



Insights from fumarole gas geochemistry on the recent volcanic unrest of Pico do Fogo, Cape Verde

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Fogo is a volcanic island of the Cape Verde archipelago and host at its center the active stratovolcano Pico do Fogo (2829 m.a.s.l.). On November 23, 2014 a new volcanic eruption started at the southwestern flank of Pico do Fogo, after 19 years of the last eruptive event. Since 2007, regular sampling and analysis of fumarole gas discharges from a fumarole (F1) has been performed in a yearly basis to monitor the chemical and isotopic gas composition. From 2008, fumarole gas sampling was also performed in a second fumarole (F2). During the period of study, outlet temperature in F1 has ranged between 62 to 159°C, whereas the F2 has ranged between 295 and 344°C. For determination of major gas species, fumarolic gases were collected in evacuated flasks containing a 5N NaOH solution. In addition, condensed steam and non-condensable gases (dry gas) were sampled by flowing the fumarolic gases through a water-cooled condenser. The isotopic composition of He ($^3\text{He}/^4\text{He}$) was determined on dry gas samples at the GRC of Tokyo University. Water vapor is by far the most abundant component, as shown by a gas/steam molar ratio between 0.08 and 0.48, followed by CO_2 (384,606 – 988,679 mmol/mol in the dry gas phase). The concentration of the other gases in the gas dry phase and expressed in $[\text{U}+\text{F}06\text{D}]$ mol/mol: Stotal varies from 3,411 to 606,054, N_2 from 835 to 84,672, H_2 from 45.6 to 68,439, CH_4 from 0 to 61,785, Cl from 4.9 to 1,729, CO from 0 to 1,396 and He from 4.4 to 617. The presence of O_2 in concentrations from 10.4 to 17,350 $[\text{U}+\text{F}06\text{D}]$ mol/mol reflects minor air contamination either during sampling or storage, or naturally in the sampled vents. Carbon isotopic composition of Pico do Fogo fumarolic CO_2 , expressed in $\delta^{13}\text{C}-\text{CO}_2$ vs. VPDB notation, varied from -4.62 to -4.06 ‰ whereas $^3\text{He}/^4\text{He}$ data, expressed as R/R_A, ranged from 5.70 to 8.81. In the classical He–Ar–N₂ triangular diagram, most of samples plot between the He, air and ASW end members, showing compositions variably contaminated by air or by ASW. Few samples show a significant increase of the relative nitrogen content toward sediment composition. Gas geothermometry, based on chemical reactions related to measured gas species, indicate equilibrium temperatures between 240 to 504°C using the $\text{H}_2/\text{H}_2\text{O}-\text{CO}/\text{CO}_2$ geothermometer and between 240 to 638°C using the $\text{CH}_4/\text{CO}_2-\text{CO}/\text{CO}_2$ geothermometer. The chemical evolution of Pico do Fogo fumarolic gases coupled with the observed increase of CO_2 soil flux, suggests the occurrence of an important increase of convective heat flux and evidences an active magmatic degassing beneath the volcano before the eruption onset. $\text{H}_2\text{O}/\text{CO}_2$ and $\text{H}_2\text{O}/\text{St}$ molar ratios showed an increasing trend towards the eruption onset, with higher values coinciding with the anomalous soil CO_2 emissions registered at the summit crater, November 2008 and March 2014, suggesting a heat pulse from the depth affected the hydrothermal reservoir before the eruption onset. This is corroborated by the sharp increase observed in the CO/CO_2 and H_2/CO_2 molar ratios in November 2013 (one year before the eruption), the last one probably due by H_2O thermal dissociation. Early degassing of new gas-rich magma batch at depth is also explained by the observed increase on the He/CO_2 molar ratio, which showed two pulses in November 2008 to February 2011 and from November 2013 to March 2014, both also coinciding with two pulses on the soil CO_2 emission. These two pulses on the He content occurred together with an increase on the $^3\text{He}/^4\text{He}$ isotopic ratio, indicating the prevalence of a magmatic dominated component during these two periods. The observed changes in the chemical and isotopic composition of Pico do Fogo fumarolic gases have proved to be clear geochemical precursory signals of the volcanic unrest occurred before the eruption onset of Pico do Fogo volcano in November 23, 2014.