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# Distinguishing contributions to diffuse $CO_2$ emissions in volcanic areas from magmatic degassing and thermal decarbonation using soil gas $^{222}$Rn–$\delta^{13}$C systematics: Application to Santorini volcano, Greece

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ABSTRACT

Between January 2011 and April 2012, Santorini volcano (Greece) experienced a period of unrest characterised by the onset of detectable seismicity and caldera-wide uplift. This episode of inflation represented the first sizeable intrusion of magma beneath Santorini in the past 50 years. We employ a new approach using $^{222}$Rn–$\delta^{13}$C systematics to identify and quantify the source of diffuse degassing at Santorini during the period of renewed activity. Soil $CO_2$ flux measurements were made across a network of sites on Nea Kameni between September 2010 and January 2012. Gas samples were collected in April and September 2011 for isotopic analysis of $CO_2$ ($\delta^{13}$C), and radon detectors were deployed during September 2011 to measure ($^{222}$Rn). Our results reveal a change in the pattern of degassing from the summit of the volcano (Nea Kameni) and suggest an increase in diffuse $CO_2$ emissions between September 2010 and January 2012. High-$CO_2$-flux soil gas samples have $\delta^{13}C \sim 0‰$. Using this value and other evidence from the literature we conclude that these $CO_2$ emissions from Santorini were a mixture between $CO_2$ sourced from magma, and $CO_2$ released by the thermal or metamorphic breakdown of crustal limestone. We suggest that this mixing of magmatic and crustal carbonate sources may account more broadly for the typical range of $\delta^{13}$C values of $CO_2$ (from $\sim -4‰$ to $\sim +1‰$) in diffuse volcanic and fumarole gas emissions around the Mediterranean, without the need to invoke unusual mantle source compositions. At Santorini a mixing model involving magmatic $CO_2$ (with $\delta^{13}$C of $-3 \pm 2‰$ and elevated ($^{222}$Rn)/$CO_2$ ratios $\sim 10^5$–$10^6$ Bq kg$^{-1}$) and $CO_2$ released from decarbonation of crustal limestone (with ($^{222}$Rn)/$CO_2$ $\sim$ 30–300 Bq kg$^{-1}$, and $\delta^{13}$C of $+5‰$) can account for the $\delta^{13}$C and ($^{222}$Rn)/$CO_2$ characteristics of the 'high flux' gas source. This model suggests $\sim 60\%$ of the carbon in the high flux deep $CO_2$ end member is of magmatic origin. This combination of $\delta^{13}$C and ($^{222}$Rn) measurements has potential to quantify magmatic and crustal contributions to the diffuse outgassing of $CO_2$ in volcanic areas, especially those where breakdown of crustal limestone is likely to contribute significantly to the $CO_2$ flux.



## 1. Introduction

Santorini is an active caldera system in the southern Aegean Volcanic Arc (Druitt et al., 1999; Vougioukalakis and Fytikas, 2005). The caldera lies close to an active normal fault system associated with the Santorini–Amorgos ridge. Historic volcanic centres in the region include the submarine Kolumbo volcano, 7 km north-east of Santorini (Nomikou et al., 2012; Nomikou et al., 2013), and the intra-caldera Kameni Islands (Fig. 1) which have been the site of the most recent eruptions in the region. The Kameni islands are formed of dacite lavas and domes, and probably began forming as a submarine shield shortly after the Minoan eruption $\sim$ 3600 yr ago. The first reported eruption associated with the Kameni islands was in 199–197 BC; and there have been 10 effusive eruptions reported during the historical period (Pyle and Elliott, 2006), the

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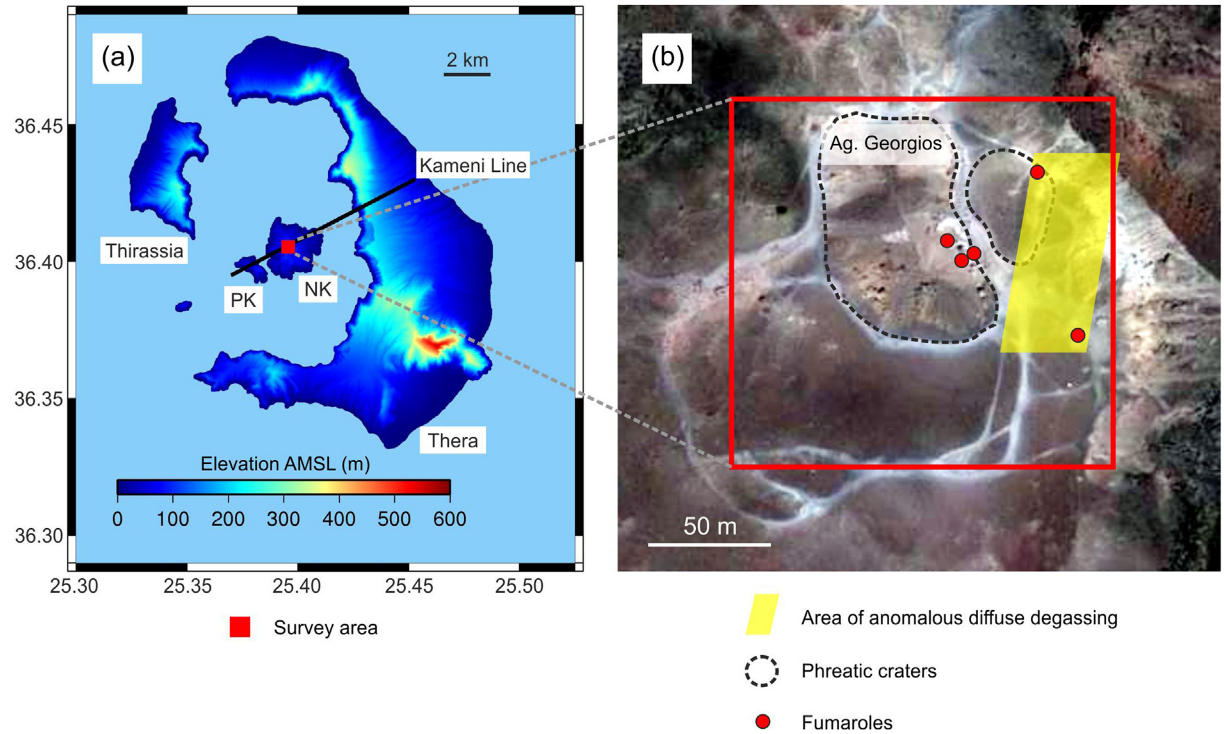


**Fig. 1.** (a) Elevation map of the islands of the Santorini volcanic centre (PK and NK denote Palaea and Nea Kameni). The Kameni line (solid black line) is an active volcano-tectonic fault/fracture zone, believed to influence vent locations of historic dome-building eruptions on Nea Kameni. The coordinates displayed on the axes are latitude and longitude, reported in decimal degrees. (b) Satellite image of the summit of Nea Kameni. The gas survey area on the summit of Nea Kameni is defined by the red box. Craters are displayed by black dashed circles and the area of elevated diffuse degassing (observed by Chiodini et al., 1998 and in this study) is displayed by the yellow box. Fumaroles NK1, 3, 4, 5 and 10 from Tassi et al. (2013) are marked as red dots. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

most recent of which occurred at Nea Kameni in 1950. A major volcano-tectonic fault system, the Kameni line, intersects the Kameni islands. This has been a controlling factor in the location of historical eruption sites, with a progression of vent locations from SW to NE along the line (Fytikas et al., 1990; Druitt et al., 1999; Vougioukalakis and Fytikas, 2005; Pyle and Elliott, 2006).

Surveys of the diffuse $CO_2$ flux from the ground have been made at numerous volcanoes to monitor flank emissions and to detect buried faults and fracture zones (Farrar et al., 1995; Chiodini et al., 1998, 2001; Hernandez et al., 2001; Rogie et al., 2001; Caliro et al., 2005; Giammanco et al., 2010). At Usu volcano, Japan, an increase in diffuse soil $CO_2$ flux from 120 to 340 $\text{t}\,\text{d}^{-1}$ was detected on the summit caldera six months before the March 2000 eruption (Hernandez et al., 2001), and continuous soil-flux measurements on Stromboli (Italy) show promise as eruption precursors (Inguaggiato et al., 2011). On Etna (Sicily), at Solfatara (Campi Flegrei, Italy) and at Lakki plain (Nisyros, Greece) buried faults have been mapped on the basis of detailed $CO_2$ flux surveys (e.g., Chiodini et al., 2001; Caliro et al., 2005; Bonforte et al., 2013).

In June 1994, Chiodini et al. (1998) carried out a $CO_2$ flux measurement campaign on Nea Kameni, using an accumulation chamber method. They discovered an anomalous zone of diffuse degassing on the summit of the volcano, in the vicinity of the craters (Fig. 1(b)) and measured $CO_2$ effluxes as high as 6.6 $\text{kg}\,\text{m}^{-2}\,\text{d}^{-1}$ with an estimated total $CO_2$ output of 15 $\text{t}\,\text{d}^{-1}$ (over an area of 2.8 ha). Three further accumulation chamber surveys were performed by the same team at Nea Kameni in April, June and September 1995, and we use these previously unpublished data in the current study.

The aim of this study was initially to repeat these earlier surveys, to establish whether or not there were any significant temporal variations in $CO_2$ flux during a quiescent phase at Santorini volcano, and to use isotopic analysis of carbon to place constraints on the source of the outgassing $CO_2$. However in early 2011, geodetic monitoring at Santorini revealed an early stage of caldera-wide uplift (Newman et al., 2012; Parks et al., 2012), accompanied by an ongoing swarm of shallow earthquakes. Modelling of GPS and InSAR displacements from March 2011 to April 2012 suggests that the observed uplift corresponds to a volume change of $\sim 1\text{–}2 \times 10^7$ $\text{m}^3$ due to a magmatic intrusion located slightly north of Nea Kameni, at a depth of $\sim 4$ km below the sea surface (Newman et al., 2012; Parks et al., 2012). The onset of a new phase of unrest, considered to be the first since the last eruptive activity in 1950 (Parks et al., 2012), offered an opportunity to observe how the soil gas flux would respond. We completed further gas-measurement campaigns during 2011 and 2012, including a radon survey in September 2011, to help determine the origin of the outgassing. In a complementary study, Tassi et al. (2013) examined the response of fumarole compositions to this unrest.

Radon is a naturally occurring noble gas, produced in the decay chains of uranium and thorium. The isotope $^{222}Rn$ is commonly used in geochemical surveys – it is produced by the decay of $^{226}Ra$ and has a half-life of 3.8 days. Radon is volatile, and will readily partition into the gas phase during degassing. It is also soluble, and will dissolve in aqueous fluids. The volatile and short-lived nature of $^{222}Rn$ means that variations in $^{222}Rn$ activity can be used to map fluid flow along active faults and fractures in volcanic areas (e.g., Burton et al., 2004; Neri et al., 2011; Bonforte et al., 2013) and to detect changes in volcanic activity (e.g., Giammanco et al., 2007; Laiolo et al., 2012).

Here we present the results of 5 soil $CO_2$ surveys undertaken on Nea Kameni between September 2010 and January 2012, along with $\delta^{13}C$ isotopic analysis of $CO_2$ samples collected in April and September 2011, and $^{222}Rn$ measurements acquired during September 2011. We also include the previously unpublished results of 3 surveys performed by the Italian team at Nea Kameni in