

**SUPPLEMENTARY INFORMATION TO THE PAPER:**

**“Caldera unrest driven by CO<sub>2</sub>-induced drying of the deep hydrothermal system”**

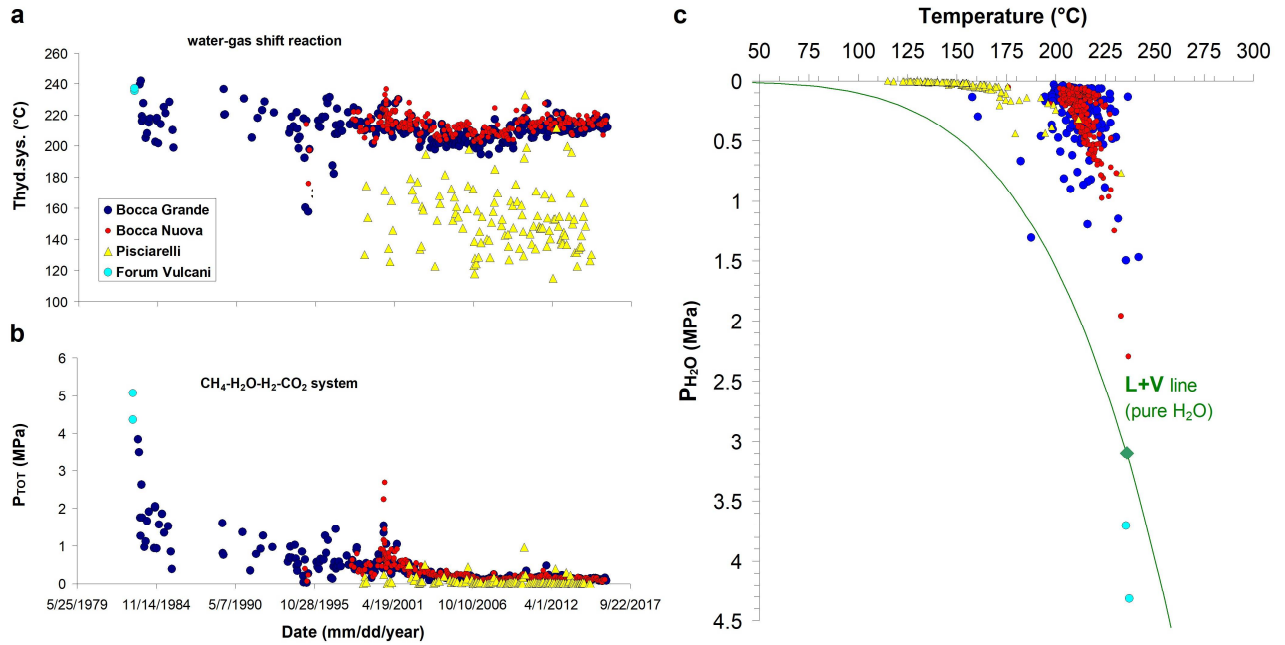
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**Supplementary Table 1**

**TABLE S1.** Rock and magma properties used in simulations of conductive/convective heat transfer. HEAT3D<sup>54</sup> default values of thermal conductivity (K) and heat capacity (Cp) are used. Rock porosity from [ref. 35](#); rock density from [ref. 36](#); magma density and initial magma temperature (T<sub>0</sub>) from [ref. 43](#).

| Rock type      | K (W/m K) | Cp (J/kgK)   | Density (kg/m <sup>3</sup> ) | porosity            |
|----------------|-----------|--------------|------------------------------|---------------------|
| Tuff           | 1         | 980          | 2000                         | 0.2                 |
| Sill intrusion | K (W/m K) | Cp (J/ kg K) | Density (kg/m <sup>3</sup> ) | T <sub>0</sub> (°C) |
| trachyte       | 1.3       | 1150         | 2750                         | 900                 |

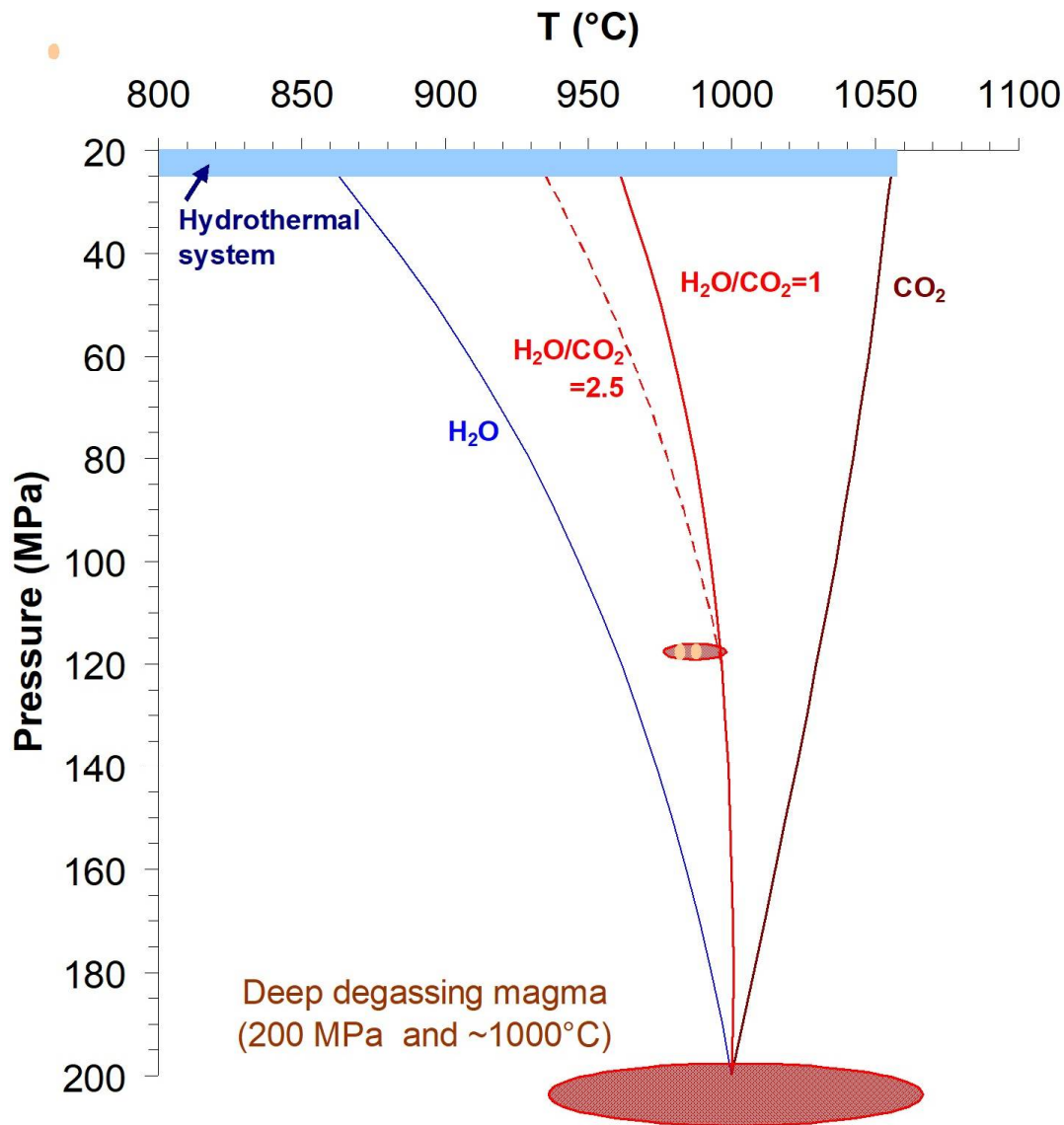
15 **Supplementary figure 1 and caption**



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17 **Supplementary figure 1 | P-T conditions of the upper hydrothermal reservoir. a.** Chronogram of  
 18 computed shallow hydrothermal equilibrium temperatures at Solfatara and Pisciarelli vents by using the  
 19 water-gas shift reaction (equation 2; see [Methods](#)). Note that the Pisciarelli system does not show any  
 20 appreciable heating, whereas Solfatara hydrothermal temperatures draw a minimum around year 2007. **b.**  
 21 Chronogram of pressures computed from thermodynamic equilibrium involving  $\text{CO}_2\text{-H}_2\text{O-H}_2\text{-CH}_4$  species in  
 22 the single gas phase (equation 4; see [Methods](#)). **c.** P-T diagram comparing results on the shallow  
 23 hydrothermal system to the liquid-vapour equilibrium of pure water (see [Methods](#)).

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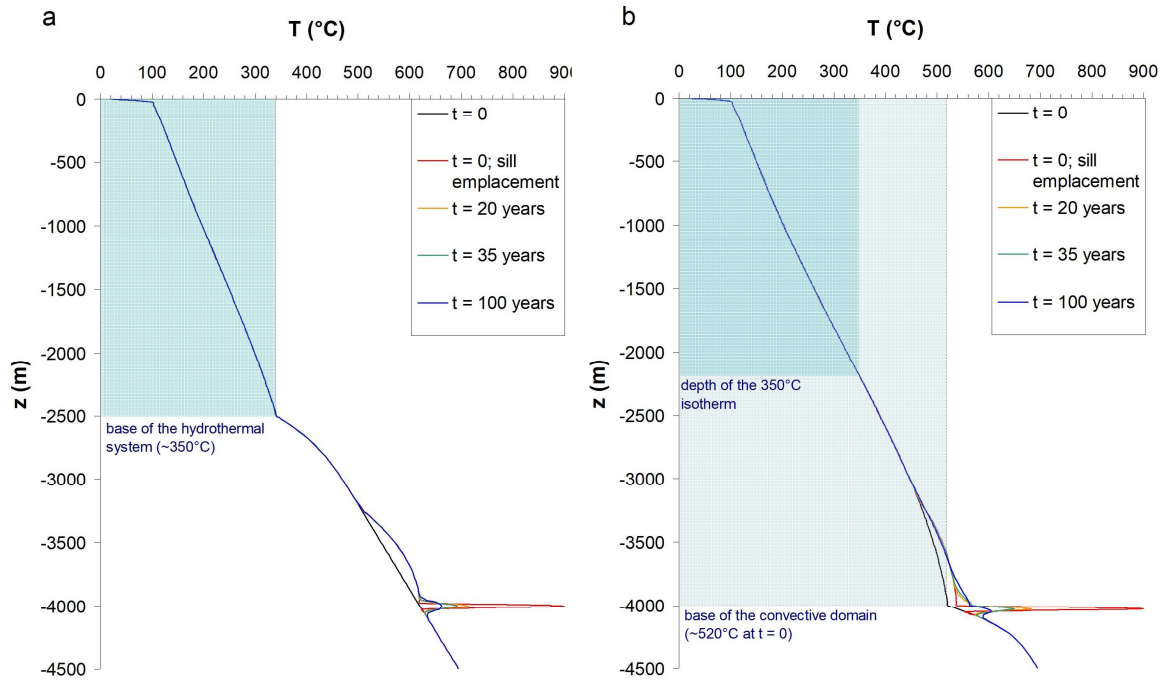


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27 **Supplementary figure 2 | P-T properties of the deep fluids.** P-T diagram reporting IAD paths (eq. 5) of  
 28 deep magmatic gas, computed from 200 MPa and 1000°C to 25 MPa (for pure-H<sub>2</sub>O, pure CO<sub>2</sub>, and 1:1 H<sub>2</sub>O-  
 29 CO<sub>2</sub> mixture) and from 120 MPa and 1000°C to 25 MPa (2.5:1 H<sub>2</sub>O-CO<sub>2</sub> mixture, as in [ref. 24](#)). The blue  
 30 stripe between 20 and 25 MPa indicate conditions attained by the gas phase right prior to interact with the  
 31 hydrothermal component to form the gas plume subsequently discharged at fumaroles<sup>22,23</sup>. The Joule-  
 32 Thomson coefficients ( $\mu_{JT}$ ) for pure components were linearly combined (i.e., ideal mixing in the P-T range  
 33 of interest) in case of 1:1 and 2.5:1 H<sub>2</sub>O-CO<sub>2</sub> mixtures (see [Methods](#)).

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35 **Supplementary figure 3 and caption**



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37 **Supplementary figure 3 | Results of conductive/convective modeling<sup>56</sup> of thin-sill emplacement at 4 km**  
 38 **depth. a.** T depth profile for hydrothermal system having its base at 2.5 km at a temperature of ~ 350°C (ref.  
 39 22). **b.** T-depth profile of a convective domain extending down to 4 km, that is, right on top of the emplacing  
 40 25 m-thick sill. Note that in this second case the 350°C isotherm is shifted ~ 250 m upward.

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## Arguments against a persistent shallow degassing magma

Several geochemical arguments play against a shallow magma that drives the current unrest at CFC by relaxing its overpressure since 1984 and releasing steam upward<sup>24,25</sup>:

1) CO<sub>2</sub> plus inert-gas (N<sub>2</sub>, He, Ar) degassing patterns modelled in [refs. 24,25](#) hold only for a primary trachybasalt or shoshonite compositions, the least represented compositions of CFC volcanism<sup>45</sup>. However, it is unrealistic that a trachybasaltic may evolve uniquely as a gas+melt system up to shallow depths.

2) A persistent shallow magmatic source would be conceptually according to some geophysical inversions of geodetic and seismic data<sup>S1-S3</sup>, but overpressure relaxation from modelled degassing patterns is such that pressure was 200 MPa in 1984 and is 120 MPa in 2014 ([ref. 24](#)), resulting in an initial overpressure of 80 MPa. This value largely overcomes the tensile strength of the overlying crustal rocks<sup>13,26</sup> and can be compatible only with a lithostatic load of about 7-8 km. Thus, if a shallow magma were triggering the current uplift, the 1982-84 unrest was hydrothermal<sup>22</sup>, in agreement with temporal trends of geochemical indicators, which point to different triggering mechanisms for these two episodes ([Fig. 2a](#)).

3) It is well established that steam is extracted from magma via “second boiling” and crystallization<sup>23,S4,S5</sup>, which causes the downward migration of a growing solid carapace surrounding the liquid residuum and then leads to a scenario completely opposite to that of a shallow decompressing magma.

4) Independently of the source of juvenile steam (magma second boiling vs continuous decompression), the amount of magma needed to sustain the steam flux of ~ 3500 tons/day ([ref. 24](#)) is not compatible with available geophysical estimates. If we consider that the amount of magma possibly emplaced in 1982-84 occupies at most the same volume as that of the inflation corresponding to maximum displacement (0.09 km<sup>3</sup>, see [Methods](#)), and using a density of 2500 kg/m<sup>3</sup>, steam flux could have been sustained for 17.5 years at most (i.e., until 2002) before

exhaustion, even under most favourable conditions, i.e., adopting the highest H<sub>2</sub>O content CFc  
magmas (4 wt%; [ref. 44](#)) and considering that ~40% of discharged steam comes from magma  
degassing<sup>22,23</sup>.

These simple arguments further dismount shallow magma hypotheses for the present unrest and  
play in favour of a deep and persistent gas contribution (H<sub>2</sub>O/CO<sub>2</sub> ratio between 1 and 1.5) from the  
8 km-deep magma regional reservoir<sup>16,23,44,45</sup>.

### **On the nature of the deep hydrothermal system**

Lacking a shallow degassing magma, the observed thermal evolution can be ascribed to either 1)  
drying of the hydrothermal low-saline liquid, now replaced by a high-T supercritical gas or vapor,  
or 2) increasing salinity of the hydrothermal boiling liquid, now replaced by a NaCl brine like at the  
nearby Vesuvius volcano<sup>S6</sup>. In the first case the increasing CO<sub>2</sub>/H<sub>2</sub>O fumarole ratio accompanies  
decreasing involvement of the hydrothermal end-member and the relative increase of the CO<sub>2</sub>-rich  
deep gas contribution<sup>16,23</sup>, whereas in the second case it may be related to CO<sub>2</sub>-solubility drop in a  
brine (salting-out effect<sup>S1,S2</sup>). In this latter scenario, temperatures in [Fig. 2c](#) would suggest that the  
brine boiling point increases with increasing salt concentration due to the progressive neutralization  
of acid magma gases. Transition to a brine may thus have occurred rapidly at the end of previous  
hot cycles (e.g., between 30 and 40 years at Vesuvius<sup>S1</sup>). We suggest however that the first scenario  
is the only one plausible, due to the very high CO<sub>2</sub>-concentrations ([Fig. 2a](#)) and magmatic fluid  
fractions (> 0.4; [refs. 22,23](#)) and because it easily accounts for high rates of gas discharges at  
surface and the widening of the CO<sub>2</sub> degassing area<sup>24</sup>. On the other hand, the second scenario  
should lead to progressive cooling of the shallow system and much lower magmatic gas fractions,  
neither of them observed.

### **Supplementary references**

- 93 S1. Amoruso, A., Crescentini L. & Sabbetta, I. Paired deformation sources of the Campi Flegrei  
94 caldera (Italy) required by recent (1980–2010) deformation history. *Journal of Geophysical*  
95 *Research: Solid Earth* **119**, 858-879 (2014).
- 96 S2. Amoruso, A. *et al.* Clues to the cause of the 2011–2013 Campi Flegrei caldera unrest, Italy,  
97 from continuous GPS data. *Geophysical Research Letters* **41**, 3081-3088 (2014).
- 98 S3. De Siena, L. *et al.* 4D imaging of the seism-geochemical dynamics leading to recent Campi  
99 Flegrei unrest. Geophysical Research Abstract 19, EGU2017-1877. EGU General Assembly  
100 2017, Vienna (2017).
- 101 S4. Bodnar, R.J. *et al.* Quantitative model for magma degassing and ground deformation  
102 (bradyseism) at Campi Flegrei, Italy: Implications for future eruptions. *Geology* **35**, 791-794  
103 (2007).
- 104 S5. Lima, A. *et al.* Thermodynamic model for uplift and deflation episodes (bradyseism) associated  
105 with magmatic–hydrothermal activity at the Campi Flegrei (Italy). *Earth-Science Reviews* **97**,  
106 44-58 (2009).
- 107 S6. Chiodini, G., Marini, L. & Russo, M. Geochemical evidence for the existence of high-  
108 temperature hydrothermal brines at Vesuvio volcano, Italy. *Geochimica et Cosmochimica Acta*  
109 **65**, 2129-2147 (2001).
- 110 S7. Truesdell, A.H. Origins of acid fluids in geothermal reservoirs. *Geotherm. Res. Counc. Trans.*  
111 **15**, 289 –296 (1991).