Tarchini Luca (Orcid ID: 0000-0001-6045-0802)

Carapezza Maria Luisa (Orcid ID: 0000-0002-0223-6012)

Fluid Geochemistry Contribution to the Interpretation of the 2011-12 Unrest of Santorini, Greece, in the frame of the dynamics of the Aegean Volcanic Arc

L. Tarchini[1,2], M. L. Carapezza[2], M. Ranaldi[1,2], F. Sortino[2], A. Gattuso[2] and V. Acocella[1]

[1] Science Department, RomaTRE University, Rome, Italy.

[2] Istituto Nazionale di Geofisica e Vulcanologia, Italy.

Corresponding author: Luca Tarchini (luca.tarchini@uniroma3.it)

Key Points:

- Extensive and systematic geochemical surveys followed the anomalous degassing during Santorini unrest, both in the caldera center and on the inner caldera walls;
- Gas ratios and isotopic composition indicate deep mafic magma refilling into the shallow dacitic plumbing system;
- Unrest has limited apparent relations with the longer-term tectonic evolution of the Arc, conversely to the 1950 eruption.

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1029/2018TC005377

Abstract

Tectonic and magmatic activity may couple at volcanic arcs, even though any relationship is less defined in smaller arcs, experiencing limited activity. Here we use gas geochemistry data collected during the 2011-2012 unrest at Santorini (Greece) to understand better the dynamics of the Aegean Volcanic Arc with regard to its tectonic setting. Since the most recent eruption in 1950 and before the unrest, minor seismicity and CO_2 degassing (mainly from the fumaroles of Nea Kameni islet) were observed at Santorini. On January 2011, anomalous seismicity along the NE-SW trending Kameni Line was accompanied by an inflation north of Nea Kameni. Fumarolic gas composition changed and gas release notably increased. We carried out geochemical study both on Kameni and Thera islands from January 2012 to June 2013. We repeated surveys of diffuse soil CO_2 degassing and of in-soil gas concentration and we analyzed fumaroles and gas dissolved in thermal waters for chemical and isotopic composition. In agreement with previous studies, our geochemical data, particularly the diffuse soil CO_2 flux increase, the increase of H_2 content and of CO_2/CH_4 and $^3He/^4He$ ratios in fumarolic gases, support geophysical data in indicating that unrest was associated with the emplacement of new mafic magma. This unrest had limited effect on the regional setting, with gas emissions focusing along the regional NE-SW structures, without triggering by any seismic event, conversely to the 1950 eruption, which probably occurred in a frame of general tectonic reorganization of the Aegean microplate.

1 Introduction

The activity of volcanic arcs relates closely to that of the converging plates responsible for the arc development. This dependence occurs at deeper and shallower levels. In the first case, the dip of the subducting slab determines the release of fluids, thus controlling the location of the overlying magmatic arc. In the second case, volcanic activity may be partly controlled by the regional tectonic activity, including the seismic cycle of the subduction zone (Acocella, 2014, and references therein). In particular, the latter feature has been object of several recent studies (Hill et al., 2002; Manga and Brodsky, 2006; Walter and Amelung, 2007; Eggert and Walter, 2009; Pritchard et al., 2013; Takada and Fukushima, 2013; Acocella et al., 2018). The consensus is that the activity of faults and the related seismicity along the subducting and the overriding plates may be responsible for extension in the overriding plate, from the trench to the area of the volcanic arc included. This extension is transient, mainly occurring during the co-seismic and post-seismic phases (thus lasting a few years), but may occur independently of the longer-term (or post-seismic, lasting from decades to centuries) regional tectonic motion along the arc. This is well exemplified by the 2011 Tohoku (Japan) mega-earthquake, which induced, on the contracting volcanic arc, a transient extension during the co- and post-seismic phases (Ozawa et al., 2011, Simons et al., 2011), also affecting magmatic activity (Takada and Fukushima, 2013). In several cases, the established relationship between the occurrence of mega-earthquakes and successive eruptions along the affected portion of the arc confirms that the local extension created by the accelerated plate motion may promote dike injection and thus eruptions, increasing the post-seismic eruptive frequency (Walter and Amelung, 2007).

While these relationships are better established at large volcanic arcs experiencing mega-earthquakes, the tectono-magmatic interactions at smaller arcs, associated with plates converging at lower velocities (and thus not producing mega-earthquakes), have been less investigated and are also less clear.

The aim of this paper is to contribute to fill this knowledge gap, exploiting a gas geochemistry dataset acquired during a recent unrest of Santorini volcano, in the Aegean Volcanic arc.

The Aegean Volcanic Arc results from the northward subduction of the oceanic African lithosphere below the continental Eurasian lithosphere, forming a slab extending to 150-200 km of depth (Fig. 1; Dimitriadis et al., 2010, and references therein). In this context, several microplates, including the Aegean one, make up the overriding plate. Aegean microplate is experiencing an overall ~N-S extension along the volcanic arc and towards the trench, as highlighted by structural data (Feuillet, 2013, and references therein), seismicity data (Kiratzi, 2014, and references therein) and GPS data (Reilinger et al., 2010). In the Santorini area, the extensional structures have a more NE-SW direction, associated with a local NW-SE extension. Evidence of these structures is given by the NE-SW trending Kameni-Kolumbo fracture zone (this zone is also partly coinciding with a low-velocity zone; Dimitriadis et al., 2010), as well as by its activation during the 2011-2012 Santorini unrest (Feuillet, 2013).

In addition, all Santorini historic eruptions occurred from vents located on two parallel NE-SW trending structures, forming the "Kameni Line", crossing Santorini caldera from the Kameni islets to the main island of Thera, and the "Kolumbo Line", running from northern Thera to the submarine Kolumbo volcano (Fig. 1). In recent years until 2011, these two structures had a marked contrasting behavior: the Kolumbo Line has been the site of an intense seismic activity, whereas the Kameni Line showed lack of seismicity (Dimitriadis et al., 2009). On January 2011, anomalous seismicity (M_L up to 3.3) began inside the caldera in the Kameni Line and continued up to April 2012 (Vallianatos et al., 2013; Kaviris et al., 2015; Papadimitriou et al., 2015). In the same time, GPS, InSAR and SqueeSAR observed a rapidly expanding radial deformation from a point located within the caldera to the north of Nea Kameni (Newman et al., 2012; Parks et al., 2012, 2015; Lagios et al., 2013; Papoutsis et al., 2013). Concurrently, fumaroles and gas discharges showed geochemical variations indicating an increase of magmatic gas output (Parks et al., 2013, Tassi et al, 2013, Rizzo et al., 2015). Such a seismic, geodetic and geochemical unrest, never recorded at Santorini, was related likely to the inflation of a magmatic source.

In order to contribute to the evaluation of this unrest, and to relate it to the general tectonic framework, we carried out an extensive geochemical study of the gas emissions of Kameni and Thera islands from 4 January 2012 to June 2013. We repeated several surveys of soil CO_2 diffuse degassing and in-soil gas concentration on established grids of measurement points. We sampled the main fumaroles and thermal waters, which we analyzed for chemical and isotopic composition either immediately in the field or in laboratory. The aim was to recognize possible variations in fluid geochemistry with respect to the pre-unrest conditions (Barberi & Carapezza, 1994; Chiodini et al., 1998a, b; D'Alessandro et al., 2010) and to discuss their meaning. In fact, unrest and crises are characterized by anomalous increase of soil CO_2 diffuse degassing and by variation in the chemical and isotopic composition of fumarolic gas, reflecting an increasing gas release from relatively shallow magma bodies, e.g. at Vulcano (Granieri et al., 2006) and at Stromboli (Carapezza et al., 2004).

2 Geologic setting

Santorini, located in the southern volcanic Aegean arc of the Meso-Cenozoic subduction zone (Jolivet and Brun, 2010), is one of the most famous volcanic complex of the world. It has been the site of the so-called Minoan eruption, a violent Plinian eruption occurred in the late Bronze Age about 1650 B.C.E., which covered all emerged near lands by thick tephra and caused a caldera collapse with associated tsunami. This eruption was considered for a long time the main cause for the vanishing of the Minoan civilization, which instead began about one century later (Heiken and McCoy, 1984; Druitt et al., 1999; Friedrich et al., 2006; Manning et al., 2006). At least three other caldera collapses, a dozen of major explosive eruptions and inter-Plinian smaller eruptions occurred at Santorini before the Minoan event

(Druitt et al., 1999; Vespa et al., 2006). Strabo in 197 B.C.E. was the first to report the Post-Minoan intracaldera volcanic activity, which built up the short-living islet of Hiera. Starting from 46 AD, two volcanic islets (Palea Kameni and Nea Kameni) were progressively formed in the center of the caldera. From 1570 to 1950, six eruptions built up Nea Kameni islet with extrusion of dacitic lava flows and domes, associated to mild Vulcanian and phreatic explosions (Fouquè, 1879; Georgalas, 1953 and references therein; Pyle and Elliot, 2006). Only the explosive eruption of Palea Kameni of 726 AD caused considerable destruction in Thera (Vougioukalakis and Fytikas, 2005). The most recent eruption started in January 1950, preceded by a nearby (~150 km) and shallow (15 km) M=7.3 earthquake in February 1948 (Fig. 1).

The 2011-2012 unrest showed shallow seismicity, surface deformation and increase in degassing. The unrest has been related to the emplacement of ~$16x10^6$ m^3 of magma at a depth between 3.5 and 6 km immediately to the north of Nea Kameni Island (see Lagios et al., 2013 for a comparison of the estimated Mogi source). Pre-unrest seismicity (period 1991-2001), characterized by M>5.5 (considered to be a lower bound to trigger any static stress variation over a distance of at least 100 km; Walter et al., 2009; Wang and Manga, 2010), is shown in Fig. 1 in terms of location, magnitude and focal mechanisms (https://earthquake.usgs.gov). While this seismicity clusters on the eastern part of the Aegean microplate, no particularly large and/or near (to Santorini) event occurred to justify a seismic trigger of the unrest.

Finally, another active submarine volcano (Kolumbo) is located outside the caldera 8 km to the NE of the main island of Thera (Fig. 2). Kolumbo most recent explosive eruption occurred in 1649-1650 AD and caused the death of 70 people and more than 1000 animals on Thera, because of severe ash fallout, volcanic gas clouds and by a tsunami generated by an underwater caldera collapse (Fouquè, 1879; Vougioukalakis and Fytikas 2005).

3 Investigation sites and methods

Fig. 2 shows the sites where we carried out geochemical investigation from January 2012 to June 2013. Preliminary soil CO_2 flux surveys were performed both on Nea Kameni islet and on Thera island (Cape Kolumbos, Firà, Cape Exomiti) from 4 to 10 January 2012 by means of 405 soil CO_2 flux measurements and 405 soil gas sampling at 50 cm depth. Based on the preliminary soil CO_2 flux maps, we established target areas for the repetition of the surveys on Nea Kameni (from now TANK= Target Area of Nea Kameni, where soil CO_2 flux and in-soil gas concentrations were measured again from 10 to 14 January 2012) and near Firà town (TAF= Target Area of Firà). TANK consists of a newly established denser network of measuring and sampling points (119 with 20 m spacing) while TAF consists of 96 points selected amongst those previously measured. During the first survey, we sampled dissolved gases from two thermal springs, one on the northern shore of Nea Kameni (Irinià) and one on the northeastern shore of Palea Kameni (Agios Nikolaos). These two springs, together with a third one (Agios Georgios) on the western shore of Nea Kameni, were then sampled for dissolved gases in all surveys from May 2012 to June 2013. Seven fumaroles of the central sector of Nea Kameni were also sampled.

We measured diffuse soil CO_2 flux with the accumulation chamber method (Chiodini et al., 1998b for method description). We derived soil flux and gas concentration maps by ordinary kriging in Golden Software Surfer®. Fumarole and soil gas samples were collected in 20 ml glass vials with rubber screw cap, and analyzed for CO_2, N_2, O_2, He, H immediately on site with an Agilent 490 Micro GC Analyzer with CP-MolSieve 5Å column channel. Fumarolic gases were also sampled in glass sampling tubes for isotopic composition. Water samples were collected in rubber-septum glass bottles for dissolved gas chemical and isotopic composition following the procedure of Inguaggiato and Rizzo (2004). Isotopic analyses were made at INGV Palermo laboratories accordingly with the procedures described in Paonita et al. (2012).

4 Results

4.1 Soil CO_2 flux and in-soil gas concentration on Thera Island

Barberi and Carapezza (1994) carried out a pioneer soil-gas investigation at Thera in 1993, in order to investigate soil-gas anomalies in deep reaching fault zones. Diffuse soil CO_2 flux was measured by the "CO_2 dynamic concentration" method (Gurrieri & Valenza, 1988); soil CO_2 and He concentrations were respectively measured in the field with IR spectrometer and in laboratory with mass spectrometer. Barberi and Carapezza (1994) detected the following three main anomalies, respectively from North to South: on the Kolumbo Line, on the Kameni Line, and in an area related to a deep faulting zone cutting across a geothermal system between Akrotiri and Exomiti. Fig. 3 shows the data of Barberi and Carapezza (1994) that we reprocessed with ordinary kriging.

In early January 2012, we carried out soil CO_2 flux and gas concentration surveys in the same anomalous zones by means of 345 flux measurements and 22 soil gas analyses. Fig. 4 shows the soil CO_2 flux maps of the preliminary survey of 4-10 January 2012. No map has been interpolated for Cape Exomiti, as only 23 measures along two transects were taken. A NE-SW oriented anomalous degassing zone was found in the area of Firà town on the Kameni Line (Fig. 4a) with values up to 224 $g*m^{-2}day^{-1}$ (compared to a maximum of 98 $g*m^{-2}day^{-1}$ found in the 1993 survey of Barberi and Carapezza, 1994), and a total soil CO_2 flux of 25.6 tonnes/day from 0.73 km^2.

Fig. 4b shows the soil CO_2 flux map of Cape Kolumbos area (1.6 km^2): few and weak NE-SW aligned flux anomalies were detected in the central investigated sector with values up to 64 $g*m^{-2}day^{-1}$ (the maximum value was 21 $g*m^{-2}day^{-1}$ in 1993; Barberi & Carapezza, 1994) and a total flux of 16.5 tonnes/day from 1.58 km^2. Diffuse soil CO_2 flux values measured at Vlychada, near Cape Exomiti, are even lower (maximum of 34 $g*m^{-2}day^{-1}$; similar to the 33 $g*m^{-2}day^{-1}$ measured by Barberi and Carapezza, 1994). However, anomalies in the soil gas concentration were recorded in the central surveyed sector ([CO_2] up to 6 vol.%; [He] up to 9 ppm; [H_2] up to 14 ppm). These anomalies are aligned NNE-SSW (Fig. 4d).

Total soil CO_2 flux of Firà of January 2012, recalculated for the TAF, sums up to 18.8 tonnes/day. In May 2012, flux reduced of nearly two-thirds (6.4 tonnes/day). Total flux continued diminishing in July 2012 (2.3 tonnes/day) and it slightly increased in October 2012 (3.7 tonnes/day) and January 2013 (6.0 tonnes/day; a value close to that of May 2012). The minimum flux added up to 2.0 tonnes/day in June 2013 (Table 1). Data therefore show that in January 2012, during the Santorini seismic unrest, anomalous degassing occurred on the prolongation of the Kameni Line on Thera.

4.2 Nea Kameni soil CO_2 flux and gas concentration

At Nea Kameni the first four soil CO_2 flux surveys using an accumulation chamber were carried out from June 1994 to September 1995 in the central part of the island where most craters and fumaroles are located (Chiodini et al., 1998a, 1998b; Parks et al. 2013). The maximum soil CO_2 flux was measured in June 1994, with 12.2 tonnes/day diffusing from a surface of 25,000 m^2. In order to compare previous and recent surveys, we recalculated fluxes with ordinary kriging from the raw data published in Chiodini et al. (1998a).

Chiodini et al. (1998b) calculated a total soil CO_2 flux of 15.4 tonnes/day for the June 1994 survey with a different geostatistical method. Parks et al. (2013) report a distinct CO_2 degassing pattern as, throughout 2011, they observed higher fractions of high-flux population and higher means of the low-flux population with respect to the 1994-1995 surveys.

In early January 2012, we first carried out a wider soil CO_2 flux survey on Nea Kameni with 60 measurements over 456,000 m^2 and an average spacing of 90 m (Fig. 4c), estimating a total soil flux of 74.6 tonnes/day of CO_2. Fig. 4c confirms that the central sector of the islet is the most degassing, but anomalous degassing also matches to past volcanic activity zones, especially south of the central crater area. On 6 January 2012, we estimated a total soil CO_2 flux from TANK of 35.9 tonnes/day with ordinary kriging and of 39.9 tonnes/day with Stochastic Gaussian Simulation (Table 1). Parks et al. (2013) estimated 38 tonnes/day with Stochastic Gaussian Simulation for their survey at the end of January 2012. They observed a change, with respect to their 2011 surveys, in the degassing pattern, which displayed anomalously high emissions over a much broader area than before, and they attributed this to the increased fracturing after the major seismic swarm of 23-24 January 2012. Fig. 5 shows the soil CO_2 flux maps of TANK from January 2012 to June 2013.

After the end of the seismic and geodetic crisis, total soil CO_2 flux from TANK decreased to 27.4 tonnes/day in May 2012, 16.4 tonnes/day in July 2012, 11 tonnes/day in October 2012 (but from a smaller area of 22,000 m^2), increased to 25.1 tonnes/day in January 2013 and reduced to 7.6 tonnes/day in June 2013. When normalized to the investigated area, total soil CO_2 flux varied from 8.8 tonnes/ha*day in January 2012 to a minimum of 3.5 tonnes/ha*day in June 2013. Maximum flux value, measured within the fumarolic area, increased from 9000 $g*m^{-2}day^{-1}$ in 1995 (Chiodini et al., 1998a) to 15,700 $g*m^{-2}day^{-1}$ in early 2012, but continued increasing in the following surveys until October 2012 (32,200 $g*m^{-2}day^{-1}$). Only in January 2013, the maximum value began diminishing (Table 1).

In the 4-10 January 2012 survey the soil gas at 50 cm depth was firstly sampled on the broad area of Nea Kameni. Very high concentrations were found (Fig. 5) up to 90 vol.% of CO_2, 2.4 vol.% of H_2 and 14.8 ppm of He, with maxima distributed in the area of high soil CO_2 flux. Another anomalous area was found several tens of meters south of it (Fig. 6), at the feeding point of two Georgios lava flows (1866-1870)

Soil gas sampling was repeated on all the TANK points from 10 to 14 January 2012, and only in the 65 most representative points in the surveys from May 2012 to June 2013 (Fig. 7). In each survey, the highest soil concentrations occurred in the eastern part of TANK, with maxima values recorded in January 2012 (Table 2 and Fig. 7).

4.3 Nea Kameni fumarole geochemistry

The main gas discharge of Nea Kameni occurs from low-pressure steaming ground in the central part of the island (Fig. 2). These fumaroles are weak gas emissions fed by a shallow hydrothermal system and undergoing in-soil steam condensation and air contamination before reaching the surface (Chiodini et al., 1998a). Maximum temperature (T) is 95-96 °C (below the water boiling point for 100 m a.s.l.) and it remained constant along the years (Nagao et al., 1991; Chiodini et al., 1998a; Tassi et al., 2013). Fumaroles were sampled in the January 2012 survey. We performed chemical analyses on site by a portable gas chromatograph for major dry gas components and in laboratory for C and He isotopes (most of the data published by Rizzo et al., 2015). For the comparison with pre-unrest composition, we used the analytical data published in Chiodini et al. (1998a), D'Alessandro et al. (2010), Tassi et al. (2013), with Fumarole FNK4 (with high T, $^3He/^4He$, CO_2 and H_2 content) used as the reference fumarole (Table 3 and Fig. 4).

The ternary plots of the major gas species show the occurrence in some samples (particularly those of 1994 and 2007) of marked air contamination (as evident in the triangular plots N_2-CO_2-CH_4 and N_2-CO_2-H_2) (Fig. 8). Ternary plots show also some variation in the hydrogen and methane concentration with respect to CO_2.

Of particular interest is the clear increase of CO_2/CH_4 ratio recorded in late 2011 and early January 2012 (Fig. 9a). Methane is relatively abundant in hydrothermal gases and has very low concentration in magmatic fluids. Increase of CO_2/CH_4 ratio in fumaroles characterizes volcanic unrest as in Campi Flegrei 1983–2008, Mammouth Mt. 1990-1992, Nisyros 1998-2002 (Chiodini et al., 2002; Chiodini et al., 2016) and indicates an increasing input of deep magmatic CO_2 in shallow hydrothermal systems. The same process clearly occurred at Nea Kameni during the 2011-2012 unrest, as already commented by Rizzo et al. (2015). The time-variation of the CO_2 and H_2 content, recalculated on air–free analyses, shows high variation in the hydrogen content of the CO_2-rich fumarole FNK4 (Fig. 9b), with the maximum (3.36 vol.%) recorded in February 2012 following an increase initiated after May 2007 (Tassi et al, 2013; Rizzo et al., 2015).

The H_2 and CO_2 content of fumarole FNK4 in January 2012 is identical to that of September 2008 (D'Alessandro et al., 2010), but we do not have data to exclude an hydrogen decrease in the period 2009-2010, before the January 2011 onset of the seismic unrest, followed by a new increase during the 2011-2012 seismic unrest.

An attempt has been made to estimate the temperature of the hydrothermal system feeding the Nea Kameni gas emissions by gas geothermometry. Owing to the lack of water concentration data in the sampled gas, we used water-independent geothermometers, as discussed in Barberi et al. (2013). As neither Ar concentration data were available (argon being the standard gas used in the field gas-chromatograph), we adopted the geothermometric functions based on the CO/CO_2 and the H_2/N_2 ratios, after Chiodini & Marini (1998) and Brombach et al (2003) respectively. For the preparation of the theoretical grids of Fig. 10, we adopted the $FeO\text{-}FeO_{1.5}$ hydrothermal gas buffer, proposed by Giggenbach (1987) as a correct assumption of the redox conditions in the gas equilibration zone. These grids indicate the H_2/N_2 and CO/CO_2 ratios expected for gas equilibration in a single-saturated liquid phase and in a single-saturated vapor phase, as well as the effects of single-step vapor phase separation at decreasing temperatures from a liquid phase of initial temperature T_0. Furthermore, arrows in Fig. 10 qualitatively indicate the effects of processes of interest, such as steam condensation accompanied by preferential dissolution of CO_2 and air addition. FNK4 gases plot close to the vapor line from 1994 to May 2007. FNK4 gases plot close to the liquid line from October 2007 to 2013 and a possible increase of the hydrothermal liquid temperature from 230 to 250-275 °C may have occurred after May 2007 (Fig. 10).

4.4 Helium isotopic composition of Nea Kameni fumarolic and dissolved gases

The highest $^3He/^4He$ value (6.84) in the fumarolic gases of the Aegean arc volcanoes has been found at the submarine Kolumbo vent (Carey et al., 2013). Shimizu et al. (2005) found another high value (6.2 Ra) at Nysiros. These values are only slightly lower than those of the mantle below typical arc volcanoes (ca. 7-8 Ra; Hilton et al., 2002; Shaw et al., 2006) but they are significantly higher than the R/Ra found at Santorini. Table 3 reports all available He isotopic analyses of the Kameni gases from 1988 to 2013. As commented by Rizzo et al. (2015) a significant $^3He/^4He$ increase up to 3.94 Ra was recorded in FNK4 in January 2012 during the seismic unrest, with a successive return to the lower pre-unrest values (≤ 3.7 Ra). We agree with their comments, but we point out that we actually found the maximum R/Ra value in the dissolved gas of Irinià spring at the northern shore of Nea Kameni (the spring closer to the deformation center). Here, $^3He/^4He$ increased from 3.86 Ra on 13 January 2012 to 4.17 Ra on 12 May 2012 and to 4.26 Ra in January 2013 (see Table 3). Unfortunately, the time-limited sampling of this spring prevents to assess whether the R/Ra increase in its dissolved gas initiated already in 2011. In any case, it persisted during the whole 2012. These data and the He isotopic ratios measured by Rizzo et al. (2015) in the fluid inclusions in olivine of mafic nodules of Kameni dacitic lavas indicate that very likely the degassing of a mafic magma was involved in the 2011-2012 unrest. To the other hand, the relatively low $^3He/^4He$ values of the Kameni fumarolic and dissolved gases (< 4.26) indicate that they underwent a significant contamination by radiogenic gases or in the mantle during magma generation or in the crust during magma ascent.

Furthermore, the isotopic composition of $\delta^{13}C_{CO2}$ (from -2.96 ‰ to -0.23 ‰, Table 3) is less negative than in a typical mantle CO_2 (-8 ‰ to -4 ‰, Mattey et al., 1984). This suggests either tapping from a mantle source contaminated by variable amounts of subducted sediments, or a contamination of the magmatic source with thermal decarbonation of carbonate rocks (the latter suggested by Parks et al. 2013 based on the ^{222}Rn-$\delta^{13}C$ systematics of the soil gases).

Klaver et al. (2016), based on a complete analysis of minero-petrographic and radiogenic features of Santorini and Kolumbo volcanic deposits, infer that these two volcanic centers have no shallow connection between their plumbing systems as they tap unrelated and distinct mantle sources, the one beneath Santorini showing more contamination by fluid-rich sediments.

5 Discussions

5.1 Interpretation of the geochemical data

Thera and Nea Kameni soil CO_2 flux, soil gas concentration and fumaroles chemical and isotopic composition show concurrent variations related to the 2011-2012 Santorini seismic and geodetic crisis. Data coherently indicate the occurrence of an episode of anomalous output of high-T deep magmatic fluids rich in CO_2 and with a radiogenic He signature.

Nea Kameni soil CO_2 flux in early January 2012 is three times higher than the pre-crisis values measured in 1994-1995 by Chiodini et al. (1998a), and 1.4 to 1.9 times higher than the values measured from September 2010 to July 2011 (Parks et al., 2013). The total soil CO_2 flux value of early January 2012 is similar to the value measured by Parks et al. (2013) three weeks later, soon after the seismic apex of 23-24 January 2012 (50 and 33 daily events respectively; Fig. 11). Therefore, the episode of maximum CO_2 degassing occurred prior to, and lasted after, the aforementioned seismic apex, likely implying that an increasing magmatic and hydrothermal degassing could have enhanced pore pressure and fostered more failures along Kameni Line faults and fractures, similarly to the inferences made at Vulcano by Alparone et al. (2010).

The surveys at Firà town show that geochemical changes occurred synchronously also in peripheral sectors of Thera Island, on the prolongation of the Kameni Line. In fact, total soil CO_2 fluxes measured from the target area (Table 1 and Fig. 11) show a decreasing trend, combined with a seasonal trend likely due to shallow biologic activity. It has to be noticed that in January 2012 the soil CO_2 flux from the target area of Nea Kameni was twenty times higher than the CO_2 flux from the target area of Firà. This ratio rose up to forty-eighty times in the following surveys (Fig. 11). Soil CO_2 output at Firà in January 2012, during the seismic crisis, likely reflected mixture of a deep gas component with a shallow organic component. In the following months, we substantially measured the seasonal emission of gas of main biologic origin by soil respiration processes.

The soil CO_2 flux maps of Nea Kameni (Fig. 6) show that the maximum gas release occurred from crater rims, whereas crater bottoms were poorly degassing, probably because of self-sealing processes, as observed at La Fossa crater of Vulcano, Italy (Granieri et al., 2006). Sealing phenomena can also explain the soil CO_2 flux behavior, which reflected a seasonal trend. In fact, as the total gas efflux diminished through 2012 (from 35.9 to 11.0 tonnes/day), flux maxima increased (Table 1) and concentrated in the eastern most degassing area, where such high flux rates from the steaming ground likely prevented soil pores and small fractures from self-sealing. Only in January 2013, total soil CO_2 flux was high again (25.1 tonnes/day; Table 1) but the maximum was lower and the degassing area was more extended than before. Presumably, the presence of more meteoric water in winter times dissolved salts, opened the sealed pores and restored higher permeability to gases even in the western parts of the target area. The reduction from 2012 to 2013 of deep gas efflux also affected the distribution of maxima in soil gas concentration, because high efflux rates prevented self-sealing processes, and conversely low rates fostered deposition and sealing.

Soil concentrations of CO_2, H_2 and He show the highest values and maximum areal extent in January 2012, compared to the following surveys (Fig. 7). Moreover, He minima increase throughout 2012-2013 as a consequence of the reduction of CO_2 deep magmatic input, that caused a relative dilution of minor species in the first survey.

CO_2/CH_4 increase in fumaroles indicates a shift from a typical hydrothermal composition to a more magmatic one, accompanied by a strong reduction in air dilution. CO_2/H_2 decrease reflects a temperature increase of the hydrothermal system due to steam and heat input from the magmatic system. Gas geothermometry of fumaroles indicates a slight temperature increase of the underground hydrothermal system in January 2012, followed by a return to the pre-crisis values.

It has to be stressed that these geochemical variations alone do not univocally reflect a mass transfer of magma to shallower levels, as they could be simply due to the intense seismic activity that enhanced the fracturing of the rocks above the stationary magma plumbing system. The resulting decrease of the lithostatic pressure could have led to a higher exsolution of steam and uncondensable gases from the magma. Granieri et al. (2006) give a similar explanation for the geochemical variations recorded during the 2005 crisis of La Fossa crater in Vulcano Island, Italy. However, when considered together with other available geophysical data, which highlight the shallow intrusion of magma during the unrest (between 3.5 and 6 km of depth; Newman et al., 2012; Parks et al., 2012; Lagios et al., 2013) and geochemical data (He isotopes in Rizzo et al. 2015) the interpretation of our measurements becomes univocal. In this context, gas composition variations are the consequence of the shallow emplacement of mafic magma and the related fracturing below the caldera. The latter, testified by the seismicity occurred during the unrest, has enhanced the upper crustal permeability, increasing the gas flux at the surface.

5.2 The regional tectonic context

Interestingly, the degassing pattern during unrest highlights, besides the central zone of gas release at Nea Kameni, also the preferred release of gas along the regional NE-SW trending tectonic systems of Santorini, the Kameni and the Kolumbo fracture zones. Therefore, even though the unrest has been a local feature occurred at Santorini, its effects may have influenced a slightly larger area, corresponding to the nearby NE-SW trending extensional systems. This is consistent with the seismic activation of the NE-SW trending Kameni and Kolumbo fracture zones during the unrest, probably depending on the static stress changes induced by the shallow emplacement of magma (Feuillet, 2013).

While any further impact of the 2011-2012 unrest has been negligible or absent outside Santorini area, or at a larger scale, this may not have been the case for the 1950 eruption. In fact, two M>7 earthquakes occurred on 9 August 1956, activating in extension the NE-SW trending structures of the Kameni-Kolumbo fracture zone. Given the rarity of high magnitude earthquakes in this specific area, and their relatively short occurrence after the eruption, it cannot be excluded that the 1950 eruption may have enhanced, or even triggered, this seismicity (Feuillet et al., 2013).

Even more intriguing is the comparison of the pre-eruptive seismicity before the 2011-2012 unrest with the Kolumbo (1650 BCE) and Santorini (1950) eruptions. Apart from the quoted 1956 large events, no significant (M>5.5) seismicity occurred within a radius of 100-150 km from Santorini before the 2011-2012 unrest (Fig. 1), suggesting that any seismic triggering of the unrest is unlikely. In fact, the regional pre-eruptive seismicity focused on the SE part of the Aegean microplate, characterized by contractional or dextral shear (the latter probably related to the SW motion of the Aegean microplate) along the subduction zone and extension or strike-slip faulting in the upper plate (Fig. 1). Therefore, this seismicity, limited in time (1991-2011) and size (M<5.5), in general supports the idea that the oblique convergence between the African and Aegean plates induces, in addition to some component of dextral shear, an overall extension in the overriding plate. However, as anticipated, no clear relationship is evident between the occurrence of the pre-unrest seismicity and the unrest itself.

Conversely, just before the 1950 eruption of Santorini , a shallow (15 km depth) M=7.3 earthquake occurred nearby (~150 km) in February 1948 (https://earthquake.usgs.gov). As for Kolumbo, an historical codex reports two strong shocks, happened presumably in Crete on January 1646 BCE, followed by minor events felt by population for the two following months. Another codex describes several seismic events at Crete through 1646 and 1647 BCE (Ambraseys, 2009). The most recent eruption of Kolumbo (VEI= 4) took place in September 1650 BCE after an unrest started in 1649, causing damages and loss of inhabitants and livestock on Santorini (Fouqué, 1879; Vougioukalakis et al., 1994). It is likely that the earthquakes before both the 1950 Santorini and 1650 BCE Kolumbo eruptions may have been associated with the extension within the overriding plate. Given their size and location, they may have even triggered or at least enhanced both eruptions.

All these data suggest a possible and preliminary working hypothesis to define the relationships between the magmatic activity of Santorini and Kolumbo volcanoes with the regional tectonic setting along this arc portion. On the one hand, the 2011-2012 Santorini unrest has a limited relationship with the regional setting. This is mainly related to minor activation of regional structures in the volcano area, as no triggering effect of the regional seismicity on the unrest is evident. Therefore, this unrest does not seem to have a trigger in any specific seismic event. This suggests that the Santorini unrest occurred during a longer-term (in the order of centuries) and minor (mm to cm/yr) convergence phase. Such an activity, which marks the interseismic period, has not enhanced any important rise of magma. On the other hand, the Kolumbo, 1650, and the Santorini, 1950, eruptions seem to have a stronger relationship with the regional setting, as following (Kolumbo and Santorini) and preceding (Santorini) important shallow and nearby earthquakes. This implies that the eruptions may have been related to a peak of seismic activity within the overriding plate, during a transient evolution that has been occurring on a shorter-term (a few years). During this transient phase, the regional tectonic stresses may have associated with magma rise and extrusion.

Therefore, the limited available data suggest a coupling between the magmatic activity along the Santorini-Kolumbo structure and the tectonic activity in the region, where eruptions may be related to the tectonic reorganization of the upper plate, whereas unrest episodes manifest themselves in periods of minor regional tectonic activity. These behaviors suggest a preliminary working hypothesis for magmatic arcs: unrest episodes may more frequently relate to regional tectonic quiescence, whereas eruptions may more likely pertain to tectonic activity phases, which also support the ascent of higher mafic magma volumes. Such hypothesis summons for additional, dedicated and systematic studies correlating eruptions and historical seismicity, at other magmatic arcs as well.

6. Conclusions

Our geochemical results, obtained during the 2011-2012 unrest, highlight:

An increase of diffuse soil CO_2 flux on the Kameni volcano tectonic Line both at Nea Kameni and on its prolongation on Thera Island (Fig. 11);

An increase of H_2 content and of CO_2/CH_4 in fumarolic gases of Nea Kameni;

An increase of $^{3}He/^{4}He$ dissolved in Irinià spring water, up to values even higher than those measured by Rizzo et al. (2015) in fluid inclusions of mafic enclaves olivines.

Coherently with geodetic evidence, our data suggest that the unrest was due to the shallow emplacement of a mafic (but enriched in fluids from the subducting plate) magma body underneath the caldera.

The unrest had only a limited effect on the regional setting, testified by anomalous gas emissions along Santorini NE-SW structures, but without any apparent seismic trigger. This is different to what happened during the 1950 eruption, characterized by large (up to M>7) crustal seismicity nearby the volcano (<150 km) both before and after the eruption, probably reflecting a general tectonic reorganization of the Aegean microplate. These two different behaviours suggest a working hypothesis for magmatic arcs, where unrest episodes may more frequently relate to tectonic quiescence, whereas eruptions may more frequently relate to tectonic activity.

Acknowledgements

We are grateful to Prof. M. Fytikas and Prof. G. Vougioukalakis, and particularly to Dr. N. Christou, Geologist at the Subprefecture of Santorini, for helping in logistic assistance. We thank the Boatmen Union of Santorini that kindly provided transports to Kameni islands. All supporting data obtained from tables, or archived in earthquakes.usgs.gov, bbnet.gein.noa.gr, or listed in references.

Our work also benefited from one of Renato Funiciello's numerous teachings: to seek into the past (books, manuscripts, codices) in order to advance research towards the future.

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Table 1. Main statistics and results of the soil CO_2 flux surveys

Date	Sector	CO_2 soil flux measures (g/m^2day) No.	Min.	Avg.	Max.	Total flux (ton/day)	Area (m^2)	Flux/Area (ton/ha day)
Preliminary surveys								
Jan.'12	Nea Kam.	60	0.7	250	7084	74.6	456,000	1.6
Jan.'12	Firà	160	1.7	36	224	25.6	730,000	0.6
Jan.'12	Kolumbos	162	1.5	11	64	16.5	1,580,000	0.1
Jan.'12	Exomiti	23	0.3	10	34	n.c.	n.c	n.c.
Target surveys								
Jan.'12	TAF	96	3.5	48	224	18.8	475,200	0.4
May'12	"	96	5	14	36	6.4	475,200	0.1
Jul.'12	"	96	0.1	5	13	2.3	475,200	0.05
Oct.'12	"	96	1.5	8	17	3.7	475,200	0.08
Jan.'13	"	96	2.5	16	101	6.0	475,200	0.1
Jun.'13	"	94	1.3	5	13	2.0	475,200	0.04
Jun.'94	TANK	63	2.0	432	6600	12.2§	28,000	4.4
Apr.'95	"	63	0.7	90	902	1.5§	29,000	0.5
Jun.'95	"	50	0.9	192	1330	2.3§	23,000	1.0
Sep.'95	"	71	0.5	879	8990	11.8§	25,000	4.7
*Sep. '10	"	n.i.	n.i.	n.i.	n.i.	26	19,600	13.3
*Apr '11	"	n.i.	n.i.	n.i.	n.i.	24	19,600	12.2
*Jul.'11	"	n.i.	n.i.	n.i.	n.i.	21	19,600	10.7
*Sep. '11	"	n.i.	n.i.	n.i.	n.i.	29	19,600	14.8
Jan.'12	"	119	1.4	935	15,700	35.6	19,600	18.2
*Jan. '12	"	n.i.	n.i.	n.i.	n.i.	38	19,600	19.4
May'12	"	119	1.4	1010	24,800	27.4	44,000	6.2
Jul.'12	"	119	0,1	632	28,500	16.4	44,000	3.7
Oct.'12	"	65	1.0	981	32,200	11.0	22,000	5.1
Jan.'13	"	119	0.6	877	21,700	25.1	44,000	5.7
Jun.'13	"	65	1.0	786	16,747	7.62	22,000	3.5

§1994-'95 values by new processing of data from Chiodini et al. (1996): Chiodini et al. (1998) calculated 15.4 ton/day for 1994 survey with a different method. *Parks et al. (2013). n.i.= not indicated. n.c.= not calculated

Table 2. Main statistics and results of the in-soil gas concentration surveys

Survey Date	Soil CO_2 (vol%) Min	Med	Max	*Area (m^2)	Soil H_2 (vol%) Min	Med	Max	#Area (m^2)	Soil He (ppm) Min	Med	Max	§Area (m^2)
Jan2012	0.05	7.29	90.36	6865	$0.2*10^{-4}$	0.09	2.50	5388	3.2	6.6	14.8	4722
May2012	0.37	14.64	85.28	9809	$0.3*10^{-4}$	0.07	0.86	4649	5.2	6.3	11	3120
Jul2012	0.07	11.13	76.56	7475	$1.1*10^{-4}$	0.05	0.74	2914	5.2	7.3	13	6285
Oct2012	0.10	9.47	66.26	7086	$0.1*10^{-4}$	0.03	0.65	2969	5.2	6.9	9	1176
Jan2013	0.10	8.78	71.80	6533	$0.1*10^{-4}$	0.04	0.74	2952	5.1	6.1	9	433
Jun2013	0.06	8.96	73.65	6997	$0.8*10^{-4}$	0.05	0.99	3371	4.3	5.5	10.4	653

Interpolated surface comprising *soil [CO_2] above 10 %; #soil [H_2] above 0.01 %; §soil [He] Above 8 ppm.

Table 3. Chemical and isotope composition of free and dissolved gases from Palea and Nea Kameni

Type	Sample	Date	[He] ppm	[Ne] ppm	R/Ra	$^4He/^{20}Ne$	Rc/Ra	Err $_{Rc/Ra}$ +/-	$\delta^{13}C$ ‰vsVPDB	H_2 ppm	O_2 %	N_2 %	CO ppm	CH_4 ppm	CO_2 %
B	[a]GSA2	04/07/,88	1.8	0.12	3.42	15.0	3.47	0.100	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	[b]PK	07/05/'96	1.1	0.28	3.34	4.0	3.57	0.050	-1.10	3580	0.10	0.60	n.a.	4	98.00
	[c]S-1-1	24/10/'01	0.4	0.05	2.61	7.7	3.77	0.060	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	[g]Irinià	13/01/'12	0.4	0.60	3.73	6.1	3.86	0.038	n.a.	2	0.05	3.50	5.4	36	50.44
	[g]Irinià	12/05/'12	8.3	3.9	3.73	2.0	4.17	0.039	n.a.	b.d.l.	0.03	2.88	0.1	38	56.36
	[g]Irinià	13/10/'12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	b.d.l.	0.04	3.14	10.0	33	52.62
	[g]Irinià	14/01/'13	6.9	4.2	3.69	1.6	4.26	0.025	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	[f]PK	09/05/'12	0.6	0.39	3.15	1.5	3.74	0.077	-0.48	b.d.l.	0.10	0.50	0.6	1	95.10
	[f]PK	17/07/'12	0.6	0.42	3.20	1.5	3.80	0.024	n.a.	0	0.70	0.40	b.d.l.	b.d.l.	97.80
	[f]PK	14/10/'12	1.8	0.16	3.73	11.0	3.82	0.024	-0.48	b.d.l.	0.30	0.60	3.1	6	98.00
	[f]PK	13/01/'13	0.6	0.06	3.64	10.4	3.73	0.023	n.a.	b.d.l.	0.10	0.40	2.7	3	99.40
	[f]PK	16/09/'13	0.6	0.131	3.47	4.5	3.66	0.036	-2.96	b.d.l.	0.30	0.80	23.0	b.d.l.	96.20
	[b]FNK4	07/'93	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4100	n.i.	n.i.	2.0	140	52.0
	[b]FNK4	06/'94	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	6400	n.i.	n.i.	3.4	n.a.	63.2
	[b]FNK4	05/'95	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	5980	n.i.	n.i.	5.0	110	47.3
	[b]FNK4	06/'95	n.a.	n.a.	2.7	0.29	3.5	n.i.	-0.68	6700	n.i.	n.i.	8.0	180	44.5
	[b]FNK4	09/'95	n.a.	n.a.	2.5	0.29	3.2	n.i.	-0.68	5250	n.i.	n.i.	5.0	95	34.3
F	[b]FNK4	12/'95	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2960	n.i.	n.i.	5.1	95	19.6
	[d]FNK4	06/10/'07	6.6	3.4	3.35	1.9	3.81	0.023	0.5	11700	4.08	17.80	n.a.	119	89.60
	[f]FNK4	07/09/'08	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	14300	5.40	23.60	n.a.	116	70.10
	[f]FNK4	22/09/'09	9.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	22200	4.10	17.80	n.a.	138	74.80
	[f]FNK4	12/05/'10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1383	15.80	62.80	n.a.	45	19.90
	[e]FNK4	05/'11	n.a.	0.37	n.a.	n.a.	n.a.	n.a.	n.a.	18500	4.13	27.5	n.a.	24	65.80

[f]FNK4	08/01/'12	9.4	1.7	3.75	5.4	3.94	0.016	n.a.	14200	1.26	7.05	5.3	114	90.71
[e]FNK4	02/'12	n.a.	0.32	n.a.	n.a.	n.a.	n.a.	n.a.	33600	3.19	26.0	n.a.	65	67.00
[e]FNK4	04/'12	n.a.	0.04	n.a.	n.a.	n.a.	n.a.	n.a.	12100	0.44	4.70	n.a.	156	93.50
[f]FNK4	09/05/'12	6.8	1.8	3.51	3.8	3.77	0.021	-0.24	12907	0.89	5.56	8.3	172	91.21
[#]FNK4	07/'12	n.a.	0.03	n.a.	n.a.	n.a.	n.a.	n.a.	10300	0.31	3.80	n.a.	204	93.50
[f]FNK4	17/07/'12	6.5	1.0	3.62	6.6	3.77	0.029	-0.26	11390	0.56	3.64	6.0	189	93.43
[f]FNK4	09/10/'12	6.2	2.3	3.44	2.7	3.80	0.021	-0.23	12300	1.44	4.01	3.6	212	87.95
[f]FNK4	13/01/'13	5.8	3.8	3.20	1.5	3.77	0.014	n.a.	11100	3.20	16.98	6.4	219	77.17
[f]FNK4	22/06/'13	6.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	11800	3.09	15.17	5.0	250	79.09
[f]FNK4	16/09/'13	5.50	2.50	3.27	2.2	3.66	0.029	-1.67	15200	1.50	11.40	43.0	285	84.00
[f]FNK4	26/04/'13	6.40	5.40	2.98	1.2	3.72	0.038	0.08	11100	4.50	24.50	3.2	295	71.90

B: bubbling and dissolved gases of thermal springs; F: fumaroles of Nea kameni; [a]Nagao et al. (1991); [b]Chiodini et al. (1998a); [c]Shimizu et al. (2005); [d]D'Alessandro et al. (2010); [e]Tassi et al. (2013); [f]Rizzo et al. (2015); [g]This work. n.a.= not analyzed; n.i.= not indicated; b.d.l.= below detection limit.

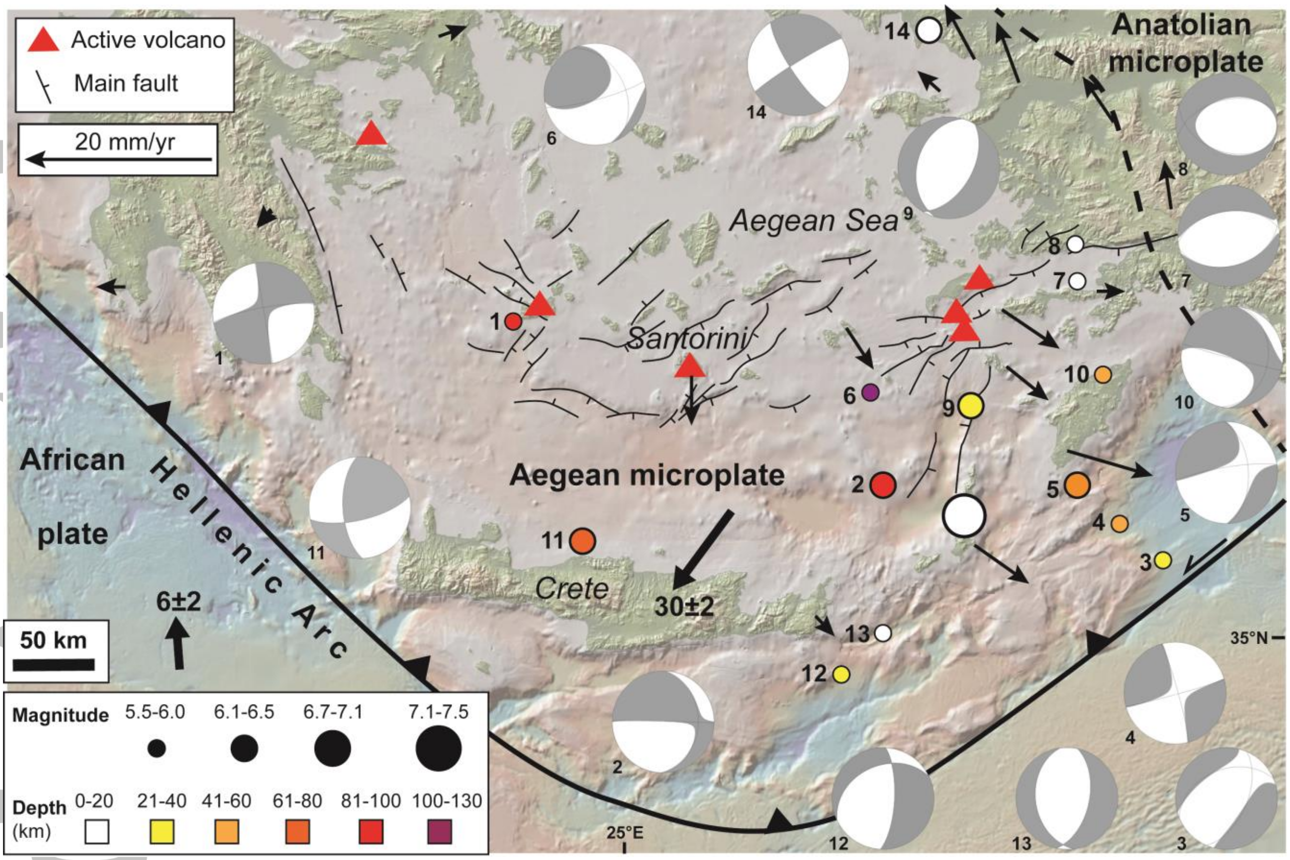

Figure 1. Tectonic setting of the southern Aegean region. Thick black arrows: plate motions (in mm) with regard to Eurasia (after McClusky et al., 2000). GPS vectors (thin black arrows; reference in upper left corner) refer to the central Aegean region (Reilinger et al., 2010). Active faults along the Aegean Volcanic Arc are from Feuillet et al., 2013, and references therein. Location and focal mechanisms of M>5.5 earthquakes occurred in the 20 years before the onset of the unrest (from 1 January 1991 to 10 January 2011) are reported as a function of depth and magnitude (https://earthquake.usgs.gov). The white circle to the east of Crete refers to the M=7.3 earthquake occurred at 15 km of depth on 9 February 1948 (no focal mechanism available).

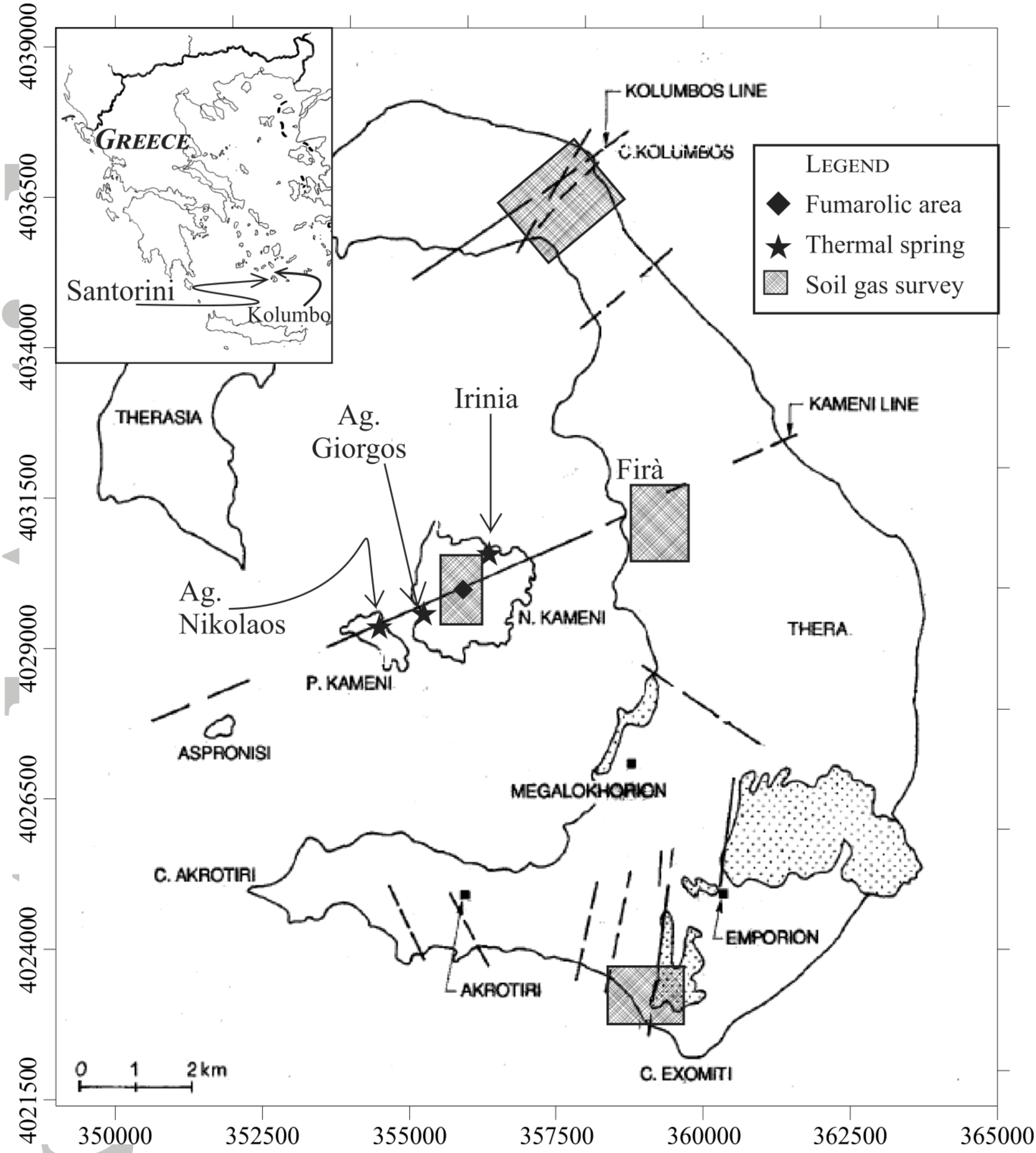

Figure 2. Santorini Island and location of the investigated areas (rectangles). Dotted areas are Mesozoic basement outcrops (modified from Barberi & Carapezza, 1994).

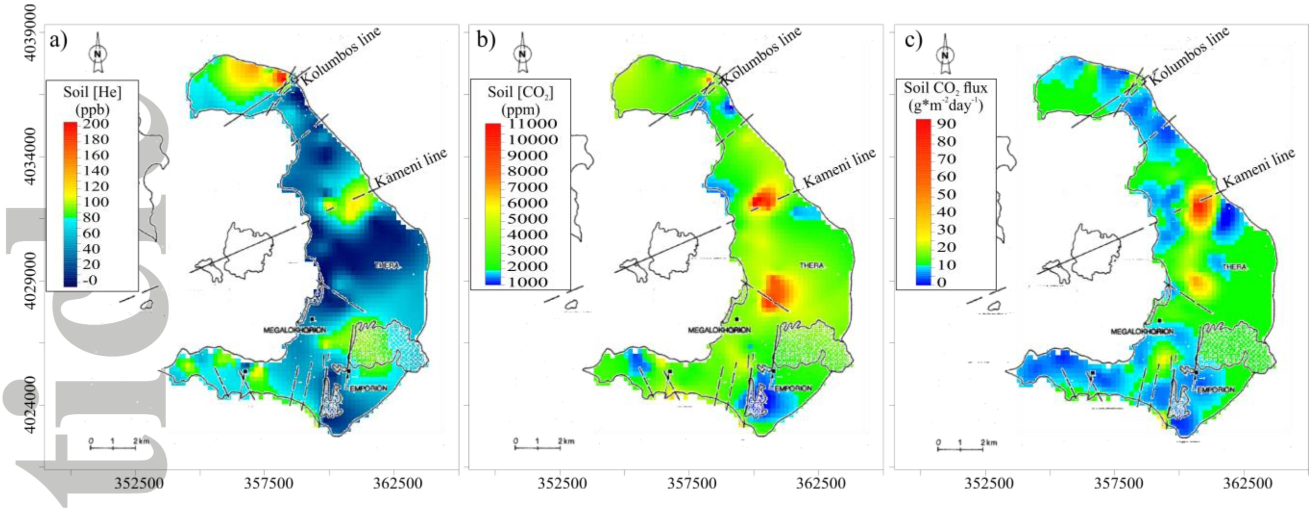

Figure 3. Maps of soil gas concentration and flux on Thera: a) He concentration in soil (ppbV); b) CO_2 concentration in soil (ppmV); Diffuse soil CO_2 flux ($g*m^{-2}day^{-1}$). Maps were reprocessed by ordinary kriging from original data of Barberi & Carapezza (1994).

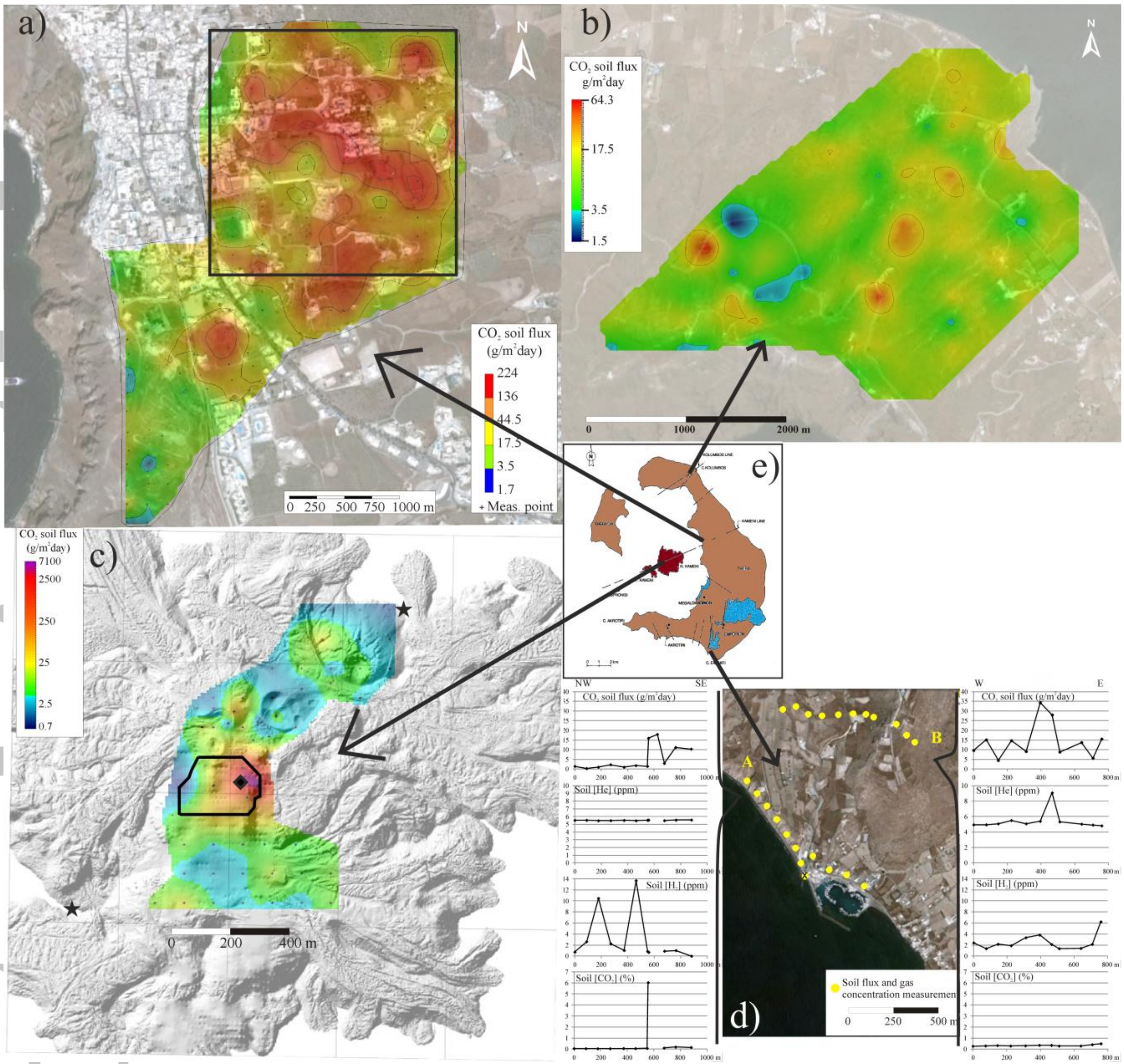

Figure 4. Soil CO_2 flux maps of the preliminary broad surveys of January 2012. a) Firà town with indication of the target area (black line); b) Cape Kolumbos; c) Nea Kameni, with indication of the target area (black line), reference fumarole (black diamond) and thermal springs (star); d) soil CO_2 flux and gas concentration along profiles at Cape Exomiti; e) Mesozoic basement outcrops (light blue), Plinian and inter-Plinian volcanics (light brown), post-Minoan dacitic pyroclastics and lavas of Kameni islets (dark brown).

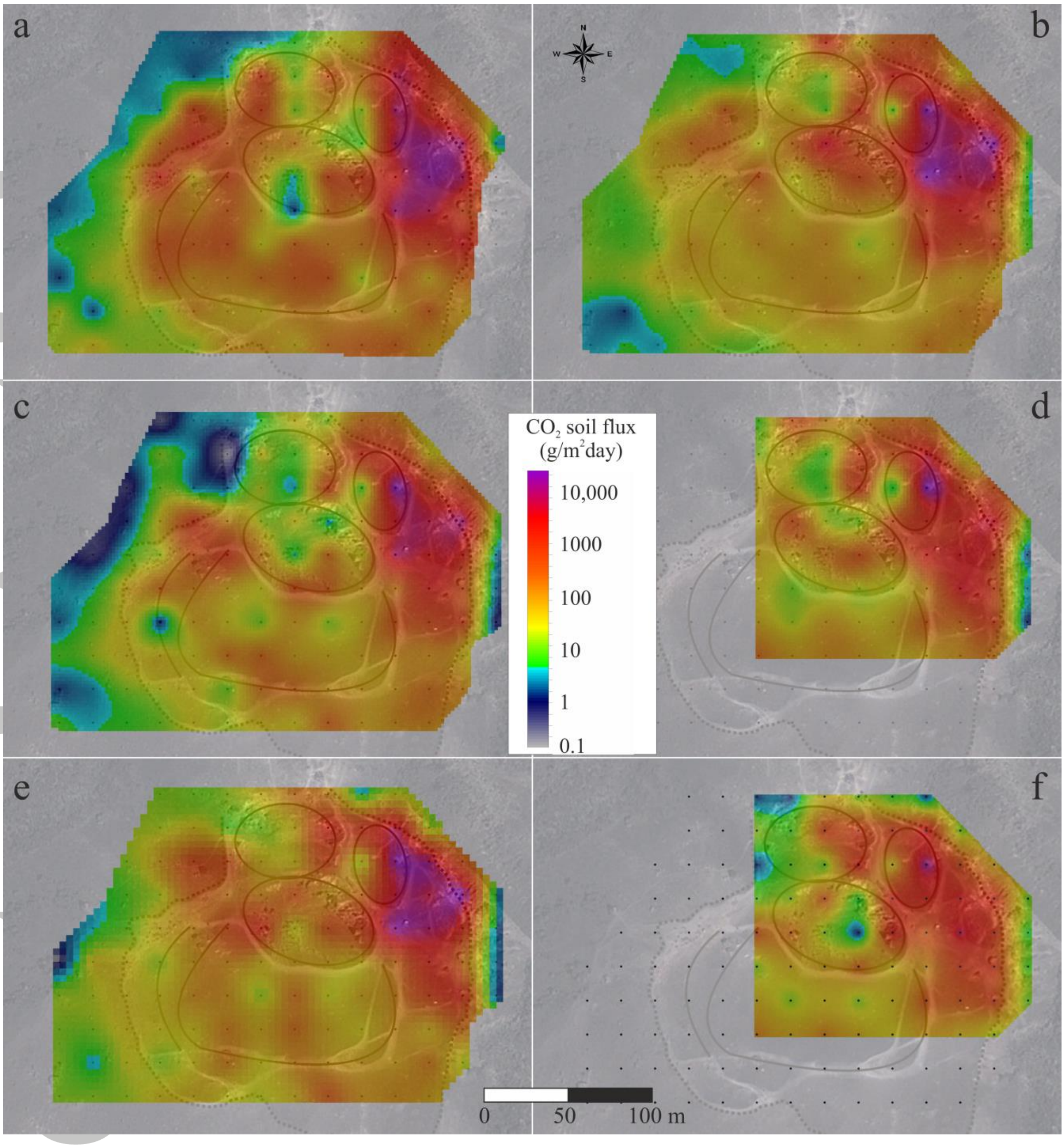

Figure 5. CO_2 soil flux maps of the TANK surveys of: a) January 2012; b) May 2012; c) July 2012; d) October 2012; e) January 2013; f) June 2013. Grey line: phreatic craters. All maps have the same color scale and scale bar.

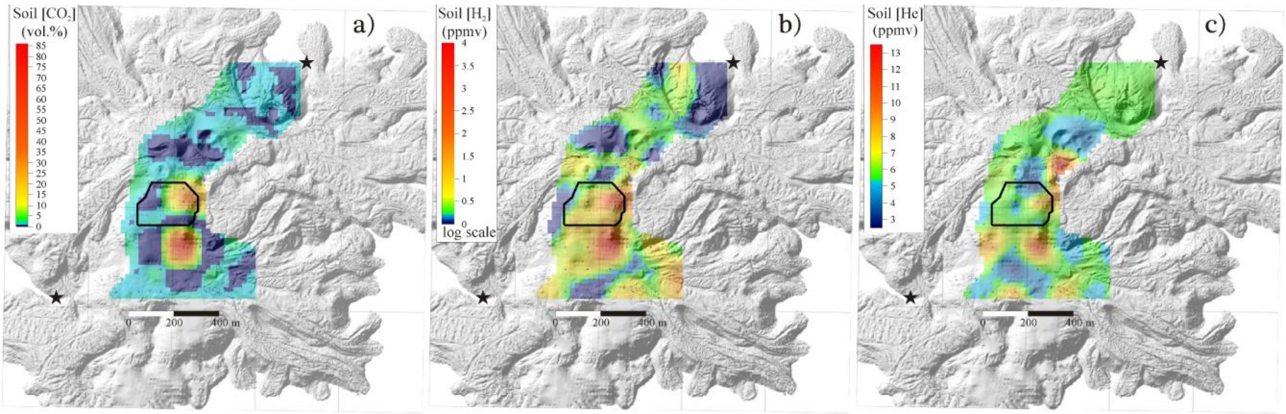

Figure 6. Soil gas concentration (at 50 cm depth) maps of Nea Kameni of 4-10 January 2012: a) [CO_2] in vol.%; b) [H_2] in ppm on a log scale; c) [He] in ppm. Black line: TANK area.

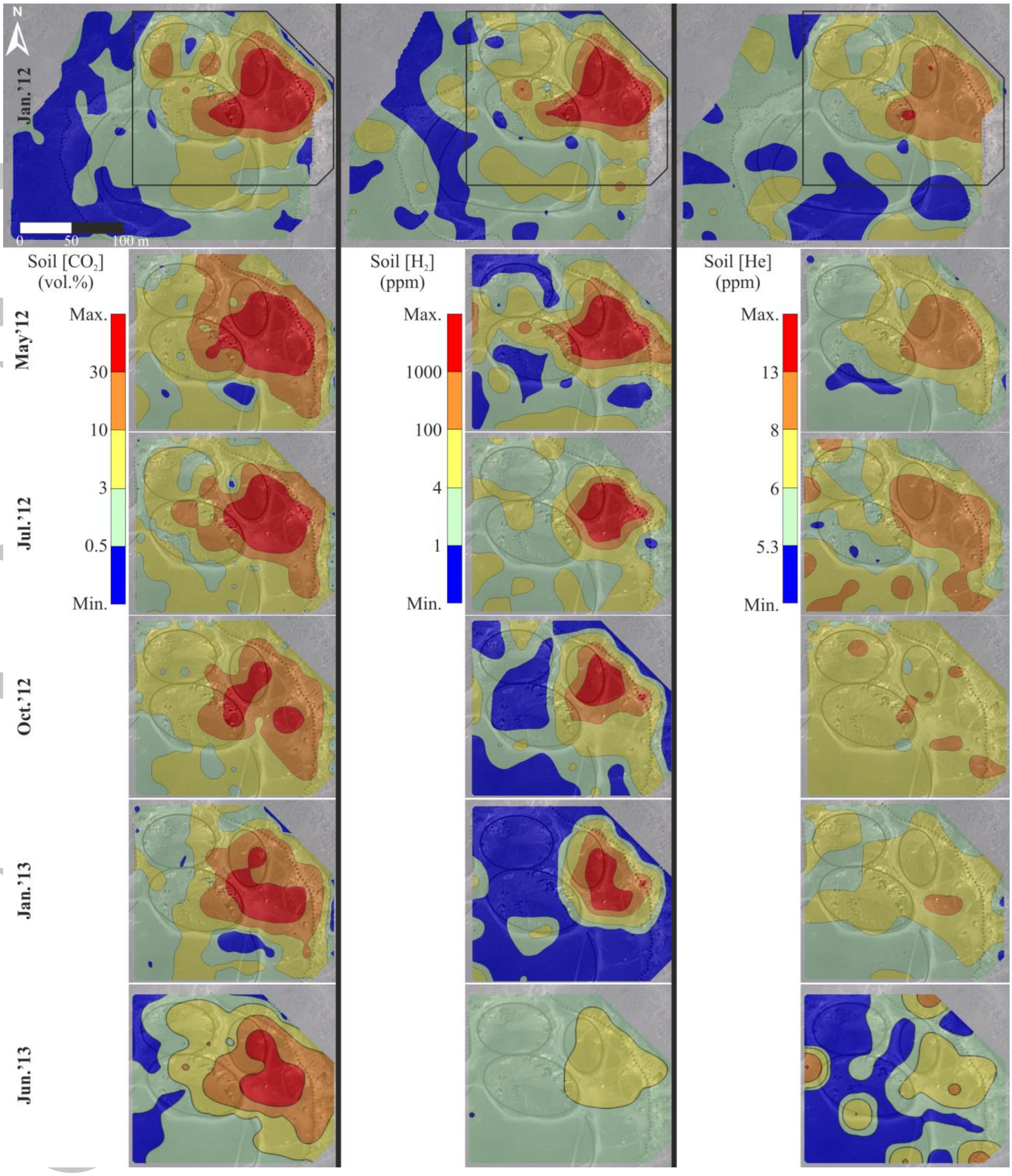

Figure 7. Time variation of soil concentration of CO_2 (left column), H_2 (central column) and He (right column) in TANK, ordered from top to bottom, from January 2012 to June 2013. Each gas species has its color scale. Meter scale bar is the same for every map. See Table 2 for minimum, average and maximum of each survey.

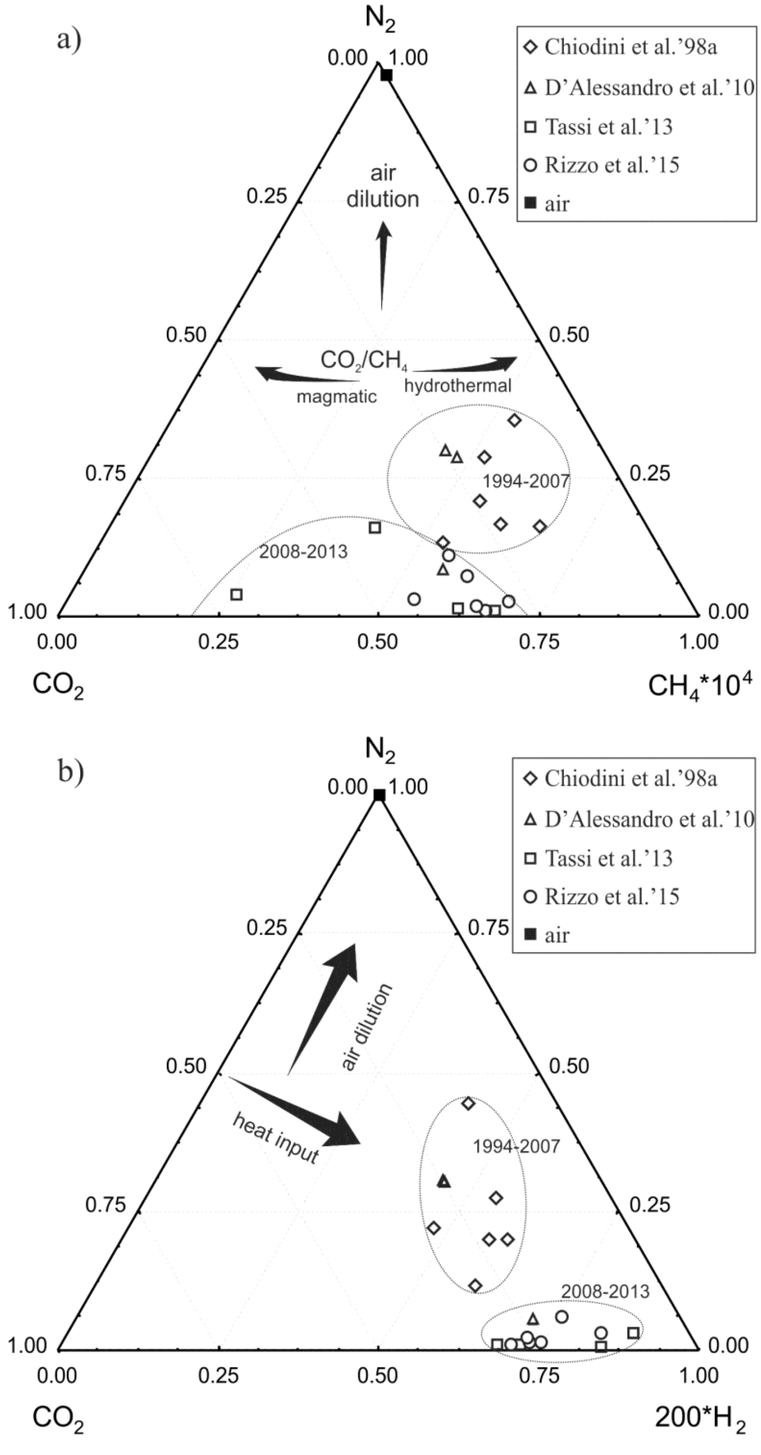

Figure 8. Ternary plots of the main gas components of Nea Kameni fumaroles. a) Plot of N_2-CO_2-10,000*CH_4; b) Plot of N_2-CO_2-200*H_2.

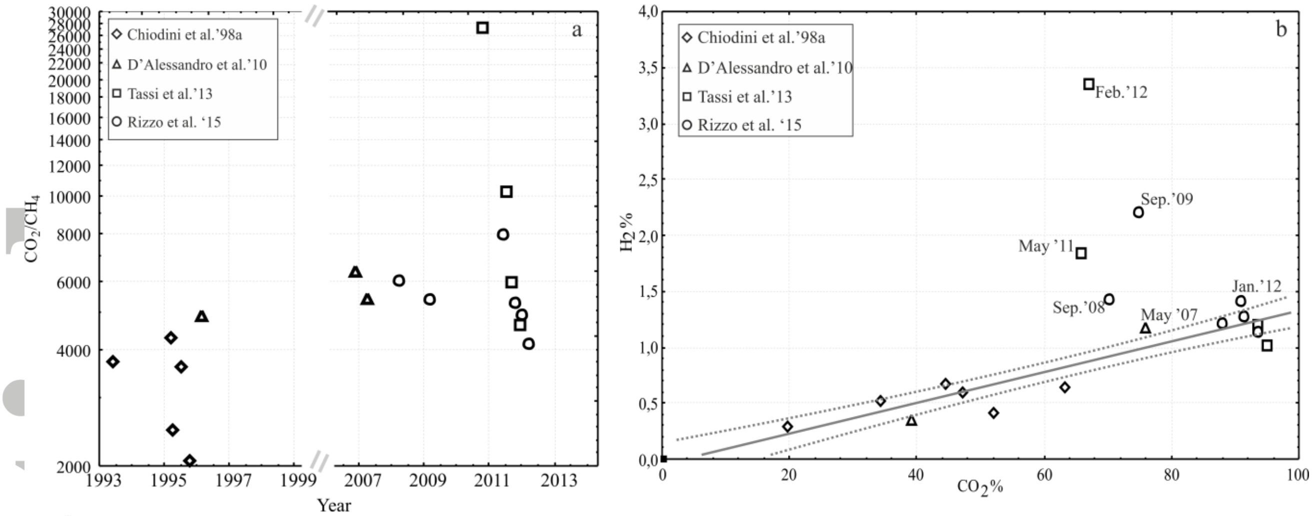

Figure 9. a) Time variation of $[CO_2]/[CH_4]$ in Nea Kameni FNK4 fumarole. b) Variation of H_2 and CO_2 concentration in air-free analyses of Nea Kameni fumaroles. Regression line with 95% confidence interval (full and stippled grey lines) separates analyses of 1994-'96 from high H_2 gases from May '07 to Feb. 2012.

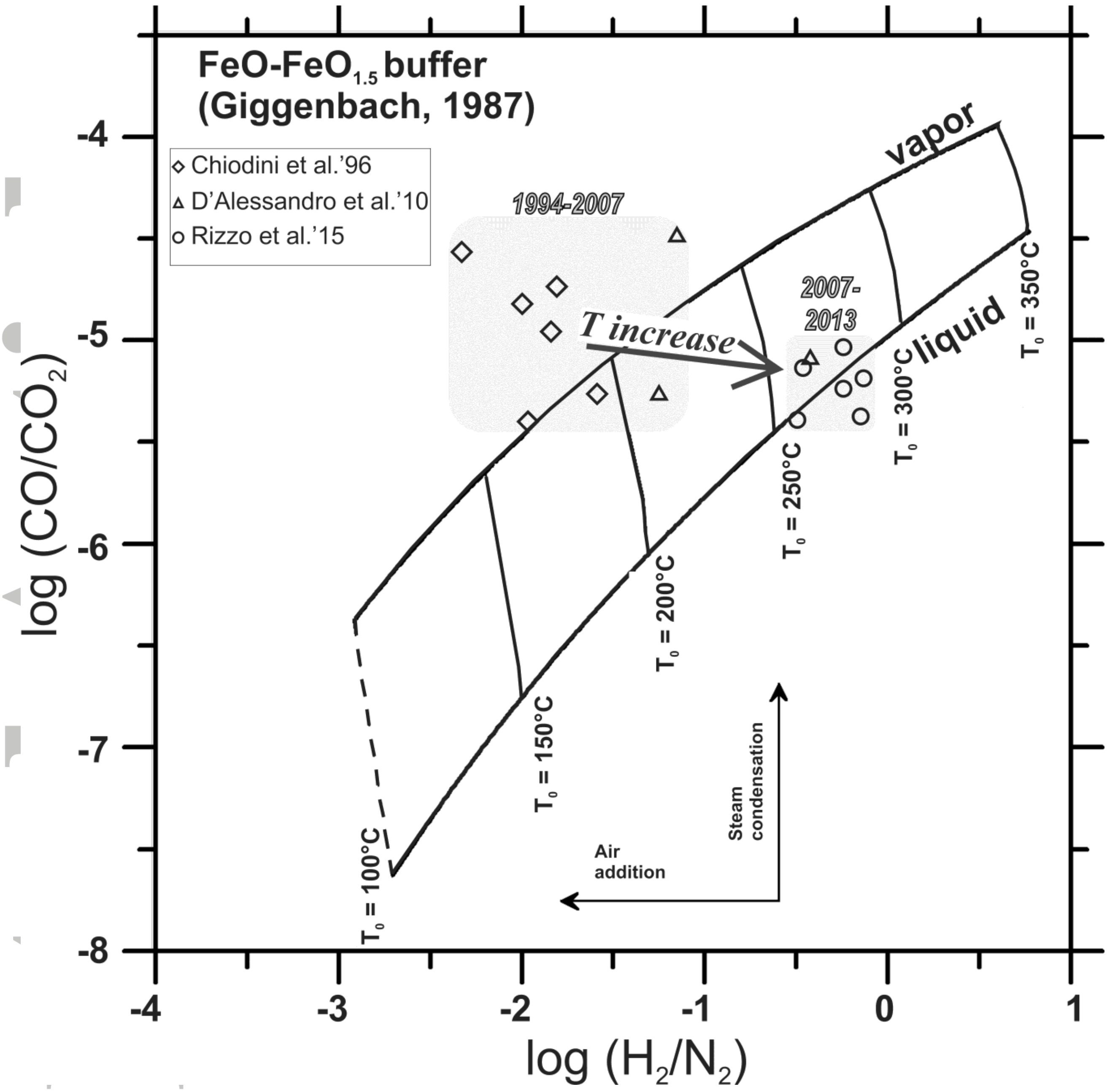

Figure 10. Plot in the log(CO/CO_2) versus log(H_2/N_2) gas geothemometer (Giggenbach, 1987) of Nea Kameni FNK4 fumarole. Left cluster of analyses: data from 1994 to May 2007. Right cluster of analyses: data from October 2007 to October 2013.

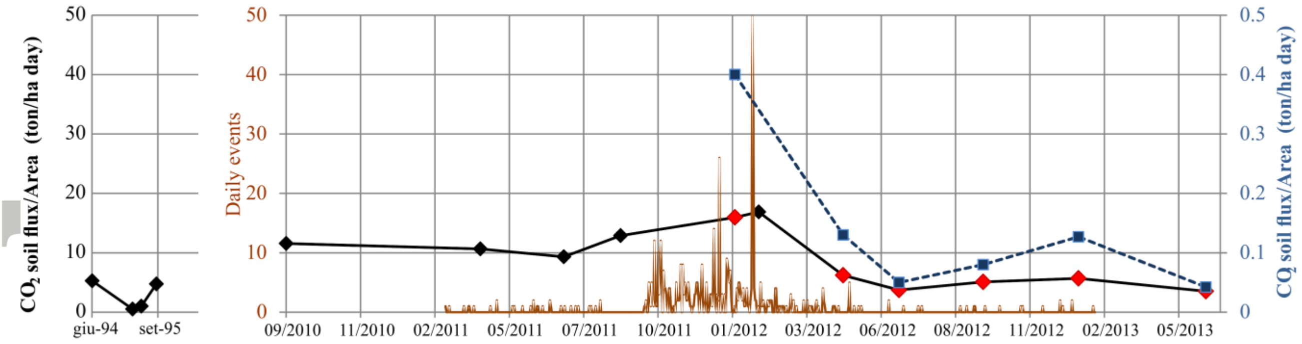

Figure 11. Time variation of diffuse soil CO_2 flux of the target areas of Nea Kameni (left axis) and of Firà (right axis) normalized to the investigated areas. The daily number of earthquakes (brown line, left axis) recorded during the 2011-2012 seismic crisis of Santorini is indicated (data after bbnet.gein.noa.gr).Red diamond: January 2012 to June 2013 soil CO_2 fluxes on Nea Kameni target area; Blue square: January 2012 to June 2013 soil CO_2 fluxes on Firà target area; Black diamonds: 1994-1995 fluxes calculated after data of Chiodini et al. (1998a) and September 2010-late January 2012 fluxes from Parks et al. (2013).