Details on the seismic station and signals at Pisciarelli

The seismic station located nearby Pisciarelli fumarole (CPIS) is equipped with a 3-component broadband sensor (Guralp CMG-40T) that has a standard response from 60 seconds to 50 Hz. The sensor is located at 8 m distance from the fumarole (Fig. DR1).

Data are sampled at 100 Hz and recorded using a 24-bit digital data-logger (Orazi et al., 2006). The signal is expressed in count units, i.e. the number returned by the data-logger that is directly proportional to the velocity of the ground. We analyse a period of about seven years (January 2010 to June 2017). Spectral analysis, exemplified by analysis conducted over a period of 4 hours on the vertical component signal recorded on April 30, 2017, shows a spectral peak at around 10 Hz (Fig. DR2).

Spectrograms calculated at different times in our time series show that the spectral peak around 10 Hz is a persistent feature of the fumarolic tremor at Pisciarelli (Fig. DR3). We thus use a filtered signal in the 5-15 Hz frequency band to focus on the component of the signal generated by the fumarole activity, and to improve the fumarolic tremor to undesired-signal ratio.

Polarization analysis of data filtered in 5-15Hz indicates that this component of the signal spectrum is clearly polarized as shown in Fig.s DR4 and DR5. By performing the same polarization analysis on the data of other periods, we note that the azimuth and incidence angle are roughly constant over time, even if modest variations can be detected (Fig. DR6). The dominant direction of ground motion is vertical. This is thus chosen for RSAM computations.

We consider each day a 4-hour data window from 00:00 to 04:00 UTC (Time Zone UTC+1), the time of the day when anthropogenic noise is lowest (lower than during daylight hours). This 4-hour time window is further divided into 8 windows of 30 minutes each. Then, we calculate the RSAM defined as (Endo and Murray, 1991; Schweitzer et al., 2002):

\[
RSAM(iT) = \frac{1}{T} \sum_{t=IT-\frac{T}{2}}^{IT-\frac{T}{2}} |s(t)|
\]
where $T$ is the averaging interval (30 min) and $s(t)$ is the 5-15 Hz bandpass filtered seismic trace. Of the 8 RSAM values obtained every day, the minimum is extracted and taken as representative of the specific measurement day.

Figure DR1. CPIS station and Pisciarelli fumarole

Figure DR2 Stacked spectra of 240 windows of the signal (vertical component) of CPIS seismic station recorded on April 30, 2017, from 00:00 to 04:00 UTC (window length = 1 minute). A remarkable spectral peak is around 10 Hz.

Figure DR3 Spectrograms of a 30-minute seismic signals recorded in eight different periods. The spectrogram window length is 1s and the overlap of sliding window is 50% of window length (i.e. 0.5s). Colorbars show spectral amplitude. The prominent spectral peak at $\sim$10 Hz frequency is evident and persistent over time.
Figure DR4 a) One-hour signal polarization analysis (Flinn 1965). The signal was recorded at the CPIS station on April 30, 2017, from 00:00 to 01:00 UTC. We filtered the data in 5-15 Hz band, based on the spectral analysis shown in Figure 2. The rectilinearity (right axis) is defined after Montalbetti and Kanasewich (1970). The planarity (right axis) is defined after Jurkevics (1988). Azimuth ranges between 0 (North) and 180 degrees, clockwise. Incidence is from the vertical direction. For polarization analysis we used the ObsPy processing routines (www.obspy.org), (Krischer et al., 2015). b) Particle motion in the vertical / east-west plane of a 2-second signal window filtered in the band 5-15 Hz.

Figure DR5 Rose diagram showing the azimuth of the polarization of the seismic signal (filtered in 5-15 Hz band, Fig. DR4) reported on the Pisciarelli map.
Figure DR6 Chronogram of azimuth (blue) and of incidence angle (red) compared with the RSAM. The azimuth and the incidence angle (with respect to the vertical) are calculated every 20 days as mean value of 30-minute time windows of the seismic signal. The plot show how in 2013 and in 2016, during periods of high RSAM, the polarization of the tremor is more vertical than in other periods, possibly suggesting a moderate deepening of the tremor source.

Figure DR7 RSAM of infrasound data (blue, Buonocunto et al., 2011) compared with RSAM of seismic data filtered in the band 5-15 Hz (red) in the period August 31, 2016 - May 12, 2017, when a peak of fumarolic tremor amplitude occurred.
Measurement of air CO2 concentration

Air CO2 concentrations are measured from the geochemical monitoring station FLXOV3, located about 20 m east from the main fumarole. The station, installed in April 2007, automatically measures every two hours the CO2 flux from the soil, using the accumulation chamber method, and the air CO2 concentration at about 40 cm above the ground. Carbon dioxide concentrations are measured with a NDIR sensor (mod. Draeger Polytron IR CO2) that is periodically calibrated during maintenance operations, at least once every year.

The raw signal shows noisy behavior due to analytical uncertainties of the sensor at low concentrations (full scale of 10% by volume), and because of the existence of periodical (daily and annual) variations in air CO2 concentrations (see the wavelet power spectrum of the series in Fig. DR8, Grinsted et al., 2004). We processed the air CO2 concentration time series with the function “stl” (B.D. Ripley; Fortran code by Cleveland et al, 1990) of the package “stats” of the “R” statistical software. This loess smoothing algorithm is specifically designed to quantify and separate seasonal and residual components (instrumental noise and daily variations in our case). This, once subtracted from the raw signal, allowed us to quantify the long-term trend in air CO2 (Fig. DR9).

Figure DR8 Wavelet power spectrum of air CO2 concentrations in the 2007-2017 period. Two omnipresent periodicities are evident: a daily periodicity and a less marked annual periodicity.
Gas equilibria at Solfatara and derivation of T-P gas geoindicators

As reference for the geochemical signals of the Solfatara-Pisciarelli hydrothermal system, we use composition of the highest temperature BG and BN fumaroles (~ 162°C and ~ 145°C, respectively) located in the Solfatara crater some hundreds meters from Pisciarelli. BG and BN fumaroles are sampled monthly and many studies demonstrated that the two fumaroles discharge fluids suitable for the application of gas-geothermometric and geobarometric techniques (e.g. Caliro et al., 2007 and references therein; Chiodini et al., 2015; Moretti et al., 2017). In contrast, the fumaroles of Pisciarelli are sampled more sporadically, and are affected by shallow secondary processes (Chiodini et al., 2011). In particular, their CO/CO$_2$ ratio (and, consequently, the P-T estimations that derive from them) exhibits marked seasonal cycles (see for example Figs. 7 and 8 in Chiodini et al., 2011), that perhaps reflect variable interactions with meteoric water during dry and wet seasons.

The geobarometric and geotermometric relations used in this study are derived considering gas-equilibria among the gas species formed by combination of H, C and O elements. We follow the approach of Chiodini et al. (2015) that considers the following formation reactions:

\[
\begin{align*}
\text{H}_2\text{O} & \leftrightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \\
\text{CO}_2 & \leftrightarrow \text{CO} + \frac{1}{2}\text{O}_2
\end{align*}
\]

(1) (2)

The equilibrium constants of reactions 1-2 can be written as:

\[
\begin{align*}
\log K_{\text{H}_2} &= \log f_{\text{H}_2} + \frac{1}{2}\log f_{\text{O}_2} - \log f_{\text{H}_2\text{O}} \\
\log K_{\text{CO}} &= \log f_{\text{CO}} + \frac{1}{2}\log f_{\text{O}_2} - \log f_{\text{CO}_2}
\end{align*}
\]

(3) (4)

Figure DR9 The raw air CO$_2$ time-series (upper panel, data in the figure) is analyzed with the Cleveland et al. (1990) algorithm. The obtained seasonal signal (seasonal in the figure) is subtracted from the raw data (data), and the residual signal is then decomposed into a noise signal of short period (reminder) and in a long-term trend of air CO$_2$ (trend).
where \( \log K_{H_2} = -12707/T + 2.548 \) and \( \log K_{CO} = -14955/T + 5.033 \) (thermodynamic data from Stull et al., 1969).

An objective of Chiodini et al. (2015) was to derive T-P functions un-affected by secondary processes involving \( H_2O \) (water condensation and/or addition). A possible large-scale condensation process was in fact suggested by an increase in the incondensable gas faction relative to water (i.e. an increase of the \( \text{CO}_2/\text{H}_2\text{O} \) ratio), by an increase of the \( \text{CO}/\text{CO}_2 \) ratio (a good indicator of temperature, and condensation is a very efficient process to heat a system), and by repeated episodes of liquid emission at Pisciarelli (Chiodini et al., 2011). For this reason, we derived T-P functions (equations 1-3 in Table DR1) based on equi-molar ratios between incondensable gases (i.e. \( H_2, \text{CO}, \text{CO}_2 \)), i.e. not dependent on eventual condensation processes. The functions are derived from equations 3 and 4 assuming \( f_{O_2} \) fixed by a typical hydrothermal redox buffer (\( \log f_{O_2} = 8.20 - 23643/T \), D’Amore and Panichi, 1980) and \( f_{H_2O} \) fixed by the vapour-liquid coexistence (\( \log f_{H2O} = 5.510 - 2048/T \), Giggenbach et al., 1980).

Table DR1. Comparison between our geothermometric-geobarometric model and that of Moretti et al. (2017). \( X_i \) indicate the fumarole molar fraction of the \( i \) gas species.

<table>
<thead>
<tr>
<th>Assumptions</th>
<th>This work</th>
<th>Moretti et al. (2017)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Presence of an equilibrated gas phase in the ‘gas equilibration zone’</td>
<td>Presence of an equilibrated gas phase in the ‘gas equilibration zone’</td>
<td></td>
</tr>
<tr>
<td>Redox conditions fixed by the rock matrix (( f_{O_2} ) -T function of D’Amore Panichi, 1980)</td>
<td>Redox conditions controlled by the gas system itself (i.e. ( \text{CH}_4 ) in equilibrium with the other gas species)</td>
<td></td>
</tr>
<tr>
<td>Secondary processes can affect ( H_2O ) (i.e. shallow water addition or vapour condensation)</td>
<td>No occurrence of secondary processes (i.e. no condensation of water)</td>
<td></td>
</tr>
<tr>
<td>Saturated vapour (i.e. ( P_{H2O} ) fixed by liquid-vapour coexistence)</td>
<td>( P_{H2O} ) not fixed</td>
<td></td>
</tr>
</tbody>
</table>

Geobarometric and geothermometric functions

1) \( T = 3133.5/(0.933- \log X_{CO}/X_{CO_2}) \)

2) \( P_{H2O} = 5.51-2048/T \)

3) \( \log P_{CO_2} = 3.025 + 201/T - \log X_{H2}/X_{CO} \)

4) \( P_{tot} = P_{CO_2} + P_{H2O} \)

Recently, a different approach to hydrothermal gas equilibria, based on the same dataset of Solfatara fumaroles, has led to contrasting temperature and pressure estimates (Moretti et al., 2017). The results of Moretti et al. (2017) would indicate a progressive depressurization of the hydrothermal system, while our estimates point to an ongoing process of heating and pressurization. These diverging results arise from different model assumptions, which in turn result into diverse geothermometric and geobarometric functions (Table DR1).
Moretti et al. (2017) use the same model of Chiodini and Marini (1998), i.e. they consider equilibrium conditions within the gas system H$_2$O-CO$_2$-H$_2$-CO-CH$_4$. In their model, redox conditions are internally fixed within the gas system, in the assumption that methane equilibrates with the other species in the gas equilibration zone. This assumption is however not obvious because CH$_4$ is much slower to react than H$_2$ and CO (Giggenbach, 1991). In particular, at Solfatara, Caliro et al. (2007), considering the reaction of carbon isotopic exchange between CO$_2$ and CH$_4$, have shown that the CH$_4$/CO$_2$ ratio does reflect much higher temperatures (360°C-430°C) than those returned by the H$_2$/H$_2$O and CO/CO$_2$ ratios (200-250°C). For this reason, and according to Chiodini et al. (2015), we here favour the assumption of redox conditions fixed by the mineral rock matrix (expressed by the empirical f$_{O2}$-T function of D’Amore and Panichi, 1980) instead of assuming that H$_2$, CO and CH$_4$ re-equilibrate at the same temperature. We note, however, that assuming a rapid CH$_4$ re-equilibration can cause different absolute T-P estimations, but not an opposite interpretation (declining v. increasing pressure) of the same set of data.

A second critical aspect determining the divergent results of Chiodini et al (2015) and Moretti et al. (2017) is that the latter authors neglect secondary process affecting the H$_2$O content of the gas (i.e. no condensation, no addition of water). This is evident from their geothermometric and geobarometric functions that are based on ratios involving measured X$_{H2O}$ (i.e. H$_2$O is considered as representative of the equilibrium conditions in equations 1$_M$ and 3$_M$ in Table DR1). We will refer to this assumption as the no-condensation assumption, while we will refer to that of Chiodini et al., (2015) as the vapour-liquid coexistence assumption.

The temperatures and pressures estimated with the two methods (equations 1$_C$-4$_C$ and equations 1$_M$-4$_M$ in Table DR1) are compared with our fumarolic tremor (RSAM) at Pisciarelli in the form of chronograms (Fig. DR10b,c) and binary diagrams (Fig. DR11a,b). The diagrams show that only the P-T estimates based on the vapour-liquid coexistence assumption are positively correlated with RSAM. In contrast, the fluid pressures computed in the no-condensation assumption negatively correlate with fumarolic tremor, and decrease in the period of observation from about 2 bar to values that are systematically lower than the atmospheric threshold of 1 bar (i.e. impracticable values for a fumarolic vent, Fig. DR11a).

From a general point of view, the above examples highlight that geochemical modelling is strongly dependent on assumptions that need to be done to transform gas concentrations in geothermometric and geobarometric estimations. The no-condensation assumption of Moretti et al., (2017) and the vapour-liquid coexistence assumption are in principle both possible. The vapour-liquid coexistence assumption coincides with the concept of the boiling point-depth curve that generally applies to the majority of the hydrothermal system of the world (Henley et al., 1984), in which a liquid phase is
present. Hydrothermal systems characterised by superheated steam, similar to those returned by the Moretti et al. (2017) approach, are rare but possible, such as in the well-known geothermal systems of Larderello (Italy; White et al., 1971) and the Geysers (California; White et al., 1971) where, however, low pressures are at least partially caused by extensive artificial extraction of the geothermal fluids.

To conclude, even if both the assumptions are valid in principle, only the vapor-liquid coexistence model returns T-P values compatible with other independent observations (Figs. DR10, DR11), including the observed increases in soil CO\textsubscript{2} output (see Fig. 7 in Cardellini et al., 2017) and fumarolic activity (see Fig. 5 in Aiuppa et al., 2015).

Figure DR10 A: Chronogram of RSAM at CPIS station compared with the temperature (panel B) and pressure (panel C) estimations based on the two different approaches of this work and of Moretti et al. (2017) (see the text). In order to better compare the geochemical and seismic signals, the RSAM trend is reported as a thick grey line in the background of panels B and C.
The fumaroles of Solfatara (BG and BN) are systematically sampled and analysed since 1983. Details on the sampling and analytical methods are reported in Caliro et al. (2007). The pre-2016 compositions used in this work are available in Chiodini et al., (2016) while here are reported the compositions updated to April 2017. The concentrations are expressed in \( \mu \text{mol/mol} \).

### Table DR2 Composition of Solfatara fumaroles

The fumaroles of Solfatara (BG and BN) are systematically sampled and analysed since 1983. Details on the sampling and analytical methods are reported in Caliro et al. (2007). The pre-2016 compositions used in this work are available in Chiodini et al., (2016) while here are reported the compositions updated to April 2017. The concentrations are expressed in \( \mu \text{mol/mol} \).

| Date       | name | T °C | H₂O | CO₂ | CH₄ | H₂ | CO | name | T °C | H₂O | CO₂ | CH₄ | H₂ | CO |
|------------|------|------|-----|-----|-----|----|----|------|------|-----|-----|-----|----|----|----|
| 26/01/2016 | BG   | 163.7| 737000 | 260200 | 14.1 | 599 | 1.49 | BN   | 145.3 | 747400 | 250200 | 10.2 | 608 | 1.44 |
| 24/02/2016 | BG   | 164.1| 746700 | 250600 | 13.8 | 572 | 1.42 | BN   | 144.8 | 729600 | 268000 | 10.9 | 626 | 1.59 |
| 31/03/2016 | BG   | 163.5| 746200 | 251100 | 13.7 | 608 | 1.49 | BN   | 143.2 | 734400 | 263100 | 11.5 | 680 | 1.57 |
| 29/04/2016 | BG   | 164.8| 734400 | 262600 | 15.2 | 679 | 1.59 | BN   | 145.0 | 743300 | 254300 | 10.5 | 628 | 1.53 |
| 20/05/2016 | BG   | 164.0| 742700 | 254500 | 14.6 | 633 | 1.62 | BN   | 145.0 | 736700 | 260900 | 10.6 | 654 | 1.70 |
| 22/06/2016 | BG   | 163.6| 745200 | 251900 | 15.4 | 676 | 1.58 | BN   | 144.0 | 741300 | 256300 | 11.6 | 653 | 1.66 |
| 06/07/2016 | BG   | 164.4| 743300 | 253800 | 14.7 | 654 | 1.63 | BN   | 144.5 | 735900 | 261600 | 11.7 | 689 | 1.71 |
| 30/08/2016 | BG   | 163.1| 739100 | 257800 | 13.1 | 641 | 1.58 | BN   | 145.1 | 740100 | 257400 | 10.3 | 643 | 1.59 |
| 26/09/2016 | BG   | 163.3| 745100 | 251900 | 14.6 | 668 | 1.54 | BN   | 145.1 | 742300 | 255200 | 11.3 | 674 | 1.60 |
| 25/10/2016 | BG   | 162.9| 742300 | 254800 | 13.4 | 605 | 1.63 | BN   | 144.9 | 744000 | 253700 | 10.0 | 621 | 1.66 |
| 28/11/2016 | BG   | 163.5| 751700 | 245400 | 12.4 | 584 | 1.50 | BN   | 143.5 | 725400 | 272000 | 10.5 | 657 | 1.70 |
| 15/12/2016 | BG   | 162.5| 743000 | 254000 | 14.1 | 663 | 1.65 | BN   | 142.9 | 728300 | 269100 | 11.6 | 723 | 1.82 |
| 11/01/2017 | BG   | 163.5| 738600 | 258600 | 13.5 | 657 | 1.73 | BN   | 144.1 | 721800 | 275600 | 11.4 | 723 | 1.80 |
| 20/02/2017 | BG   | 163.7| 748500 | 248900 | 10.8 | 581 | 1.63 | BN   | 144.2 | 732400 | 265300 | 8.95 | 630 | 1.80 |
| 16/03/2017 | BG   | 163.7| 723300 | 273700 | 12.4 | 704 | 1.77 | BN   | 144.3 | 743500 | 254200 | 9.01 | 650 | 1.58 |
| 18/04/2017 | BG   | 163.7| 741000 | 256000 | 10.9 | 659 | 1.69 | BN   | 144.7 | 742500 | 255100 | 8.42 | 669 | 1.66 |

Figure DR11. The total pressure (panel A) and temperature estimations (panel B) are plotted vs Log RSAM. The determination coefficients \( R^2 \) refer to the annual mean values.
REFERENCES CITED


