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Tracking the behaviour of persistently degassing volcanoes using noble gas analysis of Pele's hairs and tears: a case study of the Masaya volcano (Nicaragua).

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ABSTRACT

We provide evidence that noble gasses (NGs) trapped in Pele's hairs and tears can be used as a tool to monitor the degassing behaviour of persistently active volcanic systems. We investigated ^4He , ^{36}Ar , ^{40}Ar abundances and $^4\text{He}/^{40}\text{Ar}^*$ and $^{40}\text{Ar}/^{36}\text{Ar}$ isotopic ratios in samples collected in March 2015 and March 2016 from Masaya volcano (Nicaragua). The resurgence of a lava lake in December 2015 provided the opportunity to monitor NG variations during a specific volcanic event. The variations in the NG abundances of individual glass particles are here attributed to solubility-controlled NG fractionation between melt and bubbles, and consequently correlated with sample vesicularity and vesicle size. Inhomogeneous incorporation of ^{36}Ar , along with kinetic mass fractionation during magma degassing, vesiculation and fast-quenching of the samples after eruption, are the mechanisms that control the variability of the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios observed in the samples. From March 2015 to March 2016, our data indicate a general increase of mean $^{40}\text{Ar}^*$ abundances from $1.9\text{E}^{-8} \pm 1.4\text{E}^{-8}$ cc/g to $9.3\text{E}^{-8} \pm 8.9\text{E}^{-8}$ cc/g and decrease in mean $^4\text{He}/^{40}\text{Ar}^*$ ratios from 0.37 ± 0.15 to 0.18 ± 0.13 . We ascribe this to the upward migration of a gas-rich magma from depth that recharged the shallow magmatic reservoir of Masaya at some point between the two collection periods. Since this model agrees well with the physical volcanology of Masaya and with gas plume measurements spanning our collection period, we suggest that NG in Pele's hairs and tears can be further used as a valuable tool to monitor degassing processes at Masaya volcano and, when samples are available, at other persistently degassing systems (e.g. Etna, Hawaii).

Keywords

Noble gas; Masaya volcano; degassing; Pele's hairs and tears; volcanic glass.

1. Introduction

Noble gases (NG) have been used extensively to investigate the degassing of volcanic systems by inspecting different types of minerals, volcanic rocks and glass as primary sources of information (e.g., Ozima and Podosek, 2002 and references therein; Burnard, 2013 and references therein). However, not all types of volcanic materials have been equally considered. Amongst those volcanics yet to receive full consideration are Pele's hairs and tears that have not previously been examined for their NG isotopic compositions.

Pele's hairs and tears are millimetre sized glassy vesiculate pyroclasts derived from the fast-quenching of low-viscosity magmas erupted during lava-fountain Strombolian and Hawaiian eruptions of many basaltic volcanoes (e.g., Carracedo-Sánchez et al., 2016 and references therein). Several studies have investigated their morphological features (e.g., Duffield et al., 1977; Moune et al. 2007, Porritt et al., 2012; Carracedo-Sánchez et al., 2016; Cannata et al., 2019), petrography and geochemical compositions (Moune et al., 2007; Cannata et al., 2012; Porritt et al., 2012; Carracedo-Sánchez et al., 2016) and formation processes (Shimozuru, 1994; Zimanowski et al., 1997; Moune et al., 2007; Porritt et al., 2012), but little attention has been paid to the use of these particles as tracers of magmatic processes (Villemant, 2009). Pele's hairs and tears have been observed worldwide but they are specifically associated with the activity of persistently degassing basaltic volcanoes (e.g., Hawaii, Etna, Masaya, Erta' Ale, Villarrica).

Masaya Volcano (11.984°N 85.161°W, south-western Nicaragua) has been characterised by intense passive degassing activity during the last 2 centuries, and since 1853 five degassing crises occurred (Stoiber et al., 1986; Rymer et al., 1998; Williams-Jones et al., 2003), strongly impacting on the local environment, economy and human health (Delmelle et al., 1999, 2002). The release of thousands of tonnes of SO₂ per day and up to tens of tonnes of CO₂ per day, have caused respiratory problems to the surrounding population, severe damage to agricultural areas and corrosion of metal infrastructure (roofs, wires and machinery; Delmelle et al., 2002). In order to constrain the causes and source of this persistent degassing activity, several studies have investigated the structural and chemical characteristics of the Masaya volcanic system (e.g. Stoiber et al., 1986; Walker et al., 1993; Rymer et al., 1998; Williams-Jones et al., 2003; Stix, 2007; Stephens and Wauthier, 2018 and reference therein; Caravantes González et al., 2019) as well as the composition, the rates and volumes of the plume gases (e.g. H₂O, CO₂, SO₂, HCl, HF - Rymer et al., 1998; Delmelle et al., 1999; Williams-Jones et al., 2003; Martin et al., 2010; De Moor et al., 2017; Aiuppa et al., 2018; Stix et al., 2018; Zurek et al., 2019).

Ours is the first study of NG concentrations and variations in the erupted products at Masaya Volcano.

Here, we track active degassing processes at Masaya volcano by measuring NG trapped in Pele's hairs and tears. We demonstrate that, due to their high cooling rate (Porritt et al., 2012), hairs and tears can retain NG, free of the effects of post-eruptive degassing, providing a new tool for studying and monitoring the evolution of a persistently degassing system. Pele's hairs and tears were collected in two separate field campaigns in March 2015 and 2016, at Masaya Volcano. The resurgence of a lava lake in December 2015, between the two collection periods has provided the opportunity to monitor NG variations during this specific volcanic event.

2. Geological context: the Masaya Volcano

Masaya is a tholeiitic basaltic shield volcanic complex composed of a series of nested calderas formed as the result of multiple basaltic plinian eruptions (e.g., Van Wyk de Vries, 1993). At the top of the Masaya caldera are several pyroclastic cones (Fig. 1 A) made of scoria, ash and lavas erupted from fault structures (Caravantes González et al., 2019 and references therein). Vertical collapses of the crater floors of the Masaya and Nindirí cones have created Masaya, San Pedro, Nindirí and Santiago pit craters (Fig. 1 B) (Rymer et al., 1998). The most recent activity is confined to the Santiago pit crater and is represented by small Strombolian eruptions, and continuous passive degassing with periods of low gas emission that cyclically culminate in degassing crises and formation of a lava lake (Rymer et al., 1998; Williams-Jones et al., 2003; Aiuppa et al., 2018; Fering et al., 2019; Zurek et al., 2019).

Masaya volcano is an open-degassing system with a stable deep source that periodically supplies volatiles to a shallow reservoir (Williams-Jones et al., 2003; Stix, 2007). Convective overturns of the magma in the shallow reservoir with cyclical upward migration and degassing of low-density gas-rich magma from deep levels, controls the rate of degassing at the surface and the timing of degassing crisis at Masaya volcano (Rymer et al., 1998; Williams-Jones et al., 2003). Exolving gasses accumulate at the top of the upper portion of the shallow reservoir creating a foam layer just a few tens of meters below the surface (Delmelle et al., 1999; Stix, 2007). Gas crises occur when a considerable portion of the foam layer is destabilised (Stix, 2007) and starts to detach from the rest of the reservoir (Delmelle et al., 1999).

Since the beginning of the last degassing crisis in 1993 (Rymer et al., 1998) the composition of the plume has remained relatively stable with respect to H₂O, SO₂, CO₂, HCl and HF gas fluxes (1998 - 2009 period, Martin et al., 2010 and references therein; Zurek et al., 2019) with major variations recorded only prior to minor explosive eruptions (Duffel et al., 2003) or prior to minor seismic events (Padilla et al., 2014). In early 2014 gas emissions started

to increase and in December 2015 a new lava lake formed in the Santiago crater (Bulletin of the Global Volcanism Program, 2015, Aiuppa et al., 2018; Zurek et al., 2019). This resurgence was preceded by increased seismicity in April 2015, by the eruption of ash from the crater in October 2015 (Bulletin of the Global Volcanism Program, 2015), by ground deformation of the Masaya caldera (Stephens and Wauthier, 2018 and references therein), and by a high peak in CO₂ degassing at the vent in November 2015 (Aiuppa et al., 2018). In March 2016 the lava lake reached its maximum dimensions following multiple collapses of the crater floor (Bulletin of the Global Volcanism Program, 2016). At the time of writing the lava lake is still active.

3. Material and methods

Pele's hairs and tears from Masaya volcano (Fig. 1 A) were collected in March 2015 (sample suite KS15-03) and March 2016 (sample suites KS16-03 and KS16-13) around the Santiago crater (Fig. 1 B). This collection strategy was specifically designed to investigate the NG isotopic variations on a long period of time (1 year). The use of samples collected during eruptions minimizes alteration due to either extended exposure to acidic volcanic gases, or to post-eruptive hydration. The collection site was swept before each collection in order to remove any glass particles derived from earlier eruptions. This procedure ensured that only fresh samples, from the on-going activity, were recovered for the analyses. In order to minimise the alteration of the glass at ambient temperature (Fearn et al., 2004), after collection the samples were stored in plastic bags for at least a few months up to 1 year, in a dry environment at room temperature until their preparation for analysis.

Pele's hairs and tears were characterised in terms of their external texture, petrography and internal features by optical microscope observations of thin sections and backscatter electron images analysis. The latter were obtained from a total of 10 particles of each sample suite and produced from gold-coated polished thin sections. ImageJ software (Abramoff et al., 2004) was used for image processing allowing the calculation of the sample vesicularity – the ratio between the area covered by vesicles and the total area of the sample. This method has been used to characterise internal morphological features, vesicularity and vesicle size of Pele's hairs and tears (Porritt et al., 2012; Carracedo-Sánchez et al., 2016; Cannata et al., 2019) and is comparable to results obtained when 2D microscope observations have been combined with vesicularity calculation derived from bulk density measurements (Porritt et al., 2012) and from 3D image analysis performed by synchrotron radiation X-ray computed microtomography (Cannata et al., 2019).

Major element compositions of the glass were determined by electron microprobe and the Chemical Index of Alteration (CIA; Nesbit and Young, 1972) was calculated for each analysed spot in order to assess the degree of alteration of the glass.

^4He , ^{36}Ar and ^{40}Ar compositions of Pele's hairs and tears were investigated by NG mass spectrometry analysis. Pele's hairs and tears were washed with water and sieved and particles of 1 - 2 mm were handpicked for analysis. The selected samples were washed with acetone and deionized water, in an ultrasonic bath. Only the optically cleanest particles were weighted, placed grain by grain in a separate hole of an aluminium sample holder and loaded into the ultra-high vacuum extraction line of a MAP-215-50 noble gas mass spectrometer. The samples were stored under vacuum (10^{-9} Torr) for at least 5 days prior to NG analysis in order to minimise the amount of atmospheric gas adsorbed to a sample surface. Single grain total fusion analyses on Pele's hairs and tears were performed using a MAP-215-50 noble gas mass spectrometer. A focused continuous SPI 1062 nm fibre infrared laser (20 W power) was used to extract NG isotopes (^4He , ^{36}Ar , ^{40}Ar) from the samples. Two Zr-Al SAES NP10k getters (one working at room temperature, the other one working at 440 °C) and an inline cold nitrogen trap were used to capture active gases prior to admission to the mass spectrometer. An ultra-high vacuum system (10^{-9} Torr) provided the lowest blank value within the mass spectrometer. Ion counts were detected by a secondary electron multiplier in peak-hopping mode scanning the peaks at mass 4, 36 and 40. Routine peak centres on ^4He and the peak position for masses 36 and 40 were calculated relative to the ^4He peak position. During analysis we used the following parameters: 5 minutes gettering time, 10 scan and 10 measurements for each considered isotopes. Peak intensities were automatically calculated, by a LabView routine, extrapolating back to the inlet time to correct for gas adsorption onto the spectrometer walls. A homemade LabView platform, routinely used in the laboratory, was used to control the analytical parameters and to display visually ion count and regression graphs. Background levels of the machine were monitored over the entire duration of the experiments running two blank measurements after every two sample analyses. The daily average blank value was subtracted from the raw data using the in house designed *ArMaDiLo* software (Argon Macro Direct Loader – Schwanethal, 2006). A known volume (0.2 cc) of NG with standard element and isotopic ratios, contained within a specifically designed calibration bottle, was measured before each experiment in order to determine the mass spectrometer sensitivity and mass discrimination value (at 283 ± 2 for $^{40}\text{Ar}/^{36}\text{Ar}$ - uncertainty not propagated in the calculation). Calibration measurements were operated using the same operational routines and analytical conditions used for measuring NG abundances in the samples. Detection limits for the considered isotopes are related to the minimum blank level achievable during the analysis.

Average blank values measured throughout the duration of the experiments are $3.6\text{E}^{-3} \pm 8.6\text{E}^{-4}$ cc/v for ^4He , $1.1\text{E}^{-4} \pm 6.4\text{E}^{-5}$ cc/v for ^{36}Ar and $3.2\text{E}^{-2} \pm 3.0\text{E}^{-2}$ cc/v for ^{40}Ar . The average sensitivity of the mass spectrometer during the experiments was 1.21×10^{-9} cc/V for ^{40}Ar , 1.26×10^{-9} cc/V for ^{36}Ar and 4.40×10^{-8} cc/V for ^4He . After the analysis, data that have negative values after blank correction, due to gas concentrations within error of the background value, or with 1σ analytical uncertainties higher than 100 % of the absolute value are discarded from further considerations. Also excluded are those values of ^{40}Ar for which the ion detector measured an ion count close to 14 V. This value represents the saturation point of the ion detector of the MAP-215-50 mass spectrometer used in this study. For this reason, the values of ^{40}Ar close to this number are not considered reliable and thus are excluded from further considerations. Measurements of ^{36}Ar collected when the ion detector reached the saturation point (14 V) at mass ^{40}Ar are also omitted. These values can't be considered reliable because of the possible interferences caused by a Cl-based compound with mass 36 which is emitted from the detector/detector housing upon saturation. Analytical errors are reported at 1σ level and are between 3 % and 71 % for ^4He , 1 % and 39 % for ^{36}Ar and < 1 % and 18 % for ^{40}Ar . All omitted data are reported, mean blank values, raw data, weight of the samples and calibration data are included in supplementary file C for completeness.

Details of the instruments used for the analyses, analytical conditions and calibration data are reported in supplementary files A, B and C.

4. Results

4.1. Sample characterisation

Pele's hairs and tears in this study (Fig. 2) display similar external morphologies to those reported for the same type of material derived from other volcanoes (Masaya - Moune et al., 2007; Etna - Cannata et al., 2012; Kilauea - Porritt et al., 2012). Here, Pele's hairs and tears are composed of sideromelane glass (99 % - 100 %); less than 1% of the particles contain between 1 and 3 isolated microcrystals of plagioclase and/or clinopyroxene ($< 50 \mu\text{m}$). The glass generally is pristine and without structures that could be attributed to devetrification or alteration. Pele's hairs and elongated tears have elongated vesicles stretched parallel to the maximum axes of the samples (Fig. 3 A - B). Pele's tears with a tear-drop or spherical shape display multiple generations of vesicles with different dimensions: a few glass particles ($\sim 1\%$) are composed of pure glass without visible vesicles (Fig. 3 C) or have only a few round vesicles of less than $100 \mu\text{m}$ in diameter (Fig. 3 D); others have only small isolated round vesicles with a diameter equal or less than $50 \mu\text{m}$ (Fig. 3 E); another group of particles have small isolated round vesicles ($< 50 \mu\text{m}$) and bigger round isolated ($150 - 200 \mu\text{m}$) (Fig. 3 F - G);

finally, others have small isolated round vesicles ($< 50 - 100 \mu\text{m}$), bigger isolated round vesicles ($100 - 200 \mu\text{m}$) and coalescent vesicles ($200 \times 320 \mu\text{m}$) (Fig. 3 H). The vesicularity varies from one particle to another ranging from 0 % (KS16-03_5) up to 47.6 % (KS16-03_6) with weighted mean vesicularities of 17.4 % (KS15-03), 23.2% (KS16-03) and 15.3 % (KS16-13) (Fig. 4). Backscatter images of individual particles, total areas of each pyroclast and size of single vesicles are listed in supplementary file A.

4.2. Glass chemistry

Based on electron microprobe data the glass is basaltic in composition with mean SiO_2 values of $51.2 \pm 0.4 \text{ wt. \%}$ (KS15-03), $51.7 \pm 0.3 \text{ wt. \%}$ (KS16-03) and $51.1 \pm 0.4 \text{ wt. \%}$ (KS16-13). The three samples have an average total alkali content (Na + K) of $4.4 \pm 0.1 \text{ wt. \%}$ and display only minor variations in the other major elements (Table 1). Pele's hairs and tears of this study have similar chemistry to those previously collected at Masaya Volcano and analysed by Moune et al. (2007) (Table 1). Totals are between 97.07 wt. % and 99.58 wt. % (Table 1) indicating only negligible alteration, possibly related to small areas of the glass with minor exposure to plume acidic gasses; the CIA values are closely aligned to the value of 50 for unaltered glass (Nesbitt and Young, 1992) and are 50.8 ± 0.3 (KS15-03), 50.9 ± 0.3 (KS16-03) and 50.7 ± 0.3 (KS16-13) (Table 1). These data and the small variability of the more mobile elements (K, Na, Ca) demonstrate that the glass is not altered. All the data are listed in supplementary file B.

4.3. NG results

NG concentrations and proportions vary considerably from particle to particle independently from their external morphology. Minimum, maximum and mean values for each NG isotope (^4He , ^{36}Ar , ^{40}Ar , $^{40}\text{Ar}^*$) and isotopic ratios ($^{40}\text{Ar}/^{36}\text{Ar}$, $^4\text{He}/^{40}\text{Ar}^*$) obtained from the 115 Pele's hairs and tears derived from samples KS15-03, KS16-03 and KS16-13 are summarised in Table 2. NG abundances of individual particles, selection criteria for meaningful data, mean blank values, weight of the samples and calibration data are reported in supplementary file C.

^4He content varies by two orders of magnitude in samples KS15-03 and KS16-03 and by one order of magnitude in sample KS16-13. ^4He mean values of particles collected in 2015 are similar to mean values of particles from samples KS16-03 and KS16-13 collected in 2016 (Table 2); ^{36}Ar is more variable in samples KS15-03 and KS16-03 while it is less dispersed for KS16-13 (Table 2); the variability of ^{40}Ar is higher in sample KS16-03, lower for sample KS15-03 and minimal for KS16-13; at the 1σ level, all the three suites of samples display sub-

atmospheric, atmospheric and supra-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (Table 2). Particles collected in 2016 generally have higher $^{40}\text{Ar}^*$ ($^{40}\text{Ar}^* = [^{40}\text{Ar} - \text{Ar}_{\text{ATM}}] \times ^{36}\text{Ar}$; where $\text{Ar}_{\text{ATM}} = ^{40}\text{Ar}/^{36}\text{Ar}$ of 298.56 – Lee et al., 2006) concentrations and lower $^4\text{He}/^{40}\text{Ar}^*$ ratios than those collected in 2015 (Table 2). KS15-03 shows a uniform gas signature (“2015-like” signature in Fig. 5) with all the particles that have $^4\text{He}/^{40}\text{Ar}^*$ ratios > 0.2 (range 0.23 – 0.58, mean 0.37 ± 0.15) and $^{40}\text{Ar}^* < 4.1\text{E}^{-8}$ cc/g (range $3.9\text{E}^{-9} - 4.1\text{E}^{-8}$ cc/g, mean $1.9\text{E}^{-8} \pm 1.4\text{E}^{-8}$ cc/g). Samples erupted in 2016 (KS16-03 and KS16-13) display some glass particles ($n^\circ 4$) that have a gas signature similar to Pele’s hairs and tears erupted in 2015 (Low $^{40}\text{Ar}^*$ and high $^4\text{He}/^{40}\text{Ar}^*$ ratio - $^4\text{He}/^{40}\text{Ar}^*_{\text{mean}} = 0.33 \pm 0.05$, $^{40}\text{Ar}^*_{\text{mean}} = 2.8\text{E}^{-8} \pm 1.4\text{E}^{-8}$ cc/g) and others ($n^\circ 6$) that display a distinctive NG signature (“2016-like” signature in Fig. 5) characterised by lower $^4\text{He}/^{40}\text{Ar}^*$ ratios (range 0.14 – 0.03, mean 0.08 ± 0.04) and higher $^{40}\text{Ar}^*$ content (range $7.0\text{E}^{-8} - 2.9\text{E}^{-7}$, mean $1.5\text{E}^{-7} \pm 9.0\text{E}^{-8}$ cc/g). Particles with a “2016-like” signature can be further subdivided into two separate groups (Groups 1 and 2) according to their different $^{40}\text{Ar}^*$ content. Group 1 has $^{40}\text{Ar}^*$ that is between 7.0E^{-8} cc/g and 1.3E^{-7} cc/g and $^4\text{He}/^{40}\text{Ar}^*_{\text{mean}} < 0.15$, while Group 2 has $^{40}\text{Ar}^* > 2.6\text{E}^{-7}$ cc/g and $^4\text{He}/^{40}\text{Ar}^*_{\text{mean}} < 0.07$ (Fig. 5). Specifically, KS16-03 has particles that belong to Groups 1 and 2, while KS16-13 has particles with that belong to Group 1 only (Fig. 5). It is possible that the distinction between Groups 1 and 2 may be the result of a sampling bias and that a continuous transition between the two groups exists. However, with the available data this can’t be determined. A hyperbolic trend with a negative slope links those particles with a “2015-like” signature to particles that have a “2016-like” signature (Fig. 5, 6). These considerations are valid also excluding those particles with positive $^{40}\text{Ar}^*$ abundances obtained from $^{40}\text{Ar}/^{36}\text{Ar}$ ratios that are supra-atmospheric at the 1σ level but are atmospheric if considered at the 2σ level.

5. Discussion

5.1. Factors controlling the measured NG abundances

NG concentrations in volcanic materials can vary for different reasons such as changes in the chemistry of the melt (e.g., Carroll and Stolper, 1993; Carroll and Draper, 1994), H₂O and CO₂ content (e.g. Nuccio and Paonita, 2000), crystal and bubble content (e.g., Ozima and Podosek, 2002). Studies conducted on basaltic glass samples have demonstrated that when vesicularity exceeds 1 vol % the majority of magmatic NG reside in bubbles rather than in melt or crystals (Carroll and Draper, 1994; Sarda and Moreira, 2002; Aubry et al., 2013). This happens because NG behave as incompatible trace elements during magmatic processes preferentially partitioning into bubbles rather than being retained in the melt or partitioned into the crystalline phase (Ozima and Podosek, 2002). For a vesicularity of 1 %, around 90 % of Ar

atoms and 40 % of He atoms are in the vesicles while at vesicularity of ≥ 10 % more than 99 % of Ar atoms and 90 % of He atoms are trapped in the gas phase (Aubry et al., 2013). These differences are related to the rate at which different NG fractionate in bubbles that, in turn, is strictly dependant on their relative solubilities at different pressures (Carroll and Draper, 1994). On a minor scale, diffusion of NG (e.g., ^4He) out of the glass at ambient temperature after eruption (Amalberti et al., 2016) and NG loss and / or redistribution due to post-eruptive devetrification and hydration of the glass (Cerling et al., 1985) can also contribute to modification of the actual NG isotopic composition of the samples. For these reasons, it is necessary to carefully evaluate factors, other than magmatic degassing, that could have controlled the NG variations.

Since ca. 99% of the particles in this study are crystal free and the solubility of NG in melt and bubbles is higher than in crystals (Ozima and Podosek, 2002), we suggest that the amount of NG derived from the presence of possible micro-crystals inside the samples can be considered negligible compared to the total volume of gas trapped in the glass and bubbles. Large contributions of NG from any crystal phase, in specific from fluid and melt inclusions, would result in a distinct NG signature and would be different from that which would be derived from crystal-free particles.

Since the pyroclasts all have the same chemical composition, with high electron microprobe major element totals and CIA values of around 50, we can rule out the possibility that the NG variations have been controlled by major or minor compositional variations of the glass. However, H_2O and CO_2 were not measured in this study, and so it is not possible to comment upon any possible influence that these volatiles had on the solubility of the NG in these samples.

Because the samples were collected at different periods of time and analysed some 1 – 2 years after their eruption, it is possible that the observed NG abundances and ratios have been influenced by some degrees of ^4He loss or atmospheric ^{36}Ar and ^4He ingassing through diffusion, post-eruption, and prior to analysis. However, there is little variation in $^{40}\text{Ar}/^{36}\text{Ar}$ and $^4\text{He}/^{40}\text{Ar}^*$ ratios regardless of which year glass particles from different collection periods were analysed. Moreover, diffusion and ingassing of Ar during storage is unlikely due to the low diffusion rate of Ar at room temperature (Ozima and Podosek, 2002) and the short time between sample eruption and analysis with some particles analysed just a few months after their collection. This supports the idea that if ^4He loss occurred or NG with atmospheric composition have been trapped post-eruption via diffusion, these have not significantly impacted on the NG isotopic and elemental ratios. Based on these considerations, the variations

of NG abundances can be discussed in the context of magmatic degassing, and modelled as binary mixing between a gas phase dissolved in the glass and one dissolved in the bubbles.

5.2. NG variations due to magmatic degassing

NG are incompatible trace elements that, during degassing, segregate from the magma and diffuse into newly-formed CO₂-rich bubbles (Carroll and Draper, 1994). Following this, the concentration of the NG in a volcanic sample is primarily determined by the original gas content of the magma, by the volume of gas fractionated and retained in bubbles, and, by the amount of bubbles nucleated during gas-melt separation (Carroll and Draper, 1994; Aubry et al., 2013). The higher the magma vesicularity, the greater the amount of NG partitioned into the bubbles (Aubry et al., 2013). Given sufficient time, the volatiles trapped in the bubbles will reach equilibrium with the gas dissolved in the melt, and the fraction of NG that partition between the two phases will be directed by the relative solubilities (Carroll and Stolper, 1993; Carroll and Draper, 1994) and by the CO₂ and H₂O contents of the melt (Nuccio and Paonita, 2000). The light NG (e.g., He) are more soluble and preferentially remain in the melt, whilst the heavier NG (e.g., Ar) are less soluble and preferentially partition into the bubbles (Carroll and Draper, 1994). During open-system degassing buoyant bubbles rise independently of melts and are lost from the system. As a result, bubbles that formed during subsequent stages of magma evolution will incorporate NG with variably fractionated compositions (Burnard, 1999). The first nucleated bubbles, forming in the deepest levels and at relatively high pressure, incorporate gas with the most primitive composition. Bubbles formed at shallower conditions, during the later stages of magma evolution, will have a more evolved and fractionated NG signature (Burnard, 1999, 2001). If quenching happens rapidly after eruption, preventing post-eruptive degassing, it is possible that different NG signatures will be preserved in samples that have a mixture of bubbles equilibrated at different depths and that have different NG signatures. We propose that this is what controlled the variations of the NG abundances in single Pele's hairs and tears from Masaya volcano.

A model of equilibrium degassing and NG fractionation, and variable sample vesicularities, does not alone explain the increase in the ⁴⁰Ar* abundance between 2015 and 2016 (Fig. 5 and 6). Among other isotopic ratios, the ⁴He/⁴⁰Ar* ratio has been widely used to track the degassing of basaltic rocks and glass. In a persistently degassing open-system like Masaya volcano, the gas concentrations in the residual magma would be expected to remain stable or decrease with time and the ⁴He/⁴⁰Ar* ratios would be expected to increase following subsequent degassing and vesicle loss events (Carroll and Draper, 1994; Sarda and Moreira, 2002; Burnard et al., 2004). At equilibrium, Ar is preferentially incorporated into the bubbles

and lost from the system over He due to its lower solubility in the melt (Ozima and Podosek, 2002 and references therein). The higher the amount of ^{40}Ar loss (vesicle loss), the more degassed the magma and, thus the higher the $^4\text{He}/^{40}\text{Ar}^*$ ratio in the final erupted products (Carroll and Draper, 1994; Sarda and Moreira, 2002; Burnard et al., 2004) (Fig. 6 A). It follows, therefore, that simply allowing for the passage of time, the 2015 samples should be less degassed than the 2016 samples, as modelled in Figure 6 A. However, the observed $^{40}\text{Ar}^*$ concentrations generally increase from 2015 to 2016 whilst the $^4\text{He}/^{40}\text{Ar}^*$ ratios decline, and this trend suggests that a recharge event occurred between 2015 and 2016 (Fig. 6 B). Specifically, glass erupted in 2015 has only low $^{40}\text{Ar}^*$ concentrations and high $^4\text{He}/^{40}\text{Ar}^*$ ratios (“2015-like” signature, Fig. 6 B) while glass erupted in 2016 has two distinct NG signatures: one has a “2015-like” signature (low $^{40}\text{Ar}^*$ and high $^4\text{He}/^{40}\text{Ar}^*$ ratio) and the second has higher $^{40}\text{Ar}^*$ abundances and lower $^4\text{He}/^{40}\text{Ar}^*$ ratios (“2016-like” signature, Fig. 6 B). This suggests that Pele’s hairs and tears erupted in 2016 have incorporated gases derived from two different and coexisting reservoirs: one with low NG content (2015-like) and the other one more enriched in gas (2016-like). Minor variations in the daily gas supply ($^{40}\text{Ar}^*$) from the source region and / or in the samples’ vesicularity could explain the small differences in the NG composition of some glass particles having a “2016-like” signature.

Although this model seems to explain the variability of the NG in Pele’s hairs and tears, given the low $^4\text{He}/^{40}\text{Ar}^*$ ratios below the mantle production ratio (mean 2.9 - Graham, 2002), extensive non-equilibrium degassing having controlled NG ratios and abundance in the magma prior to eruption (Gonnermann and Mukhopadhyay, 2007; Weston et al., 2015) cannot be entirely ruled out. During degassing, the volatiles dissolved in the melt enter the bubbles at a rate that is controlled by their relative diffusivities. If the diffusion time of the gas species is higher than the degassing time of the magma, the melt and the bubbles will not reach solubility equilibrium and the relative diffusivities of the volatiles will control the final gas composition of a sample (Gonnermann and Mukhopadhyay, 2007). Under disequilibrium conditions, He is preferentially lost over Ar from the melt due to its higher diffusivity (Lux et al., 1987; Amalberti et al., 2016) and the $^4\text{He}/^{40}\text{Ar}^*$ ratios of the residual melt decrease, following subsequent stages of volatiles loss, reaching values that can be lower than the elemental ratios of the primordial melts (Gonnermann and Mukhopadhyay, 2007; Weston et al., 2015), and, similar to those observed in Pele’s hairs and tears and in many other volcanic glass.

An alternative model explains the low $^4\text{He}/^{40}\text{Ar}^*$ ratios as a consequence of a two-stage process. A melt with $^4\text{He}/^{40}\text{Ar}^*$ ratios, higher or equal to the Earth’s mantle, undergoes a primary fractionation of He to Ar, followed by a secondary NG fractionation, during solubility-controlled magma degassing (Fury et al., 2010; Graham, 2002; Hopp and Tieloff, 2008). In

the specific case of Masaya volcano, it is possible that primary fractionation of the melt happened during long-lasting magma storage in the shallow reservoir. Multiple stages of magma overturn recycling and degassing at depth could have favoured preferential diffusional loss of He over Ar lowering the original $^4\text{He}/^{40}\text{Ar}^*$ ratio below the mantle value. In this model, Pele's hairs and tears with a 2015-like gas signature (high $^4\text{He}/^{40}\text{Ar}^*$ ratio, low $^{40}\text{Ar}^*$) could be the result a secondary fractionation event controlled by equilibrium degassing of the magma at more superficial levels, while Pele's hairs and tears with a 2016-like gas signature would record the up-rise from depth of a less degassed magma that has increased the $^{40}\text{Ar}^*$ concentration in the superficial reservoir and even lowered the $^4\text{He}/^{40}\text{Ar}^*$ ratios up to 0.03.

5.3. Air argon contamination

Volcanic materials in equilibrium with an atmospheric reservoir at 1 atm are expected to have a $^{40}\text{Ar}/^{36}\text{Ar}$ ratio equivalent to that of the air (298.56 ± 0.31 , Lee et al., 2006). However, supra- and sub-atmospheric ratios have been frequently reported for different subaerial volcanic glass types and have been attributed to a range of processes (e.g. pumice – Krummenacher, 1970; Kaneoka, 1980; Clay et al., 2011; obsidian – Vogel et al., 2006, Morgan et al., 2009, Clay et al., 2015, Flude et al., 2018, pillow lava rinds – e.g. Kaneoka, 1994). Magma mixing with a reservoir with an air-like Ar signature (air, meteoric water or host-rocks with a ^{36}Ar component) at depth and/or at the surface, before or during eruption, and kinetic mass fractionation seems to control the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios and the ^{36}Ar content of volcanic glasses (Kaneoka, 1980, 1994; Vogel et al., 2006; Morgan et al., 2009; Brown et al., 2009; Clay et al., 2015; Flude et al., 2018). Ar diffuses from the air-like reservoir into the magma because its concentration in air (and water) is higher than in silicate melts ($\text{Ar}_{\text{solubility in air}} \gg \text{Ar}_{\text{solubility in basaltic melt}}$, Carroll and Stolper, 1993), kinetic theory (Young et al., 2002) dictates that ^{36}Ar will migrate faster than ^{40}Ar due to a higher diffusion coefficient (Amalberti et al., 2016). If quenching happens rapidly after magma extrusion, prior to complete equilibration between magmatic and air/atmospheric Ar, the sample would have a final $^{40}\text{Ar}/^{36}\text{Ar}$ ratio different from the atmospheric value with a ^{36}Ar abundance reflecting its concentration in the magma at eruption conditions.

Variable $^{40}\text{Ar}/^{36}\text{Ar}$ ratios and ^{36}Ar content of Pele's hair and tears suggest that different particles have incorporated ^{36}Ar and equilibrated with the atmosphere to varying degrees. Incomplete atmospheric equilibration is extremely likely in Pele's hairs and tears since quenching is reached rapidly soon after magma ejection (0.1 s to 5 s - Porritt et al., 2012) and, thus, degassing and fractionation are arrested. Sub-atmospheric ratios in Pele's hairs and tears may be explained by a mass fractionation process coupled with incomplete equilibration, while

supra-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratios may be associated with particles that have undergone incomplete degassing and retained a portion of the original magmatic $^{40}\text{Ar}^*$ as excess ^{40}Ar . At Masaya, meteoric water and hydrothermal fluids are circulating within the upper part of the volcano (Mauri et al., 2012); wall rocks and portions of the crater floor have collapsed into the reservoir (Rymer et al., 1998) and the magma is exposed to atmospheric contamination when it reaches the vigorously churning lava lake; any or all of these factors could contribute ^{36}Ar to the magma.

Given the debate over the location of the atmospheric Ar in volcanic samples (glass and/or bubbles - Raquin et al., 2008 and references therein) and that the Pele's hairs and tears have differing vesicularities and bubbles sizes, it may be also possible that variations in $^{40}\text{Ar}/^{36}\text{Ar}$ ratios could be related to variable amounts of ^{40}Ar and ^{36}Ar trapped in bubbles formed during subsequent stages of magma degassing and that have undergone different degrees of atmospheric contamination. Bubbles formed nearer to surface may have Ar signatures approaching that of the air, whilst bubbles formed at depth may have preserved a more primitive Ar signature less affected by ^{36}Ar uptake (Azbel and Tolstikhin, 1989). Here, the sample would have a final $^{40}\text{Ar}/^{36}\text{Ar}$ ratio and ^{36}Ar abundance reflecting the Ar signature of the trapped vesicles. Finally, potential atmospheric Ar contamination could have been introduced into the samples through micro-cracks during sampling and sample preparation (Ballentine and Barfod, 2000). However, because the NG were released from both vesicles and glass by laser-heating total fusion, it is not possible to determine the separate atmospheric contribution from these two reservoirs, and further investigation is needed to address the location of atmospheric NG in Pele's hairs and tears.

5.4. Volcanological implications of new data

The renewed activity at Masaya Volcano in 2015 seems to correlate with some changes in the gas fluxes that supply the plumbing system (Fig. 7). Basaltic glass erupted in March 2015, before the appearance of the lava lake, formed from a homogeneous reservoir that has high $^4\text{He}/^{40}\text{Ar}^*$ ratios and low $^{40}\text{Ar}^*$ content (pre-lava lake “2015-like signature” in Fig. 5 and 7 A). Samples erupted in March 2016 display two different NG signatures with some particles that have a pre-lava lake NG signature (Fig. 5) and others that show lower $^4\text{He}/^{40}\text{Ar}^*$ ratios and higher $^{40}\text{Ar}^*$ (Post-lava lake “2016-like signature” in Fig. 5 and 7 C). On this basis we propose that in early 2015 the active crater at Masaya was fed by a highly degassed magma derived from a superficial reservoir. Subsequently, a gas-rich magma ascended from depth and mixed with the degassed magma in the upper part of the volcanic system resulting in a reservoir with two distinct gas signatures that erupted the glass particles characterised by two different NG

signatures. Small variations in the daily gas supply could have controlled the variability of the NG dissolved in samples collected in 2016.

This model is consistent with cycles of upward migration of gas-rich magma from deep levels to the shallow reservoir of the Masaya volcanic system thought to have triggered previous degassing crisis and the formation of lava lakes (Rymer et al., 1998; Williams-Jones et al., 2003; Stix, 2007). It also corroborates the results of two long-term surveys of gas emissions performed between 2014 and 2017 (De Moor et al., 2017; Aiuppa et al., 2018). Low CO_2/SO_2 ratios (from 4.9 ± 2.0 to 6.3 ± 3.1 - Aiuppa et al., 2018; 3.1 ± 0.7 - De Moor et al., 2017) observed before and after the appearance of the lava lake in 2015 (Fig. 7) have been attributed to a gas source equilibrated at low pressure (0.1 - 10 MPa) (Aiuppa et al., 2018). Higher CO_2/SO_2 ratios (12.2 ± 6.3 - Aiuppa et al., 2018; 10.1 ± 1.2 - De Moor et al., 2017) measured just a few weeks prior the formation of the lava lake and the peak of the SO_2 degassing (11.4 ± 5.2 Kg/s - Aiuppa et al., 2018) observed during lake formation have been attributed to upward migration of a volatile-rich magma from the base of a shallow reservoir (0.36 - 1.4 km between 9 - 25 MPa and 15 - 35 MPa) (Aiuppa et al., 2018). This fresh, less dense, gas-rich magma reached the upper part of the Masaya volcanic system in mid-December speeding up convective movements within the upper part of the plumbing system, increasing the degassing rate at the vent and causing the resurgence of the lava lake (Aiuppa et al., 2018) (Fig. 7 B).

6. Conclusions

This study demonstrates that NG trapped in Pele's hairs and tears can be used to investigate the behaviour of a persistently degassing volcanic system such as Masaya volcano. We believe that success lies in selecting material that is chemically homogenous, not affected by post-eruptive alteration and crystal free. The samples have also variable vesicularities and display a complex mixture of bubbles of different dimensions and shapes. Sample vesicularity and vesicle size seem to be a controlling factor in the variation in the NGs along with solubility-controlled fractionation between melt and bubbles. We suggest that the variations in atmospheric argon (specifically ^{36}Ar) observed at Masaya are primary features relating to the magmatic system and not secondary processes.

Our data suggest that a gas-rich magma from depth recharged the 2015 reservoir at some point between the March 2015 and March 2016 surveys and resulted in glass erupting with two different NG signatures preserved. It is notable that this model agrees well with different evidence from Masaya such as long-term measurements of the gas-rich plume, ground deformation and gravity measurements spanning our 2015 - 2016 period, and existing models

of volcanic degassing at Masaya. Given this good agreement of observed NG in Pele's hairs and tears, with plume chemistry and physical volcanology, we propose that using NG in such materials could be a valuable addition to the tools used for monitoring long-term degassing of volcanoes (e.g., Etna, Hawaii) or to monitor the degassing of minor events such as the prolonged eruption that occurred at Kilauea along the lower East Rift Zone in May 2018 (USGS, 2018). It could also help to reveal possible precursors of renewed volcanic activity during a period of quiescence (Alvarez-Valero et al., 2018).

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Figure captions

Figure 1: A) Masaya caldera (black dashed line) with post-caldera cones (grey circles) and estimated position of the ring faults along which the cones are located (red dashed line) (after Caravantes González et al., 2019); B) Location and names of the pit craters of the Nindirí and Masaya cones (white dashed lines) - Image from Google Earth ©. Continuous red line within the Santiago pit crater indicates the lava lake active during sample collection, the orange dots indicate the collecting sites: 16N 590126 E, 1325107 N; 16N 590428 E, 1324761 N; 16N 16P 590371 E, 1325206 N. For both images, the coordinate system refers to Utm zone 16P with the grid expressed in m.

Figure 2: Pele's hairs and tears collected during this study with different morphologies A) Pele's hairs with tubular shape and displaying bifurcations. B) Pele's tears with spherical, tear-drop and elongated shapes.

Figure 3: Backscatter images of Pele's hairs and tears with different morphologies, vesicle abundance and dimension. Note the absence of crystals within the analysed samples. A) Pele's hair with elongated vesicles; B) Elongated Pele's tear with elongated vesicles; C) Pele's tear without vesicles; D) Pele's tears with isolated round vesicle; E) Pele's tear with only small ($< 50 \mu\text{m}$) isolated round vesicles; F) Pele's tear with isolated round vesicles with dimension $< 50 \mu\text{m}$ and isolated vesicles $> 50 \mu\text{m}$; G) Pele's tear with small ($< 50 \mu\text{m}$) isolated round vesicles and bigger vesicles of $100 - 200 \mu\text{m}$; H) Pele's tear with small isolated round vesicles ($< 50 - 100 \mu\text{m}$), bigger isolated round vesicles ($100 - 200 \mu\text{m}$) and coalescent vesicles ($200 \times 320 \mu\text{m}$).

Figure 4: Histogram showing the vesicularity of hairs and tears of the three sample suites (KS15-03, KS16-03, KS16-13). Particle N° 5 of sample KS16-03 has a vesicularity of 0 %, the bar in the diagram is only for illustrative purposes and not indicative of a real value.

Figure 5: Variations of the $^4\text{He}/^{40}\text{Ar}^*$ ratios with respect to $^{40}\text{Ar}^*$ abundances in Pele's hairs and tears of this study. Particles collected in 2015 display a uniform “2015-like NG signature” (in orange) with low $^{40}\text{Ar}^*$ and higher $^4\text{He}/^{40}\text{Ar}^*$ ratios, while particles collected in 2016 have 2 different NG signatures. One like those samples erupted in 2015 and the other characterised by high $^{40}\text{Ar}^*$ and lower $^4\text{He}/^{40}\text{Ar}^*$ ratios (“2016-like signature” – in grey). Groups 1 and 2

indicate particles that have a similar “2016-like NG signature” but with slightly different NG composition. Error bars are at the 1σ level.

Figure 6: A) Variations of the $^4\text{He}/^{40}\text{Ar}^*$ ratios and $^{40}\text{Ar}^*$ abundances as expected during a degassing event and modelled in Burnard et al. (2004) and Sarda and Moreira (2002). The $^4\text{He}/^{40}\text{Ar}^*$ ratios increase through time and the $^{40}\text{Ar}^*$ abundances decrease due to gas loss and bubble depletion. The black arrow indicates the theoretical degassing trend; B) Behaviour of the Masaya volcano according to NG variations in Pele’s hairs and tears. The black arrow indicates the variation of the $^4\text{He}/^{40}\text{Ar}^*$ ratios and $^{40}\text{Ar}^*$ abundances during the recharge event that occurred between 2015 and 2016. The $^4\text{He}/^{40}\text{Ar}^*$ ratios decrease between the two collections and the $^{40}\text{Ar}^*$ abundances increase indicating an accumulation of gases in the reservoir and thus, in the particles. Error bars are at the 1σ level. In A and B, dotted curved lines show the binary mixing between a melt component (high $^4\text{He}/^{40}\text{Ar}^*$ ratios and low $^{40}\text{Ar}^*$) and a component dissolved in vesicles (low $^4\text{He}/^{40}\text{Ar}^*$ ratios and high $^{40}\text{Ar}^*$).

Figure 7: Model of the behaviour of the Masaya Volcano between 2015 and 2016. The model combines NG data from this study with CO_2 , SO_2 and CO_2/SO_2 ratios measurements from Aiuppa et al. (2018). A) March 2015 - Pele’s hairs and tears with high $^4\text{He}/^{40}\text{Ar}^*$ ratios and low $^{40}\text{Ar}^*$ (“2015-like signature”) are erupted from a steady degassing vent. The gas emissions were low and the upper magma reservoir was homogeneous with respect to NG; B) December 2015 - A new batch of gas-rich magma rose from the base of the shallow reservoir causing increased degassing at the vent (higher CO_2 , SO_2 abundances in the plume) and after a few weeks, the formation of the lava lake in the Santiago crater. At this point convective movements within the surface reservoir and in the conduit started to mix the degassed magma with low NG abundance with the new magma enriched in NG; C) March 2016 - The lava lake reached its maximum dimension and Pele’s hairs and tears with 2 different NG signatures (“2015-like signature” and “2016-like signature”) erupted. CO_2 and SO_2 emissions are at the same level as they were before the appearance of the lava lake.

Supplementary data

Supplementary material 1

Supplementary material 2

Supplementary material 3

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Table 1: Major elements mean values from EMPA on selected Pele's tears and hairs from Masaya volcano.

	KS15-03 (N° 33)		KS16-03 (N° 53)		KS16-13 (N° 20)	
* Wt %	Mean	± St. Dev.	Mean	± St. Dev.	Mean	± St. Dev.
SiO ₂	51.25	0.42	51.71	0.35	51.12	0.45
Na ₂ O	2.97	0.10	3.02	0.13	3.01	0.10
K ₂ O	1.44	0.02	1.44	0.03	1.44	0.02

CaO	8.89	0.04	8.85	0.10	8.85	0.07
MgO	4.87	0.05	4.86	0.07	4.84	0.04
MnO	0.25	0.01	0.24	0.01	0.24	0.01
FeO	13.46	0.17	13.34	0.25	13.44	0.23
Al ₂ O ₃	13.71	0.13	13.81	0.11	13.69	0.11
TiO ₂	1.31	0.06	1.31	0.05	1.34	0.07
Cl	0.05	0.03	0.04	0.03	0.04	0.03
P ₂ O ₅	0.36	0.02	0.36	0.03	0.36	0.02
SO ₃	0.01	0.01	0.01	0.01	0.01	0.01
Total	98.56	0.52	98.99	0.37	98.38	0.57
CIA	50.76	0.27	50.91	0.35	50.72	0.33

N° = Number of analysis for each sample; * = Data are normalised to 100%.

Table 2: Minimum, maximum and mean NG abundance expressed as ng and isotopic ratios for KS15-03, KS16-03 and KS16-13.

Sample	⁴ He	± 1σ	³⁶ Ar	± 1σ	⁴⁰ Ar	± 1σ	⁴⁰ Ar*	± 1σ	⁴⁰ Ar/ ³⁶ Ar	± 1σ	⁴ He/ ⁴⁰ Ar*	± 1σ
KS15-03 Total N° of particles 33												
N° R _{NG}	27		10		28		4		10		3	
Min	1.0E-9	5.6E-10	9.4E-11	2.1E-11	2.5E-9	3.5E-10	4.0E-9	8.7E-11	270.0	21.8	0.23	0.03
Max	1.0E-7	3.0E-9	2.2E-8	2.4E-10	2.5E-7	2.5E-9	4.1E-8	3.8E-9	352.7	23.2	0.58	0.27
Mean	2.4E-8		4.7E-9		1.5E-6		1.9E-8		297.1		0.37	
st.dev	2.4E-8		7.4E-9		2.6E-6		1.4E-8		21.5		0.15	
KS16-03 Total N° of particles 45												
N° R _{NG}	33		11		38		6		14		5	
Min	2.4E-9	7.0E-10	4.5E-10	1.7E-10	1.1E-7	1.1E-9	9.7E-9	9.8E-11	277.3	1.2	0.03	0.01
Max	1.3E-7	2.6E-8	2.3E-8	2.2E-10	2.5E-5	9.3E-8	2.9E-7	9.1E-9	404.1	156.6	0.24	0.07
Mean	3.1E-8		5.4E-9		5.3E-6		1.4E-7		306.4		0.12	
st.dev	3.0E-8		5.3E-9		6.2E-6		1.0E-7		31.8		0.07	
KS16-13 Total N° of particles 37												
N° R _{NG}	22		10		28		6		10		5	
Min	2.7E-9	8.1E-10	9.7E-10	8.1E-11	3.2E-8	3.1E-9	2.0E-8	5.8E-10	286.8	5.3	0.04	0.01
Max	3.3E-8	9.0E-9	1.2E-8	1.7E-10	6.1E-6	3.0E-8	7.1E-8	1.5E-9	370.9	32.9	0.38	0.04
Mean	1.6E-8		4.3E-9		1.6E-6		4.5E-8		310.8		0.24	
st.dev	8.7E-9		4.1E-9		1.7E-6		2.1E-8		23.7		0.15	

Note: $^{40}\text{Ar}^* = (^{40}\text{Ar}_{\text{measured}} - \text{Ar}_{\text{ATM}}) \times ^{36}\text{Ar}_{\text{measured}}$; where Ar_{ATM} is 298.56 – Lee et al., 2006; N° R_{NG} = Number of particles that have positive NG abundance or isotopic ratio after atmospheric or blank correction (see supplementary file C for data selection criteria).

Highlights

- New tool to study persistent active volcanoes: noble gases in Pele's hairs / tears
- Monitor the degassing of Masaya volcano using noble gases in Pele's hairs and tears
- $^{40}\text{Ar}^*$ increases and $^4\text{He}/^{40}\text{Ar}^*$ ratios decrease from 2015 to 2016
- Gas variations suggest the migration of a gas-rich magma from depth in late 2015
- Noble gas content in the samples is function of solubility-controlled fractionation