducible in several samples of similar XRD-derived mineral assemblage and the can be used to identify the bands typical of specific minerals and that, based on literature information and on the well-constrained mineralogy by XRD, allow some information useful for our scopes. We particularly refer to kaolinite order and our data agree with conclusion of Madejova et al. (2002).

CH-supplement: The supplement includes XRD traces. It includes a section “Notes on XRD and FT-IR data” in which we illustrate that bands of specific minerals can be detected in the FT-IR spectra for samples already characterized by XRDP. Some bands are peculiar of molecules and these molecules can be detected in very small amount thanks to the bands in powders.

2. The spectral range >4000 cm-1 belongs to the NIR region and the bands in this region are actually combination bands (not stretching and especially not bending bands). The text referring to these results needs total re-writing. R2. Yes, we have oversimplified and we have edited the sentences annotated in the pdf by inserting the underlined words, i.e.,

CH-Lines 27-29 on page 6: Accordingly, the spectra show vibrations at ca. 4605 cm-1 ascribed to the Al-OH stretching contribution in alunite; furthermore, it is possible recognizing the OH-deformation at ca. 915 and 938 cm-1, the Si-O stretch at 1008 and 1026 cm-1, and the Al-OH bending contribution at 4523 cm-1 from kaolinite.

3. There is bad use of some references (e.g. Parafinium & Kruszewky, 2010). The band assignment in this work refers to ammonium alunite-jarosite. There are important differences with this study with the most important being the OH-stretching region. R3. You are right and we are wrong. We have moved back to our original purpose, i.e., identifying the NH4 band in the FT-IR that must be present in the NH4-sulfate mineral detected by XRD. Therefore, we have changed the sentences annotated in the pdf as it has pasted below and we discuss the assignment of other bands for these XRD-derived crystals in the new section of supplement. We also cited Weis and Ewing that have studied Mascagnite-type aerosols. The detection of this band associable to NH4 is very interesting because allows the detection of the group contained in low amount in samples.

CH-Lines 4-9 of page 6: "DRIFT-FTIR spectra collected on selected samples (Fig. S2) produce data consistent with XRDP results (Fig. S1) and furthermore allow useful details on structure and eventual minor phases or impurities (Supplement). Table S2 lists the relevant vibration modes of spectra and the proposed mineral assignments. The crystals formed by evaporation of water in the Pisciarelli pool (Fig. S2a; Supplement) show a sharp band at 1422-1411 cm-1 that is in the region of the $\nu$4(NH4+), as described in the literature (e.g., Weis and Ewing, 1996; Parafiniuk and Kruszewky, 2010) and in agreement with XRDP mineral data (Table S1; Fig S1). ".

CH-Lines 21-23 on page 6: Notably, the DRIF-FTIR spectra of muds from Pisciarelli (Fig. S2d) show a vibration in the region of 1430 cm-1. Because the muds were separated from water, as before, the band can be related to the NH4 (Weis and Ewing, 1996; Parafiniuk and Kruszewski, 2010) in tschermigite, mascagnite and letovicite (Table S1, Fig. S2, Fig. S1, Supplement).

4. I do not understand why the authors did not present XRD traces at least as a supplement, which would verify the presence of some phases. XRD is the most suitable and reliable method for this type of materials. R4. Note that the mineralogy derives from XRD data as it is clearly stated in the caption of Table 1. This is further well-stated



now because the changes at the beginning of the section 3.1 (see first sentence).

CH- line 30-31 pag 4: "New and previously published (Piochi et al., 2015) mineralogical data for the Solfatara-Pisciarelli area (Table S1, Table 1) provide information on a yearly to monthly basis since 2013 along with measurements of temperature. The mineral assemblage dataset derives from XRDP analyses (Supplement) corroborated by textural and chemical information obtained at the EDS-BSEM. DRIFT-FT-IR spectra determined on representative samples, display characteristic bands of minerals they include (see below and Supplement), and help in material characterization.".

However, we agree with you and in order to clarify we have produced a new figure in which XRD spectra and peaks with assigned minerals have shown for same samples represented in (old) figure 4.

CH-Supplement: the Supplement (as you have indicated) now includes the new figure showing XRD spectra and a section that explains the use of FT-IR technique, the limit and the advantage, therefore, evidencing the assumption and the possibility to obtain reproducible and informative FT-IR spectra on mixtures, as explained at the previous point 1.

5. The presence of illite/montmorillonite at Solfatara is at odds with the environment of acid sulfate alteration and should be explained/discussed by the authors. Also, illite and montmorillonite are very easily distinguished by XRD. This is another reason why XRD data should be presented at least in supplement. R5. The XRD are inserted in the supplementary materials, as asked. Concerning XRD, the spectra are in the Supplementary materials (see also previous point 4). We agree and we improve our discussion about the occurrence of illite/montmorillonite at the studied sites. We reports the occurrence of illite/montmorillonite within the results, without comments. In the discussion at section 4.2 we use the information on clays and in particular we implement some sentences as reported below (see R7). However, we are in disagreement with you (see your note at line 20 section 4.1 pag 8), as native sulfur has been de-

tected and reported in association with clays in various sites of the world. In any case the sentence here has a mistake and it has been modified. CH-Line 19-20 on pag 8: We recurrently detected an enrichment in pyrite, illite/montmorillonite and feldspar at Pisciarelli and in native sulfur at Solfatara.

6. In general, the distribution of clay minerals is not presented clearly. Well-ordered kaolinite seems to be present but this also has to be verified by XRD. Table 3 does not include illite and montmorillonite, although these minerals are not included in the discussion and the results sections. However, this table includes local presence of halloysite which was not described in the text. In any case, how was halloysite distinguished from (disordered) kaolinite? R6. FT-IR is adequate to detect well-structured kaolinite, as reported in the cited literature. The XRDP also support the statement and this has been clarified through the changes in relation to your annotations in the pdf.

CH-Line 18-19 on pag 5: Clays have a low relative abundance in the studied samples (Supplement). They are mostly smectite, and most common are illite/montmorillonite, while kaolinite seems least abundant (Table S1, Table 1), as derived by the XRDP spectra (see Fig. S1c,d,e) and supported by DRIFT-FT-IR study (see below; Fig. S2 and Supplement). In particular, the infrared technique is suitable to detect the kaolinite and the related bands in the OH-region, in agreement with Madejová et al. (2002).

CH-lines 30-31 of pag 6: The four vibration modes of kaolinite in Fig. S2e point for a well-ordered mineral structure (Madejová, 2003; Fitos et al., 2015), giving a strong support to the XRDP results (Fig. S1e, Supplement), also in multiphase samples (Madejová, et al., 2002).

CH-Supplement: we report the XRDP spectrum for kaolinite, for which we have FT-IR analyses.

The occurrence of hallosyite is practically not detected in our samples by XRDP. Montanaro et al (2017) reported generical kaolinite/halloysite in samples from Solfatara floor that we exclude due the anthropogenic rework. The paper by Montanaro is is the



because that induced us to include the halloysite in the discussion. We never detected kaolinite with disordered structure, until now and at the sample sites. The Table 3 has been changed in order to correctly address the raised questions. The Table 3 lists the halloysite as odd and include illite plus montmorillonite. The caption of table 3 has been changed.

CH-Table 3: Inserted information for illite and montorillonite The caption: “Table 3 – Summary of the mineralogical and isotopical features at the acid sulfate area following Rye et al. (1992); Hedenquist and Lowerstern (1994). *highest 34S and 18O during bacteriogenic reduction of sulfates with maximum fractionation in dry-wet alternating conditions. ˆ $\delta$34S reflects the H2S/SO2 and temperature of fluid. 1 always present, 2 may be associated. 3 from Valentino and Stanzione (2003; 2004), Gresse et al. (2017). ‘halloysite is indicated in Montanaro et al. (2017) and included here for completeness.”

7. Most of section 4.1 contains actually results. It has to One of the main conclusions about the role of climatic conditions (e.g. humidity) is well-known. Actually most of the sulfate salts are very soluble. Also, the discussion in sections 4.2 and 4.3 should be more focused. The biological imprint has not been verified in the text. The authors might wish to consider organic matter, present in the underlying sediments, as a potential source of N. 8. R7. The section 4.1 contains elaboration of results. It evidences that the various minerals and mineral assemblages we detected and we listed in the results section occur in particular sites of the investigated area. Through the time of our surveys, we have observed that the Solfatara area can be distinguished in several smaller realms (domains) that can be considered stable in terms of dominant minerals, temperatures and pH. This is not only a mineral assemblage constancy, but is important in the frame of the hydrothermal dynamics. This is important to evaluate eventual dynamical changes in the future. We have changed the second paragraph at the beginning of the section in order to clarify our intention and aid the reader in the correct understand of elaboration of results. Yes the role of water and humidity (weather) is important also at the Campi Flegrei and has been used now in the conclusions.

CH-Lines 9-12 pag 8: “However, the various sites further display reproducible rock geochemistry and stable isotope compositions at the timescale of survey, and with respect to oldest data (e.g., Valentino et al., 1999) as well; they can be 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. ”

As already stated before and anticipated at R5, we have implemented the section 4.2 by considering your indication on clays. In particular,

CH-Lines 17-24 pag 10: The occurrence of kaolinite and alunite at several Solfatara and Pisciarelli realms (particularly, new pool and PINT, Table 1) fits with the high sulfidation environment; in fact, the two phases usually coexist in the advanced argillic alteration zones proxy to ascent plumes (e.g., Pirajno, 2008). The evidence of K-feldspar replacement by alunite (Piochi et al., 2015), the disseminated pyrite and the presence of native S at Pisciarelli apparently support the high sulfidation - magmatic hydrothermal environment (Rye et al., 1992). Nevertheless, illites/montomorillonites are most common in intermediate argillic alteration zones (Pirajno, 2008) and their widespread occurrence in the various studied realms is among the results that contrasts this high sulfidation environment. Indeed, sampling temperature are higher than 40 °C (Tables 2 and S1) and SO2 is rare or absent (Aiuppa et al., 2013) at Campi Flegrei. Also, the lack (or rare detection) of the lower temperature (< 40 °C), disordered polymorphs (i.e., halloysite) point to limited supergene alteration. Only, the alunite coexisting with kaolinite



in the new hole pool has the finest grain sizes. Accordingly, the XRDP and DRIFT-FTIR analyses of CF samples point to slightly ordered kaolinite forms that usually occurs at temperatures < 150 °C in epithermal systems (Sillitoe, 1993), but could also represent a metastable form in hotter settings (Zotov et al., 1998). In this later case, the new pool realm with kaolinite and alunite can represent a local, well-circumscribed advanced argillic alteration condition indicative of a proxy plume. We also implement the section 4.3. In particular, our edited sentences are listed below.

CH-Lines 20-21 pag 11: Merging all available information, it appears that observations concerning the both realms’ “stationarity” and contradictory classification environment reflect the evolving conditions that have followed the last magma intrusion and eruption and that probably are overlapping through time.

CH-Lines 29-30 pags 11-12: The alteration zone locally presents high Ti, Ba, Au, As, Hg, Tl, S concentrations relative to the above parent basement lithology (Fig. 8). The zone also appears anomalous in terms of ammonium content.

CH-Lines 31-32 pag 11 and 1-3 pag 12: The presence of NH4-bearing sulfates is particularly abundant at Pisciarelli; those sulfates systematically form by drying water collected at the various pools of the area, in relation to the abundance of nitrogen species (0.2-1 g/l) in those waters (Martini et al., 1991; Celico, 1992; Valentino et al., 1999; Holloway and Dahlgren, 2002; Valentino and Stanzione, 2003; 2004; Aiuppa et al., 2006).

CH-Lines 8-11 pag 12: These fumaroles continuously emit H2S and CO2 (Allard et al., 1991; Aiuppa et al., 2013; Chiodini et al., 2016) and are the preferred location of crystallization of native S and alunite. NH4+ emissions are also present at Solfatara (Chiodini et al., 2010), although ammonium is of limited importance inside the crater waters literature data <0.001 g/l (Aiuppa et al. 2006) and crystallization of alum instead than NH4+-sulfates in the water from Solfatara pool. In agreement with these authors, the plausible source is the conventional geothermal reservoir. You are right

here about the biological imprints. But this was an oversimplification as we refer to the organic matters but, in our minds, we want indicate the possible (additional) biological contribution that there is detectable at the surface in the area. We attributed the NH4 to organic matters in sediments as the logical sequence of our previous sentences. We have made editing at the lines that the reviewer annotated in the pdf.

CH-Lines 16-20 pag 12: Fluid outflows from discrete aquifers hosted in sediments – and bearing organic imprints – feed the Pisciarelli site giving its ammonium peculiarity. Our purpose does not exclude the possible biological contribution that has been ascertained in the studied sites (e.g., Ciniglia et al., 2005; Glamoclija et al., 2004;). However, marine strata and volcano-clastic sequence intercepted by deep drillings (San Vito1, Mofete and CF23 wells; Rosi and Sbrana, 1987; Piochi et al., 2014) are the key sediments of the NH4 species. An additional supply can be the swampy sediments encountered in shallowest boreholes (de Vita et al., 1999) located in the central sector of the caldera (Fig. 11), nearest to the study area.

CH-Lines 2-3 on pag 13: This idea comes from field observations that indicate the alteration deposits locally underlying the most recent eruptive units (e.g., Astroni) that are unaltered. Therefore, the texture of the mineral assemblage, the enrichment in some metals and the lithogeochemical parameters are relict of a “high-sulfidation system”. The evolutionary dynamics within the conduit and, in particular, the water overflows from the aquifers alternating with runoff processes, explains the contradictory mineral environments with superimposed intermediate and advanced argillic alteration..

Following the reviewer’s annotations, we applied these further changes:

CH-Line 15 on pag 1 of abstract: .... and, common at Pisciarelli, pyrite, illite and NH4-sulfates.

CH-Line 23 on pag 1 of abstract: .... organic....

CH-Lines 25-26 on pag 1 of abstract: ..., point to the existence of an evolving paleo-



conduit.

CH-Line 3 on pag 3: “...1987) and the solfataric landscapes (Fig. 1a-e) have replaced the original pyroclastic sequences (e.g.,.” changed to “...1987) and the solfataric landscapes (Fig. 1a-e) have locally replaced the original pyroclastic sequences (e.g.,.”

CH-Line 7 on pag 4: The pH of water pools and soils...

CH-Line 8 on pag 4: Sampling, sample preparation and analytical techniques

CH-Lines 16 on pag 4: April 2019 (Table S1).

CH-Lines 25-27 on pag 4: Details on XRDP and DRIT-FT-IR are in the Supplement (S1) together with representative spectra (Fig. S1, S2).

CH-Lines 19-20 on pag 5: Illite/montmorillonite usually occurs in the muds at Pisciarelli (from geyser and around other emissive vents) and occasionally at Solfatara (Table 1, S1). Kaolinite characterizes the newly formed pool within the Solfatara crater and occurs locally at Pisciarelli (Fig. 1c,de and Table 1).

CH-Line 32 on pag 5: Accessory minerals include hematite, quartz, and, possibly, Fe-hydroxides and phlogopite.

CH-Lines 30-31 on pag 6: The IR spectra of samples for which XRDP confirmed illite/montmorillonite (Fig. S1, Supplement) lack of overtones at 4255 and 4081 cm-1. Following the literature (Clark et al., 1990; Madejová; 2003), these overtones are characteristics of illite and their absence can support the presence of montomorillonite.

CH-Lines 30-31 on pag 8: The kaolinite is easily discriminated also by DRIFT-FTIR spectra (not shown) that, in agreement with XRDP traces, point for a well-ordered structure. This terrain bears variably sized (up to few dm) clasts and is subject to slumping and sinking.

CH-Lines 1-5 on pag 9: A hole up to 2-3 m deep represents a distinct realm that we emphasize because it opened 180 m North from the main pool within the crater in

May 2017, by surface collapse. A grey viscously boiling mud fills the hole (Fig. 1c,d), with a minimum temperature of 70 °C; 91 °C is the temperature on April 2019. The mud is dominated by alunite with subordinate native sulfur, showing vague similarity to Solfatara mud (Table S1), although its grey colour and the occasional pyrite are reminishent of the Pisciarelli mud. However, kaolinite is the main clay mineral in the new pool (Fig. S1e; Fig. S2e, note the inset). Mud geochemistry reveals peculiarly high concentrations of Sr, Ga, Co, Th, V, REE, Sb (Fig. 9).

CH-Lines 16-17 on pag 9: Vapour effluents around the various geysers/vents at Pisciarelli are the most important factors that influence the neogenesis of the alunite-dominated realms. Pisciarelli is a decametres-deep incision on the NE Solfatara slope and the degassing vents are constrained in a gorge-like morphology. This setting favours the stagnation of the hydrothermal steam that impregnates the rock substratum and supplies elements to the formation of a variety of Na and NH4 sulphates. We detected high abundance of those phases around the pool as desiccation during the summer season.

CH-Lines 22-24 on pag 9: DRIFT-FTIR and XRDP spectra (Fig. 4d, S1a,d), however, point to the presence of NH4 in both the mud and water pools at Pisciarelli, but not at Solfatara (except for BG and BN). Alum – (K) has also been found in relation to the wet conditions at Pisciarelli. Vapour emissions outflow and the conditions of hydrothermal steam stagnation are dependent on atmospheric pressure and wind conditions.

CH-Line 4 on pag 10: Meteoric and surface waters can dilute the aggressive endogenous fluids determining alteration degree conditions low enough for the generation of illlite/montomorillonite (Pirajno, 2008) at Pisciarelli. Further studies need to be performed in order to better characterize clays as they can bear information useful to further constrain the hydrothermal setting.

CH-Line 17 on pag 11: The analysed samples do not produce bands attributable to C=H ligands (Supplement) and the carbon content is <1.25 wt% (most common < 0.2



wt%; Table S3).

CH-Lines 20-21 on pag 11: Merging all available information, it appears that observations concerning the both realms' "stationarity" and contradictory classification environment reflect the evolving conditions that have followed the last magma intrusion and eruption and that probably are overlapping through time.

CH-Line 9 on pag 13: . . ..likely to organic/biological. . ..

CH-Lines 19-18 on pag 13: The limited areal extent of the alteration zone underlying the most recent unaltered volcanic units, its mineralization texture and style, the $\delta$18O and $\delta$34S values of S-bearing minerals, and the enrichment in Ti, Ba, Au, As, Hg and Tl, are possibly attributes of the evolution of a paleo-conduit.

CH-Table S1, caption: List of samples, collection date, temperature and mineralogical associations as resulting by XRDP analyses and corroborated by FTIR and EDS-BSEM study. The sampling includes water spring sampled at Stufe di Nerone. In the temperature column: tc, thermo couple (see chapter 2.2 Sampling, sample preparation and analytical techniques), infr, infrared gun. In the mineralogy column: ?, for minerals to be validated; minerals in red are approximate attribution based on XRDP patterns. The orange cells evidence water samples. Representative XRDP spectra are in Fig. S1. Further details in this supplement. Data updated on April 2019.

CH-Table S2, caption: Vibration modes and related tentative assignment of functional groups, and mineral attribution for selected samples by DRIFT-FTIR investigations. Alu = alunite, Clay = illite/montmorillonite, Masc = NH4 - bearing sulfates, am = amorphous, Kao = kaolinite, KAl = alum - (K). ?, uncertain attribution. Note: assignments and attributions are based on mineralogy derived by XRDP study and corroborated by EDS-BSEM analyses. Further details in this supplement.

CH-Fig. 4: The old Figure with FT-IR spectra is now in the supplement; it is Figure S2. A new figure (figure 4) illustrates the kaolinite at the BSEM and we have inserted a new

caption: Figure 4 – BSEM image of kaolinite platy crystals at the new pool of Solfatara (New P, Fig. 1c,d): The kaolinite plates have tendency to assembly (a) and associated with alunite (b). Kao = Kaolinite, Al – Alunite.

CH-References: Madejová, J., Kečkéš, J., Pálková, H., and Komadel, P.: Identification of components in smectite/kaolinite mixtures. Clay Min., 37(2), 377-388, 2002. Pirajno, F.: Hydrothermal processes and mineral systems. Springer Science & Business Media, pp 1250, 2008. Weis, D. D., and Ewing, G. E.: Infrared spectroscopic signatures of (NH4)2SO4 aerosols, J. Geoph. Res., 101, 18709-18720.

Our efforts have been also done for editing and improving English; we hope to have reach results that you can accept. We hope that our reviewer will be considered suitable for publication into 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 $\delta$34S values (< 15 ‰ for alunite can derive from: (i) the light sulfur isotopic composition of H2S during boiling (steam-heated or low-sulfidation setting), (ii) $\delta$34S 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-AC2-supplement.pdf

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



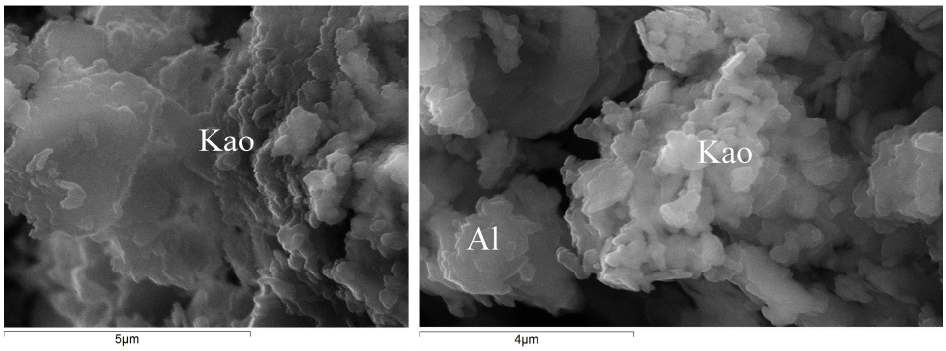


**Fig. 1.** new figure 4

**Supplementary materials**

Table S1 – List of samples, collection date, temperature and mineralogical associations as resulting by XRDP analyses corroborated by FTIR and EDS-BSEM study. The sampling includes water spring sampled at Stufe di Nerone. In the temperature column: tc, thermo couple (see chapter 2.2 Sampling, sample preparation and analytical techniques), infr, infrared gun. In the mineralogy column: ?, for minerals to be validated; minerals in red are approximate attribution based on XRDP patterns. The orange cells evidence water samples. Representative XRDP spectra are in Fig. S1. Further details in this supplement.

| Sample name | Sampled area | Location* | Details on sites and sample | Temperature (°C) tc, infr | Sampling date | Mineralogy | pH | Note |
|---|---|---|---|---|---|---|---|---|
| **Ss1** | Pisciarelli | L1 | - | - | 09-Jan-13 | Sulfur | nd | Piochi et al 2015 |
| **$S_{tot}$2** | Pisciarelli | L1 | - | - | 09-Jan-13 | Pickeringite, Alunite, Alunogen, Alum-(K), Sulfur, Amarillite, Mereiterite | nd | Piochi et al 2015 |
| **S3** | Pisciarelli | L1 | - | - | 09-Jan-13 | Alunite, Alum-(K) | nd | Piochi et al 2015 |
| **$S_{tot}$4** | Pisciarelli | L1 | - | - | 09-Jan-13 | Alunogen, Alunite, Sulfur, Kaolinite | nd | Piochi et al 2015 |
| **S5** | Pisciarelli | L2 | - | - | 09-Jan-13 | Quartz, Amorphous | nd | Piochi et al 2015 |
| **S7** | Pisciarelli | L2 | - | - | 09-Jan-13 | Alunite, Alunogen, Illite/Montmorillonite | nd | Piochi et al 2015 |
| **S10** | Pisciarelli | L2 | - | - | 21-Mar-13 | Alunite, Illite/Montmorillonite | nd | Piochi et al 2015 |
| **Sf12** | Pisciarelli | L3 - mud pool | mud | - | 21-Mar-13 | Alunite, Sulfur, K-Feldspar, Amorphous, Illite | nd | Piochi et al 2015 |
| **Sf14** | Pisciarelli | L3 - mud pool | mud | - | 10-Oct-13 | Alunite Sulfur, K-Feldspar, Amorphous, Illite | nd | Piochi et al 2015 |
| **$S_{tot}$16** | Pisciarelli | L4 | - | - | 21-Mar-13 | Quartz, Amorphous, Illite/Montmorillonite, Kaolinite | nd | Piochi et al 2015 |
| **ASA 12-3** | Solfatara | ASA | NE-slope, uppermost part | - | 11-Dec-13 | Alunite, Alunogen | nd | Piochi et al 2015 |
| **AP 12-3** | Pisciarelli | L1 | - | - | 11-Dec-13 | Alunite, Alunogen, Alum-(K) | nd | Piochi et al 2015 |

1

**Fig. 2.** new supplement with XRD spectra



| | Supergene $H_2SO_4$ production by sulphides oxidation | Steam-heated $H_2SO_4$ production by $H_2S$ oxidation | Magmatic hydrothermal $H_2SO_4$ production by $SO_2$ | Magmatic steam | Solfatara crater | Pisciarelli |
|---|---|---|---|---|---|---|
| | | Low Sulfidation | High Sulfidation | | | |
| Alunite texture age vs original rocks | Very thin-cryptocrystalline, younger | Powdery coeval | up to 250 µm coeval | rare up to 250 µm in vein coeval | thin to sub mm-sized | thin to sub mm-sized |
| Kaolinite | disordered | well-formed | - | - | well-crystallized | well-crystallized |
| Halloysite | yes | possible | - | - | odd? | - |
| Montmorillonite | not indicate | present | in medial zones | not present | rare | present |
| Illite | not indicated | diffuse | in medial and outer zones | not present | rare | widespread |
| Gossan | at the top | - | - | - | - | possibly locally |
| Sinter | - | widely | - | - | widely | widely |
| Vuggy silica | - | - | at the core | - | not present | not present |
| Al solubility | - | - highly leached - | highly leached | - | possibly not intense to absent | possibly not intense to absent |
| Sulfides - Pyrites | widespread | may be | disseminated pyrites | rare | rare | abundant pyrites |
| Pyrophillite, diaspore, covellite, enargite, lauzonite | - | - | may and must be | rare | not detected | not detected |
| $PO_4$ in alunite | - | - | yes | unknown | not detected | not detected |
| S isotope fractionation | nearly absent equilibria fractionation* rarely present in sulphide rich-rocks | similar to $H_2S$ | equilibria fractionation, $H_2S$-Sulfates and Sulfate-pyrite equilibria* | equilibria fractionation with $SO_2$ | Al-$H_2S$ no equilibrium (Fig. 11) | Al-$H_2S$ no equilibrium Py-Al no equilibrium Py-$H_2S$ nearly equilibrium (Fig. 11) |
| O isotope in Alunite | nearly absent equilibria fractionation* | equilibria fractionation | equilibria fractionation^ | equilibria fractionation with $SO_2$ | nearly equilibria fractionation (Fig. 11) | equilibria fractionation (Fig. 11) |
| pH | - | Nearly neutral | <2 | - | Generally acid, locally at very low acid, locally neutral[1] | Locally/timely acid[2] |
| Fumarole T | - | 100-to-160°C | >200°C | >200°C | Locally >160°C | Generally ≤110°C |
| Metal | - | Au[1], (Ag, Pb-Zn)[2] | (As, Ag, Cu)[1], (Hg, W, Bi, Pb, Zn)[2] | | Locally As, Hg (Fig. 9) | Hg (Fig. 9) |
| $H_2S/SO_4$ | | - | 4±2 | <1 | <1 | 1 or higher |
| S state | | Low, S° | High, S°^ | High, S°^ | <1 | 1 or higher |

**Fig. 3.** new table 3

# 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.

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**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. 4.** all revisited manuscript